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CATION EFFECTS IN ORGANOALKALI METAL CHEMISTRY

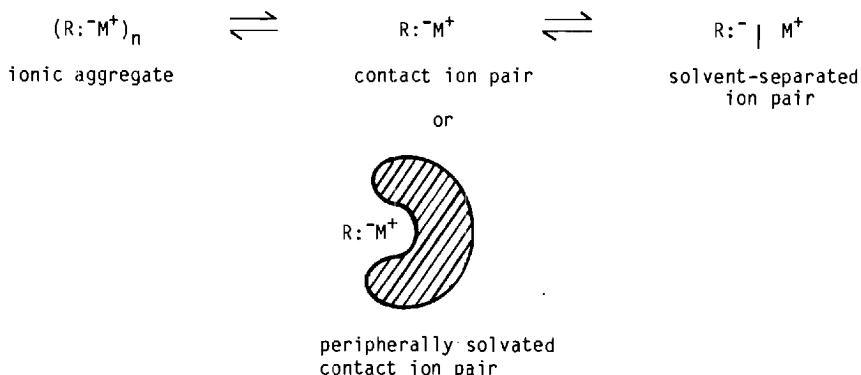
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I. INTRODUCTION

Organoalkali metal compounds can be regarded as substances in which the organic anion is joined to the counter alkali metal cation primarily by electrostatic forces between cations and anions. This generalization [1] is believed to hold even for organolithium compounds with localized negative charge, although here some small carbon-lithium covalency may enhance bonding [2]. From the simplified structure R^-M^+ , it is tempting to think that the nature of M^+ is unimportant, in other words, that one is concerned only with the chemistry of "carbanions" in discussing the reaction of R^-M^+ .

As the Arrhenius theory of ionization emphasizes, the chemistry of salts in dilute aqueous solution can be discussed in terms of kinetically "free" cations and anions; however, organoalkali metal compounds have inappreciable lifetimes in protic solvents and ordinarily are studied in ethereal or hydrocarbon solvents. In such media organoalkali metal compounds exist as ion pairs and aggregates of ion pairs as Michael Szwarc [3] and others have emphasized (see Scheme 1). It should be understood that, in ethereal

Scheme 1



solvents, all of these ionic species are solvated such that the coordination shell of the alkali metal cation is normally filled. Thus the contact ion pair of lithium would be expected to contain three ethereal oxygens in its periphery.

Some of the most informative studies concerning cation-anion interactions have come from careful measurements upon the physical properties of organoalkali metal compounds in ethereal solvents. For example, in the pioneering work of Hogen-Esch and Smid [4] upon the absorption spectra of 9-fluorenyl salts in tetrahydrofuran (THF) at 25°, the absorption maximum shifted from 374 to 349 nm in going from the free anion to the contact ion pair with lithium cation. This spectral shift most likely results from greater stabilization of the ground state than the excited state by the counter cation. A spectral shift from 374 to 349 nm is an energy change of 5.4 kcal/mole brought about by the lithium cation. This is a significant energy change which if operating in an equilibrium or rate process can effect a 10^4 fold change. Hence cation effects and the related factor of solvation or complexation of cations with ligands should be of great importance in the chemistry of organoalkali metal compounds.

The following is a brief summary of examples of cation effects in organoalkali metal chemistry. For convenience many of the examples will be taken from work in the author's laboratory. The first area for consideration will be chemical studies upon equilibria.

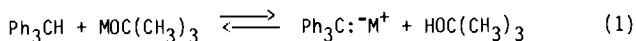
II. CHEMICAL STUDIES UPON EQUILIBRIA

(A) Reaction of Alkali Metals with Carbon

Lithium and sodium when heated with carbon form the acetylides Li_2C_2 and Na_2C_2 . The heavier alkali metals including cesium react with carbon but give non-stoichiometric interstitial compounds where the metal atoms enter between the planes of carbon atoms in the lamellar graphite structure [5]. Thermodynamic calculations suggest that Cs_2C_2 is unstable relative to its elements and attempts to make it have not met with success [6], contrary to early reports in the literature.

(B) Metalation of Hydrocarbons by Alkali Metal Alkoxides

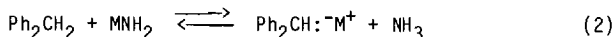
The metalation of hydrocarbons by alkali metal alkoxides [7,8] in tetrahydrofuran (eq. 1) is an equilibrium process whose equilibrium constant



increases with the alkali metal M along the series $\text{Li} < \text{Na} < \text{K} < \text{Cs}$. While exact values of the equilibrium constant are not known, the differences are quite large between lithium t-butoxide and cesium t-butoxide.

(C) Metalation of Hydrocarbons by Alkali Metal Amides

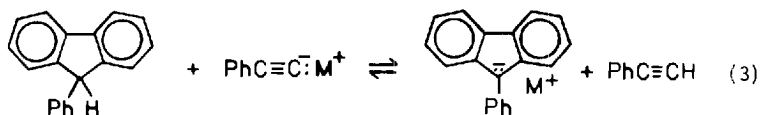
From studies upon equilibria in the reactions of diphenylmethane with alkali metal amides in liquid ammonia or diethyl ether (eq. 2), the alkali



amides increase in metalating power along the series: $\text{Li} < \text{Na} < \text{K}$. With respect to kinetic basicity, cesium cyclohexylamide is up to 35,000 times more reactive than lithium cyclohexylamide in cyclohexylamine as solvent [9].

(D) Metalation of Hydrocarbons by Alkali Metal Acetylides

The equilibrium of equation (3) is shifted toward the right [10] by



increasing the size of the alkali metal cation and by increasing the solvating ability of the solvent [$\text{Et}_2\text{O} < \text{MeOCH}_2\text{CH}_2\text{OMe} < \text{MeO}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me} < (\text{Me}_2\text{N})_3\text{PO}$].

(E) Metal-Metal Exchange of Organolithium Compounds with Alkali Metal Alkoxide, Amides, and Halides

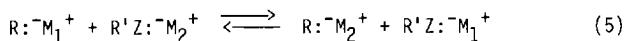
Organosodium and potassium compounds may be formed by reaction [11] of sodium and potassium alkoxides with organolithium compounds in hydrocarbon solvents (eq. 4). The conversion of organolithium compounds to organosodium,



-potassium, and -cesium compounds by sodium, potassium, and cesium *t*-butoxide respectively in THF is evidently the basis for catalysis of the rearrangement of organolithium compounds by alkali metal alkoxides [12-14].

The cation effects on the equilibrium of eq. 4 and also that on the reactions of eq. 1, 2, and 3 may be summarized by a simple generalization.

For the chemical equilibrium,



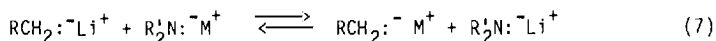
the larger cation prefers to be associated with the larger anion (frequently an anion with delocalized charge) and the smaller cation with the smaller anion (frequently an anion with localized charge). This generalization also rationalizes the reactions of alkali metals with carbon given above.

An explanation for this generalization can be found in electrostatic attraction between cations and anions. If for simplicity we assume that cations and anions behave electrostatically as point charges centered on the atoms which bear the charges in their usual structural formulas, then we can calculate the change in electrostatic energy (in atomic units) for equilibrium (5) from the expected interionic distances of the ion pairs as given in equation (6), where R_p is the distance (bohr units) between centers of

$$-\Delta E = \sum_p \frac{1}{R_p} - \sum_r \frac{1}{R_r} \quad (6)$$

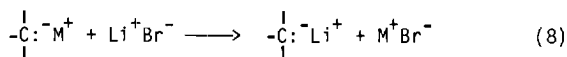
positive and negative charge in the product p and R_r is the similar distance in the reactant r , the summations being over all ion-pair products and reactants. We take 1.65 Å for the bond radius of carbon in an anion [15], 1.26 Å for the radius of oxygen in an alkoxide [16], and Pauling's crystal radii of the alkali metal cations [17]. If we assume that these radii are constant in all compounds, then $-\Delta E$ for equilibrium (4) may be calculated to be 8.4, 14.2, 15.8, and 17.8 kcal/mole for M equal to Na, K, Rb, and Cs respectively. These values appear adequate to account for the large values of the equilibrium constants of these synthetically useful reactions.

For the related reaction of eq. (7), if we take the anionic radius of



nitrogen in an amide [18] to be 1.40 Å and the other values as previously specified, the calculated values of $-\Delta E$ are 4.8, 8.3, 9.2, and 10.4 kcal/mole for M equal sodium, potassium, rubidium, and cesium respectively. These numbers are about 58% of the corresponding values calculated for equilibrium (4) and help show how sensitive the calculation is to the separation of charge in the ion pairs. The data cited for equilibrium (2) is in qualitative agreement with this calculation but involves the diphenylmethyl anion which has a delocalized charge. Such charge delocalization effectively increases the radius of the carbanion and drives equilibrium (7) further to the right.

Another metal-metal exchange reaction is the conversion of organopotassium [19] or organocesium [20] compounds to organolithium compounds by reaction with lithium bromide (eq. 8) in ethereal solvents. If we take

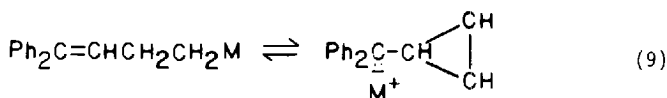


Pauling's crystal radius of bromide (1.95 Å) and the other values as previously specified, the calculated values of $-\Delta E$ from eq. 6 for equilibrium (8) are 4.1, 7.2, 8.0, and 9.2 kcal/mole for M equal Na, K, Rb, and Cs respectively. Again the calculated values appear large enough to agree with the synthetic utility of eq. (8).

It must be emphasized that, in addition to the approximations already cited, these calculations assume that the ion pairs are in the vapor phase at infinite separation from one another. In practice the ion pairs are located in a solvent whose dielectric constant is larger than that of free space; this factor will somewhat decrease the exothermicities which have been calculated from equation (6). Also the solvent, in principle, may preferentially solvate either the products or the reactants. A more important problem is that of aggregation. Since aggregation is but further Coulombic interaction between ions, the ions which form tighter ion pairs would be expected to form tighter and larger aggregates. Aggregation, therefore, would be expected to increase further the exothermicities which have been calculated by equation (6). In extreme cases the aggregates may become so large that insoluble products precipitate from solution and drive the equilibria further to completion.

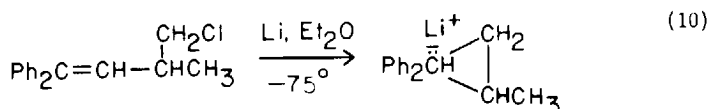
(F) Ring-Chain Tautomerism of Unsaturated Organoalkali Metal Compounds

4,4-Diphenyl-3-butenylalkali compounds undergo reversible cyclization [19] as shown in eq. (9). For M = Li in diethyl ether as solvent only the

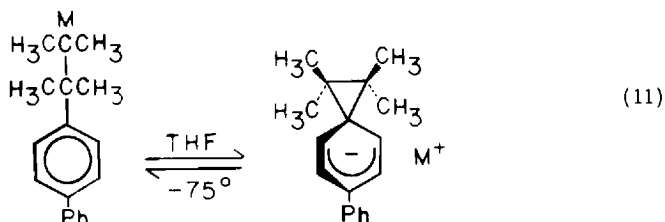


open form of the organometallic is observable at equilibrium (near room temperature) while with M = Na or K only the cyclic (cyclopropyl) compound is detectable. In THF only the cyclic compound is detectable with any of these cations. Equilibria of this type are not only cation and solvent dependent but also temperature and structure dependent. For example reaction (10) is

found [21] to give the cyclic compound with lithium in diethyl ether at



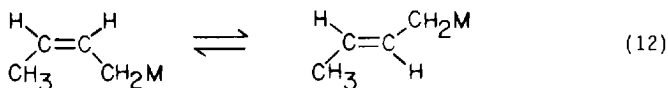
-75°C . Also in the system [20,22] of eq. (11) in THF at -75°C , with $\text{M} = \text{Li}$



only the open organoalkali compound is observed while with $\text{M} = \text{Cs}$ about a 30 to 70 ratio of open to cyclopropyl compound is found. These equilibria exemplify well the generalization given above: the larger cation prefers to be associated with the larger anion, *i.e.* the anion with delocalized charge, and the smaller cation with the smaller anion with localized charge. Also alkali metal cations can be made effectively larger by solvation which is enhanced by lowering the temperature. These equilibria are also affected by substitution, methyl groups on the cyclopropyl ring (especially *gem*-dimethyl groups) help stabilize the cyclic structure and cycloaddition to a double bond is more favorable than to an aromatic ring.

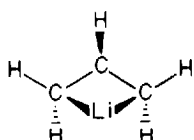
(G) cis, trans-Equilibria of Allylic Anions

The equilibrium Z/E isomeric composition of various 2-alkenylmetallic compounds is dependent upon the metal. Thus for the 2-butenyl system [23] of eq. (12) the % (Z)-isomer increases as $\text{M} = \text{H}$, MgBr , Li , Na , K , and Cs , the %

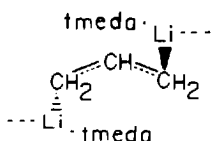


(Z)-isomer being 23, 54, 67, 93, 96, and 99.9 respectively in hexane (except for lithium in diethyl ether). The larger cation favors the (Z)-isomer. In THF Li gives 85% and K 99.2% of (Z)-isomer; again increased solvation makes the cations effectively larger. The larger cations give

decreased electrostatic stabilization of the anion which accordingly must rely more on its internal structure for stabilization. The (Z)-isomer is likely stabilized by charge-induced dipole interaction of the anionic center with the cis-methyl group [24]. It should be noted that according to ab initio calculations [25] monomeric allyllithium in the vapor phase has structure (1) whereas crystalline allyllithium as the tmeda complex [26] has



(1)



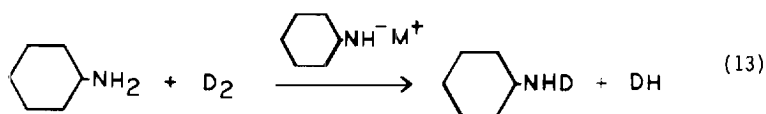
(2)

the polymeric structure (2). If the butenyllithium in the equilibration studies under discussion here has a structure similar to (1), then for the (Z)-isomer the methyl group would NOT be in the plane of the allylic carbon atoms and would be on the side of the allyl group away from the negative charge which is located largely near lithium. In this conformation charge-induced dipole interaction with the methyl group would be minimal.

III. CHEMICAL STUDIES UPON RELATIVE REACTION RATES

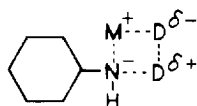
(A) Isotopic Exchange between Deuterium and Cyclohexylamine

Deuterium exchange in cyclohexylamine, eq. (13), is catalyzed by



cyclohexylamide alkali metal salts (MCHA) with the observed order being $\text{LiCHA} \ll \text{NaCHA} < \text{KCHA} < \text{CsCHA}$. The cesium salt is at least 10^3 times more reactive than the lithium salt [27]. The exchange likely proceeds via a transition state such as (3) in which the metal to nitrogen bond is stretched and the metal to deuterium bond is also extended. Hence more electrostatic energy is required to stretch the tight bonds of the smaller alkali metals to attain the transition state structure than the loose bonds of the larger alkali metals and little of this energy difference is offset by forming new

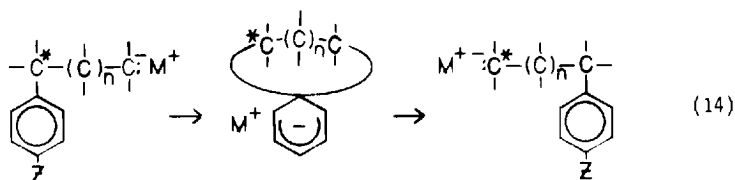
metal to deuterium bonds in the transition state.



(3)

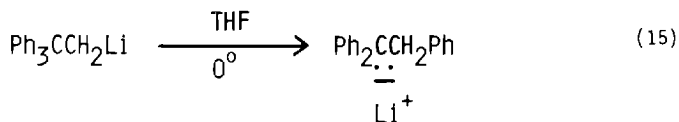
(B) Relative Rates of Migration of Aryl Groups in Organoalkali Metal Compounds

In ethereal solvents the relative rates of [1,2] and [1,4] migration of aryl groups, eq. (14), versus the rate of protonation of the organoalkali

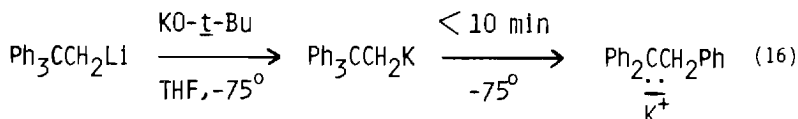


(14)

compound by solvent increases [12,28] along the series: $\text{Li} \ll \text{Na} \ll \text{K}$ or Cs . This order seems likely to be the same as the relative rate of rearrangement of the organoalkali compounds themselves. Thus 2,2,2-triphenylethyllithium rearranges [29], eq. (15), with a half-life of about 40



min. in THF at 0° ; whereas 2,2,2-triphenylethylpotassium rearranges [30] as rapidly as it is formed, eq. (16), even at -75° . The qualitative explanation



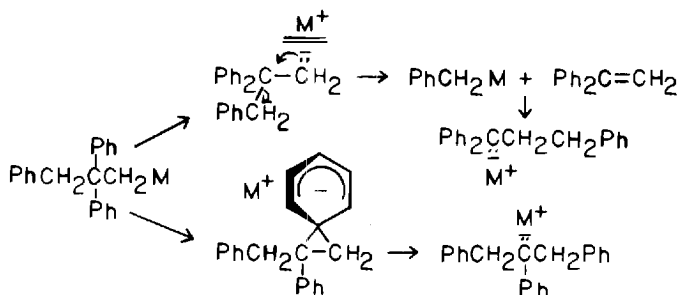
of these results is that given in the prior example (A). Of course the chemistry of organoalkali compounds is complicated by aggregation into dimers, trimers, tetramers, etc.; however the most tightly bound aggregates are expected to be formed from the tightest ion pairs. The aggregates are

expected to be less reactive than the monomeric ion pairs.

(C) Variation of Migratory Aptitudes of Groups in Organoalkali Rearrangements with Alkali Metal Cation and Solvent

1. Competitive Rearrangement of Phenyl versus Benzyl

Benzyl migration in 2,2,3-triphenylpropyllithium has been shown [31] to proceed by cleavage of benzyllithium followed by its readdition to 1,1-diphenylethene, whereas phenyl migration proceeds via an intramolecular process as shown in **Scheme 2**. The organolithium compound undergoes exclusive

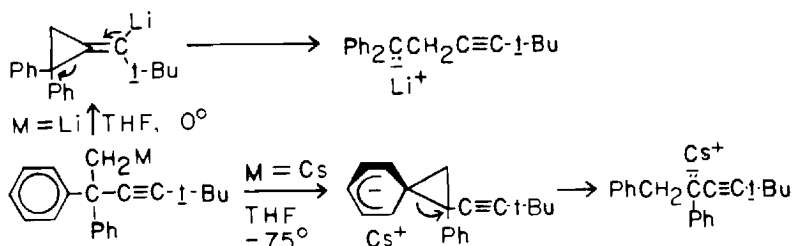


benzyl migration in THF at 0°, as does the sodium compound in THF at -75° or the potassium and cesium compounds which are complexed with 18-crown-6. In contrast the lithium compound rearranges in diethyl ether at 35° with exclusive phenyl migration and the cesium compound in THF at -75° with predominant (72%) phenyl migration. These results [13] can be understood on the basis that benzyl cleavage occurs in a loose or solvent-separated ion pair whereas phenyl migration proceeds in a tight ion pair. Thus conditions which favor loose ion pairs (small alkali metal cations, good solvents or ligands, low temperatures) favor benzyl migration whereas conditions which favor tight ion pairs (large alkali metal cations, poor solvents, high temperatures) favor phenyl migration.

2. Competitive Rearrangement of Phenyl versus Alkynyl

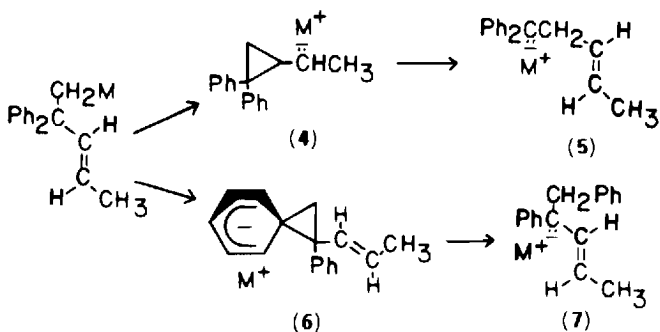
5,5-Dimethyl-2,2-diphenyl-3-hexynyllithium undergoes exclusive migration [32] of the alkynyl group by addition to the triple bond as shown in **Scheme 3**. In contrast the corresponding cesium compound undergoes phenyl migration [32] by addition to the phenyl group with no detectable (< 2%) migration of the alkynyl group (**Scheme 3**).

Scheme 3



3. Competitive Rearrangement of Phenyl versus Alkenyl

In diethyl ether at 35°C trans-2,2-diphenyl-3-pentenyllithium undergoes propenyl migration to give (5) versus phenyl migration to give (7) (see Scheme 4) in a ratio of 92 to 8. In the solvent THF at 10°C this ratio



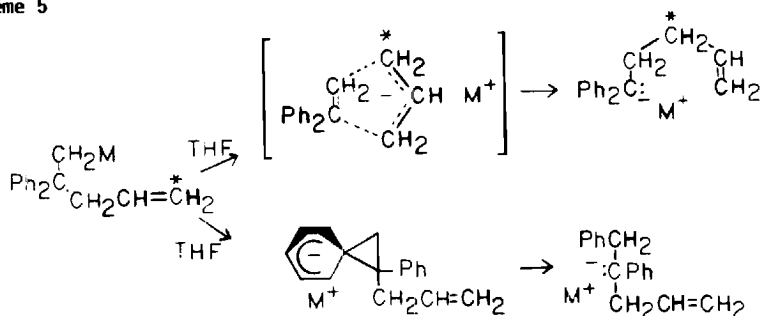
becomes 54 to 46. The corresponding potassium compound rearranges in THF at -75°C to give the product of phenyl migration (7) with no detectable propenyl migration [33].

According to Scheme 4 propenyl migration occurs via an intermediate (4) with essentially localized negative charge while phenyl migration occurs via intermediate (6) with delocalized charge. Similar intermediates are suggested in Scheme 3 for alkynyl versus phenyl migration. These results suggest a simple generalization. Rearrangements of organoalkali metal compounds tend to occur in the sense that compounds with large alkali metal cations preferentially rearrange via transition states (or reactive intermediates) with delocalized negative charge whereas compounds with small alkali metal cations rearrange via transition states (or intermediates) with localized

negative charge. This generalization is similar to that suggested earlier for cation effects upon equilibria and has a similar rationale. With small cations and carbanions of localized negative charge, the transition state or intermediate is stabilized by strong electrostatic interaction between cation and anion. With large cations, cation anion interaction is greatly reduced and hence the anion must rely on its own structure for stabilization; such stabilization is generally greater in a delocalized anion. However, the effective size of an alkali metal cation is dependent upon its state of solvation. Thus the effect upon trans-2,2-diphenyl-3-pentenyllithium of rearrangement in diethyl ether at 35° versus rearrangement in THF at 10° is that under the later set of conditions increased solvation is expected and hence more phenyl migration should and does occur. Increased solvation implies a "looser" ion pair, not necessarily a solvent-separated ion pair.

4. Competitive Rearrangement of Phenyl versus Allyl

In the solvent THF at -70 to -75°C 2,2-diphenyl-4-pentenylpotassium and cesium compounds undergo migration either of the allyl group or the phenyl group [14]. With potassium complexed with 18-crown-6 a 92 to 8 ratio of allyl to phenyl migration is observed. Without 18-crown-6 this ratio is 32 to 68 for potassium or 16 to 84 for cesium. These arrangements are believed to occur by way of the intermediates or transition states shown in **Scheme 5**.



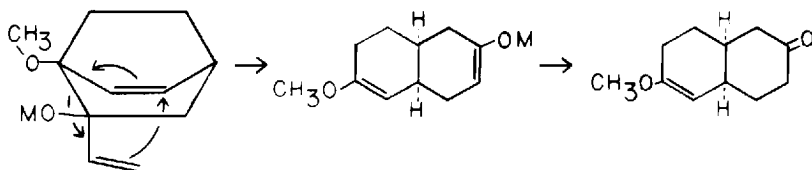
It appears that allyl migration occurs in a highly solvated transition state, likely in a solvent-separated ion pair, while phenyl migration occurs in a more weakly solvated or tight ion pair. With lithium as counter cation, rearrangement does not occur at an appreciable rate at -75°C but upon warming to near 0°C gives 96% allyl migration and only 4% phenyl migration. At this temperature the allyl group breaks free from the diphenylethylene moiety, evidently as an allyl anion, such that a carbon-14 label on the terminus of the allyl group becomes 67% scrambled and only 33% inverted (unlike the low

temperature [2,3] sigmatropic process of **Scheme 5** which gives only inversion of the allyl group as shown). Yet the non-radioactive lithium compound when allowed to rearrange in the presence of a six fold excess of allyl- ^{14}C -lithium showed only 14% incorporation of radioactive allyl group in the product of allyl migration. Hence the cleavage-readdition of allyl anion evidently occurs very rapidly largely within a solvent cage. These results show how cation and solvent (or ligand) effects can be used to control the nature of chemical reactions.

Since both allyl and phenyl migration in **Scheme 5** occur via transition states or intermediates with delocalized negative charge, prediction of the ratio of allyl to phenyl migration is somewhat difficult. For the low-temperature [2,3] sigmatropic pathway, the negative charge evidently is involved in binding the allyl group to the diphenylethylene group at both termini in an aromatic (6 π -electron) transition state in which the negative charge is concentrated in the region between the two groups and hence is shielded (by carbon and hydrogen) from close proximity to the cation. Hence strong solvation is required to attain this transition state which necessarily has the properties of a loose or solvent-separated ion pair. For the 0° elimination-readdition mechanism, the state of solvation is less clear. Perhaps now lithium ion binds the allyl anion at both termini as shown in structure (1) in a tight ion pair. Since the allyl anion is smaller than the cyclohexadienyl anion and has more concentrated negative charge, lithium prefers binding to allyl rather than cyclohexadienyl and thus brings about preferential allyl migration.

(D) The Anionic Oxy-Cope Rearrangement

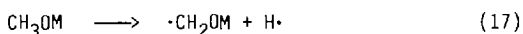
In studies upon the oxy-Cope rearrangement Evans and Golob [34] found that 1,5-hexadien-3-ols rearranged much more readily in the form of their alkoxides than the corresponding alcohols and that the rate of rearrangement was both cation and solvent (or ligand) dependent. Thus in **Scheme 6** the rate



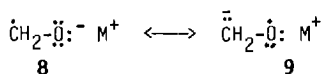
of rearrangement increased along the series $\text{M}^+ = \text{H}^+ \ll \text{Li}^+ \ll \text{Na}^+ < \text{K}^+ \ll \text{K}^+ -$

18-crown-6 with the acceleration for potassium complexed with 18-crown-6 10^{12} times that of the alcohol ($M^+ = H^+$). For a related system (**Scheme 6**, CH_3O replaced by H) the corresponding acceleration was 10^{17} fold. Similar anionic rate enhancements are observed in [3,3]-Claisen rearrangements of the enolates of α -allyloxy ketones [35], in [1,3] sigmatropic rearrangements [36], and in vinylcyclopropane rearrangements [37]. These rate enhancements are reminiscent of those discussed earlier for rearrangements of organoalkali metal compounds and likely have a similar explanation. Namely the transition states for the rearrangements have more charge delocalization than the reactants. Charge delocalization is better accommodated by large cations than by small since less energy is required to pull negative charge away from large than small cations (the proton can be viewed as the smallest cation).

A related explanation has been given by Steigerwald, Goddard, and Evans [38] who by an *ab initio* method have calculated C-H bond energies (see eq. (17) for CH_3OH , CH_3ONa , and CH_3O^- of 90.7, 70.6, 79.0 and 74.2 kcal/mole respectively. The authors note that the metal ketyl product of cleavage of



CH_3OM is a hybrid of the two structures **8** and **9** and hence is charge-






delocalized whereas the reactant alkali metal alkoxide has its charge essentially localized on oxygen. Hence large alkali metal cations offer less electrostatic resistance to bond cleavage of the alkoxide than do small cations. A similar explanation is proposed to account for cation effects upon the anionic oxy-Cope rearrangement.

(E) NMR Rotational Barriers in Benzylic and Allylic Alkali Metal Compounds

Rotational barriers about the partial double bonds of benzylic and allylic anions are dependent on the counter ion. Some of the available data [39-41] for methylene rotation are summarized in **Table I**. In all cases cited the barrier to rotation increases along the series $Li < Na < K < Cs$. Somewhat similar barriers are found in 9-(1-naphthyl)methyleneoctatrienyl-alkali metal compounds [42].

Why does the rotational barrier increase or the rate of rotation decrease with increasing size of the alkali metal? In the other cation

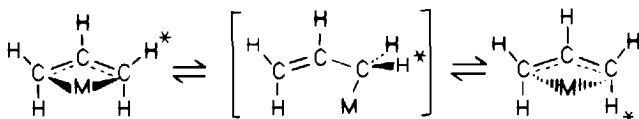
Table I. NMR Rotational Barriers in THF

M			
	ΔG^\ddagger kcal/mole		
Li	17.0 ^a	10.7 ^b	12.9 ^c
Na	> 17.8	—	14.8
K	> 20.1	16.7	(17.8)
Cs	—	18.0	—

^aRef. 39.^bRef. 40.^cRef. 41.

effects [see Sections (A), (B), and (D)], the opposite order is observed. Schleyer and coworkers [43] have made calculations of the reaction barrier for allyl compounds based on the mechanism shown in Scheme 7. These

Scheme 7



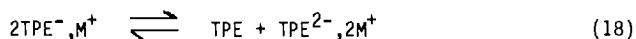
calculations pertain to monomeric species in the gas phase. The barrier for the free anion is estimated to be 22.2 kcal/mole, a value somewhat higher than that reported in Table I for allylcesium in THF. The value for allyllithium is calculated to be 17.7 kcal/mole, a barrier which is significantly higher than the observed barrier for allyllithium in THF. The value for allylsodium is 11.9 kcal/mole, not far from that which might be interpolated for the missing experimental value for allylsodium in Table I. Why is the experimental value for allyllithium much smaller than the calculated barrier? The effect under discussion is so large that the calculated barrier for lithium versus sodium is opposite the general trend of Table I. Schleyer and co-workers suggest [43b] that aggregation of allyllithium in THF may be responsible for the observed barrier being much less than that calculated. The situation may be similar to that in the

inversion of alkyllithium for which aggregation has been calculated to lower the barrier [45]. The examples cited in this section should serve as a warning that the aggregation of organoalkali metal compounds is a factor which must be considered sometimes even in simple qualitative discussions.

The observed order of increasing rotational barriers in allylalkali metal compounds can be understood on the basis that the highest barrier is expected for the solvent-separated ion pair whose barrier should be nearly the same as that calculated for the free anion. Cation-anion interactions are expected to lower the barrier because of greater stabilization of the transition state (which has localized negative charge) than the reactant (which has delocalized negative charge) - this is opposite the general situation described for rearrangements in Sections (A), (B), and (D). Two (or more) cations should have a greater effect than one in this differential stabilization; hence aggregation serves further to lower the barrier. Where aggregation stabilizes the reactant more than the transition state as in the rearrangements of Sections (A), (B), and (D), it does not have to be invoked in simple qualitative arguments since aggregates are likely to be so unreactive as to play little role in reaction. The effect of aggregation should be greatest for lithium and least for cesium. Thus the observed order of rotational barriers is commonly $\text{Li} < \text{Na} < \text{K} < \text{Cs}$. This is not an invariant order. The barrier to rotation of the phenyl group in *trans*, *trans*-1,3-diphenylallyl anion in liquid ammonia containing 15% of methyl *t*-butyl ether is essentially independent of the counter-ion (Li^+ , Na^+ , K^+), doubtlessly because these compounds exist as solvent-separated ion pairs or possibly free anions [46]. Also methylene rotation in 2-methyl-1,3-diphenylallyl anion in THF occurs more readily in the potassium salt than in the lithium salt, likely because the potassium salt exists as a contact ion pair while the lithium salt occurs as a solvent-separated ion pair [47]. Thus both solvation and aggregation play important roles in determining rotational barriers in organoalkali metal compounds.

IV. OTHER EXAMPLES OF CATION EFFECTS

Many other instances of cation effects in organoalkali metal chemistry are known and could have been cited in this brief review. For example, the disproportionation of tetraphenylethylene (TPE) radical anion into dianion, eq. (18), has a formal equilibrium constant which increases along the series



$\text{Li} < \text{Na} < \text{K} < \text{Cs}$ in THF and varies with solvent in the order 1,2-

dimethoxyethane < THF < diethyl ether [48]. For the disproportionation of stilbene radical anion into dianion, the order of cation effects is reversed while the solvent effects are similar [49]. Related cation and solvent effects have been observed in disproportionation of many other radical anions [50].

In another example, alkali metal cations have been found to catalyze the reaction of ethylene oxide with fluoradenyl anion, the reaction rate increasing at least 10^5 fold from cesium to lithium. The catalysis has been attributed to the behavior of alkali metal cations as Lewis acids in coordination with the oxygen of ethylene oxide [51].

This review has not included cation effects which are combined with the differing reducing power of the alkali metals in various solvents. This area is rich in possibilities [52].

Finally interesting cation effects [53] are observed in anionic polymerization but these effects are too well known to polymer chemists for discussion here. It is hoped that the examples of cation effects cited have been representative of those possible in organoalkali metal chemistry and that these examples will encourage chemists, including polymer chemists, to use cation effects as a convenient tool to control chemical reactions and divert them in directions useful to mankind.

V. CONCLUSIONS

The factors involved in "cation effects" in organoalkali metal chemistry are diverse and interrelated but include (a) electrostatic attraction between cation and anion, (b) the size (distance of nearest approach) of cation and anion, (c) the charge distribution and geometry of the anion, (d) solvation of cation and anion and the related problem of whether contact or solvent-separated ion pairs are involved (note that contact ion pairs are frequently solvated), (e) specific interactions between cations and anions, including mutual polarization and covalent interactions. It frequently is not possible a priori to weigh all the factors and predict the outcome but general patterns are beginning to emerge. Cations frequently have large effects upon reaction rates and equilibrium constants of anions, sometimes so large as to alter the nature of a chemical reaction. Cations suitably coordinated to solvent or ligand can be used by chemists to exercise considerable control over chemical reactions of anions. More systematic studies on the effects of cations upon the behavior of carbanions would likely prove profitable.

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REFERENCES

1. (a) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. (b) Streitwieser, A. Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (c) Bushby, R. M.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265.
2. (a) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818. (b) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (c) Schleyer, P. v. R., Royal Society of Chemistry, International Symposium on Chemistry of Carbanions, Univ. of Durham, July 20, 1984, Plenary Lecture, "Searching for the True Nature of 'Carbanions'".
3. Thus see "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Wiley-Interscience; New York, Vol. 1, 1972; Vol. 2, 1974.
4. Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1965**, *87*, 699; **1966**, *88*, 307, 318.
5. Cotton, F. A., and Wilkinson, G. "Advanced Inorganic Chemistry," 3rd ed., Wiley-Interscience, New York, 1972, p. 190.
6. Ader, M.; Hubbard, W. N. *J. Chem. Thermodynamics* **1973**, *5*, 607.
7. Steiner, E. C.; Gilbert, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 3054.
8. Schlosser, M. "Struktur und Reaktivität polarer Organometalle," Springer-Verlag, Berlin, 1973, p. 102.
9. (a) Streitwieser, A., Jr.; Hammons, J. H. *Prog. in Phys. Org. Chem.* **1965**, *3*, 41. (b) Streitwieser, A., Jr.; Caldwell, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 5394.
10. Terekhova, M. I.; Kruglyak, L. I.; Petrov, E. S.; Shatenshtein, A. I. *Chem. Abst.* **1976**, *85*, 93613.
11. (a) Lochmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257. (b) Lochmann, L.; Lim, D. *J. Organometal. Chem.* **1971**, *28*, 153.
12. Grovenstein, E., Jr.; Rhee, J.-U. *J. Am. Chem. Soc.* **1975**, *97*, 769.
13. Grovenstein, E., Jr.; Williamson, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 646.
14. Grovenstein, E., Jr.; Cottingham, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 1881.
15. This value is from the average value (2.25 Å) of the C-Li bond distance in crystalline $(CH_3Li)_4(tmeda)_2$ (Koster, H.; Thoennes, D.; Weiss, E. J. *Organomet. Chem.* **1978**, *160*, 1) or the value (2.61 Å) of the C-Na bond distance in $(CH_3Na)_4$ cluster in crystalline methylsodium (Weiss, E.; Sauermann, G.; Thirase, G. *Chem. Ber.* **1983**, *116*, 74) less Pauling's crystal radius of lithium or sodium respectively.
16. This value is from the Li-O bond distance (1.86 Å) in 1,3-dilithiobenzylketone $(tmeda)_2$ (Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 621) or the Li-O bond distance (1.87 Å) in benzophenonedilithium $\cdot tmeda \cdot THF$ (Bogdanovic, B.; Kruger, C.; Wermches, B. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 817) less Pauling's crystal radius of lithium.
17. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell Univ.: Ithaca, N.Y., 1960, p 514.
18. This value is from the average value of 2.00 Å for Li-N in $(2,2,6,6-tetramethylpiperidinato)lithium$ and $LiN(SiMe_3)_2$ (Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakier, R. *J. Am. Chem.*

- Soc. 1983, 105, 302) or in $(\text{PhCH}_2)_2\text{NLi OEt}_2$ and $(\text{PhCH}_2)_2\text{NLi}\cdot\text{HMPA}$ (Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. J. J. Chem. Soc. Chem. Commun. **1984**, 285).
19. Maercker, A.; Roberts, J. D. J. Am. Chem. Soc. **1966**, 88, 1742.
 20. Grovenstein, E., Jr.; Lu, P.-C. J. Org. Chem. **1982**, 47, 2928.
 21. Unpublished experiments with Dr. S. C. Goel.
 22. Grovenstein, E., Jr.; Lu, P.-C. J. Am. Chem. Soc. **1982**, 104, 6681.
 23. (a) Schlosser, M.; Hartmann, J. J. Am. Chem. Soc. **1976**, 98, 4674.
(b) Stahle, M.; Hartmann, J.; Schlosser, M. Helv. Chim. Acta **1977**, 60, 1730.
 24. Cf. the *o*-methylbenzyl anion: Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. J. Am. Chem. Soc. **1983**, 105, 6290.
 25. Clark, T.; Rohde, C.; Schleyer, P. v. R. Organometallics **1983**, 2, 1344.
 26. Koster, H.; Weiss, E. Chem. Ber. **1982**, 115, 3422.
 27. Symons, E. A.; Powell, M. F.; Schnittker, J. B.; Clermont, M. J. J. Am. Chem. Soc. **1979**, 101, 6704.
 28. (a) Grovenstein, E., Jr. Adv. Organomet. Chem. **1977**, 16, 167. (b) Grovenstein, E., Jr. Angew. Chem. Int. Ed. Engl. **1978**, 17, 313.
 29. Grovenstein, E., Jr.; Williams, L. P., Jr. J. Am. Chem. Soc. **1961**, 83, 2537.
 30. Unpublished experiments with Dr. R. E. Williamson.
 31. Grovenstein, E., Jr.; Wentworth, G., J. Am. Chem. Soc. **1967**, 89, 1852; ibid. **1967**, 89, 2348.
 32. Grovenstein, E., Jr.; Chiu, K.-W.; Patil, B. B. J. Am. Chem. Soc. **1980**, 102, 5848.
 33. Unpublished research with Dr. Subash C. Goel, Randall L. Hughes, John H. Northrop, and Douglas L. Streeter.
 34. Evans, D. A.; Golob, A. M. J. Am. Chem. Soc. **1975**, 97, 4765. See also Evans, D. A.; Baillargeon, D. J.; Belson, J. V. J. Am. Chem. Soc. **1978**, 100, 2242.
 35. Koreeda, M.; Luengo, J. I. J. Am. Chem. Soc. **1985**, 107, 5572.
 36. (a) Thies, R. W.; Seitz, E. P. J. Org. Chem. **1978**, 43, 1050. (b) Wilson, S. R.; Mao, D. T. J. Chem. Soc., Chem. Commun. **1978**, 479. (c) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. J. Am. Chem. Soc. **1976**, 98, 1241.
 37. Danheiser, R. L.; Martinez-Davila, C.; Morin, J. M., Jr. J. Org. Chem. **1980**, 45, 1341.
 38. Steigerwald, M. L.; Goddard, W. A.; Evans, D. A. J. American Chem. Soc. **1979**, 101, 1994. See also Evans, D. A.; Baillargeon, D. J. Tetrahedron Lett. **1978**, 3319.
 39. Sandel, V. R.; McKinley, S. V.; Freedman, H. M. J. Am. Chem. Soc. **1968**, 90, 495.
 40. Thompson, T. B.; Ford, W. T. J. Am. Chem. Soc. **1979**, 101, 5459.
 41. Kronzer, F. J.; Sandel, V. R. J. Am. Chem. Soc. **1972**, 94, 5750.
 42. Staley, S. W.; Dustman, C. K. J. Am. Chem. Soc. **1981**, 103, 4297.
 43. (a) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. J. Organomet. Chem. **1978**, 150, 1. (b) Clark, T.; Rohde, C.; Schleyer, P. v. R. Organometallics **1983**, 2, 1344.
 44. Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. J. Am. Chem. Soc. **1981**, 103, 5609.
 45. Clark, T.; Schleyer, P. v. R.; Pople, J. A. J. Chem. Soc. Chem. Comm. **1978**, 137.
 46. Bushby, R. J.; Ferber, G. J. J. Chem. Soc. Perkin II **1976**, 1688. See also (a) Boche, G.; Schneider, D. R. Tetrahedron Lett. **1976**, 3657. (b) Boche, G.; Martens, D.; Wagner, H.-V. J. Am. Chem. Soc. **1976**, 98, 2668.
 47. Burley, J. W.; Young, R. N. J. Chem. Soc. Perkin II **1972**, 1843.
 48. (a) Garst, J. F.; Zabolotny, E. R. J. Am. Chem. Soc. **1965**, 87, 495. (b) Garst, J. F.; Zabolotny, E. R.; Cole, R. S. ibid. **1964**, 86, 2257. (c) Lundgren, B.; Levin, G.; Claesson, S.; Szwarc, M. ibid. **1975**, 97, 262 and references therein cited.

49. (a) Zabolotny, E. R.; Garst, J. F. J. Am. Chem. Soc. **1984**(b) Jachimovicz, F.; Levin, G.; Szwarc, M. ibid., **1978**, 100, 5426. (c) Wang, H. C.; Levin, G.; Szwarc, M., ibid., **1978**, 100, 6137.
50. (a) Rainis, A.; Szwarc, M. J. Am. Chem. Soc. **1974**, 96, 3008. (b) Levin, G.; Holloway, B. E.; Szwarc, M. ibid., **1976**, 98, 5706. (c) Levin, G.; Szwarc, M. ibid., **1976**, 98, 4211. (d) Pola, J.; Levin, G.; Szwarc, M. J. Phy. Chem. **1976**, 80, 1690. (e) Hirota, N.; Weissman, S. I. J. Am. Chem. Soc. **1964**, 86, 2538. (f) Garst, J. F.; Walmsley, D.; Hewitt, C.; Richards, W. R.; Zabolotny, E. R. J. Am. Chem. Soc., **1964**, 86, 412.
51. Chang, C. J.; Kiesel, R. F.; Hogen-Esch, T. E. J. Am. Chem. Soc. **1973**, 95, 8446.
52. For example see: (a) Grovenstein, E., Jr.; Longfield, T. H.; Quest, D. E. J. Am. Chem. Soc. **1976**, 99, 2800. (b) Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. ibid., **1983**, 105, 6290.
53. For example see: (a) Bhattacharyya, D. N.; Smid, J.; Szwarc, M. J. Phy. Chem. **1965**, 69, 624. (b) Dyball, C. J.; Worsfold, D. J.; Bywater, S. Macromolecules **1979**, 12, 819.