REACTIONS OF CESIUM WITH AROMATIC HYDROCARBONS

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REACTIONS OF CESIUM WITH AROMATIC HYDROCARBONS

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SUMMARY

The purpose of this research was to investigate the reactions of cesium metal and a low-melting cesium alloy (mp -79.2°) containing 40.8 g-atom % Cs, 47.4 g-atom % K, and 11.8 g-atom % Na with benzene, diphenylmethane, 2,2-diphenylpropane, 1,1,1-triphenylethane, tetraphenylmethane and cis-2-heptene.

Reaction of cesium sand with excess benzene in tetrahydrofuran (THF) at -70° to -75°, with vigorous stirring, produces, after one to two hours, a 60 to 70 percent yield of cesium benzenide (I) as a black solid. Compound I, upon protonation with water, forms benzene and 1,4-dihydrobenzene; upon reaction with iodine, is oxidized to benzene; and upon carbonation and subsequent acidification, gives 1,4-dihydroterephthalic acid. Compound I is similarly formed using cesium alloy instead of cesium sand.

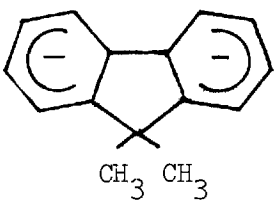
If the reaction mixture containing ca 54 mmol of I prepared from cesium sand and benzene in THF is warmed from -70° to -20° and stirred for two hours, ca 30 mmol of dicesium 1,1'-dihydrobiphenylide (II), a yellow-green solid, is formed by intermolecular coupling of I. Compound II upon protonation with water gives 1,1',4,4'-tetrahydrobiphenyl (III) whose structure was ascertained by ms, nmr, uv and elemental analysis; Compound II upon reaction with D_2O, gives 1,1',4,4'-tetrahydrobiphenyl-4,4'-d_2; and upon reaction with iodine, is oxidized to benzene.

If the reaction mixture containing II is warmed from -20° to ca 30°, and stirred for one to two hours, there is between 50 percent and 100 percent conversion of II by loss of hydrogen to dicesium biphenylide (IV), a black solid. Compound IV can also be prepared by reaction of cesium with an excess of benzene in THF at ca 30°, by reaction of cesium with benzene in excess benzene as solvent at ca 32°, and by reaction of cesium with biphenyl in THF at ca 35°. Compound IV, upon protonation with water, gives a mixture of reduced biphenyls and biphenyl; thus IV, prepared from Cs and biphenyl at 36° gave upon protonation, 0.5% of phenylcyclohexane, 13.3% of 3-phenylcyclohexene (tentative identification), 36.2% of 1,4-dihydrobiphenyl, 11.8% of 1-phenylcyclohexene, 3.8% of 3,4-dihydrobiphenyl (tentative identification) and 34.3% of biphenyl (yields are expressed as relative mole percent yields of C_{12} products).

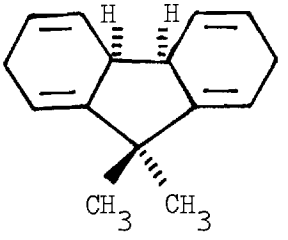
Diphenylmethane, when allowed to react with cesium alloy (ca six g-atoms of cesium to one mole of hydrocarbon) for between 20 to 60 minutes at -70° in THF, forms a dianion diradical that upon protonation with water forms, in a typical run (absolute yields based on initial diphenylmethane): 2,5-dihydrodiphenylmethane (42.1%), diphenylmethane (24.9%), and small amounts of four unidentified compounds (5.1%, 3.4%, 0.6%, and 0.7%). Warming the reaction mixture to -60° causes the dicesium diphenylmethanide to decompose partially to diphenylmethylcesium.

The compound 2,2-diphenylpropane when allowed to react with an excess of cesium alloy (ca six g-atoms of Cs to one mole of hydro-

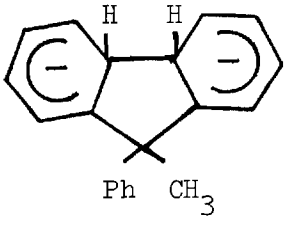
carbon) for one hour at -70° in THF, gives an intramolecularly coupled dianion (V) that upon protonation with water gives a 96 percent yield of cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene (VI) which was identified by uv, nmr, ms, elemental analysis and



V



VI



VII

dehydrogenation to 9,9-dimethylfluorene. Warming compound V to -20° causes it partially to uncouple to dicesium 2,2-diphenylpropanide according to analysis of the product from aqueous protonation.

The analogous compound VII, prepared from Cs alloy and 1,1,1-triphenylethane at -70° in THF when warmed to 0° decomposed by cleavage of phenyl to give 1,1-diphenylethylcesium, which upon protonation gave diphenylethane.

Tetraphenylmethane, when allowed to react with Cs alloy in THF for one hour at -70°, gives, after protonation with water, a complex mixture of reduced biphenyls, biphenyl, diphenylmethane, reduced triphenylmethanes and tetraphenylmethane. This result indicates that the cesium adduct of tetraphenylmethane degrades, even at -70°, to compounds of lower molecular weight.

The compound cis-2-heptene is isomerized by cesium metal to

trans-2-heptene and 1-heptene in THF at temperatures between -70° and 65° with or without the presence of cesium tert-butoxide ion. Cesium alloy does not isomerize cis-2-heptene under similar conditions.

CHAPTER I

INTRODUCTION

The purpose of this research was to investigate the reactions of cesium and a low melting alloy of cesium, potassium, and sodium[1] with aromatic hydrocarbons. The compounds investigated were benzene, diphenylmethane, 2,2-diphenylpropane, 1,1,1-triphenylethane and tetraphenylmethane. The reactions of the alkali metals, lithium, sodium and potassium with aromatic hydrocarbons are well known.[2,3,4] Alkali metals (M) reduce aromatic hydrocarbons (A) to anion radicals.

$$A + M \rightleftharpoons A^{\cdot -} + M^{+}$$

Under certain conditions, anion radicals may react further by

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(1) F. Teppler, J. King, and J. Greer, "The Alkali Metals, An International Symposium, Held at Nottingham on 19-22nd July, 1966." The Chemical Society, London, 1967, p. 25. The composition of the alloy is in g-atom %: 47.4% K, 40.8% Cs, and 11.8% Na. This is the minimum melting alloy (-79.2°).

(2) N. L. Holy and J. D. Marcum, Angew. Chem., Int. Ed. Engl. 10, 115 (1971).

(3) B. J. McClelland, Chem. Rev. 64, 301 (1964).

(4) "Ions and Ion Pairs in Organic Reactions" Vol. I, M. Szwarc, ed., Wiley Interscience, New York, N. Y., 1972.

disproportionation to form dianions and neutral molecules or couple to form dimer dianions.

$$2A^{\cdot-} \rightleftharpoons A^{2-} + A$$

$$2A^{\cdot-} \rightleftharpoons A_2^{2-}$$

Anion radicals may react with neutral molecules to form polymers.

$$A^{\cdot-} + A \rightleftharpoons A\text{-}A^{\cdot-}$$

Factors Controlling Formation of Anion Radicals

The production of anion-radical salts and their ionic form in solution is dependent upon a number of factors. The more important of these are the ability of the alkali metal to donate an electron to the hydrocarbon, the electron affinity of the hydrocarbon, the solvating power of the solvent, and the temperature of the reaction.

B. J. McClellan, in a review published in 1964,[3] contends that the reactivity of an alkali metal is inversely related to the photoelectric work function, a measure of the amount of work needed to remove an electron from the surface of a metal. The photoelectric work function for the alkali metals are: Li, 2.42 eV; Na, 2.28 eV; K, 2.24

eV; Rb, 2.09 eV; Cs, 1.96 eV.[5] Using this criterion, the order of reactivity for the alkali metals is: Cs > Rb > K > Na > Li. This explains why alkali metals are more reactive than alkaline-earth metals, e. g. magnesium (3.7 eV) or barium (2.7 eV). However, amalgams of these metals do reduce hydrocarbons. This increase in reactivity is attributed more to changes in the structure of the metal surface than to a reduction of its photoelectric work function.[6]

Since in alkali-metal aromatic-hydrocarbon reactions, the electron transfer process is also dependent on the ability of the aromatic hydrocarbon to accept an electron, the reactivity of the aromatic hydrocarbon is proportional it its electron affinity. Experimentally determined electron affinities have been found for aromatic molecules both in the gas phase and in solution.[7] Modified molecular orbital calculations have been used for theoretical determinations.[7] Consideration of both the experimental and calculated electron affinities determined by various workers,[3,6] leads to the order for simple aromatic hydrocarbons: benzene < biphenyl < naphthalene < anthracene.

There are two types of common solvents used in the study of alkali-metal reductions: ethers and amines. Since amines are generally more acidic than ethers, they were not examined as solvents

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(5) "Handbook of Chemistry and Physics" 50th edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p. E87.

(6) M. Szwarc in "Progress in Physical Organic Chemistry" Vol. 6, A. Streitwieser, Jr., R. W. Taft, Eds., Interscience Publishers, New York, p. 357.

(7) For an extensive review on methods of experimentally and theoretically determining electron affinities see reference 6, p. 323.

in the present work. The nature of solvent has a profound effect on the reaction of alkali metals with aromatic hydrocarbons. The solubility of the metal in the ethereal solvent determines whether the reaction follows a homogeneous or heterogeneous pathway. Secondly, the equilibrium concentrations in these reactions are dependent upon the ability of the solvent to solvate the ion pair. Thirdly, if the solvent has sufficient solvating power, the form of the ion pair will be solvent separated. That is, the cation is surrounded by a layer of solvent molecules which separate it from the anion.

Ethers have been found to dissolve alkali metals, especially at low temperature, to form blue solutions.[8,9,10] This is generally considered to be the formation of "solvated" electrons and metal cations. However, there is evidence that this is in equilibrium with a metal anion[10] and with a metal dimer[11] where the dimer is a salt of a metal anion and a metal cation. These reactions are shown in the next scheme. In any of these cases, the ethereal solvent promotes a removal of an electron from the metal atom and in doing so makes it more easily transferred to the atomatic hydrocarbon.

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(8) J. L. Down, J. Lewis, B. More and G. Wilkinson, J.Chem. Soc., 3767, (1959).

(9) F. S. Dainton, D. M. Wiles and A. N. Wright, J. Chem. Soc., 4283, (1960).

(10) Sivert H. Glarum and James H. Marshall, J. Chem. Phys., 52, 5555 (1969).

(11) See reference 6, p. 380.

$$M \longrightarrow M^+ + e^-$$

$$M + e^- \longrightarrow M^-$$

$$M^- + M^+ \longrightarrow M_2$$

Different ethereal solvents have quite a range of effects upon the equilibrium of the reaction between aromatic hydrocarbons and alkali metal.[12a] This is illustrated in Table 1 for the reaction between sodium and biphenyl. Investigation of this table shows that three factors are found to affect the equilibrium of this reaction. First, more basic solvents, having two oxygen atoms rather than one, generally promote reaction. Secondly, the dominant factor in the reaction appears to be steric requirements of the solvent for solvation of ion pairs. For example, MEE is a better solvent than DEE, THF is better than MeTHF or THP, 1,2-DMPr is better than 1,3 DMPr. Thirdly, a decrease in temperature increases the magnitude of the equilibrium constant. Lowering the kinetic energy of the solvent improves its ability to form solvating bonds with the resulting ion pair. Since these same factors are found to be important in alkali metal solvation to form "solvated electrons",[8,9] it seems logical to assume that there

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(12a) See reference 4, J. Smid author, Chapter 3, p. 138. Data taken from A. I. Shatenshtein, E. S. Petrov and M. I. Bulousova Organic Reactivity, 1, 191 (1964) and R. V. Slates and M. Szwarc, J. Amer. Chem. Soc., 89 6043 (1967).

Table 1. Equilibrium Constants[12a] for the Reaction:

$$Na + Biphenyl \underset{}{\overset{Ether}{\rightleftharpoons}} Na^{+}, Biphenyl^{\cdot-}.$$

T	MEE	1,2-DMPr	THF	MeTHF	DEE	THP	1,3-DMPr
40°	0.12	0.09	0.10				
30°	0.28	0.20	0.20				
20°	0.75	0.49	0.36	0.02	0.07		
10°	2.55	1.40	0.66	0.036	0.11		
0°	7.0	5.0	1.50	0.055	0.19	0.06	
-10°			2.90	0.11	0.39	0.10	0.12
-20°				0.20	1.25	0.17	0.34
-30°				0.45	8.7	0.29	1.20
-40°				1.18		0.48	

MEE = 1,2-methoxyethoxyethane; 1,2 DMPr = 1,2-dimethoxypropane; THF = tetrahydrofuran; MeTHF = 2-methyltetrahydrofuran; DEE = 1,2-diethoxyethane; THP = tetrahydropyran; 1,3-DMPr = 1,3-dimethoxypropane

is a correlation between alkali metal solvation and yield of anion radical salts.

In an extensive paper on the effect of solvent on organo-alkali metal salts Hogen-Esch and Smid report[12b] that ethereal solutions of anion radicals and carbanions contain two types of ion pairs, contact and solvent separated. The bulk of their research was concerned with the study of alkali metal salts of the fluorenyl carbanion. After establishing the nature of this carbanion in various solvents, at different temperatures, and with each of alkali metals as the counterion, these workers investigated a number of other organo-alkali metal salts including lithium naphthalide and sodium naphthalide.

In their study of the fluorenyl carbanion, Hogen-Esch and Smid found that ethereal solutions of fluorenyl alkali-metal salts possess uv absorption spectra that contain two independent bands, a lower wavelength band due to the contact ion and a higher wavelength band due to the solvent separation ion pair. The wavelength of the band due to the contact ion pair was dependent on the cation, while the wavelength of the band due to the solvent separated ion pair was independent of the cation. The solvent and the counterion have considerable effect upon the relative amounts of solvent separated and contact ion pairs present in solution.

Table 2, a summary of the results found by Hogen-Esch and Smid

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(12b) T. E. Hogen-Esch and J. Smid, J. Amer. Chem Soc., 88, 307 (1966).

Table 2. The Percentages of Solvent Separated Ion-Pairs in 9-Fluorenyl Salt Solutions at 25°.[12b]

	Solvent						
Counterion	Diox	Tol	MeTHF	THF	DME	Pyr	DMSO
Li^+	0.0%	0.0%	25%	80%	100%	100%	100%
Na^+	0.0%		0.0%	5%	95%	100%	100%
K^+				0.0%	ca 10%		
Cs^+				0.0%	0.0%		
NBu_4^+				0.0%			

Diox = dioxane; Tol = toluene; MeTHF = 2-methyltetrahydrofurane; THF = tetrahydrofuran; Pyr = pyridine; DMSO = dimethylsulfoxide

in their study of 9-fluorenyl salts, indicates that the amount of solvent separated ion-pairs increases as the size of the cation decreases. The ability of the solvents to produce solvent separated ion pairs increases in order: toluene, dioxane < MeTHF < THF < DME < DMSO, pyridine.

The unusyal result of dioxane is considered to be due to steric factors resulting from a need to be in the boat conformation in order for both oxygens to coordinate with a cation.[12b]

These workers report that sodium naphthalide and lithium naphthalide exist as both types of ion pairs. At room temperature, a sodium naphthalide exists in THF as a contact ion pair while lithium naphthalide is 60-80% in the solvent-separated form. Others have shown that the ion pair form can be determined using nmr and esr hyperfine splitting constants (HFSC) of the cations in spectra of the anion radical.[13,14] A large HFSC indicates a contact ion pair and a small or no HFSC indicates a solvent separated ion. For example, Cs has an HFSC in cesium biphenylide of 0.0 between -90° and -100° in diglyme and ca -0.8 at ca 25°.[13] In Table 3, the effect of solvents on the type of ion pair for the naphthalide ion and the biphenylide ion is summarized. This table shows that the effect of solvent on the ionic form of the anion radical salts studied is qualitatively the same as that found for the fluorenyl salts. The

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(13) See reference 4, Egbert De Boer and Jan L. Sommerdijk, authors, Chapter 7, p. 304.

(14) Noboru Hirota, J. Amer. Chem. Soc., 90, 3603 (1968)

Table 3. The Ionic Form of Naphthalide and Biphenylide Salts in Ethereal Solvents.

Counterion	Solvent	Temperature	Ionic Form	Method of Determination	Reference
Naphthalide					
Na	THP	36° to -37°	Contact	Absorption spectra	15
Na	Et_2O	-56° to -95°	Contact	Absorption spectra	15
Na	Et_2O	10°	Contact	esr-HFSC	16
Na	DME	-30°	Solvent-Separated	esr-HFSC	16
Na	THF	-70°	Solvent-Separated	esr-HFSC	16
Na	THF	20°	Contact	Absorption spectra	17
Na	THF	57°	Contact	esr-FHSC	16
Na	DMTHF	15°	Contact	esr-HFSC	16
K	THF	24°	Contact	esr-HFSC	16
K	Et_2O	-3° to -38°	Contact	Absorption spectra	15
Li	THF	-30°	Solvent-Separated	esr-HFSC	16
Li	DME	not given	Solvent-Separated	esr-HFSC	16

Table 3. (Continued)

Counterion	Solvent	Temperature	Ionic Form	Method of Determination	Reference
Naphthalide					
Cs	THF	0°	Contact	esr-HFSC	16
Biphenylide					
Na	THP	20° to -30°	Contact	Absorption spectra	17
Na	DME	< -30°	Solvent-Separated	Absorption spectra	17
Na	THF	-70°	Solvent-Separated	Absorption spectra	17
Na	THF	20°	Contact	Absorption Spectra	17

THP = tetrahydropyron; Et_2O = diethylether; DME = dimethoxyethane; THF = tetrahydrofuran; DMTHF = 2,4-dimethyltetrahydrofuran.

order of increasing solvating power of the solvent is: THP, Et_2O < THF < DME. THF is interesting because it forms solvent separated ions at -30° and contact ions at 20°.

As can be seen in Tables 1 and 3, lowering the temperature increases the equilibrium constant of the reaction between biphenyl and sodium and the solvating power of the solvents. These two observations are consistent since increasing the solvation would stabilize the ionic products. Smid and Hogen-Esch found similar results for their fluorenyl salts.[12] For example, the equilibrium constant for the equation,

$$F^- Na^+ + THF \rightleftharpoons F^-//Na^+ \text{ (solvent separated)}$$

is 0.064 at 24.1°, 0.129 at 1.8°, 0.468 at -21.8°, 1.22 at -36.2° and 6.15 at -63.0°. However, when cesium was used as a counterion, there was no solvent separation found in THF even at -70°. In DME at -70°, its spectrum indicated a "sizable fraction"[12] of solvent-separated ion pairs.

The reactions investigated in this research are those between benzene, diphenyl-methane, 1,1,1-triphenylethane, 2,2-diphenylpropane, or tetraphenylmethane and cesium either as a metal or in Cs-K-Na

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(15) M. Szwarc, J. Amer. Chem. Soc., 93, 4149 (1971).

(16) Noboru Hirota, Robert Carraway and William Schook, J. Amer. Chem. Soc., 90, 3611 (1968).

(17) Y. Karasawa, G. Levin, and M. Szwarc, J. Amer. Chem. Soc., 93, 4614 (1971).

alloy. All of these reactions are of the type where cesium reacts with a phenyl ring to form an alkali-metal anion-radical ion pair. Thus, an understanding of the reaction of benzene with cesium should be a basis for the understanding of the other reactions studied.

As stated above, the course of this type of reaction is dependent upon the electron affinity of the aromatic hydrocarbon, the electron donating ability of the metal, the solvating power of the solvent, and the reaction temperature. Cesium is the strongest reducing agent among the alkali metals while benzene has the lowest electron affinity of the aromatic hydrocarbons. Hence if benzene can be appreciably reduced to radical anion, cesium would appear to be the alkali metal of choice. Factors open for choice in study of the reaction of cesium with benzene are the solvent and temperature. As seen in the case of biphenyl and sodium, increasing the solvating power of the solvent, by either changing to a more basic solvent or lowering the temperature, increases the yield of anion radical. Solvation also controls the type of ion pair produced, that is, contact or solvent separated. The smaller metal cations are solvated more than the larger metal cations and solvent separation of cation and anion is likely to play a smaller role in the reactions of cesium than the other alkali metals.

In the next sections which discuss specific alkali-metal aromatic-hydrocarbon reactions, the desirability of contact ion pairs or solvent separated ion pairs will be considered.

Reaction of Benzene with Alkali Metals

In 1912[18a] and in 1913[18b], Louis Hackspill reported that cesium, when allowed to react with benzene for two or three days in vacuum at 28°, formed a black solid. No evolution of hydrogen was observed. This black solid reacted with water and alcohol to form biphenyl. It reacted with carbon dioxide but did not form cesium benzoate. When heated it quickly formed a resin. Addition of the black solid to chloroform produced a violent explosion. After being washed with dry pentane, this solid was found to be 65.34 percent cesium. This agreed with the formula C_6H_5Cs. Since no hydrogen was evolved in this reaction, Hackspill felt that benzene and cesium reacted to form phenylcesium and dihydrobenzene according to the following equation.

$$3C_6H_6 + 2Cs \longrightarrow 2C_6H_5Cs + C_6H_8$$

Later[18c], Hackspill questioned his supposition that phenylcesium was produced in this reaction because reaction of the black precipitate with water yielded biphenyl and hydrogen. He suggested that the reaction be further studied.

More recently, in 1946[19], Jean de Postis who worked with Louis Hackspill, reanalyzed the black solid formed in this reaction. He

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(18a) L. Hackspill, Proc. Int. Congr. Appl. Chem. 8th, 2, 113 (1912); (b) Ann. Chim. Phys. (Paris), 28, 653 (1913); (c) Helv. Chim. Acta, 11, 1026 (1928).

(19) Jean de Postis, Proc. Intl. Cong. Pure Appl. Chem., 11th, 5 867 (1947), Compt. Rend., 222, 398 (1946).

allowed cesium to react with benzene in a vacuum at 40° for between 24 and 48 hours. Analysis of the resulting black solid showed that the ratio of the mass of the solid to the mass of cesium was 1.097:1. This indicated that the formula of the product was $C_6H_6Cs_6$. Jean de Postis also observed that this solid, when quenched with water, evolves hydrogen gas. Hackspill, disregarding his previous work in a chapter on alkali metals in "Chimie Minérale"[20] published in 1956, concurs with de Postis that the formula for the black solid is $C_6H_6Cs_6$.

The reaction of benzene with alkali metals in addition to cesium in ether has been studied to some extent. The initial step in this reaction is the transfer of an electron from the alkali metal to benzene to form an anion radical. This is analogous to the same reaction in amine solvents,[21] that is, the normal Birch reduction. The anion radical produced has been observed by esr spectroscopy and trapped chemically with various quenching reagents.

The observation of benzene anion radical was first reported by Tuttle and Weisman[22] in 1958. They found that benzene reacted with potassium at -80° in DME to produce an intermediate possessing a seven line esr spectrum. The splitting of the spectrum indicated that the

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(20) L. Hackspill in "Nouveau Traite' de Chimie Minérale" Vol. 3, Paul Pascal ed., Masson, Paris, France, (1956), p. 124.

(21) O. J. Jacobus and Jerome F. Eastham, J. Amer. Chem. Soc., 87, 5799 (1965).

(22) T. R. Tuttle, Jr. and S. I. Wiessman, J. Amer. Chem. Soc., 80, 5342, (1958).

intermediate contained the six equivalent hydrogens of the benzene anion radical. This intermediate was found to slowly decompose as the temperature was raised above -80°. Subsequently, other workers in their study of this anion radical have been able to prepare stable solutions of it in THF, DME and THF-DME mixtures at temperatures as high as 30°.[23,24] It was reported[25] that this intermediate, when heated above 20° would decompose to a new compound possessing an entirely different esr spectrum. Further study[26] indicated that the appearance of the new intermediate was linked to the method of purification used for the solvent. Drying the solvent over sodium-potassium alloy would prevent formation of this new compound while drying with lithium aluminum hydride would cause its formation. Addition of either lithium chloride or lithium aluminum hydride to the reaction also caused this new intermediate to form even at temperatures below 20°. This intermediate possessed a 15-line esr spectrum in which each line was split into 12 components. Analysis indicated that the spectrum was due to a compound containing at least 13 hydrogens. Three

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(23) George L. Malinoski,Jr. and W. H. Bruning, Angew. Chem. Int. Ed. Engl., 7, 953, (1968); J. Amer. Chem. Soc., 89, 5063 (1967).

(24) George L. Malinoski, Jr. and W. H. Bruning, J. Chem. Phys, 50, 3637 (1969).

(25) Pamala Wormington and J. R. Bolton, Angew. Chem. Int. Ed. Engl., 7, 954 (1968).

(26) K. W. Boddeker, G. Lang and V. Schindewolf, Angew. Chem. Int. Ed. Engl., 7, 954 (1968).

sets of equivalent hydrogens were identified to be in the relative ratio 1:2:4. Interpretation of these data is difficult. However, this spectrum was definitely not caused by a benzene monomer. These workers stated that it possibly could be caused by a form of a benzene dimer.[26] They did not propose a structure for this dimer.

The yields of benzene anion radical produced for esr analysis in these cases were quite small. Spin concentration measurements of 1M and 0.01M solutions of benzene in DME-THF (1:2) in the presence of Na-K alloy showed that the anion radical yield ranged from 0.006% to 0.02% to 0.09% respectively, between -20° and -83°.[27]

Chemical evidence of the anion radical of benzene produced by alkali metal has been observed through the use of quenching agents. The probable pathway of the reaction of benzene anion radical with a quenching agent is outlined in the following scheme. The reaction mechanism is well established for the Birch reduction in amine solvents.[21] In the next set of reactions this mechanism is illustrated using carbon dioxide as the quenching agent.

Benzene, when allowed to react with potassium in DME at -70° for two hours and then quenched by passing CO_2 over the resulting mixture for one hour, will give (after acidification) a 54% yield of 1,4-dicarboxyl-2,5-cyclohexadiene.[28] Quenching this reaction mixture

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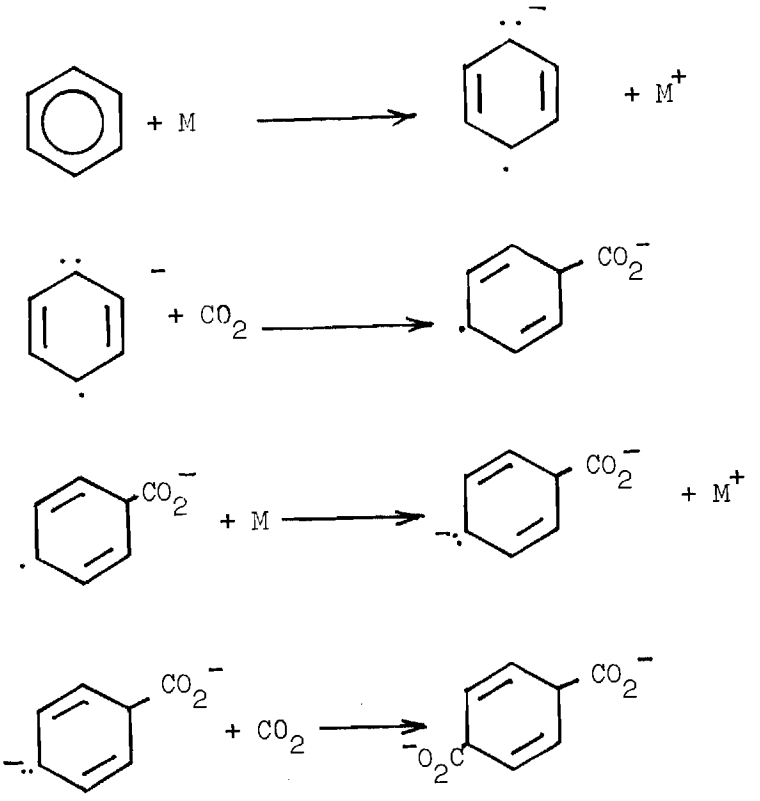
(27) Robert G. Kooser, Walter V. Volland and Jack H. Freed, J. Chem. Phys. 50, 5243 (1969).

(28) Irving L. Mador and Theodore S. Soddy, U.S. Patent 2,960,544 (November 15, 1960).



with ethylene oxide was reported to give the analogous diol derivative.[28] However, the analysis appeared incomplete. Benzene when allowed to react with lithium, potassium containing a catalytic amount of lithium, or sodium-potassium alloy in THF at 25° for two to six days in the presence of trimethylchlorosilane produced a 30-40% yield of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene.[29]

With the exception of cesium, alkali metals react with benzene to produce a small amount of benzene anion radical. Cesium, based on incomplete and contradictory reports, may react quantitatively with

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(29) Donald R. Weyenberg and Louis H. Toporcer, J. Amer. Chem. Soc., 84, 2843 (1962).

benzene.[18,19] However, the structure of the product as described in the literature is questionable.

Reaction of Pyridine and Other Nitrogen Containing Aromatic Compounds with Alkali Metals

Pyridine, the simplest nitrogen containing aromatic compound, is very similar to benzene in structure. However, it is considerably more reactive than benzene with alkali metals and thus more easily studied. The reactions of pyridine should provide an insight into the possible reactions of benzene.

In 1961, Ward[30] reported that pyridine in DME in contact with potassium metal at -70° to -50° produced an intensely purple solution. This solution was paramagnetic and produced an esr spectrum containing considerable hyperfine structure. After five to ten minutes, a yellowish solution formed that was diamagnetic. The esr spectrum observed for the purple intermediate was not that expected for the pyridine anion radical. It was consistent with the spectrum predicted for 4,4'-bipyridyl anion radical. Study of the esr spectra of DME solutions of the reaction products of deuterated pyridines with potassium confirmed that this intermediate was the 4,4'-bipyridyl anion radical. This intermediate has also been observed in THF to be stable in an absence of excess sodium.[31] Apparently the yellowish solution

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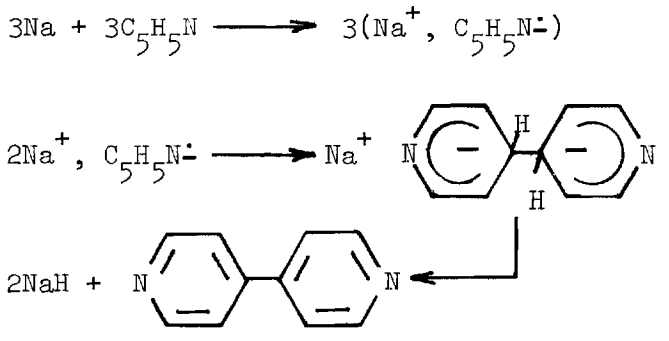
(30) Raymond L. Ward, J. Amer. Chem. Soc., 83, 3623 (1961).

(31) J. W. Dodd, F. J. Hopton and N. S. Hush, Proc. Chem. Soc.,61 (1962).

mentioned above contained the dianion of 4,4'-bipyridyl.

In a more recent investigation, it was found that the alkali metals, lithium, sodium, and cesium dissolved in pyridine at room temperature to form an unstable, pyridine-soluble, yellow solid.[32] This exhibits a broad esr signal at liquid nitrogen temperatures and an absorption band at 330 mμ. This yellow solid was identified as the anion radical of pyridine. At room temperature, the yellow solution changed without the evolution of hydrogen to an intense blue solution. This solution possessed an esr spectrum identical with the reported spectrum of 4,4'-bipyridyl anion radical. The second yellow intermediate, observed in DME, was not observed in pyridine. Since in the transition from pyridine radical anion to bipyridyl dianion there was no hydrogen evolution, it was assumed that sodium hydride was a product of the reaction. The proposed reaction mechanism is given below.[32]



(32) C. D. Schmulbach, C. C. Hindsley and David Wasmund, J. Amer. Chem. Soc., 90, 6600 (1968).

$$(Na^+, C_5H_5N^{\cdot-}) + C_{10}H_8N_2 \longrightarrow (Na^+, C_{10}H_8N_2^{\cdot-}) + C_5H_5N$$

In DME, this intermediate appears to react further to form the dianion

$$(Na^+ C_{10}H_{10}N_2^{\cdot-}) + (Na^+, C_5H_5N^{\cdot-}) \text{ or } Na \longrightarrow Na^+ \; N\bigcirc\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc N \; Na^+$$

There were different final products formed in these two investigations for the following reason. In the first investigation, there was an excess of alkali metal which favored bypyridyl dianion formation. In the second investigation there was an excess of pyridine which favored bypyridyl anion radical formation.

Szwarc[33] has found that the anion radical of the monomers of various nitrogen containing aromatic compounds can be produced. He studied the reactions of pyridine, quinoline, isoquinoline, acridine, and 9,10-diazophenanthrene with sodium and with sodium biphenylide. Two different solvents, HMPA (hexamethylphosphoramide) and THF, were used. These compounds, with the exception of pyridine, exist as monomer anion radicals in HMPA and as dimer dianions in THF. Pyridine loses hydrogen to become the dehydro-dimer dianion, i. e., bipyridyl dianion, in both solvents. In HMPA, the ion pair formed by quinoline, for example, is solvent separated. This will not react

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(33) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski and M. Szwarc, J. Amer. Chem. Soc., 90, 6421 (1968).

further because of the electron-electron repulsion in the dimerization product. In THF the salt is a contact ion pair. After dimerization (to the dihydro derivative) the cations, because they are closer, contribute more stabilization to the dianions.

Reaction of Biphenyl and Other Aromatic Hydrocarbons with Alkali Metals

Anion radicals of organic compounds are known to react further in the absence of a quenching agent by either disproportionation to dianions or intermolecular coupling to dianionic dimers. The latter reaction has just been described in the case of pyridine. Since benzene anion radical is difficult to prepare, the dianion of benzene does not appear to be an expected product. If dimerization occurred, a dihydro-biphenyl dianion would be expected. In the case of pyridine, the dimerization product lost two hydrogen atoms by some method to give bipyridyl which reacted further with alkali metal. This resulted in the observation of the bipyridyl anion radical or dianion. If benzene were analogous, biphenyl anion radical and dianion would be expected products. Therefore, an understanding of the reactions of benzene with alkali metals must include an understanding of the reactions of biphenyl with alkali metals.

Unlike benzene, the biphenyl anion radical, which has been well characterized by esr spectroscopy,[34-37] is produced in reasonable yields

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(34) M. I. Terekhova, É. S. Petrov, and A. I. Shatenshtein, Zhurnal Obshchei Khimii (Eng. Trans.) 38, 2509 (1968).

in ethereal solvents, even at room temperature. The equilibrium constants for the reaction of sodium and biphenyl in various ethers at different temperatures are compiled in Table 1. These values, determined spectrophotometrically, indicate, as previously discussed, that the yield is dependent upon the ion-pair solvating ability of the solvent. This table indicates that the ethereal solvents in the order of ability to produce ion pairs are: THP < 1,3-DMPr < Et_2O < MeTHF < THF < 1,2-DMPr < MEE. Other work upon this reaction at room temperature has given the order: DEE < THF < DME, diglyme.[35] An independent study of this reaction in THF using magnetic susceptibility for analysis has determined the equilibrium constant at 26° to be 0.366.[38] Alkali metal-biphenyl salts have also been used as reducing agents for other organic compounds.[33,34,39,40]

Biphenyl will also accept two electrons to form a dianion.

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(35) É. S. Petrov, E. A. Yakovleva and A. I. Shatenshtein, Zhurnal Obshchei Khimii (Eng. Trans.) 33, 100 (1963).

(36) M. A. Komarynsky and S. I. Weissman, Chem. Phys. Let., 7 211 (1970).

(37) F. C. Adams and C.R. Kepford, Can. J. Chem., 49, 3529 (1971).

(38) Ting Li Chu and Shan Chi Yu, J. Amer. Chem. Soc., 76, 3367 (1954).

(39) J. I. Terekhova, E. S. Petrov, and A. I. Shatenshtein, Reaktsiannaya Sposobnost' Organicheskikh Soedinenii (Eng. Trans.), 4, 263 (1967).

(40) John J. Eisch and William C. Kasha, J. Org. Chem. 27, 3745 (1962).

Lithium and sodium react in THF to form the dimetal-biphenyl adduct,[30,41] The dianion prepared from potassium in DME has been reported to be more reactive than the monoanion.[34] It will react with solvent to decompose to ca 10 percent of its initial concentration over a four hour period. This new product, the probable result of proton abstraction from the solvent, is considered to be monohydrobiphenyl anion.* Lithium biphenylide was found to be even more reactive. When this adduct comes in contact with a lithium mirror, it rapidly decomposed to a diamagnetic substance that did not have quite the same characteristics as dilithium biphenyl. This was considered to be the lithium monohydrobiphenyl anion salt.

There is a case where two diphenyl molecules apparently share one electron.[36] If biphenyl is added to a MeTHF solution of lithium biphenylide, the esr spectrum of the solution changes to a mixture of two distinct biphenyl anion radical spectra that differ only by the magnitude of the lithium hyperfine splitting constant (HFSC). Since this phenomenon is concentration dependent, this suggests that the new species is a dimer. This dimer would have to be two biphenyl molecules sharing a lithium ion and its electron since there is only a change in the HFSC.

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* This intermediate has also been postulated as an intermediate in the reaction of lithium biphenylide with triphenylmethane in THF.[40]

(41) Konrad Lühder, Z. Chem., 9, 387 (1969).

The identification of the hydrolysis products of alkali-metal-biphenyl adducts in ethereal and amine solvent has been the subject of considerable discussion.[42-44] Recently a definitive study[45] of the products of this reaction has shown that a mixture of biphenyl and reduced biphenyls is produced. The reduced biphenyls observed include phenylcyclohexane, 3-phenyl-1,4-cyclohexadiene, 1-phenyl-cyclohexene, and 2-phenyl-1,3-cyclohexadiene. In Table 4, the relative yields of the reduction products using three different methods of reduction are presented. These products were also isolated from the reaction of biphenyl and Na-K alloy in DME with water used as a quenching agent.[46]

Considering the identities of the products, the hydrolysis of the reduction product of biphenyl with alkali-metals appears to follow the reaction pathway outlined below.

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(42) Walter Hückel and Roland Schwen, Chem. Ber., 89, 150 (1956).

(43) Iu. P. Egorov, E. P. Kaplan, Z. I. Letina, V. A. Shliapochnikov and A. D. Petrov, J. Gen. Chem. USSR, 28 (1958).

(44) Walter Hückel and H. Bretschneider, Justus Liebigs Ann. Chem., 540, 173 (1939).

(45) P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras and J. L. R. Williams, J. Org. Chem., 33, 1116 (1968).

(46) S. A. deLicastro and M. A. Ruveda, J. Organmetal. Chem., 39, 225 (1972).

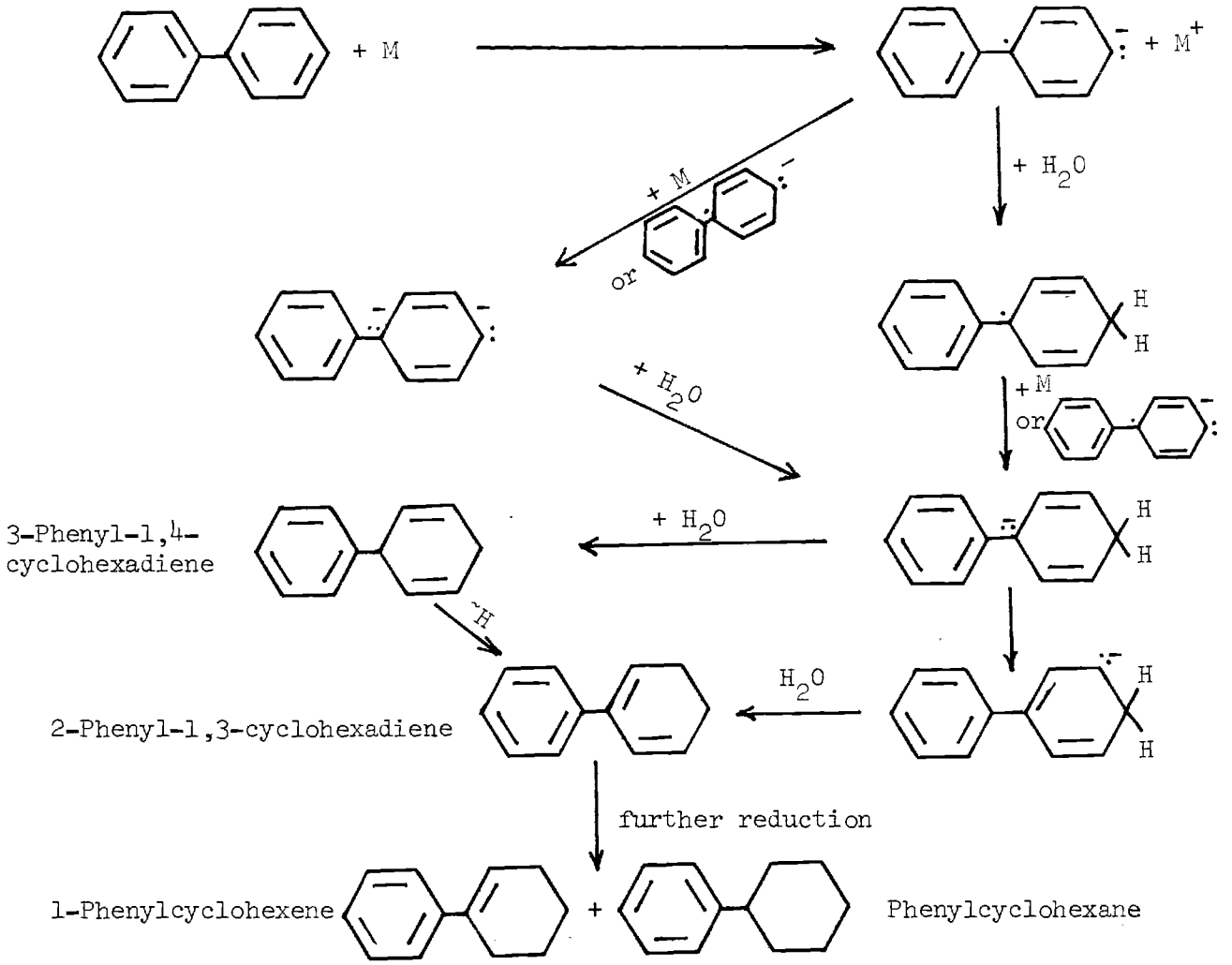
Table 4. Relative Percentage Yield of Products Formed From the Alkali Metal Reduction of Biphenyl.[45]

Product	Method A	Method B	Method C
Phenylcyclohexane	21%	0%	19%
3-Phenyl-1,4-cyclohexadiene	52%	100%	72%
1-Phenylcyclohexene	20%	0%	9%
2-Phenyl-1,3-cyclohexadiene	6%	0%	0%

Method A: Reacted biphenyl and sodium (1:2.06) in liquid ammonia at -70° to -75° and quenched with methanol after four hours.[44]

Method B: Reacted biphenyl and sodium (5:8) in ammonia and diethyl ether (500 ml: 100 ml) and quenched with ammonium chloride.[42]

Method C: Reacted biphenyl and lithium (1:5) in ether for 100 hours while shaking and decomposed with ethanol.[43]


+ M
+ M+
+ H2O
+ M
or
H
H
+ H2O
+ M
or
3-Phenyl-1,4-
cyclohexadiene
+ H2O
-H
H2O
2-Phenyl-1,3-cyclohexadiene
further reduction
1-Phenylcyclohexene
+
Phenylcyclohexane

In the formation of anion radicals of aromatic hydrocarbons, an electron is put into the lowest antibonding molecular orbital.[47-49] Thus, aromatic compounds larger than benzene and biphenyl would have a stronger tendency to form anion radicals, since they possess antibonding orbitals of lower energy. Experimentally, this has been shown with many aromatic hydrocarbons. Naphthalene reacts so well with sodium that the resulting salt is commonly used as a reducing agent.[2,39,50,51] Fluorene forms an anion radical with alkali metals at -70° in ethereal solvents.[52] Still other compounds that are known to form anion radicals, to name a few, are anthracene,[42,47] triphenylene,[30,53] tetracene,[47], pyrene,[47] and coronene.[48]

Hydrocarbon anion radicals, in the absence of quenching agents, may react further by disproportionation to dianions. A few aromatic compounds known to form dianions are tetraphenylethylene,[54]

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(47) G. J. Hoijtink, N. H. Velthorst and P. J. Zandstra, Mol. Phys, 3, 533, (1960).

(48) G. J. Hoijtink, Mol. Phys, 2, 85 (1959).

(49) M. Matsuda, J. Jagur-Grodzinski and M. Szwarc, Proc. Roy. Soc. (London), 288, 212, (1965).

(50) John F. Garst and Franklin E. Barton II, Tetrahedron Lett., 587 (1969).

(51) T. L. Staples, J. Jagur-Grodzinski and M. Szwarc, J. Amer. Chem. Soc., 91, 3721 (1969).

(52) D. Casson and B.J. Tabner, J. Chem. Soc., B, 887 (1969).

(53) E. de Boer, A. M. Grotens, and J. Smid, J. Amer. Chem. Soc., 92, 4742 (1970).

(54) John F. Garst, Ernest R. Zabolotny and Ronald S. Cole, J. Amer. Chem. Soc., 86, 2257 (1964).

naphthalene,[55] anthracene,[55] tetracene,[55] and pyrene.[55] Tetraphenylethylene (TPE) is more stable as a dianion than as an anion radical. This stability is due to the ability of the dianion to distort from planarity. Poorer solvents increase the degree of disproportionation in the equation: $2(TPE^{\cdot-}, Na^{+}) \rightleftharpoons TPE + (TPE^{-2}, 2Na)$. The equilibrium constant (K) of this disproportionation at room temperature are in this order according to solvent: diethyl ether, dioxane (K too large to measure); THF (K = 212); diglyme (K = 1); DME (K = 0.84).[54] This means that the solvents producing contact ion pairs allow the cations to give more stability to the dianion while stronger solvents which produce solvent separated cations and anions incerase the electron-electron repulsion in the dianion and therefore favor the monoanion.

Many anion radicals of aromatic compounds react intramolecularly to dianionic dimers. Lithium anthracenide at high cencentrations (12×10^{-2}M) forms a precipitate that after hydrolysis gives 9,9', 10,10'-tetrahydro-9,9'-dianthryl.[56] A possible reaction pathway for this is given below. However the dimerization process could also occur during the protonation reaction. The anion radicals of the compounds 1,1-diphenylethylene,[49,51] fulvene,[3], and styrene,[3] are also

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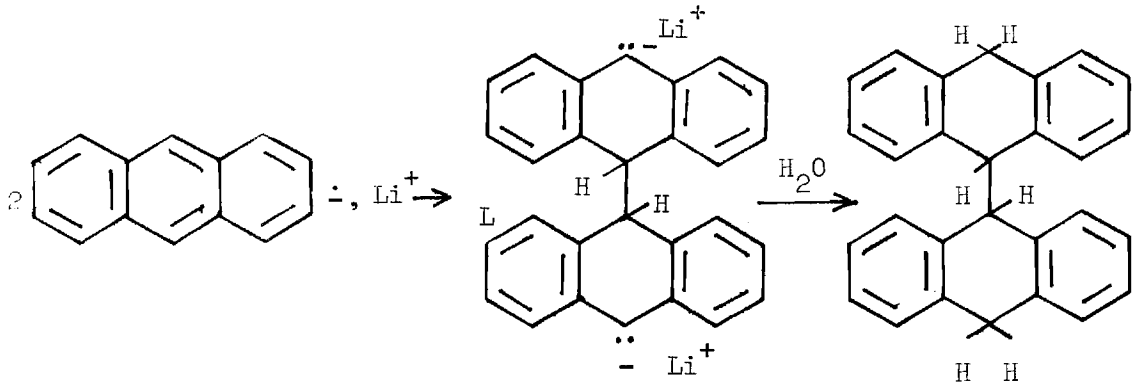
(55) N. H. Velthorst and G. J. Hoijtink, J. Amer. Chem. Soc., 87 4529 (1965).

(56) Hans J. S. Winkler and H. Winkler, J. Org. Chem., 32, 1695 (1967).



known to form dimer dianions.

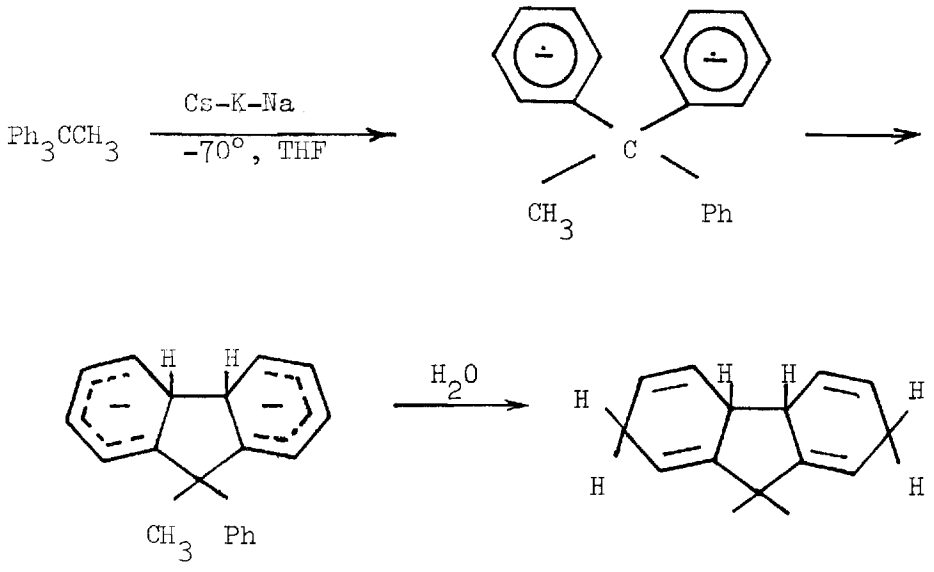
The Reaction of 1,1,1-triphenylalkanes with Ca-K-Na Alloy.

The reactions of polyphenylalkanes could lead to intermediates where at least two separate moieties within a molecule could form anion radicals. The chemistry of such dianion radicals is interesting because there is the possibility of intramolecular interaction. This is in contrast to the intermolecular reactions described in the previous section.

Grovenstein and coworkers[57] discovered that 1,1,1-triphenylethane reacts with an excess of the minimum melting alloy of cesium, potassium and sodium[29] at -70° in THF to give a red intermediate. The color of this intermediate could be discharged by addition of a 2.0 molar equivalent of tert-butyl alcohol. Quenching this intermediate by jetting to ice water gave an almost quantitative yield of one product. This product was determined to be 9-methyl-9-phenyl-2,4a,4b,7-

(57) Erling Grovenstein, James A. Beres, Yao-Ming Cheng and James A. Pegolotti, J. Org. Chem., 37, 1281 (1972).

tetrahydrofluorene by its elemental analysis, nmr spectrum, uv spectrum, and mass spectrum. Dehydrogenation of this product yielded 9-methyl-9-phenylfluorene. When the red intermediate was quenched in D_2O, a product containing two allylic deuterium atoms was isolated. The proposed mechanism for this reaction is outlined in the following scheme.



These workers found that the same type of reaction occurred with 1,1,1-triphenyl-butane and 1,1,1-triphenyl-pentane.

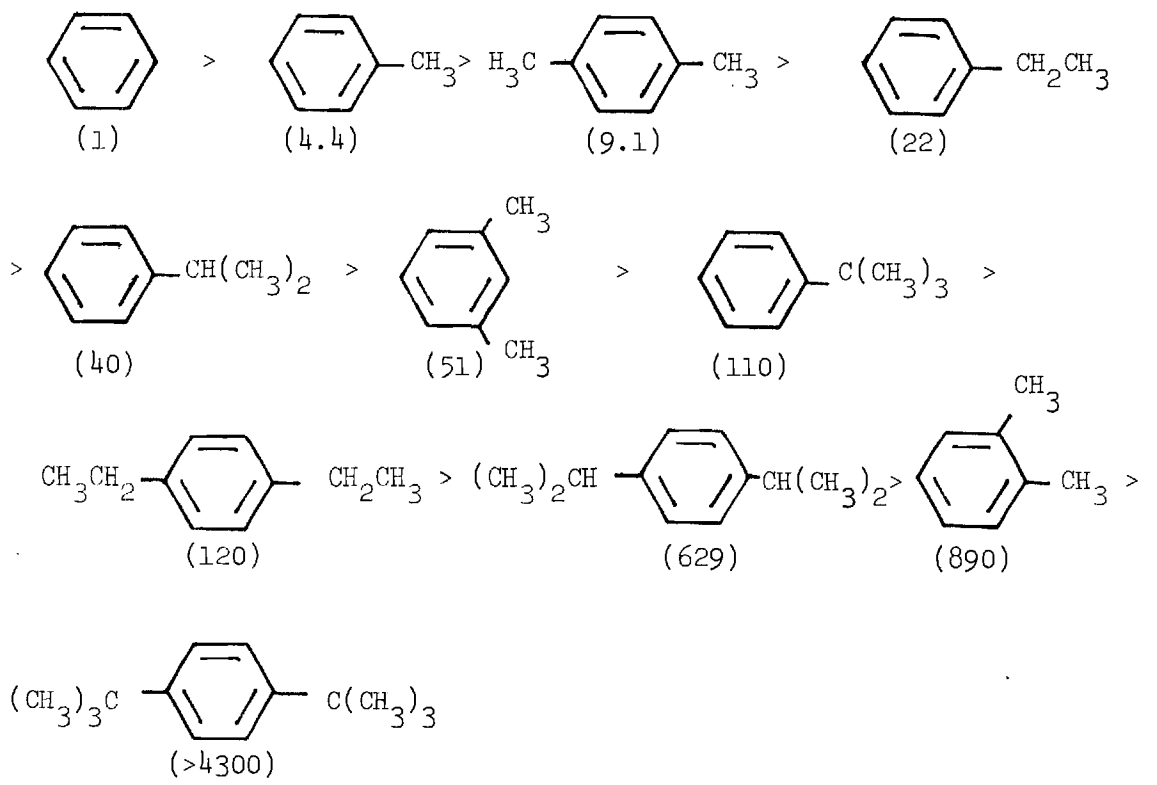
Reactions of Other Phenylalkanes and Fluorene with Alkali Metals

Tuttle[22] found that toluene reacts with potassium in DME at -80° to give an intermediate possessing an esr spectrum. This spectrum was consistent for that predicted for the anion radical of toluene. He also found esr spectra for o-, m-, and p- xylenes under the same conditions. The anion radicals of alkyl substituted benzenes are less

likely to form than benzene. This has been shown by a study[58] of the equilibrium constants (K) of the following reaction in DME at -100° using Na-K alloy as an electron source.

$$R_1R_2C_6H_4 \cdot^- + C_6H_6 \rightleftharpoons C_6H_6 \cdot^- + R_1R_2C_6H_4$$

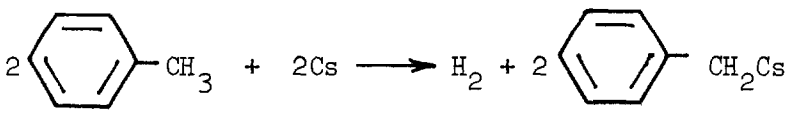
In this study the hydrocarbons were found to be in order of decreasing electron affinity (K):



(58) Ronald G. Lawler and Cynthia T. Tabit, J. Amer. Chem. Soc., 91, 5671 (1969).

The ranking of electron affinity of these compounds can be attributed to two effects: first, the inductive effect of the alkyl group which makes the molecule more resistant to addition of an electron and second, steric effects which destabilize the anion radical intermediate. Since the amount of benzene anion radical formed under these conditions is quite low[27] then the anion radicals of alkyl substituted benzenes would be even lower.

Alkali metal could also react with alkyl benzenes to form benzyllic anions by replacement of a benzyllic hydrogen. However, this has not been observed for the alkali metals lithium, sodium, or potassium. Lithium does not react with toluene under strenuous conditions.[59] Xylenes are used in preparation of Na-K alloy without any apparent reaction.[60] Cesium does react with toluene at 28.5° (the melting point of cesium) to form benzyl cesium according to the following scheme.[19]



Compounds similar to toluene will also react with cesium. Hackspill[20] reports that xylene, ethylbenzene, and tetrahydronaphthalene all form carbanions. These were isolated and identified after carbonation and acidification as the corresponding organic acids. On the other

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(59) Henry Gilman and Bernard J. Gaj, J. Org. Chem., 28, 1725 (1963).

(60) Louis F. Fieser and Mary Fieser "Reagents for Organic Synthesis" John Wiley and Sons, Inc., New York, N. Y., (1967) p. 1102.

nand, tert-butylbenzene and cumene in ether, will react[20] with cesium to form a "non carbonatable product". It appears that dicarboxylic acid derivatives were not investigated.

The benzyl anion can be prepared if there is present in the reaction a hydrogen acceptor. Morton[62,63] found that alkyl-benzenes and -naphthalenes could be metalated by potassium in excess of hydrocarbon or heptane as reaction medium if metal oxides such as Na_2O, BaO, S_2O were present as hydrogen acceptors. Similarly, anion radicals of polynuclear aromatic hydrocarbons have also been used to initiate these reactions.[64,65]

Diphenylmethane, a compound that is the result of replacing methyl hydrogen in toluene with phenyl, is considerably more acidic than toluene. It is metalated quite readily. Lithium[59] reacted with it for a period of five days in THF gives a 59 percent yield of diphenylacetic acid, after carbonation and subsequent acidification. At -20°, potassium will metalate this compound in a 2:1 ratio of THF:DME

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(61) M. R. Arick, J. A. M. van Broekhaven, F. W. Pijper and E. deBoer, J. Amer. Chem. Soc., 94, 7531 (1972).

(62) Chester E. Claff, Jr., and Avery A. Morton, J. Org. Chem., 20, 981 (1955).

(63) Chester E. Claff, Jr., and Avery A. Morton, J. Org. Chem., 20, 440 (1955).

(64) Takeo Saegusa, Tashihiko Waragai and Hideo Kawaguchi, Tetrahedron Lett., 4527 (1968).

(65) Takeo Saegusa, Tashihiko Waragai and Hideo Kawaguchi, Tetrahedron Lett.,4523 (1968).

as solvent after 80 hours in 80.5 percent yield; this was isolated as diphenylacetic acid.[70] Cesium reacts with diphenylmethane at 80-90° to give, with the liberation of hydrogen, diphenylmethyl cesium.[19]

Solutions of diphenylmethane in contact with alkali metal at low temperatures exhibit esr spectra corresponding to the diphenylmethane anion radical.[60,65-69] It has been suggested that the anion radical decomposes in DME through an intramolecular reaction to the diphenylmethyl anion by the following scheme.[70]

$$(Ph_2CH_2)\ \dot{-},\ K^+ \longrightarrow Ph_2CHK + 1/2\ H_2$$

Or, the reaction pathway follows the intermolecular route that is illustrated in this scheme.[70]

$$(Ph_2CH_2)\ \dot{-},\ K^+ + Ph_2CH_2 \longrightarrow Ph_2CHK + Ph_2CH_2 + 1/2\ H_2$$

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(66) John D. Young and Nathan L. Bauld, Tetrahedron Lett.,2251 (1971).

(67) F. Gerson and W. B. Martin, Jr., J. Amer.Chem. Soc., 91, 1883 (1969).

(68) S. P. Solodovnikov, M. I. Kabachnik, Tetrahedron Lett., 1941 (1972).

(69) John D. Young, Gerald R. Stevenson and Nathan L. Bauld, J. Amer. Chem. Soc., 94, 8790 (1972).

(70) I. I. Grandbera, V. B. Golubev, O. P. Kholova, A. B. Dimitriev, A. L. Krasnoshchek and V. A. Moskalenko, Zhurnal Organicheskoi Khimii (Eng. Trans.), 4 1375 (1967).

The assumption that the reaction occurs with the initial formation of an anion radical is supported by the following observations. Diphenylmethane is metalated much more rapidly at -20° to -40° than at 15°.[70] The low temperature promotes the formation of anion radical, as seen in the case of benzene.[27] Secondly, cesium reacts quantitatively with benzene to apparently form the anion radical and toluene reacts with cesium quantitatively to form benzylcesium. Since no other alkali metal reacts with either of these compounds to any extent, it appears that the initial formation of an anion radical is important in both reactions. Thirdly, addition of biphenyl to the reaction between diphenylmethane and potassium increases the rate of formation of diphenylmethylpotassium.[70] Since biphenyl forms a stable anion radical with potassium, this would react as an electron donor, as illustrated in the following scheme, much as diphenylmethane anion radical did in the previous schemes.[70]

$$Ph_2CH_2 + (Ph_2)^{\cdot-}, K^+ \longrightarrow Ph_2CHK + Ph_2 + 1/2\ H_2$$

It has been pointed out by Young and Bauld that the benzyl group is electron donating and therefore the anion radical of diphenylmethane should be less stable than benzene.[66] Since it is more thermodynamically stable there apparently is a stabilizing interaction between the two phenyl rings in the anion radical. These workers investigated diphenylmethane anion radicals prepared (1) with sodium-potassium alloy in MeTHF in the presence of dicyclohexyl-18-crown-6-

ether, and (2) with sodium-potassium alloy in DME. A detailed study of the esr spectra of this compound indicated that the electron was highly localized on one phenyl ring with no more than 2 percent leakage of spin to the other ring. They suggest that since the anchimeric stabilization of diphenylmethane anion radical is at least one kcal and there is apparently no electron leakage between the two rings, then there is an electrical polarization effect. That is, an attraction between a pole and it's induced pi dipole at the o-positions. Thus this o-o' interaction is the stabilizing influence in the diphenylmethane anion radical. These workers have found that 2,2-phenylpropane anion radical cyclizes to 9,9-dimethylfluorene anion radical.[66,69] This lends support to the idea of o-o' interaction between the two phenyl rings.

Although there is essentially no observable leakage of electrons from one ring to the other, there is observable electron transfer between rings.[66-68] The rate of exchange is dependent upon the nature of the ion pair formed. Solvent separated ion pairs (in DME) appear to have a faster exchange rate than contact ion pairs (in THF).[68] On the other hand, in Young and Bauld's work[66] they found no exchange in the system in which the cation is highly solvated by a crown ether and exchange when DME is a solvent. This implies that the position of the cation relative to the phenyl rings is quite important and that the electron is transferred from ring to ring through the cation. Thus, the cation is in a position to hold the two rings so that bond formation may take place as is observed in the case of 2,2-diphenyl-

propane.[66,69]

Isolation of the two phenyl rings by separating them with two methylene groups, as in 1,2-diphenylethane anion radical, eliminates the interaction between the two aromatic rings.[71] This compound is reduced readily to an anion radical in either DME or THF at -78° with potassium.[65] This intermediate adds a second electron and decomposes to benzyl anion at temperatures as low as -60°. This reaction is outlined in the following scheme.[65]

$$PhCH_2CH_2Ph \xrightarrow[-78^\circ]{K} (PhCH_2CH_2Ph)\dot{-}, 2K^+$$

$$(PhCH_2CH_2Ph)\dot{-} \xrightarrow{+K \text{ or } (PhCH_2CH_2Ph)\dot{-}} (PhCH_2CH_2Ph)^{-2}), K^+$$

$$(PhCH_2CH_2Ph)^{-2}, 2K^+ \longrightarrow 2(PhCH_2-), K^+$$

In this compound in which the methylene hydrogens are less acidic than in diphenylmethane, the carbon-carbon bond is broken instead of the carbon-hydrogen bond.

As expected, triphenylmethane is quite acidic and reacts readily with alkali metals to form the triphenylmethyl anion. This compound reacted in Et_2O:THF (20:50) at 25° for 15 minutes gives, after carbonation and acidification, a 77.6 percent yield of triphenylacetic acid.[59] When reacted with potassium in DME at room temperature

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(71) D. J. Williams, J. M. Pearson and M. Levy, J. Amer. Chem. Soc., 93, 5483 (1971).

for 16 hours, a quantitative yield of triphenylmethylpotassium is obtained.[72] Cesium reacts rapidly with triphenylmethane to form triphenylmethyl cesium.[61] The process of metalation appears to occur through an anion radical intermediate as in the case of diphenylmethane. This is supported by the fact that the anion radicals of naphthalene, biphenyl and anthracene react with triphenylmethane at -78° to form this carbanion.[39] A detailed analysis of the water quenched products of this carbanion indicate that there is a small amount of decomposition to lower molecular weight anions. These products are phenylcyclohexane (2%), biphenyl (6%), diphenylmethane (16%).[72]

D. Casson and B. J. Tabner have studied decomposition of the fluorene anion radical to the fluorenyl carbanion.[52] Fluorene, a compound similar in structure to both biphenyl and diphenylmethane, forms an anion radical at -70° in ethereal solvents such as THF, DME, THP and MeTHF. The alkali metals lithium, sodium, and potassium all react with fluorene to form this anion radical. This decomposes at temperatures above -70° to form the carbanion. The rate of decomposition, measured in THF at 25°, was found to increase as the size of the metal cation increased.

In the reaction of alkali metals with aromatic hydrocarbons

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(72) Herbert O. House and Vera Kramer, J. Org. Chem., 27, 4146 (1962).

containing potentially replaceable alkyl hydrogens, it appears that there is not competition between a metalation reaction and an anion radical formation reaction. Rather, the metalation reaction requires an initial anion radical formation. In the case of 1,2-diphenylethane, initial anion radical formation is also required before this decomposes to form benzyl anion. Thus, the anion radical formation of these types of hydrocarbons could be studied with careful control of reaction conditions.

Pyridinyl Radicals

The pyridinyl radical and the benzene anion radical are isoelectronic aromatic radicals. Kosower and coworkers,[73-76] have extensively investigated the chemical and physical properties of the pyridinyl radicals. Itoh and Nagahura have found that 1-alkyl-4-carbomethoxypyridinyl radicals will reversibly dimerize in isopentane solutions at 77°K.[77] Itoh and Kosower[76,78] have studied the

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(73) Edward M. Kosower and Edward J. Poziomek, J. Amer. Chem. Soc., 85, 2035 (1963; 86, 5515 (1964).

(74) W. M. Schwarz, Edward M. Kosower and Irving Shain, J. Amer. Chem. Soc., 83, 3164 (1961).

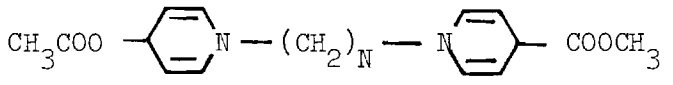
(75) Edward M. Kosower and Irving Schwager, J. Amer. Chem. Soc., 86, 5528 (1964).

(76) Michiya Itoh and Edward M. Kosower, J. Amer. Chem. Soc., 90, 1843 (1968).

(77) Michiya Itoh and Saburo Nagakura, J. Amer. Chem. Soc., 89, 3959 (1967).

(78) Edward M. Kosower and Yusaku Ikegami, J.Amer.Chem.Soc., 89, 461 (1967).

electron pairing found in α,ω-dipyridyalkyl diradicals of the form shown below, where n varies from two to five.



These diradicals were prepared by treating the bis(pyridinium diiodides) with 3 percent sodium amalgam at -40° to 0° for one hour in acetonitrile followed by standing at room temperature for about one week. The course of the reaction was monitored spectrophotometrically. The diradical was isolated by removing the acetonitrile and extracting with isopentane.

The esr spectra of these compounds in isopentane and MeTHF solutions revealed that the spin concentration of these radicals were dependent upon the number of methylene groups separating the two radicals. Since the spin concentrations are directly related to the amount of unpaired radical in solution, the percentage of unpaired radicals could be determined. They found that there was 2 percent unpaired radical when n = 3, 20 percent when n = 4 and 100 percent when n = 5. In the case of the compound where n = 2 the relative strength of the esr signal decreased with increased concentration implying that intermolecular spin coupling occurs.[78] The authors claim that it does not exist in a form that can intramolecularly couple because of steric factors.[76] The dipyridyl radicals have absorption spectra very similar to absorption spectra of pyridinyl radicals. Since the formulation of a covalent bond would have produced a gross

change in the absorption spectra, the electron pairing is proposed to be due to the formation of a charge transfer complex.[78]

Reactions of Olefins with Alkali Metals

Previous researchers[79,80] have proposed that alkali metals form allylic salts with olefins according to the pathway outlined below.

$$M + \text{impurities} \longrightarrow M^+, R^-$$

$$M^+, R^- + R'CH_2CH{=}CH_2 \longrightarrow M^+ (R'CH{=}CH{-}CH_2^-)$$

This intermediate allylic anion then either attacks a second olefin to form a dimer[79] or attacks a second olefin to form an isomeric olefin.[80] A. W. Shaw and coworkers[79] found that propylene will dimerize in the presence of potassium or cesium to 4-methyl-1-pentene in a hydrocarbon solvent at 100°-200° under a pressure of several hundred pounds per square inch. Haag and Pines[80] report that sodium dispersed on alumina, lithium dispersed on alumina, or sodium dispersion in n-octane will isomerize any of the three n-butenes to the other two. Using sodium on alumina, they found that the relative ratios of products and reactant was consistent with theoretical

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(79) A. W. Shaw, C. W. Bittner, W. V. Bush and G. Holtzman, J. Org. Chem., 30, 3286 (1965).

(80) Werner O. Haag and Herman Pines, J. Amer. Chem. Soc., 82, 387 (1960).

equilibrium concentrations.

Hackspill and Rohmer[81] found that cesium reacted with ethylene at 45° for six to eight days, forms a brown solid which these workers claim to be $C_2H_4Cs_2$. This solid reacted completely with water vapor to give C_2H_6, quantitatively, CsOH and hydrogen.

Clusius and Mullet[82] have also implied in their study of the hydrogenation of ethylene using cesium as a catalyst that the intermediate $Cs_2C_2H_4$ is formed.

Proposed Work

The chemistry of the cesium-benzene adduct is of considerable interest because of the following reasons. This possibly would be a method of producing large amounts of benzene anion radical to be used to study its chemistry. Identification of the compound formed by further reaction would provide insight into the reaction of other aromatic hydrocarbons with alkali metals. The reactions of cesium have not been explored to any extent,[83] and a knowledge of this metal's scope of reaction could lead to its utilization as a reagent in alkali metal reaction. Therefore, in this research, the reaction of benzene

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(81) L. Hackspill and R. Rohmer, Compt.Rend., 217. 152 (1943).

(82) Klaus Clusius and Hans Mullet, Helv. Chim. Acta, 39, 363 (1956).

(83) P. C. L. Thorne and K. W. Allen, J. P. Quin, ed., Mellor's Comprehensive Treatise on Inorganic Chemistry, Vol. II Suppl. III, Longman, Green and Co., New York, N. Y., (1963) p. 2287. "In 1946 the world output of cesium in the formal ore was estimated to be about 10 lb. and in 1949 the production of cesium metal in the United States was estimated to be 1 lb. with the potential production of about 1 ton."

and cesium was investigated.

To extend the observations of Grovenstein and coworkers[57] on 1,1,1-triphenylethane, the reactions of 2,2-diphenylpropane, tetraphenylmethane and diphenylmethane with cesium alloy were studied. The study of 2,2-diphenylpropane was undertaken to see if the third phenyl of 1,1,1-triphenylethane could be replaced with a methyl group. Recently, it has been reported [66,69] that the anion radical of 2,2-diphenylpropane cyclizes to 9,9-dimethylfluorene anion radical. This report suggests that the reaction of 2,2-diphenylpropane with cesium alloy may be similar to that of 1,1,1-triphenylethane. The compound tetraphenylmethane was chosen for study since this compound could form a tetra-anion which might cyclize twice to give a spiro-tetra-anion.

Diphenylmethane was selected for study since it does not have steric crowding about the central carbon atom as does 2,2-diphenylpropane, tetraphenylmethane, and 1,1,1-triphenylethane. This compound could react with cesium alloy in two ways. It might form a diradical which could cyclize as expected for the other systems or it might react further to give diphenylmethyl anion.

Since cesium is considered a good electron donor to aromatic systems, there was a possibility that this metal would donate an electron to an olefinic system. With this in mind, the study of the reaction of cis-2-heptene with cesium metal and cesium-potassium-sodium alloy was undertaken.

CHAPTER II

REAGENTS AND SOLVENTS

t-Butyl Alcohol

Baker reagent grade t-butyl alcohol redistilled from molten potassium at 81° through a 60-cm vacuum-jacketed column packed with glass helices. This was purified by Y. M. Cheng.

Biphenylene

Platz and Bauer Co. biphenylene was used without further purification.

Bibenzyl

Aldrich research grade bibenzyl, mp 52.5°, was used without further purification.

Benzoic Acid

A sample of benzoic acid was obtained from the Georgia Institute of Technology chemistry stockroom and found to be pure by gc and nmr analysis.

Benzene

Benzene of "Baker Instra-Analyzed" reagent grade, gc-spectrophotometric quality, was stored over sodium wire and used without further purification.

Biphenyl

Eastman reagent grade biphenyl, mp 69.5°-70.5° (lit[84] 71°) was used without further purification.

p,p'-Diphenyldicarboxylic Acid

A sample of p,p'-diphenyldicarboxylic acid prepared by K and K Laboratories was used without further purification.

Carbon Tetrachloride

Carbon tetrachloride, of "Baker Analyzed reagent, Instra-Analyzed", spectrophotometric grade was used without further purification.

Cesium

MSA Research Corp., 99.9 percent purity minimum, cesium was used.

1,3-Cyclohexadiene

A sample of Matheson, Coleman and Bell 1,3-cyclohexadiene, found to be pure by gc analysis, was used.

1,4-Cyclohexadiene

A sample of 1,4-cyclohexadiene prepared by Chem Samples Co., reported to be 99 percent pure, was used without further purification. This sample decomposed under refrigeration to benzene; however, the gc

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(84) See reference 5, p. C-203.

systems used would separate it from benzene and, therefore, it could be used for its gc retention time.

Cyclohexane

Phillips Petroleum, 99.5 wt. percent minimum, cyclohexane was used without further pruification.

Cyclohexene

Phillip 66, 99 percent pure, cyclohexene was distilled from a spinning band column. This was purified by A. J. Mosher.

Deuterium Oxide

Stock deuterium oxide found to be 99.4 percent isotropically pure by nmr analysis was used.

Deuterochloroform

Diaprep grade deuterochloroform was stored over 3A molecular sieve.

Dicyclohexyl

Aldrich 97 percent dicyclohexyl (mp 3-4°) was used without further purification.

2,2'-Dimethylbiphenyl

K and K Laboratories 2,2'-dimethylbiphenyl was used without further purification.

4,4'-Dimethylbiphenyl

Aldrich 97 percent 4,4'-dimethylbiphenyl, mp 118°-120°, was

used without further purification.

Dimethyl Sulfoxide

Eastman practical grade dimethyl sulfoxide was used without further purification.

Diphenic Acid

Aldrich 98 percent diphenic acid was used without further purification.

Diphenylmethane

Eastman practical grade diphenylmethane, distilled at 70° and 100 microns and stored over 4A molecular seives, was used. This was found to be pure by gc analysis.

2,2-Diphenylpropane

Aldrich 95 percent 2,2-diphenylpropane was stored over 4A molecular sieves and used without further purification. A gas chromatography analysis of this sample had 0.2 relative area percent impurities.

n-Heptane

Chemical Samples Co., 99.9 percent pure, n-heptane was used without further purification.

1-Heptene

Chemical Samples Co., 99 percent pure, 1-heptene was used without further purification.

cis-2-Heptene

Chemical Sample Co., 95 percent, cis-2-heptene was used without further purification.

trans-2-Heptene

Chemical Sample Co., 99 percent, trans-2-heptene was used without further purification.

cis-3-Heptene

Chemical Sample Co., 95.7 percent, cis-3-heptene was used without further purification.

trans-3-Heptene

Chemical Samples Co., 99 percent, trans-3-heptene was used without further purification.

Iodomethane

Eastman reagent grade iodomethane dried with 4A molecular sieves was used without further purification.

Isooctane

Phillips Petroleum Co., 99 percent plus, isooctane was used without further purification after drying over sodium wire.

Isophthalic Acid

A sample of isophthalic acid obtained from the Organic Stockroom of the School of Chemistry, Georgia Institute of Technology, was

used without further purification.

4-Methylbiphenyl

A sample of 4-methylbiphenyl prepared in Dr. E. Grovenstein's laboratory was used without further purification.

Palladium

Engelhard Industries, Inc., 5 percent Palladium on charcoal, was used.

n-Pentane

Phillip Petroleum Co. n-pentane, 99 percent minimum purity, was stored over sodium wire.

Perdeuteroacetone

A sample of incompletely labeled perdeuteroacetone (96.7 percent CD_3COCD_3) from the Organic Stockroom of the School of Chemistry, Georgia Institute of Technology, was used.

Perdeuterobenzene

Stohler Isotope Chemicals, 99.5 percent deuterium, perdeuterobenzene was distilled from potassium and stored over sodium wire.

Perdeuterobiphenyl

Merck, Sharp and Dome, Isotope Division, perdeuterobiphenyl, 99 percent D minimum isotopic purity, was used without further purification.

Perdeuterodimethylsulfoxide

Diaprep, 99.5 percent minimum isotipic purity, perdeuterodimethylsulfoxide was stored over 3A molecular sieves.

Perdeuterotetrahydrofuran

A sample of perdeuterotetrahydrofuran prepared by Norell Chemical Co., Inc., was used (99 atom percent deuterium isotopic purity).

Phenylcyclohexane

Chemical Samples Co., 99 percent, phenylcyclohexane was used without further purification.

1-Phenylcyclohexene

Chemical Samples Co., 99 percent pure, 1-phenylcyclohexene was used without further purification.

Phthalic Acid

A sample of phthalic acid from the Organic Stockroom of the School of Chemistry, Georgia Institute of Technology, was used.

Potassium

Baker reagent grade potassium was used.

p-Quaterphenyl

Aldrich, 97 percent, p-quaterphenyl was used.

Sodium

Baker reagent grade sodium was used.

Sodium Aluminum Hydride

Alfa Inorganic sodium aluminum hydride was used.

Tetrahydrofuran

Fisher certified tetrahydrofuran dried over sodium wire was used.

Tetramethylsilane

Aldrich NMR grade, 99.9 percent minimum, tetramethylsilane was used without further purification.

Tetraphenylmethane

Aldrich, 99+ percent, tetraphenylmethane was used.

Terephthalic Acid

A sample of terephthalic acid obtained from the Organic stockroom of the School of Chemistry, Georgia Institute of Technology was used.

o-Terphenyl

Eastman reagent grade o-terphenyl was used.

p-Terphenyl

Eastman reagent grade p-terphenyl was used.

Triphenylethane

Triphenylethane prepared in the laboratory of Dr. E. Grovenstein

by Mr. Ronald J. Carter, was purified by vacuum sublimation.

Triphenylmethane

Eastman reagent grade triphenylmethane was used.

Toluene

Toluene of "Baker Instra-Analyzed", gc spectrophotometric quality was used.

o-Xylene

Phillips Petroleum, 99 mole percent, o-xylene was used.

m-Xylene

Eastman reagent grade m-xylene was used.

p-Xylene

Aldrich p-xylene (99 percent) was used.

CHAPTER III

GENERAL PROCEDURE FOR REACTIONS AND INSTRUMENTAL ANALYSIS OF PRODUCTS

General Procedure

In all of the reactions of hydrocarbons and cesium or Cs-K-Na alloy studied, the experiments were carried out in a glove box under a nitrogen atmosphere. The apparatus normally consisted of either a 4- or 5-necked creased Morton flask fitted with a Morton high-speed stirrer, a pressure equilizing dropping funnel, a Friedrich condensor, a thermometer well, and a 4-mm bore Teflon stopcock for sampling, when it was needed. A nitrogen source was connected to the reaction vessel through a mercury valve.

The reaction procedure was essentially the same in all experiments. The apparatus was thoroughly flame dried under a flow of nitrogen. Then the glove box (Lab Con Co., ca 12 ft^3 volume) was sealed and flushed with ca 24 ft^3 (at 70°F and atmospheric pressure) of nitrogen until the oxygen content was too low to sustain combustion of a match. When the reaction was run in a solvent, a flask containing tetrahydrofuran (THF) and $NaAlH_4$ (ca 1 gm) was attached to the condensor and the THF was distilled into the reaction vessel. If needed, 10 to 20 ml of THF was withdrawn. The cesium or cesium alloy was added and the THF and alkali metal were heated, while stirring, at reflux for one hour. The reaction mixture was then cooled to the

reaction temperature and the hydrocarbon to be reacted was added in the withdrawn THF. During the reactions, samples were taken for further study at various intervals of time. All reactions were carried out with vigorous stirring. The reactions were terminated by fitting a syphon into the flask and jetting the contents into a flask containing a quenching reagent, usually water.

Samples quenched with H_2O or D_2O were worked up by salting out the organic phase. In most instances, this phase was used directly for gas chromatography. However, if extraction of the sample was necessary, the aqueous phase was then extracted with pentane and the organic extracts were combined, dried over magnesium sulfate and filtered. The filtrate was either analyzed as is, concentrated to a small volume or concentrated to dryness depending on the expected products.

The samples quenched with Dry Ice were extracted with ether and then acidified with concentrated HCl. The acids were isolated by extraction with ether, dried ($MgSO_4$) and the ether distilled off under vacuum. Gas chromatogarphy samples were prepared by esterification with diazomethane. The work up of samples quenched with iodine, dimethyl sulfate and methyl iodide will be described in Chapter IV.

Instrumental Analysis

All nmr spectra were obtained on a Varian Associates Model A-60 D Analytical NMR Spectrometer using tetramethylsilane as an

internal standard.

Infrared spectra were taken on a Perkin-Elmer Grating Infrared Spectrophotometer model 237B and were calibrated with the 1101.4 cm^{-1} band of polystyrene.

Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer.

A Magnion ESR Spectrometer at X Band (ca 9600MHz) was used to obtain electron spin resonance spectra. A solution of 2,2-diphenyl-1-picrylhydrazyl (free radical) in benzene was used as a standard to determine the radical concentration of the samples studied. The yield of radical anion was calculated from the radical concentration and the concentration of the limiting reagent in the reaction. The theory and calculation of esr analysis are discussed in Appendix B.

Mass spectra were obtained on a Varian A-66 mass spectrometer. When gas chromatography was used for separation for mass spectra, a Varian Aerograph Series 200 gas chromatograph with a Varian V-5500 MS/GC Interface was attached. Reference standards were perfluorotributylamine (3)* and 1,1,2,2-tetrabromoethane (8)*.

Gas chromatographic analysis of the reaction products was accomplished by using either a F & M Research Chromatograph Model 810 (F & M), a Perkin-Elmer Model 881 Gas Chromatograph (P-E) or a Perkin-Elmer Model 154 Vapor Fractometer (PE 154); both gc instruments utilized flame ionization detectors (hydrogen flame). The columns

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* Varian mass spectra reference sample numbers.

used are given in Table 5 and the typical operating conditions are given in Table 6.

Two types of yields are calculated by gas chromatography, "absolute" and "relative". An "absolute" yield is expressed as a function of the limiting reagent in the reaction. This reagent is determined by an alternate method. For example, if cesium is the limiting reagent, it is titrated as cesium hydroxide with standardized hydrochloric acid. The amounts of products formed are determined by comparison of peak area per weight of solution of each product with the peak area per weight of a standard. This standard is a product of the reaction or the aromatized form of the product determined. The assumption is made that the peak area per mole of an aromatic hydrocarbon is the same for its reduction products. The gc standards for the work with benzene was benzene and biphenyl; for work with other hydrocarbons, the starting hydrocarbon was the usual standard.

If only the approximate relative composition of the volatile products was determined, only gc area percent or area ratios were used; percentage yields so determined are called "relative area percent" yields.

Table 5. Columns for Gas Chromatographic Analysis of Reaction Products.

Column	Liquid Phase[a]	Solid Phase[b]	Mesh	Length	(Outside diameter)
I	10% Carbowax 20M	Chromosorb G	60-80	6 ft.	(1/4 in.)
II	10% Carbowax 20M	Gas Chrom Q	100-120	12 ft.	(1/8 in.)
III	10% SE30	Chromosorb G	60-80	6 ft.	(1/4 in.)
IV	5% SE30	Varaport #30	100-120	6 ft.	(1/8 in.)
V	3.6% OV17	Chromosorb W	100-120	4 ft.	(1/8 in.)
VI	3.6% OV17	Chromosorb W	100-120	12 ft.	(1/8 in.)
VII	15% FFAP	Chromosorb W	100-120	12 ft.	(1/8 in.)
VIII[c]		Silica gel		2 m.	(1/4 in.)
IX	33% Dimethylsulfolane	Chromosorb	60-80	6 ft.	(1/4 in.)
X	33% Dimethylsulfolane	Chromosorb	60-80	16 in.	(1/4 in.)
XI	10% Ucon oil LB 550X	Chromosorb W	60-80	6 ft.	(1/4 in.)
XII	10% DEGS	Diatoport S	60-80	6 ft.	(1/8 in.)
XIII	10% DEGS	Chromosorb W	60-80	22 in.	(1/4 in.)

(a) Carbowax = polyethyleneglycol, MW 20,000; SE-30 = silicon rubber gum (methyl); OV17 = silicon rubber gum (50:50-Methyl:Phenyl); FFAP = polyethylene glycol terminated with tetephthalalate esters; Ucon oil = polypropylene glycol; DEGS = diethyleglyol succinate.

(b) The solid phases except silica gel, had been acid washed and treated with dimethyl dichlorosilane.

(c) Perkin-Elmer 154, column J, no mesh size available.

Table 6. Typical Operating Conditions for Gas Chromatographic Analysis.

Material Analyzed	Column Number	Instrument	Column Temp.	Injector Temp.	Detector Temp.	Carrier gas[a] flow (mm)
Benzene and reduced benzene	XI	PE	52°	80°	85°	0.5
	VII	PE	61°	85°	78°	2.0
Biphenyls and reduced biphenyls	I	F&M	178°	225°	225°	2.0
	IV	PE	123°	198°	149°	1.0
	V	PE	160°	180°	200°	2.0
Mixtures of benzene, biphenyl and reduction products	I	F&M	60° (10 min) 40°/min to 170°	230°	230°	3.5
	V	PE	30° (3 min) 10°/min to 180°	120°	125°	2.0
Triphenylethane and reaction products	IV	PE	180°	230°	205°	1.0
	III	F&M	200°	220°	220°	3.0
	IV	PE	145°	200°	155°	2.0

Table 6. (Continued)

Material Analyzed	Column Number	Instrument	Column Temp.	Injector Temp.	Detector Temp.	Carrier gas[a] flow (mm)
Diphenylpropane and reaction products	I	F&M	50° (4 min) 40°/min to 200°	240°	240°	1.8
	III	F&M	130°	220°	220°	3.0
	I	F&M	180°	250°	230°	2.0
Diphenylmethane and reaction products	I	F&M	189°	250°	230°	2.0
	III	F&M	122°	240°	222°	2.3
	III	F&M	100° (2 min) 15°/min to 240°	250°	240°	2.3
	IV	PE	120°	200°	155°	1.6
Heptenes	XI	F&M	30°	150°	105°	0.7
	IX	F&M	55°	150°	130°	3.0
Methyl benzoate and methyl phthalates	IV	PE	130°	175°	165°	3.1
	XII	PE	179°	235°	184°	3.0

Table 6. (Concluded).

Material Analyzed	Column	Instrument	Column Temp.	Injector Temp.	Detector Temp.	Carrier gas [a] flow (mm)
Esters above, 4-methyl, 4'-biphenyl methyl-carboxylate and 4,4'-dimethylbiphenyl dicarboxylate	III	F&M	60° (1 min) °/min to 215°	245°	220°	2.2
Hydrogen	VII	PE154	25°	25°	25°	3.0, (4.0 psig)

Columns II and VI were used in gas chromatography-mass spectroscopy under conditions similar to I and V respectively.

(a)All carrier gas flows were with a gas pressure of 40 psig, except when noted.

CHAPTER IV

EXPERIMENTAL DETAILS

Reactions of Benzene and Cesium

Reaction of Benzene and Cesium in Tetrahydrofuran at -20°C

Isolation and Identification of 1,1',4,4'-Tetrahydrobiphenyl. In experiment 4-5,* an excess of benzene (43.38 g, 555.3 mmol) was added to a mixture of cesium sand** (10.60 g, 79.7 mg-atoms) and tetrahydrofuran (THF) at -75°. The reaction mixture was stirred vigorously for one hour at temperatures between -70° and -75°. This procedure produced a fine black precipitate. Quenching a sample of this with water produced a mixture of benzene, 1,4-dihydrobenzene, and traces of eight compounds of higher molecular weight. According to gc analysis on a Carbowax 20 M column (I)*** (temperature programmed: 55° for 10 minutes, then 40° per minute to 200°), the relative area percent yields (retention time in minutes) of the 1,4-dihydrobenzene were 76.6 (4.1) and eight unidentified components, 23.4 (13.6 - 16.4). Then the temperature of the reaction was raised to -20° ± 3° over a 23 minute period and maintained at this temperature for two hours. The color of

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* This first number in this code is the research notebook number and the second is the page number.

** Cesium sand was prepared by stirring molten cesium and THF at reflux for one hour and quickly cooling this mixture to between -70° and -75° without stirring.

*** A complete identification of columns is in Table 5.

the reaction gradually turned to a yellow-green. Five ml of this was quenched in five ml of D_2O. The remainder of the reaction mixture was jetted into 200 ml of H_2O through a siphon.

After pentane extraction of the H_2O quench and concentration of the extract, 3.29 g of a viscous oil was obtained. This oil contained the following compounds according to gas chromatography (gc) analysis on a temperature programmed (55° for eight minutes, then 40° per minute to 200°) Carbowax 20 M column (I) the following compounds listed as relative area percentages (retention time in minutes, identification): 9.8 (3.5, THF), 1.4 (4.6, 1,4-dihydrobenzene), 25.5 (5.5, benzene), 19.7 (14.6), 14.3 (15.8), 29.2 (16.4). This sample when analyzed by gc on a Carbowax 20 M column (I) at 165° appeared to have only one component (retention time of 6.5 minutes) besides solvent. It appears that the three components (retention times of 14.6 minutes, 15.8 minutes, and 16.4 minutes) found in the temperature programmed gc study are all due to one compound. The two components of shorter retention time are formed by pyrolysis of the third component under the conditions of the gc analysis.

Distillation of this oil on a Hickman Still at 48° to 68° (80 μ) gave 1.91 g (39.7% yield) of a clear liquid containing four components by gc analysis on column I (temperature programmed: 10 minutes at 50°, then 40° per minute to 170°). These were listed as relative area percents (retention time, identification): 10.4 (13.1, 1,4-dihydrobenzene), 5.2 (14.7, benzene), 1.4 (17.4), 84.1 (30.6, new product). Considering the conditions used for distillation there should be no

six-carbon compounds in this sample. It appears that the new product decomposes to benzene and 1,4-dihydrobenzene during gc analysis.

Anal* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92; Found: C, 90.83, 90.84; H, 9.08, 9.05.

This compound exhibited the following uv spectra max (isooctane); 260 mμ (ε 502.89**),214 mμ (ε 3034.8). The nmr spectrum (neat) [2.88τ (s, 0.04 H, benzene impurity); 4.37τ (complex m, 8.0 H, vinylic); centered at 7.38τ (m, 6.0 H, allylic)] of the protonated product and the nmr spectrum (in $CDCl_3$)[2.80τ (s, 0.1 H, benzene impurity), 4.30τ (complex 8, J=11, 8.0 H, vinylic), centered at 7.2τ (three broad peaks, 4.0 H, allylic)] of the deuterated product*** are consistent for 1,1', 4,4'-tetrahydrobiphenyl and 1,1'-dihydro-4,4'-dideuterobiphenyl, respectively. The mass spectrum [m/e (rel intensity) 81, (11); 80, (69); 79, (100); 78, (55); 77, (88)] obtained by direct introduction

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* Analysis performed by Atlantic Microlab, Inc., Atlanta, Ga.

** According to the literature,[85] the λ max and ε for 5-methyl-1,3-cyclohexadiene is 259 mμ and 4910. This chromophore could be in the product from the thermal isomerization of 1,1',4,4'-tetrahydrobiphenyl or as initial product of the reaction. With this in mind, a sample of the above oil after being refrigerated for one year was repurified by preparative gc; there had been decomposition to biphenyl and 1,4-dihydrobiphenyl. The uv spectrum of this [λ max, 261 mμ; (ε 1432)] shows an increase in compounds with this chromophore. This indicates that it is a thermal degradation product (ca 5 or 10% of the isolated material) which was apparently produced during the workup of the reaction.

*** This sample was isolated by removing the organic phase of D_2O quench; extracting the aqueous phase with pentane; then, combining the organic phases; drying ($MgSO_4$); and removing the solvent in vacuo at temperatures no greater than 30°.

(85) Harlan L. Goering, Jean P. Blanchard and Ernest F. Silverman, J. Amer. Chem. Soc., 76, 5409 (1954).

into the mass spectrum did not have a molecular ion; the most intense ion, m/e 79 ($C_6H_7^+$) is an expected cleavage product. However, when the mass spectrum was rerun by a gas chromatographic-mass spectrometry (gc-ms) on a Carbowax 20 M column (II), the molecular ion (m/e, 158) is obtained.* The gc-ms of the deuterated product indicates that it has a molecular ion of 160 under the same conditions. An IR spectrum of this compound is reported in Appendix C.

Dehydrogenation of 0.113 g of this oil with 0.112 g of 5% Pd/C by heating at 160° for 3.75 hours without solvent at atmospheric pressure yielded by sublimation 48.9 mg (44.2%) of biphenyl, mp. 67-68°, mixture mp 69°, (literature[83], 71°); molecular ion, 154. Hydrogenation of this oil (0.271 g) at atmospheric pressure and room temperature with 5% Pd/C (117.4 mg) in 50 ml of 95% EtOH gave, after filtration and removal of the solvent on a rotary evaporator, 172.5 mg of an oil. It appears the unrecovered material was absorbed on 5% Pd/C. This oil was dissolved in $CDCl_3$ for nmr analysis. The spectrum was: 2.68τ (s, 1.0 H, phenyl), 7.79τ (s, 1.7 H), 8.2τ and 8.8τ (broad multiplets, 19.5 H). This appears to be a mixture of phenylcyclohexane [nmr spectrum of authentic sample ($CDCl_3$): 2.70τ (s, 5 H), 7.5τ (broad s, 1 H), 8.0τ to 8.8τ (broad m,10 H)] and dicyclohexyl [nmr spectrum of authentic sample ($CDCl_3$): 8.25τ and 8.9τ (two overlapping broad multiplets)] in a 1:7 ratio; the broad singlet at 7.5τ of phenylcyclohexane is presumably in the overlapping spectrum of the products. The gc analysis on a

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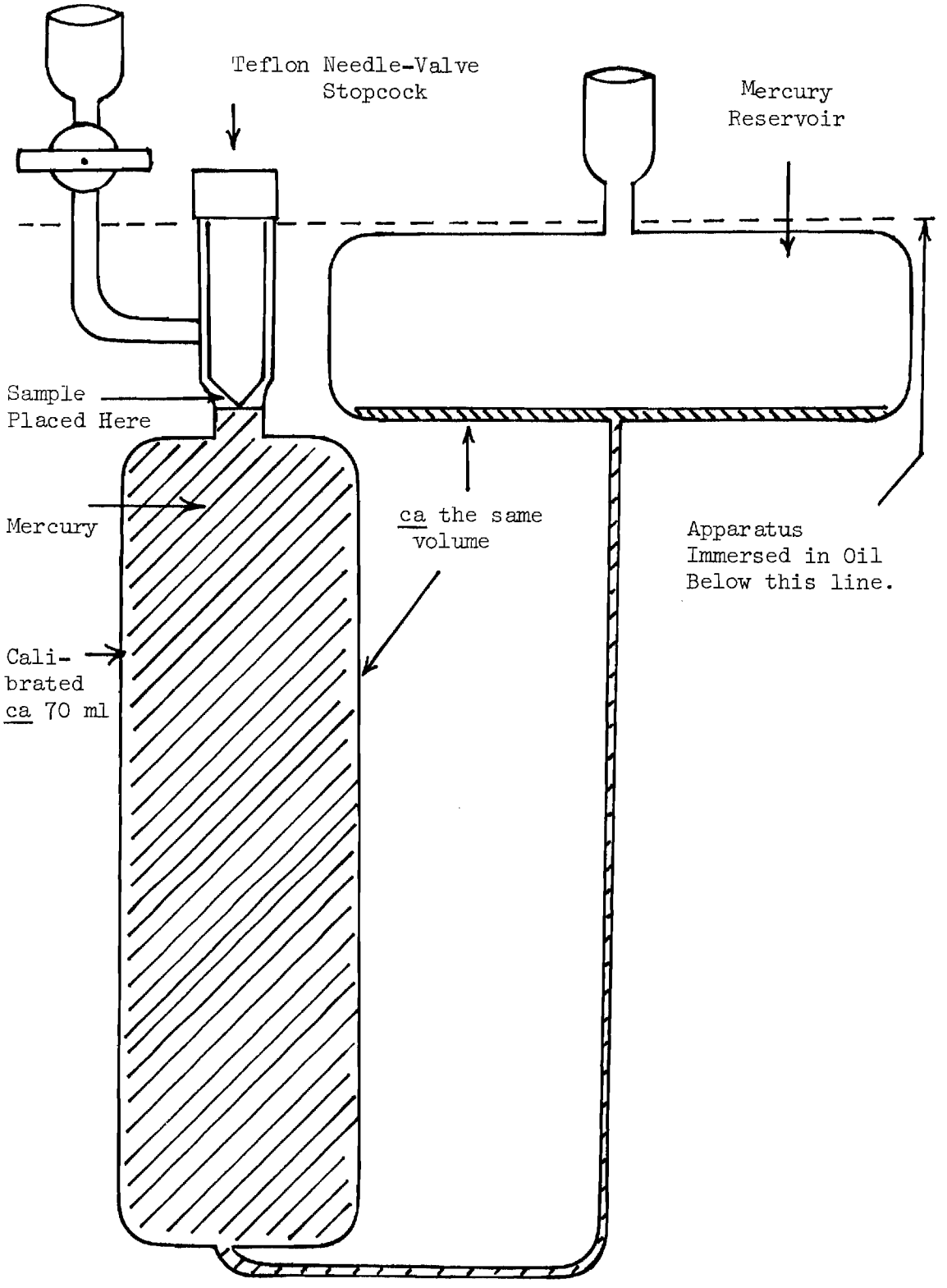
* The mass spectrum of this compound, obtained by gc-ms analysis is given in tabular form in Appendix A.

Carbowax 20 M column (I) at 172° of the nmr sample diluted in acetone indicated that it contained relative area percent yields of 22.1 for phenylcyclohexane and 77.9 for dicyclohexyl. Apparently there are hydrocarbons not observed by gc in this sample. Any cyclohexane would have been distilled off with the solvent.

The product of this reaction, supported by the evidence outlined above, is 1,1',4,4'-tetrahydrobiphenyl.

The pyrolysis of 1,1',4,4'-tetrahydrobiphenyl was performed as part of experiment 4-5; 72.34 mg (0.457 mmol) of this compound was heated in a specially designed glass pyrolysis apparatus, shown in Figure 1. The sample was placed on the mercury in the calibrated tube and this sealed with the needle valve stopcock. Then, the entire apparatus was placed in an oil bath and heated slowly to 166°. At 154° gas evolution began; after five hours at 166° gas evolution stopped to give 0.715 mmol of gas. The system was cooled to room temperature (no gas present) and the products washed out of the apparatus with pentane. Analysis of these by gc (Carbowax 20 M (I), temperature programmed, 10 minutes at 50° and then 40° per minute to 170°) gave products listed as area percents (retention time in minutes, identity by mixed gc injection) 5.5 (8.6, 1,3-cyclohexadiene), 6.0 (12.0, 1,4-cyclohexadiene), 27.7 (13.3, benzene), 8.1 (25.3), 21.4 (27.5), 13.0 (28.9), 12.6 (30.4, 1,1',4,4'-tetrahydrobiphenyl), 5.5 (35.9). The unidentified compounds are not biphenyl, 1-phenylcyclohexene, or 1,4-dihydrobiphenyl according to mixed-injection-gc studies. Their retention times indicate that these compounds are derivatives of


Teflon Needle-Valve
Stopcock
Mercury
Reservoir
Sample
Placed Here
Mercury
Cali-
brated
ca 70 ml
ca the same
volume
Apparatus
Immersed in Oil
Below this line.

biphenyl and not benzene. With the exception of the component of retention time of 35.9 minutes, the unknown compounds produced by pyrolysis have slightly shorter retention times than the starting material. This is also the case for the components found by pyrolysis during gc analysis at 200°.

Study of the Temperature Dependence of the Reaction of Cesium and Benzene in THF

The Use of H_2O, D_2O, CO_2, I_2, and $(CH_3)_2SO_4$ as Quenching Agents.

In experiment 3-162, 43.95 g of benzene (562.7 mmol) was added to 250 ml of THF containing 11.09 g of cesium sand (83.43 mg-atoms) at -72°. This was stirred at this temperature for four hours and then heated over a 10 minute period to -35° ± 5°. This temperature was maintained for 70 minutes and then heated again to 5° ± 5° in a five minute period. After 55 minutes at this temperature, it was heated to 38° over a 15 minute period and held at this temperature for an additional 50 minutes. Initially the reaction color was black; at -35°, it was also black; at 5°, the mixture had turned a reddish-brown and at 31° it again became black. The reaction was quenched in 200 ml of H_2O. Throughout the reaction, groups of three 5-ml samples were taken and quenched. The quenching reagents were 5 ml of H_2O, 5 ml of D_2O, and 600 mg of I_2. The samples were withdrawn at the temperatures: -70° after 1.5 hours; -70° after four hours; -35° after 70 minutes; 5° after 55 minutes; 38° after 50 minutes. The D_2O and H_2O quenches were separated into two phases by addition of excess NaCl and the organic phases were directly analyzed. The I_2 quench was worked up by decom-

posing the excess I_2 with aqueous acetic acid, NaI and $Na_2S_2O_3$, then making strongly basic with KOH pellets, and the top layer studied by gc analysis. All were gas chromatographed on a temperature programmed (50° for four minutes, then 40° per minute to 200°) 10% Carbowax 20 M column (I).

Table 7 gives the results of the H_2O samples. In this table the following method of calculating yields is used. The gc area of each volatile product including benzene (excluding THF) was measured. The total gc area was assumed to equal the area of the total amount of initial benzene in the reaction. The ratio of mol of a particular product to g-atom of initial cesium was then calculated by using the equation:

$$\frac{\text{mol of product}}{\text{g-atom of initial cesium}} = \frac{A_p}{A_t} \times \frac{M_{Bz}}{M_{Cs}} \times \frac{1}{S}$$

where A_p = gc area of the product in question, A_t = total gc area of all volatile material excluding THF, M_{Bz} = mol of initial benzene, M_{Cs} = g-atoms of initial cesium, and S = 1 for benzene and reduced derivatives or S = 2 for biphenyl and reduced derivatives. The formula used to calculate the mol of product per g-atom of initial cesium is based on the assumption that the gc area per mol of biphenyl and reduced derivatives equals twice the area per mol of benzene and reduced derivatives. This assumption has been substantiated experimentally in two separate experiments. In experiment 3-112, the compounds, benzene and biphenyl,

Table 7. The Yields of Products Found at Various Reaction Temperatures in Experiment 3-162 after Quenching with H_2O.

Component	Retention[a] time in min	Yields ($\frac{\text{mol of product}}{\text{g-atom of initial cesium}}$) 1.5 hr -72°	4 hr -72°	70 min -35°	55 min 5°	50 min 38°
1,4-dihydrobenzene	5.7	0.349	0.297	0.225	0.182	0.124[b]
cyclohexene	2.8	0.0085	0.0126	0.0137	-	0.0202[b]
phenylcyclohexane	ca 11.0	<0.0038	<0.0037	<0.0038	<0.004	<0.0046[b]
1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound[d]	11.1, 11.5-12.8, 12.8-13.5[c]	0.0277	0.0603	0.141	0.196	0.150[b]
1,4-dihydrobiphenyl	14.2	-	-	0.0038	0.0116	0.0782[b]
1-phenylcyclohexene	14.9	-	-	-	0.0024	0.0313[b]
$C_{12}H_{12}$, unidentified	15.9	-	-	-	0.0028	0.0175
biphenyl	17.5	-	-	-	0.0056	0.102

(a) GC analysis performed on a temperature programmed (50° for 4 minutes, then 40° per minute to 200°) Carbowax 20 M column (I).

(b) These products were identified by mixed injections.

(c) At this high column temperature, this product decomposed to three broad groups of peaks. Yields are a sum of these.

Table 7. (Concluded).

(d) The mass spectrum of the unidentified $C_{12}H_{14}$ compound, obtained by gc-ms analysis, is different in the 38° (50 minutes) sample from the mass spectrum, obtained by gc-ms analysis of the compound isolated from the reaction between benzene and cesium at -20° in expt. 4-5 although these two compounds have the same gc retention time. The mass spectra of this component of the 38° (50 minutes) sample is in Appendix A.

analyzed at the same time on a temperature programmed (four minutes at 30°, then 10° per minute to 250°) OV 17 column (V) had gc areas per mmol of 67.9 and 130, respectively. In experiment 4-59, the areas per mmol for these two compounds were respectively, 0.723 and 1.37 on a Carbowax 20 M column (I), measured at 50° for benzene and 172° for biphenyl with all other conditions the same. These relative areas of 1.92 and 1.89 differ from the assumed ratio of 2.00 by only some 5%.

Table 8 contains the results of the I_2 final quenches. The yields in mol of product per g-atom of initial cesium are calculated in this table using the same equation as for Table 7.

In Table 9, the yield (in mol of product per mol of titrated cesium hydroxide) of the H_2O quench are tabulated. The study described in Table 9 was done six months after completion of the reaction. These yields were calculated by comparison of the gc areas of products in solution with the gc area of an external biphenyl standard of known concentration. In both cases, the gc sample injected into the gas chromatograph was weighed. From this data, the molar concentration of the product in the sample is determined as if it were biphenyl. The total number of mol of each product is determined from this and the total weight of the product solution which was isolated by extraction of the aqueous reaction quench. Titration of the aqueous fraction of this with standardized HCl for CsOH, using phenophthalein as an indicator, gives the total number of g-atoms of cesium isolated. The yield is calculated from the total number of mol of each product (as

Table 8. Yields of I_2 Quenches Found at Various Reaction Temperatures in Experiment 3-162.

Component	Yield ($\frac{\text{mol of product}}{\text{g-atom of initial Cs}}$)				
	1.5 hr −70°	4 hr −70°	70 min −35°	55 min 5°	50 min 38°
1,4-dihydrobenzene	0.036	0.022	0.014	0.041	0.024
benzene			In excess		
1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound	-	-	-	-	0.0035
1,4-dihydrobiphenyl	-	-	-	-	0.005
biphenyl	-	-	-	0.0235	0.174

Table 9. Yield[a] of Final Aqueous Quench in Experiment 3-162.

Component	Retention time[b] in min.	Yield	Relative Amounts	Table 7 Relative Amounts
1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound	6.9	0.033	0.57	1.48
1,4-dihydrobiphenyl	9.2	0.042	0.74	0.77
1-phenylcyclohexene	10.6	0.02	0.34	0.37
$C_{12}H_{12}$, unknown	12.7	0.007	0.12	0.15
biphenyl	16.4	0.058	1.00	1.00

(a) This yield is in mol of product per mol of titrated CsOH.

(b) Analysis performed with a Carbowax 20 M column (I), that was at 178°.

Table 10. Molecular Ions of Compounds of H_2O and D_2O Quenches in Experiment 3-162.

Component[a]	MW of H_2O Quench		MW of D_2O Quench
	55 min, 5°	50 min, 38°	50 min, 38°
1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound (or $\underline{d}_4$)	158	158[b]	162
1,4-dihydrobiphenyl (or $\underline{d}_2$)	156	156	158
1-phenylcyclohexene (or $\underline{d}_4$)	-	158	162
$C_{12}H_{12}$ (or $\underline{d}_2$)	-	too small	158, 162 (trace)
biphenyl (or $\underline{d}_4$)	-	154	158[c]

(a) Analysis performed with a Carbowax 20 M column (II), that was at 145°.

(b) The mass spectrum of this gc component obtained by gc-ms analysis, is given in Appendix A.

(c) This is apparently due to some decomposition of tetradeuterated products to biphenyl.

biphenyl) and the total number of g-atom of cesium.

Table 10 contains the molecular weights found by gc-ms on the 55 minute, 5°; and the 50 minute, 38°; H_2O and D_2O samples.

In experiment 4-82, 43.21 g of benzene (553.2 mmol), distilled from molten potassium and stored over sodium, were added to 10.16 g of cesium sand (76.4 mg-atoms) in 250 ml of THF at -70°. This was stirred vigorously at temperatures between -70° and -75° for two hours. At this point an esr sample was taken and maintained at -70° or lower. The esr spectrum at -196° indicated a 2.3 x 10^2% yield* of anion radical. Calculation of the theoretical yield assumes that all cesium has reacted to form an anion radical, the stoichiometry between benzene and cesium is 1:1, and the product is homogeneously mixed in the reaction solvent when the sample is taken. The last assumption probably is not generally true. The mixture was warmed to

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* The general procedure used in the study of esr samples was as follows. A dry quartz esr tube is flushed with nitrogen which is led to the bottom of the tube via a canula and then cooled under a stream of nitrogen in a Dry Ice-acetone bath in the glove box. When samples are taken from reactions at room temperature, the cooling is not necessary. A sample is transferred into the esr tube through a canula fitted through a septum attached to one neck of the reaction flask. The solution is forced through the canula by increasing the nitrogen pressure in the reaction flask. The esr tube is tightly capped and removed from the glove box. In order to protect the sample from oxidation, the esr tube is flame sealed while in a Dry Ice-acetone bath. The esr spectrum of the sample is then run as soon as possible (from one to three hours) after sampling. After being sealed, the sample is stored in a liquid nitrogen bath. The spin concentration was measured relative to a 0.04828 molar solution of diphenylpicrylhydrazyl radical in benzene at a g-factor equal to ca 2.0 unless otherwise noted. This concentration divided by the concentration of the limiting reagent and multiplied by 100 gives the percent reaction. The results are considered to be accurate only within a factor of 10. The detailed method of calculation is described in Appendix B.

$-20° \pm 3°$ and stirred for 1.5 hours. During this period, the mixture slowly changed from black to a yellow-green color. A second sample was withdrawn for study by esr. Two 5 ml samples were quenched in H_2O and D_2O. The mixture was cooled to -50° or lower and stored for about two hours while esr samples were studied. Then, 50 ml of the mixture was quenched in ca 200 ml of crushed Dry Ice; it lost its color immediately. An additional 50 ml was quenched with 5 ml of dimethyl sulfate; the mixture was stored in a -20° bath for one hour and then warmed to room temperature. A 10 ml sample of the benzene-cesium reaction was also quenched in 10 ml of water. The remaining contents (approximately 75 ml had been lost accidentally) of the flask, ca 50 ml, were warmed to room temperature, stirred for one hour, and then quenched in 100 ml of water.

The -75° and -20° esr samples were studied at -75° to -105° in a cooled pentane bath. The sample taken at -75° showed a $8.5 \times 10^{-2}\%$ yield* of anion radical. The -20° sample had $3.3 \times 10^{-4}\%$ yield* of anion radical. When this was warmed to room temperature and allowed to set overnight (ca 18 hours) there was a $9.0 \times 10^{-3}\%$ yield* of anion radical (studied at -90" to -120°). Obviously, this data does not correlate with the sample taken at -196°. It has been included to show that a discrepancy was found between esr spectra obtained at -90° to -120° and -196°. This discrepancy in the data is discussed in some detail in Appendix B. For additional data taken at -196° on this

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* See footnote on page 76.

reaction, see the section on the reaction of perdeuterobenzene and cesium.

The product, which had been warmed to -20° for 1.5 hours and then carbonated, was worked up by adding 50 ml of water, extracting with pentane, acidifying the aqueous fraction with concentrated HCl, and re-extracting the solution with ether. The ether extract was dried ($MgSO_4$) and concentrated to a white solid on a rotary evaporator. This, after drying in a vacuum dessicator for two hours, weighed 0.707 g. The aqueous portion was evaporated to dryness yielding 1.46 g (8.69 mmol) of a white solid assumed to be cesium chloride.

The nmr spectrum (CMSO-$\underline{d}_6$) [2.43τ (m, 1* aromatic), 4.07τ and peak centered at 4.25τ (d, J=1, C$\underline{H}$-COOH and broad m, respectively, 44, vinyllic), 6.33τ (complex m, 17, allylic), 7.1τ (broad q, J=9, 6, allylic), and 8.2τ (m, 2)] of the mixture of isolated acids and the nmr spectrum (in perdeutero acetone)[2.45τ (m, 1, aromatic),4.07τ and peak centered at 4.28τ (d, J=1, and broad m, respectively, 20*, vinyllic), 6.20τ (s, 10, methyl and/or allylic), 6.38τ (complex m and s, 25, allylic and methyl, respectively), centered at 7.2τ (four peaks, 3.5, allylic)] of the product from diazomethane esterification of these acids indicate that there is a complex mixture of reduced acids produced. In both spectra only a tract (ca 1 integration unit) of aromatic hydrogens were observed. A gc spectrum of the methyl esters of this mixture on an SE 30 column (III) (temperature programmed: 140°

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* This value is in integration units in the nmr spectra of the acid and ester mixtures.

for three minutes, then 20° per minute to 250°) indicated it contained seven components, listed as relative area percents (retention time): 14.7 (2.0, same as benzoic acid), 10.6 (5.0), 1.9 (5.4), 2.8 (6.0), 54.5 (6.3, same as terephthalic acid), 12.6 (8.5, same as 2,2'-biphenyldicarboxylic acid), 2.9 (10.6, same as 4,4'-biphenyldicarboxylic acid).

A sample (0.238 g) of the mixture was dehydrogenated by heating it with 0.247 g of 5% Pd/C in 50 ml of toluene at reflux for ca 18 hours. The Pd/C was filtered off and washed with 5% NaOH. The toluene was also extracted with 5% NaOH. The basic solution was combined and acidified with concentrated HCl. The resulting precipitate was filtered off (yield after drying: 104.9 mg) and the aqueous fraction was extracted with ether. The ether extract was dried ($MgSO_4$), and added to the above precipitate. This was concentrated to dryness on a rotary evaporator (yield: 131.5 mg). In Table 11, the yields of various products of the carbonation after aromatization are reported.

The product, which had been warmed to -20° for 1.5 hours and then quenched with dimethyl sulfate, was worked up by adding concentrated NH_4OH to decompose the excess dimethyl sulfate. The mixture was next acidified with concentrated HCl. The THF phase was separated and the aqueous phase was extracted twice with pentane. The organic extracts were combined, dried ($MgSO_4$), and concentrated to 39.61 g on a Teflon spinning band column at pot temperatures no greater than 60°C. Analysis by gc on a temperature programmed (50° for seven minutes, then 20° per minute to 200°) Carbowax 20 M column (I) indicated that there were at

Table 11. The yield of Aromatized Carbonation Products in Experiment 4-82.

Component	Retention time in min[b]	Yield (mg)[a]	Relative Yield (wt %)
Benzoic acid	7.9	0.036	5.03
Terephthalic acid	12.1	0.405	56.56
p-Phenylbenzoic acid	14.6	0.043	6.00
Diphenic acid	15.0	0.012	1.67
Unidentified acid[c]	22.0	0.029	4.05
4,4'-Biphenyldicarboxylic acid	23.3	0.191	26.68
Total		0.716	

(a) A 2.31 mg portion of aromatized acid mixture was taken for analysis. There was a 30.1 wt % yield of volatile products from this mixture. The yields were determined by comparison of gc areas of the products with gc areas of a solution containing weighed amounts of samples of each of the components.

(b) Analyzed by gas chromatography of methyl esters prepared with diazomethane. GC conditions were: SE 30 column (III), temperature programmed (60° for one minute, then 20° per minute to 215°).

(c) Used, 4,4'-biphenyldicarboxylic acid as a standard for this component.

least 12 separate products. The aqueous portion was dried by extensive heating to give a white precipitate weighing 1.925 g (5.32 mmol Cs_2SO_4 or 11.43 mmol CsCl). A sample (15.54 g, 39.2%) of the organic extract was mixed with 0.105 g of 5% Pd/C and heated to reflux. This reaction was followed by gc analysis on Carbowax 20 M (I) column. The temperature of reflux was slowly raised to 100° by adding isooctane and distilling off the pentane, THF, and benzene. In Table 12, the products of dehydrogenation of the methylation products are displayed. It is apparent that only partial dehydrogenation was accomplished using this method.

The aqueous quench taken simultaneously with esr sample of the -20° intermediate contained 0.188 mol of 1,1',4,4'-tetrahydrobiphenyl per mol of titrated cesium hydroxide according to gc analysis*. The sample taken for an aqueous quency at the time of the methylation and carbonation quenches had a 0.177 mol of 1,1',4,4'-tetrahydrobiphenyl per mol of titrated cesium hydroxide. The final quench with water, after the reaction was warmed to room temperature, was found to contain compounds by gc analysis on a Carbowax 20 M column (I) at 171° with the ratios of mol of product per mol of titrated CsOH (retention time in minutes, identity); 0.0025 (4.2, phenylcyclohexane), 0.0845 (5.1, 1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 0.046 (7.2, 1,4-dihydrobiphenyl), 0.013 (8.4, 1-phenylcyclohexene), 0.011 (10.1, unidentified dihydrobiphenyl) and 0.0285 (13.2, biphenyl)

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* Biphenyl used as an external standard.

Table 12.[a] The Yields of Products from the Dehydrogenation of the Methylation Reaction.

Compound used as standard for calculation	Retention time (min)	mmoles of[b] products	Relative mole Percent Yield
p-xylene	3.3[c]	0.284	55.7
p-xylene	4.2	0.014	2.4
p-xylene	5.1	0.018	3.4
biphenyl	10.7		
biphenyl	10.9	0.008	1.6
biphenyl	11.4	0.048	9.4
biphenyl	11.8	0.016	3.1
biphenyl	12.7	0.008	1.5
biphenyl	13.4	0.012	2.3
biphenyl	14.4[c]	0.003	0.7
4-methylbiphenyl	15.5	0.025	5.0
4-methylbiphenyl	16.3	0.005	0.9
4-methylbiphenyl	18.4[c]	-	-
4,4'-dimethylbiphenyl	19.9	0.038	7.4
4,4'-dimethylbiphenyl	22.3[c]	0.033	6.5
Total		0.516	

(a) Calculations for this table were obtained by gc analysis on Carbowax 20 M column (I) that was temperature programmed (90° for four minutes, then 20° per minute to 200°). No toluene was observed in the analysis.

(b) The yields were calculated fro the 15.54 g of solution which was dehydrogenated and were determined by comparison of gc areas of the products with gc areas of a solution containing weighed amounts of the known components used as standards.

(c) This compound was found to be identical with the corresponding standard according to gc retention times (and mixed gc injections).

(Total: 0.184). In these samples, no attempt was made to analyze for the 1,4-dihydrobenzene present.

In experiment 4-72, 10.02 g (75.4 mg-atoms) of cesium sand was reacted with 43.52 g (557.1 mmol) of benzene in 250 ml of THF at -70°. This was stirred for two hours at this temperature. An esr sample, taken at this time, indicated a $3.8 \times 10^{+2}$% yield of anion radical.* This esr was measured at -196°. The mixture was then warmed to -20° ± 3°. After remaining at this temperature for two hours, the mixture did not change to yellow-green color found in the other reactions but remained black. Analysis by esr at -196° of a sample of this gave a 6.4×10^{-1}% yield of anion radical.* The reaction was quenched with 250 ml of H_2O. Analysis of this quench by gc on a temperature programmed Carbowax 20 M column (I) (50° then 20° per minute to 168°) indicated an approximate yield** of 0.0187 mol of 1,1',4,4'-tetrahydrobiphenyl per g-atom of initial cesium and less than 0.01 mol of 1,4-dihydrobenzene per g-atom of initial cesium. The 12 carbon compound was reanalyzed by adding a 355.1 mg of biphenyl to this solution and studying its gc spectra on a Carbowax 20 M column at 140° (II). The yields as mg of biphenyl were (retention time in minutes): 73.7 mg (3.2, 3.6, 3.9, 4.1, 4.6), 257.3 mg (5.4, 1,1',4,4'-tetrahydrobiphenyl) 67.7 mg (6.6). These yields correspond to 0.0065, 0.022, and 0.006 mol

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* See footnote on page 76.

** This yield was calculated using the formula given in the discussion of Table 7.

of product per g-atom of initial cesium, respectively. In various attempts to prepare the -20° intermediate, a significant amount of these reactions did not turn yellow-green. Since there is a correlation between this color production and product yield, as seen in the previous experiment, those reactions (experiments 4-47, 4-70*, 4-71, 4-73) that did not change from black to yellow-green were not studied.

Study of Hydrogen Evolution During Pyrolysis of Benzene-Cesium Adduct. In experiment 4-20, an excess of benzene (43.34 g, 554.9 mmol) was added to 10.48 g (78.9 mg-atoms) of cesium sand in 250 ml of THF at 70°. This was reacted for one hour at this temperature, warmed to -20° ± 5°, and then reacted for three additional hours. At -20°, the reaction color changed from black to a greenish-yellow color. After one hour at -20°, a 5 ml aliquot of the reaction mixture was withdrawn and quenched with H_2O. Analysis of this by gc on a Carbowax 20 M column (I) (temperature programmed: 10 minutes at 60°, then 40° per minute to 170°) gave the following products listed as mol of product per g-atom of initial cesium (retention time in minutes, identification): 0.102 (5.5, 1,4-dihydrobenzene), in excess (6.5, benzene),0.100 (19.5, 1,1',4,4'-tetrahydrobiphenyl). After two hours at -20°, a second sample was removed and quenched. This (measured in mol of product per g-atom

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* In experiment 4-70, the anion radical yield was 19% in the reaction between benzene (0.59 mol) and cesium (0.794 g-atoms) in 250 ml of THF at -70° after one hour. This yield was determined by esr analysis at -196°.

of initial cesium) contained 0.071 1,4-dihydrobenzene and 0.1825 1,1',4,4'-tetrahydrobiphenyl.* After three hours of stirring at -20°, the mixture was transferred under nitrogen to a second flask cooled with a Dry Ice-acetone bath. A 10 ml aliquot of this was warmed to room temperature and analyzed for gas evolution.

The sample was attached to a vacuum line manifold (10^{-5} mm pressure) containing a Toepler pumped gas collection system. The sample was evacuated (10^{-5} mm) at -196° and allowed to warm to room temperature. The solvent, benzene and THF, distilled into a liquid nitrogen-cooled trap in the line. The resulting solid residue slowly liberated gas for 2 hours. The solvent was then distilled back onto this solid. After one hour at room temperature, in this state, the liquid phase was again removed by distillation. The solid was found to be still liberating gas so the solvent was distilled back onto the solid and left for an additional 30 minutes. The benzene and THF were again removed and the solid evolved gas for after about two hours and then stopped. All of the gas evolved was collected, measured, and found to be 0.494 mmol. The solid was then quenched by distilling about 5 ml (ca 25 mmol) of D_2O upon it while it was being cooled with liquid nitrogen and then warming the mixture to room temperature. During the quenching of the solid, 0.306 mmol of gas was liberated. The results of mass spectroscopy determined isotopic analysis of the

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* This yield was calculated using the formula given in the discussion of Table 7.

hydrogen produced are in Table 13. This quenched sample contained 2.45 mmol of cesium hydroxide by titration. Analysis by gc of the products indicated 0.941 mmol of benzene had reacted. This analysis on a Carbowax 20 M column (I) (temperature programmed: 10 minutes at 60°, then 40° per minute to 170°) gave the following products listed as mol of product per mole of titrated cesium hydroxide (MW by gc-ms, identification): 0.008 (1,4-dihydrobenzene), 0.041 (benzene), 0.002 (phenylcyclohexane), 0.018 (162, $C_{12}H_{10}D_4$; tetrahydrobiphenyl-$\underline{d}_4$), 0.11 (158, $C_{12}H_{10}D_2$; dihydrobiphenyl-$\underline{d}_2$), 0.018 (162, $C_{12}H_{10}D_4$; 1-phenylcyclohexene-$\underline{d}_4$), 0.01 (158,* $C_{12}H_{10}D_2$; a dihydrobiphenyl-$\underline{d}_2$, unidentified), 0.59 (154 to 159, $C_{12}H_{10}$ to $C_{12}H_5D_5$, biphenyl).

After storing the yellow-green mixture (-20° intermediate) for a period of nine hours at -70°, it was distributed in the following manner: (1) 5 ml was quenched in 5 ml of H_2O, (2) 10 ml was added to a nitrogen-flushed flask fitted with a vacuum stopcock, and (3) the remainder was quenched by addition of Dry Ice and the mixture was allowed to stand overnight.

The 5 ml aqueous quench was found to contain a 0.06 mol of 1,4-dihydrobenzene and 0.09 mol of 1,1',4,4'-dihydrobiphenyl per mol of initial cesium. This low yield is probably caused by settling of the precipitate while standing. This would make it difficult to obtain a representative sample.

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*This contains a trace of a component with a MW of 162.

Table 13. Relative Amounts of H_2, HD and D_2 in the Gas Liberated During the D_2O Quench in Experiment 4-20[a].

m/e	Relative Peak Heights (percent abundance)		
	Run 1	Run 2	Run 3
2	62 (26.8%)	73 (31.7%)	33(15.8%)
3	100 (43.8%)	100 (43.4%)	100 (49.9%)
4	69 (29.9%)	57.5 (24.9%)	76.5(36.2%)

(a) Analyzed by Florida State University using a mass spectrometer. This analysis had poor reproducibility. Later work had vastly improved analysis.

The 10 ml sample was cooled to -78° and evacuated to about a pressure of 100μ and then allowed to warm to room temperature overnight. The gas above the -20° intermediate mixture was found to be a mixture of nitrogen (1.4 minutes) and hydrogen (0.8 minutes) by gc analysis on a silica gel column (III) at 30°.

The carbonation products were worked up in the usual manner to give 2.85 g of acid material. Acetone crystallization of this material yielded two fractions: 0.0786 g and 0.257 g (mp-chars above 248°). The nmr of the first fraction in DMSO-$\underline{d}_6$ [4.05τ (complex d, J=1, 4.0 H, C$\underline{H}$=C$\underline{H}$), 6.28τ (complex m, 1.9 H, CH=CH-C$\underline{H}_2$-), 3.9τ (0.24 H, acetone) no acidic protons were observed] was consistent with that expected for 1,4-dihydroterephthalic acid. A portion of the second fraction was esterified with diazomethane. The nmr [3.99τ (complex d, J=1, 3.9 H, C$\underline{H}$=C$\underline{H}$), 6.30τ (complex m, 8.1 H, C$\underline{H}$COOC$\underline{H}_3$)] was consistent with the expected spectrum of dimethyl 1,4-dihydroterephthalate.

A third fraction, 0.327 g of white crystalline material was isolated from the acetone mother liquor and dehydrogenated by heating with 0.306 g of 5% Pd/C in 75 ml of boiling toluene for 20 hours. A basic extract of this yielded, upon acidification, 87.5 mg of a white water-insoluble precipitate. The nmr (DMSO-$\underline{d}_6$) [1.90τ (s, aromatic)] was identical with that of a known sample of terephthalic acid.

After a period of three months, a portion of the acetone soluble material (0.318 g from 1.625 g) was sublimed at 22 mm and 147° for 18 hours to give 0.125 g of sublimate and 0.160 g of unsublimed material. The sublimed material was benzoic acid according

to ir analysis (the spectrum of this compound was identical, except for a band at 3420 cm^{-1}, with that of benzoic acid) and nmr analysis [1.9τ (complex m, 2.15 H), 2.8τ (complex m, 2.9 H)]. The unsublimed material was the same as terephthalic acid by nmr analysis as previously described. However, the ir spectrum of this was not like that of terephthalic acid. It appeared to be a mixture of terephthalic acid and some other compounds.

These results led to the study done in experiment 4-82, previously described. In experiment 4-82, a more complete analysis was performed upon the carbonation products. This experiment indicated that there was a 25.1% relative yield of reduced 4,4'-biphenyldicarboxylic acids. In the experiment described above, no investigation was made for these compounds.

Reaction of Perdeuterobenzene. In experiment 4-59, 43.36 g (515.2 mmol) of benzene-d_6 was added to 10.34 g of cesium (77.8 mg-atoms) in 250 ml of THF at -72°. This was stirred vigorously one hour and then warmed over a 20 minute period to -20° ± 3°. This reaction temperature was maintained for 1.75 hours. The color changed from black to a yellow-green mustard color. A 20 ml sample was taken and the remainder cooled to Dry Ice-acetone temperatures. The contents of the flask was cooled in a Dry Ice-acetone bath for six days to preserve the -20° intermediate.

The 20 ml sample was attached to a manifold containing a high vacuum line and a Toepler pumped gas collection system. The sample was evacuated and degassed to -70° and then allowed to warm to room

temperature. At this temperature, 0.2027 mmol of hydrogen was given off from the sample over a 12.5 hour period. The relative isotopic amounts by four analyses (respectively) of the gas were: H_2, 9.03, 9.02, 8.57, 8.89, (5.6%); HD, 51.39, 51.15, 48.98, 48.89 (31.5%); D_2, 100.00 for all four analyses (62.9%). This sample was quenched by distilling 10 ml of H_2O onto it at -196°, and then allowing the mixture to warm to room temperature. This reaction gave off 0.7482 mmol of hydrogen of the relative isotopic amounts by four analyses (respectively): H_2, 28.87, 31.92, 29.57, 30.19 (19.2%); HD, 100.00 for all four analyses (63.8%); D_2, 24.74, 27.66, 27.05, 27.36 (17.0%). The yields in terms of mol of product per mol of titrated CsOH (4.93 mg-atoms) (retention time in minutes, identification) of volatile products determined on a Carbowax 20 M column (I) were: in excess (8.4, benzene), 0.027 (6.8, 1,4-dihydrobenzene), 0.092 (6.9, 1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 0.019 (9.3, 1,4-dihydrobiphenyl), 0.007 (10.8, 1-phenylcyclohexene), 0.0215 (16.4, biphenyl). This was measured at 50° for the six-carbon compounds and at 175° for the 12-carbon compounds. The total yield of deuterium atoms evolved as HD or D_2, was 0.213 g-atom of D per mol of titrated CsOH.

Two days after the reaction, a 20 ml sample of the -20° intermediate was transferred to a flask and attached to a manifold containing a high vacuum line and a Toepler pumped gas collection system. The solvent and benzene were removed <u>in vacuo</u> (10^{-5} mm, -20°). The resulting precipitate was quenched by distilling 10 ml of

H_2O onto it. The total hydrogen evolution during this quench was 8.71 x 10^{-3} mmol. The amount of titrated CsOH was 5.02 mmol. Volatile products determined by gc analysis on a Carbowax 20 M column (I), at 50° for six-carbon compounds and at 172° for 12-carbon compounds, are listed by mol of product per mol of titrated CsOH (identification): 0.207 (1,4-dihydrobenzene), 0.239 (benzene), 0.114 (1,1',4,4'-tetrahydrobiphenyl). A 10 ml sample taken at the same time from the original flask that was being cooled at -70° for two days was jetted into H_2O. The amount of titrated CsOH was 2.60 mmol. The volatile products in mol of product per mol of titrated CsOH, (identification in protio form) were: in excess (benzene), 0.018 (1,4-dihydrobenzene), 0.200 (1,1',4,4'-tetrahydrobiphenyl).

After six days, a 20 ml sample of the -20° intermediate was again attached to the vacuum line. This was degassed as before, warmed at 60° for 10 minutes and then at 30-35° for 1.5 hours. The sample evolved 0.263 mmol of hydrogen after warming and 1.669 mmol while being quenched with 10 ml of H_2O. The amount of titrated CsOH was 5.67 mmol. The volatile products determined as in the previous analysis listed as mol of product per mol of titrated CsOH (identification) were: in excess (benzene), 0.025 (1,4-dihydrobenzene), 0.0315 (1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 0.017 (1,4-dihydrobiphenyl), 0.0095 (1-phenylcyclohexene), 0.027 (biphenyl).

In experiment 4-48, 49.21 g (537.1 mmol) of benzene-$\underline{d}_6$ was reacted with 9.607 g (72.3 mg-atoms) cesium sand in 250 ml of THF at

-70°. The -20° intermediate was prepared, as in the previous reaction, by stirring at -70° for one hour and then -20° ± 3° for 1.5 hours. Two esr samples* were taken at the end of each temperature period. The percent yield of radical anion in the -70° sample was $9.3 \times 10^{3}\%$ and in the -20° sample was $1.3 \times 10^{-4}\%$. The -20° esr sample was warmed at 25° for 18 hours and had a percent yield of radical anion $6.3 \times 10^{-2}\%$*.

A 20 ml sample of the -20° intermediate was analyzed for hydrogen evolution on the vacuum line system. Warming this for 18 hours at room temperature gave 0.207 mmol of hydrogen gas which had the relative isotopic amounts for successive analyses (respectively): H_2 16, 18, 18, 13 (10.5%); HD, 40, 36, 41, 39 (25.1%); and D_2, 100 for all four analyses (64.4%).** The amount of hydrogen gas evolved during quenching was not determined property.

The remainder of yellow-green intermediate was quenched by jetting into 300 ml of H_2O. This contained a gc volatile product on a Carbowax 20 M column (I) at 168°, having the same gc retention time by mixed injection as 1,1',4,4'-tetrahydrobiphenyl, was isolated by pentane extraction, concentration of the extracts, and distillation at 75° to 80° and 300 μ. No other 12-carbon compound was observed. The yield of this was 1.82 g or 0.166 mol per mol of initial cesium.

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* Analysis performed at -196°, see footnote on page 76.

** Analysis by Florida State University.

The mass spectrum (70 eV) m/e (rel intensity) was: 88 (6), 87 (71), 86 (73), 85 (100), 84 (44), 83 (22), 82 (29), 81 (40); others with rel intensity of five or greater: 57 (5), 56 (8), 55 (5), 54 (10), 53 (6), 52 (7), 42 (7). However, the gc-ms analysis on a Carbowax 20 M column (I) at 170° indicated the molecular ion to be 170 as expected for $C_{12}D_{12}H_2$.

Reaction in THF at Room Temperature

Reaction with Excess Benzene. In experiment 2-18, 7.40 ml (81.2 mmol) of benzene was added to a mixture of 5.396 g (40.6 mg-atoms) of cesium and 250 ml of THF at 33°. After stirring vigorously for 50 minutes, the mixture had turned dark brown and the temperature had gone to 35°. The mixture was decomposed by jetting into 400 ml of ice slush. The resulting mixture was extracted with ether, dried ($MgSO_4$) and concentrated on a spinning band column at pot temperatures no greater than 50° to give a solution containing 124.3 g. Analysis by gc of this solution on a temperature programmed (50° for five minutes, then 24° per minute to 180°) SE 30 column (IV) indicated there were four products of the relative area percents (retention time): 72.4 (10.4), 19.3 (10.9, same retention time as biphenyl on mixed injection), 4.4 (11.1), 3.8 (11.2). Absolute yield determination by gc analysis using a standard solution of biphenyl indicated that there was produced in the reaction 3.82 mmol of the major component and 0.853 mmol of the biphenyl-like component. It is assumed for this calculation that both compounds have the gc characteristics of biphenyl. About one-third of the above solution was concentrated to ca 1 ml on

a spinning band column at pot temperatures up to 150°. This mixture turned brown. GC analysis showed no new products. The mass spectrum of this mixture had the m/e values (rel intensity) of: 158 (21.5), 157 (14.3), 156 (100), 155 (55), 154 (66.7), 153 (28.6), 152 (23.8). (Since this is a mixture, there are ca 90 peaks in this spectrum. Only the highest valued group of peaks is described here.)

In experiment 3-20, 13.18 g (168.8 mmol) of benzene was added to a mixture of 5.296 g (39.8 mg-atoms) of cesium in 100 ml of THF at 35°. In order to have a good nitrogen atmosphere, the glove box was flushed with 240 ft^3 (one tank) of nitrogen before the reaction was started. The reaction mixture turned black immediately and the reaction heated to 38°. This was stirred for two hours. The unreacted benzene was washed from the black precipitate under an atmosphere of nitrogen by repeatedly adding isooctane, mixing it well with the black precipitate, allowing the precipitate to settle, and removing the wash solvent with a siphon. This operation was repeated until the calculated amount of benzene was 0.1 mmol. The whole wash procedure took 21 hours. The black precipitate was transferred to a mercury-displacement gas measurement apparatus. It yielded 9.23 mmol of hydrogen when quenched with 15 ml of H_2O.

The quenched products were separated into organic and aqueous phases by washing the isooctane phase three times with 10 ml of water and then washing the combined aqueous extract three times with 10 ml of isooctane. The CsOH contained in the aqueous portion was found to be 32.59 mmol by titration with standardized HCl. The products were

identified and the number of mol of product per mol of titrated CsOH calculated by gc analysis on Ucon Oil LB 550 X (XI), SE 30 (III), and Carbowax 20 M (I) (in this analysis the extract had been stored in the refrigerator for 16 months after the reaction) and ms-gc analysis on OV 17 (V). The products, listed as mol of product per mol of titrated CsOH (retention time in minutes on a Ucon Oil LB 550 X at 52° for six-carbon compounds and on SE 30 at 126° for 12-carbon compounds, molecular weight determined by ms-gc, identification) were: 0.0598 (5.9, 78, benzene), 0.0065 (7.2, 80, 1,4-dihydrobiphenyl), 0.0372 (4.1, 158, 1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 0.0678 (6.9, 158, 1-phenylcyclohexene), 0.1316 (6.2, biphenyl), 0.0134 (8.1, unidentified $C_{12}H_{12}$ compound). The 12-carbon products found by gc on a Carbowax 20 M column at 180° listed as relative area percents (retention time in minutes, identification) were: 14.7 (6.7, 1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 28.1 (10.1, 1-phenylcyclohexene), 57.2 (15.5, biphenyl). The relative ratio of yields of 1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound: 1-phenylcyclohexene: biphenyl for the SE 30 column is 1:1.8:3.5 and for the Carbowax 20 M column is 1:1.9:3.9. This indicates that there was only a small amount of product decomposition during the six-month period between the two analyses.

Reaction with Excess of Cesium. In experiment 3-106, 1.00 g (12.8 mmol) of benzene was reacted with an excess of cesium (5.93 g, 44.7 mg-atoms) in 250 ml of THF at 40° for one hour. The reaction was

quenched in 200 ml of H_2O. Analysis by gc on an FFAP column at 77° and a Carbowax 20 M column (I) at 215° of the ether extract, obtained in the usual manner, showed these products listed as relative area percents (identification): 21.8 (1,4-dihydrobenzene), 73.3 (benzene), 0.2 (phenylcyclohexane), 0.1 (1,1',4,4'-tetrahydrobiphenyl and/or an unidentified $C_{12}H_{14}$ compound), 3.3 (1,4-dihydrobiphenyl), 0.2 (1-phenylcyclohexene), 0.3 (unidentified $C_{12}H_{12}$compound), 0.7 (biphenyl). The total relative area percent yield of reduced biphenyls and biphenyl is 4.8%. After 10 months, absolute yield based on initial benzene, for the conversion of benzene to reduced biphenyls and biphenyl was found to be 6.3% by analysis on a Carbowax 20 M column (I) at 178°. This calculations is based on initial benzene with the assumptions that the stoichiometry between benzene and these compounds are 2:1. It appears that the 12-carbon compounds had decomposed during gc analysis at 215°.

Reaction at Room Temperature Without Solvent

In experiment 2-140, 5.185 g (39.1 mg-atoms) of cesium was added to 50 ml (0.562 mol) of benzene at 30°. Within 10 minutes, the mixture turned black and the temperature rose to 35°. The stirring was stopped after 100 minutes and the benzene removed in vacuo over a one hour period. The resulting solid was black streaked with white and grey. An attempt to scrape the precipitate off the sides of the flask caused the mixture to explode! Apparently oxygen had gotten into the flask during evacuation and formed the explosive cesium superoxide. This same reaction was observed by L. Hackspill in his

study of the reaction between benzene and cesium.[18a]

In experiment 2-130, 6.169 g (51.3 mg-atoms) of cesium was added to 250 ml (2.81 mol) of benzene at 25°. The mixture turned black and the temperature rose to 39°. After stirring for two hours, the mixture appeared to contain a black precipitate and no cesium. The black precipitate was washed four times with ca 110 ml portions of pentane in the reaction flask. While washing, as much benzene as possible was being removed. Then, the black precipitate was transferred to a 125 ml flask and the remaining liquid decanted off. The precipitate was washed an additional three times with 100-ml portions of pentane. After decanting as much pentane as possible from the precipitate, it was dried in vacuo (1.5 mm, 25°). The dried product was a grey-brown solid. Two weighed samples of this were quenched in water to give a brown solution with a black precipitate in it. The samples contained 4.7% and 6.8% by weight of this precipitate. Titration with standardized HCl of these solutions indicated that the grey-brown solid was 16.4% and 16.7% by weight of cesium* respectively. The water was boiled from the titrated solution and the contents were dried to a white powder. Assuming the white powder to be CsCl, the weight percentages of Cs in the initial grey brown solid were 74.1 and 69.4, respectively. Hackspill reports[18a] that he found 65.3 wt % cesium and DePostis[19] reported 91.2 wt % cesium in the

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* Comparison of the titration with the gravimetric analysis indicates that the pH meter used for the titration was probably not working properly.

precipitate isolated in this reaction.

In experiment 3-112, 5.73 g (43.1 mg-atom) of cesium were added to 100 ml (1.12 mol) of benzene at 28° in a glove box flushed with 240 ft^3 of nitrogen. The mixture was stirred vigorously for one hour. The temperature rose from 28° to 35° during the first 10 minutes of reaction. At this point the mixture was black. A black precipitate was isolated by adding 130 ml of isooctane to the reaction flask, mixing well, and transferring to a calibrated glass filtering vessel which contained a coarse sintered glass filter. This apparatus is shown in Figure 2. Additional isooctane was added to the reaction flask to get the remaining precipitate. It took about 300 ml of isooctane to effect a good transfer. This operation was done completely in an atmosphere of nitrogen. The solvent was drained off and portions of isooctane added for a series of washes. The precipitate was washed until the calculated amount of benzene left in the precipitate was 0.05 mmol. About 30 ml of isooctane was left above the black precipitate. A scoopula full of precipitate was decomposed in each of the quenching agents in Table 14. The work up of each of these reactions is described in this table.

Table 15 contains the relative yields of products by gc on OV 17 (V) and Carbowax 20 M column (I) for the H_2O quench. Table 16 contains a tabulation of gc-ms and gc data on OV 17 column (VI) of the D_2O quench. The methanol quench was performed a day after all of the other quenches. The gc results of this are tabulated in Table 16. The relative area percentages according to gc analysis on an OV 17 column

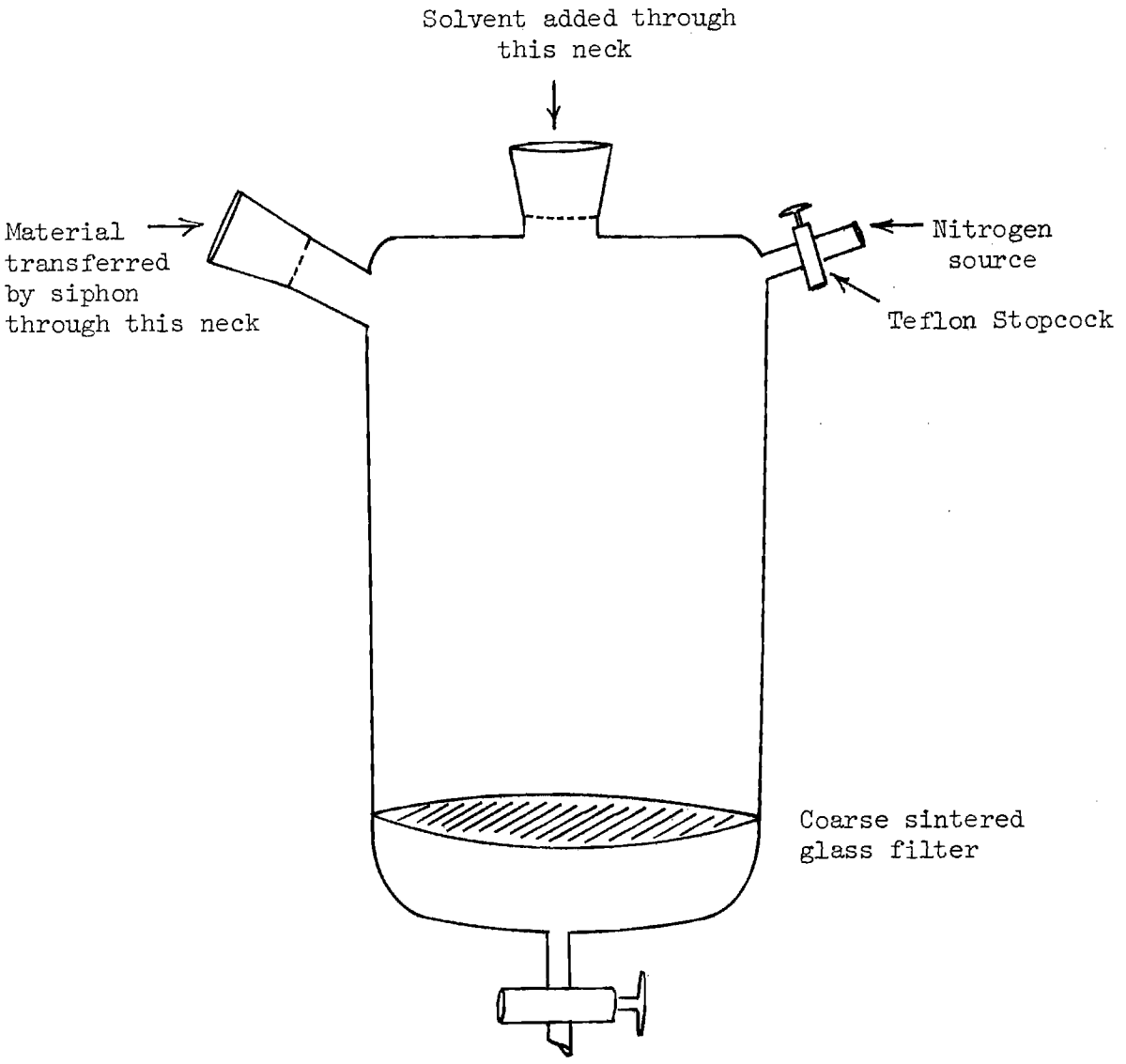

Figure 2. Apparatus Used to Filter Benzene-Cesium Adduct.

Table 14. The Quenching Methods Used in the Study of the Black Precipitate Isolated from the Reaction of Benzene and Cesium at Room Temperature in Experiment 3-112.

Quenching Agent	Reaction	Work Up
5 ml of H_2O	reacted slowly relative to cesium metal	Removed isooctane layer, extracted aqueous portion with 3 ml of pentane three times, combined and dried ($CaSO_4$)
5 ml of D_2O	same as above	Added 1 ml of pentane and proceed as with H_2O.
5 ml of $(CH_3)_2SO_4$	gas given off	Added 0.5 ml of H_2O; extracted four times with 3 ml of pentane. Decomposed excess $(CH_3)_2SO_4$ with dilute NH_4OH; extracted this with 5 ml of pentane, combined extracts. Washed with dilute NH_4OH, 1 N HCl and dried ($CaSO_4$).
5 ml of MeI	reacts rapidly giving a grey precipitate	Added 0.5 ml of H_2O, washed three times with ca 3 ml of H_2O and dried ($CaSO_4$).
10 ml of MeOH	reacts rapidly	Removed isooctane layer; extracted twice with pentane and washed twice with 2 ml H_2O; dried ($CaSO_4$).
5 ml of "I_2 dissolved in isooctane" plus solid I_2	yielded a red precipitate	Decomposed I_2 with NaI, HOAc and $Na_2S_2O_3$. Removed organic layer washed with H_2O; dried ($CaSO_4$).

Table 15. Relative Area Percent Yields of Products of H_2O Quench in Experiment 3-112.

Component[a]	Relative area % Yield Carbowax 20 M column[b] (I) (Retention time in minutes)	Relative area % Yield OV 17[c] (V) (Retention time in minutes)	Molecular ion, m/e ms-gc on an OV 17 (VI) column
benzene	13.0 (6.1)	13.9 (1.8)	78
1,4-dihydrobenzene	12.4 (5.5)	15.5 (2.4)	80
phenylcyclohexane and 1,1',4,4'-tetrahydrobiphenyl[d]	20.1[e] (7 peaks, 10.9-12.9)	12.0 (16.4)	160
unknown reduced biphenyl	1.4 (13.4)	too small to determine	
1,4-dihydrobiphenyl	32.1 (14.0)	33.1 (16.8)	156
1-phenylcyclohexene	2.6 (14.7)	18.8[e,f] (17.7)	158
biphenyl	10.2 (17.2)		
unidentified dihydrobiphenyl	9.4 (15.6)	6.7 (18.4)	156

The total cesium hydroxide found by titration was 2.39 mmol and the absolute amount of reacted benzene (calculated by use of benzene and biphenyl as external standards and assuming the stoichiometry of one to one between benzene and dihydrobenzene and two to one between benzene and 12-carbon compounds) was 1.42 mmol which is 59.4% reaction of cesium assuming one cesium atom reacts with one molecule of benzene.

(a) These compounds were identified by mixed-gc injections and ms-gc analysis.

(b) This column was temperature programmed (4 minutes at 55°, then 40° per minute to 206°).

Table 15. (Concluded).

(c) This column was temperature programmed (4 minutes at 30°, then 12° per minute to 250°).

(d) The phenylcyclohexane is a shoulder and less than 5% of two components on OV 17 column and buried in the pyrolysis products on Carbowax 20 M column. 1,1',4,4'-tetrahydrobiphenyl was later found to decompose in gas chromatography higher than 175°.

(e) Apparently there is an unidentified $C_{12}H_{14}$ compound that has a retention time of ca 11.9 minutes on Carbowax 20 M and 18.8 minutes on OV 17.

(f) These compounds have the same retention time on OV 17.

Table 16. Relative Area Percent Yields of D_2O Quench and MeOH Quench Calculated From GC and GC-MS Spectra on an OV 17 Column (VII) in Experiment 3-112.

Component	MeOH Quench		D_2O Quench	
	Rel. yield (Retention time in minutes)[a]	Mol. Ion	Rel. yield (Retention time in minutes)[a]	Highest Mol. ion
benzene	8.0 (1.7)		14.2 (1.5)	78
1,4-dihydrobenzene (and $\underline{d}_2$)	10.2 (2.3)		16.4 (2.0)	82
phenylcyclohexane[b] (and $\underline{d}_6$) and 1,1',4,4'-tetrahydrobiphenyl (and $\underline{d}_4$)	9.7 (15.0)	160	10.7 (15.9)	166
1,4-dihydrobiphenyl (and $\underline{d}_2$)	33.6 (15.6)	156	39.9 (16.2)	158
1-phenylcyclohexene (and $\underline{d}_4$), biphenyl and an unidentified tetrahydrobiphenyl ($\underline{d}_4$)	29.2 (16.3)	158	13.0 (17.2)	162
unidentified dihydrobiphenyl (and $\underline{d}_2$)	9.1 (17.0)	156	5.9 (17.9)	158

The total cesium in MeOH quench was 6.36 mg atoms and amount of benzene needed to produce volatile product was 4.49 mmol.[c] This corresponds to a 70.6% reaction of cesium.

The total titrated cesium in D_2O quench was 3.63 mg atoms and amount of benzene needed to give the various volatile products was 2.18 mmol.[c] This means there is a 60.2% reaction of cesium with benzene.

(a) Temperature programmed as described in Table 15.

Table 16. (Concluded)

(b) This is less than 5% (relative) of the two components.

(c) The method of calculation is the same as in Table 15.

(VI) using conditions described in Table 15 of volatile products from the iodine quench were benzene, 27% and biphenyl, 73%. The relative area percentages* (retention times in minutes, gc-ms determined molecular weights, identification) from the methyl iodide and dimethyl sulfate quenches are for CH_3I: 24.9 (2.4, 78, benzene); 62.4 (14.5, 154 and 168, biphenyl and methyl biphenyl); 11.4 (15.8, 168, methylbiphenyl); 1.2 (17.0, 182, dimethylbiphenyl); and for $(CH_3)_2SO_4$: 36.7 (2.0, 78, benzene); 45.5 (11.0, 182 and 184, dimethylbiphenyl and a reduced derivative); 6.5 (11.5, 182, dimethylbiphenyl); 12.2 (12.3, 184, dihydrodimethylbiphenyl).

A second batch of the black precipitate was prepared (experiment 3-130) using 6.396 g of cesium, (44.1 mg-atoms) and 100 ml of benzene according to the same procedure as the previous experiment. Samples were taken for esr spectroscopy (measured at room temperature) before and after the black precipitate was washed with isooctane. The spin concentration after the washing step was ca 400 times higher than before the washing step. In the isolated black precipitate, the spin concentration was 3×10^{19} spin/liter** or ca 5.0×10^{-5} M in unpaired electrons. Assuming the density of the precipitate is at a minimum, the density of benzene (0.9 g/ml), then the concentration of electrons is no greater than 5.5×10^{-8} mol of electrons/g. If 1 g-atom of

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* Yields are in terms of moles of reacted benzene are therefore adjusted for the substituted methyls by multiplying the area of each methyl substituted compound by the ratio of 12 to the number of carbons in this compound.

** See footnote on page 76.

cesium reacts with 1 mol of benzene, then 6.40 g of cesium would combine with 3.43 g of benzene to give 9.8 g of precipitate. Thus, maximum amount of anion radical in the two samples would be 5.4×10^{-7} mol and 5.4×10^{-4} mmol. In this experiment, 44.1 mg-atoms of cesium were reacted. Therefore, the maximum yield of anion radical would be 1.2×10^{-3}%. In the precipitate before washing with isooctane, the yield is 3×10^{-6}%. The anion radical concentration of the precipitate is too small to be an important intermediate.

The washed black precipitate in one scoopula amounts was quenched in a variety of reagents: 3 ml cold MeOH, -70° (1st day of experiment) took ca 1 minute to react; 3 ml of MeOH, 25°,(1st day of experiment), almost instantaneous reaction; 5 ml of H_2O (1st day of experiment), reacted slowly; 5 ml of D_2O (1st day of experiment), reacted slowly; 3 ml of H_2O, (2nd day of experiment); 3 ml of D_2O ice slush (2nd day of experiment), I_2 crystals and isooctane (2nd day of experiment), yielded a red precipitate. The work up procedures were the same as in the previous experiment in Table 14. Table 17 shows the relative area yields of the various quenches determined by gc.

Reaction of Benzene and Cs Alloy

Reaction at -70°. In experiment 2-72, 567 mg (7.27 mmol) of benzene was added to 2.0 ml of Cs-K-Na alloy (15.9 mg-atoms of Cs) in 250 ml of THF at -70° and reacted for one hour. The reaction turned blue-green. The mixture was then jetted into 500 ml of H_2O. Analysis of the pentane extract by gc on a Ucon Oil LB 550 X (XI) column at 40° gave the products, listed as relative area percents (retention time in

Table 17. Quenching Agents and Relative Area Percent Yields of Products in Experiment 3-130.[a]

Component[a]	MeOH -70°	MeOH 25°	H_2O 1st Day	D_2O 1st Day	H_2O 2nd Day	Cold D_2O 2nd Day	I_2 2nd Day
benzene	12.7	12.3	12.5	8.6	6.7	8.2	15.4
1,4-dihydrobenzene	13.2	16.4	11.9	8.0	4.0	8.6	none
phenylcyclohexane (less than 5%) and 1,1',4,4'-tetrahydrobiphenyl	18.8	12.3	11.3	14.7	13.5	14.7	none
1,4-dihydrobiphenyl	32.4	31.2	32.7	49.7	46.1	41.2	none
unidentified product (new)	1.6	4.1	0.6	none	none	none	none
biphenyl, 1-phenylcyclohexene, and an unidentified $C_{12}H_{14}$ compound	16.2	19.7	24.7	11.0	20.8	17.1	84.6 (probably biphenyl only)
unidentified dihydrobiphenyl	3.1	4.1	6.2	8.0	8.4	10.2	none

(a) This was analyzed on a temperature programmed OV 17 column (V). (30° until 1,4-dihydrobenzene is eluted and then 10° per minute to 180°).

minutes, identification): 62 (13.3, benzene), 38 (11.9, 1,4-dihydrobenzene). No 1,3-cyclohexadiene or cyclohexene was found by gc analysis. The product was not analyzed for biphenyl and reduced biphenyls.

In experiment 2-110, 1.134 g (14.2 mmol) of benzene was added to a mixture of 4.0 ml of Cs-K-Na alloy (31.8 mg atoms of cesium) in 250 ml of THF at -70°. A sample was taken immediately after benzene addition and quenched in water, extracted with pentane and dried ($CaSO_4$). Analysis of the pentane extract by gc on a Ucon Oil LB 550 X column (XI) at 50° showed relative area percentages (retention time in minutes) for the compounds: benzene, 89.1 (10.2) and 1,4-dihydrobenzene, 10.9 (11.7). The reaction mixture was stirred for four hours. A sample quenched after two hours of reaction showed relative gc area yields of 19.5% 1,4-dihydrobenzene and 80.5% benzene. After four hours, a similar analysis showed 30.6% of 1,4-dihydrobenzene and 69.4% of benzene. At the same time (four hours), a sample was withdrawn from the reaction with a pipette containing a glass wool filter. This was an attempt to keep any precipitate from being taken into the sample. Analysis by gc of the pentane extract of the aqueous quench of this sample showed it to contain 1,4-dihydrobenzene and benzene with relative area percents of 6.5% and 93.5%, respectively.

In experiment 3-100, 1.00 g (12.8 mmol) of benzene was added to a mixture of 4.0 ml of Cs-K-Na alloy (Cs: 31.8 mg-atoms) in 250 ml of THF at -70°. The mixture was stirred for one hour. The reaction turned from blue to dark black green immediately. The reaction was

terminated by jetting into 250 ml of H_2O. The products were extracted in the usual manner using ether as the extraction solvent. Analysis of the products by gc on a FFAP column (VII) at 78° gave the absolute yields (based on initial benzene assuming a 1:1 stoichiometry between benzene and product), listed as percents (retention time in minutes, identification): 39.0 (5.0, benzene), 28.1 (4.4, 1,4-dihydrobenzene). No biphenyl or reduced biphenyls were observed on a temperature programmed (four minutes at 60°, then 40° per minute to 206°) Carbowax 20 M column (I).

In experiment 2-44, 567 mg (7.27 mmol) of benzene was allowed to react with 2.0 ml (Cs: 15.9 mg-atoms) of Cs-K-Na alloy at -70° in 250 ml of THF for four hours. The mixture was quenched by jetting onto 22 g of crushed Dry Ice. After two hours, 10 ml of H_2O was added to the carbonated mixture to decompose any residual alkali metal. The THF phase was separated from the aqueous phase and ether was added to the THF phase to promote separation of additional aqueous phase. The aqueous phases were combined, acidified with concentrated HCl, and extracted three times with 10 ml of ether. The ether extract was dried ($MgSO_4$) and concentrated. The THF-ether mixture containing the neutral fraction was also concentrated. The gc-ms on an SE 30 column (IV) that was temperature programmed (110° for 10 minutes, then 12° per minute to ca 130°), of the methyl esters indicated there was a major (1.5 minute) and minor (1.2 minute) component with molecular weights of 136 ($C_8H_8O_2$) and 138 ($C_8H_{10}O_2$), respectively, and three components (5.1 minutes, 9.3 minutes, 12.0 minutes) with

molecular weights of 194, ($C_{10}H_{10}O_4$). However, gc analysis on an SE 30 column (IV) at 124° indicated that the products of molecular weight 194 were not the methyl esters of phthalic acid, isophthalic acid, and terephthalic acid. Further investigation indicated that these three compounds were probably reduced forms of dimethyl terephthalate which dehydrogenated under the conditions used for gc-ms. Dehydrogenation of the above mixture of acids with 5% Pd/C (1.0g) in boiling toluene yielded, after esterification with diazomethane, only dimethyl terephthalate by gc analysis on an SE 30 column (IV) at 130° (retention time: 6.2 minutes). The absolute percent yields of acids from the carbonation reaction (percent reaction of benzene) as determined by analysis on a DEGS column (XIII) at 179° were (retention time in minutes, identification): 12.1 (4.0 and 8.2 min, the third component had decomposed by the time of the analysis, one month after the reaction, to one of these two terephthalic acids), 1.7 (1.0, benzoic acid). A reduced benzoic acid was only present in trace amounts. In the neutral fraction, there was no biphenyl, dihydrobiphenyl, or tetrahydrobiphenyl by gc or gc-ms analysis on an SE 30 column at 120°.

Reaction at Room Temperature. In experiment 3-90, 1.00 g (12.8 mmol) of benzene is added to a mixture of 4.0 ml (Cs: 78.0 mg-atoms) of Cs-K-Na alloy at 34° in 250 ml of THF and reacted for one hour. This is quenched in 250 ml of H_2O. Analysis by gc [15% FFAP column (VII) at 61° and a Carbowax 20 M temperature programmed column (I) (four minutes at 60°, then 40° per minute to 206°)] of the salted-out THF phase indicated

that there were no reduced biphenyls, biphenyl, or reduced benzene present. In other words, there was no reaction.

The Reaction of Biphenyl and Cesium

Study in THF at Room Temperature

In experiment 4-16, 2.337 g (15.15 mmol) of biphenyl was added to a mixture of 4.434 g (33.36 mg-atoms) of cesium in 100 ml of THF at 48°. The mixture was stirred without heating for 1.5 hours and thereby cooled down to 32°. The reaction mixture was black. A 5 ml sample was withdrawn and quenched in 5 ml of D_2O. The remainder was quenched in 100 ml of H_2O. The quenches were worked up in the usual manner. Table 18 outlines the relative and absolute yields of product found by gc and gc-ms.

In experiment 4-66, the reaction of biphenyl and cesium was repeated; however, the amount of unreacted biphenyl was followed in the reaction. In this case, 4.999 g (32.42 mmol) of biphenyl was added to a mixture of 10.80 g (81.3 mg-atoms) of cesium in 250 ml of THF at 36°. Small samples (ca 1 ml) of the reaction mixture were removed periodically and gas chromatographed after centrifuging. Table 19 contains the results of these samples. The reaction was found to have gone to completion (> 97%) after two hours, that is, there was no free biphenyl in the reaction mixture. Five ml of this was quenched in five ml of D_2O and remainder quenched in 250 ml of H_2O. Samples for esr spectroscopy were removed from the THF-Cs mixture before addition of biphenyl (no detectable esr spectrum) and before

Table 18. Calculations of Yields for the Reaction of Biphenyl and Cesium in Experiment 4-16.

Product (Retention time on a Carbowax 20 M column (I) at 178°)	D_2O quench Rel. area % (MW)[a]	H_2O quench Rel. area % (MW)[a]	H_2O quench Absolute Yield[b]
phenylcyclohexane (8.6)	0.19 (-)	0.26 (160)	0.32
unidentified tetrahydrobiphenyl[c] (9.7)	7.47 (162)	9.71 (158)[c]	10.76
1,4-dihydrobiphenyl (12.7)	43.25 (158)	29.31 (156)	27.65
1-phenylcyclohexene (14.6)	6.31 (162)	9.65 (158)	8.63
unidentified dihydrobiphenyl[d] (17.5)	5.07 (158)	3.15 (156)	3.43
biphenyl (22.5)	37.70 (154)	45.2 (154)	41.94
Total			92.73

(a) Molecular ion by gc-ms on a Carbowax 20 M column (II) at 170°. All of the products are results of addition of deuterium or protium to biphenyl.

(b) This work performed five months after the reaction. The absolute yield is measured relative to titrated cesium and assumes the stoichiometry of two cesiums to biphenyl.

(c) The mass spectrum of this compound, obtained by gc-ms analysis, is in Appendix A in tabular form. Comparison of the mass spectrum of this compound with the mass spectrum of 1,1',4,4'-tetrahydrobiphenyl (both have the same gc retention time on Carbowax 20 M) indicates that these two compounds are different. The structure of this compound is assumed to be 3-phenylcyclohexene for the reasons presented in Appendix A.

(d) This compound is probably 3,4-dihydrobiphenyl, a product observed in the methanol quench of the reaction between lithium and biphenyl[45].

Table 19. Relative Amount of Biphenyl Remaining in One ml Aliquots of the Reaction Mixture at Various Times of Reaction. Analysis on an SE 30 Column at 168° for Experiment 4-66.

Sample	Retention Time (in minutes)	GC Area
biphenyl std, 100 mg/5 ml[a]	3.7	369
#1, 30 sec reaction	3.7	180 (three other components of ca 10 units each)
#2, 1 hour	3.8	10 (Same as above)
#3, 1.5 hours	3.9	6 (Same as above)
#4, 2.0 hours	3.9	9 (Same as above)

(a) This concentration is the same as the initial concentration of the reaction.

Table 20. The Absolute Percent Yields of Final Products Found in Experiment 4-66 by Analysis on a Carbowax 20 M Column (I) at 170°

Product (Retention time)	H_2O Quench Absolute yield[a] (Relative area percents)	D_2O Quench Absolute yields[b] Relative area percents)
Phenylcyclohexane (3.9)	0.35 (0.54)	0.36 (0.42)
3-phenylcyclohexene[c] (4.6)	8.65 (13.33)	10.17 (11.95)
1,4-dihydrobiphenyl (6.0)	23.47 (36.17)	39.83 (46.79)
1-phenylcyclohexene (7.1)	7.67 (11.82)	7.01 (8.23)
3,4-dihydrobiphenyl[c] (8.5)	2.49 (3.84)	4.92 (5.78)
biphenyl (11.0)	22.26 (34.30)	22.84 (26.82)
Total	64.9 (100.00)	85.13 (100.00)
Percent of initial cesium present in the sample by titration of cesium hydroxide	66.3	2.975 mmol CsOH

(a) Based on biphenyl as limiting reagent and assuming a one to one stoichiometry between biphenyl and each product.

(b) Based on titrated cesium hydroxide and assuming the stoichiometry of two cesiums to each product. The yields are not adjusted to account for the fact that cesium is in excess in this reaction.

(c) These are tentative identifications. See footnotes (c) and (d) of Table 19.

the reaction was quenched (6×10^{-4}% yield of anion radical).* The liquid above the black precipitate in the esr sample also had no detectable esr spectrum. The spectra were measured at room temperature, ca 25°. The yields of products in the H_2O and D_2O quench are given in Table 20.

Study of Perdeuterobiphenyl in Tetrahydrofuran-d_8

In experiment 4-30, 35.4 mg (0.22 mmol) of perdeuterobiphenyl was added as a powder to 0.08 ml (1.13 mg-atoms) of cesium in 1 ml of perdeuterotetrahydrofuran. The reaction was carried out in a one dram vial containing a magnetic stirrer and capped with a rubber septum at ca 32°. After 1.5 hours of reaction, the blue-black mixture was quenched by pouring into 5 ml of H_2O. The extract of this was studied on a Carbowax 20 M column (I) by gc at 160° and by gc-ms (II) at 155°. The products, listed as relative area percent (retention time at 160° in minutes, molecular weight, identification) were: 2.0 (9.0, 170, phenylcyclohexane-d_{10}); 13.8 (10.2, 168, 3-phenylcyclohexene-d_{10}**), 29.2 (13.9, 166, 1,4-dihydrobiphenyl-d_{10}); 14.1 (16.2, 168, 1-phenylcyclohexene-d_{10}); 3.8 (19.8, 164 3,4-dihydrobiphenyl-d_{10})**,*** ; 37.0 (25.8, 164, biphenyl-d_{10}). There is no evidence of deuterium addition from the solvent during the reaction. These results show

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* See footnote on page 76.

** These are tentative identifications. See footnotes (c) and (d) of Table 19.

*** This compound decomposes after the chromatography module and before the mass spectra module when studied on gc-ms. The molecular ion of the decomposition product was 164 m/e ($C_{12}D_{10}$) or biphenyl-d_{10}.

that the solvent does not take part, even in a minor way, as a proton donor in the reaction between cesium and biphenyl.

Preparation of 1,4-Dihydrobiphenyl

The compound 1,4-dihydrobiphenyl was prepared by Birch reduction of biphenyl according to the procedure of Kaplan, Petrov and coworkers[43] (expt.3-142). This was prepared using 6.230g (0.897 g-atoms) of lithium and 40.0 g (0.259 mol) of biphenyl in 350 ml of ether. Methyl iodide (3.0 ml, 0.048) was used to initiate the reaction. The reaction was carried out for six hours and then quenched with 120 ml of methanol followed by 80 ml of water. The mixture was extracted with ether and washed with water; the extract was dried ($MgSO_4$), filtered, concentrated, and refrigerated. The crystals of biphenyl that had precipitated out were filtered away and the remainder distilled on a spinning band column under vacuum (ca 1 mm) until crystals started to appear in the column head. Three fractions were collected: #1, 0.9 mm, 63°, 2.143 g; #2, 1.2 mm, 68°, 3.760 g; #3, 1.2 mm, 68°, 3.452 g (contained crystals). The nmr spectrum of sample #1 (neat) [2.9τ (complex m, 7.3 H, aromatic); 4.35τ (complex m, 4.1 H, vinyl); 6.12τ (complex t, 0.9 H, J=8.5, allyl); 7.4τ (complex d, 2.0 H, J=8.5, allyl)] is consistent for a mixture of biphenyl and 1,4-dihydrobiphenyl in the ratio 19:81. The allyl and vinyl regions are identical to the nmr spectrum found in the literature[46] for 1,4-dihydrobiphenyl [(CCl_4), 4.3τ (s), 6.2τ (complex t), 7.4τ (complex d)];the reproduction of the spectrum in the literature was too small to get J values and it was not integrated. Fraction #2 had a similar nmr spectrum and contained 83.5% product. Fraction #1 was used

as a gc standard for the retention time of "authentic" 1,4-dihydrobiphenyl. No further attempts at isolation of pure 1,4-dihydrobiphenyl in this mixture were made.

Reactions of Polyphenylalkanes with Cesium

Reaction of 1,1,1-Triphenylethane and Cs-K-Na Alloy

ESR Study of Products at -70° in THF. In expt. 4-80, 1.219g (4.73 mmol) of 1,1,1-triphenylethane was reacted with 4 ml (31.8 mg-atoms of Cs) of Cs-K-Na alloy in 250 ml of THF at -70° for one hour, according to the method of Grovenstein et al.[57] At this point, an esr spectrum of a sample from the reaction showed 4.1×10^{-5}% anion radical* present. This esr was taken at -95°± 5°. Results at this temperature were later found to possibly be inaccurate. Mr. Dean Quest has shown that the esr of this intermediate studied at -196° had a yield of 2.2×10^{2}%. This esr study by Mr. Quest also indicated that the radical was in the doublet state (g = 1.9966) and not the triplet state (no half-wave absorption).** The reaction was quenched in 250 ml of ice water and worked up by salting out the organic phase and then extracting the aqueous phase with pentane. The solvent was removed in vacuo. The nmr spectrum (CS_2)[2.85τ (m, 5.0 H, aromatic); 4.33τ (complex m, 5.3 H, vinylic); 7.3τ (complex m, 5.44 H, allylic); 8.7τ (s, 3.0 H, C-CH_3)] of the crude product (1.058 g of white precipitate)

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* See footnote on page 76.

** For further explanation of the esr spectra of triplet state radical, see Appendix B.

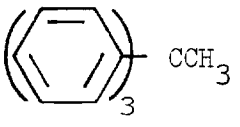
indicates there is ca 98 percent yield of the intramolecular coupling product. Gas chromatography on SE 30 (IV) at 200° shows only one volatile product (retention time: 8.6 minutes). Crystallization of this product from EtOH yielded 0.724 g (58.9%) of a white crystalline material, mp 94° (lit.[57] 96.5-97.5). The nmr spectrum [2.83τ (m, 5.1 H, phenyl); 4.25τ and 4.33τ (complex multiplets, 6.0 H, vinylic); 7.25τ (broad m, 6.0 H, allylic); 8.65τ (s, 2.9 H, C-CH_3) is consistent with the literature[57] for 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene.

NMR Study of Products at -70° in THF. In experiment 2-32, 2.58 g (10.0 mmol) of 1,1,1-triphenylethane was reacted with 7.5 ml of Cs-K-Na alloy (60.0 gm-atoms of Cs) in 50 ml of THF at -70° to -75° for one hour. A sample of this, studied by nmr (at -40°) showed only the spectrum due to THF. The contents of the nmr tube at this temperature had precipitated out and it was impossible to obtain a spectrum of the alkali metal-hydrocarbon adduct. This project was dropped for this reason.

Reaction of Cesium Metal in Liquid Ammonia. In experiment 2-162, 600.3 mg (4.23 mmol) of 1,1,1-triphenylethane was added to a reaction flask containing 0.562 g (2.326 mg-atoms) of cesium in 100 ml of liquid ammonia at -70°. This was stirred at -70° to -75° for 1.75 hours, until the blue color disappeared, and then quenched with ammonium chloride. Analysis by gc on an SE 30 column (IV) at 192° of the volatile products indicated that there was no reaction.

The Temperature Dependence of this Reaction in THF. In this experiment (2-96), 611.5 mg (2.37 mmol) of 1,1,1-triphenylethane was

added to 2.0 ml of Cs-K-Na alloy (15.9 mg-atoms of cesium) in 250 ml of THF at -70°. The reaction temperature was raised in 20° increments over a three-hour period to room temperature and then held at this temperature without stirring for an additional 25 hours. During the reaction, 5 ml samples were withdrawn from it and quenched in 5 ml of H_2O. The reaction was terminated by jetting the contents of the flask into 100 ml of H_2O. Table 21 contains the heating procedure and sampling schedule during this reaction. The small samples were separated into two phases with NaCl. The organic phase was removed, dried ($MgSO_4$) and gas chromatographed. The final quench was extracted with ether; this extract was dried and concentrated on a spinning band column. Table 22 outlines the results obtained from the samples taken in this experiment.



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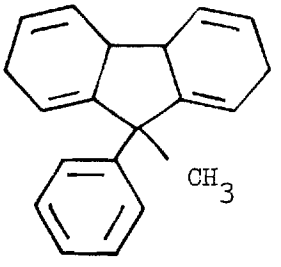

II

A mass spectrum sample of the off-scale component described was isolated from the final quench of the reaction by preparative gc on an SE 30 column at 145°. The major ions in mass spectrum (70 eV)[m/e (rel intensity, ion) 183 (7, $M^+ + 1$), 182 (46, M^+), 168 (16, $M^+ - CH_2$): 167 (104, $M^+ - CH_3$); 165 (24, $M^+ - CH_3 - H$), 152 (17, $C_{12}H_8^+$),

Table 21. Heating Procedure and Sampling Schedule for the Reaction Between 1,1,1-Triphenylethane and Cs-K-Na Alloy (Experiment 2-96).

Sample	Time of Reaction	Temperature	Time at this Temperature	Time taken to raise to next temperature
0	5 min	-70° to -72°	5 min	-
1	1 hr	-70° to -72°	1 hr	10 min
2	1 hr 20 min	-50° ± 4°	30 min	10 min
3	2 hr 25 min	-30° ± 4°	35 min	5 min
4	3 hr	-10° ± 4°	30 min	15 min
5	3 hr 45 min	10° ± 4°	30 min	25 min
6[a]	4 hr 40 min	25°	30 min	-
7	27 hr 20 min	25°	23 hr 30 min	-
Final quench	29 hr 40 min	25°	24 hr 30 min	-

(a) Turned off stirrer after this sample.

Table 22. The Percent Yields[a] of Products in the Reaction of 1,1,1-Triphenylethane with Cesium Alloy at Various Temperatures.

Sample	Retention time[b] in minutes	Yield[a]	Identification
0; 5 min	8.2	69.3	I
	10.7	30.7	II
1; 1 hr, -70°	8.2	2.1	I
	10.7	43.2	II
2; 30 min, -50°	8.1	2.8	I
	10.7	36.3	II
3; 35 min, -30°	0.8 - 1.0	off scale[c]	1,1-diphenylethane[d]
	7.9	6.2	I
	10.8	18.4	II
4; 30 min, -10°	0.8 - 1.0	off scale	1,1-diphenylethane
	7.9	4.7	I
	11.5	0.9	unidentified no II
5; 30 min, 10°	1.0 - 1.3	off scale	1,1-diphenylethane
	2.4	0.6	unidentified
	3.5	1.2	unidentified
	5.8	8.3	unidentified
6; 30 min, 25°	1.1 - 1.4	off scale	1,1-diphenylethane
	2.3	0.6	unidentified
	3.5	0.8	unidentified
	5.8	16.6	unidentified
7; 23 hr 30 min, 25°	1.0 - 1.5	off scale	1,1-diphenylethane
	2.2	0.4	unidentified
	3.7	2.8	unidentified
	6.2	19.5	unidentified

(a) This is an approximated yield arrived at by comparison of the areas of the peaks and the amounts injected and by making the assumptions that all components have the same response factor per mole

Table 22. (Concluded).

and the five minute sample represents a 100% yield of starting material and product. A low yield of product, for example, in sample 1, is possibly due to precipitation of alkali metal hydrocarbon adduct and thereby causing unrepresentative sampling.

(b) This is for an SE 30 column (III) at 180°.

(c) The yield of 1,1-diphenylethane is determined in the next experiment discussed.

(d) This compound was identified by mixed gc injections with a known standard of 1,1-diphenylethane.

105 (16, $M^+ - C_6H_5$), 77 (12, $C_6H_5^+$)] indicate that the compound is 1,1-diphenylethane.

In experiment 2-142, 610.6 mg (2.34 mmol) of 1,1,1-triphenylethane was added to 2 ml (15.9 mg-atoms of cesium) of cesium alloy in 250 ml of THF. This was stirred for one hour at -70° and then warmed to 0° over a 10-minute period and reacted for an additional two hours. The reaction was terminated by jetting into 250 ml of ice water. Two volatile products were found. The absolute percent yields (retention time in minutes) of these products, as determined by analysis on an SE 30 column (IV) at 128° and at 185°, were: 55.6 (8.1, 128°) and 6.0* (8.6, 185°). The product of 55.6% yield has the same molecular weight (182, determined by ms-gc analysis on an OV 17 column (VI)) and the same gc retention time as 1,1-diphenylethane. The minor component is unidentified. It has a longer retention time than triphenylmethane (8.5) in this gc system.

Reaction of 2,2-Diphenylpropane and Cs-K-Na Alloy in THF

Reaction at -70°. In experiment 3-44, 470 mg (2.39 mmol) of 2,2-diphenylpropane was reacted with 2.0 ml of Cs-K-Na alloy (15.9 mg-atoms of cesium) in 250 ml of THF for one hour at temperatures between -65° and -70°. After 35 minutes of reaction, the mixture was a deep rusty brown-orange. Before the mixture was quenched, it had turned a dark blue-black and appeared to contain a finely divided solid. The mixture was quenched after one hour by jetting into 250 ml of ice

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* This calculation assumes that the response per mole of this compound is the same as triphenylmethane.

water. Gas chromatography on an SE-30 column (III) at 165° of the THF phase of the quenched solution showed three volatile products that, listed as relative area percents (retention time in minutes, identification), were: 94.6 (6.6, isolated product $C_{15}H_{18}$, see later discussion); 3.2 (5.8, unknown); 2.1 (5.0, same as 2,2-diphenylpropane). Pentane extraction and concentration of the extract yielded a brown solid. Brown crystals (234.7 mg; mp, 70-72°) were isolated after crystallization from hot aqueous acetone. Two further recrystallizations from hot ethanol produced 111.3 mg (23.7% yield) of white needles, mp 75°-76.5°.

Anal. Calculated for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 9.25, 9.17.

The nmr spectrum (CS_2) [3.9 - 4.8τ (four peaked multiplet, 5.9 H, vinylic), 6.5 - 6.8τ (m, 2.1 H, allylic), 7.3 - 7.6τ (m, 3.8 H, allylic), 8.91τ (s, 3.1 H, C-CH_3), 8.82τ (s, 3.1 H, C-CH_3)] is consistent for cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene. The mass spectrum of this compound had major fragments of m/e (rel. intensity): 200 (4, M^+ +2), 199 (7, M^+ +1), 198 (50, $C_{15}H_{18}^+$), 183 (59, $C_{14}H_{15}^+$), 119 (64, $C_9H_{11}^+$), 105 (100, $C_8H_9^+$), 91 (50, $C_7H_7^+$). The uv spectrum max are (95% C_2H_5OH): 265 mμ (ε 9.14), 272 mμ (ε 10.97).[86] An IR of this compound is reported in Appendix C.

The solvent was evaporated from the mother liquor from the second recrystallization from hot ethanol to give 117.3 mg of crude product.

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(86) "Organic Electronic Spectral Data, Vol. IV," J. P. Phillips and F. C. Nachad, ed., Interscience Publishers, New York (1963), p. 185. The uv spectrum max of 1,2-dimethyl-1,4-cyclohexadiene are (C_2H_5OH): 262.5 mμ (ε 276) and 270 mμ (ε 224).

This was dehydrogenated by heating with 111.5 mg of 5 percent Pd/C in 30 ml of isooctane for 5.5 hours at reflux. The Pd/C was removed by filtration and isooctane removed by distillation in vacuo. There was isolated 36.1 mg of product, mp 66-68° (lit 71°).[87] The nmr spectrum [2.2 - 2.9τ (m, 8.2 H) and 7.2 (s, 6.0 H)], the mass spectrum m/e (rel. intensity) [195 (6, M^+ +1), 194 (37, $C_{15}H_{14}^+$), 180 (20, $C_{14}H_{12}^+$), 179 (100, $C_{14}H_{11}^+$), 178 (46, $C_{14}H_{10}^+$), 177 (8, $C_{14}H_9^+$), 179 (12, $C_{14}H_8^+$)] and the uv spectrum max (95% C_2H_5OH) [301 mμ (ε 132 x 10^4), 289 mμ (ε7.71 x 10^3), 262 mμ (ε 1.99 x 10^4), 228 mμ (ε 8.45 x 10^3)][88] are consistent with 9,9-dimethylfluorene.

In experiment 4-74, 0.9434 g (4.81 mmol) of 2,2-diphenylpropane was reacted with 4.0 ml (31.8 mg-atoms of Cs) of Cs-K-Na alloy in 250 ml of THF for one hour at -70°. In this reaction, a sample for esr study was taken after the Cs-K-Na alloy and THF was stirred for 20 minutes before the hydrocarbon was added to the reaction. During the reaction with hydrocarbon, the mixture turned black. A second esr sample was removed immediately before the contents of the flask were quenched with 250 ml of ice water. The esr of THF-cesium alloy sample contained a

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(87) Marjorie Anchel and A. A. Blatt, J. Amer. Chem. Soc., 63, 1948 (1941). These authors report that the mp of 1,1-dimethylfluorene increases to 95-96° upon standing. This was not found to be the case with the crystals isolates.
with the cry

(88) E. J. Greenhow and D. McNeil, J. Chem. Soc., 3204 (1956). The authors report that the uv spectrum max of 9,9-dimethylfluorene to be (95% EtOH): 301 mμ (ε 1.26 x 10^4), 296 mμ (ε 6.92 x 10^3), 264 mμ (ε 1.78 x 10^4), 228 mμ(ε7.08 x 10^3).

1.63×10^{-6} molar radical concentration* and the esr sample taken after one hour of reaction of 2,2-diphenylpropane contained a 9.34×10^{-5} molar radical concentration (0.43% yield).*

The pentane extract of the quenched solution was concentrated. This gave a brown crystalline material (1.23 g) after removal of the solvent. The nmr spectrum of this material [2.85τ (broad s, 0.4 H due to impurity), 3.9 - 4.8τ (four complex peaks, 6.0 H), 6.5 - 6.8τ (broad s, 2.0 H, allylic), 7.25 - 7.6τ (broad m, 4.0 H, allylic), 8.78τ (s, 3.0 H, $C-CH_3$), and 8.87τ (s, 3.0 $C-CH_3$)] was consistent for cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene. Crystallization out of hot ethanol yielded 0.118 g of white crystals, mp 75-76°. Addition of water to the mother liquor gave 0.110 g of white needles, mp 75-76°. Two more fractions were obtained by this method: 0.215 g, mp 74-75°, and 0.130 g, mp 64-68°.

The third fraction of crystals (0.215 g, mp 74-75°) was dehydrogenated in 50 ml of isooctane using 0.262 g of 5% Pd/C by heating at reflux for 13 hours. The 5% Pd/C was filtered off and the isooctane removed by distillation. The resulting oil was sublimed. This gave 98.1 mg of oily looking crystals, mp 68°. The nmr of this was the same as that of 9,9-dimethylfluorene found in experiment 3-44.

The Temperature Dependence of this Reaction. In experiment 4-41, 1.176 g (5.99 mmol) of 2,2-diphenylpropane was added to 5 ml (39.8 mg-

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* This sample was studied at -100° ± 10°. Unfortunately, it was later found that esr spectra obtained at this temperature may be unreliable. See footnote on page 76.

atoms of Cs) of Cs-K-Na alloy in 250 ml of THF at -70°. The mixture was stirred vigorously for one hour at -72° ± 2°; the reaction mixture turned reddish-brown and then black. At this point, two 5 ml samples were removed and quenched in 5 ml of H_2O and 5 ml of D_2O. These were samples numbered 1 and 2 respectively. The temperature of the reaction was raised in 10° increments to -20°. At each temperature increment, that temperature (± 2°) was maintained for 0.5 or 1.0 hour. Five ml samples were withdrawn from the reaction vessel at each temperature and were quenched. Table 23 contains the sampling schedule.

The contents of the reaction flask were then, right after sample No. 9 was withdrawn, jetted into 250 ml of water. Also, 150 ml of water was added to the material remaining in the reaction flask. The THF phase of each of the small samples was salted out and analyzed. The "flask residue" and "final quench" were similarly separated into two phases. The aqueous phase was extracted with pentane. The combined organic extracts of each were analyzed. The total yield of products containing 15 carbons found in the "final quench" and "final wash" was calculated to be 44.0% by gas chromatography analysis on a Carbowax 20 M column (I) at 180°. The "final quench" contained a 35.6% yield of two products, listed as relative area percents (retention time): 24.0 (4.6), 76.0 (7.6). The "flask wash" contained an 8.4% yield of six different components, listed as relative area percents (retention time): 1.8 (3.4), 29.9 (4.7), 18.4 (6.6), 33.2 (7.7), 7.6 (9.5), 9.0 (11.2). In Table 24, the results of gc on an SE 30 column (III) at 160° are tabulated for the samples taken during the reaction.

Table 23. Schedule of Reactions Between 2,2-Diphenylpropane and Cs-K-Na Alloy.

Sample No.	Reaction Time (hr:min)	Temperature	Quenching Agent
1	1:00	$-72° \pm 2°$	H_2O
2	1:00 1:00 to 1:35	$-72° \pm 2°$ warming to $-60° \pm 2°$	D_2O
3	2:05 2:05 to 2:25	$-60° \pm 2°$ warming to $-50° \pm 2°$	H_2O
4	2:55 2:55 to 3:10	$-50° \pm 2°$ warming to $-40° \pm 2°$	H_2O
5	3:40	$-40° \pm 2°$	H_2O
6	4:10 4:27	$-40° \pm 2°$ warming to $-30° \pm 2°$	H_2O
7	5:27 5:39	$-30° \pm 2°$ warming to $-20° \pm 2°$	H_2O
8	6:09	$-20° \pm 2°$	H_2O
9	6:39	$-20 \pm 2°$	D_2O

Table 24. Percent Yields of Products in the Reaction Between 2,2-Diphenylpropane and Cs-K-Na Alloy (Experiment 4-41) as Determined by GC Analysis Using an SE 30 Column (III) at 160°.

Sample Number (Description)	Retention Time in Minutes of Products[a]	Relative Percent Yield	Absolute Percent Yield[b] of Products
1(-72° ± 2°, 1 hr)	3.9 4.9	2.6 97.4	84.3
3(-60° ± 2°, 30 min)	3.9 4.9	7.0 93.0	98.9
4(-50° ± 2°, 30 min)	3.9 5.0	9.0 91.0	79.7
5(-40° ± 2°, 30 min)	3.8 4.9	9.5 90.5	72.4
6(-40° ± 2°, 1 hr)	3.9 4.9	13.6 86.4	61.0
7(-30° ± 2°, 1 hr)	4.1 5.1	13.6 86.1	49.5
8(-20° ± 2°, 30 min)	3.9 5.1	22.5 77.5	46.0
9(-20° ± 2°, 1 hr)	4.0 5.2	28.7 72.3	44.0[b]

(a) The first product in these pairs has the retention time of 2,2-diphenylpropane. However, the data in Table 25 indicates that it is a mixture of two different tetrahydro-2,2-diphenylpropanes. The second product is cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene.

(b) Assumed sample #9 yield to be same as yield found in analysis of "final quench" and "flask wash". Absolute yields in samples #1 through #8 are based on this value.

Table 25. GC-MS of Products in the Reaction Between 2,2-Diphenylpropane and Cs-K-Na Alloy (Experiment 4-41) as Determined by GC Analysis Using a Carbowax 20 M Column (I) at 178°.

Sample (Description)	Retention time of Products in minutes	Relative Area Percents	Molecular Ion	Identification by gc and ms
1(-72° ± 2°, 1 hr)	5.3	1.4	200	$Ph_2C(CH_3)_2$ + 4H
	5.9	2.4	200	$Ph_2C(CH_3)_2$ + 4H
	8.4	96.2	198	$Ph_2C(CH_3)_2$ + 2H[a]
2(-72° ± 2°, 1 hr)	5.1	1.3	204	$Ph_2C(CH_3)_2$ + 4D
	5.8	2.5	204	$Ph_2C(CH_3)_2$ + 4D
	8.7	96.2	200	$Ph_2C(CH_3)_2$ + 2D[a]
3(-60° ± 2°, 30 min)	4.7	4.8	200	Same as sample #1
	5.9	3.0	200	
	8.8	92.2	198	
4(-50° ± 2°, 30 min)	5.1	7.7	200	Same as sample #1
	5.8	5.7	200	
	8.6	86.6	198	
5(-40° ± 2°, 30 min)	5.0	9.6	200	Same as sample #1
	5.8	3.1	200	
	8.5	87.3	198	
6(-40° ± 2°, 1 hr)	5.3	9.1	200	Same as sample #1
	6.0	2.8	200	
	8.4	88.1	198	
7(-30° ± 2°, 1 hr)	4.7	11.8	200	Same as sample #1
	6.0	2.4	200	
	8.4	85.8	198	
8(-20° ± 2°, 30 min)	5.5[b]	13.5	200	Same as sample #1
	6.2	2.3	200	
	9.0	84.2	198	
9(-20° ± 2°, 1 hr)	5.1	30.1	204	Same as sample #2
	5.8	0.0	-	
	8.6	69.9	200	

(a) Identified in proteo form as cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene. The starting material 2,2-diphenylpropane has the same retention as this compound on this column; however, a comparison of Table 24 with Table 25 indicates there is no 2,2-diphenylpropane in these samples.

Table 25. (Concluded).

(b) Slower flow rate than other samples.

The results of the study of the nine samples taken during the reaction on Carbowax 20 M columns(I, II) at 178° in gc and gc-ms analysis are shown in Table 25.

Comparison of the gc of sample #9 and the compounds benzene, biphenyl and diphenylmethane on a temperature programmed (50° for six minutes, then 4° per minute to 180°) Carbowax 20 M column (I) shows that these compounds are not produced in the reaction. However, gc analysis on this column at 70° does indicate that there are traces of ethylbenzene in samples 1 and 9 and a trace of isopropylbenzene in sample 9.

Reaction of Diphenylmethane and Cs-K-Na Alloy in THF

Reaction at -70°. In experiment 3-62, 0.8188 g (4.87 mmol) of diphenylmethane was reacted with 4.0 ml (31.9 mg-atoms of Cs) of Cs-K-Na alloy in 250 ml of THF. The diphenylmethane was added to a mixture of Cs-K-Na alloy and THF at -70° and this was stirred at this temperature for 20 minutes. The mixture turned blue-black within five minutes after the diphenylmethane was added. The reaction was quenched by jetting the contents of the flask into 250 ml of H_2O. The THF layer was salted out and removed. The aqueous fraction was then extracted twice with anhydrous ether. The organic extracts were combined and dried ($MgSO_4$). The solvent was removed by distillation in vacuo to give an oil. Analysis by gc and gc-ms on a SE-30 column (III) at 120° and an OV-17 (V) column at 175°, respectively, of this oil determined that there were the products, listed as relative area percents (retention time in minutes on OV-17 (V), MW, identification):

2.7 (4.6, 172, $C_{13}H_{16}$), 77.7 (6.6, 170, $C_{13}H_{14}$), 19.6 (4.9, 168, $C_{13}H_{12}$, diphenylmethane).

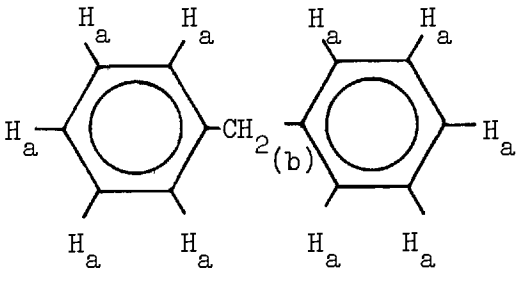
This reaction was repeated in experiment 4-51, using 1.228 g (7.301 mmol) of diphenylmethane and 6 ml (47.7 mg-atoms Cs) of Cs-K-Na alloy in 250 ml THF. The time and temperature of reaction were the same. In this experiment, 10 ml of the reaction mixture was quenched with 10 ml of H_2O. The remainder was quenched with water as before. Two samples were worked up using pentane as an extraction solvent rather than ether as in the previous reaction. They were dried and concentrated by the usual procedure. The nmr (neat) of the proteo products and the nmr (in $CDCl_3$) of the deutero products are shown in Table 26 and Table 27. These two nmr's indicate that the products are a mixture of 2,5-dihydrodiphenylmethane and diphenylmethane. The two allylic hydrogens are replaced by deuterium in the deuterium oxide quench. The relative yields according to nmr are 33% diphenylmethane and 67% the dihydro derivative. The absolute yields (assuming all products are derivatives of diphenylmethane and based on initial diphenylmethane as limiting reagent) from gc analysis on a Carbowax 20 M (I) at 189° were (retention time in minutes, identification): 24.9 (15.1, diphenylmethane), 42.1 (13.1, 2,5-dihydrodiphenylmethane), 5.1 (16.7), 3.4 (8.4 and 9.0, two unresolved peaks), 0.6 (6.1), and 0.7 (5.6). Four-fifths of the solution of protonated products used for gas chromatography was concentrated to remove solvent and dissolved in 100 ml benzene. The solution was dehydrogenated with 0.416 g of 5% Pd/C by heating at reflux for 20 hours. The mixture was then filtered

Table 26. Interpretation of the NMR Spectrum of Protonated Products (Neat) in the Reaction Between Diphenylmethane and Cs-K-Na Alloy (Experiment 4-51).

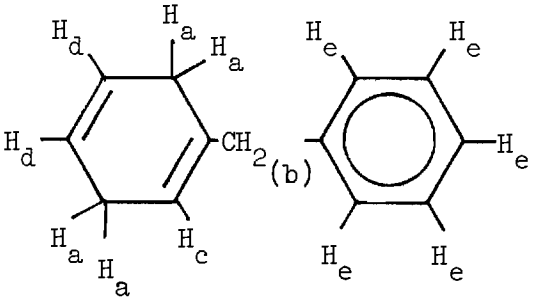
	Multiplicity	Integration Rel. Areas	Relative Numbers of Hydrogens	Identification[a]
7.5	complex q	40	4.0	IV, H_a
6.9	s	20.5	2.0	IV, H_b
6.2	s	10	1.0	III, H_b[b]
4.5	broad s	10.7	1.1	IV, H_c
4.4	complex s	21.3	2.1	IV, H_d
2.9	two peaks separated by 1 Hz	100 (50 + 50)	5.0 + 5.0	III, H_a[b] and II, H_e

(a) This spectrum is consistent for a 33:67 ratio of III:IV.

(b) Identical with nmr spectrum of diphenylmethane. It appears the down field peak is due to diphenylmethane.



III



IV

Table 27. Interpretation of the NMR Spectrum of Deuterated Products ($CDCl_3$) in the Reaction Between Diphenylmethane and Cs-K-Na Alloy (Experiment 4-51).

τ	Multiplicity	Integration Rel. Areas	Relative Numbers of Hydrogens	Identification[a]
7.4	broad d	10.5	2.1	IV, H_a
6.7	s	9.5	1.9	IV, H_b
6.0	s	4.6	1.0[b]	III, H_b[b]
4.5	broad s	4.5	0.9	IV, H_c
4.3	t (J=0.67 Hz)	10.0	2.0	IV, H_d
2.8	s	50.0 (25.4 + 24.6)	5.1[b] + 4.9	III, H_a[b] and II, H_e

(a) This spectrum is consistent for a 33:67 ratio III:IV where IV is dideuterated in allylic positions.

(b) Identical with nmr spectrum of diphenylmethane.

and concentrated. NMR spectroscopy and gc analysis on a Carbowax 20 M (I) column at 193° indicated that the dihydrodiphenylmethane and the unknown, yield of 5.1%, (retention time of 16.7 minutes), were aromatized to diphenylmethane. The other products found (4.7% yield) were not. The products found by gc analysis, listed as relative area percents (retention time in minutes, identification), were: 1.6 (4.2), 14.2 (5.2), 11.7 (6.1), 1.9 (7.0), 70.6 (11.1, diphenylmethane). The sample before dehydrogenation had under the same gc conditions the products, listed as relative area percents (retention time) were: 1.3 (4.4), 2.4 (6.2), 6.7 (8.0), 55.0 (9.5), 34.6 (11.4). Analysis by gc on this column at 210° indicate that the dehydrogenated sample did not contain fluorene (14.0 min).

In experiment 4-77, 0.8274 g of diphenylmethane (4.918 mmol) was reacted with 4.0 ml (31.8 mg-atoms) of Cs-K-Na alloy at -70° for one hour in 250 ml THF. Electron spin resonance spectroscopy of a sample at -95° $\pm$ 5° from this reaction showed 0.5 percent anion radical present.* The reaction was quenched in water, extracted and concentrated as in the previous reactions. The nmr spectrum of resulting oil (0.948 g) indicates that it is consistent with a 80:20 mixture of 2,5-dihydrodiphenylmethane and diphenylmethane. A small sample of the 2,5-dihydrodiphenylmethane (1.21 mg) was isolated by preparative

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* This is based on the assumption that one electron is added to one molecule of diphenylmethane. Further esr studies indicated that the spectra obtained at this temperature may be unreliable. See footnote on page 76.

gc on a Carbowax column (I) for uv analysis in isooctane. The uv spectrum max were: 248 mμ (ε 161.7), 253 mμ (ε 215.1), 258 mμ (ε 253.1), 262 mμ (ε 240.4), 264 mμ (ε 206.7), 268 mμ (ε 196.8). This is similar to the uv spectrum max (isooctane) of ethyl benzene[89]: 242 (shoulder) mμ (ε 63.1), 248 mμ (ε 125.9), 253 mμ (ε 158.5), 258 mμ (ε 199.5), 262 mμ (ε 199.5), 264 mμ (ε 158.5), 268 mμ (ε 199.5). The uv spectrum max (isooctane) of diphenylmethane is[90]: 254 mμ (ε 389), 256 mμ (ε 398), 260 mμ (ε 468), 263 mμ (ε 468), 269 mμ (ε 380).

In experiment 2-165, 0.8277 g (4.927 mmol) of diphenylmethane was added to a mixture of 6.628 g (35.7 mg-atoms of cesium) of Cs-K-Na alloy in 250 ml of THF at -70°. This was stirred vigorously for one hour and two esr samples were withdrawn. The remainder was quenched in 250 ml of water. Analysis of the esr samples at -196° indicated percent yields of anion radical of 6.4×10^2 and 1.3×10^3 based on the addition of one electron to one diphenylmethane molecule. Relative area percent yields (retention time in minutes) of 18.2% (4.8) diphenylmethane and 81.8% (5.6) 2,5-dihydrodiphenylmethane were obtained by gc analysis, using an SE-30 column (III) at 132°, of the water quench.

The Effect of Warming this Reaction from -70° to -60°. In experiment 4-54, 1.217 g (7.236 mmol) of diphenylmethane was added to

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(89) Mortimer J. Komlet "Organic Electronic Spectra Data" Vol. I, Interscience, New York (1960), p. 202.

(90) Reference 86, p. 510.

6 ml (47.7 mg-atoms Cs) of Cs-K-Na alloy in 250 ml of THF. This was stirred for 1.33 hours at -70° ± 2° and then heated to -60° ± 2° over a two minute period. This last reaction temperature was maintained for two hours. Upon addition of the diphenylmethane, the mixture turned deep greenish-blue. This had changed to black within the first hour of the reaction. Aliquots were periodically removed from the reaction: (1) after one hour at -70°, (5 ml), (2) after one hour at -60° (5 ml), and (3) after two hours at -60° (10 ml). Samples No. 1 and 2 were quenched in 5 ml of water while sample No. 3 was quenched in 10 ml of D_2O. After the D_2O quench, the remainder of the mixture was jetted into 250 ml of water. The samples No. 1 and No. 3 and the final quench were extracted, dried ($MgSO_4$) and concentrated. The material remaining in the reaction flask was quenched with water and the products were isolated in the same manner. Analysis by gc on a Carbowax 20 M column (I) at 193° of the "final" and "flask wash" aqueous quenches indicated that the products, listed as absolute percent yields, based on initial diphenylmethane as the limiting reagent, (retention time in minutes, identification) were: 4.0 (6.9), 3.9 (8.9), 39.9 (10.7, 2,5-dihydrodiphenylmethane), 47.3 (12.6, diphenylmethane). This final quench analyzed by gc on a temperature programmed SE 30 column (III) (two minutes at 100°, then 15° per minute to 240°) indicated that the products, listed as relative area percents (retention time in minutes, identification) were: 1.5 (7.0),58.7 (8.2, diphenylmethane), 32.2 (8.7, 2,5-dihydrodiphenylmethane), 11.5 (6.0), 13.8 (1.5). The relative area percent (retention time in minutes,

identification) yields of products by gc analysis on a Carbowax 20 M column (I) at 195° in the three small quenches were:

Sample 1 (-70°, 1 hour): 6.0 (6.8), 6.7 (8.2), 62.3 (9.8, 2,5-dihydrodiphenylmethane), 24.9 (11.5, diphenylmethane).

Sample 2 (-70°, 1.33 hours; -60°, 1 hour): 4.3 (6.8), 4.7 (8.6), 53.1 (10.2, 2,5-dihydrodiphenylmethane), 37.9 (12.0, diphenylmethane).

Sample 3 (-70°, 1.33 hours; -60°, 2 hours): 2.8 (6.6), 5.1 (8.6), 47.4 (10.2, 2,5-dihydrodiphenylmethane), 44.7 (12.1, diphenylmethane).

The nmr spectrum (neat) of the final quench had a similar spectrum to that outlined in Table 26 for experiment 4-51. The relative yields of diphenylmethane and 2,5-dihydrodiphenylmethane calculated from the nmr spectrum were 48° and 52%, respectively. The nmr spectrum of Sample 1 in $CDCl_3$ (-70°, 1 hour) showed this sample contained 73% 2,5-dihydrodiphenylmethane and 27% diphenylmethane. The nmr spectrum ($CDCl_3$) of sample 3 (-70°, 1.33 hours, -60°, 2 hours; quenched with D_2O) is outlined in Table 28. This indicates there is ca a 63% monodeuteration of diphenylmethane.

Reaction of Tetraphenylmethane with Cesium in THF

Reaction at -70° with Cs-K-Na Alloy. In experiment 4-27, 199.3 mg of tetraphenylmethane (0.622 mmol)* was reacted with 1 ml of Cs-K-Na alloy (7.95 mg-atoms of Cs) in 250 ml of THF at -70° ± 2° for one hour. The mixture turned black during the course of the reaction. A 5 ml

* Amount limited by solubility in THF. The solubility of tetraphenylmethane is ca 100 mg/20 ml of THF at room temperature.

Table 28. NMR Spectrum of Sample 3, Experiment 4-54.

τ	Multiplicity	I	H	Interpretation
7.5	broad	15	2.2	IV, H_a
6.8	s	12	1.8	IV, H_b
6.1	broad s	9	1.3	III, H_b
4.6	broad s			
4.4	s	21	3.1	IV, H_c
2.9	s	100 (65.8; 34.2)	14.7	III, H_a; IV, H_c

The ratio of products is 51% diphenylmethane and 49% 2,5-dihydrodiphenylmethane by nmr analysis.

sample of this was quenched in 5 ml of D_2O and the remainder quenched in 220 ml of H_2O.

The D_2O quench was separated* into two phases by addition of NaCl. The aqueous phase was extracted with pentane. The extracts were combined, dried ($MgSO_4$) and concentrated. The H_2O quenched sample was worked up in the same manner. Table 29 contains the reaction products found by gc on a temperature programmed OV 17 column (V). Table 30 contains the results of analysis on a temperature programmed Carbowax 20 M column (I).

Analysis by ms-gc of the sample quenched with D_2O on a temperature programmed (50° until the solvent eluted, then 50° per minute to 150°) Carbowax 20 M column (II) indicated that the product, diphenylmethane, contained two deuterium atoms (a MW of 170). Since the D_2O quenched material was worked a month after the reaction, the deuterium in the compound could be due to base catalyzed exchange occurring after the quenching step.

Reaction with Cesium at 36°. In experiment 3-56, 2.001 g of tetraphenylmethane (6.264 mmol) was added as a powder to 5.22 g of cesium (39.3 mg-atoms) in 250 ml of THF at 32 to 36°. This reaction was stirred for four hours and quenched in 250 ml of water. The mixture had turned a deep brown-green before it was quenched. This was worked up in the usual manner and studied by gc on a temperature programmed SE 30 column (III) (two minutes at 70°, then 24° per minute

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* One month after the reaction performed.

Table 29. Analysis of the Reaction of Tetraphenylmethane and Cesium Alloy at -70° (Experiment 4-27) Using a Temperature Programmed OV 17 Column (V) (90° for four minutes, then 10° per minute to 290°).

Component[a]	Retention Time in minutes	Yield (mg)	Yield[b]
reduced biphenyls[c]	9 0, 9.4, 9.8	28.9	30.2%
biphenyl	11.2	11.8	11.8%
diphenylmethane	12.2	29.2	28.0%
1,2-diphenylethane	13.2	0.0	0.0
unknown C_{13} compound[d]	14.6	3.84	3.7%
triphenylmethane	20.3	1.57	1.0%
tetraphenylmethane plus small shoulders	26.5	11.09	5.6%
Total			80.3%

(There is also a low broad peak (15.5 minutes to 34 minutes) which would be indicative of decomposition of high molecular products.)

(a) The components were identified by retention time and mixed injections. The amount of each component was determined by comparison of gc areas with a known amount of an authentic sample of each component.

(b) Absolute yield assumes each product comes from tetraphenylmethane.

(c) Biphenyl is used as a standard for calculations in this case.

(d) This is assumed by gc retention time. No attempt was made to determine the number of carbon atoms in the products. In this case, diphenylmethane was used as a standard for calculations.

Table 30. Gas Chromatography Results on a Temperature Programmed Carbowax 20 M Column (I) (50° for 10 minutes, then 40° per minute to 170°) of Tetraphenylmethane and Cesium Alloy (Experiment 4-27).

Component	Retention Time in Minutes	Yield (mg)	Absolute Yield[a]
benzene	4.1	0.28	0.6%
phenylcyclohexane	18.2	5.40	5.6%
an unidentified tetrahydrobiphenyl	19.0	2.12	2.2%
1,4-dihydrobiphenyl	20.6	6.99	7.3%
unknown reduced biphenyl[b]	23.0	0.63	0.7%
unknown reduced biphenyl[b]	24.2	0.43	0.5%
biphenyl, diphenylmethane	26.3	-	-
Total			16.9%

No toluene of 1,2-diphenylmethane found.

(a) Absolute yield assumes each product comes from tetraphenylmethane. Biphenyl is used as a standard for calculations.

(b) This is assumed for yield calculations. This could be reduced diphenylmethanes.

Table 31. GC-MS[a] Results in the Reaction of Tetraphenylmethane and Cesium at 36° in Experiment 3-56.

Retention Time in Minutes	Relative Area Percent	Molecular Ion (m/e)	Possible Product
12.1	0.2	160	$C_{12}H_{16}$
12.2	0.9	160	$C_{12}H_{16}$
12.3	6.5	158	$C_{12}H_{14}$
12.9	15.2	156	$C_{12}H_{12}$
14.0	3.2	158	$C_{12}H_{14}$
14.1	15.1	154[b]	$C_{12}H_{12}$
15.0	44.2	168	diphenylmethane
19.8	1.1	168[c]	unknown
25.0	1.8	242[c]	9-phenylfluorene
27.3	3.1	244[c]	triphenylmethane[d]
29-31	8.6	244 or 320[c]	tetraphenylmethane and reduction product

(a) Analyzed on a temperature programmed OV-17 column (VI) (3 minutes at 90°, then 8° per minute to 300°).

(b) This has the gc retention time of an unknown $C_{12}H_{12}$ compound.

(c) It has apparently dehydrogenated during the gc-ms determination. The high molecular weight compounds have a tendency to stick in the instrument and to dehydrogenate to aromatic molecules, thereby giving false spectra.

(d) Not triphenylmethane by gc analysis.

to 290°)and ms-gc on a temperature programmed OV 17 column (VI) (three minutes at 90°, then 8° per minute to 300°). Table 31 contains the results of this study.

Reactions of cis-2-Heptene with Cesium Metal and Cs-K-Na Alloy in THF

Reaction with Cesium Alloy

In experiment 2-60, 0.695 g (7.08 mmol) of cis-2-heptene was added to a mixture of 20 ml of Cs-K-Na alloy (15.9 mg-atoms of Cs) and 250 ml of THF at -70°. This was stirred for eight hours at temperatures between -70° and -75° and then quenched in 250 g of ice slush. The pentane extract of this was washed with water, dried ($MgSO_4$) and concentrated to ca 7 ml on a vacuum jacketed column and then a spinning band column. Analysis by gc on a Ucon Oil LB 550 X column (XI) at 30° for the various heptenes shows that there was no apparent reaction. The retention time in minutes of the possible products in this gc system were: n-heptane, 9.8; 1-heptene, 13.4; trans-3-heptene, 13.6; cis-3-heptene, 14.5; trans-2-heptene, 15.0; cis-2-heptene, 16.8.

A second run, experiment 2-76, used the same amounts of starting reagents plus 0.708 mmol of tert-butanol. The cis-2-heptene, cesium alloy, and tert-butanol were stirred in THF for four hours at -65° and then warmed over 0.5 hour to 29° and stirred an additional two hours. There was no apparent reaction by gc analysis at 28° on a Ucon Oil LB 550 X column (XI). A third run, experiment 2-82, used

the same amounts of reagents as in the second. This reaction was cooled at -72° ± 1° for four hours and then warmed to 26° over a 1.25 hour period, where it was stirred for an additional 2.5 hours. There was no apparent reaction by gc analysis for the various heptenes on a dimethylsulfolane column at 55°. The retention time in minutes of the possible products at a column temperature of 50° were: heptane, 6.2; trans-3-heptene*, 8.3; 1-heptene*, 8.6; cis-3-heptene**, 9.0; trans-2-heptene**, 9.6; cis-2-heptene, 10.4.

Reaction with Cesium Metal

In experiment 2-64, 1.165 g (11.9 mmol) of cis-2-heptene was added to a mixture of 4.73 g (35.6 mg-stoms) of cesium in 250 ml of THF and was stirred for 1.25 hours at 35-37°. Then, 0.1061 g (1.19 mmol) of tert-butanol was added and stirred at this temperature for 80 minutes more. This was cooled to -70° and kept between -70° and -60° for two hours. This turned wine-red. This was quenched in 500 ml of ice water. Analysis of the dried ($MgSO_4$) pentane extract on a dimethylsulfolane column (IX) at 55°, after it was concentrated to about 30 ml, indicated that three seven-carbon compounds were present. They were listed as relative area percents (retention time in minutes, identification); 6.87 (8.8, 1-heptene), 6.87 (10.1, trans-2-heptene) and 86.26 (10.9, cis-2-heptene). There were no 14-carbon compounds formed.

In experiment 2-90, 1.241 g (12.6 mmol) of cis-2-heptene was

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* and ** These two pairs of compounds had the same retention time in a mixed sample.

added to a mixture of 5.04 g (35.9 mg-atoms) of Cs, and 143 µl (1.26 mmol) of tert-butanol and 250 ml of THF. This was studied in the following manner: heated for hour hours at ca 33°; heated at reflux for one hour; tried to cool but metal coagulated; stood overnight without stirring; 100 µl of oleic acid was added (ca 2% of the amount of Cs); stirred at 45° to get an immulsion; cooled to -72°; and allowed to warm up and stand for an additional two days.

Table 32 contains an outline of the reaction procedure and the relative area percent yields of products determined by analysis on a dimethylsulfolane column (IX) at 55° found in 5 ml samples quenched periodically throughout the reaction.

In experiment 2-140, 1.222 g (12.5 mmol) of cis-2-heptene is added to a mixture of 4.98 g (37.4 mg-atoms) of cesium and 250 ml of THF at 37°. This was heated to ca 40° for four hours, heated at reflux for 2.5 hours, and let stand without stirring for 62 hours. Samples were withdrawn and quenched throughout the experiment. Table 33 outlines the results of analysis on a dimethylsulfolane column (IX) at 55°. The remaining solution was quenched by jetting over 200 g of CO_2.

Table 32. Relative Area Percent Yields of Heptenes in Experiment 2-90.

Sample	Temperature (°C)	Time (hr:min)	% cis-2-heptene (retention time in minutes)	% trans-2-heptene (retention time in min)	% 1-heptene (retention time in min)	Comment
-	-	0:00	100.0 (8.0)	-	-	standard
0	37°	0:05	96.7 (8.0)	1.8 (7.2)	1.5 (6.6)	
1	33°	1:00	95.7 (7.8)	2.5 (7.1)	1.8 (6.2)	
2	33°	2:03	93.7 (7.7)	3.8 (7.0)	2.5 (6.3)	
3	32°	3:00	91.7 (7.5)	6.2 (6.9)	2.1 (6.2)	
4	32°	3:55	89.0 (7.9)	7.7 (7.2)	3.3 (6.5)	
5	30°	5:13	71.8 (7.5)	23.3 (6.9)	4.9 (6.1)	had just kept at reflux for 1 hour
6	ca 30°	7:05	67.6 (7.4)	24.3 (6.8)	7.9 (6.0)	attempted to cool to -70°
7	ca 30°	20:40	32.5 (7.2)	60.9 (6.8)	6.6 (6.0)	had set overnight without stirring
8	-72°	21:30	33.3 (7.2)	60.4 (6.8)	6.3 (6.1)	added oleic acid stirred at 45° for 15 minutes and cooled at -72° for 15 minutes.

Table 32. (Concluded).

Sample	Temperature (°C)	Time (hr:min)	% cis-2-heptene (retention time in minutes)	% trans-2-heptene (retention time in minutes)	% 1-heptene (retention time in minutes)	Comment
9	-70°	23:30	27.6 (7.3)	64.1 (6.7)	8.3 (5.9)	
10	30°	69:00	23.0 (8.9)	68.9 (7.8)	8.1 (7.0)	had left two days, no stirring, decomposed in 250 ml of H_2O

Table 33. Relative Area Percent Yields of Heptenes Found in Experiment 2-104.

Sample	Temperature	Time (hr:min)	% cis-2-heptene (retention time in minutes)	% trans-2-heptene (retention time in minutes)	% 1-heptene (retention time in minutes)	Comment
0	41°	0:02	98.0 (7.8)	0.7 (6.9)	1.3 (6.3)	
1	41°	1:05	96.2 (7.7)	1.7 (7.0)	2.1 (6.2)	
2	42°	2:05	94.8 (7.8)	2.6 (7.0)	2.6 (6.3)	
3	42°	3:05	92.9 (7.9)	4.5 (7.2)	2.6 (6.4)	
4	42°	4:05	89.9 (7.8)	6.2 (7.0)	4.0 (6.4)	
5	67°	5:05	81.7 (7.6)	13.1 (7.0)	5.0 (6.2)	had heated at reflux one hour
6	67°	6:35	73.5 (7.7)	20.0 (6.8)	6.3 (6.2)	had heated at reflux 2.5 hours
7	25°	19:45	74.7 (6.6)	20.6 (6.0)	4.7 (5.2)	no stirring from sample 7 on
8	25°	68:33	72.5 (6.5)	22.4 (6.0)	5.1 (5.5)	
9	25°	71:50	60.8 (7.4)	32.3 (6.8)	6.9 (6.0)	neutral fraction of carbonated solution[a]

(a) Isolation of the carbonation products from this reaction yielded 43.1 mg of crude material. This amount was considered too small to pursue any further.

CHAPTER V

DISCUSSION

The Reactions of Benzene and Cesium

The experimentation, described in the previous chapter indicates that the course of the reaction of cesium with benzene is temperature dependent. This reaction was studied at three different temperatures: -70°, -20°, and room temperature (25° to 35°).

The Reaction at -70° in THF

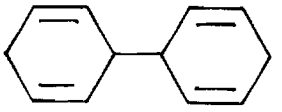
The reaction at -70° was studied in a few experiments whose original purpose was to investigate the course of the reaction at -20° and above. The reaction at -20° was performed by first reacting cesium sand with a seven-fold excess of benzene in THF at -70° to give a black precipitate and then warming this to -20°. Table 34 outlines the results of the study of the reaction at -70°. According to the data presented in this table, the black precipitate produced at -70° has a high radical concentration in a doublet state, this fact along with the high chemical yield of products (ca 75% based on cesium) indicated that there is a high yield of monoanion radical. No triplet radical was observed. This black precipitate, when decomposed by water, becomes 1,4-dihydrobenzene (VI) (the expected product in Birch reduction of benzene[21]), cyclohexene (VIII), and 1,1',4,4'-tetrahydrobiphenyl (VIII) (the major product formed in this reaction at -20°). In experiment 3-162, the yield (in mol of product per g-atom of initial

cesium) of 1,4-dihydrobenzene was only 0.036 (after 1.5 hours) and 0.222 (after 4 hours) when the -70° black intermediate was quenched with iodine, rather than the much higher yields given in Table 34 for quenching with water. The only other volatile product found in the reaction with iodine was the starting material, benzene.

Benzene
V

1,4-dihydrobenzene
VI

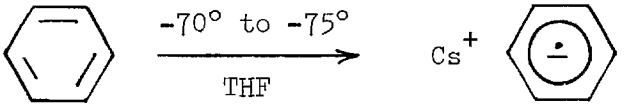
cyclohexene
VII



1,1',4,4'-tetrahydrobiphenyl
VIII

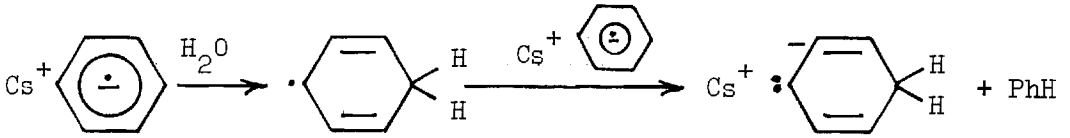
These observations indicate that the product of the reaction of benzene with cesium at -70° to -75° is primarily cesium benzenide, the product of transfer of an electron from one cesium atom to one benzene molecule. This reaction is illustrated in equation 1. The role of cesium benzenide in forming compound VI is shown in equation 2.

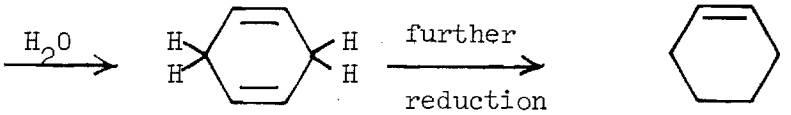
1



V

2





VI VII

Table 34. Results of the Reaction of Cesium Metal with Benzene in THF at -70° when Quenched with Water.

Expt.	Conditions	Yield of Products[a] VI	VII	VIII[c]	Anion Radical Yield[b] (Temp. of esr measurement)
4-5	1 hr, -70° to -75°	76.6%[d]	0.0%	23.4%[d]	NA[e]
3-162	1.5 hr, -72°	0.333[f]	0.00847[f]	0.0277[f]	NA
	4 hr, -72°	0.297[f]	0.0125[f]	0.0603[f]	NA
4-82	2 hr, -70° to -75°	NA	NA	NA	200% (-196°) 0.08% (-105° ± 15°)
4-72[g]	2 hr, -70°	NA	NA	NA	400% (-196°)
4-70[g]	1 hr, -70°	NA	NA	NA	19% (-196°)
4-48	1 hr, -70° (benzene-$\underline{d}_6$)	NA	NA	NA	9000% (-196°)

(a) Benzene is not reported because it is in excess.

(b) These are doublet state radicals; an esr investigation in experiment 4-82 indicated there was no half-field signal which means there was no triplet-state radical present. The yields were calculated by dividing the radical concentration by the initial cesium concentration and multiplying by 100.

(c) The gc analysis was at 200°. There is pyrolysis of VIII to up to 10 components at this temperature.

Table 34. (Concluded).

(d) This is a relative area percent yield.

(e) No analysis was performed.

(f) This yield is expressed in mol of product per g-atom of initial cesium.

(g) The color of the reaction did not change from black to yellow-green when the reaction mixture was warmed from -70° to -20°.

According to the data in Table 34 and assuming the stoichiometry of equation 2, the yield of VI indicates that there is a 60 percent to 67 percent yield of cesium benzenide in the reaction of cesium and benzene. The formation of benzenide ion in alkali metal-benzene reactions is not unusual. Potassium and benzene are known to form potassium benzenide;[22-27] however, a high yield of cesium benzenide is quite unusual for an alkali metal-benzene reaction. For example, potassium (from Na-K alloy) and benzene yield, at the most, 0.01 percent potassium benzenide in vacuum line experiments.[27] The high yield of cesium benzenide is probably due to a number of factors. The production of a THF-insoluble precipitate may facilitate reaction by lowering the potential energy of the cesium benzenide salt and thereby shifting the equilibrium towards the products. The higher electron donor ability of cesium than potassium[3] promotes a larger formation of anion radical. The vigorous stirring used during the present reactions provided good contact between benzene and cesium and thereby made possible a high yield of products.

It appears that iodine acts as an electron acceptor and oxidizes the benzenide ion to benzene. There is a small amount of VI produced in this reaction. This product is probably formed as a result of the presence of water as a minor impurity during the quenching reaction with iodine. The reaction of cesium benzenide with iodine is shown in equation 3.

3 

There is some question as to the source of the second electron that is transferred to benzene in equation 2. Since the esr measurements indicate quantitative yields of cesium benzenide, it is implied that there is no free cesium available to participate in further reduction. This conjecture is supported by the results found when an excess amount of cesium alloy is reacted with benzene. In this case, there was never more than a 40 percent relative yield (Table 39) of 1,4-dihydrobenzene even though there was at least a two-fold molar ratio of cesium (in Cs-K-Na alloy) to benzene. Therefore, it appears that the second electron is transferred from cesium benzenide and not from free cesium.

The Reaction of Cesium with Benzene in THF at -20°

After cesium benzenide is produced at -70° to -75°, warming of this black intermediate to -20° promotes an apparent second reaction because a yellow-green precipitate is produced. This reaction was found to be hard to reproduce; however, it did occur in ca 70 percent of the reactions attempted. Analysis by gc of a reaction product that did not change color (experiment 4-72, see Table 35) indicated that only a small amount of products VI, VII, and VIII were formed. No attempt was made to determine why this reaction was not reproducible; however, it seems reasonable to assume that the poor reaction at -20° is due to a low yield of cesium benzenide at -70°. This assumption is supported by the observation of the low anion radical concentration (at -70°) found by esr measurement in experiment 4-70 (Table 34, a reaction that does not change from black to yellow-green at -20°). On

the other hand, the esr results found in experiment 4-72 (Tables 34 and 35) appear to indicate that the anion radical concentration (at -70°) of a reaction that does not change color (at -20°) can be quite high. Since these values found by esr measurements are only accurate within a factor of some ten-fold and there is low yield of products (after quenching with water at -20°) in experiment 4-72, it is probable that the actual anion radical yield is more like 10 percent.

There is a report in the literature that further reaction of potassium benzenide is catalyzed by lithium ion;[26] it was found that drying the solvent of the reaction by distilling from $LiAlH_4$ provided enough lithium ion to catalyze potassium benzenide to form some sort of dimer. Since in the present reactions of cesium and benzene the solvent was dried with $NaAlH_4$, the presence of lithium ion should not be a factor.

The properties of the yellow-green intermediate were quite different from those of the product found at -70°, cesium benzenide. The anion radical concentration, for example, was negligible. The measurement made in experiment 4-48, showed only a 1.3×10^{-6} ratio of radical to initial cesium in this precipitate. In experiment 4-5, the precipitate was quenched with water to yield a new compound that had an elemental analysis of $C_{12}H_{14}$. Dehydrogenation of this with Pd/C yielded biphenyl and hydrogenation with hydrogen over Pd/C in ethanol gave dicyclohexyl and phenylcyclohexane. NMR analysis of the compound $C_{12}H_{14}$ showed eight vinyl hydrogens and six allylic hydrogens. When the yellow-green intermediate was quenched with D_2O, the nmr spectrum of

Table 35. Results of the Reaction of Cesium Metal with Benzene in THF at -20° when Quenched with Water.

Experiment	Conditions	Yield of Products[a] VI	VII	VIII	Anion Radical Yield[b] (Temp. of esr measurement)
4-5	1 hr, -70° to -75° 2 hr, -20° ± 3°	1.4%	0.0	63.2% 0.198[h]	NA[e]
3-162	4 hr, -72° 70 min, -35°	0.224	0.0136	0.141[f] (-35°)	NA
4-82	2 hr, -70° to -75° 1.5 hr, -20° ± 3°	NA	NA	0.188[i]	33×10^{-4}% (-105° ± 15°)
4-82	above conditions stored for 2 hr at -70°	NA	NA	0.177[i]	NA
4-72[g]	2 hr, -70° 2 hr, -20° ± 3°	<0.01	-	0.022[i]	6.4×10^{-1}% (-196°)
4-59	perdeuterobenzene, 1 hr, -72° 1.75 hr, -20° ± 3°	0.018	-	0.200[i]	NA
4-48	perdeuterobenzene, 1 hr, -70° 1.5 hr, -20° ± 3°	NA	NA	0.166[h]	1.3×10^{-4}% (-196°)
4-20	1 hr, -70°	0.102 (after 1 hr)	-	0.100[f]	NA
	3 hr, -20° ± 5°	0.071 (after 2 hrs)	-	0.182[f]	NA

Table 35. (Concluded).

Experiment	Conditions	Yield of Products[a] VI	VII	VIII	Anion Radical Yield[b] (Temp. of esr measurement)
4-20	above condition stored for 9 hr at -70°	0.060	-	0.090[f]	NA

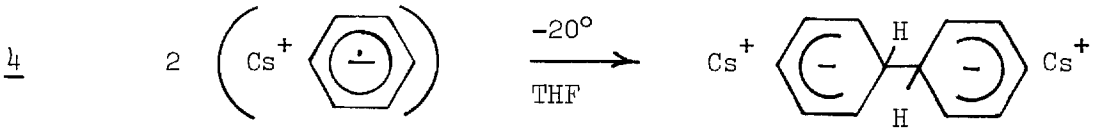
(a),(b),(e),(f),(g) Same as (a),(b),(e),(f),(g), respectively, in previous table.

(h) This was isolated as an oil by distillation. The yield is expressed in mol of product per g-atom of initial cesium. The percentage yields are relative area percentage of products contained in the isolated mixture before distillation. There is also THF and benzene in this mixture.

(i) This yield is based on titrated cesium in the sample and is expressed in mol of product per g-atom of titrated cesium.

the product indicated that two of the allylic hydrogens were replaced by deuterium. The structure of the product from quenching by water is indicated by this data to be 1,1',4,4'-tetrahydrobiphenyl (VIII). The product from a D_2O quench would be 1,1',4,4'-tetrahydrobiphenyl-$\underline{d}_2$ (VIII-$\underline{d}_2$). In Table 35, the yields of VIII are outlined for the different experiments performed. The absolute yields of VIII, determined from this table, are found by calculation, using the stoichiometry in equation 4, generally to range between 33% and 40%, in reactions that turned yellow-green.

Considering the evidence outlined above, the intermediate formed at -20°* is the dimer of cesium benzenide, i. e. dicesium 1,1'-dihydrobiphenylide (IX). This reaction is shown in equation 4. The same type of reaction has been reported to occur

4 

IX

with pyridine and alkali metals.[30-33] In this case, the dimer dianion loses two hydride ion to form bipyridyl.

In the work with the yellow-green intermediate, three other

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* According to the data in Table 34, this intermediate is also produced at -70°; however, the concentration of this is not high enough to change the color of the reaction.

quenching reagents were investigated. They were iodine, dimethyl sulfate, and carbon dioxide. Iodine gave the simplest results. This reagent appears to act as an electron acceptor to give as products: benzene and traces of 1,4-dihydrobenzene.* Carbon dioxide quenching of the intermediate yielded a complex mixture of acids. An nmr analysis of these acids showed no aromatic acids present. The products were tentatively identified by dehydrogenation with Pd/C and then gc analysis of the methyl esters of the resulting aromatic acids. The acids found were (relative weight percents): benzoic acid (5.0), terephthalic acid (56.6), p-phenylbenzoic acid (6.0), 2,2'-diphenyldicarboxylic acid (1.7), 4,4'-diphenyldicarboxylic acid (26.7), and an unidentified acid derivative of biphenyl (4.0). The yellow-green intermediate, when quenched with dimethyl sulfate, yielded at least 12 different gc-volatile products. Dehydrogenation of this mixture with Pd/C made this mixture even more complex. However, the major known products were, in their aromatized forms, p-xylene and 4,4'-dimethylbiphenyl in relative molar yields of 61:14.

The probable reactions of the yellow-green intermediate (IX) are summarized in equations 5 to 9.

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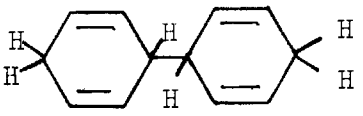
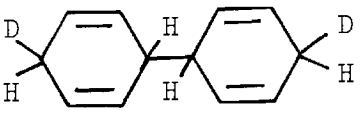
* In experiment 3-162, there was produced a 0.014 molar ratio of 1,4-dihydrobenzene to initial cesium. This could result from traces of water present during the quenching step. In view of the fact that a large excess benzene was present in the reaction mixture, the formation of benzene as product of the reaction with iodine in the present experiment can only be conjectured on the basis that no other products were found (other than traces of 1,4-dihydrobenzene).

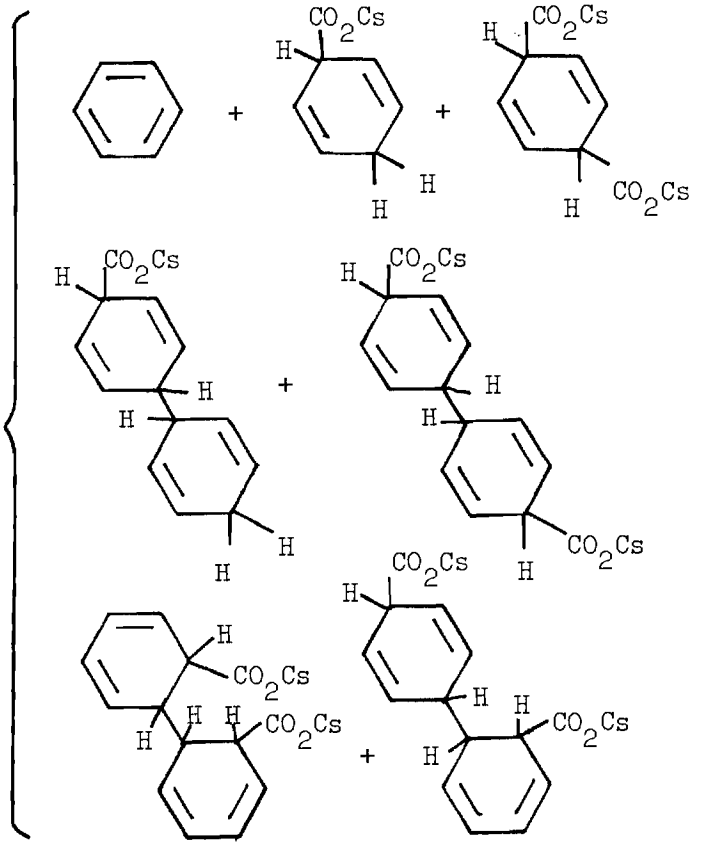
5 IX + $2H_2O$ ⟶  + 2CsOH

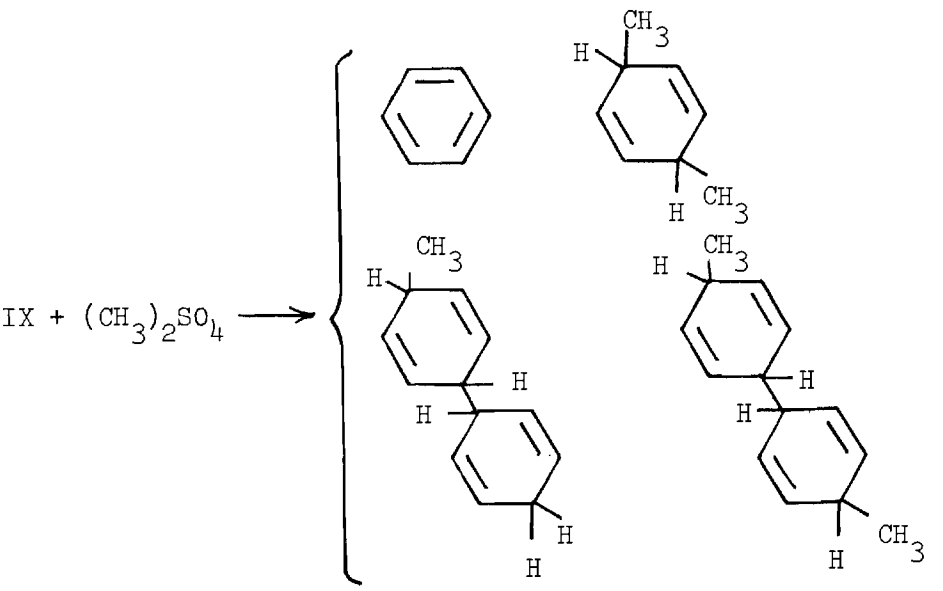
VIII

6 IX + $2D_2O$ ⟶  + 2CsOD

VIII-$\underline{d}_2$

7 IX + I_2 ⟶ 2  + 2CsI

8 IX + CO_2 ⟶ 

9 

There seems to be a correlation between product complexity and rate of reaction. Water which reacts instantaneously with the intermediate gives primarily compound VIII. In gc analysis of VIII (isolated in experiment 4-5), there was benzene (V) (5.2 rel. area percent) and 1,4-dihydrobenzene (VI) (10.4 rel. area percent) present. However, these are also thermal decomposition products of VIII. Pyrolysis of compound VIII, produced in experiment 4-5, has shown that V (27.7 rel. area percent) and VI (6.0 rel. area percent) are among the products formed after five hours at 166°. An nmr spectrum of this same sample of VIII indicates that it contains ca 0.7 mol percent benzene. It is more likely that these products come from pyrolysis on the gc column rather than from the reaction with water. Carbon dioxide which is somewhat slower in reacting than water allows the 1,1'-carbon-carbon bond to be broken before quenching has been accomplished. Dimethyl sulfate, a reagent that appears to be slower

than carbon dioxide at discharging the yellow-green color, also allows the 1,1'-carbon-carbon bond to be broken. Iodine, which acts as an electron acceptor, promotes the breaking of this bond to give the starting material, benzene.

In experiment 4-59, a sample of the -20° intermediate prepared from perdeuterobenzene was attached to a vacuum line and the solvent was removed at temperatures below -20°. When the intermediate was quenched by slow distillation of water into the evacuated flask at -196°, the products (measured as mol of product per g-atom of titrated CsOH), were found to be: benzene (0.207), 1,4-dihydrobenzene (0.239), and 1,1',4,4'-tetrahydrobiphenyl (0.114) (all by gc analysis). Analysis of a sample (with solvent) that was quenched at the same time by jetting into water showed (in mol of product per g-atom of titrated CsOH): 1,4-dihydrobenzene (0.018) and 1,1',4,4'-tetrahydrobiphenyl (0.200)(benzene is in excess). This discrepancy in total yield (mol of benzene needed to form the product per g-atom of titrated CsOH), 0.673 as opposed to 0.419, could be explained by either of two conjectures: (1) removal of the THF promotes further reaction to produce additional dicesium 1,1'-dihydrobiphenyl-d_{-12} and in the latter compound the 1,1'-carbon-carbon bond breaks under the slow quenching conditions, or (2) there is produced in this reaction a cesium benzenide polymer which when quenched quickly with water gives some non-volatile product but when quenched slowly yields products volatile enough to be studied by gc.

The Reaction at Room Temperature

Warming dicesium 1,1'-dihydrobiphenyl to room temperature or slightly above (25° to 35°)* and holding at this temperature for one to two hours, caused the reaction mixture to turn from yellow-green to black. While the mixture was being warmed, hydrogen gas was evolved. In Table 36, the results of four studies of the gas evolved during warming from -20° to 25° are tabulated. When this black precipitate was quenched with water, the products appeared to be a mixture of 1,1',4,4'-tetrahydrobiphenyl (VIII), 1,4-dihydrobiphenyl (X), phenylcyclohexane (XI), 1-phenylcyclohexene (XII), a dihydrobiphenyl, tentatively identified as 3,4-dihydrobiphenyl (XVI), and biphenyl (XIII) by mixed gc injections of reaction product mixtures with solutions of known compounds. The molecular ions of these products, found by ms-gc analysis of various runs of this reaction, are consistent with the assigned structures given to each component in the reaction mixture. However, a close examination of the mass spectra obtained by gc-ms analysis, indicates that there are significant differences in the cracking patterns of: (1) VIII produced after quenching with water from the product of the reaction between benzene and cesium after warming to -20°; (2) a compound produced after quenching with water from the product of the reaction between biphenyl and cesium, this compound has the same gc retention time and molecular ion as VIII; and (3) the compound described above as

* In experiment 3-162, this change was found to be occurring to some extent at -5°.

Table 36. Studies of Gas Evolution During the Reaction of Benzene and Cesium in THF.

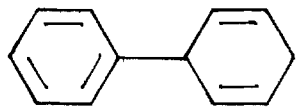
	Experiment Number			
	4-59	4-48	4-20	3-20
Conditions	C_6D_6 - 20°, sample warmed at 25° for 12.5 hrs.	C_6D_6 -20°, sample warmed at 25° for 18 hrs.	C_6H_6 -20°, sample warmed without solvent 2 hrs and with solvent 3.5 hrs.	C_6H_6, only at 35° reacted for 2 hrs and isolated by washing over a 21 hour period with isooctane.
Amount of Cesium in the sample (mg-atoms)	4.93	4.24	2.45	32.59
Yield of VIII at -20° (in mol of product/mg-atoms of Cs.	0.200	0.166	0.181	-
Amount of gas evolved when warmed from -20° to 25°	0.2027 mmol (determined to be hydrogen by gc analysis)	0.263	0.4944 mmol	-
Relative Isotopic amounts of hydrogen (described above)	5.6% H_2 31.5% HD 62.9% D_2	10.5% H_2 25.1% HD 64.4% D_2	-	-
Amount of gas evolved when quenched with H_2O	0.7482 mmol	poor analysis	Quenched with D_2O 0.3061 mmol	9.23 mmol

Table 36. (Concluded).

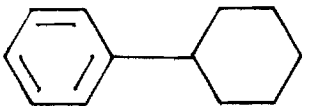
	Experiment Number			
	4-59	5-48	4-20	3-20
Relative Isotopic amounts of hydrogen (described above)	19.2% H_2 63.8% HD 17.0% D_2	did not analyze	25% H_2 [a] 45% HD 30% D_2	-

(a) This sample was poorly analyzed. These values only indicate trends.

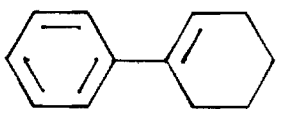
VIII, a product of the reaction between benzene and cesium at 25° to 35°. The three mass spectra are in Appendix A. It appears that the "single" gc component found in the product mixture from benzene-cesium reaction at 25° to 35° is a mixture of VIII and a new component produced in the biphenyl-cesium reaction. This product is tentatively identified as 3-phenylcyclohexene (XIV), this identification is discussed in more detail in Appendix A.



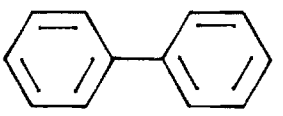
1,4-dihydrobiphenyl (X)



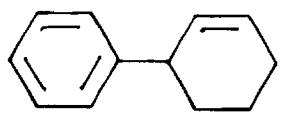
phenylcyclohexane (XI)



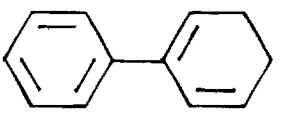
1-phenylcyclohexene (XII)



biphenyl (XIII)



3-phenylcyclohexene (XIV)



3,4-dihydrobiphenyl (XVI)

Table 37 outlined the yields of products from the quenching of the precipitate at room temperature with water. Analysis by esr of a sample (taken in experiment 4-48) of this black precipitate

Table 37. Results of Aqueous Quench of the Product from the Reaction of Cesium with Benzene at Room Temperature in THF.

	Experiment Number				
	4-82	4-20	4-59	4-59	3-20
Conditions	Warmed from -20° to 25° in Morton flask with stirring, one hour.	Decomposed after study of gas evolution during heating from -20° to 25° on a vacuum line.	Starting material: C_6D_6; decomposed after study of gas evolution during heating from -20° to 25° on a vacuum line.	Starting material: C_6D_6; decomposed at 60° for 10 minutes 30° to 35°, 1.5 hrs.	Reacted benzene and cesium only at 35° and for two hrs and isolated by washing over a 21 hr period with isooctane
	Yield[a] of VIII at -20°				
	0.188, 0.177	0.18	0.200	0.200	-
	Yield[a] of Products at 25° to 35°				
VIII and/or XIV $C_{12}H_{14}$	0.0845	0.018	0.092	0.0315	0.037
X $C_{12}H_{12}$	0.046	0.056	0.019	0.017	0.003
XI $C_{12}H_{16}$	0.0025	0.002	-	-	-

Table 37. (Concluded).

	Experiment Number				
	4-82	4-20	4-59	4-59	3-20
	Yield[a] of Products at 25° to 35° (Continued)				
XII $C_{12}H_{14}$	0.0105	0.0185	0.007	0.0095	0.068
XVI $C_{12}H_{12}$	0.011	0.01	-	-	0.014
XIII $C_{12}H_{10}$	0.0295	0.059	0.0215	0.027	0.132
Total	0.184	0.164	0.140	0.085	0.284[b]

(a) The yields are expressed in mol of product per mol of titrated cesium hydroxide in the sample.

(b) There was also 0.06 mole of benzene per mole of CsOH.

showed 6 x 10^{-2}%* anion radical yield (measured at -196°) and another sample (experiment 3-82) showed 9.0 x 10^{-3}%* anion radical yield (measured at -120° to -90°). The black precipitate, when reacted with iodine in experiment 3-162, gave yields (in mol of product per g-atom of initial cesium) of 0.174 XIII, 0.005 VI, 0.0035 VIII and/or XIV. In this same experiment, when the black precipitate was quenched with water, the product distribution (in mol of product per g-atom of initial cesium) was VI (0.124), VII (0.0202), XI (0.0046), VIII and/or XIV (0.150), X (0.0782), XII (0.0313), XVI (0.0161), and XIII (0.102). In this and in experiment 4-20, the room temperature intermediate was also quenched with D_2O and studied by gc-ms. The products were found to be the result of the reduction of biphenyl ($C_{12}H_{10}$) with deuterium. The higher m/e peaks in the spectra of each of the above products indicated that they were composed of 12 carbons, 10 hydrogens and two or four deuteriums depending on the extent of reduction. The only exception to this was biphenyl itself which had a highest molecular ion of 158 in experiment 3-162 and of 159 in experiment 4-20. This is apparently due to some decomposition of tetradeuterated and hexadeuterated products to biphenyl. The compound phenylcyclohexane was in too small a yield to find its molecular ion in either experiment.

The results outlined in Tables 36 and 37 and in the previous

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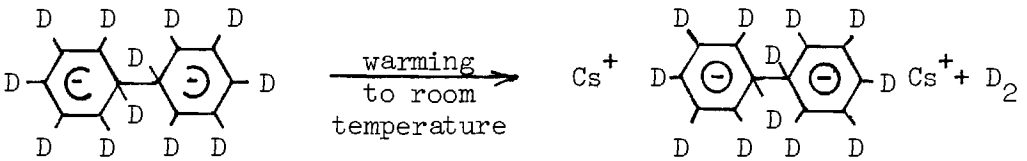
* This is calculated by multiplying 100 times the ratio of radical concentration to the initial cesium concentration.

discussion indicate that a new intermediate is prepared at room temperature. It does not have the properties of cesium benzenide or dicesium 1,1'-dihydrobiphenylide.

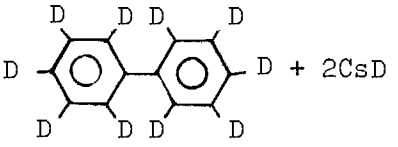
When the -20° intermediate is warmed to room temperature, there is a loss of hydrogen. If this is quenched with water, there is a further loss of hydrogen. Studies of this hydrogen evolution are outlined in Table 36. The isotropic form of hydrogen evolved from the warming step of the perdeutero product (produced by starting with benzene-$\underline{d}_6$) is primarily D_2. This data could indicate that the hydrogen is lost directly from the -20° intermediate to form the room temperature intermediate as is illustrated in equation 10.

10 

IX-$\underline{d}_{12}$

When the perdeutero product obtained at room temperature is quenched with water, the major isotropic form of hydrogen produced is HD. There is however, H_2 and D_2 also evolved in this reaction. If protio-benzene is used as starting material for this reaction and the reaction quenched with D_2O, then HD is the major form of hydrogen gas evolved. The evolution of a large amount of HD upon quenching the room temperature intermediate indicates that there is CsD (or CsH in the protio case) present in the reaction mixture. This implies that the

reaction follows the course outline in reaction 11.

11 IX-d_{12} $\xrightarrow[\text{to room temperature}]{\text{warming}}$  + 2CsD

This same type of reaction has been postulated for the reaction between pyridine and sodium.[32]

When the intermediate produced in the reaction between benzene and cesium at room temperature is allowed to react with water, five reduced biphenyls and biphenyl in varying amounts are the products as seen in Table 37. These same products with the exception of VIII were found in experiments 4-16, 4-66, and 4-30 when biphenyl was reacted with cesium in THF and this was quenched with water (in Table 40). This same correlation between the products of the reaction of cesium with benzene at room temperature and the products of the reaction of cesium with biphenyl at room temperature was found when both reactions were quenched with D_2O and studied by gc and gc-ms. These products, with the exception of 3-phenylcyclohexene, have also been observed in the literature in the reaction of biphenyl with lithium[45] and sodium-potassium alloy.[46] This observation indicates that there is a common intermediate in the two reactions. If the reaction followed the pathway outlined in equation 10, the common intermediate would be biphenyl dianion. On the other hand, if the reaction went according to equation 11, biphenyl would be the common

intermediate. This intermediate (biphenyl) would have to react with cesium to form biphenyl dianion; however, at -20°, there was found to be very little free cesium present. Thus, in experiment 4-59,a sample of the -20° intermediate was attached to a vacuum line. The solvent and excess benzene were removed by distillation. Upon quenching the resulting solid with water, there was given off ca 0.0005 mol of hydrogen per mol of titrated CsOH in the sample.

Equation 11 could not be ruled out as a possible reaction pathway if there is present in the reaction mixture, an alternate source of cesium. Since it is established that cesium deuteride is produced in the reaction using perdeuterobenzene, then this salt would possibly be decomposing to cesium metal and deuterium[91] shown in equation 12.

12 $$2CsD \longrightarrow 2Cs + D_2$$

This supposition would explain the mixture of gases (H_2, HD, D_2) evolved when the benzene-d_6-cesium reaction is quenched with water at room temperature. These gases would come from intermolecular decomposition of cesium deuteride and the reactions of cesium and cesium deuteride with water. As stated previously, the major product of

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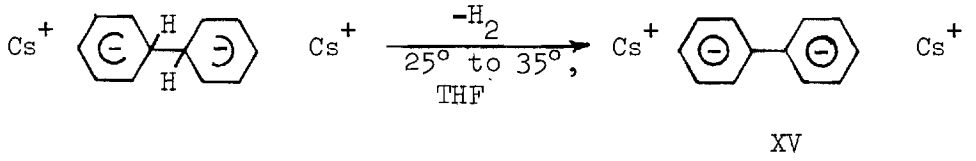
(91) According to available data, this reaction does not occur for pure CsH at this temperature and pressure (10^{-5} mm). The dissociation pressure is 1.7×10^{-8} mm at 25°. Reference 83, p. 2330.

the room temperature aqueous quench is HD. This would be a product of the reaction of cesium deuteride and water. The D_2 could be produced by intermolecular decomposition of cesium deuteride and the H_2 could result in the reaction between cesium and water.

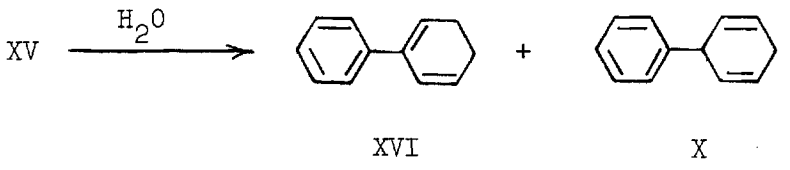
At this point, the gas evolution results are quite complex and there is no difinitive evidence for either reaction 10 in which there is a direct loss of deuterium gas from the cesium benzenide dimer ($\underline{d}_{12}$) to give the dicarbanion of biphenyl or reaction 11 in which the cesium benzenide dimer ($\underline{d}_{12}$) loses CsD to form biphenyl-$\underline{d}_{10}$ which reacts with free cesium formed according to equation 12 to give the biphenyl dicarbanion. In fact, both reactions may be occurring.

The above data indicates that the compound formed at room temperature is dicesium biphenylide. This intermediate could possibly react further to give cesium monohydrobiphenylide. In fact, Shatenshtein and coworkers[34] have claimed to have prepared the mono metal monohydrobiphenyl anion from the biphenyl dianion of the alkali metals, lithium and sodium, by abstraction of a hydrogen from the solvent (DME). In an attempt to determine if this was the species found in the reaction with cesium, experiment 4-30 was performed. In this experiment, perdeuterobiphenyl was reacted with cesium in THF-$\underline{d}_8$ for 1.5 hours and then quenched with water. The products listed as relative area percents (identification by gc-ms) were: 2.0 (phenylcyclohexane-$\underline{d}_{10}$), 13.8 (3-phenylcyclohexene-$\underline{d}_{10}$), 29.2 (1,4-dihydrobiphenyl-$\underline{d}_{10}$), 14.1 (1-phenylcyclohexene-$\underline{d}_{10}$), 3.7 (3,4-dihydrobiphenyl-$\underline{d}_{10}$), 37.0 (biphenyl-$\underline{d}_{10}$). These products were

identified by gc and gc-ms. Since none of the products had more deuterium than the starting material had, the products are not the result of an intermediate that had abstracted deuterium atoms from the solvent. Therefore, dicesium biphenylide does not react further to form cesium monohydrobiphenylide under the conditions of the present experiments. The reactions discussed concerning dicesium biphenylide are illustrated in equations 13 through 16.

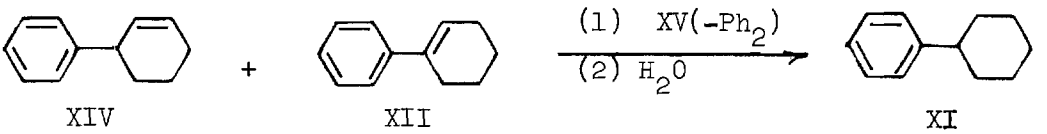
13 

XV

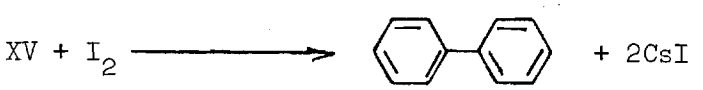
14 

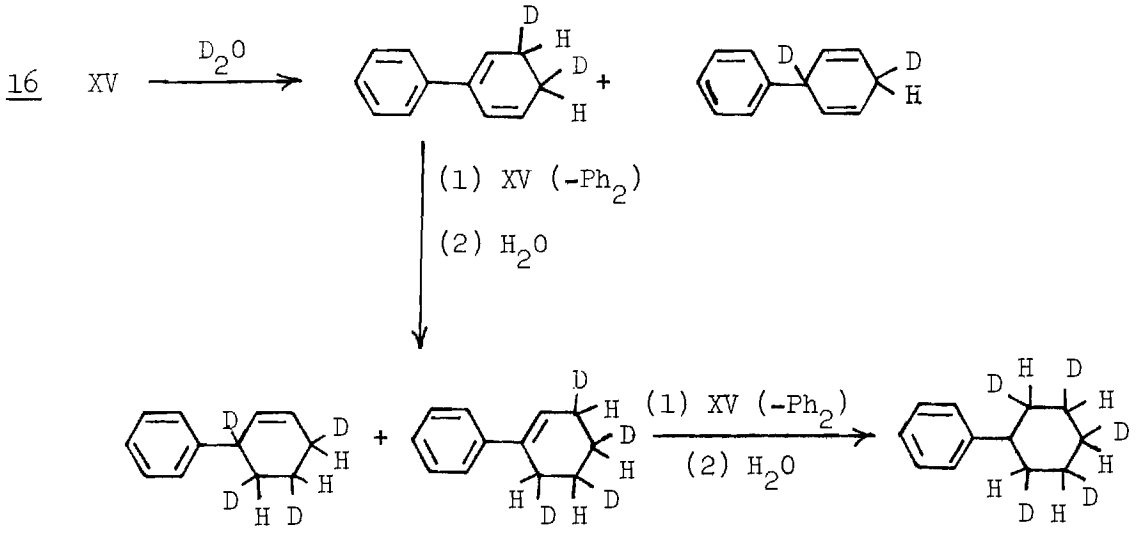
XVI X

(1) XV(-Ph_2)
(2) H_2O



XIV XII XI

15 



In the reaction between biphenyl and cesium metal at ca 35° (when quenched with water), the relative area percent yield of XIV, according to the data in Table 40, ranges between 7.5% and 13.8%. In the reaction between benzene and cesium at 25° to 35° (when quenched with water), the relative area percent yield of VIII and XIV (both have the same gc retention time) calculated from the data in Table 37, for the five reactions listed are: 45% (experiment 4-82), 66% (experiment 4-59, 25°), 37% (experiment 4-59, 60° for 10 minutes), 11% (experiment 4-20), and 13% (experiment 3-20). A comparison of these two sets of data shows that the first three reactions listed above from Table 37, have relative area percent yields of VIII and XIV that are much higher than found for the reaction of biphenyl with cesium; while, the latter two reactions, in this list from Table 37, have relative area percent yields of VIII and XIV that are within the range of yields of XIV found in the biphenyl-cesium reaction. This variation of relative area percent yields of the gc component

corresponding to VIII and XIV indicates that, at times, IX does not completely decompose to XV as shown in reaction 13. In fact, it appears that, in the three cases containing "high" yields of VIII and XIV, the amount of VIII in this mixture ranges between 25% and 50% of the total amount of volatile material isolated. Therefore, the possibility that reaction 13 has not gone to completion in these reactions of cesium and benzene at 25° to 35°, must be considered in the interpretation of the results.

The Reaction of Cesium with Benzene in Excess Benzene as Solvent at Room Temperature

In experiments 3-112 and 3-130, cesium when added to an excess of pure benzene gave a black precipitate. This precipitate was washed with isooctane to remove any unreacted benzene and reacted with the reagents: H_2O, D_2O, methyl iodide, dimethyl sulfate, and iodine. In Table 38, representative results of the products of these reactions are tabulated. When quenched with H_2O, D_2O, and MeOH, the black precipitate has shown ratios of benzene appearing in the products to titrated cesium hydroxide of 0.594, 0.602 and 0.706, respectively. The esr spectrum indicated that this black precipitate contained a 1.2×10^{-5} ratio of radical to initial cesium. Although this work was analyzed on a poorer gc column than the previous work in THF, the reaction is apparently the same. Benzene reacts with cesium to produce cesium benzenide. This dimerizes to form dicesium 1,1'-dihydrobiphenylide which (to about 75%) loses hydrogen to form dicesium biphenylide. The reactions of I_2, D_2O and H_2O are very similar to the

Table 38. Representative Yields of the Reactions of the Black Precipitate Isolated from the Reaction of Benzene and Cesium at Room Temperature.

Reagent	Relative Area Percent Yields of Products[a]
H_2O	13.9% V; 15.5% VI; <0.6% XI; 11.4% VIII and/or XIV; 33.1% X; 18.8% XII and XIII; 6.7% XVI.
D_2O	14.2% V; 16.4% VI-$\underline{d}_2$; <0.5% XI-$\underline{d}_6$; 10.2% VIII-$\underline{d}_4$ and/or XIV-$\underline{d}_4$; 39.9% X-$\underline{d}_2$; 13.0% XII-$\underline{d}_4$ and XIII; 5.9% XVI-$\underline{d}_2$.
MeOH	12.5% V; 13.2% VI; <0.9% XI; 17.9% VIII and/or XIV; 32.4% X; 1.6% unidentified reduced biphenyl; 16.2% XIII and XII; 3.1% XVI.
I_2	27.0% V; 73.0% XIII.
$(CH_3)_2SO_4$	36.7% benzene; 45.5% dimethylbiphenyl and reduced derivative; 6.5% dimethylbiphenyl; 12.7% dihydrodimethylbiphenyl.
CH_3I	24.9% benzene; 11.4% methylbiphenyl; 62.4% biphenyl and methylbiphenyl; 1.2% dimethylbiphenyl[b].

(a) The yields represent the percent of the reacted benzene which appears in the various products.

(b) Products aromatized in gc.

reaction of these reagents with the room temperature intermediate found in the reaction with THF. The reagents methyl iodide and dimethyl sulfate were incompletely studied as quenching reagents. However, the high yield of biphenyl in the methyl iodide quench indicates that it may be performing primarily as an electron acceptor rather than a methylating agent. Dimethyl sulfate on the other hand, seems to be primarily a methylating agent.

In 1912,[18a] and in 1913,[18b] Louis Hackspill reported that cesium, when reacted with benzene for two or three days at 28°, formed a black precipitate. Gravimetric analysis of this black precipitate indicated that it contained 65.34% cesium which agreed with the formula C_6H_5Cs. More recently, in 1946,[19] Jean de Postis (in Hackspill's laboratory) analyzed this black precipitate and claimed that it had the chemical formula $C_6H_6Cs_6$. In a chapter in "Chimie Minerale" written on alkali metals in 1956, Hackspill[20] concurred with de Postis that the formula for the black solid is $C_6H_6Cs_6$. It appears in our present study of the reaction of cesium and benzene that the chemical formula of the black precipitate is $C_{12}H_{10}Cs_2$ (dicesium biphenylide). This agrees, in empirical formula, with the chemical formula reported by Hackspill. Evidently, de Postis had analyzed the product of only a partial reaction of cesium with benzene.

The Reaction of Benzene with Cs-K-Na Alloy

This reaction was studied at two temperatures, -70° and 34° with an excess of Cs-K-Na alloy two-fold or greater in cesium. Three reactions were performed at -70° with the final product quenched by water. Table

39 outlines the results found in these reactions. Although there is an excess of cesium alloy, the yield 1,4-dihydrobenzene is always less than 50 percent. This indicates that the second electron transferred in the reduction of benzene (equation 2) comes from a benzenide ion and not from an alkali metal. In a fourth reaction, carbonation yielded 12.1% of reduced terephthalic acids and 1.7% of benzoic acid.

In the reaction between benzene and excess Cs-K-Na alloy (two-fold in cesium) at 34°, the only product isolated was unreacted benzene. There are two factors that may account for the lack of reaction in experiments at room temperature. In all other experiments at room temperature with benzene and cesium metal, with one exception,* there has been a large excess of benzene, at least seven-fold, relative to cesium. An excess of benzene, since it is soluble in the reaction solvent, would provide for more contact between the alkali metal and this aromatic hydrocarbon. Also, cesium present in an alloy rather than as the pure metal would be diluted and therefore, less reactive. This diminishment of reactivity was also found when cis-2-heptene was reacted with these two forms of cesium.

At -70°, with Cs-K-Na alloy, there can be up to an 84 percent conversion to anion radical of benzene while at 34°, there is no anion radical of benzene formed. This temperature dependence of anion radical production is consistent with observations of other

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* In experiment 3-106, benzene was reacted with a three-fold excess of cesium metal at 40° for one hour. Analysis of the products by gc indicated only a 6.3% yield of biphenyl and reduced biphenyls.

Table 39. Results of the Aqueous Quench of Benzene and Cs-K-Na Alloy Reaction at -70° in THF.

Experiment	Time of Reaction	Relative Area Percent Yield of Products V	VI
2-72	1 hr	62	38
2-110	ca 5 min	89.1	10.9
	2 hr	80.5	19.5
	4 hr	69.4	30.6
	4 hr[a]	93.5	6.5
3-100[b]	1 hr	58.1	41.9

(a) This sample was withdrawn with a pipette containing a glass-wool filter. This result indicates that the cesium-benzene adduct is insoluble in THF.

(b) Absolute yield analysis, by gc, based on initial benzene as the limiting reagent indicates that there is a 39.0% yield of benzene (V) and a 28.1% yield on 1,4-dihydrobenzene (VI). No biphenyl or reduced biphenyl were found in this sample when it was analyzed by gc for 12-carbon compounds.

alkali-metal-aromatic hydrocarbon systems.[4] Cesium metal, on the other hand, reacts with benzene in the temperature range -70° to 35° and only the extent of reaction is temperature dependent.

The Reaction of Biphenyl and Cesium

The results of the reaction between cesium and biphenyl (followed by aqueous quenching) are tabulated in Table 40. In these reactions, biphenyl reacts with excess cesium in THF at temperatures above the melting point of cesium to form a black precipitate. (In experiment 4-66, the amount of unreacted biphenyl was followed by gc analysis of the liquid portion of the reaction mixture; after one hour of reaction, 97.5 of the biphenyl had reacted.) Analysis of this black precipitate (experiment 4-66) by esr spectroscopy indicated that only 0.0006% of the biphenyl had become anion radical. This precipitate, when quenched with water, gives the same products that were found in the reaction of benzene and cesium at room temperature.

In this reaction, a method of determining the number of cesium atoms reacting with each biphenyl molecule is to calculate the ratio of g-atoms of H atoms added to biphenyl during the aqueous quench per mol of biphenyl required to form the products, biphenyl and reduced biphenyls. This ratio is for the various experiments*: 1.50 (experiment 4-16, H_2O quench), 1.53 (experiment 4-16, D_2O quench), 1.83 (experiment 4-66, H_2O quench), 1.88 (experiment 4-66, D_2O quench),

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* The conditions for these experiments are in Table 40.

Table 40. The Products Found in the Reaction of Biphenyl (XIII) and Cesium when Quenched with Water.

Experiment	Conditions	Relative Area Percent Yields of Products					
		XIV	X	XI	XII	XIII	XVI[a]
4-16[b]	15.1:33.4 molar ratio of XIII: Cs; 48° to 32°, 1.5 hr.; H_2O quench	9.7	29.3	0.3	9.6	45.2	3.2
	above; D_2O quench[c] taken at same time as H_2O quench	7.5	43.2	0.2	6.3	37.7	5.1
4-66	32.4:81.3 molar ratio of XIII: Cs; 36°; 2.0 hr; H_2O quench	13.3	36.2	0.5	11.8	34.3	3.8
	above; D_2O quench[c] taken at same time as H_2O quench	12.0	46.8	0.4	8.2	26.8	5.8
4-30	0.22:1.13 molar ratio of XIII-$\underline{d}_{10}$: Cs; ca 32° 1.5 hr; H_2O quench[d]	13.8	29.2	2.0	14.1	37.0	3.8

(a) Compound XVI is tentatively identified as 3,4-dihydrobiphenyl because possible reduction products (XI, XII, and XIV) of this compound are found in the protonation products and this compound is a product in the reduction of biphenyl with lithium after protonation with methanol.[45]

(b) In this experiment, the percent recovery of biphenyl (absolute yield) as products (biphenyl and reduced biphenyls) is 92.7%.

Table 40. (Concluded).

(c) GC-MS results indicate that products are the result of addition of two, four, or six deuterium atoms to biphenyl ($C_{12}H_{10}$) to give XIV-$\underline{d}_4$, X-$\underline{d}_2$, XI-$\underline{d}_6$, XII-$\underline{d}_4$, and the XV, $C_{12}H_{10}D_2$.

(d) GC-MS results indicate that the products are the result of addition of two, four, or six protium atoms to biphenyl-$\underline{d}_{10}$ ($C_{12}D_{10}$) to give XIV-$\underline{d}_{10}\underline{h}_4$, X-$\underline{d}_{10}\underline{h}_2$, XI-$\underline{d}_{10}\underline{h}_6$, XII-$\underline{d}_{10}\underline{h}_4$ and XV, $C_{12}H_2D_{10}$.

1.62 (experiment 4-30, H_2O quench). These ratios together with the esr data indicate that two cesium atoms react with one biphenyl molecule to give dicesium biphenylide under the reaction conditions studied. These calculated values are less than 2.0 for three possible reasons: (1) a portion of dicesium biphenylide acts like cesium metal and reacts with water to give biphenyl, cesium hydroxide, and hydrogen gas; (2) there is possible incomplete reaction of cesium with biphenyl (in experiments 4-16 and 4-30); and (3) there is some aromatization of the products before gc analysis.

The esr data implies that the product of the reaction between biphenyl and cesium has added an even number of electrons, most likely two. According to Hückel molecular orbital calculations,[92] the lowest unfilled molecular orbital of biphenyl is non-degenerate and the next higher molecular orbital is doubly degenerate. Therefore, the diamagnetic species must be the result of addition of two or six electrons to biphenyl. Hence the most likely diamagnetic species is dicesium biphenylide. This reaction is illustrated in reaction 17. The

cesium-biphenyl adduct is decomposed by H_2O and D_2O according to the schemes shown in equations 14 and 16.

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(92) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-electron Calculations" W.H. Freeman Co., San Francisco (1965) p. 91.

In the reaction between benzene and cesium at 25° to 35°, it would be interesting to determine the ratio of "added" hydrogen atoms to "reacted" biphenyl. That is, the ratio of g-atoms of H atoms added to biphenyl (in the aqueous quench) per mole of biphenyl required to form the products (biphenyl and reduced biphenyl). This ratio is for various experiments*: 2.77 (experiment 4-82), 1.58 (experiment 4-20, 3.11 (experiment 4-59), 2.32 (experiment 4-59, decomposed at 60° for 10 minutes), 1.59 (experiment 3-20). In all except two of these experiments, the ratio is above 2.0. These experiments, compared to the reaction of biphenyl (Table 40) had large relative yields [45% (experiment 4-82), 66% (experiment 4-59, 25°), 37% (experiment 4-59, 60° for 10 minutes)] of the single gc component that has been attributed to both VIII and XIV. The correlation, in the reaction of benzene, between the ratios (above 2.0) of "added" H atoms to "reacted" biphenyl with the "large" yields of the mixture of VIII and XIV supports the supposition that this mixture contains a significant amount of VIII. Compound VIII would cause these ratios to be high because it would have two extra "added" hydrogens per biphenyl since it would be due to incomplete decomposition of dicesium 1,1'-dihydrobiphenylide (IX) to dicesium biphenylide (XV). In the other two experiments, the relative yields [11.0% (experiment 4-20) and 13.0% (experiment 3-20)] of this (VIII and/or XIV) gc component, which are in the same range

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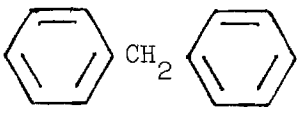
* The conditions for these experiments are in Table 37.

as the relative yields of XIV found in the biphenyl-cesium reaction, in conjunction with the "added" hydrogen atoms to "reacted" biphenyl ratios of less than 2.0, indicate that there was only a minor amount of dicesium 1,1'-dihydrobiphenylide left in the black precipitate at the time of the aqueous quenching step.

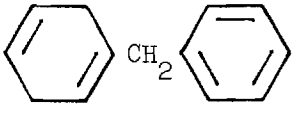
The Reaction of Polyphenylalkanes with Cesium Alloy or Cesium Metal

The Reaction of Diphenylmethane with Cesium Alloy

Diphenylmethane, when allowed to react with an excess of cesium alloy (ca six g-atoms of Cs to one mol of diphenylmethane) in THF for 20 minutes to one hour yields a black precipitate. Four separate runs were made upon this reaction. Table 41 outlines the experimental results of this study. Quenching the black precipitate with water yielded a major product, up to four minor products, and unreacted diphenylmethane.



diphenylmethane (XVII)



2,5-dihydrodiphenylmethane (XVIII)

The major product was identified by nmr analysis of the mixture of compounds isolated from this reaction. The amounts of minor products were not large enough to interfere with the nmr analysis. A typical nmr spectrum of the products of an aqueous quench is outlined in Table 42. Diphenylmethane has an nmr spectrum of 6.2τ (s, 2 H, methylene)

Table 41. Results of the Study of the Reaction of Cesium Alloy with Diphenylmethane.

Experiment	Conditions	Results
3-62	20 min, -70° quenched in H_2O	GC analysis: 2.7% $C_{13}H_{16}$; 77.7% XVIII; 19.6% XVII (relative area percent yields)
4-51	20 min, -70° quenched in H_2O	GC analysis: 42.1% XVIII; 24.9% XVIII; four unidentified components in 5.1%, 3.4%, 0.6%, 0.7% yield (all absolute yields based on initial hydrocarbon) NMR analysis: 33% XVII, 67% XVIII (relative yields)[a]
4-51	20 min, -70° quenched in D_2O	NMR analysis: 33% XVII, 67% XVIII, two allylic protons replaced by deuterium in XVIII. No deuterated XVII was observed.
4-77	1 hr, -70° quenched with H_2O	NMR analysis: 20% XVII, 80% XVIII. ESR analysis: 0.5%[b] (analyzed at 95° ± 5°)
2-165	1 hr, -70° quenched with H_2O	GC analysis: 18.2% XVII, 81.8% XVIII (relative yields) ESR analysis: 6.3×10^2%, 1.26×10^3%[b] (analyzed at -196°).

(a) Comparison of the gc and nmr data suggests that the unknowns are tetrahydrodiphenylmethanes.

(b) This is a absolute percent yield, based on initial diphenylmethane as the limiting reagent.

Table 42. NMR Spectrum of Protonated Products in Experiment 4-51. The Reaction Between Diphenylmethane and Cesium Alloy.

	Multiplicity	Integration	Relative Number of H Atoms
7.5	complex q	40.0	4.0
6.9	s	20.5	2.0
6.2	s	10.0	1.0
4.5	broad s	10.7	1.1
4.4	complex s	21.3	2.1
2.9	d (J=1)	100.0 (50 + 50)	10.0

and 2.9τ (s,10 H, aromatic). These values were subtracted from the nmr spectrum of the mixture in Table 42 give: 7.5τ (complex q, 4.0 H), 6.9τ (s, 2.0 H),4.5τ (broad s,1.1 H), 4.4τ (complex s,2.1 H), 2.9τ (s, 5.0 H). The spectrum was consistent with that expected for 2,5-dihydrodiphenylmethane; in Figure 3, the nmr spectral assignments are shown. When the black precipitate was quenched with D_2O

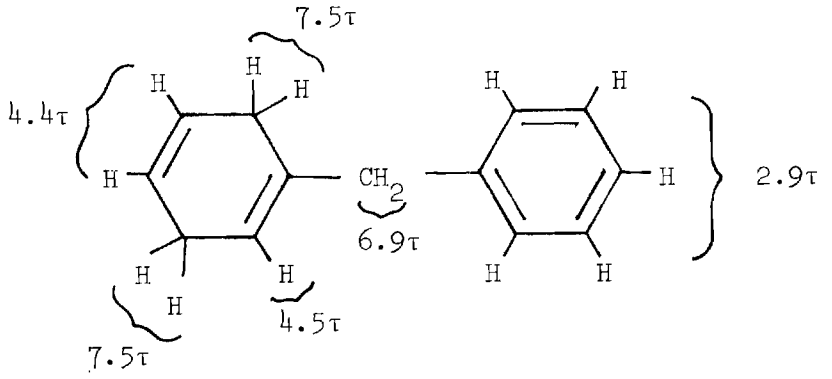


Figure 3. Assignment of nmr τ-values in 2,5-dihydrodiphenylmethane.

and the nmr spectrum of the product mixture analyzed in the same manner, it was found that two of the allylic protium atoms in the products were replaced by deuterium atoms. The production of 2,5-dihydrobiphenyl is as expected for Birch reduction of diphenylmethane. Ethyl benzene gives the same sort of Birch reduction product;[93] that is, reaction with lithium in methylamine in the presence of propanol gives 1-ethyl-2,5-dihydrobenzene.

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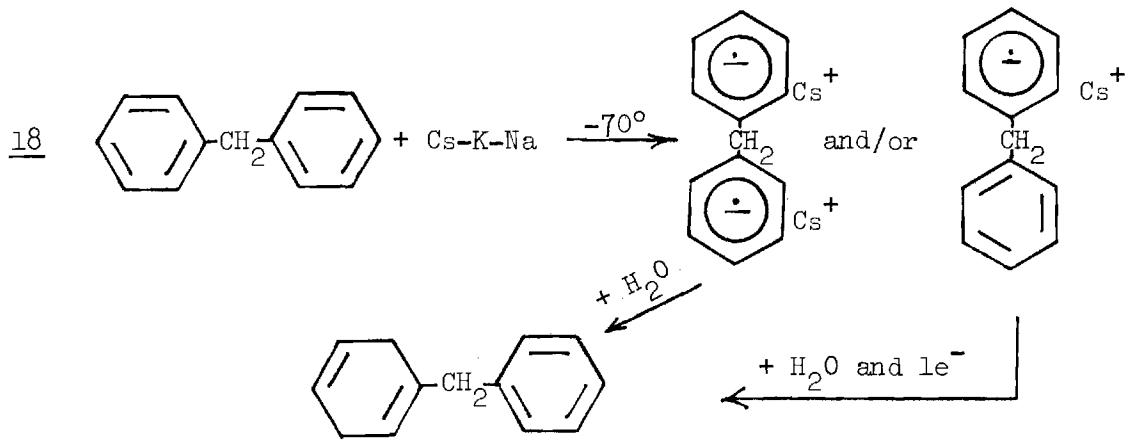
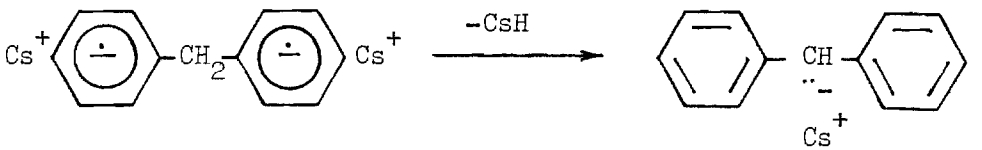
(93) H. O. House "Modern Synthetic Reactions, Second Ed.", W. A. Benjamin, Inc., Menlo Park, California, (1972) p. 196.

The esr spectrum of the product from reaction of diphenylmethane with cesium alloy, as obtained on two separate samples measured at -196°, shows anion radical yields of $6.4 \times 10^{2}\%$ and $1.3 \times 10^{3}\%$. These yields are calculated assuming one electron is added to each diphenylmethane molecule. On the basis of the data which has been presented, the reaction occurring at -70° between cesium alloy and diphenylmethane with subsequent quenching is likely to proceed as outlined in equation 18.



The esr data at -196° indicates that there is a high concentration of anion radical produced. Thus, assuming the species present is the mono anion radical, there would be needed a second electron transfer to effect the Birch reduction upon quenching with water. If the dianion radical is present, a fact which is admissible from the esr measurements and appears to be the case in the reaction of 1,1,1-triphenylethane and 2,2-diphenylpropane, then warming the intermediate

should effect intramolecular coupling. This type of coupling would be analogous to the intermolecular coupling found in the benzene anion radical. With this analogy in mind, warming of the -70° intermediate was investigated in experiment 4-54. The results outlined in Table 43 show that when the reaction is warmed to -60° and followed by quenching with water, there is a decrease in the relative amounts of products and increase in the amount of starting material. Sample 3, the result of quenching with D_2O, was concentrated and analyzed by nmr. This sample has the same mixture of major products found at -70° when the precipitate was quenched with water; however, in this case, the methylene hydrogens contain ca 30% deuterium according to nmr analysis. This result would correspond to 60% mono-deuteration at this carbon. The warming of the intermediate has caused a new species to be formed in this reaction, the diphenylmethyl anion. A possible pathway to this product is outlined in equation 19. This

19 

reaction probably prevents intramolecular coupling which is found in other compounds such as 1,1,1-triphenylmethane.

The Reaction of 2,2-Diphenylpropane with Cs-K-Na Alloy

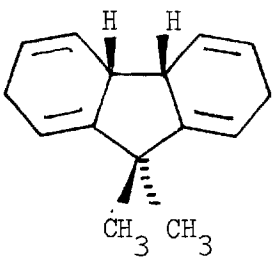
The compound, 2,2-diphenylpropane, reacts with an excess of cesium alloy (ca a seven-fold excess in cesium metal) in THF at temper-

Table 43. Results of the Study of Warming of the Reaction of Cesium Alloy with Diphenylmethane to -60°.

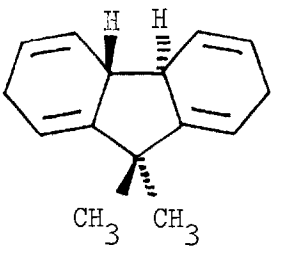
Sample	Conditions	Results (gc analysis, relative yield)
1	-70°, 1 hr H_2O quench	two unidentified products 6.0%, 6.7%; 62.3% XVIII; 24.9% XVII
2	-70°, 1.33 hr -60°, 1 hr; H_2O quench	two unidentified products 4.3%, 4.7%; 53.1% XVIII; 37.9% XVII
3	-70°, 1.33 hr -60°, 2 hr D_2O quench	two unidentified products 2.8%, 5.1%; 47.7% XVIII; 44.7% XVII
4	same as sample 3 consisting of contents of reaction flask jetted in H_2O	two unidentified products 4.0%, 3.9%; 39.5% XVIII; 44.2% XVII (absolute yields based on initial hydrocarbon)

atures between -65° and -70° to form a precipitate. The color of this was observed to be, at various times in the study of the reaction, rusty brown-orange, black and brownish-red. There was no observed correlation between reactivity and color. The progress of the reaction was followed by quenching with H_2O or D_2O. In reaction 3-44, a crystalline solid, isolated after quenching with water in 23.7% yield, was identified by uv, ms, elemental analysis, nmr, and dehydrogenation to be cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene (XIX)(See Table 44 and the following discussion).

The stereochemistry of the H_2O quenched product was determined from the nmr spectrum [3.9 - 4.8τ (four peaked multiplet, 5.9 H), 6.5 - 6.8τ (m,2.1 H); 7.3 - 7.6τ (m,3.8 H); 8.91τ (s,3.1 H); 8.82τ (s,3.1 H)]. The 3 H peaks at 8.91 and 8.82τ are assigned to two methyl groups. The quenched product could be either cis-fused, trans-fused, or a mixture of both. In the trans-fused product (XX),



cis-fused product (XIX)



trans-fused product (XX)

there is a two-fold axis of symmetry passing through C-9. In this product both methyl groups at C-9 would be equivalent in an nmr

Table 44. Analysis of the Crystalline Product of the Reaction of 2,2-Diphenylpropane with Cs-K-Na Alloy at -70°.

Method of Analysis	Results
Elemental analysis	Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15 Found: C, 90.75, 90.47; H, 9.25, 9.17
mass spectrum	m/e (rel intensity, identity); 200 (4, $C_{15}H_{18}^{+}$ + 2); 199 (7, $C_{15}H_{18}^{+}$ + 1); 198 (50, $C_{15}H_{18}^{+}$); 183 (59, $C_{14}H_{15}^{+}$); 119 (64, $C_9H_{11}^{+}$); 105 (100, $C_8H_9^{+}$); 91 (50, $C_7H_7^{+}$)
uv spectrum	λ max (ε): 265 mμ (9.14), 272 mμ (10.97)
Pd/C dehydrogenation	Isolated product identical in properties to 9,9-dimethylfluorene.
gas chromatography and gas chromatography-mass spectrum	Relative yields: 96.2%, cis-9,9-dimethyl-4a, 4b,2,7-tetrahydrofluorene; 2.4% and 1.4% unknowns, both result of addition of four hydrogens to 2,2-diphenylpropane according to gc-ms analysis.

spectrum. The cis-fused product (XIX) has a plane of symmetry passing through C-9, perpendicular to the rings. In this case, the environment around the two C-9 methyl groups is different. Therefore, each methyl should have a different chemical shift. The nmr spectrum of this compound has two different peaks of equal peak areas in the C-CH_3 regions. Therefore, the only possible products could be XIX or some mixture of XIX and XX. However, a mixture of two products would contain three different peaks because there would be methyl groups in three different enviornments or, because of similarity of environment, might have two peaks of unequal peak areas. Since neither of these was found to be the case, the product must be XIX*. In Figure 4 the structure of the product and the τ-values of its hydrogens are shown. The other methods of analysis

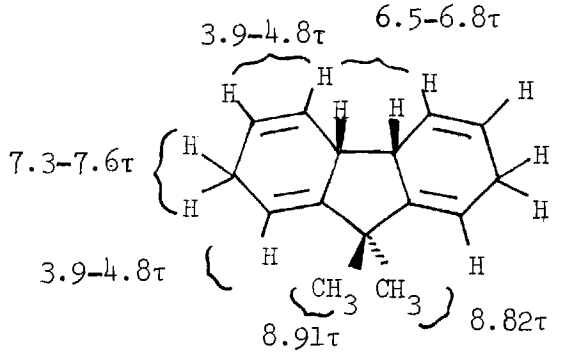


Figure 4. Assignment of nmr τ-values in cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene.

* There is the possibility that the isolated component could contain a small amount of XX and the nmr peak of the methyl groups in question is buried between the peaks of the methyl groups of XIX. This probably is not the case because the melting point of the isolated product is sharp (75°-76°).

used to determine the structure of this compound are outlined in Table 44.

The reaction of 2,2-diphenylpropane with cesium alloy was repeated in experiment 4-74. Improvement of the isolation technique increased the yield of the quenched product to 61 percent. This product was found to be identical with the major product of the first reaction, cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene.

The intermediate produced in this reaction is apparently of a form different from the intermediate with diphenylmethane. In the diphenylmethane reaction, the quenched product was the result of the Birch reduction of one of the phenyl groups. In the reaction of 2,2-diphenylpropane intramolecular coupling occurs similar to the reaction of benzene and cesium to form a new bond. This bond is formed stereochemically in only one way. Equation 20 outlines the pathway of this reaction. The second intermediate in this scheme is shown as having one of the cesium ions between the two phenyl radical anions. This cesium ion holds the phenyl rings in position for the intramolecular coupling to occur to give only the cis-fused product. A somewhat similar reaction has been observed with the anion radical of 2,2-diphenylpropane[66,69] which is reported to cyclize to 9,9-dimethylfluorene anion radical.

The products of this reaction can be altered by preparation of the -70° intermediate in the usual manner and then warming it up. In experiment 4-41, this intermediate was warmed to -20° in 10° increments and studied by quenching samples with water. This caused

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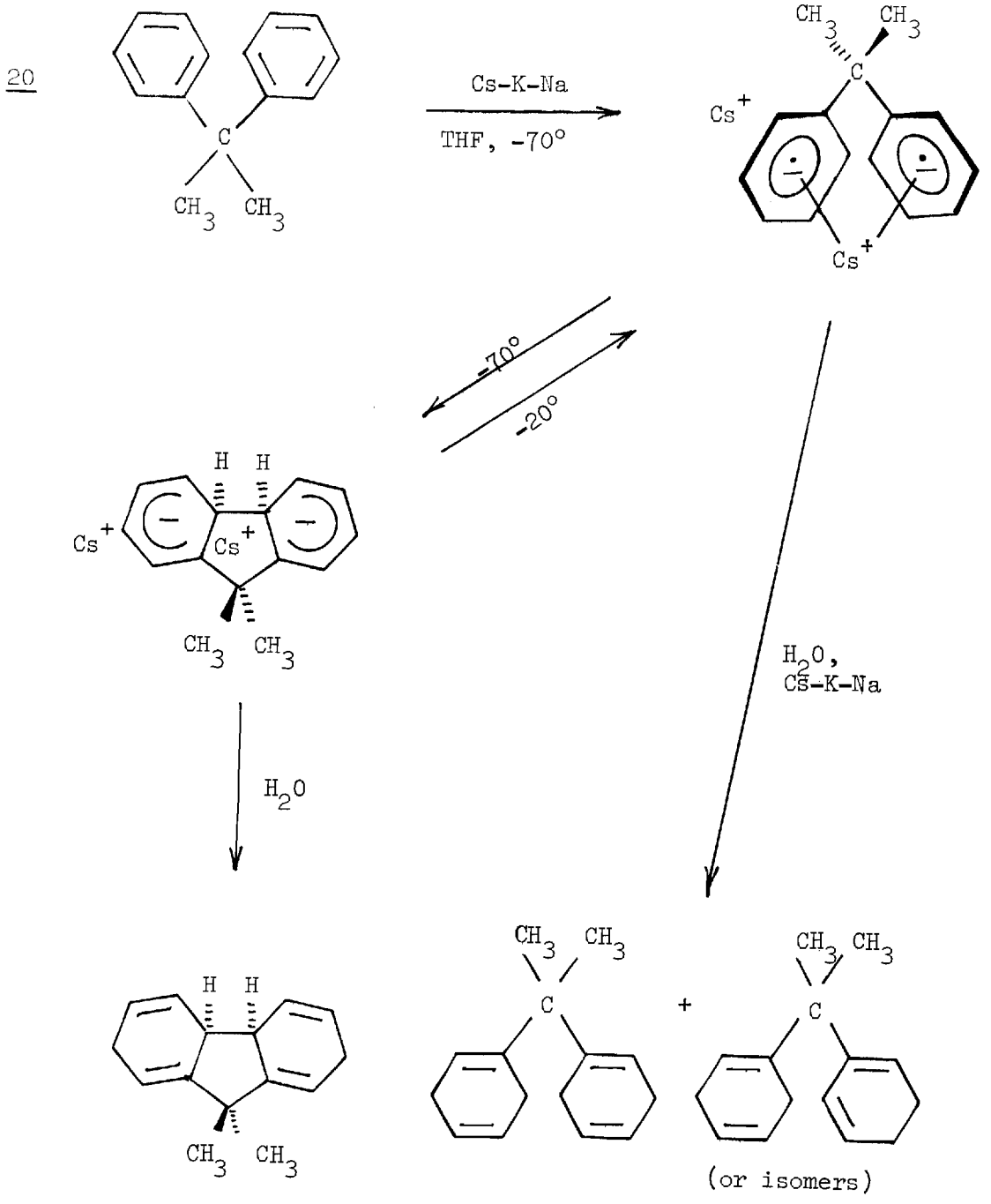

a gradual decrease in absolute yield of volatile products, from 84.3% to 44.0% and a decrease in the relative amount of cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene from 97.4 percent to 72.8 percent. The relative yield of one of the two minor products that were both the result of addition of four hydrogens to 2,2-diphenylpropane increased to 30.1%; the other stayed around 2.5%. When quenched with D_2O, these products were found to contain four deuterium atoms. The intramolecular coupling product, XIX, only contained two deuterium atoms. Thus, the products, with four additional hydrogen atoms were likely the result of Birch-type reduction of the aromatic rings in the starting material. This implies that a new intermediate, probably the dianion diradical of 2,2-diphenylpropane (equation 20) is being produced when the reaction if studied at higher temperature. The loss of product could be the result of polymerization due to an intermolecular reaction or degradation of the intermediate. No evidence besides the low yield was found for the polymerization; however, traces of ethylbenzene and isopropylbenzene were found when the reaction was warmed to -20°. These would be expected degradation products.

The Reaction of 1,1,1-Triphenylethane with Cs-K-Na Alloy in THF

Grovenstein and coworkers[57] have found that the reaction of 1,1,1-triphenylethane with Cs-K-Na alloy (ca 7:1 molar ratio of Cs to hydrocarbon) at -70° gives the same type of product as reported in this thesis for 2,2-diphenylpropane. Studies of this intermediate by quenching with water showed that a product, 9-methyl-9-phenyl-2,4a,4b,7-

tetrahydrofluorene[57] (XXI), of intramolecular coupling is prepared.

It was of interest, to study the nmr spectrum of the -70° intermediate, as a means of investigating its structure before quenching with water. A sample of this was prepared at -70° to -75° for one hour and then studied at -40° by nmr. Unfortunately, the spectrum obtained had only solvent peaks. Since there was a large amount of red precipitate in the nmr tube, it could be concluded either that the precipitate interferred with the nmr spectrum or that the intermediate was insufficiently soluble for nmr studies. The project was not pursued any further.

Mr. Quest in Dr. Grovenstein's laboratory has shown that the esr determined yield at -196° of anion radical in this reaction at -70° was $2.2 \times 10^{2}\%$. It was found to be only a doublet state radical with no triplet state radical. One explanation for this relatively high yield of anion radical concentration would be that the phenyl ring that does not take part in the intramolecular coupling reacts with cesium to form an anion radical. Some evidence for this reaction is the reported isolation[57] of 3 percent yield of a product thought to be 9-methyl-9(2,5-dihydrophenyl)-2,4a,4b,7-tetrahydrofluorene. An alternate explanation is that the intramolecular bond formed in this reaction breaks apart at -196° to give the dianion diradical form of the molecule.

The reaction of 1,1,1-triphenylethane did not occur with cesium metal when liquid ammonia was used as a solvent. Analysis by gas chromatography of the volatile products indicated that there was no

compound present besides 1,1,1-triphenylethane.

Two studies were performed on the pyrolysis of the carbanion produced from reaction of 1,1,1-triphenylethane in THF with Cs-K-Na alloy at -70°. In the first run, the reaction was maintained at -70° for one hour and then warmed in 20° increments to 25°. The reaction was kept at each temperature for 30 minutes before sampling. After the temperature of 25° was obtained, a second sample was taken after 23.5 hours at this temperature. Approximation of the yields of the H_2O quenched intermediates indicated that the intermediate produced at -70° was stable up to around -50°. A new product was first observed at -30°; the product was isolated by preparative gas chromatography and was characterized as 1,1,-diphenylethane by its nmr spectrum. The yield of this product appeared to increase with increased temperature. Three other minor products were also observed. A second run was performed with the intention of finding the absolute yield of diphenylmethane and any other products of this reaction. In this experiment 1,1,1-triphenylethane and Cs-K-Na alloy were reacted for one hour at -70° in THF and then the mixture was warmed to 0° over a 10 minute period and was held at this temperature for an additional two hours. The reaction was terminated by jetting to water. Gas chromatographic analysis showed that 55.6 percent of the initial 1,1,1-triphenylethane reacted to form diphenylethane. A second product which was not identified was found in 6.0 percent yield.*

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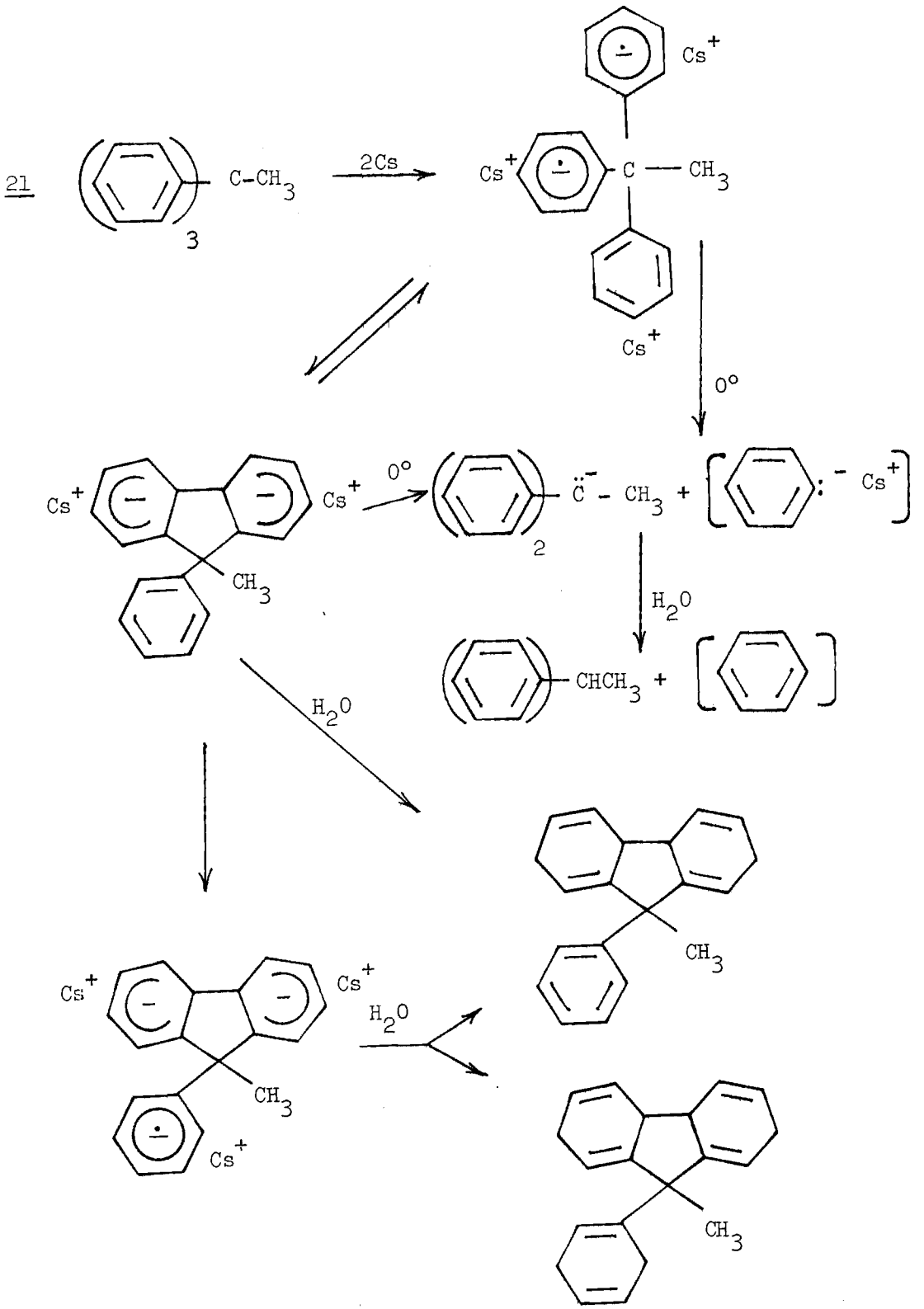
* This product was similar in gc retention time to triphenylmethane. The yield calculation assumes the gc response per mole to be the same as for triphenylmethane.


21
C-CH3
3
2Cs
Cs+
C
CH3
0°
Cs+
CH3
2
H2O
CHCH3
H2O
CH3
H2O
CH3

This study indicates that the intermediate produced when 1,1,1-triphenylethane is reacted with Cs-K-Na alloy at -70° in THF is similar in nature to that found in the reaction of 2,2-diphenylpropane under similar conditions. There is an intramolecular coupling of anion radicals of two of the benzene rings to form a dianion of a tetrahydrofluorene. This intermediate when quenched with water yields 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene. Probable paths for the observed reactions are outlined in equation 21.

The Reaction of Tetraphenylmethane with Cs-K-Na Alloy or Cesium Metal in THF

In experiment 4-27, 0.62 mol of tetraphenylmethane was allowed to react with 1 ml of Cs-K-Na alloy containing 8.0 mg-atoms of Cs in 250 ml of THF at -70° for one hour. The mixture was quenched with 220 ml of water. The products, analyzed by gc on an OV 17 column, were determined to be a complex mixture:* 30.2 percent of reduced biphenyls, 11.8 percent of biphenyl, 28.0 percent of diphenylmethane, 3.7 percent of an unknown, apparently C_{13} compound, 1.0 percent of triphenylmethane, and 5.6 percent of tetraphenylmethane and tetraphenylmethane-like products (total yield, 80.3 percent). Study of these products on a 10 percent Carbowax gc column showed a 16.9 percent yield of benzene and reduced biphenyls: 0.6 percent benzene,

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* These absolute yields were calculated relative to initial tetraphenylmethane and based on the assumption of a 1:1 relationship between reactant hydrocarbon and product. It was also assumed that reduced aromatic compounds had the same gc response factor as the corresponding aromatic compound. The nature of the unknown C_{13} compound was assumed by gc retention time with no attempt to determine the actual number of carbon atoms in the compound.

5.6% phenylcyclohexane, 2.2% 1,1',4,4'-tetrahydrobiphenyl, 5.6% 1,4-dihydrobiphenyl, 0.7% and 0.5% of two unknown reduced biphenyls. On the Carbowax column, biphenyl and diphenylmethane had the same retention time; the yields of these therefore were not calculated for this column. Also there was no toluene or 1,2-diphenylethane found. The discrepancy between the yields of reduced biphenyls determined on the Carbowax 20 M column and the yields determined on the OV 17 column can not be explained. It appears that Cs-K-Na alloy decomposes tetraphenylmethane even at the low temperature of -70°. This study was initiated with the thought that the products of the reaction might be similar in nature to those of 2,2-diphenylpropane and 1,1,1-tetraphenylmethane. This is not the case as the results show. In addition, the study of tetraphenylmethane under these conditions was found to be difficult because this hydrocarbon is not very soluble* in THF or ether. The low solubility made quantitative isolation of the reduced tetraphenylmethane derivatives hard to accomplish.

Tetraphenylmethane was allowed to react in a second reaction, with cesium metal in THF at 32° to 36°. The tetraphenylmethane was added as a powder to the mixture cesium and THF. The reaction mixture was quenched with water after four hours of reaction. The products were analyzed by gc and gc-ms and found to be a mixture of two hexahydrobiphenyls (0.2% and 0.9%), two tetrahydrobiphenyls (6.5% and 3.2%) two dihydrobiphenyls (15.2% and 15.1%) diphenylmethane (44.2%), a

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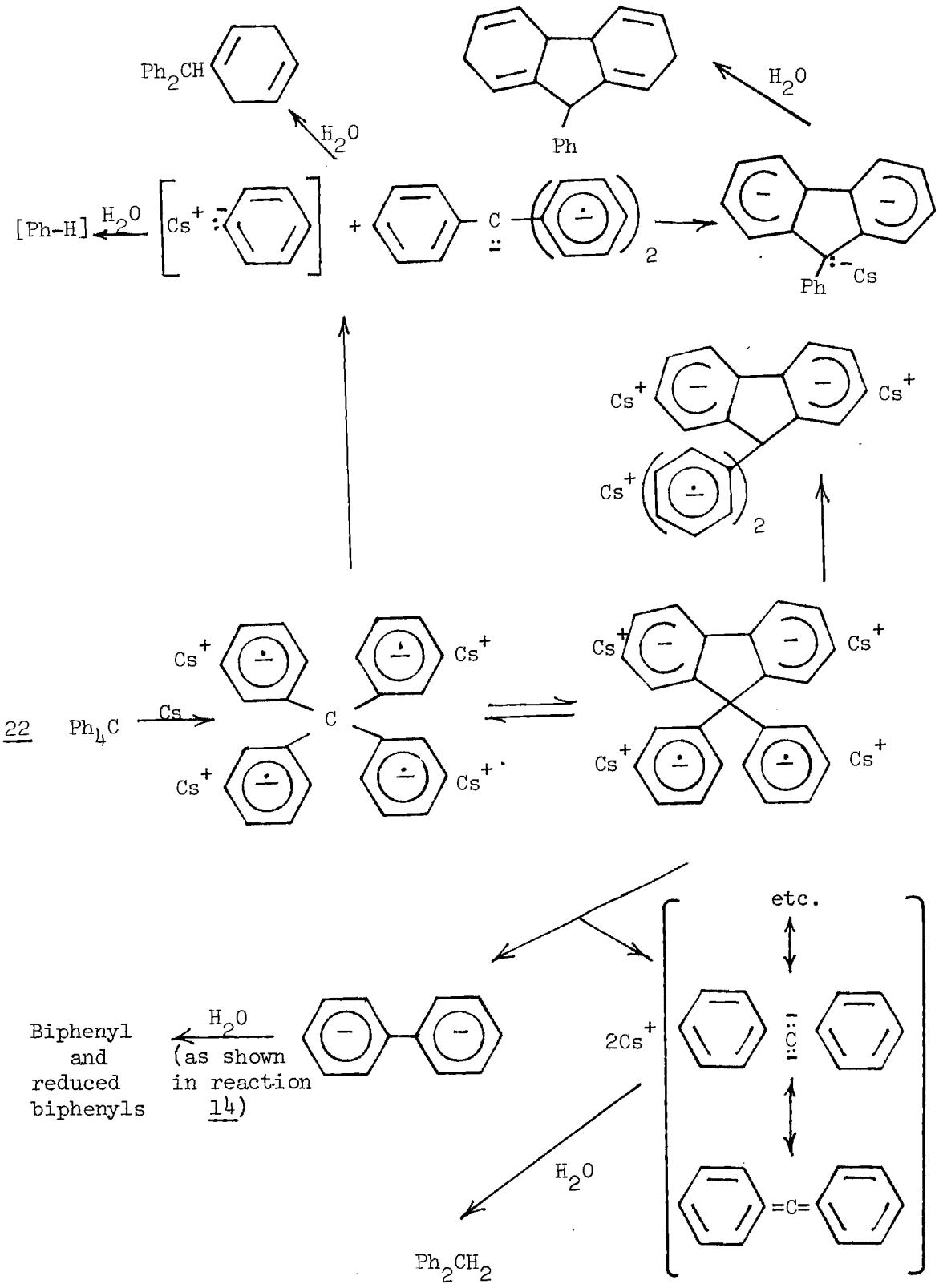
* Solubility is ca 100 mg per 20 ml of THF at room temperature.


Ph2CH
H2O
Ph
H2O
[Ph-H]
H2O
Cs+
C
2
Ph
Cs
Cs+
Cs+
Cs+
2
22
Ph4C
Cs
Cs+
Cs+
C
Cs+
Cs+
Cs+
Cs+
Cs+
etc.
2Cs+
C
=C=
Biphenyl and reduced biphenyls
H2O
(as shown in reaction 14)
H2O
Ph2CH2

small amount of a reduced triphenylmethane derivative (3.1%), a small amount of a reduced 9-phenylfluorene (1.8%), and tetraphenylmethane and reduction products (8.6%)*. This reaction gave the same types of products which were found in the reaction of cesium alloy with tetraphenylmethane at -70°. Possible reactions of tetraphenylmethane with cesium are shown in equation 22. Here a tetracesium adduct is postulated as an intermediate giving rise to cleavage product. Alternatively, the cleavage could be explained in terms of a tricesium adduct. Facial cleavage of the tri-or tetra-cesium adducts is likely promoted by forces of electrostatic repulsion of like charges within the same molecule.

Summary of the Reactions of Aromatic Hydrocarbons with Cesium

Cesium and Cs-K-Na alloy give the same types of products in reactions with aromatic hydrocarbons. Where differences exist, yields are lower with the cesium alloy. These results suggest that in reaction with the present hydrocarbons, it is the cesium contained in the alloy which is the reactive component and that the activity of cesium is diminished upon dilution with the less active alkali metals sodium and potassium.

The primary reaction of cesium and Cs-K-Na alloy with aromatic hydrocarbons at -70° is formation of hydrocarbon radical anions. With benzene, cesium benzenide is produced in good yield. With polyphenylalkanes, two, sometimes three, and possibly even four phenyl groups

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* These yields are all relative area percentages.

are reduced per molecule to radical anions.

With cesium benzenide at about -20° and with the primary reduction products of 2,2-diphenylpropane and 1,1,1-triphenylethane at -70°, secondary coupling reactions occur between the radical anions. Cesium benzenide gives, by intermolecular coupling, dicesium 1,1'-dihydrobiphenylide; 2,2-diphenylpropane gives, by intramolecular coupling, dicesium cis-9,9-dimethyl-4a,4b-dihydrofluorenide. In contrast, dicesium diphenylmethanide does not undergo appreciable intermolecular coupling at -70°, possibly because the phenyl groups (in absence of a quaternary carbon bearing phenyl and methyl groups) are effectively further apart in the unsubstituted diphenylmethane derivative than in dicesium 2,2-diphenylpropanide and dicesium 1,1,1-triphenylethanide.

All of the present cesium-aromatic hydrocarbon derivatives undergo fragmentation reactions. The cesium adduct of tetraphenylmethane (a tetracesium compound?) fragments even at -70° into anions derived from diphenylmethane and biphenyl. Dicesium diphenylmethanide undergoes hydride cleavage to give diphenylmethylcesium at -60°. Dicesium cis-9,9-dimethyl-4a,4b-dihydrofluorenide at -20° and dicesium 9-methyl-9-phenyl-4a,4b-dihydrofluorenide at -30° undergo phenyl cleavage to give 1-phenylethylcesium and 1,1-diphenylethylcesium respectively. Dicesium 1,1'-dihydrobiphenylide cleaves out the elements of hydrogen (and/or cesium hydride) at room temperature to give dicesium biphenylide.

The unique power of cesium to form radical anions of benzene and

polyphenylalkanes in good yield, in contrast to the behavior of other alkali metals, is due in part to the lower ionization potential of cesium than of the other alkali metals. Also the size of a cesium cation is about the same as that of a benzene ring. The near similarity in size of the cesium cation and the benzenide anion together with the general tendency of cesium to give contact (as opposed to solvent-separated) ion pairs likely leads to very strong electrostatic attraction (stabilization) between cesium ions and benzenide ions. The result is formation of a stable insoluble ionic aggregate. Such products appear to exist only as insoluble ionic aggregates; an attempt to form cesium benzenide in liquid ammonia (which is a much better solvent for cesium metal and, therefore, cesium cations than is THF) was unsuccessful.

The Reaction of cis-2-Heptene with Cesium and Cs-K-Na Alloy

In the reaction of 7.1 mmol of cis-2-heptene with 20 ml of Cs-K-Na alloy, containing 15.9 mg-atoms of cesium, at -70° to -75° for eight hours, there was found to be no apparent reaction. In a second run, using the same amounts of starting reagents, attempts were made to promote a reaction. Adding t-BuOH and then heating to 29° failed to cause the reagents to react. A repeat of this procedure gave the same negative results.

However when cesium was used as the source of alkali metal, the products found after quenching with water contained, besides cis-2-heptene, 1-heptene and trans-2-heptene but no 14-carbon compounds.

Three separate runs of this reaction were studied. In experiment 2-109, 12.5 mmol of cis-2-heptene was added to a mixture of 37.4 mg-atoms of cesium and 250 ml of THF at 37°. After four hours of stirring, this produced 6.2 percent trans-2-heptene and 2.6 percent 1-heptene* upon quenching with water. Heating this mixture at 67° for 1.5 hours increased the yields to 20.0 percent trans-2-heptene and 6.3 percent 1-heptene*. Then upon setting at room temperature for 62 additional hours, the ratio of products after quenching became 60.8 percent cis-2-heptene, 32.3 percent trans-2-heptene and 6.9 percent 1-heptene.**

In the second run of this reaction, 11.9 mmol of cis-2-heptene was allowed to react with 35.6 mg-atoms of cesium in 250 ml of THF. The reaction mixture was stirred for 1.25 hours at 35° - 37°. Then, 1.19 mmol of t-butanol was added and the mixture was stirred for an additional 80 minutes. At this point, the mixture was cooled to -70° and kept between -60° and -70° for two hours. The mixture turned red. The reaction mixture was quenched with water. Analysis by gc showed relative area percent of 6.9 percent 1-heptene, 6.9 percent trans-2-

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* These are the relative area percentages. The remainder of material isolated is cis-2-heptene.

** Thermodynamic equilibrium data is not available for the isomerization between these three heptenes; however, this data is available for the 1-, cis-2-, and trans-2-butenes[81] and hexenes[94]. The equilibrium concentrations for the butenes are: 3% 1-butene, 75% trans-2-butene and 22% cis-2-butene; and for the hexenes are: 1.4% 1-hexene, 70.0% trans-2-hexene, 28.6% cis-2-hexene.

(94) "API 44 Tables" American Petroleum Institute, Texas A and M Research Foundation, College Station, Texas, Table 8p.

heptene and 86.3 percent cis-2-heptene present.

In the third run, 12.6 mmol of cis-2-heptene was added to a mixture of 35.9 mg-atoms of cesium, 1.26 mmol of tert-butanol and 250 ml of THF. Various methods were used to promote reaction. Stirring this mixture at ca 33° for four hours gave products, after quenching, with relative yields of 7.7 percent trans-2-heptene, 3.3 percent 1-heptene and 89.0 percent cis-2-heptene. After heating this at reflux temperature for one hour and quenching a small sample, the product distribution was 23.3 percent trans-2-heptene, 4.9 percent 1-heptene and 71.8 percent cis-2-heptene. The mixture then set at room temperature for ca 26 hours; the products obtained for a quenched sample were 60.9 percent trans-2-heptene, 6.6 percent 1-heptene, and 32.5 percent cis-2-heptene. In this reaction, it was difficult to cool the reaction to dry ice-acetone temperatures without coagulating the metal. In an attempt to overcome this difficulty, oleic acid (ca 2 mol percent of the amount of Cs) was added to the reaction.This seemed to prevent coagulation. The reaction was maintained at ca -70° for two hours. A sample of this showed little change in the products (60.4 percent trans-2-heptene, 6.3 percent 1-heptene, and 33.3 cis-2-heptene). Finally, the mixture was left for two days at room temperature without stirring. This was quenched in water. The product distribution was 68.9 percent trans-2-heptene, 8.1 percent 1-heptene and 24.0 percent cis-2-heptene.

These studies indicate that Cs-K-Na alloy does not isomerize cis-2-heptene at an appreciable rate. An attempt to promote this

reaction by addition of tert-butanol failed. Since there was isomerization using cesium metal, this implies that cesium alloy is less reactive than cesium metal. Thus, the dilution of cesium metal with the other alkali metals has decreased its activity. The data indicates that cesium metal will cause a small amount of isomerization at room temperature. If run 1 and run 2 are compared, it is evident that addition of tert-butanol had little effect on this isomerization. This isomerization was promoted by heat. At this point, the mechanism can only be speculated upon. A probable mechanism is outlined in equation 23. It is proposed that an intermediate is formed by addition of an electron from cesium to the olefin.* The electron goes into the pi* (anti-bonding) orbital of the double bond and thereby decreases the strength of the double bond such that geometrical isomerization is promoted.

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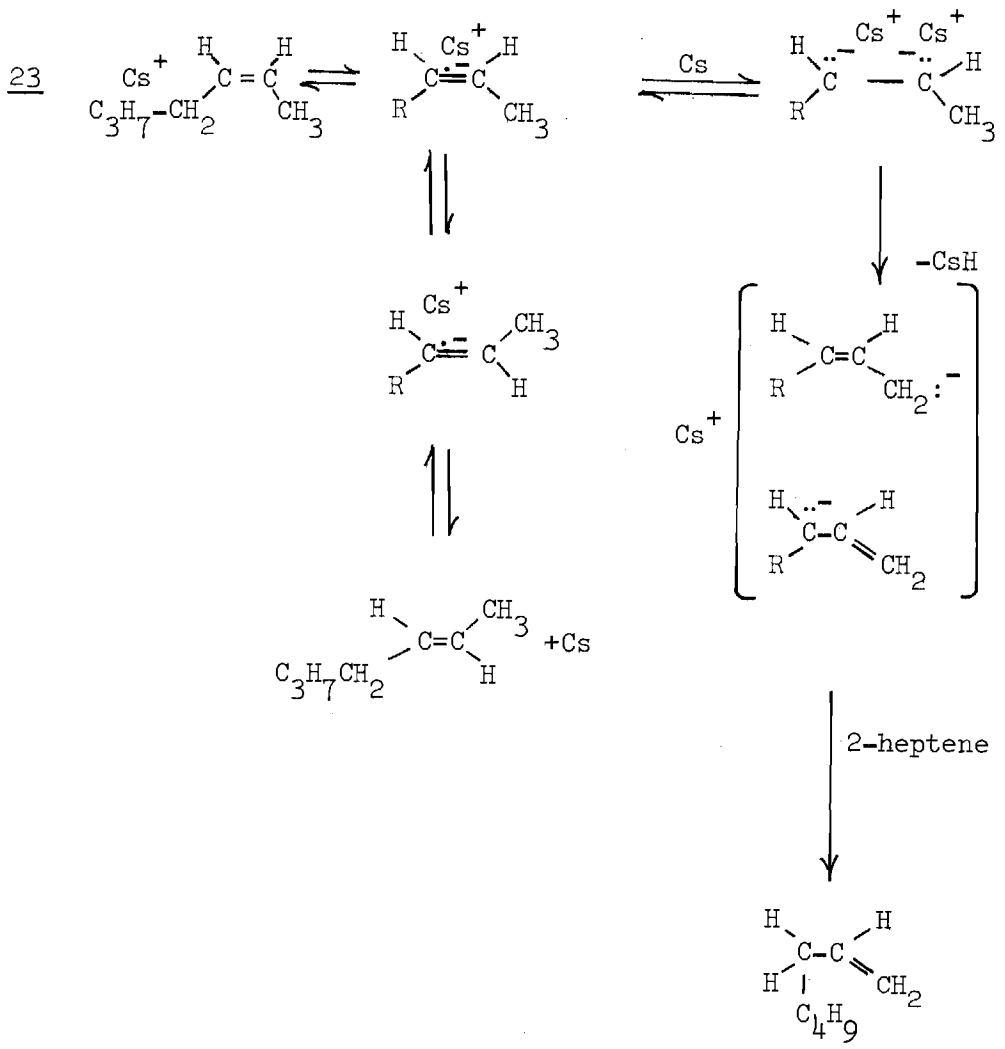
* The product of the reaction between cesium and ethylene has been claimed to be $C_2H_4Cs_2$.[81]

23

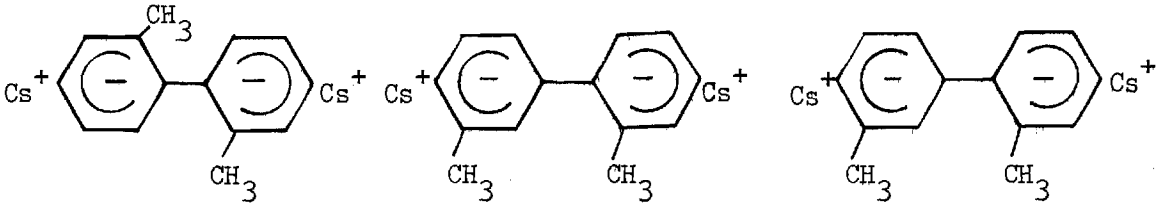


CHAPTER VI

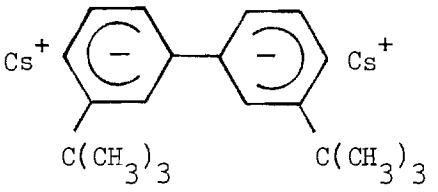
RECOMMENDATIONS

It would be interesting to extend the study of the reaction of cesium metal and Cs-K-Na alloy to include a number of compounds similar to the hydrocarbons investigated in this work. These hydrocarbons would be in two categories, compounds possibly able to form anion radicals which could couple intermolecularly and compounds possibly able to form dianion radicals which could couple intramolecularly.

Toluene, a compound in the first category, would be interesting to study because it is chemically similar to benzene. J. de Postis has found that toluene reacts with cesium at 28.5°[19] to form benzyl cesium. At -70°, judging from our results with the cesium alloy-diphenylmethane reaction, cesium should react with toluene to form cesium toluenide in high yield. Cesium toluenide would presumably couple intermolecularly, if the reaction temperature were increased, to form three possible products having the following structures:

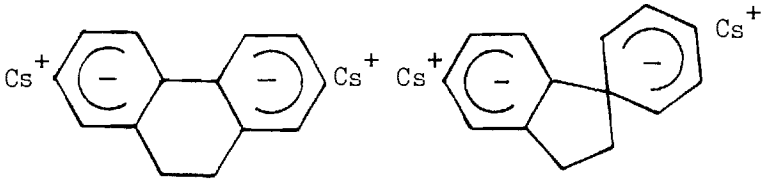


Along this same line of investigation, tert-butylbenzene has been reported to react with cesium[20]; however, no product was isolated from the reaction. This compound would be interesting to study because the tert-butyl group should provide sufficient steric hindrance to prevent two of the three possible dianion dimers from being formed. The remaining possible product, i. e.,



might provide a good synthetic route to 3,3'-di-t-butylbiphenyl.

In the category of intermolecular coupling reactions, the study of the reaction of cesium with diphenylalkanes that could couple to form six-membered rings would be interesting. The simplest compound of this type would be 1,2-diphenylethane. The intramolecular coupling product could have one of the following structures:



It has been reported[65] that 1,2-diphenylethane reacts with potassium at -70° in DME or THF to form an anion radical which decomposes to benzyl potassium when warmed to temperatures as low as -60°. Cesium,

because of its unique properties, could conceivable cause the coupling reaction rather than the bond cleavage reaction to occur at -70°. Since there appears to be a steric requirement for the intramolecular coupling reaction, 2,3-dimethyl-2,3-diphenylbutane would also be an interesting compound to study.

In this research, the reacting metal in Cs-K-Na alloy has been assumed to be cesium. This assumption is supported by the similarity between the reactions of cesium metal and the reactions of Cs-K-Na alloy; however, there is no proof that this assumption is true. Therefore, definitive identification of the alkali metal counterion in the alkali metal-hydrocarbon adducts from Cs-K-Na alloy would be of interest.

APPENDIX A

MASS SPECTRA OF 1,1',4,4'-TETRAHYDROBIPHENYL AND THE COMPOUND THOUGHT TO BE 3-PHENYLCYCLOHEXENE

1. 1,1',4,4'-Tetrahydrobiphenyl

Source: Isolated from the reaction of benzene and cesium at -20° in experiment 4-5 and analyzed by gc-ms on a Carbowax 20 M column (II).

Molecular formula: $C_{12}H_{14}$

m/e	Relative Intensity	Possible Chemical Formula
159	1.2	$C_{12}H_{14}^{+}$ + 1
158	11	$C_{12}H_{14}^{+}$
157	5	$C_{12}H_{13}^{+}$
156	18	$C_{12}H_{12}^{+}$
155	54	$C_{12}H_{11}^{+}$
154	off scale	$C_{12}H_{10}^{+}$
153	100	$C_{12}H_{9}^{+}$
152	69	$C_{12}H_{8}^{+}$
151	8	$C_{12}H_{7}^{+}$
143	4	$C_{11}H_{11}^{+}$
141	14	$C_{11}H_{9}^{+}$
130	8	$C_{10}H_{10}^{+}$
129	33	$C_{10}H_{9}^{+}$
128	13	$C_{10}H_{8}^{+}$
127	8,	$C_{10}H_{7}^{+}$
117	5	$C_{9}H_{9}^{+}$
116	5	$C_{9}H_{8}^{+}$
115	33	$C_{9}H_{7}^{+}$

m/e	Relative Intensity	Possible Chemical Formula
104	31	$C_8H_8^+$
91	20	$C_7H_7^+$
81	7	$C_6H_9^+$
80	79	$C_6H_8^+$
79	off scale	$C_6H_7^+$
78	off scale	$C_6H_6^+$
77	95	$C_6H_5^+$
76	48	$C_6H_4^+$
75	10	$C_6H_3^+$
74	9	$C_6H_2^+$

2. Compound Suspected to be 3-Phenylcyclohexene

Source: Produced in the reaction of biphenyl and cesium at 32° to 48° in experiment 4-16 and analyzed by gc-ms on a Carbowax 20 M column (II). This compound has the same gc retention time on this column as 1,1',4,4'-tetrahydrobiphenyl.

Molecular formula: $C_{12}H_{14}$

m/e	Relative Intensity	Possible Chemical Formula
159	15	$C_{12}H_{14}^+ + 1$
158	100	$C_{12}H_{14}^+$
157	10	$C_{12}H_{13}^+$
156	3	$C_{12}H_{12}^+$
155	6	$C_{12}H_{11}^+$
154	14	$C_{12}H_{10}^+$
153	6	$C_{12}H_9^+$
152	6	$C_{12}H_8^+$
143	41	$C_{11}H_{11}^+$
130	75	$C_{10}H_{10}^+$

m/e	Relative Intensity	Possible Chemical Formula
129	87	$C_{10}H_9^+$
128	33	$C_{10}H_8^+$
117	25	$C_9H_9^+$
115	70	$C_9H_7^+$
104	25	$C_8H_8^+$
91	40	$C_7H_7^+$
81	7	$C_6H_8^+$
80	15	$C_6H_7^+$
79	18	$C_6H_6^+$
78	12	$C_6H_5^+$
77	26	$C_6H_4^+$
76	6	$C_6H_3^+$

This compound is proposed to be 3-phenylcyclohexene for the following reasons: (a) the compound has the same gc retention time and molecular formula as 1,1',4,4'-tetrahydrobiphenyl but does not have the same mass spectrum; (b) the compound is not 1,2',4,5'-tetrahydrobiphenyl, a possible Birch reduction product of 1,4-dihydrobiphenyl, because the mass spectrum of this compound would be expected to be quite similar to 1,1',4,4'-tetrahydrobiphenyl, i.e., high relative amounts of m/e 154; (c) the compound does not have the same retention time as 1-phenylcyclohexene, but has a similar mass spectrum (3).

3. 1-Phenylcyclohexene

Source: Produced in the reaction of biphenyl and cesium at 32° to 48° in experiment 4-16 and analyzed by gc-ms on a Carbowax 20 M

column (II).

Molecular formula: $C_{12}H_{14}$

m/e	Relative Intensity	Possible Chemical Formula
159	13	$C_{12}H_{14}^{+}$ + 1
158	100	$C_{12}H_{14}^{+}$
157	10	$C_{12}H_{13}^{+}$
156	4	$C_{12}H_{12}^{+}$
155	5	$C_{12}H_{11}^{+}$
154	13	$C_{12}H_{10}$
153	6	$C_{12}H_{9}^{+}$
152	4	$C_{12}H_{8}^{+}$
151	2	$C_{12}H_{7}^{+}$
143	40	$C_{11}H_{11}^{+}$
130	68	$C_{10}H_{10}$
129	70	$C_{10}H_{9}^{+}$
128	30	$C_{10}H_{8}$
117	19	$C_{9}H_{9}^{+}$
115	50	$C_{9}H_{7}^{+}$
104	15	$C_{8}H_{8}^{+}$
91	24	$C_{7}H_{7}^{+}$
81	2	$C_{6}H_{9}^{+}$
80	8	$C_{6}H_{8}^{+}$
79	10	$C_{6}H_{7}^{+}$
78	7	$C_{6}H_{6}^{+}$
77	15	$C_{6}H_{5}^{+}$
76	6	$C_{6}H_{4}$

4. Mixture of 1,1',4,4'-Tetrahydrobiphenyl and 3-Phenylcyclohexene

Source: Produced in the reaction of cesium and benzene at 35° in experiment 3-162 and analyzed by gc-ms on a Carbowax 20 M column (II).

This component has the same retention time as the compounds presented in parts 1 and 2 of this Appendix.

m/e	Relative Intensity	Possible Chemical Formula
159	12	$C_{12}H_{14}^{+}$ + 1
158	100	$C_{12}H_{14}^{+}$
157	9	$C_{12}H_{13}^{+}$
156	1	$C_{12}H_{12}^{+}$
155	5	$C_{12}H_{11}^{+}$
154	48	$C_{12}H_{10}$
153	15	$C_{12}H_{9}^{+}$
152	9	$C_{12}H_{8}^{+}$
143	32	$C_{11}H_{11}^{+}$
130	57	$C_{10}H_{10}$
129	60	$C_{10}H_{9}^{+}$
128	20	$C_{10}H_{8}^{+}$
117	13	$C_{9}H_{9}^{+}$
115	18	$C_{9}H_{7}^{+}$
104	15	$C_{8}H_{8}^{+}$
91	12	$C_{7}H_{7}^{+}$
81	5	$C_{6}H_{8}$
80	3	$C_{6}H_{7}^{+}$
79	3	$C_{6}H_{6}^{+}$
78	3	$C_{6}H_{5}^{+}$
77	6	$C_{6}H_{4}^{+}$
76	3	$C_{6}H_{4}^{+}$

Comparison of this spectrum with the first two spectra indicate that the major component in the mixture is 3-phenylcyclohexene. Judging from the large relative intensity of the 154 m/e, this gc component apparently contains a small amount of 1,1',4,4'-tetrahydrobiphenyl.

APPENDIX B

DISCUSSION OF CALCULATION OF ANION RADICAL CONCENTRATIONS DETERMINED BY ESR ANALYSIS

Electron Spin Resonance (esr) spectroscopic studies of the anion radicals formed were made in a number of the experiments. This technique was used to provide two types of information, the concentration of the anion radical in the samples studied and the spin state of the radicals observed (doublet or triplet).

ESR spectroscopy is based on the fact that an unpaired electron has two energy states in an applied magnetic field because the orientation of the magnetic moment of the electron can either be parallel (α) or antiparallel (β) to the applied magnetic field. The magnitude of the energy that separates these two states depends on the strength of the applied magnetic field (H), the value of the electronic Bohr magneton (β_e) and a proportionality factor (g). The energy that will be absorbed by an electron in going from the lower energy state to the higher energy state is related to these three quentities by the formula

$$E = g\ \beta_e\ H$$

In esr spectroscopy, a microwave generator is used as an energy source. Thus, the above formula becomes, in terms of frequency,

$$h\nu = g\,\beta_e\,H$$

where h is Planck's constant. In the instrument used, the microwave frequency (ca 9000 MHz) is kept constant and the magnetic field (around 3000 gauss) was varied.

Since β_e and h are constants, this equation can be expressed in terms of g.

$$g = \frac{h\nu}{\beta_e H} = 7.14451 \times 10^{-7}\ \frac{\nu}{H}$$

The value of the g-factor for a free electron is 2.0032. In most organic radicals in the doublet spin state the g-factor is close to this value.

Triplet radicals also have a g-factor close to 2.000; however, these radicals have a second absorption at half-field (ca 1500 gauss). A triplet spin state in a magnetic field has three separate electron orientations: both electrons with their magnetic moment vectors parallel to the applied magnetic field ($\alpha\alpha$), one electron parallel and one electron antiparallel, ($\alpha\beta$), and both electrons antiparallel, ($\beta\beta$). The energy absorption at half-field is a transition from $\alpha\alpha$ to $\beta\beta$. Since in this transition, there are two electrons that have to change orientation, then only half of the magnetic field is required to achieve the proper separation of the energy states.

Table 45 is a compilation of the g-factors found in esr studies

Table 45. G-Values Determined from ESR Studies of Various Anion Radicals.

Experiment	Reaction	Reaction Temperature	Temp of esr Measurement	G-Factor
4-72	Ph-H, Cs	-70°	-196°	2.0010
4-82	Ph-H, Cs	-70°	-75° to -105°	1.9984[a]
		-20°	-75° to -105°	2.0052
		ca 30°	-90° to -120°	2.0006
3-130	Ph-H, CS (in isooctane)	ca 30°	ca 25°	2.0025
	Ph-H, Cs (in benzene)	ca 30°	ca 25°	2.0025
4-66	Ph-Ph, Cs	ca 30°	ca 25°	2.0010
4-80	Ph_3CCH_3, Cs alloy	-70°	-90° to 100°	1.9855
DQ[b]	Ph_3CCH_3, Cs alloy	-70°	-196°	1.9966[a]
4-74	$Ph_2C(CH_3)_2$, Cs alloy	-70°	-100 to -120°	2.0040
4-77	Ph_2CH_2, Cs alloy	-70°	-90° to -100°	1.9998

(a) This sample contained no half-field signal.

(b) Sample prepared by Mr. Dean Quest.

from various experiments. These g-factors were calculated using the formula, $g = 7.14451 \times 10^{-7} \frac{\nu}{H}$, where ν is in Hz and H is in gauss.

As in any other absorption spectroscopy, the amount of absorbing species is proportional to the number of energy quanta absorbed in esr spectroscopy. The concentrations of anion radical present in the sample studied were determined using the formula,

$$\frac{R_1}{R_2} = \left(\frac{10^{SA_1}}{10^{SA_2}}\right) \times \left(\frac{hm_2}{hm_1}\right) \times \left(\frac{Y\ scale_2}{Y\ scale_1}\right) \times \left(\frac{S_1}{S_2}\right) \times \left(\frac{\Delta H_1}{\Delta H_2}\right)^2$$

where subscript 1 represents the sample and subscript 2 represents a standard of known radical concentration. The variables in this equation are defined as:

R = number of radicals per unit volume

SA = log of spectrum amplitude

hm = modulation amplitude

Y scale = scale used for Y axis of the recorder (in/mv or cm/mv)

S = esr first derivative curve amplitude

H = line width (peak to peak magnetic field strength difference in gauss)

The standard solution of radical used for these calculations was a 0.04828 M solution of 2,2-diphenyl-1-picrylhydrazyl (free radical) in benzene.

In Table 46 the anion radical concentrations of samples taken during various reactions are based on the limiting reagent in the reaction.

Table 46. Compilation of Anion Radical Yields in Various Reactions.

Experiment	Reaction	Reaction Temperature	Temperature of esr Measurement	Percent Yield
4-82	Ph-H, Cs	-70° to -75°	-196°	2.3×10^{2}
		-70° to -75°	-75° to -105°	8.5×10^{-2}
		-20°	-75° to -105°	3.3×10^{-4}
		ca 25°	-90° to -120°	9.0×10^{-3}
4-72[a]	Ph-H, Cs	-70° to -75°	-196°	3.8×10^{2}
4-70[a]	Ph-H, Cs	-70°	-196°	1.9×10^{1}
4-48	Ph-H-d_6, Cs	-70°	-196°	9.3×10^{3}
		-20°	-196°	1.3×10^{-4}
		25°	-196°	6.3×10^{-2}
3-130	Ph-H, Cs (in isooctane)	25°	25°	1.2×10^{-3}
	Ph-H, Cs (in benzene)	25°	25°	3×10^{-6}
4-66	Ph-Ph, Cs	36°	ca 25°	6×10^{-4}
4-80	Ph_3CCH_3, Cs alloy	-70°	-90° to -100°	4.1×10^{-5}

Table 46. (Concluded).

Experiment	Reaction	Reaction Temperature	Temperature of esr Measurement	Percent Yield
DQ[b]	Ph_3CCH_3, Cs alloy	-70°	-196°	2.2×10^{2}
4-74	Cs alloy	-70°	-90° to -110°	1.6×10^{-6} M[c]
	$Ph_2C(CH_3)_2$ Cs alloy	-70°	-90° to -110°	9.4×10^{-5}
4-77	Ph_2CH_2, Cs alloy	-70°	-90° to -100°	5×10^{-1}
2-165	Ph_2CH_2, Cs alloy	-70°	-196°	6.4×10^{2} and 1.3×10^{3}

(a) This reaction gave a poor yield of products at -20°.

(b) Sample prepared by Mr. Dean Quest.

(c) This yield is in moles/liter.

These results are considered accurate only within a factor of about 10.

The data in Table 43 indicates that there is a discrepancy between esr measurements taken at -196° and at ca -95°. If the chemistry of the reaction is considered, the results appear to be reliable at -196°; e. g., the products of the benzene-cesium reaction at -70°, -20° and 25° are more consistent with esr results found in experiment 4-48 (-196°) than in experiment 4-82 (ca -95°).

There are problems with measurements taken at both temperatures. At -95°, the temperature of the sample is close to the freezing point of THF (-108.5°) which makes it difficult to keep a consistent microwave signal upon the sample because variations in temperature cause changes in the dielectric constant of the solvent which affect the microwave signal. Since a Dewar of cold pentane was used to cool the sample, it was impossible to maintain the sample temperature without variation. If measurements are made at -196° (liquid nitrogen), there is the possibility that the intermediate produced at -70° has changed to a different intermediate at the lower temperature; e. g., in the 1,1,1-triphenylethane-cesium alloy reaction, the dianionic species may have become a dianion diradical species and thereby giving a high esr result.

This problem could possibly be circumvented by using an instrument with a variable temperature probe that would maintain esr samples at a constant temperature. Such a temperature probe would provide the option of studying these intermediates at the reaction temperature or, if this is unsatisfactory, at temperatures slightly below the freezing point of the solvent.

APPENDIX C

IR SPECTRA OF cis-9,9-DIMETHYL-4a,4b,2,7-TETRAHYDROFLUORENE AND 1,1',4,4'-TETRAHYDROBIPHENYL

Compound	Absorption Maxima in cm^{-1} and Relative Intensity in Parentheses
cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene (KBr pellet)	3380 (m, broad), 3010 (s), 2940 (s), 2900 (m), 2860 (s), 2820 (m), 2790 (s), 1670 (w), 1630 (m), 1450 (m), 1440 (w), 1420 (m), 1385 (w), 1380 (w), 1370 (w), 1355 (m), 1290 (m), 1090 (w), 1015 (m), 975 (m), 945 (s), 930 (s), 905 (w), 830 (s), 815 (w), 775 (s), 690 (s).
1,1',4,4'-tetrahydrobiphenyl[a] (neat)	3340 (m, broad), 2970 (s), 2940 (s), 2870 (m), 1700 (m), 1640 (w), 1590 (w), 1480 (w), 1440 (m), 1380 (s), 1325 (w), 1290 (w), 1260 (m), 1210 (w), 1175 (w), 1125 (s), 1100 (s), 1080 (w), 1040 (w), 985 (w), 950 (m), 910 (w), 885 (w), 845 (m), 800 (m), 755 (w), 740 (m), 700 (m).

(a) Isolated by Mr. Dean Quest.

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