

Aliphatic Semidiones. XXIII. Perfluorobiacetyl Radical Anions¹

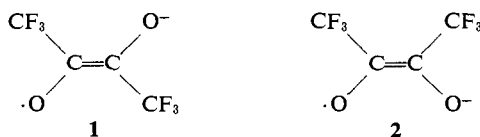
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Abstract: Perfluorobiacetyl has yielded six different radical anions detected by esr spectroscopy. In solvents such as dimethyl sulfoxide or hexamethylphosphoric triamide the radical anions are observed with a trans/cis ratio >100 unaffected by the nature or concentration of the gegenion. In ethereal solvents at low degrees of reduction *cis*-perfluorobiacetylsemidione is tightly associated with one lithium cation while ion pairing with the trans isomer is deduced by the detection of time-averaged nonequivalent trifluoromethyl groups. The trans/cis ratio of ~ 0.5 with lithium as the counterion decreases to 0.1 with sodium cations and then increases to ~ 3 as the gegenion is changed to potassium and to >100 with cesium. In the presence of mixtures of lithium and either sodium, potassium, or rubidium cations, four discrete 1:1 ion pairs are observed in which the two counterions are each complexed with the *cis*- and *trans*-perfluorobiacetyl radical anions with no evidence of time averaging between the ion pairs. At high degrees of reduction by lithium metal or lithium iodide additional *cis* and *trans* species are observed which are believed to involve quadruple ions consisting of one semidione moiety, one enedione dianion, and two lithium cations. Various combinations of the four ionically associated species can be observed depending on the solvent. In 2-methyltetrahydrofuran the four species can be observed simultaneously. Reduction with lithium metal in tetrahydrofuran initially leads mainly to the quadruple ions which slowly are converted to, and equilibrate with, the 1:1 ion pairs.

We were originally attracted to the synthesis of perfluorobiacetyl radical anion in connection with theoretical problems connected with the magnitude of esr hyperfine fluorine interaction in fluoro-substituted radicals or radical ions.² The perfluoroacetone ketyl has been prepared^{3,4} and values of $a^F = 34.9$, $a_{CF_3}^C = 8.0$, and $a_{CO}^C = 23.3$ G measured in acetonitrile. Corresponding values for the trans isomer of perfluorobiacetyl radical anion in hexamethylphosphoric triamide were determined to be $a^F = 8.60$, $a_{CF_3}^C = 4.7$, and $a_{CO}^C = 2.1$ G. During the course of this work we made a number of observations concerning the reaction of one-electron reducing agents with perfluorobiacetyl.⁵ Moreover, we have come to recognize the existence of a number of different ionically associated species involving the perfluorobiacetyl radical anion and lithium cation in ethereal solvents. The perfluorobiacetyl radical anion is the first alkali metal semidione that we have been able to thoroughly study in ethereal solvents by esr. This is due primarily to the greater stability and/or ease of preparation of the perfluorobiacetyl semidione relative to its hydrogen analog.

Methods of Reducing Perfluorobiacetyl. Electrolytic reduction of the dione⁶ in DMSO or THF at a platinum spoon electrode² in the presence of tetra-*n*-butylammonium perchlorate gave strong signals of the trans semidione, **1**, $a^F = 8.50$ – 8.55 G. The *cis* isomer **2** was



(1) This work was supported by grants from the National Science Foundation and the National Institutes of Health.

(2) G. A. Russell, J. L. Gerlock, and G. R. Underwood, *J. Amer. Chem. Soc.*, **94**, 5209 (1972).

(3) E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967).

(4) E. R. Knolle and J. R. Bolton, *J. Amer. Chem. Soc.*, **91**, 5411 (1969).

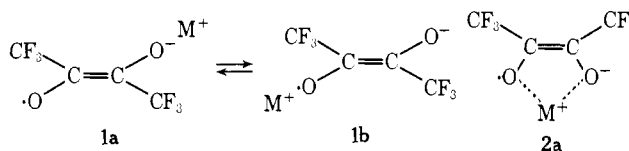
(5) G. A. Russell, J. L. Gerlock, and D. F. Lawson, *J. Amer. Chem. Soc.*, **93**, 4088 (1971).

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

barely detectable (trans/cis > 100) in either solvent, $a^F \cong 12.0$ G. The trans/cis ratio is thus considerably higher than for biacetyl radical anion itself (trans/cis ≈ 35 in DMSO with 0.1 *M* (CH₃)₄NOH).⁷ Upon interruption of the electrolysis in DMSO the esr signal of **1** disappeared after a few minutes.

Treatment of the diketone with iodide ion in DMSO or HMPA produced **1** and less than 1% of **2** with counterions such as Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺, or Et₄N⁺. In DMSO treatment of the diketone with the alkali metal *tert*-butoxides also produced the trans semidione, presumably from the reaction of methylsulfinylmethide ion (Figure 1). The observation of the same esr signal with lithium or potassium or ammonium counterions in DMSO or HMPA indicates that ion pairing which could affect the ratio of **1/2** is much less important in the case of the perfluorobiacetyl radical anion than for biacetyl radical ion.⁷

In DMF the iodide ion reduced the diketone but now the effect of the counterion was apparent. With ammonium iodide the esr signal of **1** faded quite rapidly while with lithium or sodium the ratio of **1/2** was considerably less than 100:1 and decreased with an increase in the concentration of the gegenion. Furthermore, the spectrum of **1** at high lithium ion concentration showed line width alternation with a loss in intensity of the second, fourth, and sixth peaks of the septet. We conclude that in DMF association between lithium or sodium cations and **1** and **2** occurs. In ethereal solvents the evidence for the 1:1 ion pairs **1a**, **b** and **2a** becomes quite conclusive.



(7) G. A. Russell, D. F. Lawson, H. L. Malkus, R. D. Stephens, G. R. Underwood, T. Takano, and V. Malatesta, *J. Amer. Chem. Soc.*, **96**, 5830 (1974).

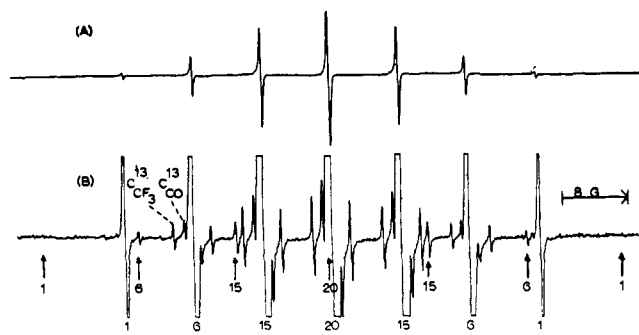


Figure 1. ESR first derivative spectra of **1** and **2** generated from perfluorobiacetyl and potassium *tert*-butoxide in DMSO at 25°: (a) the spectrum of **1** observed at high signal/noise, (b) detection of **2** by amplification of the esr signal. In addition to the septet splitting from **2** the natural abundance ^{13}C hfs of **1** is seen.

In acetonitrile reduction of the dione by lithium iodide gives evidence of more extensive ion pairing than in DMF. The spectrum of $\mathbf{1a} \rightleftharpoons \mathbf{1b}$ shows a more pronounced line width alternation in the fast exchange mode; the lines from **2** show some broadening perhaps from an unresolved lithium hfs, and the ratio of $1/2$ decreases still further to ~ 7 (Table I).

Perfluorobiacetyl is rapidly reduced by lithium iodide in dimethoxyethane, tetraglyme, THF, 2-MeTHF, or ethyl ether. The color of iodine or I_3^- is quite pronounced as it is in DMSO or HMPA solutions. No reaction is observed with potassium iodide in ethereal



solvents. However, when irradiated with a Hanovia medium pressure mercury lamp with quartz cells and lenses there was an immediate production of the semidione at a steady state concentration. Interruption of the irradiation caused the signal to disappear completely in a few seconds at most. Under similar conditions there is no reduction of biacetyl or benzil by either lithium iodide or by potassium iodide and light. *p*-Benzoquinone behaves similar to perfluorobiacetyl and is reduced spontaneously by lithium iodide or photochemically by potassium iodide in THF solution.

Sodium iodide spontaneously reduced the dione in DME, THF, or 2-MeTHF but not in ethyl ether. Reduction of the dione by calcium iodide and by anhydrous magnesium bromide in THF as well as by the alkali metals in a variety of ethereal solvents was also observed.

Detection of Ionic Association in THF. When a saturated THF solution of lithium iodide is added in aliquots to a THF solution of perfluorobiacetyl such that its concentration relative to the dione varies widely, a series of distinct spectral changes is observed. Adding a small amount of lithium iodide gives rise to the esr signals of $\mathbf{1a,b}$ and $\mathbf{2a}$, $\Delta g(\mathbf{1a,b} - \mathbf{2a}) = 0.00015$ (Figure 2A). The spectrum of $\mathbf{2a}$ is a septet split into unit intensity quartets by lithium ion ($a^{\text{Li}} = 11.22 \pm 0.03$ and $a^{\text{Li}} = 0.54$ G). The spectrum of $\mathbf{1a,b}$ shows no Li^+ hfs and clearly exhibits line width alternation in the slow exchange mode, *i.e.*, below the coalescence temperature ($a_{\text{av}}^{\text{F}} = 8.25$ G). Additional lithium iodide increases the intensity of these signals and introduces a third semidione ($\mathbf{2c}$) (Figure 2B) whose value of $a^{\text{F}} = 10.85$ G

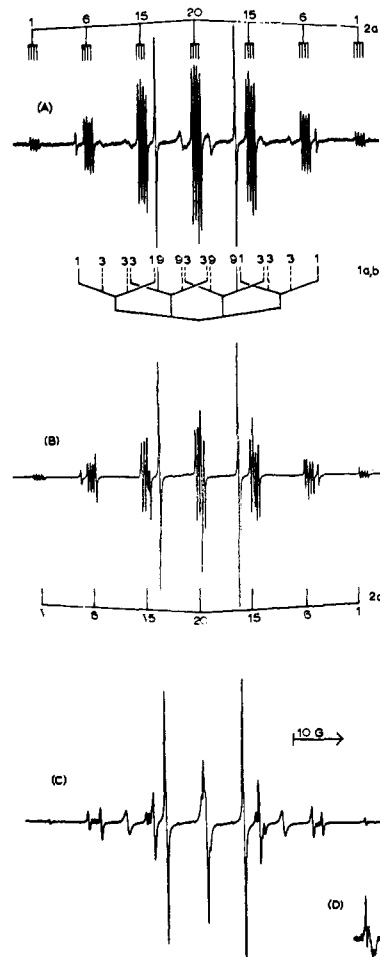


Figure 2. The esr spectra observed upon the addition of lithium iodide to perfluorobiacetyl in THF: (A) the mixture of $\mathbf{1a,b}$ (slow exchange mode) and $\mathbf{2a}$ observed at low lithium iodide concentrations; (B) the appearance of a new *cis* species $\mathbf{2c}$ at higher degrees of reduction ($\mathbf{1a,b}$ is in a faster exchange than in spectrum A); (C) at still higher lithium iodide concentrations the *trans* semidione(s) is in the fast exchange mode ($\mathbf{2c}$ now predominates over $\mathbf{2a}$); (D) wing peak only (loss of lithium hfs in $\mathbf{2a}$ and the observation of a mixture of $\mathbf{2c}$ and $\mathbf{2a}$ at highest lithium iodide concentrations).

for six equivalent fluorines with $\Delta g(\mathbf{1a,b} - \mathbf{2c}) = 0.00022$ is suggestive of a *cis* semidione moiety. No lithium hfs is detectable for this species. As lithium iodide is added the appearance of the *trans* isomer (Figure 2c) changes in that line width alternation appears to be less pronounced and the magnitude of the fluorine coupling decreases slightly. The spectrum becomes slightly asymmetric with the sharp high-field lines being somewhat more intense than the corresponding low-field lines. This is suggestive of a mixture of two species with slightly different g values and fluorine hfs. At high lithium iodide concentrations the *trans* isomer is in the fast exchange mode. Continued addition of lithium iodide first broadens the lithium hfs in $\mathbf{2a}$ and then removes it completely to yield a septet ($a^{\text{F}} = 11.2$ G) which can be observed in the presence of $\mathbf{2c}$. The ratio of $\mathbf{2c}/\mathbf{2a}$ is a function of the concentrations of diketone and lithium iodide employed. In a typical experiment the ratio reaches a maximum value of $\sim 4:1$ reasonably early in the reduction and remains at about this value even when the lithium iodide is present in a large excess. At low degrees of reduction where sharp

Table I. Semidiones Observed Under a Variety of Conditions

Solvent ^a	Reductant	Semidiones detected	a^F	a^{M^+}	a^C	Line width alternation ^b	[1a,b]/[2a]	Δg - (1a,b-2a) $\times 10^5$
DMSO	LiO- <i>t</i> -Bu	1	8.54	<i>d</i>	2.0, 4.7	None	>100	<i>e</i>
		2	11.8	<i>d</i>	<i>d</i>	None		
DMSO	NaO- <i>t</i> -Bu	1	8.50	<i>d</i>	1.9, 4.7	None	>100	<i>e</i>
		2	11.6	<i>d</i>	<i>d</i>	None		
DMSO	KO- <i>t</i> -Bu	1	8.45	<i>d</i>	2.0, 4.6	None	>100	<i>e</i>
		2	11.8	<i>d</i>	<i>d</i>	None		
DMSO	RbO- <i>t</i> -Bu	1	8.45	<i>d</i>	1.8, 4.6	None	>100	<i>e</i>
		2	11.8	<i>d</i>	<i>d</i>	None		
DMSO	CsO- <i>t</i> -Bu	1	8.50	<i>d</i>	1.9, 4.7	None	>100	<i>e</i>
		2	11.9	<i>d</i>	<i>d</i>	None		
DMSO	Electrolytic, (<i>n</i> -C ₄ H ₉) ₄ N ⁺ ClO ₄ ⁻	1	8.55	<i>d</i>	4.74	None	>100	<i>e</i>
		2	~12	<i>d</i>	<i>d</i>	None		
THF	Electrolytic, (<i>n</i> -C ₄ H ₉) ₄ N ⁺ ClO ₄ ⁻	1	8.50	<i>d</i>	4.70	None	<i>e</i>	<i>e</i>
		2						
HMPA	M ⁺ I ⁻	1	8.60	<i>d</i>	2.1, 4.7	None	>100	<i>e</i>
		2	11.97	<i>d</i>	<i>d</i>	None		
DMF	LiI	1a,b	8.50	<i>d</i>	<i>d</i>	Fast	<i>e</i>	<i>e</i>
DMF	NaI	1	8.45	<i>d</i>	4.75	None	~30	<i>e</i>
		2	11.62	<i>d</i>	<i>d</i>	None		
DMF	KI	1	8.50	<i>d</i>	4.75	None	>100	<i>e</i>
AN	LiI	1a,b	8.08	<i>d</i>	<i>d</i>	Fast	6.8	<i>e</i>
		2a	11.05	<i>d</i>	<i>d</i>	None		
TG	LiI	1a,b	8.31	<i>d</i>	<i>d</i>	Fast	1.3	<i>e</i>
		2a	11.28	0.6	<i>d</i>	None		
DME	LiI	1a,b	8.25	<i>d</i>	<i>d</i>	Slow-fast	0.3 ± 0.1	<i>e</i>
		2a	11.26	0.5	4.23	None		
DME	NaI	1a,b	8.35	<i>d</i>	<i>d</i>	Fast	0.5	<i>e</i>
		2a	11.35	0.5	<i>d</i>	None		
THF	Li or LiI or LiI + KI	1a,b	8.26	<i>d</i>	<i>d</i>	Slow'	0.5 ± 0.3	15
		2a	11.20	0.56	5.3	None		
		2c	10.90	<i>d</i>	<i>d</i>	None		
THF	Na or NaI	1a,b	8.35	<i>d</i>	<i>d</i>	Fast	0.1 ± 0.05	12
		2a	11.35	0.54	5.2	None		
THF	K or KI + <i>hν</i>	1a,b	8.15	<i>d</i>	5.1	Fast	3 ± 2	12
		2a or 3	11.17	<i>d</i>	4.7	None		
THF	Cs	1a,b or 1	8.22	<i>d</i>	1.5, 4.7	None	>100	
THF	Li + K, or K + LiCl	1a,b-Li	8.29	<i>d</i>	<i>d</i>	Slow	<i>e</i>	<i>e</i>
		1a,b-K	8.29	<i>d</i>	<i>d</i>	Fast		
		2a-Li	11.28	0.58	<i>d</i>	None		
		(2a or 3)-K	11.50	<i>d</i>	<i>d</i>	None		
THF	Li + Na or LiI + NaI or LiI + NaI + KI	1a,b-Li	8.26	<i>d</i>	<i>d</i>	Slow	<i>e</i>	<i>e</i>
		1a,b-Na	8.26	<i>d</i>	<i>d</i>	Fast		
		2a-Li	11.14	0.56	<i>d</i>	None		
		2a-Na	11.36	0.49	<i>d</i>	None		
THF	Li + RbO- <i>t</i> -Bu	1a,b-Li	8.09	<i>d</i>	<i>d</i>	Slow	~0.4 (Li)	<i>e</i>
		(1a,b or 1)-Rb	8.22	<i>d</i>	<i>d</i>	None		
		2a-Li	10.81	0.51	<i>d</i>	None		
		(2a or 3)-Rb	11.23	<i>d</i>	<i>d</i>	None		
2-MeTHF	LiI	1a,b	8.22	<i>d</i>	<i>d</i>	Slow-fast	~0.01	<i>e</i>
		2a	10.98	0.62	<i>d</i>	None		
2-MeTHF	Li	1a,b	8.25	<i>d</i>	<i>d</i>	Slow	0.07 ± 0.02	12
		1c	7.85	<i>g</i>	<i>d</i>	None		
		2a	10.95	0.70	5.2	None		
		2c	10.75	<i>d</i>	<i>d</i>	None		
2-MeTHF	Na	1a,b	8.2	<i>d</i>	<i>d</i>	Slow	0.1 ± 0.05	9
		2a	11.14	0.50	5.3	None		
2-MeTHF	K	1a,b	8.2	<i>d</i>	<i>d</i>	Fast	1.4 ± 0.5	11
		2a or 3	11.25	<i>d</i>	<i>d</i>	None		
2,5-DiMeTHF	Li	2a	10.88	0.69	5.4	None	<0.01	
2,5-DiMeTHF	Na	1c	7.94	<i>d</i>	2.9, 4.9	None	~10 ^h	<i>e</i>
		2a	11.36	0.50	<i>d</i>	None		
		2c	11.25	<i>d</i>	<i>d</i>	None		
2,5-DiMeTHF	K	1c	8.21	<i>d</i>	4.9	None	~3 ^h	11 ⁱ
		2a or 3	11.35	<i>d</i>	5.3	None		
EE	Li	1c	7.88	0.24 (2)	<i>d</i>	None	<0.01	7 ⁱ
		2a	10.72	0.70	<i>d</i>	None		
EE	Na	1a,b	8.00	<i>d</i>	<i>d</i>	Fast	~0.2	<i>e</i>
		2a	11.05	0.58	<i>d</i>	None		
		2c	11.00	<i>d</i>	<i>d</i>	None		
EE	K	1a,b	8.15	<i>d</i>	<i>d</i>	Fast	1 ± 0.3	11.5
		2a or 3	11.1	<i>d</i>	5.5	None		
EE	Cs	1a,b or 1 2c(?)	8.26 ~11	<i>d</i> 0.7 (2) ⁱ	<i>d</i> <i>d</i>	None <i>d</i>	>20	

Table I (Continued)

Solvent ^a	Reductant	Semidiones detected	a^F	a^{M^+}	a^C	Line width alternation ^b	[1a,b] ^c /[2a]	Δg - (1a,b-2a) $\times 10^6$
IPE	Li	1c	7.75	0.32 (2)	<i>d</i>	None	<0.01	0 ⁱ
IPE	K	2a	10.76	0.75	<i>d</i>	None	<0.01	0 ⁱ
		1a,b	8.20	<i>d</i>	<i>d</i>	Fast	~1	14
		2a or 3	10.87	<i>d</i>	5.4	None	~1	14
C ₆ H ₆ + dibenzo-18-crown-6	K	1a,b	8.27	<i>d</i>	<i>d</i>	None	0.7	<i>e</i>
		2a or 3	11.27	<i>d</i>	<i>d</i>	None	0.7	<i>e</i>

^a DMSO = dimethyl sulfoxide; THF = tetrahydrofuran; HMPA = hexamethylphosphoric triamide; DMF = *N,N*-dimethylformamide; AN = acetonitrile; TG = tetraglyme; DME = dimethoxyethane; EE = ethyl ether; IPE = isopropyl ether. ^b At low degrees of reduction: slow = separation of broadened lines below coalescence temperature; slow-fast = sharp 1:9:9:1 quartet without observation of broadened lines; fast = broadening of second, fourth, and sixth peak of the septet above the coalescence temperature. ^c Ratio observed at low degree of reduction and low total gegenion concentration. ^d Not observed. ^e Not measured. ^f $a^F = 5.25$ (3) and 11.35 (3) with some alternation in line widths. ^g At high degrees of reduction, broadened lines suggest unresolved lithium hfs. ^h [1c]/[2a]. ⁱ $\Delta g(1c-2a)$. ^j Resolved by cooling to -40° .

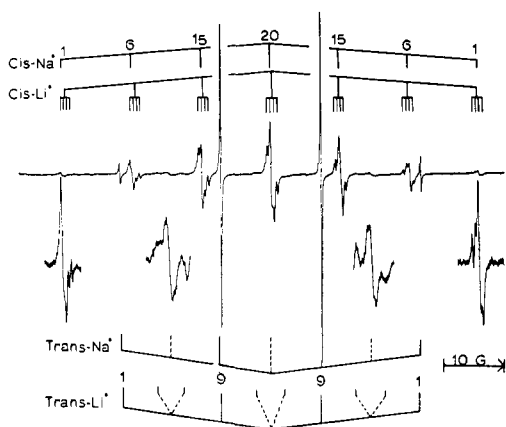
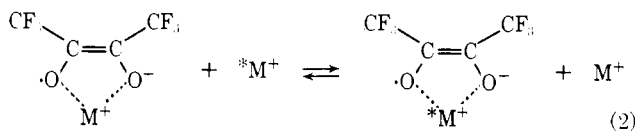
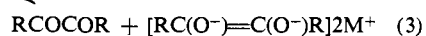


Figure 3. Reduction of perfluorobiacetyl in THF by a mixture of sodium and lithium iodides to give a mixture of four species, **2a**-Li⁺, **2a**-Na⁺, **1a,b**-Li⁺, and **1a,b**-Na⁺. The sodium hfs in **2a** has been lost by exchange with free Na⁺. This hfs is restored by the addition of dibenzo-18-crown-6 ether. **1a,b**-Li⁺ is in the slow exchange mode but **1a,b**-Na⁺ is in the fast exchange mode.

well-resolved esr lines are observed and **2c** cannot be detected, the ratio of **1a,b**/**2a** is ~ 0.6 . Based on observed peak heights the apparent ratio of **1a,b**/(**2a** + **2c**) increases to as much as 10:1 upon extensive reduction, an effect which may be at least partially caused by broadening of the peaks of **2a** by lithium exchange (reaction 2).



In an attempt to separate the effects resulting from increased lithium ion concentration from those of the degree of reduction (*i.e.*, the concentration of radical anion and/or dianion) a series of experiments was performed in which lithium chloride, a nonreducing salt, was added at some stage in a lithium iodide reduction. Addition of a saturated THF solution of lithium chloride caused a decrease in total signal intensity undoubtedly connected with the effect of gegenion on the equilibrium of reaction 3. If spectra with the same esr signal

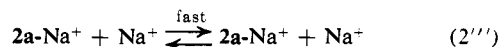
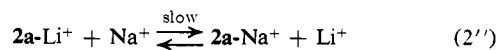
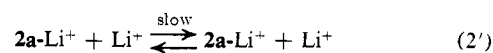


intensity are compared it is obvious that: (a) lithium

chloride does not increase the rate of the process responsible for the line width alternation in **1a,b** and (b) lithium chloride causes a decrease in the ratio of **2c**/**2a**. The macrocyclic ether dibenzo-18-crown-6 had no effect on the observed spectra. We conclude that the appearance of **2c** and the increase in the rate of time averaging process for **1a,b** observed upon continued addition of lithium iodide to the diketone are results of the increased degree of reduction and do not result from increased lithium ion concentration. This conclusion is supported by dilution experiments. If THF is added at any point in the reduction a decrease in the ratio of **2c**/**2a** is observed as well as a decrease in the rate of the process responsible for the line width alternation in **1a,b**.

Reduction of perfluorobiacetyl by sodium iodide in THF gives a spectrum containing **2a**-Na⁺ and **1a,b**-Na⁺ (**1a,b**/**2a** ~ 0.1) and with no indication of **2c**-Na⁺. It is observed that **1a,b**-Na⁺ in THF shows line width alternation such that the second, fourth, and sixth peaks of the septet are difficult to observe at 25° . Alkali metal exchange occurs more easily in **2a**-Na⁺ than in **2a**-Li⁺ and only at very low concentrations of sodium iodide can $a^{\text{Na}} = 0.50$ G be resolved. Addition of dibenzo-18-crown-6 ether restores the sodium hfs, presumably by reducing the activity of free sodium ions in reaction 2.⁷ In tetraglyme solvent there is also no evidence of sodium cation exchange even at high sodium iodide concentrations.

The addition of sodium iodide to a solution previously reduced with lithium iodide yields interesting results. The abnormal cis species (**2c**-Li⁺) disappears and a composite spectrum containing **2a**-Li⁺ (with Li hfs), **2a**-Na⁺ (no Na hfs), **1a,b**-Li⁺ (slow exchange mode) and **1a,b**-Na⁺ (fast exchange mode) is observed (Figure 3). The lack of time averaging between **2a**-Na⁺ and **2a**-Li⁺ is surprising when the consequences of cation exchange in **2a**-Na⁺ but not in **2a**-Li⁺ are considered. We are forced to conclude that $k_2, k_2', k_{-2} \ll k_2''$.



Since the line width alternation observed for **1a,b**-Li⁺ was unaffected by large excesses of lithium chloride, and since the line width alternation also occurs with-

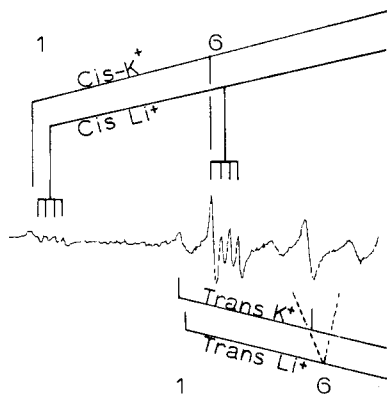
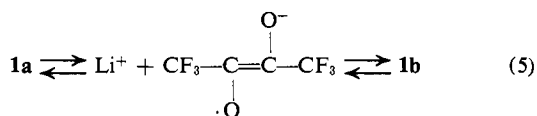
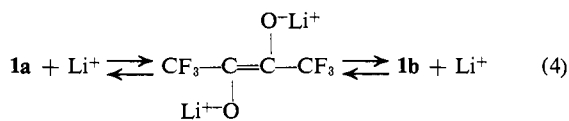


Figure 4. Wing peaks of the esr spectrum observed by reduction of perfluorobiacetyl with lithium and potassium metal in THF or by the addition of lithium chloride to the solution initially reduced by potassium.

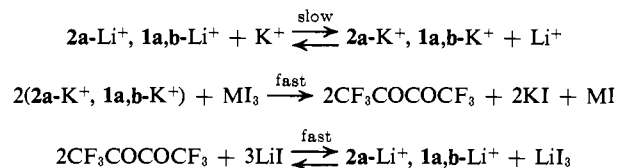
out time-averaging $1a, b-Li^+$ and $1a, b-Na^+$, we conclude that reactions 4 and 5 cannot be responsible for the



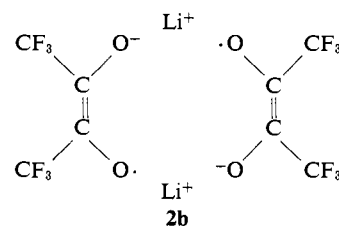
modulation of the CF_3 groups in **1** which is reflected in the observed line width alternation. One process which can be identified as being involved in the $1a \rightleftharpoons 1b$ interconversion increases with the concentration of reduced species and hence is polymolecular in reduced species. The possibility of a competing unimolecular reaction in which the lithium jumps between oxygen atoms cannot be excluded but this must be a fairly slow process because at low concentrations of $1a, b-Li^+$ two different CF_3 groups are found with $a_{CF_3^F} = 5.25$ and 11.35 G with a coalescence temperature ($\tau > 10^{-7}$ sec) above 80° .

Mixtures of lithium and potassium iodide gave spectra consisting of only $2a-Li^+$ and $1a, b-Li^+$ even when the potassium ion was present in excess. In a similar fashion mixtures of sodium and potassium iodide gave only the sodium salts of **2a** and **1a, b**. These results are surprising because reduction of the dione in THF by mixtures of lithium and potassium metals does yield a mixture of the four species (Figure 4) $2a-Li^+$ (with a^{Li}), $2a-K^+$ (no a^K), $1a, b-Li^+$ (slow exchange mode), and $1a, b-K^+$ (line width alternation barely detectable). Four species were also observed in the absence of iodide or triiodide ions for mixtures of lithium and sodium, as well as for mixtures of lithium and rubidium cations (Table I). Since not even a trace of the semidione was observed in the reaction of potassium iodide with perfluorobiacetyl (except with uv irradiation) it is obvious that the equilibrium of reaction 1 lies far on the side of the dione when $M^+ = K^+$. It follows that the absence of any species with potassium gegenion in the reduction by mixtures of lithium or sodium and potassium iodides is the result of the rapid destruction of $2a-K^+$ and $1a, b-K^+$ by I_3^- . We picture the kinetic situation as shown in Scheme I.

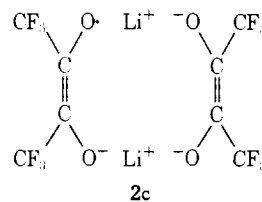
Scheme I



The structural assignment of **2c** cannot be made uniquely. Ionic aggregates including quadruple ions are possible for this "cis-like" semidione which is observed only at high degrees of reduction in THF. We have previously reported this same abnormal species in the reduction of perfluorobiacetyl by lithium metal under essentially a kinetically controlled situation,² which we will presently discuss in more detail. A suggestion was made² that this species had structure **2b** for



which we can imagine geometries in which the semidione moieties are in the same plane or at right angles to each other. However, the absence of any appreciable dipolar broadening in the esr spectrum and the absence of any coupling between the electrons which should lead to additional hfs by the second set of six fluorine atoms⁸ make structure **2b** difficult to accept.⁹ We have been unable to detect any esr transitions characteristic of $\Delta M = 1$ or 2 transitions for a triplet state in frozen (quenched) THF solutions which contained significant quantities of **2c** before cooling. Unfortunately, slow



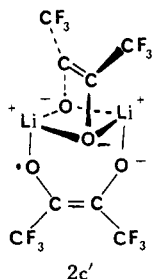
cooling results in a considerable diminution in the esr signal of THF solutions of perfluorobiacetyl semidione such that the signal can be barely detected at -40° . Moreover, the dimeric structure **2b** does not explain the observed effect of excess lithium ions in yielding a lower ratio of $2c/2a$ at the same total radical anion concentration. The dependence of $[2c]$ on the concentration of reduced species and on excess lithium ions seems to be well rationalized in terms of a 1:1 complex between the dianion and the radical anion. Again either a planar structure or a structure in which the dione moieties are at right angles to each other, or a dynamic equilibrium between these structures, could be imagined.

(8) R. Brière, R.-M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

(9) However, similarly well resolved solution spectra for the quadruple ion, $[R_2CO^-M^+]_2$, in THF at 25° are reported for the lithium and potassium salts of hexamethylacetone wherein hfs is observed for one ketone and two cations.¹⁰ This hyperfine pattern is also observed in HMPA.¹¹

(10) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960); **86**, 2558 (1964), N. Hirota, *ibid.*, **89**, 32 (1967).

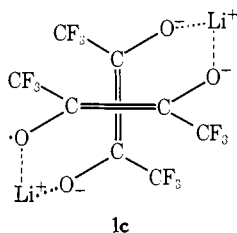
(11) Unpublished results with Dr. V. Malatesta.



Structure 2c' is our preference. The effect of lithium ion on the concentration of 2c is rationalized in eq 6.



The quadrupole ion structure 1c also deserves con-



sideration. At intermediate degrees of reduction 1a,b and 1c may have independent existence on the esr time scale. Slightly lower values for the g factor and a^F in 1c relative to 1a,b nicely explain the asymmetry noted in the esr spectrum of the trans semidione and the decrease in a^F with the degree of reduction in THF. High degrees of reduction where the concentrations of $\text{CF}_3\text{C}(\text{O}^-\text{Li}^+)=\text{C}(\text{O}^\cdot)\text{CF}_3$ and $\text{CF}_3\text{C}(\text{O}^-\text{Li}^+)=\text{C}(\text{O}^-\text{Li}^+)\text{CF}_3$ are both substantial lead to time averaging between 1a,b and 1c and hence to a substantial increase in the rate of the process leading to the magnetic equivalence of the two CF_3 groups. Addition of excess lithium ions in the form of lithium chloride in THF experimentally decreased the rate of this process. This would be consistent with the occurrence of the equilibrium described in reaction 7.



Radical Anions Observed in Alkali Metal Reductions.

The reduction of perfluorobiacetyl by lithium metal yields esr spectra which differ in detail from those observed by lithium iodide reduction. Reductions were performed in the multichambered cell described in the Experimental Section. The process involved reaction under high vacuum with a metal mirror or powder, filtration, and final esr observation. This technique allows the preparation of stable solutions of the sodium, potassium, cesium, rubidium, calcium, barium, or strontium salts of perfluorobiacetyl in THF and other ethereal solvents.

Immediately after reduction at 0–25° in THF by lithium powder mixtures the two forms of the cis semidione (2a and 2c) and the trans semidione are observed even at low degrees of reduction. Much higher ratios of 2c/2a can be observed than in the lithium iodide system. However, the initially observed ratio of 2c/2b decreases with time until 2c essentially disappears (Figure 5). As the ratio of 2c/2a decreases the rate of the process which time averages the trifluoromethyl groups in the trans semidione also undergoes a decrease. This is consistent with the presence of 1c and a concurrent



Figure 5. Effect of time on the products observed in the reduction of perfluorobiacetyl with lithium metal in THF, (A) immediately after reduction. The cis species is mainly 2c, the trans species is in the fast exchange mode, (B) after 10 min at 25°; 2a is now clearly seen; the trans species is in the slow exchange mode; (C) after 30 min there is no longer any evidence for 1c or 2c. The spectrum no longer changes with time.

decrease in the ratio of 1c/1a,b with time. The drastic change in the ratio of 2c/2a is accompanied with little change in overall radical concentration or in the ratio of total cis species to total trans species. Experimentally the decay of 2c at room temperature is first order in the concentration of 2c. Addition of excess lithium chloride to a freshly reduced solution immediately yields a mixture of 2a and 1a,b free of 2c or 1c.

When the reduction of the dione is performed below –80° with lithium powder in ethereal solvents only the trans isomer(s) can be detected at the reduction temperature. Warming to room temperature results in a dramatic increase in total radical anion concentration, particularly for the cis species. The initial cis species detected upon warming to room temperature in THF or 2-MeTHF is 2c nearly free of 2a. With time in THF 2a free of 2c is formed. The period of time over which 2c can be detected increases with the degree of reduction. If the solution is cooled after 2c has disappeared, complete loss in the esr signal is observed at about –40° in THF even though in the initial reduction the trans semidione could be detected at –80°. Upon rewarming the solution to room temperature only 2a and 1a,b can be detected even though 2c had been the major cis species observed upon the initial warming to room temperature

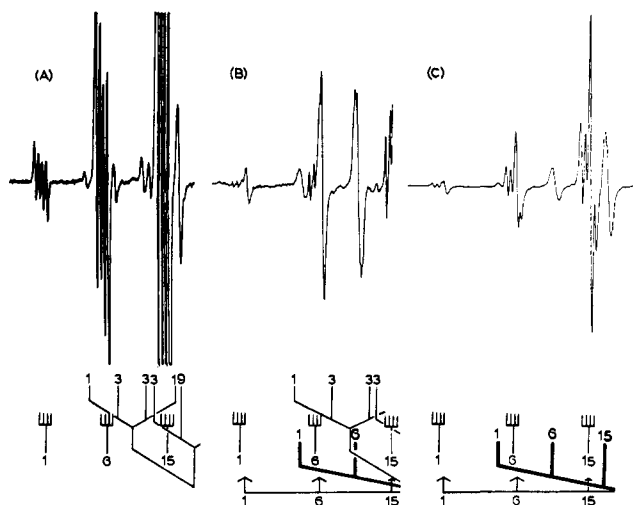
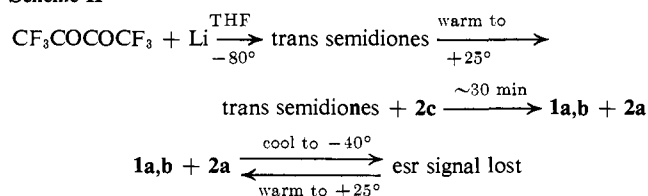


Figure 6. The observation of a stable mixture of four species in 2-MeTHF by the reduction of perfluorobiacetyl with lithium metal (partial spectra only): (A) **1a,b** (slow exchange mode) and **2a** observed at low degrees of reduction; (B) the appearance of **2c** and **1c** at higher degrees of reduction; (C) the mixture of **2a**, **2c**, and **1c** observed at the highest degree of reduction.

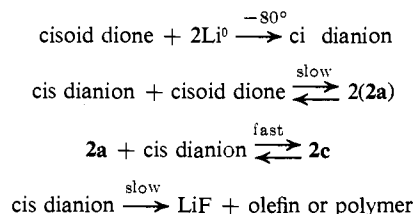
(Scheme II). The absence of **2a** (or **2c**) in the low-tem-

Scheme II



perature reduction suggests that the reduction of the cisoid conformation of the diketone at the lithium surface proceeds to the dianion whereas the transoid conformation is at least partially reduced in a stepwise manner. The irreversibility in the formation of **2c** in THF upon warming, cooling, and warming seems to be connected with the concentration of the cis dianion. The mechanism of Scheme III seems to present a rea-

Scheme III



sonable rationalization of these facts. It also appears that after reduction has occurred there is barely any interconversion between the cis and trans reduced species.

As mentioned previously indications of a similar process can be observed in the esr spectrum of the trans semidione. In THF the initial spectrum observed upon reduction or warming to room temperature is in the fast exchange mode or shows no exchange as would be expected for structure **1c**. Rapidly at 25° the spectrum changes to that of **1a,b** where two distinct trifluoromethyl groups are present. In 2-MeTHF the situation is more clean-cut. Here it is possible to observe the four distinct species at 25° (Figure 6) since in this solvent

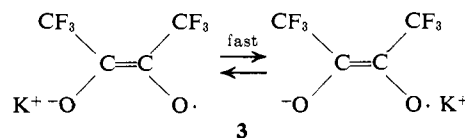


Figure 7. Reduction of perfluorobiacetyl by lithium in isopropyl ether. A mixture of **2a** and **1c** (with hfs by 2Li^+) is observed at 25°.

the trans species **1a,b** and **1c** are not appreciably time averaged. The reduction of the dione in 2-MeTHF at -100° shows first **1c** (no line width alternation). Upon warming to -55° first **2c** and then **2a** appear. Upon reaching 25°, **1a,b** (slow exchange mode) can be detected. In 2-MeTHF mixtures of these four species can be observed for long periods of time. Moreover, the broadened 1:6:15:20:15:6:1 multiplet observed for **1c** can sometimes be resolved at low temperature to give a spectrum with hfs by two lithium cations, $a^{\text{Li}} = 0.2 \text{ G}$ at -30° . In ethyl or isopropyl ethers the hfs by 2Li^+ ($a^{\text{Li}} = 0.24\text{--}0.32 \text{ G}$) in **1c** is fully resolved at 25° (Figure 7). In these solvents **1c** is the only trans species detected. In the dialkyl ethers the only cis semidione detected has structure **2a** with $a^{\text{Li}} = 0.70\text{--}0.75 \text{ G}$. High degrees of reduction or reduction and observation at low temperatures favor the dimeric trans species **1c** over the monomeric species **1a,b**. In the case of ethyl ether reduction and detection at -60° yield a pure spectrum of **1c**, which upon warming and standing at 25° gives a spectrum of **2a** in which **1c** can be barely detected.

Reduction of the diketone by other alkali metals in ethereal solvents is summarized in Table I. Sodium at 25° in THF gives mixtures of **2a** and **1a,b** in which **2a** greatly predominates. Sodium is apparently more effective in stabilizing the cis semidione than is lithium. The exchange rate of **1a,b** increased with the degree of reduction, even in the presence of dibenzo-18-crown-6, implicating the existence of **1c**. With potassium in THF **1a,b** predominates over **2a** whereas with cesium as the reductant only **1a,b** can be observed in either THF or ethyl ether. The rate of the process resulting in the modulation of the CF_3 groups in **1a,b** increases as the gegenion is changed from lithium to sodium to potassium. With cesium line width alternation is not observed, even in ethyl ether solution.

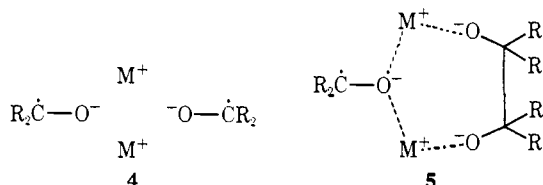
The cis species shows no hfs by potassium in THF or any of the solvents investigated. Because of the size of the gegenion a chelated structure such as **2a** may not be involved and **3** may be a better representation of the ion pair involved.



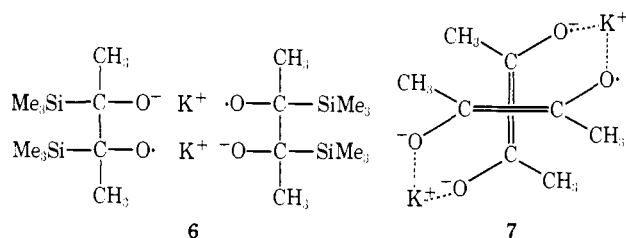
With sodium or potassium in 2-MeTHF, 2,5-DiMe-

THF, ethyl ether, or isopropyl ether, mixtures of **1a,b** and **2a** are observed. The abnormal cis species **2c** has also been observed with sodium as the cation (Table I). In fact sodium in ethyl ether behaves very similarly to lithium in THF as far as ionic association with the semidione radical anion is concerned. The fast exchange mode observed for **1a,b-Na⁺** in ethyl ether also suggests the presence of **1c** in this system, but sufficient work to identify its presence has not been performed.

In view of the present results it would appear that caution should be exercised in the interpretation of ketyl esr solution spectra in terms of only two species: the ion pair and the diradical quadruple ion. For example, the well-resolved solution spectrum observed upon reduction of di-*tert*-butyl ketone and attributed to **4**¹⁰ can also be rationalized by structure **5**. We have never



observed hfs by two alkali metal cations for **2c** in THF. However, in ethyl ether we have observed a cis species with hfs by two cesium ions, $a^{Cs} = 0.7$ G, upon cooling solutions which contain predominantly the cesium salts of **1a,b** at 25°. We have previously commented¹² on structure **6** reportedly formed by the reduction of trimethylsilyl methyl ketone in DME.¹³ The reported $a^{CH_3} = 4.5$ (2) G is quite suggestive of the *trans*-dimethylsemidione **7** while the potassium hfs of $a^K = 1.3$ (2) G is perhaps consistent with structure **7**.



The observation of hfs by only six equivalent fluorine atoms in the aggregate species **1c** and **2c** is perhaps connected with the fact that electron exchange between semidione radical anions and the dianion is seldom observed as a fast process in solution, even at relatively high concentrations. However, when the radical anion and dianion are held in close proximity in a quadruple ion it seems that such transfer should be important. One partial solution to this dilemma is to place the radical anion and dianion moieties at right angles to each other as in structure **2c'**. Now one π system is in the nodal plane of the other and direct orbital overlap is prevented. The orbital symmetries do not allow for a spiroconjugative delocalization of the unpaired electron. As drawn in structure **2c'**, the two lithium ions are also in the nodal plane of the semidione π system and this may explain why lithium hfs has not been observed in **2c**. The problem of direct orbital overlap is partially solved in **1c** by placing the two π systems in parallel planes but with a 90° rotation of the two dione

(12) G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

(13) P. R. Jones and R. West, *J. Amer. Chem. Soc.*, **90**, 6978 (1968).

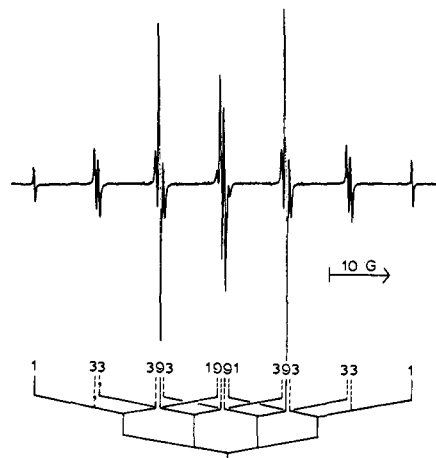
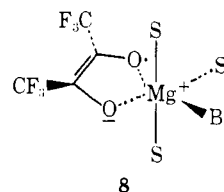


Figure 8. Esr spectrum of the product of reduction of perfluorobiacetyl by anhydrous magnesium bromide in THF at 25°.

moieties. Still another possible formulation for the abnormal *trans* species is a complex between one cis dianion and the *trans* radical anion in which the two π systems are in orthogonal planes.

In the presence of macrocyclic ethers the potassium salts of perfluorobiacetyl can apparently be formed in a wide variety of inert solvents. Thus, in benzene in the presence of dibenzo-18-crown-6-ether potassium reduces the dione to yield a mixture of semidiones without metal hfs or line width alternation, *cis/trans* $\cong 1.5$. No reduction is observed in the absence of the ether. Under the reaction conditions biacetyl itself fails to yield an esr signal.

Alkaline Earth Metal Salts of Perfluorobiacetyl Radical Anion. The diketone is reduced to *cis* semidiones in THF solution by barium, strontium, and calcium metals or by calcium iodide. Anhydrous magnesium bromide in THF also gives a spectrum, Figure 8, attributed to a *cis* semidione having slightly nonequivalent trifluoromethyl groups, showing evidence of slow exchange. A structure such as **8** may be involved where S is the ethereal solvent.



$$a_{CF_3^F} = 10.13, 10.71; a_{CF_3^C} = 5.28; a_{CO^C} = 1.78 \text{ G}$$

The surprising reducing ability of magnesium bromide may somehow be connected with the formation of $Mg^{2+}Br^-$ during the dehydration step (see Experimental Section). The anhydrous salt used did give an esr signal at $g \sim 2$ not present in hydrated magnesium bromide. The hydrate gave no evidence of reduction of the dione.

With calcium iodide two *cis* species are observed, each with six equivalent fluorine atoms, $a^F = 10.50$ and 10.88 G. Addition of dibenzo-18-crown-6 slowly replaces these species with a third *cis* complex, $a^F = 10.60$ G. All three species can be seen simultaneously. Reduction with calcium metal forms two species with $a^F = 10.54$ and 10.72 G. The possibility of ion pairs involving one or two iodide or fluoride ions associated with the calcium cation seems to be a reasonable inter-

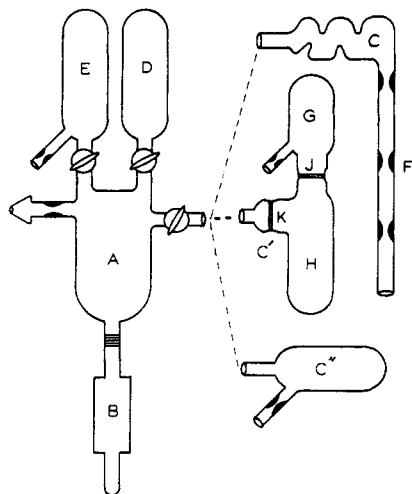


Figure 9. Cells used for the reduction of perfluorobiacetyl.

pretation. Reduction with strontium gave two species with very similar hfs by six fluorine atoms. Only one coupling constant, $a^F = 10.87$, could be measured accurately. A value of $a_{CF_3}^C = 5.37$ was observed as a hfs by ^{87}Sr ($I = 9/2, 7\%$ abundance) of 0.35 G. Barium reduction gave three similar cis species with a^F for six equivalent fluorine atoms = 10.61, 10.88, 10.93 G. In this case addition of dibenzo-18-crown-6-ether had no effect on the esr spectrum. A value of $a_{CF_3}^C = 5.30$ G was observed as well as an average value of $a^{Ba} = 1.25$ G ($^{135}\text{Ba}, I = 3/2, 6.6\%$; $^{137}\text{Ba}, I = 3/2, 11.3\%$).

Experimental Section

Materials. Perfluorobiacetyl was prepared from 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene (Columbia Organic Co.) according to the literature preparation.⁸ Bulb-to-bulb vacuum transfers gave material that showed no impurities by glpc. Purified material was stored in a vacuum line and vacuum transferred to the reaction cell when needed. Solvents except HMPA were distilled from calcium hydride. Etheral solvents were stored over benzophenone ketyl

in a vacuum line and vacuum transferred to sample cells. Other solvents were degassed in the reaction cells by the freeze-thaw method. Metal *tert*-butoxides prepared by reaction of the metals with *tert*-butyl alcohol were held under high vacuum to remove unreacted alcohol. Inorganic salts were dried under high vacuum in tubes heated by a gas torch to just below the softening temperature of Pyrex glass.

Instrumentation. ESR spectra were recorded using a Varian E-3 spectrometer calibrated with Fremy's salt in 10% aqueous sodium carbonate ($a^N = 13.00$ G). Electrolysis experiments were conducted directly in the spectrometer cavity using a platinum spoon electrode and cell previously described.³ Photolysis experiments involved the use of a focused 800-W Hanovia mercury lamp with quartz optics.

Chemical Reductions. Reductions were conducted in high vacuum Pyrex cells (Figure 9) consisting of mixing chamber A joined to a high volume fused silica ESR flat cell B with side-arm chambers adapted to contain a reducing agent (chamber C, C', or C''), perfluorobiacetyl (chamber D), and an additional reagent chamber E. Depending upon the experiment, solvent was added to one or all chambers. Each chamber was separated from the mixing chamber by a high vacuum stopcock. Mixing chamber A when attached to a vacuum line through a ground joint could be rotated so as to place either B or D and E in the down position.

Chamber C was used for standard "metal-mirror" reductions with sodium and potassium. The metals were distilled up tube F under high vacuum to the deposition surface and tube F was then removed. No attempts to purify cesium metal were made. Chamber C' was used to produce finely divided forms of lithium, barium, calcium, and strontium. Bulk metal was sealed in G and the cell assembly attached to the vacuum system with G in the down position. Several milliliters of liquid ammonia (stored over lithium metal on the vacuum line) was condensed in G producing a deep blue solution. After freezing this solution the cell was rotated to place chamber H in the down position and H cooled as chamber G began to warm. Upon thawing the metal ammonia solution (under ammonia pressure) passed through the course fritted disk J joining G and H to remove insoluble oxides. Finally the ammonia was vaporized and the powdered metal deposit warmed under vacuum for several minutes. The course fritted disk K prevented transfer of particulate metal between A and H during reduction. Care was taken to avoid contact of the diketone solution with G.

When iodides or bromides were used as reducing agents the salts were sealed in C'' and heated until dry. Salts placed in the additional reagents chamber (E) received the same treatment. Dibenzo-18-crown-6 ether (Aldrich Chemical Co.) was purified by gently distilling it up a tube to E under vacuum.

Acid-Catalyzed Hydrogen Exchange of Acetophenones. Evidence for the Inapplicability of the Reactivity-Selectivity Principle

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Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England. Received February 8, 1974

Abstract: The dependence of rate on acidity for the 3- and 5-hydrogen exchange of some 4-substituted acetophenones in aqueous deuteriosulfuric acid has been determined. Reaction is shown to occur on the keto free base form, the enol form being in such small concentration that if it were sufficiently reactive to undergo observable exchange it would direct the reaction into the 2 and 6 positions. Treatment of the data in terms of standard acidity function theory demonstrates apparent lack of dependence of transition state structure on the rate of hydrogen exchange in aromatic substrates, in contradiction of the widely accepted reactivity-selectivity principle, and thus by implication the Hammond postulate. Related data bearing on the thermodynamic acidity function theory are also discussed.

Decrease in the nuclear hydrogen exchange reactivity of aromatic compounds is commonly connected with increased resemblance of transition state structure

to the Wheland intermediate, considered discernable by isotope effect variation denoting the increased degree of proton transfer, the low C basicity of the aromatic sub-