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(10) Postdoctoral Research Associate, 1968–1969.

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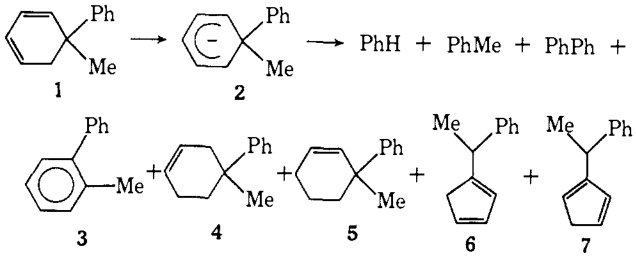
Reactions of the 6-Methyl-6-phenylcyclohexadienyl Anion. Role of the Counterion

Sir:

The elucidation of the factors[1] (*e.g.*, charge distribution,[2] ion pairing[3]) which determine the reactivity of carbanions has received an increasing amount of attention. We wish to report results which demonstrate that the title anion can undergo a variety of competitive inter- and intramolecular reactions at ambient temperature and that these reactions are greatly influenced by the counterion.

When 5-methyl-5-phenyl-1,3-cyclohexadiene[4] (**1**) is added to an approximately threefold excess of potassium amide in liquid ammonia at *ca.* −33° a deep-red solution is produced, the nmr spectrum[5] of which corresponds to what is expected for the 6-methyl-6-phenylcyclohexadienyl anion (**2**): multiplet at τ 2.3–3.2 (5 H, phenyl), apparent doublet of doublets (XX′ portion of an AA′BXX′ system) at 4.08 (2 H, C_2 and C_4 vinyl, J_{12} = 8 Hz, J_{23} = 6 Hz), complex multiplet at 6.16–6.54 (3 H, C_1, C_3, and C_5 vinyl), and singlet at 8.75 (methyl), partially obscured by the solvent absorption. Although there are no other peaks if the spectrum is obtained immediately after formation of the anion, additional signals can be observed after several hours.

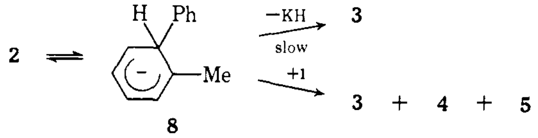
When the potassium salt of **1** is allowed to stand at 25° for 49 hr with a *ca.* tenfold excess of potassium amide a complex mixture of at least eight compounds is obtained in 75–90% yield.[6] Each component which was >1–2% of the mixture was isolated by glpc and identified by comparison of its infrared or nmr spectrum with that of an authentic sample.[7] Cyclopentadienes **6** and **7** were identified as an equilibrium mixture since they are readily interconverted (thermally)[8] under the glpc conditions used for isolation.



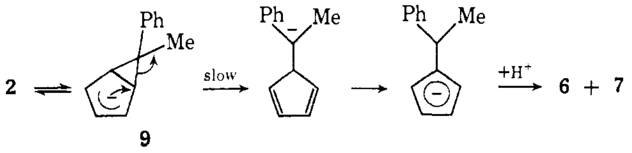
The formation of benzene and toluene and of biphenyl can be explained by loss of phenylpotassium and of methylpotassium,[9] respectively. *o*-Methylbiphenyl (**3**) can arise by intramolecular[10] migration of a substituent at C_6 (probably phenyl[1,11,12]) in **2**, followed by loss of potassium hydride.

Cyclohexenes **4** and **5** are very minor products but, along with **3**, are much more prominent when **1** (rather than potassium amide) is in excess. This is consistent with a relatively rapid (and reversible[13]) 1,2-phenyl migration followed by intermolecular hydride transfer to **1** (Scheme I).[14] The formation of cyclopentadienes **6** and **7** is particularly noteworthy and can be explained by an initial disrotatory electrocyclic ring closure,[15] followed by a rate-limiting cleavage of a perimetrical cyclopropyl bond.[16]

Scheme I



Scheme II



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[1] Reviews: (a) H. E. Zimmerman, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 345; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (c) H. F. Ebel, *Fortschr. Chem. Forsch.*, **12**, 387 (1969).

[2] J. Hine, *J. Org. Chem.*, **31**, 1236 (1966), and references cited.

[3] (a) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969); (b) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Wiley, New York, N. Y., 1968, Chapter V.

[4] Prepared from 4-methyl-4-phenyl-2-cyclohexenone ((a) R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 4765 (1967); (b) F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *ibid.*, **89**, 6704 (1967)) by lithium aluminum hydride reduction followed by *p*-toluenesulfonic acid catalyzed dehydration.

[5] Trimethylamine, taken as τ 7.87, was used as an internal standard.

[6] Undecane and tridecane were present as internal standards.

[7] (a) *o*-Methylbiphenyl (**3**): I. R. Sherwood, W. F. Short, and R. Stansfield, *J. Chem. Soc.*, 1832 (1932); (b) cyclopentadienes **6** and **7**: K. Hafner, *Justus Liebigs Ann. Chem.*, **606**, 79 (1957); (c) cyclohexenes **4** and **5** were prepared from 4-methyl-4-phenylcyclohexanone[4b] by reduction, acetylation, pyrolysis, and base-promoted isomerization (*cf.* S. W. Staley, *J. Amer. Chem. Soc.*, **89**, 1532 (1967)).

[8] (a) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); (b) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); (c) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

[9] *Cf.* (a) H. Pines and H. E. Eschinazi, *J. Amer. Chem. Soc.*, **78**, 5950 (1956); (b) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

[10] The product mixture did not change significantly under conditions of 40-fold dilution nor was any *m*- or *p*-methylbiphenyl detected.

[11] (a) E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 1852, 2348 (1967), and earlier papers; (b) T. F. Crimmins, W. S. Murphy, and C. R. Hauser, *J. Org. Chem.*, **31**, 4273 (1966).

[12] Phenyl migration is preferred over methyl migration because the activated complex for the former process is "aromatic" due to a "Möbius" interaction of the C_1, C_6, and phenyl p orbitals. For molecular orbital calculations see ref 1a and N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, **44**, 626 (1967).

[13] The reversibility of this migration derives from the expected greater stability of **2** relative to **8**.

[14] *Cf.* J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Lett.*, 1005 (1964).

[15] For electrocyclizations of pentadienyl anions, see (a) R. B. Bates and D. A. McCombs, *ibid.*, 977 (1969); (b) D. H. Hunter and S. K. Sim, *J. Amer. Chem. Soc.*, **91**, 6202 (1969).

[16] Recent evidence suggests that **9** should preferentially revert to **2** (D. J. Atkinson, M. J. Perkins, and P. Ward, *Chem. Commun.*, 1390 (1969)).

Of perhaps greatest interest is the fact that the distribution of products varies significantly when different counterions are present (see Table I). It can be seen that the relative yields of **3**, biphenyl, and **6** + **7** are greatest with lithium, sodium, and cesium amides, respectively. These results cannot be correlated by a straightforward application of the principle of hard and soft acids and bases[17] (HSAB) since the "hardest" cation (lithium)[18] appears to be paired with the "softest" activated complex (elimination of hydride).[17,19] However, a correlation can be made *if one considers the solvation of the counterions in the activated complexes.* By this analysis elimination of "hard" methide and the somewhat "softer" cyclopropyl ring cleavage proceed (relatively) fastest when present as contact ion pairs (or higher aggregates) involving sodium and cesium, respectively, whereas elimination of "soft" hydride is fastest with "soft" solvated lithium.[20]

Table I. Relative Yields of Major Products from the Reaction of 0.08 *M* 5-Methyl-5-phenyl-1,3-cyclohexadiene (**1**) with 0.8 *M* Alkali Metal Amide in Liquid Ammonia at 25° for 49 Hr

	Relative yield, %[a]			
Products[b]	$LiNH_2$[c]	$NaNH_2$	KNH_2	$CsNH_2$
Toluene[d]	53	62	60	60
Biphenyl	18	26	20	7
3	24	6	6	3
6 + **7**	5[e]	6	14	30

[a] Average of at least two runs; generally reproducible to ±10% of the listed value. All values are corrected for glpc molar response factors. [b] All products are stable under the reaction conditions. [c] Largely heterogeneous but not affected by a 40-fold dilution. [d] There was normally 5-35% less benzene than toluene. [e] Approximate value.

This interpretation was tested and given strong support by the observation that when 0.08 *M* **1** is caused to react with 0.8 *M* potassium amide in the presence of 0.8 *M* dicyclohexyl-18-crown-6, a cyclic polyether capable of complexing with potassium ions,[21,22] the relative yield of **3** increases to 22%, similar to that for lithium amide.[23] Although the reasons for HSAB correlations are not entirely clear,[15,16a] this analysis nevertheless does provide evidence for the nature of the ion pairing in the various activated complexes.[24]

Acknowledgment. Support of this research by the National Science Foundation and the Advanced Research Projects Agency is gratefully acknowledged.

(17) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

(18) (a) R. G. Pearson, *ibid.*, **85**, 3533 (1963); (b) W. S. Murphy and C. R. Hauser, *Chem. Ind.* (London), 832 (1969).

(19) H. Gilman, A. L. Jacoby, and H. Ludeman, *J. Amer. Chem. Soc.*, **60**, 2336 (1938).

(20) (a) T. E. Hogen Esch and J. Smid, *ibid.*, **87**, 669 (1965); **88**, 307, 318 (1966); (b) J. B. Grutzner, Ph.D. Thesis, University of Melbourne, 1967.

(21) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 2495, 7017 (1967).

(22) We thank Drs. H. E. Simmons and D. J. Sam of E. I. du Pont de Nemours and Co. for providing a sample of this compound.

(23) The other relative yields were 59% toluene, 9% biphenyl, and 10% **6** + **7**; in this case the yield of benzene exceeded that of toluene.

(24) Each of these processes can, in principle, occur *via* both contact and solvent-separated ion-pair activated complexes; this is perhaps most probable in the formation of benzene and toluene and the cyclopentadienes.

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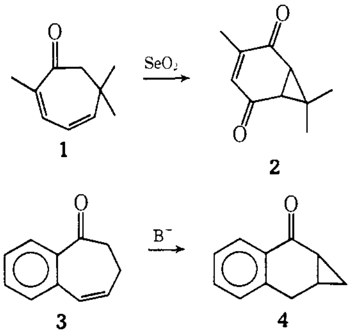
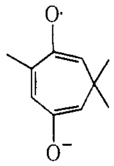
Application of Electron Spin Resonance Spectroscopy to Studies of Valence Isomerization. II. Bicyclo[4.1.0]heptene-2,5-semidiones[1]

Sir:

Valence isomerizations of the enolate anions derived from eurcarvone (**1**) or 2,3-benzocyclohepta-2,4-dienone (**3**) are known.[2,3] Treatment of **1** with base followed by a trace of oxygen yields a semidione that is also produced by treatment of **2** with potassium *t*-butoxide in DMSO solution. The semidione could have structure **5** or **6**. In a similar fashion treatment of **3** or **4** with base followed by a trace of oxygen yields a semidione that can have either structures **7** or **8**.



1 **2** **3** **4**



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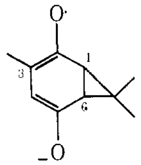

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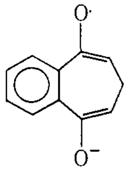

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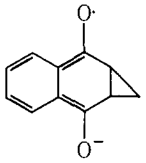

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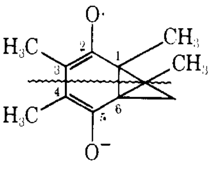
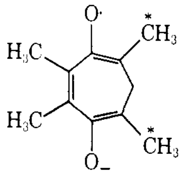
$a^H = 3.15, 3.45, 4.68$; $a_{CH_3}{}^H = 0.82, 4.95$ G

$a^H = 0.10, 0.10, 0.86, 1.64, 2.38, 2.38, 3.20, 3.20$ G

Structures **6** and **8** for the semidiones are instinctively preferred because the parent diones must have these bi- and tricyclic structures. The magnetic nonequivalence of the methylene hydrogen atoms in **7** and **8**, or of the *gem*-dimethyl groups in **5** and **6**, is more consistent with structures **6** and **8** than **5** and **7**. Final proof of structure is furnished by semidione **9** prepared by treatment of the bicyclic dione[4] with base in DMSO.



9



10

$a^H = 1.95, 0.87$ G
$a_{CH_3}{}^H = 5.20, 5.20, 0.25, 0.25$ G
〰 = nodal plane in ψ_4

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(1) This work was supported by grants from the National Science Foundation and the Army Research Office (Durham); part I: G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **91**, 2813 (1969).

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(3) S. Julia and Y. Bonnet, *Bull. Soc. Chim. France*, 1340 (1957); E. E. van Tamelen, J. McNary and F. A. Lornitzo, *J. Amer. Chem. Soc.*, **79**, 1231 (1957).

(4) W. C. Howell, M. Ktenas, and J. M. MacDonald, *Tetrahedron Lett.*, 1722 (1964).