tionally induced circular dichroism which is generally weaker than the configurational optical activity. We have found in most cases studied that the neighbor-induced optical activity is at least an order of magnitude less than the conformational (or vicinal) optical activity.[6]

It is possible that the present technique may be useful in identifying magnetic dipole transitions of metal complexes which are optically inactive. Thus we have found that the distrychnine salt of the [PtCl$_4$]$^{2-}$ ion gives appreciable circular dichroism in the regions of the spin-allowed magnetic dipole transitions of the anion.

The CD spectra were recorded on a Durrum-Jasco SS20 modified CD instrument at a sensitivity of 1 mdeg/cm.

Acknowledgment. We thank the National Research Council of Canada for financial support.

(6) B. Bosnich and J. MacB. Harrowfield, unpublished results.

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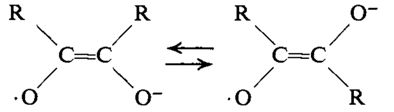
Ion Pairing in Alkali Metal Salts of Biacetyl and Perfluorobiacetyl. Mechanism of the Homogeneous Reduction of an α-Diketone by Lithium Metal and an Example of a Remarkably Slow Equilibration between Paramagnetic Lithium Salts in Tetrahydrofuran Solution[1,2]

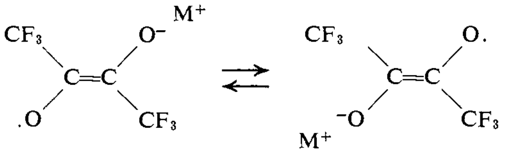
Sir:



Biacetyl semidone (10^{-5} *M*, 25°) exists as a mixture of cis (a^{H} = 7.0 G, DMSO) and trans (a^{H} = 5.6 G, DMSO) isomers.[3] In the presence of tetraalkylammonium alkoxides the ratio of trans–cis isomers is 35 in DMSO solution at 25°. We presume this reflects the stability of the free anions because the cis–trans ratio observed in the presence of R$_4$N$^+$ is not particularly solvent dependent. Rubidium and cesium cations (0.1 *M*) favor the trans isomer by preferential association since trans–cis ratios of 40 and >200, respectively, were observed in DMSO. Smaller alkali metal cations such as potassium, and, to a much greater extent, sodium and lithium gegenions favor the cis structure; trans/cis = 18, 1.8, <0.01 for 0.1 *M* K$^+$, Na$^+$, Li$^+$, DMSO, 25°.[4] Changes in solvent had a large effect on these cis–trans ratios.[3] The lithium salt (cis) exists as a tight ion pair with hyperfine splitting (hfs) by a single lithium atom, a^{Li} = 0.58 G (DMSO, 25°). The cis sodium salt shows a sodium hfs, a^{Na} = 0.23 G, DMSO, 25°. However, the sodium hfs consists of much broader lines than the lithium hfs, presumably the result of exchange with free sodium ions. Addition of dibenzo-18-crown-6 ether[5] (0.1 *M*) to a DMSO solution causes the sodium hfs to become quite sharp, apparently because the free sodium ions are now complexed by the cyclic ether and no longer exchange readily with the ion pair. The ether (0.1 *M*) also had an appreciable effect on the trans–cis ratio in DMSO increasing it from 18 to 40 for 0.1 *M* K$^+$ and from 1.8 to 7.2 for 0.1 *M* Na$^+$. In the presence of the ether the trans–cis ratios approach more closely those expected for the free anions. No alkali metal splittings have been observed for any of the trans isomers.

Perfluorobiacetyl[6] radical anion gave additional evidence for the formation of several kinds of ion pairs. Electrolytic reduction in THF (R$_4$N$^+$ cation) gave a trans (a^{F} = 8.30 G, a^{C} = 4.5, 1.8 G)–cis (a^{F} = 10.92 G) ratio of 170, whereas in DMSO the ratio was 120. Again Cs$^+$ or Rb$^+$ seemed to favor the trans structure since trans/cis = 150 (DMSO, Rb$^+$), >200 (THF, Cs$^+$).

In THF, perfluorobiacetyl was readily reduced by the group Ia and certain group IIa metals, a process which does not yield reasonable spectra for biacetyl itself. In THF the equilibrium trans–cis ratios at 25° were 1.5, 0.4, and 1.2 for Li$^+$, Na$^+$, and K$^+$, respectively. Hyperfine splitting from Li$^+$ and Na$^+$ was well resolved in the cis structure while the trans isomers showed pronounced broadening of certain lines, a phenomenon interpreted as the result of magnetic nonequivalence of the CF$_3$ groups because of movement of the gegenion in **1**.[7] For Na$^+$ the trans isomer spectrum consisted of four sharp lines in the ratio 1:9:9:1 separated by 2(8.05) G, apparently the result of extensive alternate line broadening in the fast exchange mode. The line-width alternation was more pronounced for Na$^+$ than for K$^+$. With Li$^+$, ten lines were observed which were consistent with a^{F} = 10.38 (3), 5.38 (3) G (8.11 G av) and with the broadening expected for the slow exchange mode (Figure 1a). The rate constant for interconversion of the isomeric structures of **1** is ~10^7 sec^{-1}.



1

The esr spectra of the lithium salts of perfluorobiacetyl radical anion showed an unexpected variation with time following reduction by lithium metal. Immediately after reduction at 25° the spectrum of Figure 1a was observed. This spectrum slowly changed to 1b. Spectrum 1a is interpreted as being a mixture of **1** (with line broadening), a tight ion pair **2** with a^{Li} = 0.48 G, and another species, **3**, with sharp lines the result of hfs by six equivalent fluorine atoms (without lithium splitting), a^{F} = 10.67 G. Spectrum 1b contains only **1** and **2** without a trace of **3**. The hfs of **3** strongly suggests a cis structure for the perfluorobiacetyl fragment(s).

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(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXIII

(2) This work was supported by a grant from the National Science Foundation.

(3) G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, 70, 1320 (1966).

(4) The lithium salt is most conveniently prepared by the addition of lithium iodide to a solution of the semidione prepared from the disproportionation of acetoin by some other base, *e.g.*, triton B. The other gegenions were investigated by use of appropriate alkali metal *tert*-butoxide in the disproportionation of acetoin.

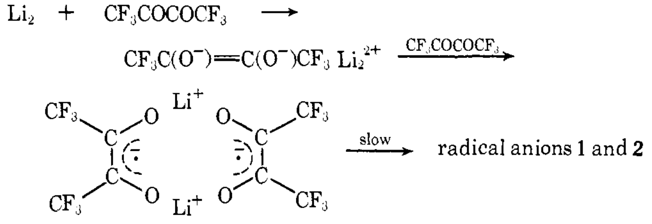
(5) C. J. Pedersen, *J. Amer. Chem. Soc.*, **92**, 386, 396 (1970).

(6) L. O. Moore and J. W. Clark, *J. Org. Chem.*, **30**, 2472 (1965).

(7) Similar effects have been observed for the benzosemiquinones: J. Oakes and M. C. R. Symons, *Trans. Faraday Soc.*, **66**, 10 (1970).

Possible structures for **3** are the loose cis ion pair or a polymeric species, such as the triplet molecule, $[CF_3C(O\cdot)=C(O^-)CF_3]_2Li_2^{2+}$ 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**.



$$Li_2 + CF_3COCOCF_3 \longrightarrow CF_3C(O^-)=C(O^-)CF_3\ Li_2^{2+} \xrightarrow{CF_3COCOCF_3}$$

3

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

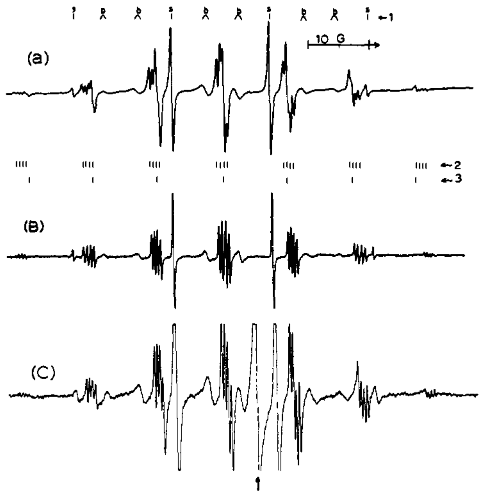
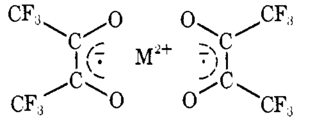


Figure 1. Esr spectra of the lithium salt of perfluorobiacetyl radical anion in THF solution: (a) immediately after reaction of the dione with lithium metal at 25°, s and b refer to sharp and broad lines; (b) the spectrum observed 45 min later; (c) initial spectrum observed by reduction at −60°; ↑ indicates absorption of the dissolved lithium metal. Upon warming, c changes initially to a and finally to b.



3

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

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[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.

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

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Received April 9, 1971

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

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(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.