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A handwritten signature, possibly "J. L. Smith", written in dark ink. The signature is stylized with a large, looped initial "J" and a long horizontal stroke extending to the right.

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THE MECHANISMS OF REARRANGEMENT
OF 2,2,3-TRIPHENYLPROPYLLITHIUM,
2,2,2-TRIPHENYLETHYLLITHIUM, AND
2-m-BIPHENYLYL-2,2-BIS(p-BIPHENYLYL)ETHYLLITHIUM

A THESIS

Presented to

The Faculty of the Graduate Division

by

Gary Wentworth

In Partial Fulfillment

of the Requirements for the Degree

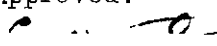
Doctor of Philosophy in the School of Chemistry

Georgia Institute of Technology

March, 1966

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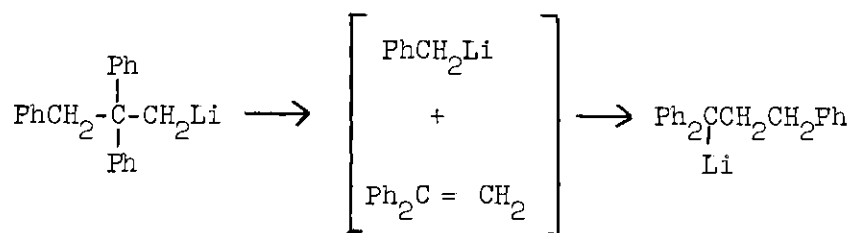
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SUMMARY

The purpose of this research was to determine the mechanism of the rearrangement of certain organolithium compounds. A 1,2-shift of phenyl in 2,2,2-triphenylethyllithium and an analogous 1,2-migration of benzyl in 2,2,3-triphenylpropyllithium have been generally assumed to take place by an intramolecular mechanism.

2,2,3-Triphenylpropyllithium was generated at -65° by the reaction of 1-chloro-2,2,3-triphenylpropane with lithium and allowed to rearrange at 0° in the presence of radioactive benzyllithium. The products of the reaction were assayed for carbon-14 after preliminary reaction with carbon dioxide to convert the organolithium compounds to carboxylic acids. The activity of the starting benzyllithium was $2.94 \mu\text{c}/\text{mmole}$; the activities of the benzyllithium and the 1,1,3-triphenylpropyllithium after the rearrangement was complete were 0.326 and $1.19 \mu\text{c}/\text{mmole}$, respectively. Thus, the rearranged compound gained radioactivity at the expense of the benzyllithium. The 1,1,3-triphenylpropyllithium is not at radiochemical equilibrium with the benzyllithium at the end of this experiment, however, since its molar activity is greater than the final activity of the benzyllithium. For the same reason, 2,2,3-triphenylpropyllithium is not at radiochemical equilibrium with benzyllithium before the rearrangement. Rather, an irreversible exchange of benzyl groups takes place during the rearrangement itself, suitably by way of the following intermolecular, elimination-readdition mechanism:



The radioactivity data are in good quantitative agreement with this conclusion, providing that the benzyllithium which re-adds to the 1,1-diphenylethene intermediate has the same activity as that of the benzyllithium in the bulk of the solution. The molar activities of 1,1,3-triphenylpropyllithium and benzyllithium calculated on the basis of these conclusions and the initial quantities and activities of reactants are 1.20 and 0.335 $\mu\text{c}/\text{mmole}$, respectively. Oxidation of the 2,2,4-triphenylbutanoic acid (derived from 1,1,3-triphenylpropyllithium) of specific activity 1.19 $\mu\text{c}/\text{mmole}$ gave benzoic acid of specific activity 1.18 $\mu\text{c}/\text{mmole}$ and benzophenone of no detectable activity. Thus, all of the carbon-14 in the 2,2,4-triphenylbutanoic acid is contained in the 4-position.

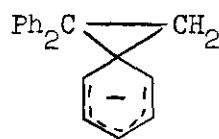
It was of interest to determine why the more basic 2,2,3-triphenylpropyllithium, which is present initially in high concentration, does not compete successfully with benzyllithium in the addition to 1,1-diphenylethene. Accordingly, the rearrangement of 2,2,3-triphenylpropyllithium was carried out in the presence of a number of other organolithium compounds and the relative extents of incorporation determined. The values of the rate constants, relative to benzyllithium ($k_{\text{RLi}}/k_{\text{PhCH}_2\text{Li}}$), were: $\text{PhLi} < 0.00083$, $\text{EtLi} < 0.00022$, $n\text{-BuLi} < 0.00019$, and $i\text{-PrLi} = 0.062 \pm 0.35$. The steric and electronic effects of the phenyl groups on 2,2,3-triphenylpropyllithium may make it even less reactive than n -butyllithium toward addition to 1,1-

diphenylethene.

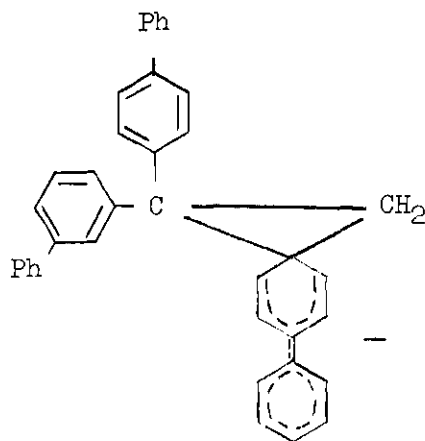
The direct addition of some organolithium compounds to 1,1-diphenylethene was carried out under the experimental conditions of the incorporation experiments. Benzylolithium and isopropylolithium formed adducts in high yield; phenylolithium and *n*-butylolithium gave much lower yields of adducts. These results are qualitatively in agreement with the results of the incorporation experiments.

2,2,2-Triphenylethylolithium was prepared in tetrahydrofuran at -60° by the reaction of 2-chloro-1,1,1-triphenylethane with lithium and allowed to rearrange at 0° in the presence of radioactive phenylolithium. The products of the reaction were assayed for carbon-14 after preliminary reaction with carbon dioxide to convert the organolithium compounds to carboxylic acids. The activity of the starting phenylolithium ($1.87 \mu\text{c}/\text{mmole}$) was identical to the activity of the phenylolithium after the rearrangement was complete. The 1,1,2-triphenylethylolithium contained less than 0.05 percent (if any) of the activity of the starting phenylolithium.

Since benzylolithium had been found to be an excellent nucleophile toward 1,1-diphenylethene, the rearrangement of 2,2,2-triphenylethylolithium was carried out in the presence of this reactive compound. Examination of the products of the rearrangement revealed that less than 0.5 percent (if any) of the benzylolithium was incorporated during the rearrangement. On the basis of these tests, the rearrangement of 2,2,2-triphenylethylolithium could be said to take place by an intramolecular mechanism, involving a bridged intermediate or transition state:



The reaction of 2-chloro-1-m-biphenyl-1,1-bis-(p-biphenyl)ethane with lithium in tetrahydrofuran at -65° generated 2-m-biphenyl-2,2-bis-(p-biphenyl)ethylolithium, as demonstrated by isolation of 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid in 23.7 percent yield upon carbonation. When the solution of this organolithium compound was allowed to warm to 0° for four hours, rearrangement occurred; the 2-m-biphenyl-2,2-bis(p-biphenyl)ethylolithium underwent migration of p-biphenyl to give 1-m-biphenyl-1,2-bis(p-biphenyl)ethylolithium, as demonstrated by carbonation to give 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid in 38 percent yield. Isotopic dilution analysis showed that this product of p-biphenyl migration accounted for at least 98.6 percent of the acidic product isolated. The predominance of p-biphenyl migration provides evidence for an intramolecular mechanism for the rearrangement, involving a bridged intermediate or transition state:



This intermediate is expected to be much more stable than the corresponding bridged intermediate for m-biphenyl migration. On the other hand, if the rearrangement of 2-m-biphenyl-2,2-bis(p-biphenyl)ethyl lithium had taken place by an elimination-readdition mechanism, m-biphenyl migration would have been expected to compete favorably with p-biphenyl migration, since the intermediate 3-lithiobiphenyl would be more stable than the alternative 4-lithiobiphenyl.

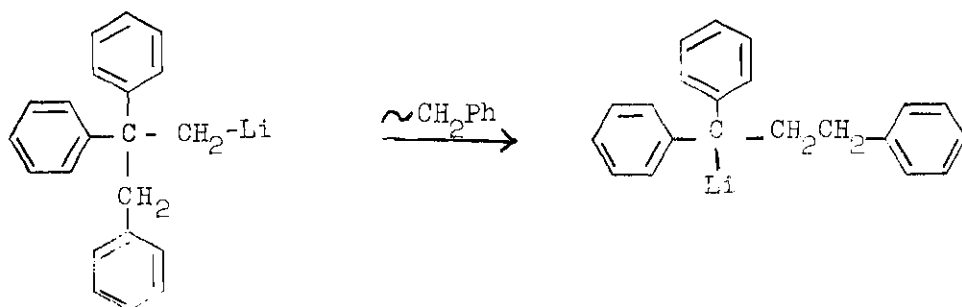
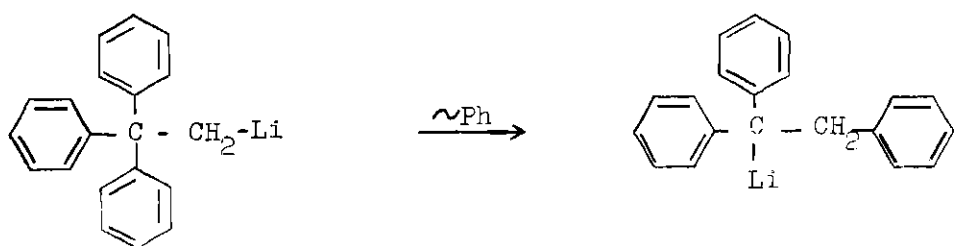
In view of the clear-cut preference for p-biphenyl over m-biphenyl migration, it is very likely that the migration of phenyl in 2,2,2-triphenylethyl lithium also takes place by an intramolecular mechanism involving a bridged intermediate on transition state. Thus, the previously allowed possibility of an elimination-readdition mechanism involving an anion plus olefin in a solvent "cage" has been eliminated.

The elimination-readdition mechanism for the Stevens rearrangement of dibenzyl dimethyl ammonium bromide and iodide was tested by allowing these compounds to react with excess radioactive benzyl lithium in tetrahydrofuran at 20°. In two runs--one in which the quaternary ammonium bromide was largely undissolved and the other in which the quaternary ammonium iodide was completely dissolved--the products dimethyl(o-methylbenzhydryl)amine and dimethyl(1,2-diphenylethyl)amine in each case showed no detectable radioactivity (0.02 percent or less of the activity of the starting benzyl lithium). The activity of the benzyl lithium after the rearrangement had taken place was identical to the activity of the starting benzyl lithium. Hence it may be concluded that these reactions are intramolecular processes under the conditions tested. This conclusion is in accord with the currently accepted intramolecular mechanism for the Stevens rearrangement of a number of other quaternary ammonium salts.

CHAPTER I

INTRODUCTION

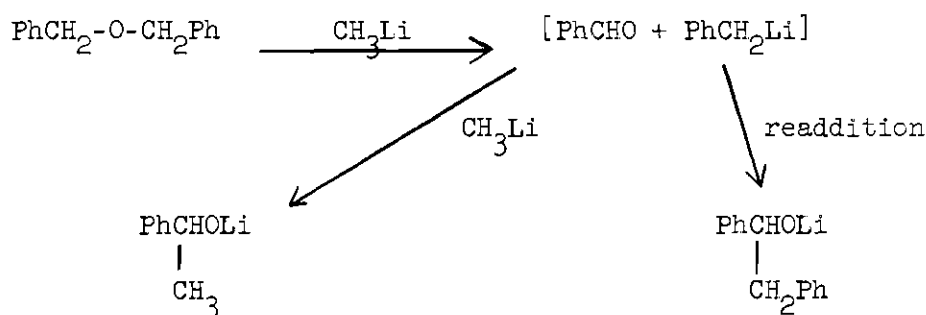
The purpose of this investigation is to determine the mechanism of the rearrangement of certain organolithium compounds. A 1,2-shift of phenyl has been observed¹ in 2,2,2-triphenylethyllithium; an analogous 1,2-migration of benzyl has been observed² in 2,2,3-triphenylpropyllithium. These rearrangements have generally been assumed to be intramolecular in character.



1. E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 412 (1961).

2. E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 2537 (1961).

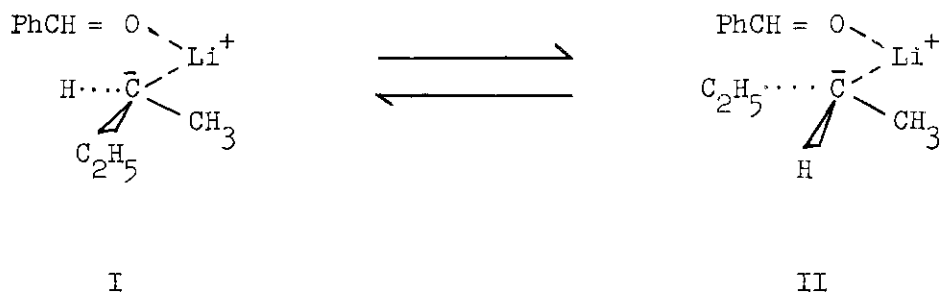
Recent work on the Wittig rearrangement³ of ethers provides strong argument for an elimination-readdition mechanism in the cases studied. In the reaction of dibenzyl ether with excess methyllithium, Lansbury and Pattison^{4,5} were able to isolate a carbinol corresponding to "trapping" of a carbonyl intermediate by the metallating agent. As the solvent was varied from 1:1 ether:tetrahydrofuran to 1:1 tetrahydrofuran:dimethoxyethane, the amount of methylphenylcarbinol produced increased from 3 to 25 percent. Schoellkopf and co-workers⁶⁻⁹ obtained strong support for the elimination-



readdition mechanism involving intimate ion pairs. Rearrangement of optically active benzyl s-butyl ether with butyllithium in a variety of

-
3. G. Wittig and L. Loeman, Ann., 550, 260 (1942).
 4. P. T. Lansbury and V. A. Pattison, J. Am. Chem. Soc., 84, 4295 (1962).
 5. P. T. Lansbury and V. A. Pattison, J. Org. Chem., 27, 1933 (1962).
 6. U. Schoellkopf and W. Fabian, Ann., 642, 1 (1961).
 7. U. Schoellkopf, Angew. Chem. (Intern. Ed. Eng.), 1, 126 (1962).
 8. U. Schoellkopf and D. Walter, Angew. Chem., 73, 545 (1961).
 9. U. Schoellkopf and D. Walter, Ann., 654, 27 (1962).

solvents proceeds with 67-82 percent racemization, presumably⁹ via the intermediates I and II. Control experiments showed that the observed racemization occurred only during the rearrangement.



The Stevens rearrangement¹⁰ of quaternary ammonium salts has been reported¹¹⁻¹⁴ to be an intramolecular carbanion rearrangement. Johnstone and Stevens^{12,13} could isolate no "cross-bred products" when two compounds with similar isomerization rates were allowed to rearrange simultaneously. Brewster and Kline¹⁴ observed that treatment of the optically active quaternary ammonium salt III with aqueous NaOH gave the amine IV with 97 per-

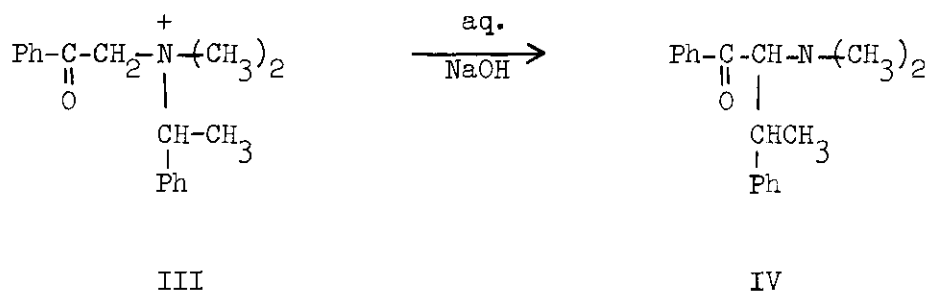
10. T. S. Stevens, E. M. Creighton, A. B. Gordon and H. MacNicol, J. Chem. Soc., 3193 (1928).

11. J. L. Dunn and T. S. Stevens, J. Chem. Soc., 279 (1934).

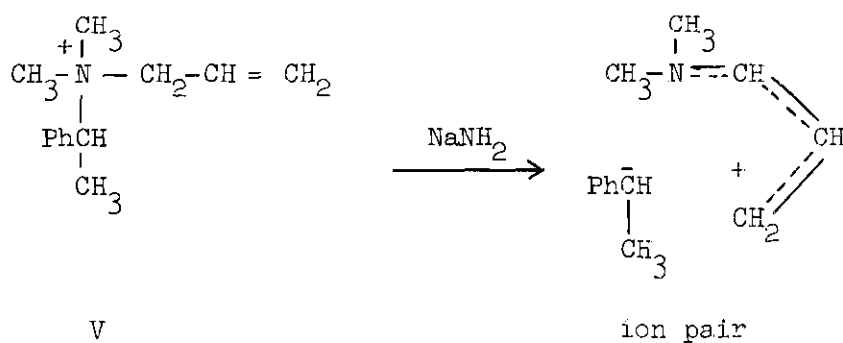
12. T. S. Stevens, J. Chem. Soc., 2107 (1930).

13. R. A. W. Johnstone and T. S. Stevens, J. Chem. Soc., 4487 (1955).

14. J. H. Brewster and M. W. Kline, J. Am. Chem. Soc., 74, 5179 (1952).

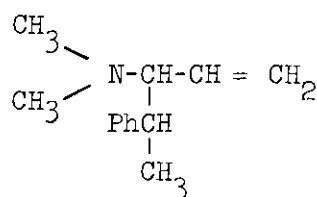


cent retention of configuration about the asymmetric carbon. Jenny and Druey¹⁵ found that treatment of optically active quaternary ammonium salt V with sodamide gave a product of 1,2-shift (VI) and a product of 1,4-shift (VII). The asymmetric carbon in product VI had retained its configuration to the extent of over 90 percent in both benzene and liquid ammonia, and that in product VII, about 80 percent in benzene and 72 percent in liquid ammonia. These results have been interpreted^{15,16} in terms of an intimate ion pair mechanism:

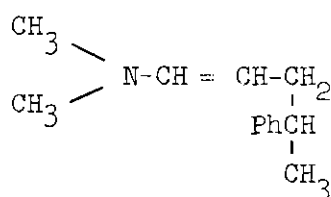


15. E. F. Jenny and J. Druey, Angew. Chem. (Intern. Ed. Engl.), 1, 155 (1962).

16. D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, p. 226.

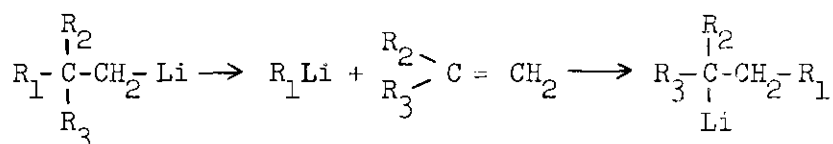


VI



VII

In the present case, the organolithium compound VIII could eliminate an organolithium compound IX to form an olefin which could combine with IX in the inverse manner, to give the final product of rearrangement X. The general argument¹⁷ in opposition to such a mechanism is that if addition of



VIII

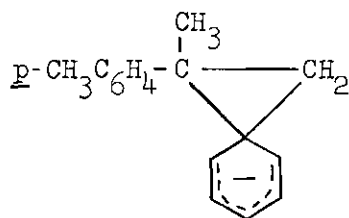
IX

X

organolithium compound IX to the olefin were possible, then the more basic organolithium compound VIII, which is present initially in high concentration, should compete successfully in addition to the olefin; however, no products corresponding to the addition of VIII have been found. As a further test for the elimination-readdition mechanism, Zimmerman and Zweig¹⁷ obtained little, if any, reaction of *p*-tolyllithium with α -methylstyrene using conditions under which 2-phenyl-2-(*p*-tolyl)propyllithium had undergone much rearrangement. These workers proposed an intramolecular mechanism

¹⁷. H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

for the rearrangement, involving the reactive intermediate or transition state XI.

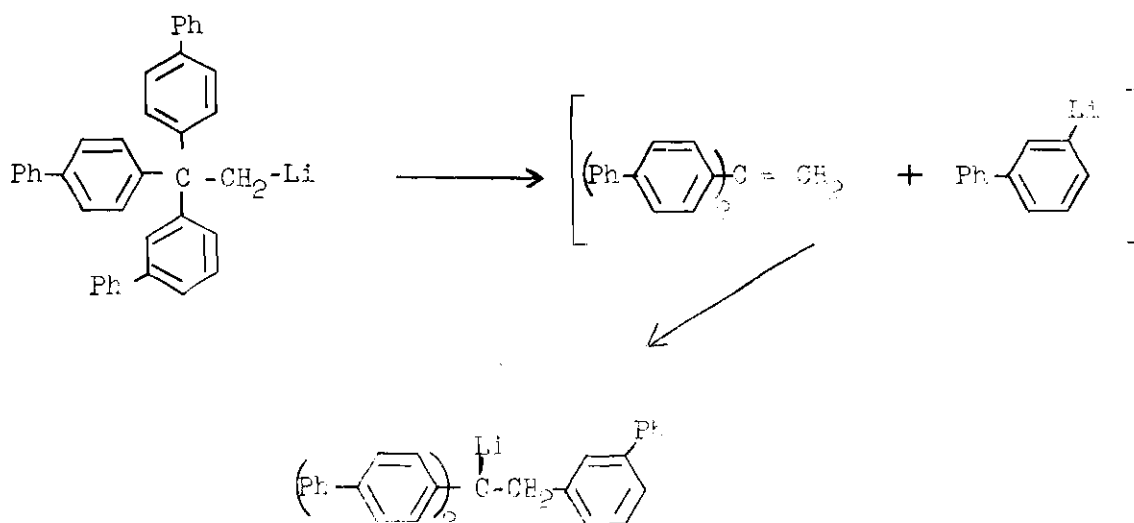


XI

In the first part of this research, the elimination-readdition mechanism for the rearrangement of 2,2,3-triphenylpropyllithium and 2,2,2-triphenylethyllithium was tested by allowing these compounds to rearrange in the presence of radioactive benzyllithium and phenyllithium, respectively. Detection of carbon-14 in the products of the rearrangements would provide strong evidence for the intermolecular mechanism. Since it was desirable to explain the lack of addition of unrearranged organolithium compound to an intermediate olefin, 2,2,3-triphenylpropyllithium was allowed to rearrange in the presence of a number of organolithium compounds and the relative extent of incorporation was determined. Phenyllithium, ethyllithium, n-butyllithium and isopropyllithium were tested. n-Butyllithium should be a good model for 2,2,3-triphenylpropyllithium, except for the steric effect of the phenyl groups on the latter compound.

In the second part of this research, 2-m-biphenyl-2,2-bis(p-biphenyl)ethyllithium was generated by reaction of 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane with lithium, and the relative migration aptitude

of m-biphenyl vs. p-biphenyl was determined. Streitwieser and Lawler^{18,19} have reported the relative rates of deuterium exchange with lithium cyclohexylamide in cyclohexyl amine on the various positions of biphenyl. Relative to 1.0 for a single position of benzene, the rate of exchange at the 4-position was 2.3 and at the 3-position, 3.7. Shatenshtein²⁰ has reported similar results for the exchange with potassium amide in liquid ammonia. These findings indicate that 3-lithiobiphenyl is more stable than 4-lithiobiphenyl. Consequently, if the rearrangement of 2-m-biphenyl-2,2-bis(p-biphenyl)ethyl lithium proceeds by an elimination-readdition mechanism, m-biphenyl migration would be expected to occur somewhat more readily than p-biphenyl migration.

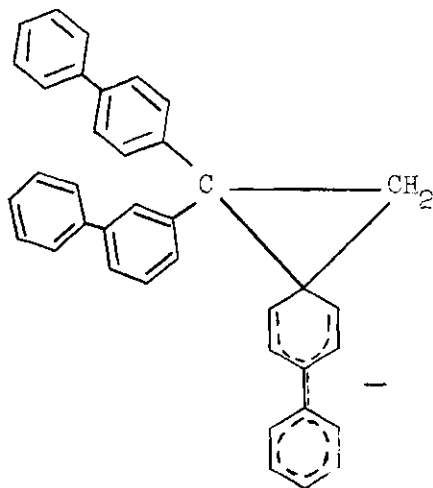


18. A. Streitwieser, Jr. and R. G. Lawler, J. Am. Chem. Soc., **85**, 2854 (1963).

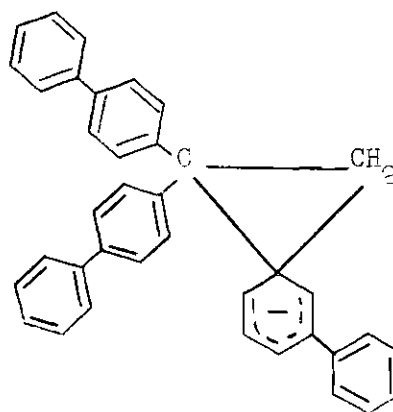
19. A. Streitwieser, Jr. and R. G. Lawler, J. Am. Chem. Soc., **87**, 5388 (1965).

20. A. I. Shatenshtein, Advan. Phys. Org. Chem., **1**, 155 (1963).

If the rearrangement proceeds by an intramolecular mechanism, p-biphenyl migration should predominate, since the reactive intermediate XII should be more stable than XIII. There are six contributing structures for the resonance hybrid XII and only three for the corresponding hybrid XIII. The Hammett σ_m constant²¹ for the β -styryl group (vinylog of a phenyl group) is +0.141; the σ^- constant²¹ for p-(β -styryl) is +0.619.* For the ionization



XII



XIII

* Constants determined for the acid hydrolysis of arylsulfuric acids at 78° ($\rho = -0.467$).

21. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, pp. 188-190.

of substituted phenols, σ_m and σ_p for a phenyl substituent are +0.124 and +0.205, respectively. (These values were calculated from the reported²² pKa values for m-phenyl- and p-phenylphenol, by extrapolation on a plot of pKa vs. σ .^{23, 24})

The products from the rearrangement were allowed to react with carbon dioxide to convert the organoalkali compounds to carboxylic acids. These acids were analyzed by an isotopic dilution technique. Independently synthesized, radioactive acids corresponding to m-biphenyl and to p-biphenyl migration were added to the crude reaction product and the resulting mixtures recrystallized to constant specific activity. A quantitative analysis of the rearrangement products was made from the extent of isotopic dilution.

The elimination-readdition mechanism for the Stevens rearrangements of dibenzyltrimethylammonium bromide²⁵ and iodide in tetrahydrofuran was tested by allowing the compounds to react with excess radioactive benzyl-lithium, and assaying the amine products for carbon-14.

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22. F. Kieffer and P. Rumpf, Compt. rend., 238, 360 (1954).
23. L. A. Cohen and W. M. Jones, J. Am. Chem. Soc., 85, 3397 (1963).
24. A. Bryson and R. W. Matthews, Australian J. Chem., 16, 401 (1963).
25. G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig, Ann., 572, 1 (1951).

CHAPTER II

REAGENTS AND SOLVENTS

Acetic Acid, Glacial

Baker reagent grade glacial acetic acid was used without further purification.

Acetic Anhydride

Eastman white label grade acetic anhydride was redistilled at 140°.

Acetone

Commercial grade acetone was redistilled at 56° from potassium permanganate through a 30-cm Vigreux column.

Acetonitrile

Eastman white label grade acetonitrile was redistilled at 81° from phosphorus pentoxide through a 30-cm Vigreux column.

Acetyl Chloride

Baker practical grade acetyl chloride was redistilled at 51° through a 30-cm column packed with glass helices.

Ammonia

Matheson Company, Inc., anhydrous ammonia (99.9 percent minimum purity) was distilled from the cylinder and condensed in the reaction vessel in which it was to be used.

Benzene

Matheson, Coleman & Bell, Inc., industrial grade (thiophene free) benzene was stored over sodium wire.

Benzoic Acid - Carboxyl-C-14

A mixture of radioactive benzoic acid from Tracerlab, Inc. and "cold" Eastman white label grade benzoic acid was dissolved in ether and the resulting solution allowed to evaporate to dryness.

Benzophenone

Eastman white label grade benzophenone was used without further purification.

Benzyl Alcohol

Baker reagent grade benzyl alcohol was redistilled at 203-204° through a 20-cm Vigreux column.

Benzyl Bromide

Eastman white label grade benzyl bromide was redistilled at 197° through a 20-cm Vigreux column.

Benzyl Chloride

Eastman white label grade benzyl chloride was redistilled at 179° through a 20-cm Vigreux column.

Benzyl dimethylamine

Eastman white label grade benzyl dimethylamine was used without further purification.

Biphenyl

Eastman white label grade biphenyl was used without further purification.

4-Biphenylcarboxylic Acid

Kent Chemicals, Ltd. (Vancouver) reagent grade 4-biphenylcarboxylic acid was used without further purification.

3-Bromobiphenyl

3-Bromobiphenyl from K&K Chemicals, Inc., was twice redistilled at 85-87° under 5 mm pressure. The vapor phase chromatogram showed three other peaks with areas totaling less than 3 percent of the total areas.

N-Bromosuccinimide

Aldrich reagent grade N-bromosuccinimide was used without further purification.

Butyric Anhydride

Eastman white label grade butyric anhydride was redistilled at 197-198° through a 20-cm Vigreux column.

Carbon Disulfide

Baker reagent grade carbon disulfide was used without further purification.

Carbon Tetrachloride

Matheson, Coleman & Bell, Inc., industrial grade carbon tetrachloride was used without further purification.

Chlorobenzene

Fisher reagent grade chlorobenzene was redistilled at 131° through a 30-cm Vigreux column.

Chlorobenzene-C-14

Chlorobenzene (labeled in the ring) from New England Nuclear Corporation was diluted with Fisher reagent grade chlorobenzene.

1-Chlorobutane

Fisher reagent grade 1-chlorobutane was redistilled at 77° through a 30-cm Vigreux column.

1-Chloro-2-methyl-2-phenylpropane

A sample prepared by L. P. Williams, Jr.²⁶ was redistilled at 101° under 15 mm pressure through a 30-cm Vigreux column.

1-Chloropropane

Fisher reagent grade 1-chloropropane was redistilled at 46.5-47.0° through a 30-cm column packed with glass helices.

2-Chloropropane

Fisher reagent grade 2-chloropropane was redistilled at 34.5-35.0° through a 30-cm column packed with glass helices.

1-Chloro-2,2,2-triphenylethane

A sample prepared by E. Grovenstein, Jr.²⁷ was recrystallized from ethanol to give white solid of m.p. 100-101°.

26. L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, p. 56 (1962).

27. E. Grovenstein, Jr., J. Am. Chem. Soc., 79, 4985 (1957).

Cyclohexane

Fisher purified grade cyclohexane was used without further purification.

Deuteriochloroform

Merck, Sharp & Dohme of Canada, Ltd., 99.5 percent pure deuteriochloroform was used without further purification.

Dibenzoyl Peroxide

Eastman white label grade dibenzoyl peroxide was used without further purification.

Diethylene Glycol

Fisher purified grade diethylene glycol was used without further purification.

Diethyl Ether

Baker reagent grade anhydrous ether was stored over sodium wire in an amber bottle.

Dimethyl Sulfoxide

Matheson, Coleman & Bell reagent grade dimethyl sulfoxide was used without further purification.

Diphenylacetic Acid

Aldrich reagent grade diphenylacetic acid was used without further purification.

Ethanol

Commercial absolute ethanol was distilled from magnesium through a 30-cm column packed with glass helices.

Ethyl Bromide

Baker reagent grade ethyl bromide was redistilled at 37-38° through a 30-cm Vigreux column.

Hydrazine

Matheson, Coleman & Bell (95 percent) hydrazine was used without further purification.

Isobutyric Acid

Eastman white label grade isobutyric acid was redistilled at 154°.

Lithium

Lithium Corporation of America, 0.05 percent sodium maximum, lithium wire was used.

Lithium Aluminum Hydride

Metal Hydrides, Inc., 95 percent, lithium aluminum hydride was used without further purification.

Magnesium

Eastman white label magnesium was used without further purification.

Malonic Acid

Fisher reagent grade malonic acid was used without further purification.

Methanol

Matheson, Coleman & Bell commercial grade methanol was redistilled at 64° from magnesium through a 30-cm Vigreux column.

Methyl Benzoate

Fisher reagent grade methyl benzoate was used without further purification.

3-Methylbiphenyl

Aldrich reagent grade 3-methylbiphenyl was used without further purification.

Methylene Chloride

Matheson, Coleman & Bell commercial grade methylene chloride was extracted with sulfuric acid and redistilled at 39-40° through a 30-cm column packed with glass helices.

Methyl Iodide

Baker reagent grade methyl iodide was used without further purification.

Methyl Isobutyrate

Fisher reagent grade methyl isobutyrate was used without further purification.

N-Methyl-N-nitroso-p-toluenesulfonamide

Aldrich reagent grade N-methyl-N-nitroso-p-toluenesulfonamide was used without further purification.

Methyl Phenylacetate

Fisher reagent grade methyl phenylacetate was used without further purification.

Methyl Propionate

Baker reagent grade methyl propionate was used without further purification.

Picric Acid

Baker reagent grade picric acid was used without further purification.

Potassium

Baker reagent grade potassium was used without further purification.

Propionic Acid

Fisher reagent grade propionic acid was used without further purification.

Pyridine

Baker reagent grade pyridine was redistilled at 115° through a 20-cm Vigreux column and stored over potassium hydroxide pellets.

Sodium

Baker reagent grade sodium was used without further purification.

Sodium Aluminum Hydride

Metal Hydrides, Inc., pure grade sodium aluminum hydride was used without further purification.

Tetrahydrofuran

Matheson, Coleman & Bell commercial grade tetrahydrofuran was redistilled from molten potassium through a 30-cm Vigreux column and stored over sodium wire.

Thionyl Chloride

Eastman white label grade thionyl chloride was redistilled at 76-77° through a 30-cm column packed with glass helices.

Toluene

Fisher reagent grade toluene was redistilled at 110° through a 20-cm Vigreux column and stored over sodium wire.

p-Toluidine

Aldrich reagent grade p-toluidine was used without further purification.

Triethylene Glycol

Fisher purified grade triethylene glycol was used without further purification.

CHAPTER III

SYNTHESES

Synthesis of 1-Chloro-2,2,3-triphenylpropane

This halide, reported by Grovenstein and Williams,²⁸ was prepared by the reaction of 2,2,3-triphenylethylpotassium with methylene chloride according to the new procedure which follows.

Triphenylethylene

This olefin was synthesized according to the procedure given in Organic Syntheses.²⁹ In a 3-l. Morton flask equipped with Morton high-speed stirrer, reflux condenser and dropping funnel, benzylmagnesium chloride was prepared by the reaction of 29.16 g (1.20 g atoms) of magnesium turnings and 152 g (1.20 moles) of benzyl chloride in 800 ml of anhydrous ether. A solution of 182 g (1.00 mole) of benzophenone in 500 ml of anhydrous ether was added to the Grignard reagent over a period of two hours. The adduct was decomposed to the olefin by the addition of 500 ml of cold 20 percent sulfuric acid. The organic phase was separated, the ether removed by distillation through a 20-cm Vigreux column, and the residue distilled at 1.0 mm. The fraction boiling at 170-180° weighed 200 g. This yellow, viscous liquid, after crystallization from 95 percent

28. E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., **83**, 2537 (1961).

29. A. H. Blatt (ed.-in-chief), Organic Syntheses, John Wiley & Sons, Inc., New York, Collective Vol. II, 1955, p. 606.

ethanol, gave 183 g of white crystalline solid, m.p.* 69-70° (71.0 percent yield). In a similar preparation, a 78.8 percent yield of olefin melting at 68.5-69.5° was obtained. A 65-70 percent yield is reported²⁹ in

Organic Syntheses.

1-Chloro-2,2,3-triphenylpropane

In a 250-ml flask equipped with mechanical stirrer and Dry Ice-acetone condenser, 125 ml of anhydrous ammonia was condensed upon 12.8 g (0.050 mole) of triphenylethylene. Under an atmosphere of dry nitrogen, 2.43 g (0.106 g atom) of sodium was added rapidly in pieces of about 0.2 g. The solution turned red in color immediately upon addition of the sodium. The mixture was stirred for ten minutes and then siphoned into a flask containing 75 ml of methylene chloride at -50°. The red color of the ammonia solution discharged rapidly. The ammonia was allowed to evaporate from the solution and 10 ml of 95 percent ethanol was added to destroy any unreacted sodium. The mixture was washed with 200 ml of water, the organic phase separated and the aqueous phase extracted with methylene chloride. Evaporation of the combined methylene chloride solutions to dryness and recrystallization of the yellow-orange solid residue from acetone gave 5.89 g (0.019 mole) of white solid (39.9 percent yield), m.p. 127-128.5°. In three similar preparations using potassium instead of sodium, the average yield was 45.6 percent.

Synthesis of 1,1-Diphenylethene

Benzophenone

Benzophenone was prepared according to the procedure of Rubidge and

*All melting points were taken on an apparatus checked with known compounds.

Qua.³⁰ In this procedure, the benzoyl chloride formed by the action of thionyl chloride on benzoic acid was not purified, but reacted immediately with aluminum chloride and benzene. Reaction of 9.00 g (0.0737 mole) of benzoic acid, 4.77 g (0.110 mole) of thionyl chloride, 9.70 g (0.0737 mole) of aluminum chloride, and 114 g (1.46 moles) of benzene afforded 8.70 g (0.0477 mole) of benzophenone (64.8 percent yield), m.p. 48-49°.

1,1-Diphenylethene

The synthesis of 1,1-diphenylethene from benzophenone and methylmagnesium iodide was carried out according to the general procedure given in Organic Syntheses,²⁹ but with use of a Morton stirrer and 500-ml Morton flask. The reaction of 10.0 g (0.055 mole) of benzophenone, 1.61 g (0.066 g atom) of magnesium turnings and 9.35 g (0.066 mole) of methyl iodide gave, after the usual work-up and redistillation, 6.94 g (0.0385 mole) of 1,1-diphenylethene (70.2 percent yield, based on benzophenone), b.p. 86-90° at 0.25 mm. In a similar preparation, the reaction of 30.0 g (0.165 mole) of benzophenone, 4.80 g (0.198 g atom) of magnesium turnings and 30.4 g (0.214 mole) of methyl iodide gave 20.9 g (0.116 mole) of 1,1-diphenylethene (71.3 percent yield, based on benzophenone), b.p. 112-118° at 1.5 mm. This was combined with the product from the previous run and distilled at 0.06 mm. The fraction boiling at 81-85° had $n_D^{27.5^\circ}$ 1.6045, or by extrapolation, $n_D^{14^\circ}$ 1.6100 (reported³¹ value, $n_D^{14^\circ}$ 1.6092).

30. C. R. Rubidge and C. N. Qua, J. Am. Chem. Soc., **36**, 734 (1914).

31. C. D. Hodgman (ed.-in-chief), "Handbook of Chemistry and Physics," Chem. Rubber Publishing Co., Cleveland, Ohio, 42nd edition, 1960, p. 989.

Synthesis of Benzyl Methyl Ether- α -C-14

The synthesis of this ether was first carried out using benzoic acid- α -C-14 as a starting material. In succeeding preparations, benzyl chloride- α -C-14 was purchased and the ether generated by the action of sodium methoxide on the chloride. The intermediates in the synthesis were purified by distillation through a 10-cm Vigreux column. After each distillation, a small portion of "cold" compound was distilled through the same apparatus and the distillate combined with the radioactive distillate. This procedure minimized mechanical loss of radioactive compound.

Benzyl Alcohol- α -C-14

Benzoic acid- α -C-14 of specific activity 1.76 mc/mole was diluted with "cold" benzoic acid to give an acid of specific activity 17.09 μ c/mole. The reduction of this benzoic acid with lithium aluminum hydride was carried out according to the procedure of Nystrom,³² except that the Morton stirring apparatus was used and the reaction carried out under an atmosphere of dry nitrogen, with tetrahydrofuran as solvent. The reaction of 4.25 g (0.0348 mole) of benzoic acid- α -C-14 with 3.96 g (0.104 mole) of lithium aluminum hydride gave 2.30 g (0.0213 mole) of benzyl alcohol- α -C-14 (61.2 percent yield), b.p. 202-203°. This was diluted (during distillation) with 0.200 g (0.00185 mole) of "cold" benzyl alcohol. In three similar preparations, the average yield was 55.6 percent (Nystrom³² reports 60-70 percent yield).

Benzyl Chloride- α -C-14

Benzyl chloride- α -C-14 was synthesized from benzyl alcohol- α -C-14

32. R. F. Nystrom, J. Am. Chem. Soc., 69, 2548 (1947).

by the method of Norris.³³ The reaction of 12.6 g (0.116 mole) of benzyl alcohol- α -C-14 with 42.5 g (1.16 moles) of hydrochloric acid (sp. gr. 1.18) gave 11.2 g (0.0885 mole) of benzyl chloride- α -C-14 (96.6 percent yield). This was diluted (during distillation) with 0.500 g (0.00395 mole) of "cold" benzyl chloride. In a similar preparation, a 92.2 percent yield was observed (Norris³³ reports quantitative yields).

Benzyl Methyl Ether- α -C-14

Benzyl methyl ether- α -C-14 was prepared by the reaction of sodium methoxide and benzyl chloride- α -C-14, according to the procedure of Olson and co-workers.³⁴ The reaction of 3.95 g (0.172 g atom) of sodium, 37.2 g (1.19 moles) of anhydrous methanol and 15.1 g (0.119 mole) of benzyl chloride- α -C-14 gave 10.4 g (0.0854 mole) of benzyl methyl ether- α -C-14 (71.2 percent yield), b.p. 170-171°. This was diluted (during distillation) with 0.500 g (0.0041 mole) of "cold" benzyl methyl ether. In three other preparations, the average yield was 70.6 percent (Olson³⁴ reports 70-75 percent yields).

Synthesis of 2,2-Diphenylpentanoic Acid

This acid was prepared according to the general method outlined by Hauser,³⁵ in which the potassium salt of ethyl diphenylacetate is alkylated with a halide.

In a 500-ml, 3-necked, round-bottomed flask equipped with stirrer, dropping funnel and Dry Ice-acetone condenser, 200 ml of anhydrous ammonia

33. J. F. Norris, Am. Chem. Journal, 38, 638 (1907).

34. W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, J. Am. Chem. Soc., 69, 2451 (1947).

35. W. G. Kenyon, R. B. Meyer and C. R. Hauser, J. Org. Chem., 28, 3108 (1963).

was condensed. Under an atmosphere of dry nitrogen, 0.657 g (0.0168 g atom) of potassium was added rapidly in pieces of about 0.1 g each. After the first piece of potassium had dissolved, a small crystal of ferric nitrate was added to catalyze the formation of potassium amide. The blue color of potassium in liquid ammonia changed to grey-brown after 40 minutes of stirring. A solution of 4.03 g (0.0168 mole) of ethyl diphenylacetate in 30 ml of anhydrous ether was added dropwise over a period of ten minutes and the resulting solution stirred for 30 minutes. A solution of 1.32 g (0.0168 mole) of 1-chloropropane in 25 ml of anhydrous ether was added dropwise over a period of ten minutes and the resulting solution stirred for two hours. Solid ammonium chloride (1.07 g, 0.020 mole) was added to neutralize unreacted potassium amide. The ammonia was allowed to evaporate from the mixture and 50 ml of 5 percent HCl was added. The aqueous layer was separated and extracted with two 25 ml portions of ether. The ether extracts were combined with the original ether layer, dried over anhydrous magnesium sulfate and allowed to evaporate to dryness, whereupon a sticky yellow solid appeared. This material was allowed to reflux for five hours with 250 ml of 15 percent aqueous KOH. The resulting clear solution was acidified with cold concd. HCl and extracted with four 100 ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate and allowed to evaporate to dryness to give 3.16 g (0.0124 mole) of off-white solid, m.p. 250-254° (74.0 percent yield). Two recrystallizations from aqueous ethanol gave 2.66 g white powder, m.p. 153-155° (reported³⁶ melting point of 2,2-diphenylpentanoic acid: 155.5°).

36. A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. Kh. Bostandzhyan, Doklady Akad. Nauk Armyan. S.S.R., 28, No. 1, 11 (1959).

Attempted Synthesis of Chloro-m-biphenylbis(p-biphenyl)methane

4,4'-Diphenylbenzophenone

This ketone was prepared by the method of Calzolari and Furlani,³⁷ in which the intermediate p-phenylbenzoyl chloride is not purified, but is used immediately to acetylate biphenyl. The reaction of 100 g (0.504 mole) of p-phenylbenzoic acid and 337 g (2.78 moles) of thionyl chloride gave p-phenylbenzoyl chloride, which, after removal of the excess thionyl chloride by distillation, was reacted with 80.6 g (0.605 mole) of aluminum chloride and 155.7 g (1.01 moles) of biphenyl in 500 ml of carbon disulfide. The black tar-like adduct was isolated by filtration, washed with carbon disulfide and decomposed with cold concd. HCl to give, after a recrystallization from benzene, 129.0 g (0.386 mole) of 4,4'-diphenylbenzophenone (76.7 percent yield), m.p. 235-237° (Calzolari and Furlani report m.p. 235°). In four similar preparations, an average yield of 75.2 percent was obtained (reported³⁷ yield: 75 percent).

m-Biphenylbis(p-biphenyl)carbinol

The synthesis of this carbinol was first attempted by reacting a solution of m-phenylphenylmagnesium bromide in diethyl ether with a slurry of 4,4'-diphenylbenzophenone in diethyl ether. The resulting mixture was stirred at reflux for three hours. Biphenyl and somewhat impure 4,4'-diphenylbenzophenone (85 percent recovery) were the only products isolated from the mixture.

37. C. Calzolari and C. Furlani, Ann. triest. cura. univ. Trieste, Sez. 2, 22-23, 63 (1953)

In another unsuccessful attempt to synthesize the carbinol, the homogeneity of the reaction was ensured by placing the ketone in a Soxhlet extraction apparatus on the side arm of a Morton flask containing a solution of *m*-phenylphenylmagnesium bromide in tetrahydrofuran. The solution was heated at reflux for five hours, at which time all of the ketone had dissolved. Biphenyl and somewhat impure 4,4'-diphenylbenzophenone (80 percent recovery) were again the only products isolated from the mixture.

In a 1000-ml Morton flask, 42.0 g (0.180 mole) of 3-bromobiphenyl was allowed to react under an atmosphere of dry nitrogen with 3.33 g (0.480 g atom) of lithium in 550 ml of tetrahydrofuran (freshly distilled from NaAlH₄) at 5°. The organolithium solution was purple in color, but at times during the addition of the bromide the solution turned blue in color (perhaps due to formation of the radical-anion). After the addition of about one-third of the bromide, the reaction temperature was lowered to -25° and the remaining bromide added rapidly. Under these conditions, the blue color was replaced by a deep purple color which persisted to the end of the reaction. After the addition of the bromide was completed, the mixture was stirred at -25° for one hour. At this point, analysis according to the method of Gilman^{38, 39} showed that 105 mmoles of 3-lithiobiphenyl (58.5 percent yield) had been formed. This solution was passed through a siphon tube containing a glass wool plug (to remove unreacted lithium) into a 3-l. Morton flask. A solution of 30.1 g (0.090 mole) of 4,4'-diphenyl-

38. H. Gilman and A. H. Haubein, J. Am. Chem. Soc., **66**, 1515 (1944).

39. H. Gilman and F. K. Cartledge, J. Organometal. Chem., **2**, 447 (1964); see also Appendix A of this thesis.

benzophenone in 1000 ml of dry tetrahydrofuran was added, at a flask temperature of 5°, over a period of one hour, and the resulting green solution was stirred vigorously at room temperature for one hour. The product mixture was acidified with 400 ml of 5 percent HCl and the tetrahydrofuran removed on the spin evaporator. The remaining aqueous suspension of solid was extracted with ether. A quantity of off-white solid (17.8 g) which was insoluble in both aqueous and ether phases was isolated by filtration and dried in vacuo. The ether extract was allowed to evaporate to dryness and the orange solid residue was washed with cyclohexane, to remove biphenyl. Total weight of product isolated by this procedure was 28.6 g (m.p. 201-229°) of a mixture of carbinol and unreacted ketone. Repeated recrystallizations from benzene removed most of the ketone, and gave 11.0 g (0.0221 mole) of white powder, m.p. 227-231° (24.5 percent yield, based on 4,4'-diphenylbenzophenone). A 2.00 g sample of this solid was subjected to vacuum sublimation at a bath temperature of 225-235° and 0.02 mm. The sublimate, after four recrystallizations from benzene, weighed 0.83 g, m.p. 231-233°. The infrared spectrum of this substance was substantially different from that of 4,4'-diphenylbenzophenone. The ketone carbonyl peak at 6.1 μ was missing in the spectrum of the compound of m.p. 231-233°, the aromatic substitution region was different, and there was a peak at 2.75 μ (O-H stretch). A mixture of the compound with 4,4'-diphenylbenzophenone of m.p. 235-237° had m.p. 203-222°.

Anal. * Calcd. for $C_{37}H_{28}O$: C, 90.99; H, 5.83.

Found: C, 90.93, 90.90; H, 5.79, 5.88.

* Analysis by Galbraith Laboratories, Knoxville, Tennessee.

In three other preparations, 3-lithiobiphenyl was synthesized by the reaction of 3-bromobiphenyl with lithium at -35° . 4,4'-Diphenylbenzophenone was added (as a powder) to the tetrahydrofuran solution of the organolithium compound at room temperature, in five equal portions, and stirred for 30 minutes after the addition of each portion. The yield of carbinol was difficult to determine because of contamination by unreacted ketone. The ketone could be removed by vacuum sublimation and several recrystallizations of the sublimate from benzene, but only a 20 percent yield of carbinol was obtained following this purification procedure.

Chloro-m-biphenylylbis(p-biphenylyl)methane

The synthesis of this halide was first attempted according to the procedure in Organic Syntheses⁴⁰ for the preparation of trityl chloride. In a 200 ml-flask, 100 g (1.27 moles) of freshly distilled acetyl chloride was added to a slurry of 12.0 g (0.0241 mole) of impure (contaminated by 4,4'-diphenylbenzophenone) m-biphenylylbis(p-biphenylyl)carbinol in 25 ml of dry benzene. The mixture was heated at reflux for four hours, the solvents removed by distillation, and the residue treated with 25 ml of dry benzene. The undissolved solid, weighing 2.30 g (m.p. $236-238^{\circ}$) was identified as 4,4'-diphenylbenzophenone, on the basis of its infrared spectrum. The benzene solution of product was condensed to a volume of 20 ml and chilled overnight in a refrigerator. The off-white solid which recrystallized weighed 8.31 g and had m.p. $125-133^{\circ}$ (with decomposition). A small sample of the unknown, dissolved in ethanol and treated with acidified

40. E. C. Horning (Ed.), Organic Syntheses, Collective Volume III, John Wiley & Sons, Inc., New York, 1955, p. 841.

silver nitrate solution, gave no precipitate. (Trityl chloride under the same conditions gave an instantaneous white precipitate.) An infrared spectrum of the unknown showed a strong band at $7.9\ \mu$ (C-O stretching frequency). A nuclear magnetic resonance spectrum showed the complete absence of aliphatic hydrogens, and contamination by unreacted carbinol. Two recrystallizations of the product from benzene gave 6.23 g of white powder, m.p. $128-133^\circ$ (with decomposition). On the basis of the above spectral data, the product likely is bis[m-biphenylyl]bis(p-biphenylyl)methyl ether, formed in 36 percent yield (based on the impure carbinol).

In another attempt to synthesize the trityl chloride derivative, the general procedure of Clark and Streight⁴¹ was followed. To a solution of 13.2 g (0.027 mole) of impure (contaminated with 4,4'-diphenylbenzophenone) m-biphenylyl]bis(p-biphenylyl)carbinol in 250 ml of dry benzene and 2.13 g (0.027 mole) of dry pyridine was added 4.76 g (0.040 mole) of freshly distilled thionyl chloride, and the reaction mixture allowed to reflux for 20 hours. A quantity of undissolved solid (pyridinium hydrochloride, m.p. $81-82^\circ$) was removed from the hot benzene solution by filtration. When the filtrate was allowed to cool to room temperature, 2.43 g of off-white solid crystallized and was isolated by filtration. This product, m.p. $236-238^\circ$, was identified as 4,4'-diphenylbenzophenone, according to its infrared spectrum. The filtrate was diluted with 100 ml of petroleum ether (b.p. $30-60^\circ$) and chilled in an ice bath for several hours. Light brown solid (6.41 g) crystallized and had m.p. $191-200^\circ$; another 4.11 g of product, m.p. $187-206^\circ$, was isolated from the mother liquor (total yield: 10.41 g, 81.7 percent,

⁴¹. R. H. Clark and H. R. L. Streight, Trans. Royal Soc. Canada (3), 23, III, 77 (1929).

based on 13.2-2.43 g = 10.8 g of carbinol). An infrared spectrum of each fraction of product indicated considerable contamination by 4,4'-diphenylbenzophenone. A sodium fusion test for halide⁴² was strongly positive. The product of m.p. 191-200°, after five recrystallizations from benzene-petroleum ether, gave ketone-contaminated, off-white solid of m.p. 194-203°. An attempted vacuum sublimation (200-210°, 0.02 mm) of a small sample of this material resulted in extensive decomposition.

Synthesis of 2-Chloro-1-m-biphenyl-1,2-bis(p-biphenyl)ethane
Bis(p-biphenyl)methane

The preparation of this hydrocarbon was first attempted via a modified Clemmenson reduction of 4,4'-diphenylbenzophenone, according to the general procedure of Martin.⁴³ A mixture of 50 g (0.765 g atom) of mossy zinc, 5.00 g (0.018 mole) of mercuric chloride, 100 ml of water and 5 ml of concd. HCl was agitated in a mechanical shaker for five minutes. The solution was removed by decantation, and the amalgamated zinc placed in a one-l., round-bottomed flask equipped with reflux condenser and mechanical stirrer. To the amalgamated zinc was added 50 ml of water, 125 ml of concd. HCl, 200 ml of toluene, 10 ml of glacial acetic acid and 10.0 g (0.030 mole) of 4,4'-diphenylbenzophenone. The mixture was stirred at gentle reflux for 48 hours; three additional 25 ml portions of concd. HCl were added, at 16 hour intervals. Most of the starting material (9.52 g)

42. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley & Sons, Inc., New York, 1956, p. 60.

43. E. L. Martin, J. Am. Chem. Soc., 58, 1438 (1936).

was recovered unchanged from the toluene phase.

The reduction of 4,4'-diphenylbenzophenone with zinc-NaOH was attempted following the general procedure of Martin.⁴³ In a one-l., round-bottomed flask, 25.0 g (0.383 g atom) of zinc dust, activated by treatment with dilute copper sulfate solution, was allowed to react with 10.0 g (0.030 mole) of 4,4'-diphenylbenzophenone in a refluxing mixture of 400 ml of 2 N NaOH and 200 ml of toluene for 24 hours. Most of the starting material (9.93 g) was recovered unchanged from the toluene phase.

A modified Wolff-Kishner reduction of 4,4'-diphenylbenzophenone was carried out following the method of Huang-Minlon.⁴⁴ To a solution of 10.0 g (0.030 mole) of 4,4'-diphenylbenzophenone in triethylene glycol at 110° was added 6.00 g (0.120 mole) of hydrazine hydrate and 5.05 g (0.090 mole) of potassium hydroxide, and the resulting mixture heated at 170° for two hours. The excess hydrazine was allowed to distill from the reaction mixture, whereupon the pot temperature was raised to 200-210° and maintained at that temperature for 20 hours. The solution was diluted with an equal volume of water and the 9.52 g (99.3 percent yield) of white solid which separated was isolated by filtration, m.p. 149-158°. One recrystallization from absolute ethanol gave 8.78 g of white crystalline solid, m.p. 160-162° (reported⁴⁵ m.p. of bis(p-biphenyl) methane: 162°). An infrared spectrum of the product showed no carbonyl absorption. The average yield of five similar preparations was 96.2 percent.

Bromobis(p-biphenyl) methane

This halide was prepared by the reaction of bis(p-biphenyl) methane

44. Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

45. J. Weiler, Ber., 7, 1188 (1874).

with N-bromosuccinimide. The general procedure of Zervas and Dilaris⁴⁶ was followed, except that a trace of peroxide was used to catalyze the reaction. In a 500-ml, round-bottomed flask, 11.0 g (0.0343 mole) of bis(p-biphenylyl)methane, 6.71 g (0.0377 mole) of N-bromosuccinimide, 0.05 g of dibenzoyl peroxide, and 250 ml of carbon tetrachloride were combined and heated at reflux for 48 hours. An additional 0.05 g portion of benzoyl peroxide was added after the first six hours of reaction. Insoluble succinimide, formed in the reaction, was removed by filtration and the filtrate evaporated to dryness on the spin evaporator. The light-tan solid residue, after a recrystallization from benzene-petroleum ether, gave 11.5 g (0.0290 mole) of off-white solid, m.p. 138-141° (77.0 percent yield). A further recrystallization of this solid from benzene-petroleum ether gave 10.3 g of off-white crystals, m.p. 142-144° [reported⁴⁷ m.p. for bromobis(p-biphenylyl)methane: 143°]. The average yield of six other preparations was 72.8 percent.

m-Biphenylylbis(p-biphenylyl)methane

From the reaction of 9.32 g (0.040 mole) of 3-bromobiphenyl with 0.610 g (0.088 g atom) of lithium, a solution of 24.1 mmoles (60.2 percent yield) of 3-lithiobiphenyl in 300 ml of tetrahydrofuran was prepared at -20°. A solution of 8.00 g (0.020 mole) of bromobis(p-biphenylyl)methane in 50 ml of tetrahydrofuran was added to the organolithium compound at -20°, over a period of 20 minutes. The resulting mixture was stirred for 10 minutes, and then 50 ml of water was added to destroy unreacted lithium.

46. L. Zervas and I. Dilaris, J. Am. Chem. Soc., 77, 5354 (1955).

47. W. Schlenk, J. Renning and G. Packy, Ber., 44, 1180 (1911).

A quantity of solid (5.44 g), insoluble in the aqueous tetrahydrofuran, was isolated by filtration and had m.p. 260-270°. A 1.00 g sample of this solid, after two recrystallizations from chloroform, gave 0.62 g of white powder, m.p. 275-279° [reported⁴⁷ m.p. for 1,1,2,2-tetrakis(p-biphenylyl)-ethane: 276-279°]. The crude yield of this coupling product was 85.3 percent. Somewhat impure biphenyl (2.64 g, m.p. 65-68°) was isolated from the aqueous tetrahydrofuran.

The Grignard reagent of 3-bromobiphenyl was prepared in 500 ml of ether by the reaction of 18.6 g (0.080 mole) of 3-bromobiphenyl with 2.04 g (0.084 g atom) of magnesium turnings. To the solution of m-biphenylyl-magnesium bromide in refluxing ether was added a slurry of 16.0 g (0.040 mole) of bromobis(p-biphenylyl)methane in 200 ml of ether and the resulting mixture stirred for six hours. Unreacted magnesium was destroyed by the addition of 100 ml of 5 percent HCl. White solid (12.1 g), insoluble in both aqueous and ether phases, was isolated by filtration and had m.p. 203-227°. The ether phase of the filtrate was condensed to 100 ml and 2.46 g of white solid, m.p. 201-229°, precipitated. The two fractions of product were combined (14.56 g, 77 percent yield) and subjected to vacuum sublimation of 0.03 mm and 210-230°. The sublimate weighed 8.31 g and had m.p. 202-210°; the residue turned dark brown under these conditions. A further vacuum sublimation of the material of m.p. 202-210° gave 8.02 g of white powder, m.p. 203-210°. Two recrystallizations of this material from chloroform-ethanol gave 7.52 g of white solid, m.p. 205-211°. A chloroform solution of this solid was extracted with several portions of 94 percent sulfuric acid; a small amount of ethanol was then added and the chloroform solution chilled overnight in an ice bath. This deposited

5.90 g of white solid, m.p. 211-213°. A vacuum sublimation of this solid at 0.02 mm and 230-240° gave 4.86 g of white powder, m.p. 212.0-213.5°.

Anal.* Calcd. for $C_{37}H_{28}$: C, 94.07; H, 5.93.

Found: C, 93.71, 93.87; H, 6.18, 6.02.

In order to achieve homogeneous conditions, the coupling reaction was attempted in tetrahydrofuran. A solution of m-biphenylmagnesium bromide in 500 ml of tetrahydrofuran was prepared by the reaction of 13.3 g (0.0572 mole) of 3-bromobiphenyl with 2.53 g (0.104 g atom) of magnesium turnings at the reflux temperature of the solvent. A solution of 11.4 g (0.0286 mole) of bromobis(p-biphenyl)methane in 150 ml of tetrahydrofuran was added to the Grignard reagent at 25° and the resulting solution stirred for four hours. After unreacted magnesium had been destroyed by addition of 100 ml of 5 percent HCl, undissolved solid (7.55 g) was isolated by filtration and had m.p. 270-276° [82.6 percent yield of 1,1,2,2-tetrakis-(p-biphenyl)ethane, identified by infrared spectral comparison with the previous sample of the hydrocarbon].

A solution of m-biphenylmagnesium bromide in 250 ml of tetrahydrofuran was prepared by the reaction of 9.32 g (0.040 mole) of 3-bromobiphenyl with 1.94 g (0.080 g atom) of magnesium turnings at the reflux temperature of the solvent. This solution was filtered through a glass wool plug to remove unreacted magnesium, and the filtered solution was allowed to react at room temperature with a solution of 8.00 g (0.040 mole) of bromobis(p-biphenyl)methane in 75 ml of tetrahydrofuran for one hour. After 100 ml

* Analysis by Bernhardt Analytical Laboratories, West Germany.

of water was added, undissolved solid (5.35 g) was isolated by filtration and had m.p. 271-277° [84.0 percent yield of 1,1,2,2-tetrakis(p-biphenyl)-ethane]. Thus, this product is formed in high yield by the reaction of the Grignard reagent with the bromide, even in the absence of magnesium.

The synthesis of the desired m-biphenylbis(p-biphenyl)methane was most successfully carried out using benzene as a co-solvent for the coupling reaction, according to the general procedure of Bachmann.⁴⁸ From the reaction of 11.65 g (0.050 mole) of 3-bromobiphenyl with 1.22 g (0.050 g atom) of magnesium turnings, a solution of 0.042 mole (94.0 percent yield) of m-biphenylmagnesium bromide in 250 ml of ethyl ether was prepared. (The quantitative analysis⁴⁹ of the Grignard reagent was carried out by hydrolyzing an aliquot with water and titrating the resulting solution with the disodium salt of ethylenediaminetetraacetic acid to an endpoint marked by Eriochrome Black T.) A solution of 14.0 g (0.035 mole) of bromobis(p-biphenyl)methane in 100 ml of dry benzene was added to the Grignard reagent and the resulting mixture stirred at reflux for one hour. Unreacted Grignard reagent was destroyed by adding 100 ml of water, and white solid (13.03 g), insoluble in both aqueous and organic phases, was isolated by filtration and had m.p. 196-238°. This solid was subjected to vacuum sublimation at 0.10 mm and 230-245°. The sublimate consisted of 10.43 g (63.3 percent yield) of m-biphenylbis(p-biphenyl)methane, m.p. 202-209°; the residue consisted of 2.33 g (20.8 percent yield) of 1,1,2,2-tetrakis(p-biphenyl)ethane, m.p. 265-275°. From the ether-benzene filtrate, 1.26 g

48. W. E. Bachmann, J. Am. Chem. Soc., 55, 2135 (1933).

49. Dr. E. C. Ashby, private communication.

of white solid was isolated and had m.p. 147-150° [10.7 percent yield of bis(p-biphenylyl)carbinol, identified by its infrared spectrum]. The reported⁵⁰ m.p. of the carbinol is 151°. In a similar preparation, the yields observed were: m-biphenylylbis(p-biphenylyl)methane, 72.0 percent; 1,1,2,2-tetrakis(p-biphenylyl)ethane, 17.2 percent; bis(p-biphenylyl)carbinol, 8.1 percent.

2-Chloro-1-m-biphenylyl-1,1-bis(p-biphenylyl)ethane

In a 500-ml flask equipped with mechanical stirrer and Dry Ice-acetone condenser, 250 ml of anhydrous ammonia was condensed. Under an atmosphere of dry nitrogen, 2.11 g (0.054 g atom) of potassium was added rapidly, in pieces of about 0.2 g each. After the first piece of potassium had dissolved, a small crystal of ferric nitrate was added to catalyze the formation of potassium amide. The blue color of potassium in liquid ammonia had changed to grey-brown after 90 minutes of stirring. m-Biphenylylbis(p-biphenylyl)methane (6.14 g, 0.013 mole) was dusted into the refluxing solution of potassium amide in liquid ammonia. The color of the solution changed rapidly from grey to royal blue. After ten hours of stirring, the color of the solution had deepened considerably, but there was still a substantial quantity of undissolved hydrocarbon suspended in the solution. The addition of 50 ml of dry ether caused the solid to dissolve after about 30 minutes of stirring. The deep purple-blue solution was siphoned into a flask containing 650 ml of methylene chloride at -60° under an atmosphere of dry nitrogen. The purple-blue color disappeared almost instantly. Ammonium chloride (5.35 g, 0.100 mole) was added to destroy unreacted potassium

50. J. Weiler, Ber., 7, 1188 (1874).

amide. After 100 ml of water was added, the methylene chloride phase was separated and allowed to evaporate to dryness. The yellow solid residue weighed 5.93 g and had m.p. 205-211°. This material gave a negative sodium fusion test for halide; it was identified as unreacted m-biphenylbis(p-biphenyl)methane by an examination of its infrared spectrum. Evidently, the large excess of methylene chloride contained enough water to react with the purple-blue solution of organopotassium compound.

The synthesis of potassium amide was carried out as described above, using 2.74 g (0.070 g atom) of potassium and 250 ml of anhydrous ammonia. A slurry of 4.00 g (0.0085 mole) of m-biphenylbis(p-biphenyl)methane in 50 ml of dry ether was added and the resulting mixture stirred for nine hours. The deep purple-blue solution was siphoned into a flask containing 30 ml of freshly-distilled methylene chloride at -30° under an atmosphere of dry nitrogen. After the solution was stirred for ten minutes, the blue color had disappeared. Unreacted potassium amide was destroyed by the addition of 5.35 g (0.100 mole) of solid ammonium chloride. After 100 ml of water was added, the methylene chloride phase was separated and allowed to evaporate to dryness. The brown solid residue, after two recrystallizations from chloroform, gave 3.63 g of tan solid, m.p. 213-220°. This material, after seven recrystallizations from methyl ethyl ketone, gave 0.636 g of white powder, m.p. 218.7-220.0°. Examination of the nuclear magnetic resonance spectrum of a solution of this solid in deuterochloroform revealed that it likely was about a 50:50 mixture of m-biphenylbis(p-biphenyl)methane and 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane. The aliphatic proton absorption band of the hydrocarbon appeared at 7.85 τ ; that of the chloride appeared at 5.38 .

Potassium amide was prepared in a 500-ml Morton flask equipped with a Morton stainless steel, high-speed stirrer, from the reaction of 3.91 g (0.100 g atom) of potassium with 250 ml of anhydrous liquid ammonia. A slurry of 4.72 g (0.010 mole) of m-biphenylbis(p-biphenyl)methane in 100 ml of dry ether was added and the resulting mixture stirred vigorously at reflux for eight hours. The deep purple-blue solution was siphoned into a flask containing 30 ml of freshly distilled methylene chloride at -30° under an atmosphere of dry nitrogen. After the solution had been stirred for 15 minutes, the blue color had disappeared. Unreacted potassium amide was destroyed by adding 5.35 g (0.100 mole) of solid ammonium chloride. After 100 ml of water was added, the methylene chloride phase was separated and allowed to evaporate to dryness. The tan solid residue, after a recrystallization from methyl ethyl ketone, gave 4.61 g (0.0886 mole) of off-white solid, m.p. $219-223^{\circ}$ (88.6 percent yield). This material, after five recrystallizations from methyl ethyl ketone, gave 3.33 g of white powder, m.p. $223.2-224.3^{\circ}$. Examination of its nuclear magnetic resonance spectrum showed that the product was contaminated by a maximum of 2 percent (if any) of unreacted hydrocarbon.

Anal.* Calcd. for $C_{38}H_{29}Cl$: C, 87.62; H, 5.57; Cl, 6.81.

Found: C, 87.41, 87.35; H, 5.81, 5.67; Cl, 7.10, 6.97.

In a similar preparation, an 84.0 percent yield of chloride of m.p. $218-222^{\circ}$ was obtained.

Synthesis of 3-m-Biphenyl-3,3-bis(p-biphenyl)propanoic Acid

The synthesis of this acid was attempted by the reaction of m-bi-

* Analysis by Bernhardt Analytical Laboratories, West Germany.

phenylylbis(p-biphenylyl)carbinol with malonic acid, according to the general procedure of Hellerman.⁵¹ A finely ground mixture of 2.44 g (0.0050 mole) of m-biphenylylbis(p-biphenylyl)carbinol and 10.4 g (0.100 mole) of malonic acid was placed in a 50-ml, round-bottomed flask and heated in an oil bath at 220° for 12 hours. The molten mixture was poured into 250 ml of 1.5 N NaOH with vigorous stirring. Undissolved solid (2.33 g) was isolated by filtration and had m.p. 229-233° (unreacted carbinol, identified by its infrared spectrum). Acidification of the filtrate with HCl failed to cause any carboxylic acid to precipitate.

In a modification of Hellerman's procedure, suggested by Gagnon,⁵² the above reaction was repeated in the presence of 0.510 g (0.0050 mole) of acetic anhydride. No melt was formed at the boiling point of the anhydride (140°), and no water-insoluble carboxylic acid could be isolated from the product mixture.

A mixture of 1.00 g (2.05 mmoles) of m-biphenylylbis(p-biphenylyl)-carbinol, 2.13 g (20.5 mmoles) of malonic acid, and 0.350 g (2.22 mmoles) of butyric anhydride (b.p. 198°) was placed in a 25-ml, pear-shaped flask and heated in an oil bath at 200° until gas evolution had ceased (15 minutes). The mixture was allowed to cool to room temperature and was then stirred with 200 ml of warm 2 N KOH. Undissolved solid (0.732 g) was isolated by filtration and had m.p. 227-229°. This was identified as unreacted carbinol by an examination of its infrared spectrum. The alkaline filtrate was acidified with HCl and the solid (0.198 g, 0.340 mmole) which precipitated was

51. L. Hellerman, J. Am. Chem. Soc., 49, 1735 (1927).

52. P. Gagnon, Ann. Chim. (Paris) [10], 12, 299 (1929).

isolated by filtration and had m.p. 223-227° (16.6 percent yield). This material, after three recrystallizations from ethanol, gave 0.082 g of white crystalline solid, m.p. 225-227°. Two further recrystallizations from ethanol gave 0.049 g of white solid, m.p. 226.4-228.1°.

Anal.* Calcd. for $C_{39}H_{30}O_2$: C, 88.31; H, 5.66.

Found: C, 88.13, 88.01; H, 5.69, 5.60.

Synthesis of 3-m-Biphenyl-2,2-bis(p-biphenyl)propanoic Acid-1-C-14
Cuprous Cyanide-C-14

The synthesis of cuprous cyanide was carried out following the procedure given in Organic Syntheses.⁵³ The reaction of 24.96 g (0.100 mole) of $CuSO_4 \cdot 5H_2O$ with 9.80 g (0.200 mole) of sodium cyanide in 175 ml of distilled water yielded 7.70 g (0.086 mole, 86.0 percent yield) of cuprous cyanide. The reaction was repeated on the same scale, using sodium cyanide-C-14 (specific activity 9.612 μ c/mole). A yield of 7.43 g (0.083 mole, 83.0 percent yield) of cuprous cyanide-C-14 was observed.

Bis(p-biphenyl)ethanenitrile-1-C-14

The synthesis of this nitrile was first attempted following the general procedure of Cope and Mehta.⁵⁴ A solution of 0.553 g (11.3 mmoles) of sodium cyanide in 25 ml of dimethylsulfoxide (DMSO) was added to a solution of 3.00 g (7.53 mmoles) of bromobis(p-biphenyl)methane in 75 ml of DMSO, and the resulting solution stirred at 30° for 72 hours. The DMSO

*Analysis by Bernhardt Analytical Laboratories, West Germany.

53. A. H. Blatt (Ed.), Organic Syntheses, John Wiley & Sons, Inc., New York, Collective Volume I, 1958, p. 46.

54. A. C. Cope and A. S. Mehta, J. Am. Chem. Soc., **86**, 5626 (1964).

solution was diluted with 500 ml of water and extracted with ether. The ether extracts were allowed to evaporate to dryness, leaving 2.21 g of yellow powder, m.p. 98-134°. This powder, after two recrystallizations from ethanol, gave 1.90 g of off-white powder, m.p. 107-137°. A small portion of this sample was subjected to sodium fusion and the resulting aqueous solution gave a black precipitate when treated with lead(II) acetate, a result indicating that the compound contained sulfur. An attempted vacuum sublimation at 0.03 mm and 110-140° resulted in decomposition of most of the material. A small quantity of sublimate (0.56 g) had m.p. 148-150°; this was identified as bis(p-biphenylyl)carbinol, by its infrared spectrum.

In a second run, a solution of 0.980 g (0.020 mole) of sodium cyanide in 200 ml of DMSO was added to a solution of 4.00 g (0.010 mole) of bromobis(p-biphenylyl)methane in 100 ml of DMSO. The resulting solution, protected from moisture by a drying tube filled with anhydrous CaSO_4 , was stirred at 60° for 36 hours. The solution was diluted with 500 ml of water and the solid which separated from the solution was isolated by filtration. A recrystallization of the solid from ethanol gave 0.90 g (2.69 mmoles) of 4,4'-diphenylbenzophenone (26.9 percent yield), identified by its infrared spectrum. (An infrared spectrum of the starting material used in the reaction showed the compound to be uncontaminated by ketone.) The mother liquor was condensed and 2.42 g (7.21 mmoles) of yellow solid crystallized, m.p. 145-150° [72.1 percent yield of bis(p-biphenylyl)carbinol, identified by its infrared spectrum].

A solution of 0.980 g (0.020 mole) of sodium cyanide in 150 ml of acetone (freshly distilled from P_2O_5) was added to a solution of 4.00 g

(0.010 mole) bromobis(p-biphenyl) methane in 100 ml of acetone and the mixture allowed to reflux gently for 72 hours under an atmosphere of dry nitrogen. The acetone solution was then diluted with 500 ml of water and the solid (2.94 g) which separated from solution was isolated by filtration and had m.p. 137-142°. A recrystallization of this solid from n-hexane gave 2.49 g of white powder, m.p. 140-144°. This material was identified as slightly impure bis(p-biphenyl)carbinol, on the basis of its infrared spectrum.

Freshly dried cuprous cyanide (0.542 g, 6.05 mmoles) was mixed with 2.20 g (5.50 mmoles) of bromobis(p-biphenyl) methane and the mixture heated at 160° under an atmosphere of dry nitrogen for eight hours. Organic product was extracted with chloroform, the chloroform solution evaporated to dryness, and the residue subjected to vacuum sublimation at 0.03 mm. The fraction collected at 140-160° weighed 0.32 g and had m.p. 147-151°; this was identified as impure bis(p-biphenyl)carbinol by its infrared spectrum. The fraction collected at 170-190° weighed 1.08 g (3.13 mmoles) and had m.p. 182-186° (57.0 percent yield). A recrystallization of this material from ethanol gave 0.992 g of white crystalline bis(p-biphenyl)ethanenitrile, m.p. 185.5-187.0°.

Anal.* Calcd. for $C_{26}H_{19}N$: C, 90.44; H, 5.50; N, 4.06.

Found: C, 90.42, 90.37; H, 5.74, 5.74; N, 3.75, 3.78.

In six similar preparations (two using cuprous cyanide-C-14 of specific activity 9.612 μ c/mmole), an average yield of 55.7 percent was obtained.

Bis(p-biphenyl)ethanoic Acid-1-C-14

The synthesis of this acid was first attempted by the treatment of

* Analysis by Bernhardt Analytical Laboratories, West Germany.

the corresponding nitrile with base, according to the general procedure given in Organic Syntheses.⁵⁵ A solution of 0.890 g (2.56 mmoles) of bis(p-biphenyl)ethanenitrile and 0.562 g (10.2 mmoles) of KOH in 125 ml of diethylene glycol was heated at 80° for ten hours. The glycol solution was diluted with 150 ml of water and the solid (0.883 g) which separated from solution was isolated by filtration and had m.p. 181-184° (unreacted nitrile, identified by its infrared spectrum).

A solution of 0.890 g (2.56 mmoles) of bis(p-biphenyl)ethanenitrile and 0.562 g (10.2 mmoles) of KOH in 125 ml of diethylene glycol was heated at 160° for eight hours. When the solution had cooled to room temperature, it was diluted with 150 ml of water. The solid which separated from solution was isolated by filtration and had m.p. 159-161°. A mixture of this solid with bis(p-biphenyl)methane had m.p. 159-162°. This product of decarboxylation weighed 0.770 g (2.41 mmoles, 94.2 percent yield).

A solution of 0.910 g (2.63 mmoles) of bis(p-biphenyl)ethanenitrile and 0.258 g (2.63 mmoles) of concd. sulfuric acid in 100 ml of 95 percent ethanol was heated at reflux for 36 hours. The mixture was diluted with 25 ml of water and allowed to cool to room temperature. The white solid (0.900 g, m.p. 183.5-186°) which crystallized was identified as unreacted nitrile.

The synthesis of the carboxylic acid was attempted following the general procedure of Berger and Olivier.⁵⁶ In a 200-ml, round-bottomed

55. N. Babjohn (ed.-in-chief), Organic Syntheses, Collective Volume IV, John Wiley & Sons, Inc., New York, 1963, p. 95.

56. G. Berger and S. C. J. Olivier, Rec. trav. chim., 46, 600 (1927).

flask containing 1.00 g (2.90 mmoles) of bis(p-biphenyl)ethanenitrile, 70 g (0.608 mole) of 85 percent phosphoric acid was combined with 30 g (0.211 mole) of phosphorus pentoxide, and the resulting mixture heated at 150-160° for 72 hours. The mixture was allowed to cool to room temperature and was poured into 100 ml of ice water. Suspended solid (0.966 g) was isolated by filtration (m.p. 181-185°) and was identified as unreacted nitrile.

The next attempt to prepare the carboxylic acid was by the general method of McElvain and Nelson.⁵⁷ Dry HCl gas was passed into a solution of 0.500 g (1.45 mmoles) of bis(p-biphenyl)ethanenitrile in 500 ml of absolute ethanol for one hour and the resulting solution heated at 50-60° for three hours and allowed to stand overnight. After 25 ml of water had been added, the solution was heated at reflux for 20 hours. When the solution was allowed to cool to room temperature, 0.485 g of white solid crystallized and had m.p. 184-186° (identified as unreacted nitrile).

The acid was prepared in modest yield following the general procedure of Speigel.⁵⁸ A mixture of 2.00 g (5.80 mmoles) of bis(p-biphenyl)ethanenitrile, 250 ml of absolute ethanol and 35.0 g (0.339 mole) of concd. sulfuric acid was heated in a sealed tube at 130° for 24 hours. The diethyl ether phase formed in the reaction was separated and allowed to evaporate to dryness. The off-white solid residue weighed 1.91 g and had m.p. 81-172°. Examination of the infrared spectrum of this material indicated that it was a mixture of carboxylic acid and ester. The mixture was

57. S. M. McElvain and J. W. Nelson, J. Am. Chem. Soc., 64, 1827 (1942).

58. L. Speigel, Ber., 51, 296 (1918).

heated at reflux for 16 hours with 300 ml of 15 percent KOH. A quantity of undissolved black resin was removed by filtration and the filtrate acidified with HCl. The off-white solid driven out of solution weighed 1.22 g (3.55 mmoles, 61.2 percent yield, m.p. 202-206°). A recrystallization from aqueous ethanol gave 0.980 g of white solid, m.p. 205-207.5° [reported⁵⁹ m.p. of bis(p-biphenyl)ethanoic acid: 208°].

A solution of 28.0 g (0.500 mole) of KOH in 50 ml of water was added to a solution of 2.00 g (5.80 mmoles) of bis(p-biphenyl)ethanenitrile in 200 ml of diethylene glycol and the resulting solution heated at 130° for 48 hours. The solution was allowed to cool to room temperature and was then diluted with 500 ml of water. Undissolved solid (0.752 g) was isolated by filtration, m.p. 138-171°, and was then subjected to vacuum sublimation at 0.05 mm. The fraction collected at 155-165° weighed 0.170 g (0.53 mmoles) and had m.p. 160-162° [9.15 percent yield of bis(p-biphenyl)methane]. The fraction collected at 170-190° weighed 0.450 g (1.30 mmoles) and had m.p. 180-183° [22.5 percent recovery of bis(p-biphenyl)ethanenitrile]. The alkaline filtrate was acidified with HCl and the solid (1.29 g, 3.75 mmoles) which separated from solution was isolated by filtration and had m.p. 201-206° (64.7 percent yield). Two recrystallizations from ethanol gave 0.986 g of off-white crystalline solid, m.p. 206.0-207.5°. The reaction was repeated, using bis(p-biphenyl)ethanenitrile-1-C-14, and a 63.3 percent yield of bis(p-biphenyl)ethanoic acid-1-C-14 was obtained.

59. E. Shilov and S. Burmistrov, Ber., 68B, 582 (1935).

Methyl Bis(p-biphenyl)ethanoate-1-C-14

An ether solution of diazomethane was prepared by the method of deBoer and Backer.⁶⁰ A solution of 2.14 g (10.0 mmoles) of N-methyl-N-nitroso-p-toluenesulfonamide in 25 ml of ether was added dropwise to a solution of 5.00 g (89.0 mmoles) of KOH in 8.0 ml of water and 50 ml of ethanol at 65°. The diazomethane co-distilled with the ether, and the resulting solution was added, with caution, to a solution of 2.32 g (6.74 mmoles) of bis(p-biphenyl)ethanoic acid-1-C-14 in 50 ml of ether at 0°. The solution of product was allowed to evaporate to dryness and the residue, after a recrystallization from methanol, gave 2.08 g of off-white powder, m.p. 125-127° (5.83 mmoles, 86.4 percent yield). A small sample of this material, after two further recrystallizations from methanol, gave a product of m.p. 126.3-127.8°.

Anal.* Calcd. for $C_{27}H_{22}O_2$: C, 85.72; H, 5.82.

Found: C, 86.00, 85.76; H, 5.67, 5.73.

3-(Bromomethyl)biphenyl

The general procedure of Zervas and Dilaris⁴⁶ was followed, except that dibenzoyl peroxide was used to catalyze the reaction. A solution of 75.0 g (0.446 mole) of 3-methylbiphenyl, 87.2 g (0.490 mole) of N-bromosuccinimide and 0.4 g of dibenzoyl peroxide in 400 ml of carbon tetrachloride was heated at reflux for 25 hours. An additional 0.2 g of dibenzoyl peroxide was added after the first six hours of reaction. Insoluble succinimide formed in the reaction was removed by filtration and the fil-

60. T. J. DeBoer and H. J. Backer, Rec. trav. chim., **73**, 229 (1954).

* Analysis by Bernhardt Analytical Laboratories, West Germany.

trate evaporated to dryness on a spin evaporator. The residue, a dark brown oil, was distilled in vacuo. The fraction boiling at 165-180° and 1.5 mm weighed 82.3 g (0.333 mole, 74.6 percent yield), and solidified upon standing for three to four hours. This orange solid, after three recrystallizations from petroleum ether, gave off-white crystalline solid of m.p. 56.5-58.0°.

Anal.* Calcd. for $C_{13}H_{11}Br$: C, 63.20; H, 4.45; Br, 32.35.

Found: C, 63.13, 63.33; H, 4.49, 4.55; Br, 32.48, 32.60.

3-m-Biphenyl-1-2-bis(p-biphenyl)propanoic Acid-1-C-14

The synthesis of this acid was carried out following the general procedure of Hauser.³⁵ In a 500-ml Morton flask equipped with Morton high-speed stirrer and Dry Ice-acetone condenser, 200 ml of anhydrous ammonia was condensed. Under an atmosphere of dry nitrogen, 0.340 g (8.70 mg atoms) of potassium was added. A small crystal of ferric nitrate was added and the solution stirred for one hour. A solution of 2.08 g (5.80 mmoles) of methyl bis(p-biphenyl)ethanoate-1-C-14 in 50 ml of anhydrous ether was added over a period of ten minutes, and the resulting solution stirred for two hours. A solution of 1.43 g (5.80 mmoles) of 3-(bromomethyl)biphenyl in 50 ml of anhydrous ether was added over a period of 30 minutes, and the resulting solution stirred for 30 minutes. Unreacted potassium amide was destroyed by adding 0.535 g (10.0 mmoles) of solid ammonium chloride and the ammonia was allowed to evaporate from the mixture. After 100 ml of water was added, the ether phase was separated and allowed to evaporate to dryness. The yellow solid residue was heated at reflux for 15 hours with

* Analysis by Bernhardt Analytical Laboratories, West Germany.

250 ml of 15 percent aqueous KOH. A small amount of brown, undissolved solid was removed by filtration and the filtrate acidified with HCl. The white solid (2.17 g) which separated from solution was isolated by filtration and had m.p. 192-218°. This material was subjected to partial vacuum sublimation at 0.04 mm and 200-220°. The sublimate, after a recrystallization from ethanol, weighed 0.238 g (0.692 mmole) and had m.p. 205-207°. The reported⁵⁹ m.p. of bis(p-biphenyl)ethanoic acid-1-C-14 is 208°. The residue, after two recrystallizations from absolute ethanol, gave 1.28 g (2.41 mmoles) of white solid, m.p. 202-204.5° (41.6 percent yield). A 0.2 g portion of this material, after two recrystallizations from ethanol, gave an analytical sample of m.p. 203.5-204.5°.

Anal.* Calcd. for $C_{39}H_{30}O_2$: C, 88.31; H, 5.66.

Found: C, 88.22, 88.34; H, 5.60, 5.68.

Synthesis of 2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14
3-Biphenylcarboxylic Acid

A solution of m-biphenylmagnesium bromide in 250 ml of ether was prepared by the reaction of 23.3 g (0.100 mole) of 3-bromobiphenyl with 2.55 g (0.105 g atom) of magnesium turnings. The Grignard reagent was siphoned into a flask containing a large excess of cracked Dry Ice. Unreacted magnesium was destroyed by adding 200 ml of five percent HCl. The ether layer was separated and extracted with six 50-ml portions of KOH. The alkaline extract was acidified with HCl and the solid (10.6 g, 0.0535 mole) which separated from solution was isolated by filtration and had m.p. 160-163° (53.5 percent yield). Two recrystallizations of this solid

* Analysis by Bernhardt Analytical Laboratories, West Germany.

from ethanol gave 8.73 g of white crystalline solid, m.p. 162-163° (reported⁶¹ m.p. of 3-biphenylcarboxylic acid: 160-162°). In a similar preparation, a 51.9 percent yield of the acid was obtained. This preparation of 3-biphenylcarboxylic acid is believed to be the first synthesis of this acid by carbonation of the Grignard reagent.

3,4'-Diphenylbenzophenone

This ketone was synthesized by the general procedure of Calzolari and Furlani³⁷ for 4-4'-diphenylbenzophenone. The reaction of 18.0 g (0.091 mole) of 3-biphenylcarboxylic acid and 150 g (1.26 moles) of thionyl chloride gave m-phenylbenzoyl chloride, which, after removal of the excess thionyl chloride by distillation, was reacted with 14.6 g (0.109 mole) of anhydrous aluminum chloride and 28.1 g (0.182 mole) of biphenyl in 250 ml of carbon disulfide. The black tar-like adduct was isolated by filtration, washed with carbon disulfide and decomposed with cold concd. HCl to give 20.2 g (0.0605 mole) of white powder, m.p. 138-141° (66.5 percent yield). Two recrystallizations from ethanol gave 15.5 g of white crystalline solid, m.p. 142-144°. A small sample of this solid, after a recrystallization from ethanol and a vacuum sublimation at 0.02 mm and 145-155°, gave ketone of m.p. 143.8-145.0°

Anal.* Calcd. for $C_{25}H_{18}O$: C, 89.83; H, 6.38.

Found: C, 89.68, 89.56; H, 6.08, 6.22.

m-Biphenylyl-p-biphenylylmethane

A modified Wolff-Kisher reduction of 3,4'-diphenylbenzophenone was

61. H. Schmidt and G. Schultz, Ann., 203, 132 (1880).

* Analysis by Bernhardt Analytical Laboratories, West Germany.

carried out following the procedure of Huang-Minlon.⁴⁴ A solution of 14.2 g (0.0425 mole) of 3,4'-diphenylbenzophenone, 8.50 g (0.170 mole) of hydrazine hydrate, and 7.18 g (0.128 mole) of KOH in 600 ml of triethylene glycol was heated at 170° for two hours. The excess hydrazine was allowed to distil from the reaction mixture, whereupon the pot temperature was raised to 200° and maintained at that temperature for 20 hours. The solution was diluted with an equal volume of water and the 13.0 g (0.0406 mole) of white solid, m.p. 92-96°, which precipitated was isolated by filtration (95.6 percent yield). Two recrystallizations from ethanol gave 9.92 g of white crystalline solid, m.p. 98-100°. A small portion of this compound, after vacuum sublimation at 0.03 mm and 120-125°, gave an analytical sample of m.p. 99.3-100.4°.

Anal.* Calcd. for C₂₅H₂₀: C, 93.75; H, 6.25.

Found: C, 93.61, 93.55; H, 6.43, 6.31.

Bromo-m-biphenyl-yl-p-biphenylmethane

This halide was prepared following the general procedure of Zervas and Dilaris,⁴⁶ except that dibenzoyl peroxide was used to catalyze the reaction. A solution of 9.10 g (0.0285 mole) of m-biphenyl-yl-p-biphenyl-ylmethane, 5.35 g (0.0313 mole) of N-bromosuccinimide, and 0.1 g of dibenzoyl peroxide in 250 ml of carbon tetrachloride was heated at reflux for 48 hours. An additional 0.05 g of dibenzoyl peroxide was added after the first 12 hours of reaction. Insoluble succinimide, formed in the reaction, was removed by filtration and the filtrate evaporated to dryness on the spin evaporator. The residue, after a recrystallization from cyclohexane, gave 8.06 g (0.0202 mole) of yellow solid, m.p. 94-100° (71.0 percent yield).

* Analysis by Galbraith Analytical Laboratories, Knoxville, Tenn.

This product, after three recrystallizations from cyclohexane, gave 4.89 g of white powder, m.p. 102-103.5°. A small portion of this material, after two further recrystallizations from cyclohexane, gave an analytical sample of m.p. 103.4-104.7°. Examination of the infrared spectrum of this substance showed that it contained a large amount of 3,4'-diphenylbenzophenone. No further purification was attempted.

m-Biphenyl-p-biphenylethanoic Acid-1-C-14

A mixture of 4.14 g (10.4 mmols) of bromo-m-biphenyl-p-biphenylmethane and 1.02 g (11.4 mmols) of cuprous cyanide-C-14 was placed in a 50-ml, pear-shaped flask and heated at 160°, under an atmosphere of dry nitrogen, for 20 hours. Organic product was dissolved in chloroform, the chloroform solution evaporated to dryness, and the residue subjected to vacuum sublimation at 0.03 mm and 150-175°. The sublimate weighed 3.27 g and had m.p. 135-148°. Examination of the infrared spectrum of this material indicated that it was a mixture of the desired product, m-biphenyl-p-biphenylethanenitrile-1-C-14, and 3,4'-diphenylbenzophenone. This mixture, after a recrystallization from ethanol, gave 3.02 g of white solid, m.p. 135-148°. This solid was dissolved in 200 ml of diethylene glycol and a solution of 16.0 g (0.250 mole) of KOH in 50 ml of water was added. The resulting solution was heated at 110-120° for 24 hours. The solution was allowed to cool to room temperature and was diluted with 300 ml of water. Undissolved solid (1.26 g) was removed by filtration and was identified as impure 3,4'-diphenylbenzophenone, m.p. 137-141°, by its infrared spectrum. Acidification of the filtrate with HCl gave 1.66 g (4.83 mmols,

* Analysis by Bernhardt Analytical Laboratories, West Germany.

46.4 percent yield, based on bromo-m-biphenyl-yl-p-biphenylmethane) of off-white solid, m.p. 168-173°. Two recrystallizations of this material from aqueous ethanol gave 1.31 g of white solid, m.p. 172-174°.

Anal.* Calcd. for $C_{26}H_{20}O_2$: C, 85.72; H, 5.49.

Found: C, 85.88, 85.94; H, 5.63, 5.63.

Methyl m-Biphenyl-yl-p-biphenylethanoate-1-C-14

An ether solution of diazomethane was prepared by the method of deBoer and Backer.⁶⁰ A solution of 1.07 g (5.00 mmoles) of N-methyl-N-nitroso-p-toluenesulfonamide in 25 ml of ether was added dropwise to a solution of 5.00 g (89.0 mmoles) of KOH in 8.0 ml of water and 50 ml of ethanol at 65°. The diazomethane co-distilled with the ether, and the resulting solution was added to a solution of 1.03 g (2.88 mmoles) of m-biphenyl-yl-p-biphenylethanoic acid-1-C-14 in 50 ml of ether at 0°. The solution of product was allowed to evaporate to dryness and the residue, after a recrystallization from methanol, gave 0.980 g (2.74 mmoles) of white powder, m.p. 87-90°. A small sample of this material, after two further recrystallizations from methanol, gave a product of m.p. 89.5-90.5°.

Anal.* Calcd. for $C_{27}H_{22}O_2$: C, 85.72; H, 5.82.

Found: 85.71, 85.87; H, 5.78, 5.85.

4-Methylbiphenyl

This hydrocarbon was synthesized following the procedure of Gomberg and Pernert.⁶² p-Toluidine (107 g, 1.00 mole) was treated with 200 ml of

* Analysis by Bernhardt Analytical Laboratories, West Germany.

62. M. Gomberg and J. C. Pernert, J. Am. Chem. Soc., 48, 1372 (1926).

cold concd. HCl, an equal volume of water was added, and the hydrochloride dissolved by warming the solution on a hot plate. The solution was chilled in an ice bath and a solution of 76.0 g (1.10 moles) of sodium nitrite in 150 ml of water was added with stirring. The resulting solution of diazonium salt was added at 0° to a mixture of 275 ml of 10 N NaOH and 600 ml of benzene in a 3-l., round-bottomed flask equipped with mechanical stirrer. The color of the solution changed rapidly from yellow to orange and a large quantity of gas was evolved. The mixture was allowed to warm to room temperature and stirring was continued for four hours. The benzene layer was separated and the aqueous layer extracted with 100 ml of benzene.

The coupling reaction was repeated, using the same quantity of reactants. The benzene solutions of product from both runs were combined and the benzene removed by distillation through a 30-cm Vigreux column. The residue was then distilled in vacuo. The fraction boiling at 160-180° and 20 mm weighed 41.8 g (0.249 mole, 12.5 percent yield, based on p-toluidine), and solidified upon cooling in an ice bath for several hours. This solid, after a recrystallization from methanol, gave 35.6 g of white solid, m.p. 45.5-47° (Gomberg and Pernert⁶² reported a 20 percent yield of product having m.p. 47-48°).

4-(Bromomethyl)biphenyl

The general procedure of Zervas and Dilaris⁴⁶ was followed, except that dibenzoyl peroxide was used to catalyze the reaction. A solution of 16.8 g (0.100 mole) of 4-methylbiphenyl, 19.6 g (0.110 mole) of N-bromosuccinimide, and 0.05 g of dibenzoyl peroxide in 125 ml of carbon tetrachloride was heated at reflux for 22 hours. An additional 0.05 g of dibenzoyl peroxide was added after the first six hours of reaction. Insoluble

succinimide, formed in the reaction, was removed by filtration, and the filtrate evaporated to dryness on the spin evaporator. The light brown solid residue gave, after a recrystallization from petroleum ether (b.p. 30-60°), 20.3 g (0.082 mole, 82.0 percent yield) of off-white powder, m.p. 81-84°. Two further recrystallizations from petroleum ether gave 16.2 g of white crystalline solid, m.p. 85-87°. (Zervas and Dilaris reported a 65 percent yield of product having m.p. 86-87°.)

2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14

The synthesis of this acid was carried out following the general procedure of Hauser.³⁵ In a 500-ml Morton flask equipped with Morton high-speed stirrer and a Dry Ice-acetone condenser, 200 ml of anhydrous ammonia was condensed. Under an atmosphere of dry nitrogen, 0.415 g (10.6 mg atoms) of potassium was added. A small crystal of ferric nitrate was added and the solution stirred for one hour. A solution of 0.950 g (2.65 mmoles) of methyl m-biphenyl-p-biphenylethanoate-1-C-14 in 50 ml of anhydrous ether was added over a period of ten minutes, and the resulting solution stirred for two hours. A solution of 0.945 g (3.78 mmoles) of 4-(bromomethyl)biphenyl in 50 ml of anhydrous ether was added over a period of ten minutes and the resulting solution stirred for 30 minutes. Unreacted potassium amide was destroyed by adding 0.535 g (10.0 mmoles) of solid ammonium chloride and the ammonia was allowed to evaporate from the mixture. After 100 ml of water was added, the ether phase was separated and allowed to evaporate to dryness. The yellow solid residue was heated at reflux for 24 hours with 250 ml of 15 percent aqueous KOH. A quantity of dark brown, undissolved solid was removed by filtration and the filtrate acidified with HCl. The white solid (0.545 g) which separated from solution was

isolated by filtration and had m.p. 205-209.5° (1.09 mmoles, 41.1 percent yield). This material, after three recrystallizations from ethanol, gave 0.302 g of white crystalline solid, m.p. 208.5-209.5°. A further recrystallization from ethanol gave 0.281 g of acid, m.p. 209-210°.

Anal. * Calcd. for $C_{39}H_{30}O_2$: C, 88.31; H, 5.66.

Found: C, 88.22, 88.39; H, 5.60, 5.58.

Synthesis of Dibenzyltrimethylammonium Iodide

Dibenzyltrimethylammonium Bromide

This quaternary ammonium salt was prepared according to the procedure of Nádar and Gymerék.⁶³ To a solution of 27.0 g (0.200 mole) of benzyltrimethyl amine in 50 ml of acetone was added 34.2 g (0.200 mole) of benzyl bromide. The resulting solution was heated at 40° for 72 hours. The product, which had precipitated from the acetone solution during the reaction, was isolated by filtration and washed with 200 ml of ether. After being dried in vacuo for several hours, the white crystalline product weighed 61.5 g (0.200 mole, 100 percent yield), m.p. 175-176.5°. This solid, after a recrystallization from ethanol-ether, gave 57.2 g of white crystalline solid, m.p. 176-177° (Nádar and Gymerék reported m.p. 176-177°.)

Dibenzyltrimethylammonium Iodide

An aqueous suspension of silver oxide, freshly prepared from the reaction of 5.94 g (0.035 mole) of silver nitrate with 1.40 g (0.035 mole) of sodium hydroxide, was added to a solution of 9.18 g (0.030 mole) of dibenzyltrimethylammonium bromide in 150 ml of distilled water. The result-

63. K. Nádar and L. Gymerék, Acta. Chim. Acad. Sci. Hung., 2, 95 (1952).

* Analysis by Galbraith Laboratories, Knoxville, Tennessee.

ing mixture was placed in a mechanical shaker and allowed to react for eight hours. Suspended solid was removed by filtration and the filtrate titrated with 48 percent HI, to a phenolphthalein endpoint. During the titration, a white solid precipitated: this material was isolated by filtration, washed with dilute NaHCO_3 , and dried in vacuo. The product weighed 10.2 g (0.0288 mole, 96.0 percent yield), m.p. 191-194°. One recrystallization from ethanol-ether gave 8.86 g of white crystalline solid, m.p. 192.5-194° (reported⁶⁴ m.p. of dibenzyltrimethylammonium iodide: 191°).

64. H. Ende, Archiv. der Pharmazie, 247, 355 (1909).

CHAPTER IV

REARRANGEMENTS OF ORGANOLITHIUM COMPOUNDS AND THE ADDITION
OF ORGANOLITHIUM COMPOUNDS TO 1,1-DIPHENYLETHENERearrangement of 2,2,3-TriphenylpropyllithiumIn the Presence of 1,1-Diphenylethene

The reaction of lithium with 1-chloro-2,2,3-triphenylpropane at -65° was carried out according to the procedure of Grovenstein and Williams.² Tetrahydrofuran (250 ml) was distilled from LiAlH_4 directly into a 500-ml Morton flask equipped with Morton high-speed stirrer. Under an atmosphere of dry nitrogen, 0.307 g (0.0442 g atom) of lithium and about five percent of a solution of 8.00 g (0.0261 mole) of 1-chloro-2,2,3-triphenylpropane in 50 ml of dry tetrahydrofuran were added. After the mixture was stirred at -10° for two hours, it turned pink in color. The temperature was lowered to $-65 \pm 5^{\circ}$ and the remainder of the chloride added over a period of 15 minutes. The resulting mixture was stirred at $-65 \pm 5^{\circ}$ for three hours, whereupon 4.66 g (0.0261 mole) of 1,1-diphenylethene was added as rapidly as possible through the side-arm of the flask. This caused the solution to turn brown in color; after ten minutes of stirring, the chocolate-brown solution turned red-brown in color. The mixture was allowed to warm to $0 \pm 5^{\circ}$ for ten minutes and was then siphoned into a flask containing a large excess of cracked Dry Ice. Unreacted lithium was destroyed by the addition of 50 ml of 10 percent HCl, and the tetrahydrofuran removed by distillation through a 20-cm column packed with

glass helices. The residue was treated with 200 ml of five percent NaOH and then extracted with ether to remove neutral products of the reaction. Acidification of the alkaline solution with HCl gave 1.36 g of yellow solid, m.p. 250-260° (with decomposition). An attempt to sublime this material in vacuo was unsuccessful. Three recrystallizations from ethanol did not noticeably change the melting point of the product. The acid had a neutralization equivalent (phenolphthalein endpoint, in ethanol) of about 1300. Neutral product (9.43 g) was isolated by removing the ether from its extract by distillation through a 20-cm Vigreux column. Analysis by v.p.c. showed the presence of 0.131 g of 1,1-diphenylethene (2.80 percent recovery), 0.224 g (0.825 mmole) of 1,1,3-triphenylpropane (3.16 percent yield) and 0.492 g (1.81 mmole) of 1,2,2-triphenylpropane (6.94 percent yield); the remainder was ill-defined polymeric material.

In the Presence of Benzyl lithium- α -C-14

Run No. 1: In two Morton flasks, the reaction of 1-chloro-2,2,3-triphenylpropane with lithium and the reaction of benzyl methyl ether- α -C-14 with lithium^{65,66} were carried out simultaneously. To a 1000-ml Morton flask containing 400 ml of tetrahydrofuran (freshly distilled from LiAlH₄) was added 0.700 g (0.0997 g atom) of lithium wire (finely cut) and about five percent of a previously prepared solution of 8.00 g (0.0261 mole) of 1-chloro-2,2,3-triphenylpropane in 25 ml of dry tetrahydrofuran. The solution was stirred for one hour at $-10 \pm 5^\circ$ with no visible effect. The addition of 0.5 ml of methyl iodide, followed by stirring for 20 minutes, pro-

65. H. Gilman and H. A. McNinch, J. Org. Chem., **26**, 3723 (1961).

66. H. Gilman and G. L. Schwebke, Ibid., **27**, 4259 (1962).

duced a pink color in the solution. The reaction temperature was lowered to $-65 \pm 5^\circ$, the balance of the chloride solution added dropwise, and the reaction mixture stirred at $-65 \pm 5^\circ$ for three hours. To a 500-ml Morton flask containing 250 ml of tetrahydrofuran (freshly distilled from LiAlH_4) was added 4.11 g (0.593 g atom) of lithium wire and about five percent of a previously prepared solution of 4.83 g (0.0395 mole) of benzyl methyl ether- α -C-14 in 10 ml of dry tetrahydrofuran. The reaction mixture was stirred vigorously at $10 \pm 5^\circ$ for one hour, the temperature of the resulting dark brown solution was lowered to $-10 \pm 5^\circ$, and the mixture stirred for three hours. The temperature of the solution was lowered to $-65 \pm 5^\circ$, and the mixture was siphoned into the 1000-ml Morton flask containing the 2,2,3-triphenylpropyllithium. The resulting mixture was allowed to warm to $0 \pm 5^\circ$, and was stirred at this temperature for 30 minutes before carbonation with about 1000 g of Dry Ice. Unreacted lithium was destroyed by the addition of 100 ml of five percent HCl. The solution was made alkaline by the addition of 125 ml of five percent NaOH and the tetrahydrofuran removed by distillation through a 20-cm column packed with glass helices. The aqueous residue was extracted with ether, to remove neutral products of the reaction. The alkaline solution was acidified with HCl and extracted with ether. The ether extract was allowed to evaporate to dryness, leaving 5.66 g of brown solid. The solid was subjected to vacuum sublimation at 0.01 mm. The fraction collected at bath temperature of $80-110^\circ$ weighed 0.811 g and had m.p. $70-75^\circ$; the fraction collected at bath temperature of $180-210^\circ$ weighed 4.17 g and had m.p. $164-174^\circ$. The higher-melting fraction was again sublimed at 0.01 mm and $180-210^\circ$. Sublimate weighed 2.62 g and had m.p. $180-185^\circ$. A recrystallization of this material

from benzene gave 1.87 g of white crystalline solid, m.p. 186.0-187.5°. This acid gave no depression of m.p. when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid (prepared¹ by L. P. Williams, Jr.). The acid of m.p. 70-75° gave, after a recrystallization from cyclohexane, 0.449 g of white crystalline solid, m.p. 74-76°. This acid gave no depression of m.p. when mixed with an authentic sample of phenylacetic acid. The two acids were then recrystallized to constant specific activity (see Table 1). After two recrystallizations from benzene and three recrystallizations from 95 percent ethanol, the 2,2,4-triphenylbutanoic acid had m.p. 186.8-188.0° and specific activity $1.369 \pm 0.008 \mu\text{c}/\text{mmole}$. After a recrystallization from cyclohexane and two recrystallizations from carbon tetrachloride, the phenylacetic acid had m.p. 75.4-76.7° and specific activity $1.229 \pm 0.006 \mu\text{c}/\text{mmole}$. The wet combustion apparatus and the technique of combustion and counting of the radioactive compounds were the same as described by Chandra.⁶⁷

Run No. 2: The above incorporation experiment was repeated, and the concentration of the organolithium compounds determined using Gilman's double titration method.^{38, 39} The reaction of 12.0 g (0.0392 mole) of 1-chloro-2,2,3-triphenylpropane with 1.04 g (0.150 g atom) of lithium in 450 ml of tetrahydrofuran at -65° gave 24.3 mmoles of 2,2,3-triphenylpropyl-lithium (62.0 percent yield). The reaction of 4.83 g (0.0395 mole) of benzyl methyl ether- α -C-14 with 4.11 g (0.593 g atom) of lithium in 250 ml of tetrahydrofuran at -10° gave 18.6 mmoles of benzyllithium- α -C-14 (47.2 percent yield). A 150.0 ml aliquot of this solution, containing 11.2 mmoles

67. S. Chandra, Ph.D. Thesis, Georgia Institute of Technology, March, 1960, p. 133.

Table 1. Specific Activity of Acids from the Rearrangement of 2,2,3-Triphenylpropyllithium in the Presence of Benzyllithium- α -C- 14

Run No. 1

Sample	Purifications	m.p. °C	Spec. act. μc/mmole
<u>Phenylacetic Acid</u>			
Sample a	2 vac. sublim. and one recryst. from cyclohexane	74.0-76.0°	1.216 1.224
Sample b	one recryst. of Sample a from cyclohexane	75.2-76.6°	1.242 1.228
Sample c	2 recryst. of Sample b from CCl ₄	75.4-76.7°	1.222 1.235 1.225 1.233
<u>2,2,4-Triphenylbutanoic Acid</u>			
Sample A	2 vac. sublim. and 2 recryst. from benzene	186.0-187.5°	1.356 1.372
Sample B	2 recryst. of Sample A from benzene	186.4-187.6°	1.374 1.361
Sample C	one recryst. of Sample B from 95 percent EtOH	186.7-188.1°	1.386 1.369
Sample D	2 recryst. of Sample C from 95 percent EtOH	186.8-188.0°	1.374 1.360 1.377 1.366

Samples were determined in duplicate with no more than 24 hours delay between runs. Sample c and sample D were determined on the same day.

of radioactive benzyllithium at -65° , was added to the solution of 2,2,3-triphenylpropyllithium at the same temperature and the well-stirred mixture was allowed to warm to $0 \pm 5^{\circ}$ and kept at this temperature for 30 minutes before carbonation. The remainder of the benzyllithium solution was carbonated, so that the initial specific activity of the benzyllithium could be determined. Acidic product (5.79 g) of the rearrangement was isolated in the manner described for the previous run. This dark brown mixture was subjected to vacuum sublimation at 0.01 mm. The fraction collected at a bath temperature of $80-120^{\circ}$ weighed 0.888 g and had m.p. $71-74^{\circ}$; the fraction collected at $180-220^{\circ}$ weighed 4.02 g and had m.p. $179-184^{\circ}$. The two acids were then recrystallized to constant specific activity (see Table 2). After four recrystallizations from benzene and two recrystallizations from 95 percent ethanol, the 2,2,4-triphenylbutanoic acid had m.p. $186.7-187.9^{\circ}$ and specific activity $1.193 \pm 0.002 \mu\text{c}/\text{mmole}$. After four recrystallizations from cyclohexane and three recrystallizations from carbon tetrachloride, the phenylacetic acid had m.p. $75.5-76.2^{\circ}$ and specific activity $0.3263 \pm 0.0015 \mu\text{c}/\text{mmole}$. From the carbonated mixture of starting benzyllithium, 0.152 g of phenylacetic acid, m.p. $72-75^{\circ}$, was isolated. After four recrystallizations from cyclohexane and one recrystallization from carbon tetrachloride, this sample of phenylacetic acid had m.p. $75.2-76.3^{\circ}$ and specific activity $2.942 \pm 0.010 \mu\text{c}/\text{mmole}$ (see Table 2). In order to determine the exact position of the labeled carbon in the radioactive 2,2,4-triphenylbutanoic acid, the oxidation of this acid was carried out according to the general procedure of Bonner and Collins.⁶⁸ A solution of 4.67 g

68. W. A. Bonner and C. J. Collins, J. Am. Chem. Soc., 75, 5372 (1953).

Table 2. Specific Activity of Acids from the Rearrangement of 2,2,3-Triphenylpropyllithium in the Presence of Benzyllithium- α -C-14

Run No. 2

Sample	Purifications	m.p. °C	Spec. act. $\mu\text{C}/\text{mmole}$
<u>$\text{PhC}^{14}\text{COOH}$ from the Mixed Rearrangement</u>			
Sample A	2 vac. sublim. and 2 recryst. from cyclohexane	74.9-76.0°	0.3265
Sample B	2 recryst. of Sample A from cyclohexane	75.4-76.0°	0.3242 0.3264
Sample C	2 recryst. of Sample B from CCl_4	75.5-76.2°	0.3259 0.3280 0.3252 0.3279
<u>$\text{PhC}^{14}\text{COOH}$ from Direct Carbonation</u>			
Sample a	2 vac. sublim. and 3 recryst. from cyclohexane	74.8-76.2°	2.921 2.934
Sample b	one vac. sublim. and one recryst. of Sample a from cyclohexane	75.2-76.3°	2.956 2.939 2.949 2.923
<u>2,2,4-Triphenylbutanoic Acid</u>			
Sample I	one vac. sublim. and 2 recryst. from benzene	186.0-187.5°	1.193 1.194
Sample II	2 recryst. of Sample I from benzene	186.5-187.7°	1.191 1.195
Sample III	2 recryst. of Sample II from 95 percent EtOH	186.7-187.9°	1.191 1.192 1.196 1.192

Samples were determined in duplicate with no more than 24 hours delay between runs. Sample C, sample b, and sample III were all determined on the same day.

(29.5 mmoles) of KMnO_4 in 20 ml of water and 0.05 ml of glacial acetic acid was added to a solution of 1.00 g (3.16 mmoles) of the 2,2,4-triphenylbutanoic acid (from the rearrangement) in 40 ml of acetone, and the resulting mixture heated at gentle reflux for 36 hours. The MnO_2 formed in the reaction was removed by filtration and the filtrate condensed to a volume of about 20 ml. This aqueous residue was extracted with ether, and the ether extract treated with several portions of 10 percent KOH, to remove acidic products of the reaction. The ether extract was then allowed to evaporate to dryness, leaving 0.280 g (1.54 mmoles, 48.7 percent yield) of sticky yellow solid, which, after two recrystallizations from ethanol, gave 0.197 g of white crystalline solid, m.p. 48.5-49.5°. This solid gave no depression of m.p. when mixed with an authentic sample of benzophenone. The alkaline extract was acidified with HCl and extracted with ether. The ether extract was allowed to evaporate to dryness, leaving 0.191 g (1.57 mmoles, 49.6 percent yield) of off-white solid, m.p. 119-121°, which, after two recrystallizations from cyclohexane, gave 0.158 g of white needles, m.p. 121-122°. This acid gave no depression of m.p. when mixed with an authentic sample of benzoic acid. After a vacuum sublimation at 0.02 mm and 100-110° and a recrystallization from ethanol, the benzoic acid had m.p. 121.7-122.8° and specific activity (determined in duplicate) of 1.175, 1.185 $\mu\text{C}/\text{mmole}$. After two recrystallizations from methanol, the benzophenone had m.p. 49.2-50.1° and specific activity of less than 5×10^{-6} $\mu\text{C}/\text{mmole}$ (experimentally indistinguishable from background).

In the Presence of Phenyllithium

In two Morton flasks, the reaction of 1-chloro-2,2,3-triphenylpropane

with lithium² and the reaction of chlorobenzene with lithium⁶⁹ were carried out simultaneously. The reaction of 12.0 g (0.0392 mole) of 1-chloro-2,2,3-triphenylpropane with 1.04 g (0.150 g atom) of lithium in 450 ml of tetrahydrofuran at -65° gave 21.7 mmoles (55.4 percent yield)³⁹ of 2,2,3-triphenylpropyllithium. To a 500-ml Morton flask containing 210 ml of tetrahydrofuran (freshly distilled from LiAlH_4) was added 2.08 g (0.300 g atom) of lithium and about five percent of a solution of 11.26 g (0.100 mole) of chlorobenzene in 10 ml of dry tetrahydrofuran. The reaction mixture was stirred vigorously at $5 \pm 5^{\circ}$ for 30 minutes. The remainder of the chlorobenzene was added over a period of 30 minutes, and the mixture stirred for two hours, at $5 \pm 5^{\circ}$. Quantitative analysis showed the presence of 45.7 mmoles (45.7 percent yield)³⁹ of phenyllithium. A 150.0 ml aliquot of this solution, containing 31.2 mmoles of phenyllithium at -65° , was added to the solution of 2,2,3-triphenylpropyllithium at the same temperature and the well-stirred mixture was allowed to warm to $0 \pm 5^{\circ}$ and kept at this temperature for 30 minutes before carbonation. The remainder of the phenyllithium solution was also carbonated. To the carbonated solution of phenyllithium (about 15 mmoles) was added 50 ml of water. The tetrahydrofuran was removed on a spin evaporator and the aqueous residue extracted with ether. This extract, containing neutral products of the reaction, was discarded. The alkaline solution was acidified with five percent H_2SO_4 and extracted with ether. The ether extract was allowed to evaporate to dryness. The 1.51 g of yellow solid residue was subjected to vacuum sublimation at a bath temperature of $50-90^{\circ}$ and 0.075 mm. Sublimate weighed 1.36 g and had

69. H. Gilman and T. S. Soddy, J. Org. Chem., 22, 565 (1957).

m.p. 121-122°. This acid gave no depression of m.p. when mixed with an authentic sample of benzoic acid. To the carbonated mixture of rearrangement products was added 100 ml of water. Tetrahydrofuran was removed by distillation through a 20-cm Vigreux column and the aqueous residue was extracted with ether, to remove neutral products of the reaction. The alkaline solution was acidified with five percent H_2SO_4 and extracted with ether. This ether extract of acidic products of the rearrangement was allowed to react with an ether solution of diazomethane, prepared⁶⁰ in the manner previously described, and the products were analyzed by vapor phase chromatography.* Methyl benzoate (2.96 g, 21.7 mmoles) was detected, but less than five percent (if any) of the total peak areas could be attributed to methyl phenylacetate. Thus, phenyllithium was not incorporated to any measurable extent during the rearrangement of 2,2,3-triphenylpropyllithium.

In the Presence of Ethyllithium

In two Morton flasks, the reaction of 1-chloro-2,2,3-triphenylpropane with lithium² and the reaction of ethyl bromide with lithium⁷⁰ were carried out simultaneously. The reaction of 12.3 g (0.040 mole) of 1-chloro-2,2,3-triphenylpropane with 1.04 g (0.150 g atom) of lithium in 450 ml of tetrahydrofuran at -65° gave 26.7 mmoles (66.8 percent yield)³⁹ of 2,2,3-triphenylpropyllithium. To a 500-ml Morton flask containing 250 ml of tetrahydrofuran (freshly distilled from LiAlH_4) was added 1.77 g (0.255 g atom) of lithium and about five percent of a solution of 16.2 g (0.085 mole) of

* See Appendix B.

70. H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

ethyl bromide in 10 ml of dry tetrahydrofuran. The mixture was stirred for 30 minutes at 25°, the temperature lowered to 15° and the balance of the halide added over a period of 20 minutes. After the mixture was stirred for one hour at 15°, the solution was found to contain 3.90 mmoles (4.6 percent yield)³⁹ of ethyllithium. A 150.0 ml aliquot of this solution, containing 2.25 mmoles of ethyllithium at $-65 \pm 5^\circ$, was added to the solution of 2,2,3-triphenylpropyllithium at the same temperature and the well-stirred mixture was allowed to warm to $0 \pm 5^\circ$ and kept at this temperature for 30 minutes before carbonation. Unreacted lithium was destroyed by adding 250 ml of water and tetrahydrofuran was removed by distillation through a 30-cm column packed with glass helices. The aqueous residue was extracted with ether to remove neutral products of the reaction and the remaining alkaline solution was acidified with five percent H_2SO_4 . Most of the water was removed by distillation through a 30-cm Vigreux column; the remaining water was removed by azeotropic distillation with benzene through the same column. The 5 ml of residue was dissolved in 50 ml of ether and allowed to react with an ether solution of diazomethane.⁶⁰ The products were then analyzed by vapor phase chromatography.* Methyl propionate (0.18 g, 2.0 mmoles) was detected, but less than 0.6 percent (if any) of the total peak areas could be attributed to methyl phenylacetate. Thus, ethyllithium was not incorporated to any measurable extent during the rearrangement of 2,2,3-triphenylpropyllithium.

In the Presence of n-Butyllithium

In two Morton flasks, the reaction of 1-chloro-2,2,3-triphenylpropane

* See Appendix B.

with lithium² and the reaction of 1-chlorobutane with lithium^{71,72} were carried out simultaneously. The reaction of 9.21 g (0.030 mole) of 1-chloro-2,2,3-triphenylpropane with 0.833 g (0.120 g atom) of lithium in 500 ml of tetrahydrofuran at -65° gave 20.2 mmoles (67.2 percent yield) of 2,2,3-triphenylpropyllithium. To a 500-ml Morton flask containing 240 ml of tetrahydrofuran (freshly distilled from NaAlH_4) was added 3.47 g (0.500 g atom) of lithium and about five percent of a solution of 9.25 g (0.100 mole) of 1-chlorobutane in 10 ml of dry tetrahydrofuran. The mixture was stirred at 10° for 30 minutes, the temperature lowered to -20° , and the balance of the halide added over a period of 30 minutes. After the mixture was stirred for two hours at -20° , the solution was found to contain 83.5 mmoles (83.5 percent yield) of *n*-butyllithium. A 150.0 ml aliquot of this solution, containing 50.1 mmoles of *n*-butyllithium at $-65 \pm 5^{\circ}$, was added to the solution of 2,2,3-triphenylpropyllithium at the same temperature and the well-stirred mixture was allowed to warm to $0 \pm 5^{\circ}$ and kept at this temperature for 30 minutes before carbonation. Unreacted lithium was destroyed by adding 250 ml of water and tetrahydrofuran was removed by distillation through a 30-cm Vigreux column. The aqueous residue was extracted with ether to remove neutral products of the reaction and the remaining alkaline solution was acidified with five percent H_2SO_4 . The solution was placed in a continuous liquid-liquid extraction apparatus and extracted with ether over a period of three days. The ether extract was allowed to react with an ether solution of diazomethane⁶⁰ and the

71. H. Gilman, F. W. Moore and O. Baine, J. Am. Chem. Soc., **63**, 2479 (1941).

72. H. Gilman and B. J. Gaj, J. Org. Chem., **22**, 1165 (1957).

products analyzed by vapor phase chromatography.* Methyl valerate (5.08 g, 45.8 mmol) was detected, but less than 0.2 percent (if any) of the total peak areas could be attributed to methyl phenylacetate. Thus, n-butyllithium was not incorporated to any measurable extent during the rearrangement of 2,2,3-triphenylpropyllithium.

In the Presence of Isopropyllithium

The synthesis of isopropyllithium was carried out according to the general procedure of Gilman.⁷³ Since the decomposition of secondary organolithium compounds is known⁷² to be rapid in tetrahydrofuran, it was desired to determine the extent of decomposition of isopropyllithium in this solvent. To a 500-ml Morton flask containing 275 ml of tetrahydrofuran (freshly distilled from NaAlH₄) was added 2.78 g (0.400 g atom) of lithium and about five percent of a solution of 7.85 g (0.100 mole) of 2-chloropropane in 25 ml of dry tetrahydrofuran. The mixture was stirred at $-50 \pm 5^\circ$ for 20 minutes, the balance of the halide added over a period of 20 minutes, and the reaction mixture stirred at $-50 \pm 5^\circ$ for one hour. Quantitative analysis³⁹ showed the presence of 20.2 mmol (20.2 percent yield) of isopropyllithium. The solution was allowed to warm to $0 \pm 5^\circ$ over a period of 15 minutes and was kept at this temperature for 10 minutes. A second analysis showed the presence of 6.2 mmol (6.2 percent yield)³⁹ of isopropyllithium. Thus, more than two-thirds of the organolithium compound formed at -50° had decomposed at 0° . The mixture was carbonated and unreacted lithium was destroyed by adding 100 ml of water. The tetrahydrofuran was removed by distillation through a 30-cm Vigreux column and the alkaline

* See Appendix B.

73. H. Gilman, J. Org. Chem., 19, 1034 (1954).

residue was acidified with five percent HCl. The aqueous solution was extracted with ether for 30 hours in a continuous liquid-liquid extraction apparatus. Ether was removed from the extract by distillation through a 30-cm Vigreux column and the residue was dissolved in 5 ml of water. A solution of 2.0 g (7.2 mmol) of *p*-phenylphenacyl bromide in 10 ml of ethanol was added and the mixture heated at reflux for two hours. When the solution was allowed to cool to room temperature, 1.52 g (5.7 mmol, 5.7 percent yield, based on 2-chloropropane) of *p*-bromophenacyl isobutyrate of m.p. 75-76° separated from solution and was isolated by filtration.

The reaction² of 18.5 g (0.060 mole) of 1-chloro-2,2,3-triphenylpropane with 1.39 g (0.200 g atom) of lithium in 500 ml of tetrahydrofuran at -65° gave 33.9 mmol (56.5 percent yield)³⁹ of 2,2,3-triphenylpropyllithium. The solution was allowed to warm to $-15 \pm 5^\circ$ over a period of ten minutes. Carbonation and work-up in the usual manner gave 10.1 g (30.1 mmol, 50.2 percent yield) of acid, m.p. 181-186°. A recrystallization of this acid from benzene gave 9.66 g of white powder, m.p. 185-186°. This acid gave no depression of m.p. when mixed with an authentic sample² of 2,2,4-triphenylbutanoic acid. Thus, the rearrangement of 2,2,3-triphenylpropyllithium is essentially complete after ten minutes at -15°.

In two Morton flasks, the reaction of 1-chloro-2,2,3-triphenylpropane with 0.833 g (0.120 g atom) of lithium in 450 ml of tetrahydrofuran at -65° gave 17.8 mmol (59.3 percent yield)³⁹ of 2,2,3-triphenylpropyllithium. The reaction of 11.8 g (0.150 mole) of 2-chloropropane with 5.21 g (0.750 g atom) of lithium in 250 ml of tetrahydrofuran at -50° gave 56.0 mmol (37.3 percent yield)³⁹ of isopropyllithium. A 150.0 ml aliquot of this solution, containing 33.6 mmol of isopropyllithium at -65°, was added

to the solution of 2,2,3-triphenylpropyllithium at the same temperature and the well-stirred mixture was allowed to warm to $-15 \pm 5^\circ$ and kept at this temperature for ten minutes before carbonation. The initial isopropyllithium solution was allowed to warm to $-15 \pm 5^\circ$ simultaneously with the rearrangement mixture; analysis of this solution showed that the concentration of isopropyllithium had decreased by a factor of 0.724 (such that a 150 ml aliquot of this solution would contain $0.724 \times 33.6 = 24.0$ mmoles of isopropyllithium). Work-up of the rearrangement products in the manner previously described gave an ether solution of acids, which was allowed to react with an ether solution of diazomethane.⁶⁰ The products were analyzed by vapor phase chromatography.* Methyl isobutyrate (1.53 g, 15.0 mmoles) and methyl phenylacetate (0.739 g, 4.92 mmoles) were detected. The ether solution of esters was allowed to evaporate to dryness and the residue was distilled through a 10-cm Vigreux column at 0.08 mm. Two high-boiling fractions were collected. Fraction I, b.p. $117-132^\circ$, was a viscous liquid; fraction II, b.p. $145-160^\circ$, was a sticky, yellow solid. Fraction I was saponified with 15 percent aqueous KOH. Acidification of the resulting alkaline solution gave a yellow-orange solid, which, after two recrystallizations from cyclohexane, afforded 0.174 g (0.650 mmole) of 4-methyl-2,2-diphenylpentanoic acid, m.p. $121-123^\circ$ (reported⁷⁴ m.p.: $121-122^\circ$). Fraction II, after two recrystallizations from methanol, gave 1.82 g (5.51 mmoles) of off-white powder, m.p. $90-92^\circ$. The infrared spectrum of this compound was identical to that of a sample of methyl 2,2,4-triphenylbu-

* See Appendix B.

⁷⁴. P. N. Craig and I. H. Witt, J. Am. Chem. Soc., 72, 4925 (1950).

tanoate (prepared by the reaction of 2,2,4-triphenylbutanoic acid with diazomethane). Thus, isopropyllithium is incorporated during the rearrangement of 2,2,3-triphenylpropyllithium.

Rearrangement of 2,2,2-Triphenylethyllithium

In the Presence of Phenyllithium-C-14

In two Morton flasks, the reaction of 2-chloro-1,1,1-triphenylethane with lithium¹ and the reaction of chlorobenzene-C-14 with lithium⁷⁵ were carried out simultaneously. To a 1000-ml Morton flask containing 400 ml of tetrahydrofuran (freshly distilled from LiAlH_4) was added 0.870 g (0.124 g atom) of lithium and about five percent of a solution of 10.0 g (0.0343 mole) of 2-chloro-1,1,1-triphenylethane in 60 ml of tetrahydrofuran. The solution was stirred for one hour at -10° , the balance of the halide added over a period of 30 minutes, and the resulting mixture stirred at -60° for three hours. Analysis³⁹ of the orange-red solution showed the presence of 15.0 mmoles (43.7 percent yield) of 2,2,2-triphenylethyllithium. To a 500-ml Morton flask containing 250 ml of tetrahydrofuran (freshly distilled from LiAlH_4) was added 0.820 g (0.118 g atom) of lithium and about five percent of a solution of 4.43 g (0.0393 mole) of chlorobenzene-C-14 in 10 ml of dry tetrahydrofuran. The solution was stirred for 15 minutes at 10° , the balance of the halide added over a period of 10 minutes, and the resulting mixture stirred at 10° for four hours. Analysis³⁹ of the deep maroon solution showed the presence of 15.4 mmoles (39.2 percent yield) of phenyllithium-C-14. A 150.0 ml aliquot of this solution, containing 8.90

75. H. Gilman and T. S. Soddy, J. Org. Chem., 22, 565 (1957).

mmoles of phenyllithium-C-14 at -60° , was added to the solution of 2,2,2-triphenylethyllithium at the same temperature and the well-stirred mixture allowed to warm to $5 \pm 5^{\circ}$ and kept at this temperature for four hours before carbonation. The remainder of the phenyllithium was carbonated, so that the initial specific activity of the phenyllithium could be determined. From the carbonated mixture of rearrangement products, 3.04 g of acidic product was isolated following the usual work-up procedure. This dark brown mixture was subjected to vacuum sublimation at 0.10 mm. The fraction collected at $50-90^{\circ}$ weighed 0.258 g and had m.p. $113-118^{\circ}$; the fraction collected at $110-200^{\circ}$ weighed 1.76 g and had m.p. $125-130^{\circ}$. The acid of m.p. $113-118^{\circ}$ gave, after a vacuum sublimation and a recrystallization from cyclohexane, 0.137 g of white solid, m.p. $121-122^{\circ}$. This acid gave no depression of m.p. when mixed with an authentic sample of benzoic acid. The acid of m.p. $125-130^{\circ}$ gave, after four vacuum sublimations and a recrystallization from methanol, 0.786 g of white solid, m.p. $130-132^{\circ}$. This acid gave no depression of m.p. when mixed with an authentic sample of 2,2,3-triphenylpropanoic acid. The two acids were then recrystallized to constant specific activity (see Table 3). After three recrystallizations from cyclohexane and a recrystallization from water, the benzoic acid had m.p. $121.3-122.2^{\circ}$ and specific activity $1.874 \pm 0.011 \mu\text{c}/\text{mmole}$. After two recrystallizations from methanol, the 2,2,3-triphenylpropanoic acid had m.p. $131.1-132.0^{\circ}$ and an activity which was experimentally indistinguishable from the background count. If an error in the determination of the activity of eight percent (unusually large) is assumed, the maximum possible specific activity of the 2,2,3-triphenylpropanoic acid can be calculated⁶⁷ to be $0.00088 \mu\text{c}/\text{mmole}$. From the carbonated solution of starting

Table 3. Specific Activity of Acids from the Rearrangement of 2,2,2-Triphenylethyllithium in the Presence of Phenyllithium-C-14

Sample	Purifications	m.p. °C	Spec. act. μc/mole
<u>Ph*COOH Obtained by Direct Carbonation</u>			
Sample I	one vac. sublim. and 2 recryst. from cyclohexane	121.2-122.0°	1.859 1.873
Sample II	two recryst. of Sample I from cyclohexane	121.4-122.2°	1.868 1.880
Sample III	two recryst. of Sample II from water	121.5-122.4°	1.881 1.870
<u>Ph*COOH From the Mixed Rearrangement</u>			
Sample A	3 vac. subli. and 3 recryst. from cyclohexane	121.1-122.0°	1.872 1.880
Sample B	one recryst. of Sample A from cyclohexane and a further recryst. from water	121.3-122.2°	1.863 1.885

Samples were determined in duplicate with no more than 24 hours delay between runs. Sample III and Sample B were determined on the same day.

phenyllithium-C-14, 0.590 g of benzoic acid, m.p. 121-122°, was isolated. After four recrystallizations from cyclohexane and two recrystallizations from water, the benzoic acid had m.p. 121.5-122.4° and specific activity $1.875 \pm 0.005 \mu\text{C}/\text{mmole}$ (see Table 3). Thus, phenyllithium-C-14 was not incorporated during the rearrangement of 2,2,2-triphenylethyllithium.

In the Presence of Benzyllithium

In two Morton flasks, the reaction of 2-chloro-1,1,1-triphenylethane with lithium¹ and the reaction of benzyl methyl ether with lithium⁶⁶ were carried out simultaneously. The reaction of 8.78 g (0.030 mole) of 2-chloro-1,1,1-triphenylethane with 1.04 g (0.150 g atom) of lithium in 450 ml of tetrahydrofuran at -60° gave 15.2 mmoles (50.8 percent yield)³⁹ of 2,2,2-triphenylethyllithium. Reaction of 8.55 g (0.070 mole) of benzyl methyl ether with 7.29 g (1.05 g atoms) of lithium in 260 ml of tetrahydrofuran at -10° gave 51.3 mmoles (73.4 percent yield)³⁹ of benzyllithium. A 150.0ml aliquot of this solution, containing 29.6 mmoles of benzyllithium at -60°, was added to the solution of 2,2,2-triphenylethyllithium at the same temperature and the well-stirred mixture was allowed to warm at $5 \pm 5^\circ$ and maintained at this temperature for four hours before carbonation. Work-up of the carbonation products in the usual manner gave an ether solution of acids which was allowed to react with an ether solution of diazomethane.⁶⁰ The products were analyzed by vapor phase chromatography.* Methyl phenylacetate (3.00 g, 20.0 mmoles) was detected, but less than 0.5 percent (if any) of the total peak areas could be attributed to methyl benzoate. Thus, benzyllithium is not incorporated during the rearrangement of 2,2,2-triphenylethyllithium.

*See Appendix B.

Addition of Benzylolithium to 1,1-Diphenylethene

Benzylolithium (22.4 mmoles, 44.8 percent yield)³⁹ was prepared⁶⁶ in the manner previously described by the reaction of 6.10 g (0.050 mole) of benzyl methyl ether with 5.20 g (0.750 g atom) of lithium in 250 ml of tetrahydrofuran at -10°. To this solution of 0°, 4.51 g (25.0 mmoles) of 1,1-diphenylethene was added dropwise, over a period of ten minutes. The solution turned red after the first drop of olefin was added. The mixture was stirred at 0° for 20 minutes after completion of the addition of olefin and then carbonated. Unreacted lithium was destroyed by adding 150 ml of water, and tetrahydrofuran was removed on a spin evaporator. The aqueous residue was extracted with ether, to remove neutral products of the reaction. The remaining alkaline solution was acidified with 10 percent H₂SO₄ and extracted with ether. Evaporation of the ether extract to dryness gave 5.14 g (16.3 mmoles) of off-white powder, m.p. 183-186° (72.8 percent yield, based on benzylolithium). One recrystallization from benzene gave 4.67 g of white solid, m.p. 185-187°. This acid gave no depression of m.p. when mixed with an authentic sample² of 2,2,4-triphenylbutanoic acid. Thus, benzylolithium adds to 1,1-diphenylethene in tetrahydrofuran in good yield. This addition reaction has been reported⁷⁶ to proceed in good yield in refluxing ethyl ether.

Addition of Phenyllithium to 1,1-Diphenylethene

Phenyllithium (33.9 mmoles, 67.9 percent yield)³⁹ was prepared⁷⁵ in the manner previously described by the reaction of 5.63 g (0.050 mole) of chlorobenzene with 1.04 g (0.150 g atom) of lithium in 250 ml of tetrahydro-

76. K. Ziegler and F. Dersch, Ber., 64, 448 (1931).

furan at 10°. To this solution at 0°, 7.21 g (40.0 mmoles) of 1,1-diphenylethene was added dropwise, over a period of 30 minutes. The mixture was stirred at 0° for 30 minutes and the resulting maroon solution was carbonated. Unreacted lithium was destroyed by adding 200 ml of water, and tetrahydrofuran was removed on a spin evaporator. The aqueous residue was extracted with ether, to remove neutral products of the reaction. The alkaline solution remaining was acidified with 10 percent HCl and extracted with ether. Evaporation of the ether extract to dryness gave 7.12 g of yellow solid. This product was subjected to vacuum sublimation at 0.01 mm. The fraction collected at 50-100° weighed 1.42 g (11.6 mmoles, 34.4 percent yield) and had m.p. 120-122°. A mixture of this acid with an authentic sample of benzoic acid showed no depression of m.p. The fraction collected at 120-200° weighed 3.63 g (11.8 mmoles, 35.0 percent yield). This sticky yellow solid gave, after three recrystallizations from methanol, 1.82 g of white powder, m.p. 130.0-131.5°. The infrared spectrum of this acid was identical to that of an authentic sample of 2,2,3-triphenylpropanoic acid.* This is believed to be the first successful addition of phenyllithium to 1,1-diphenylethene, although the addition of phenyllithium to other conjugated olefins has been reported.⁷⁷ Ziegler and Dersch⁷⁶ reported that phenyllithium does not add to 1,1-diphenylethene in refluxing diethyl ether.

Addition of *n*-Butyllithium to 1,1-Diphenylethene

n-Butyllithium (38.0 mmoles, 76.0 percent yield)³⁹ was prepared⁷¹ in the manner previously described by the reaction of 4.67 g (0.050 mole) of

* Synthesized by L. P. Williams, Jr.¹

77. K. Ziegler and W. Schaefer, Ann., 511, 101 (1934).

1-chlorobutane with 1.73 g (0.250 g atom) of lithium in 250 ml of tetrahydrofuran at 10°. To this solution at 0°, 7.21 g (40.0 mmoles) of 1,1-diphenylethene was added dropwise, over a period of 20 minutes. The mixture was stirred at 0° for 30 minutes and the resulting red solution was carbonated. Work-up in the usual manner* gave 3.93 g of viscous oil, which, after crystallization from ethanol, afforded 2.73 g (10.2 mmoles, 26.8 percent yield, based on n-butyllithium) of off-white powder, m.p. 128-131°. Three further recrystallizations from ethanol gave 1.39 g of white solid, m.p. 131-133° (reported⁷⁸ m.p. of 2,2-diphenylhexanoic acid: 130-132°). Waack and Stevenson⁷⁹ observed that n-butyllithium adds very readily to 1,1-diphenylethene in tetrahydrofuran at 20° (no yield given).

Addition of Isopropyllithium to 1,1-Diphenylethene

Isopropyllithium (30.3 mmoles, 20.2 percent yield)³⁹ was prepared⁷³ in the manner previously described from the reaction of 11.8 g (0.150 mole) of 2-chloropropane with 5.21 g (0.750 g atom) of lithium in tetrahydrofuran at -50°. To this solution at -15° (containing 8.01 mmoles of isopropyllithium), a solution of 1.44 g (8.00 mmoles) of 1,1-diphenylethene in 25 ml of dry tetrahydrofuran was added over a period of ten minutes. The resulting purple solution was stirred at -15° for ten minutes and then carbonated. Work-up in the usual manner** gave 3.29 g of sticky, yellow solid, which,

* No attempt was made to isolate valeric acid.

78. A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan and R. Kh. Bostandzhyan, Doklady Akad. Nauk Armyan. S.S.R., 28, No. 1, 11 (1959).

79. R. Waack and P. E. Stevenson, J. Am. Chem. Soc., 87, 1183 (1965).

** No attempt was made to isolate isobutyric acid.

after a recrystallization from cyclohexane, afforded 2.03 g (7.57 mmoles, 94.6 percent yield, based on isopropyllithium) of white powder, m.p. 120-122°. The infrared spectrum of this acid was identical to that of a sample of 4-methyl-2,2-diphenylpentanoic acid from the mixed rearrangement of 2,2,3-triphenylpropyllithium with added isopropyllithium. Thus, isopropyllithium adds to 1,1-diphenylethene in tetrahydrofuran in nearly quantitative yield. Ziegler and Dersch reported⁷⁶ the addition of isopropyllithium to 1,1-diphenylethene in refluxing ethyl ether, but the yield of the adduct was not given.

2-m-Biphenyl-2,2-bis(p-biphenyl)ethylolithium

Formation and Carbonation at -65°

To a 500-ml Morton flask (previously flame-dried under a stream of dry nitrogen) containing 200 ml of tetrahydrofuran (freshly distilled from NaAlH_4) was added 0.153 g (22.0 mg atoms) of lithium and about two percent of a solution of 3.00 g (5.75 mmoles) of 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane in 100 ml of dry tetrahydrofuran. The entire apparatus was under an atmosphere of dry nitrogen. The solution was stirred vigorously at $0 \pm 5^\circ$ until a faint purple color appeared (two hours). The reaction temperature was lowered to $-65 \pm 5^\circ$ and the balance of the chloride added over a period of 30 minutes. The resulting solution was stirred at $-65 \pm 5^\circ$ for three hours and then carbonated. The color of the solution just prior to carbonation was deep purple; analysis³⁹ showed the presence of 2.88 mmoles (50.1 percent yield) of 2-m-biphenyl-2,2-bis(p-biphenyl)-ethylolithium. Unreacted lithium was destroyed by adding 200 ml of 10 percent H_2SO_4 . Ether (200 ml) was added and the organic phase was separated

and allowed to evaporate to dryness. The yellow solid residue (2.96 g) was stirred (magnetic stirrer) for three hours with 500 ml of two percent aqueous KOH. Undissolved solid (2.08 g) was isolated by filtration and had m.p. 190-225°. The filtrate was acidified with HCl and the solid (0.722 g, 1.36 mmoles, 23.7 percent yield) which separated from solution was isolated by filtration and had m.p. 225-228°. This acid, after three recrystallizations from ethanol, gave 0.322 g of white crystalline solid, m.p. 226.5-228.0°. This acid gave no depression of m.p. when mixed with an authentic sample of 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid. Moreover, infrared spectra of the acid from the rearrangement and the independently synthesized sample were identical.

Formation and Rearrangement at 0°

To a 500-ml Morton flask (previously flame-dried under a stream of dry nitrogen) containing 200 ml of tetrahydrofuran (freshly distilled from NaAlH_4) was added 0.133 g (19.2 mg atoms) of lithium and about 10 percent of a solution of 2.50 g (4.80 mmoles) of 2-chloro-1-m-biphenyl-1,1-bis-(p-biphenyl)ethane in 100 ml of dry tetrahydrofuran. The entire apparatus was under an atmosphere of dry nitrogen. The solution was stirred vigorously at $0 \pm 5^\circ$ until a purple color appeared (one hour). The balance of the chloride was added over a period of 30 minutes at 0° , and the solution was stirred at that temperature for six hours before carbonation. The color of the solution just prior to carbonation was blue-purple; analysis³⁹ showed the presence of 2.17 mmoles (45.2 percent yield) of organolithium compound. Work-up in the manner described for the previous reaction gave 1.88 g of neutral product, m.p. 109-177°, and 0.995 g (1.87 mmoles, 39.0 percent yield) of acidic product, m.p. 208.0-209.5°. This acid showed no depression of m.p.

when mixed with an independently synthesized sample of 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid. Mixtures (about 50-50) of this rearrangement product with 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid and with 3-m-biphenyl-2,2-bis(p-biphenyl)propanoic acid had m.p. 201-219° and 180-202°, respectively. The infrared spectrum of the acid was identical to the spectrum of an independently synthesized sample of 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid. The infrared spectrum showed strong absorptions at 3.3 μ (broad), 5.95 μ , 7.84 μ , 10.7 μ (broad), 13.40 μ and 14.41 μ . The infrared spectrum of 3-m-biphenyl-2,2-bis(p-biphenyl)propanoic acid was identical to the above spectrum, except that the absorptions at 13.4 μ and 14.4 μ were broadened. The infrared spectrum of 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid was rather different from the above two spectra, and it showed strong absorptions at 3.5 μ (broad), 5.95 μ , 7.8 μ (broad), 10.7 μ (broad), 13.34 μ , and 14.40 μ . The crude rearrangement product (0.9861 g, m.p. 208.0-209.5°) was diluted with 0.1368 g (0.2613 mmole) of 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid-1-C-14 (specific activity $9.793 \pm 0.002 \mu\text{c}/\text{mmole}$) and m.p. 209.0-210.0°, and the mixture was dissolved in ethanol and recrystallized to constant specific activity (see Table 4). After four recrystallizations from ethanol and a recrystallization from benzene, the acid had m.p. 209.0-210.0° and specific activity $1.227 \pm 0.005 \mu\text{c}/\text{mmole}$. From this data, it follows that 98.1 ± 0.5 percent of the crude rearrangement acid was 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid.

$$\text{total activity } (\mu\text{c}) = aA = (a+b)C$$

where a = mmoles of tracer added

b = mmoles of diluent

Table 4. Isotopic Dilution Analysis of the Products of the Rearrangement of 2-m-Biphenyl-2,2-bis(p-biphenyl)ethylolithium

Sample	Purification	m.p. °C	Spec. act. μc/mole
<u>2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14</u>			
Sample I	4 recryst. from ethanol	209.0-210.0°	9.791 9.793
Sample II	2 recryst. of Sample I from benzene	209.1-210.0°	9.788 9.794
<u>2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14 Diluted with the Acidic Product of the Rearrangement at 0°</u>			
Sample A	4 recryst. from ethanol	209.0-210.0°	1.222 1.232
Sample B	one recryst. of Sample A from benzene	209.0-210.0°	1.225 1.229
<u>2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14 Diluted with the Acidic Product of the Reaction at -65°, Then Rearrangement at 0°</u>			
Sample a	4 recryst. from ethanol	209.0-210.0°	1.512 1.503
Sample b	two recryst. of Sample a from benzene	209.2-210.1°	1.502 1.509

Samples were determined in duplicate with no more than 24 hours delay between runs.

A = specific activity of tracer ($\mu\text{c}/\text{mmole}$)

C = specific activity of mixture ($\mu\text{c}/\text{mmole}$)

$$(0.2613)(9.793) = (0.2613 + b)(1.227)$$

$$b = 1.824 \text{ mmoles} = 0.9674 \text{ g}$$

$$\frac{0.9674}{0.9861} \times 100 = 98.1\%$$

Formation at -65° and Rearrangement at 0°

To a 500-ml Morton flask (previously flame-dried under a stream of dry nitrogen) containing 200 ml of tetrahydrofuran (freshly distilled from NaAlH_4) was added 0.106 g (15.4 mg atoms) of lithium and about two percent of a solution of 2.00 g (3.84 mmoles) of 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane in 100 ml of dry tetrahydrofuran. The entire apparatus was under an atmosphere of dry nitrogen. The solution was stirred vigorously at $0 \pm 5^\circ$ until a faint blue color appeared (one hour). The reaction temperature was lowered to $-65 \pm 5^\circ$ and the balance of the chloride added over a period of 20 minutes. The resulting solution was stirred at $-65 \pm 5^\circ$ for three hours. Analysis³⁹ showed the presence of 1.49 mmoles (38.8 percent yield) of 2-m-biphenyl-2,2-bis(p-biphenyl)ethylolithium. The dark blue solution was allowed to warm to $0 \pm 5^\circ$ and was stirred at that temperature for four hours before carbonation. Work-up in the manner previously described gave 1.33 g of neutral product, m.p. $79-132^\circ$, and 0.781 g (1.47 mmoles, 38.3 percent yield) of acidic product, m.p. $205-208^\circ$. This acid showed no depression of m.p. when mixed with an authentic sample of 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid; its infrared spectrum was identical to that of the authentic sample. Mixtures of this re-

arrangement product with 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid and with 3-m-biphenyl-2,2-bis(p-biphenyl)propanoic acid showed large depressions of melting point. The crude rearrangement product (0.7802 g, m.p. 205-208°) was diluted with 0.1400 g (0.2640 mmole) of 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid-1-C-14 (specific activity 9.793 ± 0.002 $\mu\text{C}/\text{mmole}$ and m.p. 209.0-210.0°), and the mixture was dissolved in ethanol and recrystallized to constant specific activity (see Table 4). After four recrystallizations from ethanol and two recrystallizations from benzene, the acid had m.p. 209.2-210.1° and specific activity 1.508 ± 0.005 $\mu\text{C}/\text{mmole}$. From this data, it can be calculated (see previous run) that $98.6 \pm 0.4\%$ of the crude rearrangement acid was 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid.

Dibenzyltrimethylammonium Halides

Heterogeneous Reaction of Dibenzyltrimethylammonium Bromide with Benzyl-lithium- α -C-14

Benzyl-lithium- α -C-14 (70.3 mmoles, 64.0 percent yield) was prepared⁶⁶ in the manner previously described by the reaction of 13.8 g (0.110 mole) of benzyl methyl ether- α -C-14 with 11.4 g (1.65 g atoms) of lithium in 600 ml of tetrahydrofuran at -10°. A 225 ml aliquot of this solution, containing 26.3 mmoles of benzyl-lithium- α -C-14, was carbonated. To the remaining 44.0 mmoles of benzyl-lithium- α -C-14 in 375 ml of tetrahydrofuran at 10° was rapidly added 9.57 g (29.3 mmoles) of solid dibenzyltrimethylammonium bromide. The reaction was not noticeably exothermal at this temperature, so the reaction temperature was raised to 20° and the mixture stirred vigorously for two and one-half hours. The reaction was quenched by adding

50 ml of water and the products worked up according to the procedure of Wittig and co-workers.²⁵ The tetrahydrofuran was removed by distillation through a 30-cm Vigreux column and the aqueous residue was extracted with ether. The ether extract was allowed to evaporate to dryness, and the yellow, oily residue was dissolved in 50 ml of 2N H_2SO_4 . Addition of 7 ml of concd. HCl caused the hydrochloride of the product of Sommelet rearrangement, dimethyl(o-methylbenzhydryl)amine, to precipitate. Treatment of the hydrochloride with 50 ml of five percent NaOH generated the amine (3.50 g, 15.6 mmoles, 53.2 percent yield), m.p. 48-50°. The product of Stevens rearrangement, dimethyl(1,2-diphenylethyl)amine, was recovered from the H_2SO_4 -HCl solution by treating the solution with NaOH, extracting the amine with ether, and evaporating the ether solution to dryness. The resulting yellow oil (2.01 g, 8.95 mmoles, 30.5 percent yield) was dissolved in 10 ml of 95 percent ethanol and this solution added to 10 ml of a saturated solution of picric acid in 95 percent ethanol. The dark yellow solid (1.80 g) which precipitated immediately was isolated by filtration and had m.p. 155-156° (reported²⁵ m.p. of the picrate of dimethyl(1,2-diphenylethyl)amine: 156°). The bright yellow picrate of dimethyl(o-methylbenzhydryl)amine (1.30 g) was formed in the same manner and had m.p. 176-177° (reported²⁵ m.p.: 178°). Phenylacetic acid (0.420 g, m.p. 75-76°) was isolated in the usual manner from the carbonated solution of benzyllithium- α -C-14. After three recrystallizations from carbon tetrachloride, the acid had m.p. 75.6-76.4° and specific activity 2.226 ± 0.004 $\mu\text{c}/\text{mmole}$. Both picrates were assayed, and the activity of each was indistinguishable from background activity. If 15 percent of the background activity is attributed to the picrates, the maximum specific activity of the picrates is calculated to be

0.0005 $\mu\text{C}/\text{mmole}$.

Homogeneous Reaction of Dibenzyltrimethylammonium Iodide with Benzylolithium- α -C-14

Benzylolithium- α -C-14 (86.8 mmoles, 86.8 percent yield) was prepared⁶⁶ in the manner previously described by the reaction of 12.2 g (0.100 mole) of benzyl methyl ether- α -C-14 with 10.4 g (1.50 g atoms) of lithium in 550 ml of tetrahydrofuran at -10° . A 300 ml aliquot of this solution, containing 47.4 mmoles of benzylolithium at 25° , was added rapidly to a 1000-ml Morton flask containing a solution of 1.00 g (2.84 mmoles) of dibenzyltrimethylammonium iodide in 550 ml of dry tetrahydrofuran at the same temperature. The resulting solution was stirred at 25° for three hours before carbonation. The remainder of the initial solution of benzylolithium- α -C-14 was also carbonated. Water (150 ml) was added to the carbonated mixture of rearrangement products, and the tetrahydrofuran was removed by distillation through a 20-cm Vigreux column. The alkaline residue was extracted with ether to remove neutral and basic products of the reaction. The ether extract was condensed to an oily residue which was dissolved in 25 ml of 2N H_2SO_4 . The addition of 5 ml of concd. HCl caused precipitation of the hydrochloride of one of the amines. Treatment of this hydrochloride with 10 percent NaOH afforded 0.183 g (0.904 mmole) of dimethyl(o-methylbenzhydryl)amine, m.p. $49.5-51.0^\circ$ (28.6 percent yield). The acid solution of the other amine was made alkaline with 15 percent KOH and extracted with ether. Evaporation of the ether extract gave 0.384 g (1.96 mmoles, 60.0 percent yield) of orange oil, assumed to be dimethyl(1,2-diphenylethyl)amine. The picrate of each of the amines was formed by combining an ethanol solution of the amine with a saturated ethanol solution of picric acid and chilling

the resulting solution in an ice bath for several hours. The crude picrate of dimethyl(o-methylbenzhydryl)amine (0.360 g, m.p. 176-178°) gave, after three recrystallizations from ethanol, 0.302 g (88.5 percent yield, based on the amine) of yellow crystals, m.p. 177.0-178.0°. The crude picrate of dimethyl(1,2-diphenylethyl)amine (0.673 g, m.p. 152-155°) gave, after three recrystallizations from ethanol, 0.496 g (56.3 percent yield, based on the amine) of dark yellow crystals, m.p. 155.2-156.5°. The phenylacetic acid- α -C-14 from the rearrangement was isolated by acidification of the aqueous alkaline solution remaining after the removal of the amine by ether extraction. A yellow solid (2.04 g, 15.0 μ moles) was isolated. This acid was purified to constant specific activity (see Table 5). After a vacuum sublimation (50-80° and 0.01 mm) and three recrystallizations from cyclohexane, this sample of phenylacetic acid had m.p. 76.5-77.5° and specific activity $2.711 \pm 0.013 \mu\text{c}/\text{mmole}$. The phenylacetic acid- α -C-14 obtained by direct carbonation (3.12 g, 22.9 μ moles) was isolated in the usual manner and had m.p. 70-75°. After a vacuum sublimation at 50-80° and 0.01 mm, the acid had m.p. 74-76°; it was then recrystallized to constant specific activity (see Table 5). After two recrystallizations from cyclohexane, this sample of phenylacetic acid had m.p. 76.0-77.4° and specific activity $2.713 \pm 0.008 \mu\text{c}/\text{mmole}$. Both picrates were assayed and the activity of each was indistinguishable from background activity. If 15 percent of the background activity is attributed to the picrates, the maximum specific activity of the picrates is calculated to be $0.0004 \mu\text{c}/\text{mmole}$. Thus, benzyl-lithium- α -C-14 is not incorporated during the rearrangement of dibenzyl-dimethylammonium iodide in tetrahydrofuran.

Table 5. Specific Activity of Phenylacetic Acids
from the Rearrangement of Dibenzyl-di-
methylanmonium Iodide

Sample	Purification	m.p. °C	Spec. act. μc/mmole
<u>Phenylacetic Acid from Direct Carbonation</u>			
Sample A	one vac. sublim. and a recryst. from cyclohexane	74-76°	2.711
Sample B	two recryst. of Sample A from cyclohexane	76.0-77.4°	2.706 2.723
<u>Phenylacetic Acid from the Rearrangement</u>			
Sample a	one vac. sublim. and a recryst. from cyclohexane	75.0-76.5°	2.715
Sample b	two recryst. of Sample a from cyclohexane	76.5-77.5°	2.698 2.724

Sample B and Sample b were assayed, in duplicate, on the same day.

CHAPTER V

DISCUSSION

Syntheses2-Chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane

This halide, the precursor to 2-m-biphenyl-2,2-bis(p-biphenyl)-ethylolithium, was prepared in an overall yield of about 20 percent from 4-biphenylcarboxylic acid, according to the synthetic route shown in Figure 1. The intermediate bromobis(p-biphenyl)methane was readily prepared from the starting material, 4-biphenylcarboxylic acid. An attempt to couple this bromide with 3-lithiobiphenyl gave only the product of halogen-metal interchange,⁸⁰ 1,1,2,2-tetrakis(p-biphenyl)ethane, in 70 percent yield. The reaction of bromobis(p-biphenyl)methane with 3-m-biphenylmagnesium bromide in tetrahydrofuran gave 1,1,2,2-tetrakis(p-biphenyl)ethane in 85 percent yield. Although halogen-metal interchange in reactions of Grignard reagents has been reported⁸¹ to be more facile in tetrahydrofuran than in ether, the high yield of symmetrical coupling product observed in this reaction was somewhat surprising. The reaction of bromobis(p-biphenyl)methane with m-biphenylmagnesium bromide in ether-benzene gave the desired unsymmetrical coupling product, m-biphenyl-bis(p-biphenyl)methane, in 60 percent yield. The metalation of this

80. R. Adams (Ed.-in-Chief), Organic Reactions, Vol. VIII, John Wiley & Sons, Inc., New York, 1954, p. 258.

81. L. I. Zakharkin, O. Yu. Okhlobystin and K. A. Bilevitch, J. Organometal. Chem., 2, 309 (1964).

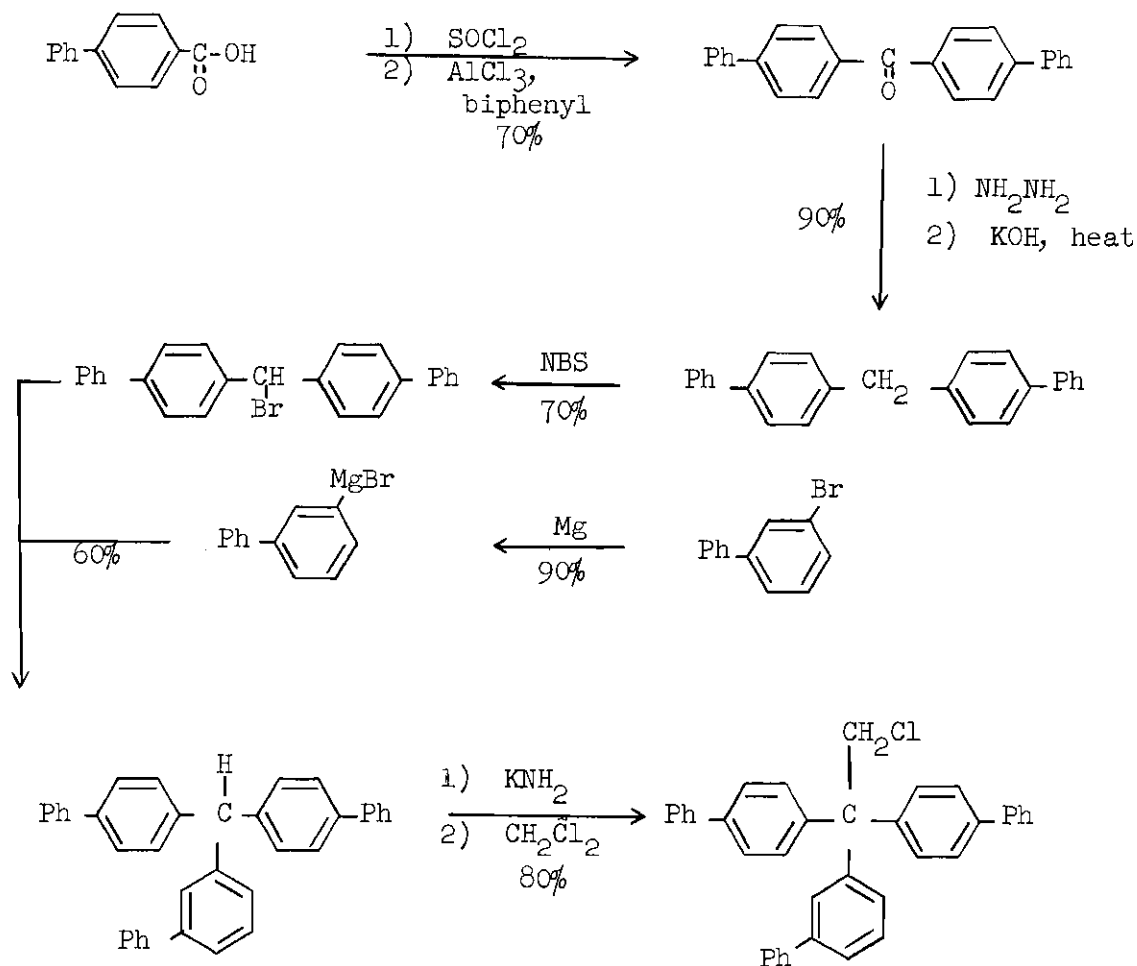


Figure 1. Synthetic Route to 2-Chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane

hydrocarbon by potassium amide was successfully carried out in liquid ammonia-ether, and the resulting deep blue solution of organopotassium compound reacted readily with carefully purified methylene chloride to give the desired 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane.

3-m-Biphenyl-3,3-bis(p-biphenyl)propanoic Acid

This carboxylic acid was prepared following the synthetic route shown in Figure 2. The reaction of 3-lithiobiphenyl with 4,4'-biphenylbenzophenone gave fair yields (50-60 percent) of m-biphenylbis(p-biphenyl)carbinol which was highly contaminated with unreacted ketone. High-

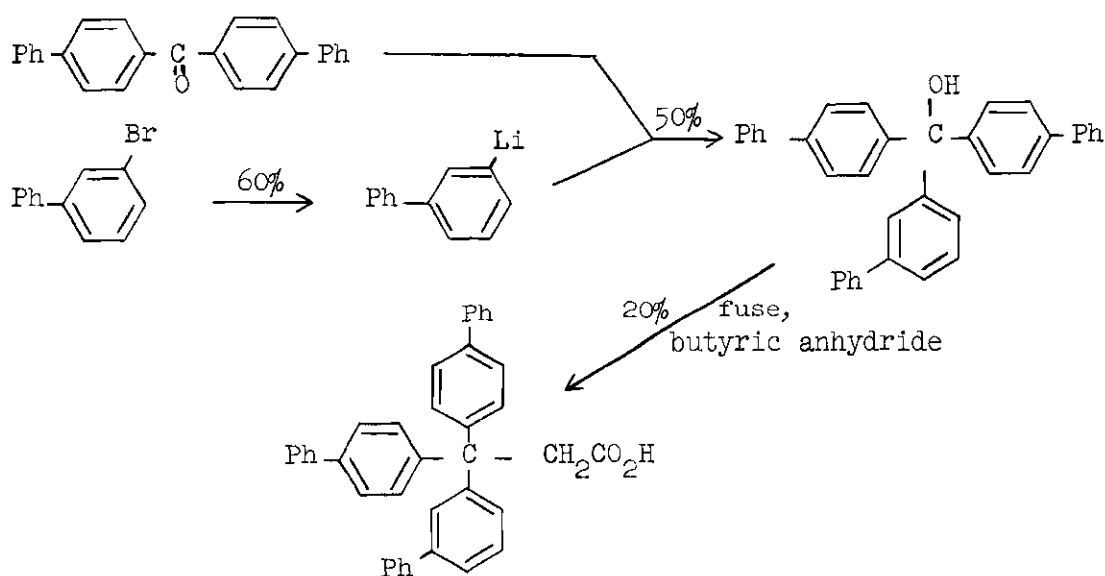


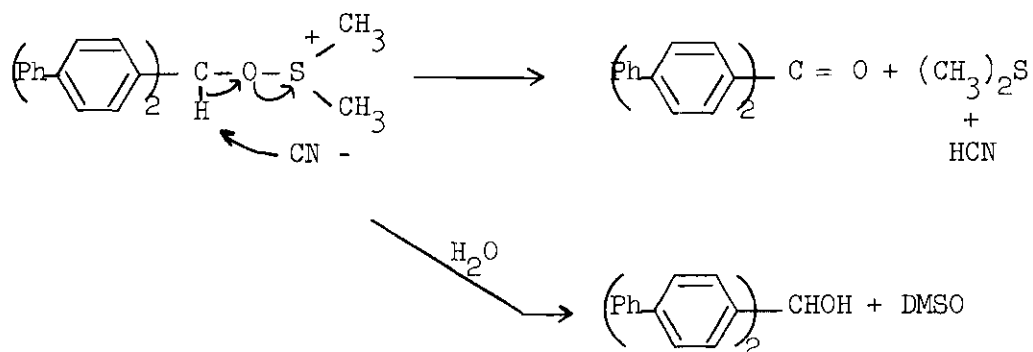
Figure 2. Synthetic Route to 3-m-Biphenyl-3,3-bis-(p)-biphenylpropanoic Acid

speed stirring and long reaction times did not improve the yield or purity of the product, probably because the adduct formed was insoluble in tetrahydrofuran and coated over sparingly soluble, unreacted ketone as the reaction progressed. The ketone contaminating the product could be removed by repeated recrystallization from benzene, but only a 20 percent yield of pure carbinol was obtained following this purification procedure. The fusion of this carbinol with malonic acid,⁵¹ with or without added acetic anhydride,⁵² gave only unreacted starting materials. In the presence of the higher-boiling butyric anhydride, however, the carbinol reacted with malonic acid to give the desired 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid.

3-m-Biphenyl-2,2-bis(p-biphenyl)propanoic Acid-1-C-14

This carboxylic acid was prepared following the synthetic route outlined in Figure 3. The intermediate bromobis(p-biphenyl)methane was readily obtained from the starting material, 4-biphenylcarboxylic acid. This benzhydrylic bromide, upon fusion with cuprous cyanide,⁵³ gave the corresponding nitrile. Attempts to form the nitrile by an ionic reaction of the bromide with sodium cyanide were all unsuccessful. The reaction of bromobis(p-biphenyl)methane with sodium cyanide in dimethyl sulfoxide* (followed by the addition of water) gave 4,4'-diphenylbenzophenone and bis(p-biphenyl)carbinol, possibly via alkylation of the solvent, followed by base-catalyzed elimination:

*Y. M. Cheng, following the procedure of Cope [A. C. Cope and A. S. Mehta, J. Am. Chem. Soc., **86**, 5626 (1964)], synthesized 4,4,4-triphenylpentanenitrile by the reaction of the corresponding chloride with NaCN and NaI in dimethyl sulfoxide.



Bis(p-biphenyl)ethanenitrile-1-C-14 was somewhat resistant to hydrolysis, but gave the corresponding carboxylic acid when treated with 1M KOH in diethylene glycol at 120° (at 150°, decarboxylation was observed). Methyl bis(p-biphenyl)ethanoate-1-C-14, prepared from the acid by reaction with diazomethane, was alkylated with 3-(bromomethyl)biphenyl, following the general procedure of Hauser.³⁵ Saponification of the adduct gave the desired 3-m-biphenyl-2,2-bis(p-biphenyl)propanoic acid-1-C-14. The overall yield in the synthesis (based on 4-biphenylcarboxylic acid) was about five percent.

2-m-Biphenyl-2,3-bis(p-biphenyl)propanoic Acid-1-C-14

This carboxylic acid was prepared following the synthetic route outlined in Figure 4. The synthesis was entirely analogous to the synthesis of 3-m-biphenyl-2,2-bis(p-biphenyl)propanoic acid-1-C-14. The overall yield was about four percent (based on 3-bromobiphenyl).

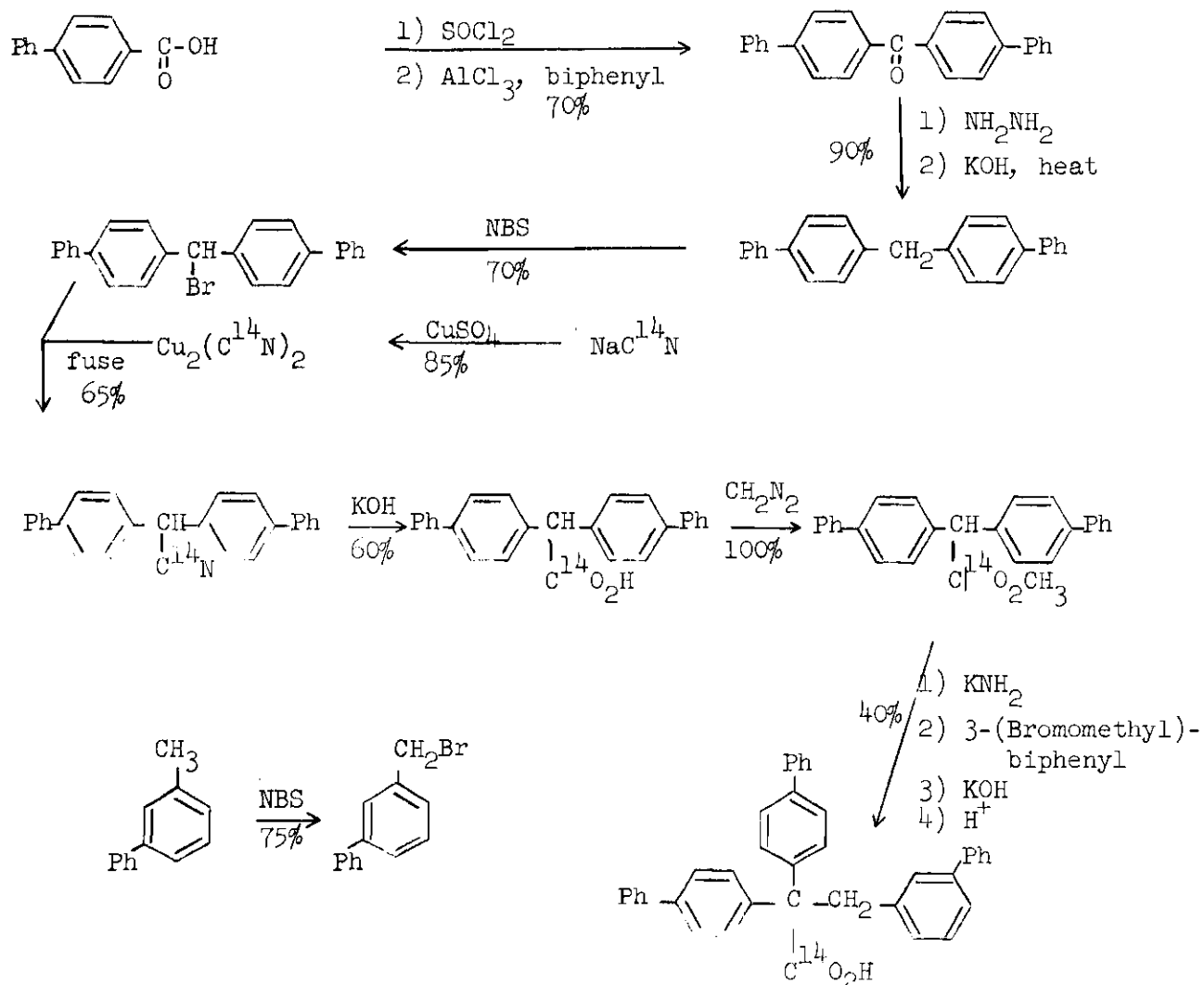


Figure 3. Synthetic Route to 3-m-Biphenyl-1,2-bis(p-biphenyl)propānoic Acid-1-C-¹⁴

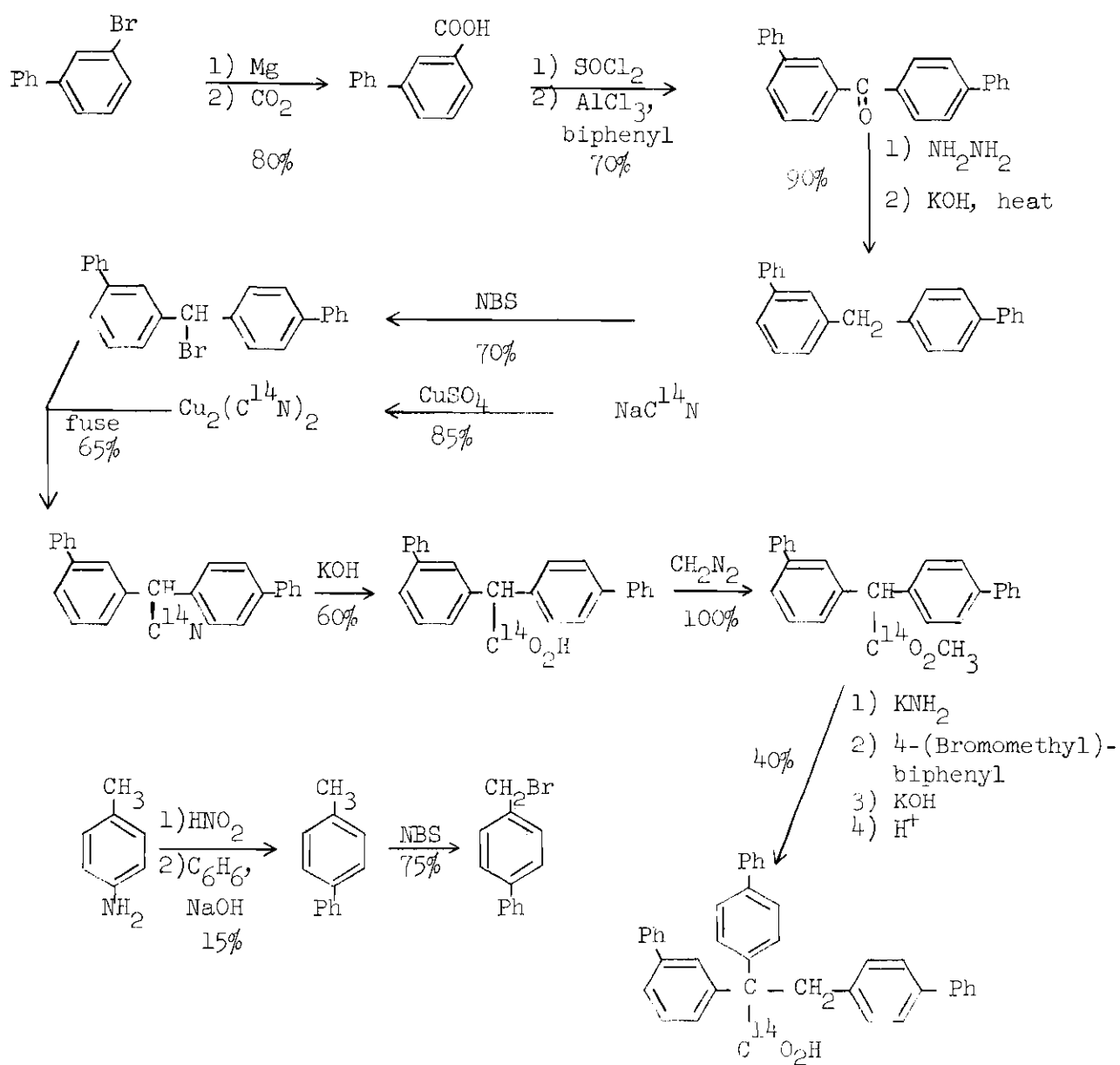
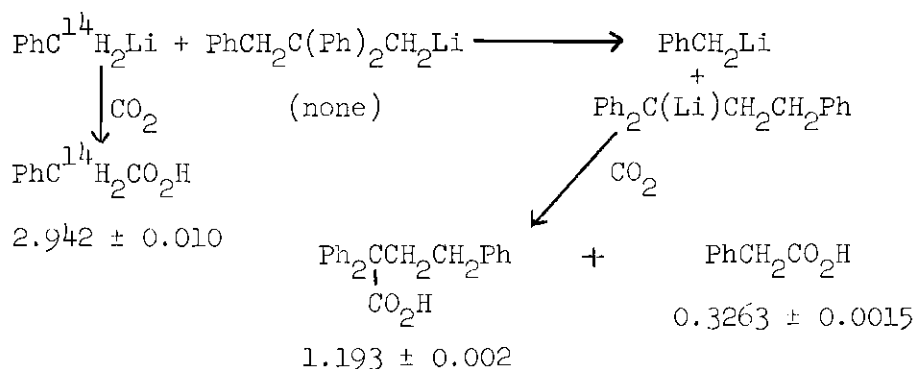


Figure 4. Synthetic Route to 2-m-Biphenyl-2,3-bis(p-biphenyl)propionic Acid-1-C-14

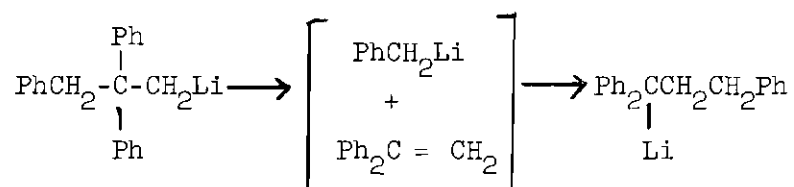
Rearrangements

2,2,3-Triphenylpropyllithium

2,2,3-Triphenylpropyllithium was prepared in tetrahydrofuran at -65° and was allowed to rearrange² at 0° in the presence of radioactive benzyllithium. After preliminary reaction with carbon dioxide, the products of the rearrangement were assayed for carbon-14. The 2,2,4-triphenylbutanoic acid (derived from 1,1,3-triphenylpropyllithium) had specific activity $1.369 \pm 0.008 \mu\text{C}/\text{mmole}$ and the phenylacetic acid (derived from benzyllithium) had specific activity $1.229 \pm 0.006 \mu\text{C}/\text{mmole}$. This preliminary experiment was repeated, since the molar activities of the two products were so similar that radiochemical equilibrium between the benzyllithium and the 1,1,3-triphenylpropyllithium (or between benzyllithium and 2,2,3-triphenylpropyllithium) could not be ruled out. In the second run, the concentrations of the benzyllithium and the 2,2,3-triphenylpropyllithium were determined³⁹ by Gilman titration and the initial activity of the benzyllithium was determined by carbonating a portion of the solution and assaying the resulting phenylacetic acid. In the following reaction sequence, the activities of reactants and products are indicated below each compound assayed in units of microcuries/mmmole. Obviously, the rearranged organolithium compound gained radioactivity at the expense



of the benzyllithium. The 1,1,3-triphenylpropyllithium is not at radiochemical equilibrium with the benzyllithium in solution at the end of this experiment, however, since its molar activity is greater than the final activity of the benzyllithium. For the same reason, 2,2,3-triphenylpropyllithium is not at radiochemical equilibrium with benzyllithium before the rearrangement. Thus, an irreversible exchange of benzyl groups in the reactants takes place during the rearrangement itself, suitably by way of an intermolecular, elimination-readdition mechanism.⁸²

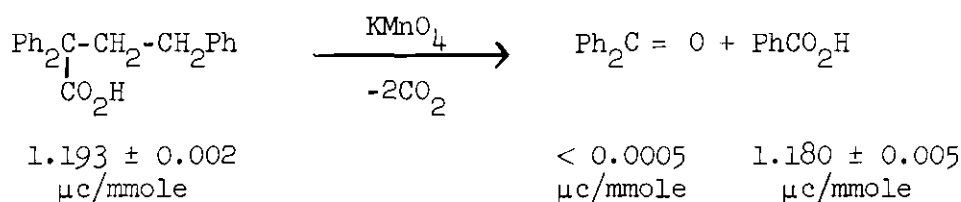


The radioactivity data are in good quantitative agreement with this conclusion, providing that the benzyllithium which re-adds to the 1,1-diphenylethene intermediate has the same activity as that of the benzyllithium in the bulk of the solution. Assuming that the isotope effect is negligible, one can derive the expression $dx/dy = (A-x)/B$, where A and B are the number of microcuries and millimoles, respectively, of benzyllithium at the start of the reaction; x and y are the number of microcuries and millimoles, respectively, of 1,1,3-triphenylpropyllithium formed. Integration of this expression gives $y = B \ln [A/(A-x)]$, where A and B are known. Since rearrangement is complete under the conditions of the experiment, y

82. E. Grovenstein, Jr. and G. Wentworth, J. Am. Chem. Soc., **85**, 3305 (1963).

is taken to be equal to the number of millimoles of 2,2,3-triphenylpropyl-lithium initially present. The molar activities of 2,2,4-triphenylbutanoic acid and phenylacetic acid calculated using this expression are 1.20 ± 0.03 and 0.335 ± 0.010 $\mu\text{c}/\text{mmole}$, respectively^{*}; these values are in excellent agreement with the experimental data.

The 2,2,4-triphenylbutanoic acid from the rearrangement gave, upon oxidation with KMnO_4 , benzophenone and benzoic acid. It was found that all of the activity of the 2,2,4-triphenylbutanoic acid was contained in the benzoic acid; i.e., the carbon-14 was originally in the 4-position of the 2,2,4-triphenylbutanoic acid. The slightly low value for the specific

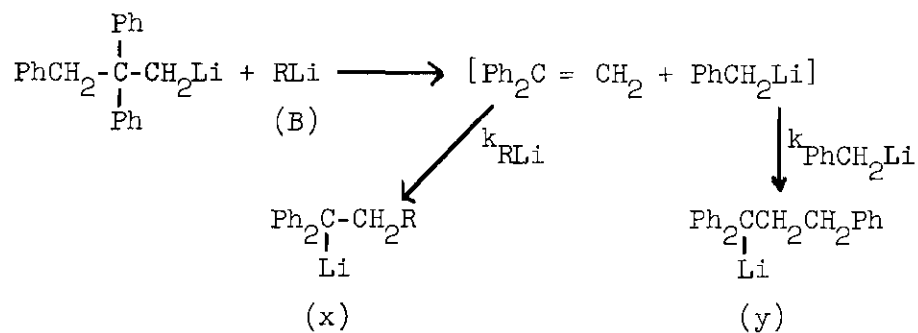


activity of the benzoic acid may be due to oxidation of a small amount of benzophenone to benzoic acid.

It was of interest to determine why 2,2,3-triphenylpropyllithium, which is present initially in high concentration, does not compete successfully with benzyllithium in the addition to 1,1-diphenylethene. Accordingly, a series of incorporation experiments, analogous to the above experiment involving radioactive benzyllithium, were run in which 2,2,3-triphenylpropyllithium was allowed to rearrange in the presence of a number of organolithium

^{*}The rather large limits of error are due primarily to uncertainties in the determination of the concentrations of organolithium compounds by Gilman titration (See Appendix B).

compounds and the relative extents of incorporation were determined. The relative rate constants (Table 6) were calculated from the following expression:



$$\frac{dy}{dx} = \frac{k_{\text{PhCH}_2\text{Li}}}{k_{\text{RLi}}} \left(\frac{x}{B-x} \right) = K \left(\frac{x}{B-x} \right)$$

which upon integration gives

$$y = -Kx - BK \ln(B-x) + BK \ln B$$

Table 6. Relative Rate Constants for Addition of RLi to 1,1-Diphenylethene and for Metalation of Triphenylmethane

RLi	Addition to 1,1-Diphenylethene	Metalation of Triphenylmethane ⁸³
PhLi	< 0.00083 (0°)	0.022 (22°)
EtLi	< 0.00022 (0°)	---
<u>n</u> -BuLi	< 0.00019 (0°)	0.066 (22°)
<u>i</u> -PrLi	0.062 ± 0.035	---
PhCH ₂ Li	1.00	1.00

83. R. Waack and P. West, J. Am. Chem. Soc., 86, 4494 (1964).

The constants for phenyllithium, ethyllithium and butyllithium represent maximum values; i.e., no incorporation was observed. The uncertainty in the value for isopropyllithium is due primarily to the fact that the precise concentration of isopropyllithium at the time of the rearrangement is unknown. This is because of the instability of isopropyllithium in tetrahydrofuran at -15° . Ethyl- and n-butyllithium should be good models for 2,2,3-triphenylpropyllithium, except for the steric and electronic effects of the phenyl groups on the latter compound, which should tend to make it even less reactive than n-butyllithium toward addition to 1,1-diphenylethene.

In spite of the low inherent basicity of resonance-stabilized benzyl-lithium,⁸⁴ it has been observed to have a high relative reactivity as an initiator of vinyl polymerization,⁸⁵ and as a nucleophile in the Wurtz coupling reaction with benzyl chloride.⁶⁶ In Table 6, the relative rates of metalation of triphenylmethane by various organolithium compounds⁸³ are given. The relative rates of metalation are in qualitative agreement with the relative rates of addition to 1,1-diphenylethene, but the magnitude of the difference in rates is much greater in the latter case.

The relative reactivity of organolithium compounds should also be influenced by the degree of clustering in solution. Thus, vinylolithium⁷⁹ and butyllithium⁸³ are associated species in tetrahydrofuran, whereas α -styryllithium⁸⁶ is monomeric in the same solvent. Presumably, charge delocalization in the latter compound reduces dipolar attractive forces and favors solvation of the incipient lithium cation.

84. H. Gilman, J. Org. Chem., 27, 1260 (1962).

85. R. Waack and M. A. Doran, Polymers, 2, 365 (1961).

86. S. Bywater and D. J. Worsfold, Can. J. Chem., 40, 1564 (1962).

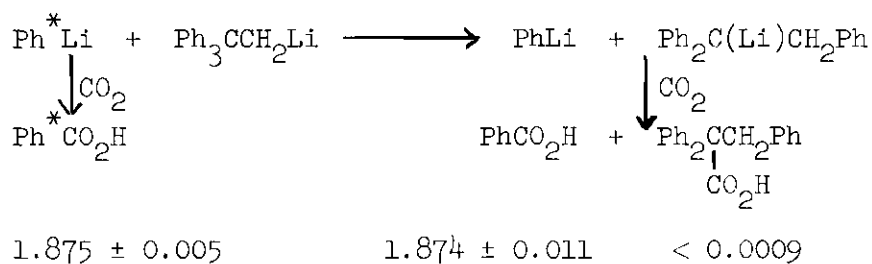
In view of the inertness of most of the alkyllithium compounds tested in Table 6, it seemed advisable to look for the direct addition of these compounds to 1,1-diphenylethene under the conditions of the incorporation experiments. The results are given in Table 7. The yield of adduct was determined by isolation of the corresponding carboxylic acid. The results are qualitatively in agreement with the results of the incorporation experiments.

Table 7. The Direct Addition of Some Organolithium Compounds to 1,1-Diphenylethene in Tetrahydrofuran

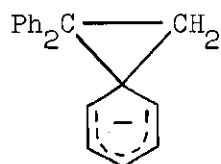
RLi	Reaction Time	Temp.	Yield of Adduct (%)
PhLi	30 min.	0°	35.0
<u>n</u> -BuLi	30 min.	0°	26.8
<u>i</u> -PrLi	10 min.	-15°	94.6
PhCH ₂ Li	20 min.	0°	72.8

2,2,2-Triphenylethyllithium

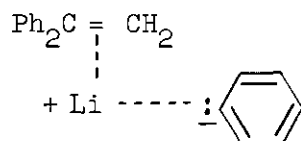
2,2,2-Triphenylethyllithium was prepared in tetrahydrofuran at -60° and was allowed to rearrange¹ in the presence of radioactive phenyllithium at 0°. In the following reaction sequence the activities of reactants and products are indicated below each compound assayed in units of microcuries/mmole.



The 2,2,3-triphenylpropanoic acid obtained was indistinguishable in radioactivity from background radioactivity. It is estimated that less than 0.05 percent (if any) of the activity of the starting phenyllithium could have become incorporated in the 1,1,2-triphenylethyllithium. On the basis of this test, the rearrangement of 2,2,2-triphenylethyllithium could be said to take place by an intramolecular process, involving a bridged intermediate or transition state:



Alternatively,⁸³ 2,2,2-triphenylethyllithium could undergo elimination of phenyl anion and 1,1-diphenylethene in a solvent "cage," and recombination could take place before radioactive phenyllithium could diffuse into the cage. In a recent textbook, Cram⁸⁷ has extended the above argument somewhat, and writes the intramolecular intermediate as an ion pair:



On the basis of the previous experiments, benzyllithium is expected to be

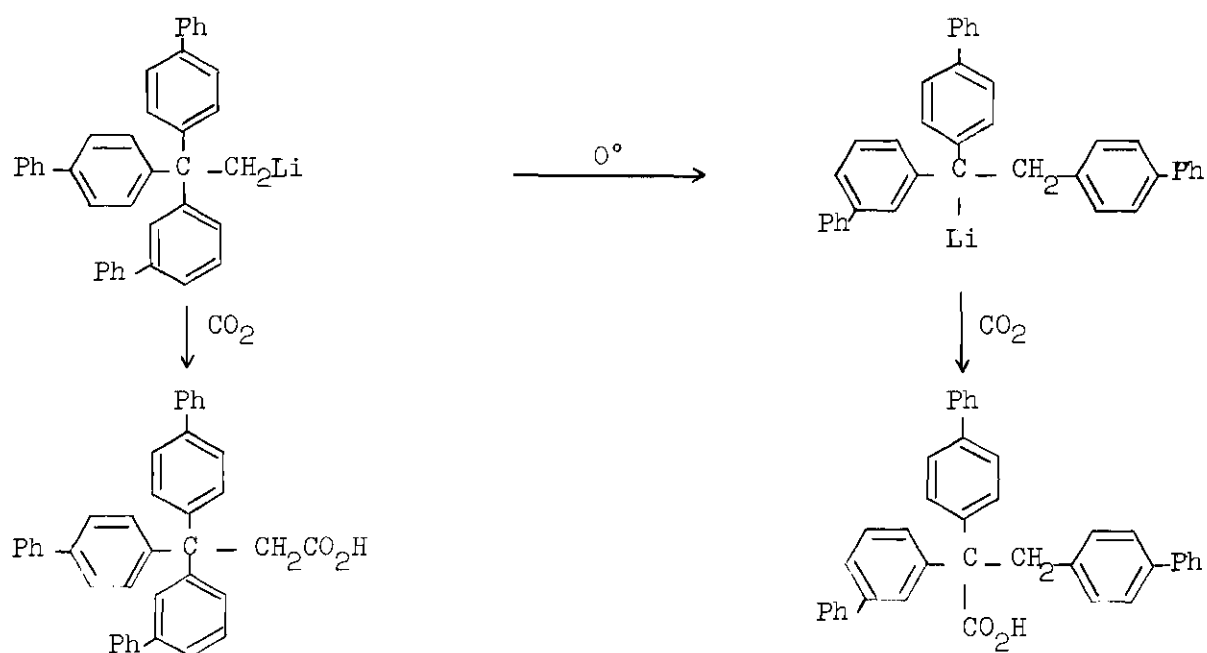
87. D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, p. 237.

much more reactive than phenyllithium toward 1,1-diphenylethene and might, therefore, be able to compete with phenyl anion for the intermediate olefin. Accordingly, 2,2,2-triphenylethyllithium was allowed to rearrange in the presence of benzyllithium. Examination of the products of the rearrangement revealed that less than 0.5 percent (if any) of the benzyllithium had become incorporated during the rearrangement. This constitutes further supporting evidence for an intramolecular mechanism for the rearrangement.

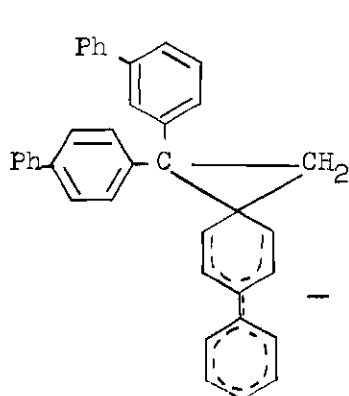
2-m-Biphenyl-2,2-bis(p-biphenyl)ethyllithium

The reaction of 2-chloro-1-m-biphenyl-1,1-bis(p-biphenyl)ethane with lithium in tetrahydrofuran at -65° generated 2-m-biphenyl-2,2-bis(p-biphenyl)ethyllithium, as demonstrated by isolation of 3-m-biphenyl-3,3-bis(p-biphenyl)propanoic acid in 23.7 percent yield upon carbonation. When the solution of this organolithium compound was allowed to warm to 0° for four hours, rearrangement occurred; the 2-m-biphenyl-2,2-bis(p-biphenyl)ethyllithium underwent migration of p-biphenyl to give 1-m-biphenyl-1,2-bis(p-biphenyl)ethyllithium, as demonstrated by carbonation to give 2-m-biphenyl-2,3-bis(p-biphenyl)propanoic acid in 38 percent yield. Isotopic dilution analysis showed that this product of p-biphenyl migration accounted for at least 98.6 ± 0.4 percent of the acidic product isolated.

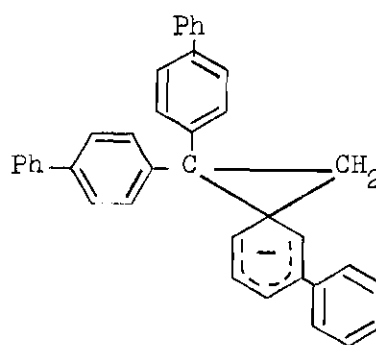
The predominance of p-biphenyl migration provides evidence for the intramolecular mechanism for the rearrangement, involving the intermediate or transition state XII. This intermediate is expected to be of



much lower energy than the corresponding structure for m-biphenyl migration, XIII. There are six contributing structures for the resonance hybrid XII and only three for the corresponding hybrid XIII.

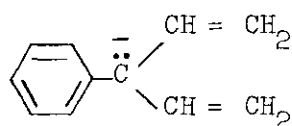


XII



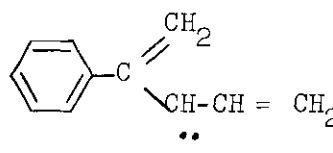
XIII

Molecular orbital calculations⁸⁸ show that the anion XIV is lower in energy than anion XV by 0.097 β . These anions should be good models for anions XVI and XVII, respectively.



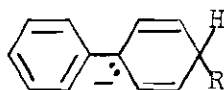
(13.9362344 β)

XIV

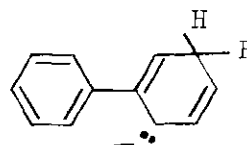


(13.8392282 β)

XV



XVI



XVII

If β for the process of localizing an electron pair in XVI or XVII is taken to be roughly equal to β for the process of localizing a proton in forming the corresponding σ -complex (35 kcal/mole),⁸⁹ a ratio of the equilibrium constants of formation of XVI (K_p) to formation of XVII (K_m) can be calculated:

88. A. Streitwieser, Jr. and J. I. Bauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, New York, 1965, pp. 92, 94.

89. A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, Inc., New York, 1962, p. 342.

$$\Delta F_p^{\circ} = -RT \ln K_p \qquad 0.097 \beta = 3.395 \text{ Kcal/mole}$$

$$\Delta F_m^{\circ} = -RT \ln K_m$$

$$\Delta(\Delta F^{\circ}) = -RT \ln(K_p/K_m) = 3395 \text{ cal.}$$

$$\ln(K_p/K_m) = \frac{3395}{(1.987)(273)} = 6.26$$

$$K_p/K_m = 525$$

This value is to be compared to the minimum ratio (calculated from observed product distribution) of $K_p/K_m \geq (98.6/2)/1.4 \geq 35.2$ for the rearrangement of 2-m-biphenyl-2,2-bis(p-biphenyl)ethylolithium. It is quite possible that 35 kcal/mole is too high a value of β to use in these calculations, since this localization energy refers to the formation of a σ -complex intermediate, an equilibrium process. Since the energy difference between the transition states leading to XVI and XVII is very likely to be less than the energy difference between the intermediates themselves, a smaller value of β should be chosen. If a value of 20 kcal/mole is taken for β , the corresponding value for K_p/K_m is calculated to be 35.7.

A consideration of Hammett σ constants also leads to the conclusion that the intermediate XII should be more stable than the intermediate XIII. For the ionization of substituted phenols, the values for σ_m and σ_p for a phenyl substituent are +0.124 and +0.205, respectively. (These values were calculated from the reported²² pKa values for m-phenyl- and p-phenyl-phenol, by extrapolation on a plot of pKa vs. σ . See references 23 and 24 for a list of the σ_m and σ_p values used in the plot.)

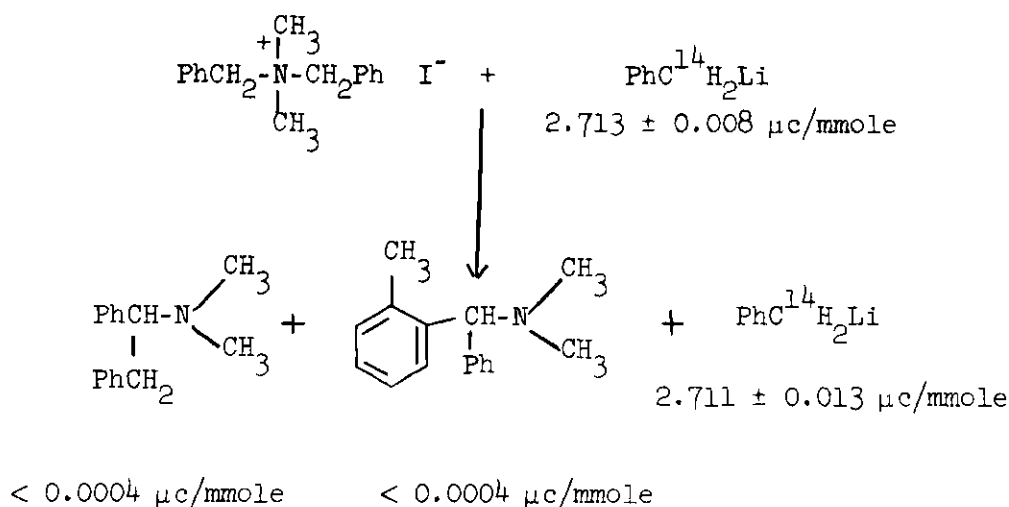
On the other hand, if the rearrangement of 2-m-biphenyl-2,2-bis-

(p-biphenyl)ethylolithium had taken place by an elimination-readdition mechanism, m-biphenyl migration would have been expected to compete favorably with p-biphenyl migration, since the intermediate 3-lithiobiphenyl would be more stable than the alternative 4-lithiobiphenyl.^{18,19} In conclusion, therefore, the rearrangement of 2-m-biphenyl-2,2-bis(p-biphenyl)ethylolithium is believed to occur by way of the bridged intermediate or transition state XII.

In view of the clear-cut preference for p-biphenyl over m-biphenyl migration, it is very likely that the migration of phenyl in 2,2,2-triphenylethylolithium also takes place by an intramolecular mechanism involving a bridged intermediate or transition state. Thus, the previously allowed⁸² possibility of an elimination-readdition mechanism involving an anion plus olefin in a solvent "cage" has been eliminated.

Dibenzyltrimethylammonium Halides

The elimination-readdition mechanism for the Stevens rearrangement of dibenzyltrimethylammonium bromide²⁵ and iodide was tested by allowing the compounds to react with excess radioactive benzylolithium in tetrahydrofuran at 20°. In two runs--one in which the quaternary ammonium bromide was largely undissolved and the other in which the quaternary ammonium iodide was completely dissolved--the products dimethyl(o-methylbenzhydryl)amine and dimethyl(1,2-diphenylethyl)amine in each case showed no detectable radioactivity (0.02 percent or less of the activity of the starting benzylolithium). The activity of the benzylolithium after the rearrangement had taken place was identical to the activity of the starting benzylolithium. Hence it may be concluded that these reactions are intramolecular processes under the conditions tested. This conclusion is in accord with the currently accepted



intramolecular mechanism for the Stevens rearrangement of a number of quaternary ammonium salts.⁹⁰ In a recent communication, Hill and Chan⁹¹ have reported that the potassium t-butoxide-catalyzed rearrangement of optically active allylbenzylmethylphenylammonium iodide in dimethyl sulfoxide gave optically active 3-(N-methylanilino)-4-phenylbutene-1. This transfer of asymmetry from nitrogen to carbon requires either that the rearrangement take place by an S_Ni mechanism, or that a tight unsymmetrical ion pair intermediate be largely undissociated in dimethyl sulfoxide.

Conclusions

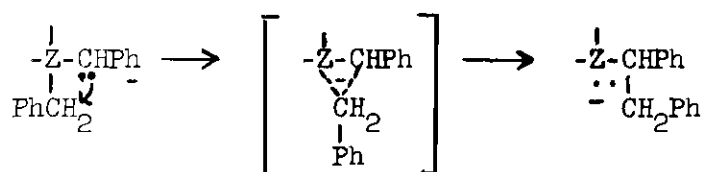
It has been found that the 1,2-migration of benzyl in 2,2,3-triphenylpropyllithium takes place by way of an intermolecular elimination-readdition mechanism. The analogous 1,2-shift of phenyl in 2,2,2-triphenylethyllithium,

90. D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, pp. 223-226, and references cited therein.

91. R. K. Hill and T. Chan, J. Am. Chem. Soc., 88, 866 (1966).

however, takes place by way of an intramolecular mechanism, very likely involving an intermediate "phenanion." Zimmerman¹⁷ has demonstrated, using simple molecular orbital calculations in which the energy of reactants was compared with the energy of the corresponding intramolecular bridged intermediates, that intramolecular 1,2-alkyl migration is expected to be energetically less favorable than the corresponding 1,2-phenyl migration. In the case of benzyl migration, however, an energetically favorable, alternative pathway is available; the migrating alkyl group in this instance is eliminated as a carbanion capable of resonance stabilization. It has been observed² that benzyl migration in 2,2,3-triphenylpropyllithium is much faster than phenyl migration in 2,2,2-triphenylethyllithium, even though the products of the rearrangement in both cases are benzhydryl carbanions. Evidently, the free energy of activation for the intermolecular process (benzyl migration) is lower than that for the intramolecular process (phenyl migration).

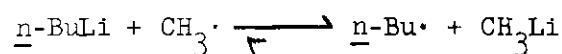
It is of interest to compare the mechanism of the rearrangement of hydrocarbon carbanions with the mechanisms of the analogous Stevens and Wittig rearrangements. In contrast to the observation of an intermolecular process for the 1,2-shift of benzyl in 2,2,3-triphenylpropyllithium, it has been demonstrated that the 1,2-migration of benzyl in the anion of dibenzyltrimethylammonium iodide is an intramolecular process. Lansbury and Pattison^{4,5} obtained good evidence for an intermolecular process for the 1,2-shift of benzyl in the anion of benzyl ether. If the intramolecular process is viewed as an internal nucleophilic displacement, it seems clear that an amine (structure XVIII, $Z = N^+$) would be a much better leaving group than either an alkoxide ($Z = O$) or a carbanion ($Z = C$). Thus, the



XVIII

intramolecular process is predicted to be the most likely in the case of the Stevens rearrangement.

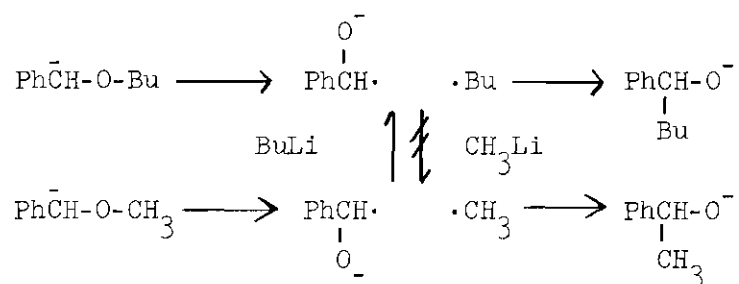
Finally, Lansbury and co-workers⁹² have obtained evidence for an elimination-readdition mechanism involving free radical pairs for the Wittig rearrangement of benzyl t-alkyl ethers. About seven percent n-butylphenylcarbinol is formed in the n-butyllithium-induced rearrangement of benzyl methyl ether, but no methylphenylcarbinol is formed in the methyllithium-induced rearrangement of benzyl n-butyl ether. This agrees with the known⁹³ relative stabilities of these radicals (n-butyl > methyl) and anions (methyl > n-butyl). While this mechanism fits the data for the rearrange-



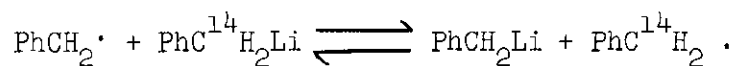
ment of benzyl t-alkyl ethers (and perhaps, for benzyl sec-alkyl ethers),

92. P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, J. Am. Chem. Soc., 88, 78 (1966).

93. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1962, p. 422.



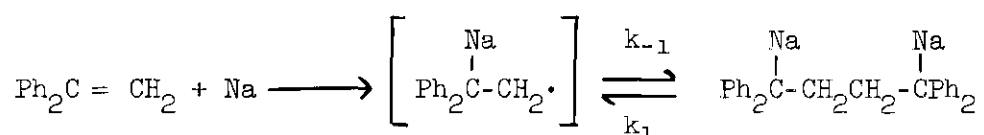
it does not explain the observed^{4,5} incorporation of methyl in the methyl-lithium-induced rearrangement of dibenzyl ether. Rather, the elimination-readdition mechanism involving free radical pairs appears to be one extreme in a whole spectrum of mechanisms. On the basis of present evidence, this mechanism cannot be positively ruled out for the rearrangement of 2,2,3-triphenylpropyllithium, but such a mechanistic complication is not required by the data. Indeed, it seems unlikely, since it would require sufficiently long-lived benzyl free radicals to bring about complete equilibration of carbon-14 prior to readdition:



Moreover, the radical-elimination mechanism would demand that benzyl radicals not combine with other benzyl radicals and also that 1,1-diphenylethene radical-anion not dimerize. Inconsistent with this requirement is the report of Szwarc and co-workers⁹⁴ that radical-anion of 1,1-diphenylethene

⁹⁴. J. Jagur, M. Levy, M. Feld and M. Szwarc, Trans. Faraday Soc., **58**, 2168 (1962).

dimerizes readily. Treatment of 1,1-diphenylethene with sodium in tetrahydrofuran at 28° rapidly produced 98-100 percent yields of the dianion, as determined by titration with methyl iodide. These workers were able to detect the intermediacy of the radical-anion by using electron spin resonance.



The rate constant of dissociation of the dianion, k_1 , was determined to be $8 \times 10^{-7} \text{ sec.}^{-1}$, and the equilibrium constant for the dissociation, $K_{\text{eq}} = 1 \times 10^{-7}$. It thus seems very likely that, if the radical-elimination mechanism were operative in the present case, some 2,2,5,5-tetraphenyladipic acid (m.p. 208°) would be found in the carbonated products of the rearrangement of 2,2,3-triphenylpropyllithium. However, the 2,2,4-triphenylbutanoic acid (m.p. 188°) isolated from this rearrangement has routinely been observed to melt quite cleanly (m.p. 182-186°) without extensive purification.

CHAPTER VI

RECOMMENDATIONS

It would be of interest to determine the kinetics of the rearrangement of 2,2,3-triphenylpropyllithium and 2,2,2-triphenylethyllithium, in order to shed light on some of the more detailed aspects of the rearrangement mechanism. Organosodium and -potassium compounds have been observed^{1,2} to rearrange much more readily than the corresponding organolithium compounds, presumably because the sodium and potassium compounds are more ionic in character. It therefore seems likely that the rate determining step in the rearrangement of the organolithium compounds is a preliminary ionization of the carbon-lithium bond. If such is the case, the rate of rearrangement should vary markedly as the solvating ability of the solvent for cations is increased (*i.e.*, diethyl ether < tetrahydrofuran < dimethoxyethane < dimethyl sulfoxide⁹⁵). Also, the rate should be retarded by the addition of lithium salts. The energy and the entropy of activation of each rearrangement could be determined by a study of the rates of rearrangement at different temperatures.

Waack and co-workers^{79,83,85} have determined the kinetics of a number of organoalkali reactions by following the appearance of a colored, resonance-stabilized carbanion spectroscopically. With suitable modifica-

95. T. E. Hogen-Esch and J. Smid, J. Am. Chem. Soc., 88, 307 (1966).

tions, the techniques described by these workers could be applied to the present systems. The nuclear magnetic resonance spectra of a number of arylmethyl carbanions have been reported by Sandel and Freedman.⁹⁶ It is possible that this analytical tool could be of use in following the kinetics of the rearrangements.

⁹⁶. V. R. Sandel and H. H. Freedman, J. Am. Chem. Soc., 85, 2328 (1963).

APPENDICES

APPENDIX A

ANALYSIS OF ORGANOLITHIUM COMPOUNDS

The concentration of organolithium compounds was determined according to the method of Gilman.^{38, 39} Two 5.00 ml aliquots of the solution of organolithium compound were each added to 25 ml portions of distilled water. Two additional 5.00 ml aliquots were allowed to react with solutions of 1.0 g of benzyl chloride in 10 ml of dry ether for five minutes before the addition of 10 ml of distilled water. The resulting alkaline solutions were then titrated with dilute HCl to a phenolphthalein endpoint. The first titration gives the titer of acid required for base produced by hydrolysis of the organolithium compound, as well as by hydrolysis of excess lithium and lithium oxide which inevitably accompanies the synthesis of an organolithium compound ("total alkali"). The second titration gives the titer of acid required for lithium hydroxide (from lithium metal and lithium oxide) left after the organolithium compound has combined with benzyl chloride ("spurious alkali"). The difference between "total alkali" and "spurious alkali" gives the titer for the organolithium compound.

The Morton flasks used in the synthesis of the organolithium compounds were calibrated to a volume of ± 10 ml. Consequently, the number of millimoles of organolithium compound synthesized could be calculated.

APPENDIX B

ANALYSES BY VAPOR-PHASE CHROMATOGRAPHY

A Perkin-Elmer Vapor Fractometer Model 154D was utilized for these analyses. For the separation of the various methyl esters of low molecular weight carboxylic acids, a Perkin-Elmer Column O was used. This column was two meters in length, and made of 1/4 inch O. D. stainless steel tubing packed with diatomaceous earth, supporting silicone grease. Relative peak areas were measured with a planimeter.

Methyl benzoate (retention time, 4.7 minutes) could be separated from methyl phenylacetate (retention time, 7.6 minutes) by using the following conditions: column O, 135°, flow rate 85 cc/min of helium.

Methyl propionate (retention time, 0.7 minute) could be separated from methyl phenylacetate (retention time, 10.1 minutes) by using the following conditions: column O, 125°, flow rate 62 cc/min of helium.

Methyl valerate (retention time, 2.2 minutes) could be separated from methyl phenylacetate (retention time, 8.6 minutes) by using the following conditions: column O, 155°, flow rate 53 cc/min of helium.

Methyl isobutyrate (retention time, 2.6 minutes) could be separated from methyl phenylacetate (retention time, 9.8 minutes) by using the following conditions: column O, 135°, flow rate 42 cc/min of helium.

*
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1. E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 412 (1961).
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VITA

Gary Wentworth, the son of Mr. and Mrs. J. Vernon Wentworth, was born August 3, 1939, in Orange, Massachusetts. From 1939, he resided in Orange, Massachusetts and attended public schools until his graduation from Orange High School in June, 1957. He entered Rensselaer Polytechnic Institute in September of 1957 and graduated with a B.S. in Chemistry in June of 1961. He entered the graduate school of the Georgia Institute of Technology in September of 1961 and completed requirements for the degree Doctor of Philosophy in Chemistry in March, 1966. He is a member of the Society of the Sigma Xi and the American Chemical Society.

On August 19, 1961, he married the former Carolee Hecht of Loudonville, New York. He has accepted employment with the Chemicals Division of Union Carbide Corporation at South Charleston, West Virginia.