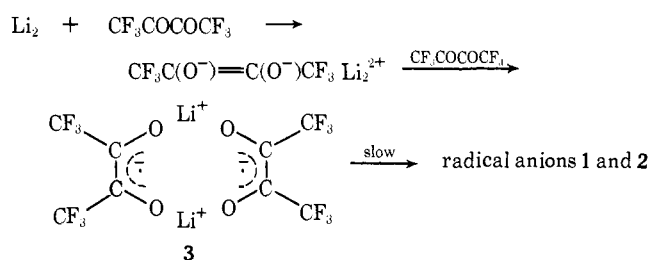Possible structures for **3** are the loose cis ion pair or a polymeric species, such as the triplet molecule, [CF$_3$C-(O·)=C(O$^-$)CF$_3$]$_2$Li$_2^{2+}$ with a singlet–triplet energy separation $J \ll a^F$.[8] We are unable to accept the assignment of **3** to a loose ion pair because we believe such a species would be in equilibrium with **1** (and probably **2**) under all conditions employed. We therefore assign the triplet structure to **3**.

Even more dramatic and startling observations were made during reduction by lithium in THF at low temperature. The solution containing an excess of perfluorobiacetyl was filtered through a glass frit after brief contact with finely divided lithium near the freezing point of THF, to yield spectrum 1c at $-60°$.[9] Spectrum 1c is composed of **1** and **2** and a sharp symmetrical singlet which we attribute to dissolved lithium atoms (or solvated electrons).[10] Very little **3** was detected as an initial reaction product at $-60°$. The reaction of lithium metal (surface) with the dione thus proceeds to yield **1** and **2** directly since we have already shown that the conversion of **3** to **1** and **2** is a slow process. Moreover, apparently dissolved lithium metal reacts only slowly with the dione at this temperature. Upon warming to $25°$ the symmetrical esr absorption of the dissolved lithium metal rapidly disappeared while the signal from **3** increased in relative intensity. Figure 1a resulted when the solution had warmed to $25°$. The reaction of the dissolved lithium metal with the dione thus proceeds to yield **3** in preference to **2**. Upon standing, spectrum 1a changed to 1b as **3** was converted to **2** and **1**, a process requiring ~45 min for completion at $25°$. The observed spectral changes are the results of kinetic effects because once a solution giving spectrum 1b (a mixture of only **1** and **2**) has been obtained, lowering the temperature to $-60°$ does not regenerate species **3** or the sharp singlet assigned to the lithium atom. A possible reaction sequence which explains the observed results of dissolved lithium metal → **3** → **1** and **2** involves the reduction of the diketone to a dianion followed by reaction with a second diketone molecule to yield **3**.

Li$_2$ + CF$_3$COCOCF$_3$ ⟶

CF$_3$C(O$^-$)=C(O$^-$)CF$_3$ Li$_2^{2+}$ $\xrightarrow{\text{CF}_3\text{COCOCF}_3}$

3

$\xrightarrow{\text{slow}}$ radical anions **1** and **2**

Soluble paramagnetic salts of perfluorobiacetyl with Ca^{2+}, Sr^{2+}, and Ba^{2+} have been prepared in THF. These spectra show hfs by six equivalent fluorines ($a^F \sim 10.5$ G) and a further second-order splitting not

(8) Triplet species with $J \ll a$ are recognized as components of alkali metal ketyls: N. Hirota and S. I. Weissmann, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

(9) The lithium was prepared by vacuum evaporation of a solution of lithium–ammonia in a tube attached to the esr cell. Sodium or potassium mirrors were generated in similar tubes by standard techniques.

(10) Undissolved lithium produces a broad unsymmetrical signal. Some polymeric aggregate involving radical anion(s), dianion, diketone, and gegenion could perhaps be invoked to explain this narrow line provided such a species possesses rapid electron exchange or a very short relaxation time. However, the *g* value of this line seems to exclude this interpretation.
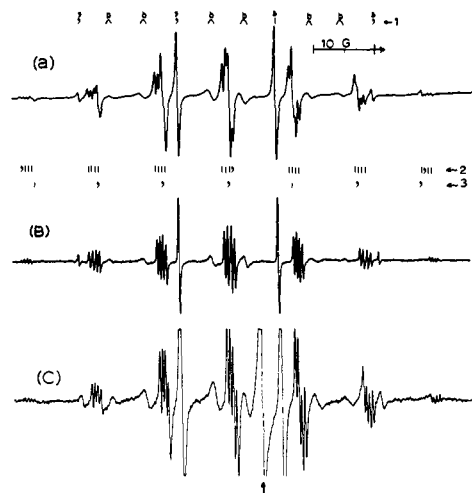
Figure 1. Esr spectra of the lithium salt of perfluorobiacetyl radical anion in THF solution: (a) immediately after reaction of the dione with lithium metal at $25°$, s and b refer to sharp and broad lines; (b) the spectrum observed 45 min later; (c) initial spectrum observed by reduction at $-60°$; ↑ indicates absorption of the dissolved lithium metal. Upon warming, c changes initially to a and finally to b.

yet analyzed. Apparently, biradical **4** exists with a singlet–triplet energy separation $\ll a^F$.[11]

3
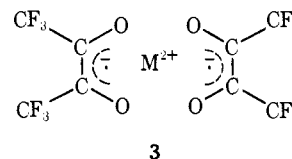
Acknowledgment. Some of the initial experiments were performed by Dr. D. Lini and G. Underwood. Dr. R. Rieke provided valuable comments.

(11) H. Lemaire, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 886 (1968).

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Kinetic Evidence for a Bishomotropylium Ion

Sir:

While the monohomotropylium[1a] ion has been the subject of much recent interest,[2] the direct observation of the 1,4-bishomotropylium ion Ia in our laboratory last year[3] has led to the characterization of a number of other ions of this type in strong acid media.[4] Whether

(1) (a) For a definition of the nomenclature and a review on homoaromaticity please refer to: S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) bishomotropylium ions will be extensively discussed in a forthcoming paper.

(2) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references therein.
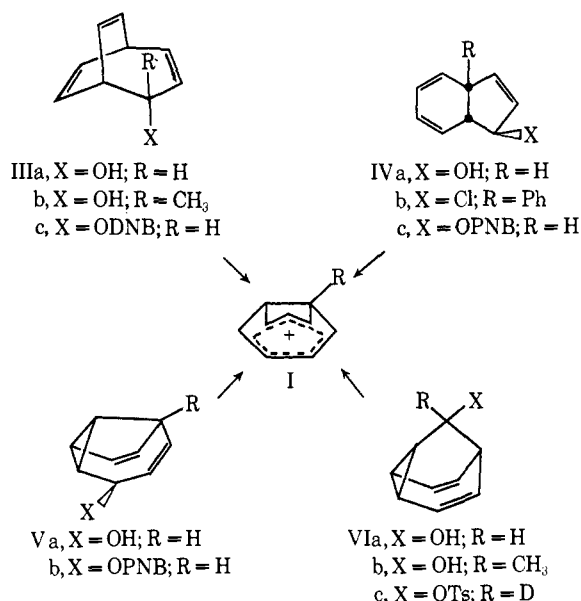
(3) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146 (1970).

(4) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4452 (1970); (b) M. Roberts, H. Hamberger, and S. Winstein, *ibid.*, **92**, 6346 (1970); (c) G. Schroeder, U. Prange, N. S. Bowman, and J. F. M. Oth, *Tetrahedron Lett.*, 3251 (1970); (d) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971); (e) D. L. Harris, D. Cook, J. Dirlam, and S. Winstein, unpublished results.

Communications to the Editor

the bishomotropylium ion also exists under other conditions had, until now, not been established. In fact, the solvolysis of potential precursors failed to reveal any unusual rate enhancements.[5] We now wish to report our studies on the epimeric 7-bicyclo[4.3.1]deca-2,-4,8-trienyl *p*-nitrobenzoates and provide evidence for the formation of the bishomotropylium ion II under conditions of short life and considerable nucleophilicity.[6,7]

Ia, R = CH₃
b, R = H

II
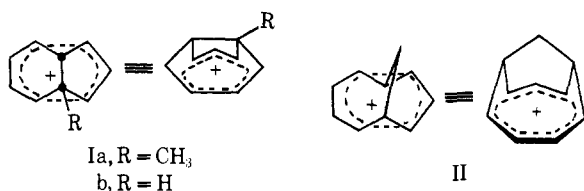
Although I could be generated in strong acid from IIIa,[4a] IIIb,[3] IVa,[4e] Va,[4a] and VIb,[3] the rates of solvolysis of IIIc,[5b] IVb,[5d] IVc,[5e] Vb,[5e] and VIc[5a] did not differ appreciably from model compounds. However,

IIIa, X = OH; R = H
b, X = OH; R = CH₃
c, X = ODNB; R = H

IVa, X = OH; R = H
b, X = Cl; R = Ph
c, X = OPNB; R = H

Va, X = OH; R = H
b, X = OPNB; R = H

VIa, X = OH; R = H
b, X = OH; R = CH₃
c, X = OTs; R = D

whereas Ia decomposes at −50° and Ib at −90°, II is stable above room temperature, raising the possibility that it might also survive other reaction conditions. To investigate this and provide suitable models for comparison, the synthesis of system VII was undertaken.
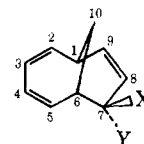
Reduction of the mercurial from the reaction between bullvalene[8] and mercuric acetate in methanol by sodium borohydride leads to 7-methoxybicyclo[4.3.1]-deca-2,4,8-triene (VIIc).[7b] The oxymercuration reaction, combined with reduction of the oxymercurial intermediate by sodium borohydride, *in situ*, provides a

VIIa, X = OPNB; Y = H
b, X = OH; Y = H
c, X = OMe; Y = H
d, X = H; Y = OH
e, X = H; Y = OPNB

convenient mild method for hydration of carbon-carbon double bonds.[9] The addition of mercuric acetate to bullvalene in tetrahydrofuran–water at room temperature followed by reduction of the mercurial with sodium borohydride leads to *exo*-bicyclo[4.3.1]-deca-2,4,8-trien-7-ol (VIIb) and an isomeric alcohol as a minor product.[10] The desired alcohol was separated by column chromatography. Oxidation by chromic anhydride–pyridine complex[11] in methylene chloride leads to the corresponding ketone, which was reduced to the endo isomer (VIId) by lithium aluminum hydride in diethyl ether at room temperature. Glc showed no trace of the exo isomer under conditions in which 1% could have been detected. *p*-Nitrobenzoates were prepared in the usual manner.[12]
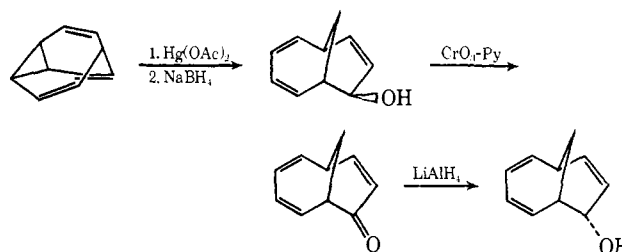
The structure and configuration of both isomers were assigned by pmr. In the exo alcohol, no coupling between H₆ and H₇ was observed, as is expected since the dihedral angle between the C₆–H₆ bond and the C₇–H₇ bond is approximately 90°.[13] In the endo alcohol, this angle is about 25° and the coupling constant, 6 Hz.

Solvolysis of *exo*-7-bicyclo[4.3.1]deca-2,4,8-trienyl *p*-nitrobenzoate (VIIa) was carried out in 80% aqueous acetone. The rate data gave good first-order plots. Rate constants at 41.4 and 65.0° were, respectively, 5.3×10^{-5} and 5.3×10^{-4} sec^{-1}. Product analysis revealed that the exo alcohol (VIIb) was the only detectable species formed under these conditions (quenching of ion II in methanol gave only the corresponding *exo*-methoxy ether (VIIc)).[4b,c] At 100.0° the *endo*-*p*-nitrobenzoate (VIIe) gave a rate constant of 6.6×10^{-7} sec^{-1}. These results are compared to other similar allylic systems in Table I.

(5) (a) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (b) J. C. Barborak and P. v. R. Schleyer, *ibid.*, **92**, 3184 (1970); (c) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970); (d) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967); (e) D. Cook, A. Diaz, J. P. Dirlam, D.L. Harris, M. Sakai, S. Winstein, J. C. Barborak, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1405 (1971).

(6) We cannot rule out the possibility that bishomotropylium ions are present in the solvolysis of IVc and Vb.[5e]

(7) (a) There are indications that II may also play a part in electrophilic additions.[7b] (b) H.-P. Loeffler and G. Schroeder, *Tetrahedron Lett.*, 2119 (1970).

(8) G. Schroeder, *Angew. Chem.*, **75**, 722 (1963).

(9) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(10) Structures involving three-membered rings, though attractive, are ruled out by the presence of six olefinic protons on the pmr spectrum, as is the epimer by comparison with VIId. The instability of this alcohol has hampered our efforts at the elucidation of its structure. Work is being continued in this direction.

(11) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

(12) Satisfactory analytical and spectroscopic data were obtained for new compounds.

(13) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, pp 103–105.

Table I. Solvolysis Rates for Allylic Systems in 80%
Aqueous Acetone

| Compd	$10^7 k$ at 100°, sec^{-1}	k_{rel} at 100°
exo-VII	3.5×10^6 [a]	1.2×10^6
endo-VII	6.6	2.3
exo-VIII[c]	176	63
endo-VIII[c]	47	17
exo-IX[c]	2.8	1[b]
endo-IX[c]	2.7	1[b]
X[d]	37	13

[a] Extrapolated. [b] These values are not corrected for acyl–oxygen cleavage. [c] Reference 14. [d] E. C. Friedrich, Ph.D. Thesis, University of California, Los Angeles, Calif., 1961.

Taking the *exo*-2-bicyclo[3.2.1]oct-3-enyl *p*-nitrobenzoate (*exo*-VIII)[14] as a standard for rates of solvolysis of allylic *p*-nitrobenzoates in fused six-membered ring systems, we find that the butadiene moiety in VII, while inductively destabilizing, actually enhances the rate by at least 10³. Further insight is gained by comparing the effects of one and two double bonds on the stability of the allylic cation. Whereas in going from *exo*-VIII to *exo*-IX the solvolysis rate is lowered by a factor of 240, the opposite effect is observed by comparison with *exo*-VII. The rate ratio of *exo*- and *endo*-VII bears out our choice of models and the fact that we are indeed dealing with anchimeric assistance to solvolysis since we would not expect backside participation in the endo case.

These results are consistent with the intervention of the bishomotropylium ion II, in which charge is delocalized significantly into the butadiene moiety,[15] in the rate-determining step. We ascribe the greater stability

(14) A. F. Diaz, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 7477 (1970).
(15) An unsymmetrical homoconjugative-type charge delocalization can be ruled out by the opposite effects of two and one double bonds in systems VII and IX, respectively, as compared to VIII, and the magnitude of these (*vide infra*).[1b] A theoretical explanation for the lower energy of the symmetrical species has been provided by perturbation theory calculations: D. Blagdon, S. Yoneda, and S. Winstein, submitted for publication.

VII

exo, 3×10^3
endo, 9×10^{-2}

VIII

exo, 1
endo, 3×10^{-1}

IX

exo, 4×10^{-3}
endo, 4×10^{-3}

X

0.2
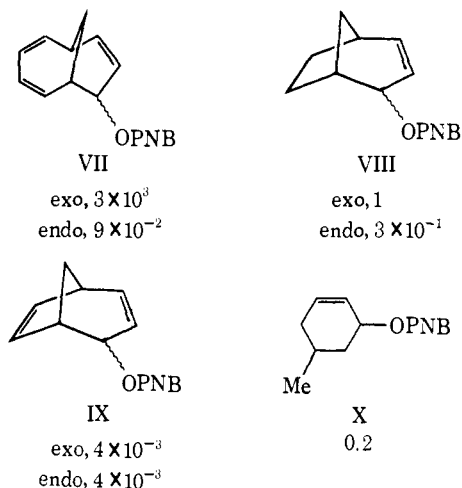
of II over I to the more favorable overlap of p orbitals on C_5 and C_7 (and C_2 and C_9) as evidenced by models of both ions.[1b]

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Book Reviews

Organometallic Reactions. Volumes 1 & 2. Edited by E. I. Becker (University of Massachusetts) and M. Tsutsui (Texas A&M University). Wiley-Interscience, New York, N. Y. 1971. Volume I: x + 389 pp. $17.95. Volume 2: x + 450 pp. $17.95.

This new series proposes, in the editors' words, "to provide complete chapters on selected categories of organometallic compounds, describing the methods by which they have been synthesized, and the reactions they undergo. The emphasis is on the preparative aspects, although structures of compounds and mechanisms of reactions are briefly discussed and referenced. Tables of all of the compounds prepared in the category under consideration and detailed directions for specific types make these chapters particularly helpful to the preparative chemist." Furthermore, the book jacket promises, "for the first time, a single source to which the preparative chemist may refer for information on reaction mechanisms, references to analogous reactions, and particularly the experimental details of the typical reactions."

The foregoing purposes of the new series echo the goals of the highly successful and classic series, "Organic Reactions," and

invite comparison with similar existing reviews in the field of organometallic chemistry. In this series the word "reaction" is interpreted far more broadly than in individual chapters of "Organic Reactions," where the focus is narrowed to a well-defined reaction of broad applicability. "Organometallic Reactions," on the other hand, includes treatments of specific classes of carbon–metal bonds and often tries to cover broad aspects of their behavior in monographic style. Volume I contains chapters on the redistribution reactions of organoaluminum compounds (T. Mole) and on the chemical fixation of molecular nitrogen (M. E. Vol'pin and V. B. Shur). An eleven-chapter treatment of the reactions of organomercury compounds (L. G. Makarova), comprising two-thirds of the book, is an extensive survey of carbon–mercury bond cleavage reactions. Volume II contains an additional six chapters on this same theme covering 90 pages. The balance of Volume II consists of a general survey of the redistribution reaction (K. Moedritzer) and an account of the reactions of organotellurium compounds (K. J. Irgolic and R. A. Zingaro). Although the real utility of an author index in compilations of this kind can be questioned, it is curious that Volume I has such an index while Volume II does not.