M. Iwaizumi, T. Matsuzaki, and T. Isobe, *Bull. Chem. Soc. Jpn.*, **45**, 1030 (1972); (c) F. C. Adam, *Can. J. Chem.*, **49**, 3524 (1971).
(9) (a) T. H. Goodwin and D. A. Morton-Blake, *Theor. Chim. Acta*, **1**, 458 (1963); (b) I. Fischer-Hjalmars, *Tetrahedron*, **19**, 1805 (1963); (c) A. Imamura and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5379 (1968); (d) G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, **15**, 339 (1968); (e) D. Perahia and A. Pullman, *Chem. Phvs. Lett.*, **19**, 73 (1973); (f) A. Golebiewski and A. Parczewski, *Z. Naturforsch. A*, **25**, 1710 (1970); (g) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **95**, 3893 (1973).
(10) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).
(11) A. d'Annibale, L. Lunazzi, A. C. Boicelli, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1396 (1973), and references cited therein.

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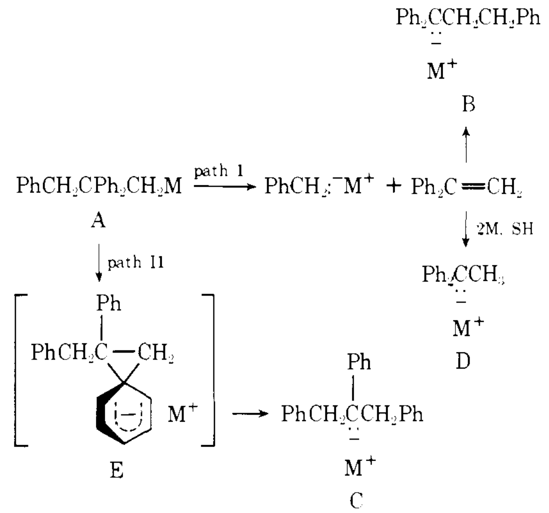
Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds[1]

Sir:

Whereas 2,2,3-triphenylpropyllithium (A), prepared from reaction of 1-chloro-2,2,3-triphenylpropane with lithium at −65 to −75°, has been reported[2] to rearrange in tetrahydrofuran (THF) at 0° with at least 98% 1,2-migration of benzyl, we now find that reaction of the same chloride with cesium in THF at 65° gives 96% 1,2-migration of phenyl rather than benzyl. In order better to understand the phenomena responsible for such diverse migratory aptitudes, the rearrangement has been studied under widely variable conditions as reported in Table I. Previous work[3] has indicated (see Scheme I) that benzyl migration proceeds by elimination of benzyl anion and readdition of this anion to 1,1-diphenylethene to give B (path I) while aryl migration proceeds intramolecularly *via* a spiro anion to C (path II). In the present work 1,1-diphenylethyl anion (D) has been identified; indeed D is a major product under strongly reducing conditions with solutions[4] of alkali metals (*e.g.*, potassium plus 18-crown-6 in THF). It is reasonable to suppose that this anion results from reduction of intermediate 1,1-diphenylethylene. The appearance of D along with benzyl anion[5] constitutes additional evidence for the occurrence of path I.

Scheme I



Examination of Table I reveals that 2,2,3-triphenylpropyllithium does not rearrange at an appreciable rate upon standing in the THF at −75°, even upon addition of 18-crown-6 ether;[6] however, sodium *tert*-butoxide or better potassium and cesium *tert*-butoxides are effective catalysts, with the product being notably dependent upon the cation present. For a related rearrangement, lithium *tert*-butoxide, unlike potassium or cesium *tert*-butoxides was an ineffective catalyst.[7] These pronounced cation effects suggest that the cation plays an important role in determining the fate of the anion and imply that the cation must be geometrically close to the anion during the rearrangement process. This could be understood, for example, if the rearrangement catalyzed by cesium *tert*-butoxide took place in the corresponding organocesium compound; therefore, the following metathetical reaction appears to occur under our conditions

$$PhCH_2CPh_2CH_2Li + MO\text{-}t\text{-}Bu \longrightarrow PhCH_2CPhCH_2M + LiO\text{-}t\text{-}Bu \quad (1)$$

Additional evidence (see Table I) for this metathesis comes from the similar ratio (equal within likely experimental errors) of products of path I to path II observed for the reaction of cesium metal with the chloride at −75° as compared to the reaction of cesium *tert*-butoxide with the organolithium compound at the same temperature.

Table I. Rearrangements of 2,2,3-Triphenylpropyl Alkali Metal Compounds

		Products,[a] rel mol %			
Conditions	Temp, °C	A	B	C	D
$PhCH_2CPh_2CH_2Li$, 7 hr, THF	−75	100	0	0	0
$PhCH_2CPh_2CH_2Li$ + 2(18-crown-6), 3.3 hr, THF	−75	100	0	0	0
$PhCH_2CPh_2CH_2Li$, 30 min, THF	0	0	100	0	0
$PhCH_2CPh_2CH_2Li$, 3 hr, Et_2O	+35	0	0	100	0
$PhCH_2CPh_2CH_2Li$ + 2NaO-*t*-Bu, 30 min, THF	−75	33	58	0	9
$PhCH_2CPh_2CH_2Li$ + 2KO-*t*-Bu, 30 min, THF	−75	0	63	37	0
$PhCH_2CPh_2CH_2Li$ + 2CsO-*t*-Bu, 30 min, THF	−75	0	25	72	3
$PhCH_2CPh_2CH_2Li$ + 2KO-*t*-Bu + 2(18-crown-6), 30 min, THF	−75	0	100	0	0
$PhCH_2CPh_2CH_2Li$ + 2CsO-*t*-Bu + 2(18-crown-6), 30 min, THF	−75	20[b]	77	0	3
$PhCH_2CPh_2CH_2Cl$, K, THF	+65	0	10	90	0
$PhCH_2CPh_2CH_2Cl$, Cs, THF	+65	0	2	96	2
$PhCH_2CPh_2CH_2Cl$, Cs,[c] THF	−75	0	5	67	28
$PhCH_2CPh_2CH_2Cl$ + 2(18-crown-6), excess K, THF	−75		2	0	98
$PhCH_2CPh_2CH_2Cl$ + 2(18-crown-6), excess Cs,[c] THF	−75	0	0	<8	>92[d]

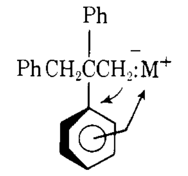
[a] Yields are based only on acidic products from carbonation; the entry "0" % means that none was detected by the nmr and glpc techniques used and therefore less than 1 or 2% was present. [b] The reaction is apparently retarded by precipitation of a cesium *tert*-butoxide complex with the 18-crown-6. [c] The organoalkali product was treated with excess mercury to lower activity of cesium (destruction of radical anions) prior to carbonation. [d] The measured ratio of **C**:**D** was 8:92 in this run; however, since the ratio of Cs:18-crown-6 was 1.15:1 and the adventitious presence of an impurity caused most of the cesium to react, it is thought that the yield of C would have been reduced if an excess of 18-crown-6 over cesium had been present.

While the present work is to our knowledge the first report[1] of the use of alkali metal alkoxides as catalysts for the rearrangement of organolithium compounds, potassium *tert*-butoxide has been previously reported to activate *n*-butyllithium toward metalation of hydrocarbons such as toluene[8] and benzene.[9] Treatment of a heptane solution of *n*-butyllithium with an equimolar amount of potassium *tert*-butoxide is reported[8] to give a precipitate which has roughly a composition corresponding to a one to one adduct of the alkoxide with the organolithium compound; similar treatment with potassium *l*-menthoxide[10] gives a relatively pure precipitate of *n*-butylpotassium. While the mechanism of potassium alkoxide catalyzed reactions has not been previously elucidated, it has been interpreted as involving formation and facile reactions of either an organopotassium compound[10,11] or a one to one adduct of organolithium reagent with potassium alkoxide.[9] The present work favors the former interpretation (eq 1) for reactions in solution in tetrahydrofuran. We find that with a two to one ratio by formula weight of potassium *tert*-butoxide to 2,2,3-triphenylpropyllithium, rearrangement goes to 74% completion in 9 min or 100% (±3%) completion in 30 min, while with a one to one ratio rearrangement goes to only 15% completion in 9 min. Since only one formula weight of alkoxide is required per formula weight of organolithium reagent according to eq 1, the reason why a second formula weight of alkoxide is required for effective catalysis is evidently that it combines with the lithium chloride which is always present in an amount equivalent to the 2,2,3-triphenylpropyllithium in our preparations of organolithium reagent.

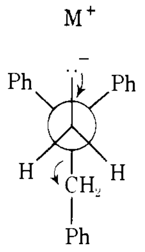
In conjunction with the above discussion on the nature of alkoxide ion catalysis, an examination of Table I reveals that the following systems undergo reaction almost exclusively by path I of Scheme I: 2,2,3-triphenylpropyllithium and -sodium in THF at 0 and −75°, respectively; 2,2,3-triphenylpropylpotassium and -cesium 18-crown-6 compounds [12] in THF at −75°, whether prepared *via* the chloride and alkali metal-crown procedure or *via* the lithium compound with alkali metal *t*-butoxide-crown complex. The following undergo rearrangement almost exclusively by path II: 2,2,3-triphenylpropyllithium in ethyl ether at 35°; 2,2,3-triphenylpropylpotassium and -cesium in THF at 65°. The following undergo reaction in comparable amounts by paths I and II: 2,2,3-triphenylpropylpotassium and -cesium in THF at −75°.

A restatement of these observations is that low temperatures, good solvents for solvating cations, coordination of cations by 18-crown-6, and Li^+ and Na^+ as opposed to K^+ and Cs^+ favor reaction by path I while high temperatures, poorly solvating solvents, absence of good ligands such as 18-crown-6, and large rather than small alkali metal cations favor reaction by path II. The conditions which favor path I are precisely those which favor loose or separated ion pairs while those which favor path II are those which favor tight or contact ion pairs.[13] Hence, we propose that path I has a transition state resembling a loose ion pair, while path II has a transition state resembling a tight ion pair.

In retrospect it is logical that phenyl migration occurs largely or exclusively in a tight ion pair while benzyl elimination occurs preferentially in a loose ion pair. Thus in the rearrangement leading to the spiro anion, E, the alkali metal cation in the tight ion pair may accompany the anionic center during bridging (see sketch F) such that no great separation of charged centers is necessary at any time for cyclization. In contrast for elimination of benzyl anion from the ion pair, the cleavage reaction gives rise to an alkali metal cation separated from benzyl anion by a molecule of diphenylethylene; this is most obvious if the elimination reaction occurs in the usual *anti-periplanar*[14] conformation G. In order for elimination of benzyl anion (which possesses a delocalized charge) to occur from a conformation such as G extensive solvation is required to overcome the unfavorable separation of charge in the resulting transition state. Conditions which are ideal for solvating the dipolar transition state are just those required for formation of solvent separated ion pairs. It is tempting to suggest that loose and tight ion pairs are the species which are the immediate precursors respectively for the transition states which resemble loose and tight ion pairs; however, this plausible microscopic picture is not required by thermodynamic arguments.[15]



F



G

Recently Biellmann and Schmitt[16] have emphasized the importance of solvation in competitive Stevens and Sommelet rearrangements. The intramolecular Sommelet rearrangement was favored by conditions which strongly solvated the cation while the Stevens rearrangement was favored by conditions of weaker solvation.

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References and Notes

(1) Presented in part at the First Fall Organic Conference, American Chemical Society, N. Falmouth, Mass., Sept 30, 1973, Abstracts, p **48**.

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

(3) H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961); E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **85**, 3305 (1963); **89**, 1852, 2348 (1967); E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, *ibid.*, **94**, 4734 (1972).

(4) J. L. Dye, M. G. DeBacker, and V. A. Nicely, *J. Amer. Chem. Soc.*, **92**, 5226 (1970); M. T. Lok, F. J. Tehan, and J. L. Dye, *J. Phys. Chem.*, **76**, 2975 (1972).

(5) Benzyl anion is not included among the products reported in Table I because its carbonation product, phenylacetic acid, is moderately volatile and requires special conditions to avoid loss during isolation. When such conditions were utilized (*e.g.*, the last entry of Table I with Cs and 18-crown-6), phenylacetic acid was found in a yield just equal to that of the 2,2-diphenylpropanoic acid (D) reported.

(6) G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974). We are indebted to the authors for directions for the preparation and purification of 18-crown-6 prior to publication and Liotta, Harris, and Cook for samples and encouragement in the use of 18-crown-6.

(7) Unpublished experiments by Mr. A. B. Cottingham.

(8) L. Lochmann, J. Pospisil, and D. Lim, *Tetrahedron Lett.*, 257 (1966).

(9) M. Schlosser, *J. Organometal. Chem.*, **8**, 9 (1967).

(10) L. Lochmann and D. Lim, *J. Organometal. Chem.*, **28**, 153 (1971).

(11) W. J. Trepka, J. A. Favre, and R. E. Sonnenfeld, *J. Organometal. Chem.*, **55**, 221 (1973).

(12) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).

(13) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions," Vol. 1, Wiley-Interscience, New York, N.Y. 1972, especially pp 1–26 and 85–151. Since the state of solvation of loose ion pairs and free ions is similar, the present work is also in accord with path I occurring in a free anion.

(14) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions," Wiley, New York, N.Y., 1973, pp 105–124.

(15) *Cf.* the Curtin-Hammett principle, L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N.Y., 1970, pp 116–120.

(16) J. F. Biellmann and J. L. Schmitt, *Tetrahedron Lett.*, 4615 (1973).

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