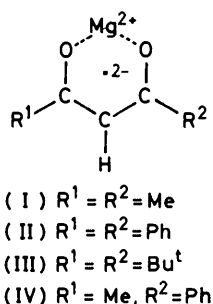


Photolytic Generation of Radical Anions and Dianions and Group IVB Organometallic Adducts of β -Diketones. An Electron Spin Resonance Study on the Effects of Fluorine Substitution and Crown Ethers

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Using $\text{CF}_3\text{COCH}_2\text{COCF}_3$, 2-thienyl- $\text{COCH}_2\text{COCF}_3$ and model diketones, we have successfully demonstrated the formation and the observation of the e.s.r. of radical anions by photoreduction with amines and the radical dianions by photochemical reactions with THF and alkali-metal tetraphenylborates. The e.s.r. results shed some light on the reaction mechanisms of these photochemical processes. The chemical selectivity of different organometallic radicals towards the tautomers of $\text{CF}_3\text{COCH}_2\text{COCF}_3$ is further illustrated by having organosilyl radicals add mainly to the enol form while the organotin radicals co-ordinate only to the keto-form of the diketone.

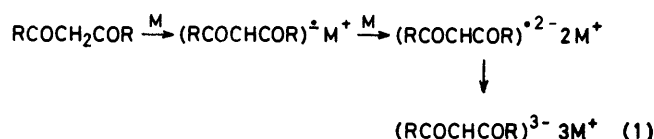
NUMEROUS studies have been concerned with the keto-enol tautomerism of β -diketones and their chemical reactions in solution. It is generally recognized that molecules such as acetylacetone exist at room temperature mainly in the enol form,¹ although photoisomerization of β -diketones and β -keto-esters has been demonstrated.² The role of keto-enol tautomerism is obviously very important in the chemistry of these compounds. For example, the addition of organosilyl radicals to β -diketones will depend upon the most stable conformation of the β -diketones.³ While the electrochemical reduction of 1,3-diketones such as $\text{PhCOC}(\text{CH}_3)_2\text{COPh}$ which can only exist in the keto-form generates the keto-radical anions⁴ only, the well known reductive methods such as the use of an alkali-metal mirror and cathodic electrolysis have either failed or led to ambiguous results about the generation of radical dianions from the β -keto-enolates.⁵ However, when the corresponding metal keto-enolates were reduced by Grignard reagents the radical dianions (I)–(IV) derived from the β -diketones were observed by e.s.r. in solution.⁶ Under



the same conditions radical dianions were not observed with $\text{R}^1 = \text{R}^2 = \text{CF}_3$ and $\text{R}^1 = \text{CF}_3, \text{R}^2 = \text{CH}_3$.

While the difficulty of observing radical dianions in these systems using conventional alkali-metal reduction is probably due to the rapid transformation of the radical dianion to the diamagnetic trianion [reaction (1)]⁷ we have demonstrated that a photochemical reduction method⁸ does lead to formation and observation of both the radical anion and the radical dianion of some substituted acetylacetones. Furthermore, we

have shown that the addition of some crown ethers to the system enhanced the stability of these radical dianions by reducing their interaction with the metal



cations. In some cases the presence of crown ether is necessary to obtain the e.s.r. spectra of the radical dianion. While the conformation of these β -diketones is important in reactions with organometallic compounds, we have further demonstrated the significance of chemical selectivity towards different keto-enol conformations by different organometallic radicals. Thus, the organosilyl radicals can add to the enol form of the β -diketones but the organostannyl radicals prefer to add to the keto-form of the same ketones.

EXPERIMENTAL

Alkali metal was supplied by Alfa Inorganic Ltd. and was vacuum sublimed. Fisher reagent grade THF was dried repeatedly over Na-K alloy and vacuum distilled into sample tubes. Substituted β -diketones, crown ethers, organometallic compounds, and sodium tetraphenylborate were used as received from Aldrich. The preparation of potassium, lithium, cesium, and ammonium tetraphenylborates was given by Chen and Hirota.⁹ The method of alkali-metal reduction and the photolytic reduction procedures of the diketones in THF on a high-vacuum line have been previously described.⁸

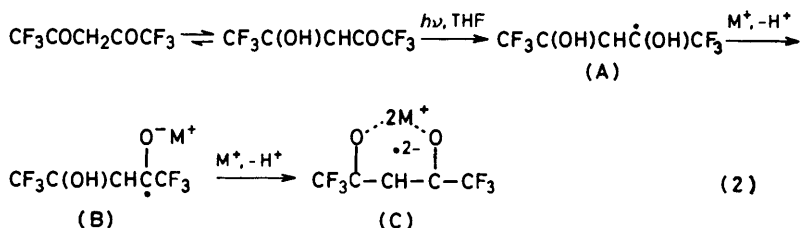
E.s.r. measurements were recorded on a Bruker 420 X-band spectrometer with 100 kHz field modulation. The temperature was varied by flowing thermostatted nitrogen past the sample. g Factors were measured using a Bruker n.m.r. oscillator, a Hewlett-Packard electronic microwave frequency counter, and a potassium naphthalene ion pair in THF as an external standard.

RESULTS AND DISCUSSION

(I) *Photoreduction of $\text{CF}_3\text{COCH}_2\text{COCF}_3$ in THF.*—
 1 *Conventional alkali-metal reduction experiments.* No

e.s.r. spectra were observed at -65°C for the alkali-metal reduction of $\text{CF}_3\text{COCH}_2\text{COCF}_3$ in the following systems in THF: (a) $\text{CF}_3\text{COCH}_2\text{COCF}_3$ alone, (b) diketone with excess of sodium tetraphenylborate, (c) diketone with excess of triethylamine, and (d) diketone with excess

solution containing the diketone $\text{CF}_3\text{COCH}_2\text{COCF}_3$, alkali-metal tetraphenylborate, and with or without crown ether led to various e.s.r. observations at low temperatures. The results are summarized in Table 1. A control experiment was performed by photolysing the



of 18-crown-6 ether. The failure to observe any e.s.r. signals in these metal reduction systems can be ascribed to the rapid reaction sequence leading to the efficient formation of the diamagnetic trianion.⁷

2 Photolytic experiments. The photolysis of a THF

TABLE 1

E.s.r. parameters of radical dianion (C) in THF *

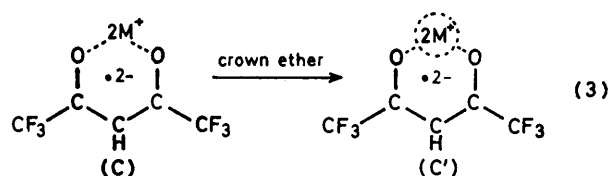
Crown ether	E.s.r. parameters of radical dianion (C) in THF *			
	None	12-Crown-4	15-Crown-5	12-Crown-6
MBPh ₄ LiBPh ₄	No signal	At -48°C $a^{\text{F}}(6\text{F})$ 18.51 G $a^{\text{H}}(1\text{H})$ 3.08 G g 2.0034		
NaBPh ₄	At -55°C $a^{\text{F}}(6\text{F})$ 18.44 G $a^{\text{H}}(1\text{H})$ 3.04 G g 2.0034	At -60°C $a^{\text{F}}(6\text{F})$ 21.55 G $a^{\text{H}}(1\text{H})$ 2.51 G g 2.0035	At -55°C $a^{\text{F}}(6\text{F})$ 21.44 G $a^{\text{H}}(1\text{H})$ 2.36 G g 2.0035	
KBPh ₄	No signal		At -47°C $a^{\text{F}}(6\text{F})$ 21.55 G $a^{\text{H}}(1\text{H})$ 2.36 G g 2.0035	At -58°C $a^{\text{F}}(6\text{F})$ 21.59 G $a^{\text{H}}(1\text{H})$ 2.43 G g 2.0035
CsBPh ₄	At -58°C $a^{\text{F}}(6\text{F})$ 18.54 G $a^{\text{H}}(1\text{H})$ 3.22 G g 2.0035		At -47°C Too weak to be analysed	
NH ₄ BPh ₄	At -47°C $a^{\text{F}}(6\text{F})$ 20.80 G $a^{\text{H}}(1\text{H})$ 2.36 G g 2.0035			
Bu ₄ NBPh ₄	At -50°C $a^{\text{F}}(6\text{F})$ 21.41 G $a^{\text{H}}(1\text{H})$ 2.51 G g 2.0033		At -43°C $a^{\text{F}}(6\text{F})$ 21.16 G $a^{\text{H}}(1\text{H})$ 2.36 G g 2.0033	

* Blanks in the Table indicate no experiments were attempted.

diketone in THF alone at temperatures ranging from -80 to 20°C ; no e.s.r. signals were seen.

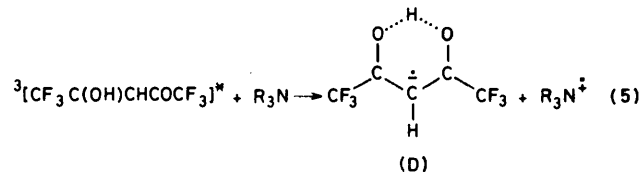
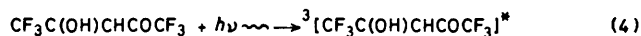
In the presence of a hydrogen donor solvent such as THF, the photochemical reaction between a ketone and metal tetraphenylborate has been shown to yield paramagnetic ion pair or triple ions.⁸ In the present system the photoreduction would proceed *via* a number of stages [reactions (2)].

There are three different paramagnetic reaction intermediates involved in the photoreduction: the neutral keto-radical (A), the radical anion (B), and the radical dianion (C). Only radical dianion (C) would have hyperfine patterns showing six equivalent fluorines and one proton as observed experimentally (Table 1). That only the radical dianion (C) (a triplet ion involving one dianion and two M^+ ions) is observed is consistent with a previous study⁸ demonstrating that the photoreduction usually proceeds directly to the 'triple ion' stage. The transformation of the radical dianion (C) to a diamagnetic trianion is probably inefficient in the absence of alkali-metal.



The effect of the presence of crown ether in these systems is very conclusive. For the lithium and potassium tetraphenylborate systems, no e.s.r. signal of the dianion was observed until crown ether was added (Table 1). In the other systems, the addition of crown ether clearly altered the hyperfine coupling constants of the radical dianion, indicating the reduced interaction between the now solvated metal cation and the dianion radical [reaction (3)]. The reduced interaction from the metal cation in (C') is expected⁶ to increase the fluorine hyperfine splitting and simultaneously decrease the proton coupling constant. This is in good agreement with the experimental observations in Table 1. In the *t*-butylammonium tetraphenylborate system, the addi-

tion of crown ether appeared to have no effect on the hyperfine values of the radical dianion. This is consistent with other observations involving ammonium cations¹⁰ and crown ethers and it is probably due to the already very weak interaction between the ammonium cation and the radical dianion in (C).



When the same photolytic reduction was carried out with the diketones $\text{CF}_3\text{COCH}_2\text{COCH}_3$ and $\text{CH}_3\text{COCH}_2\text{COCH}_3$, the formation of radical dianions was not observable by e.s.r., either with or without the addition of crown ether. The requirement of two strongly electron-withdrawing groups such as CF_3 and 2-thienyl may indeed play a critical role in the formation of (C), as has been discussed¹¹ in the formation of ammonium pairs.

3 Photoreduction in the presence of amines. The photolysis of a THF solution containing $\text{CF}_3\text{COCH}_2\text{COCF}_3$ and trimethyl- or triethyl-amine at low temperatures led to the e.s.r. observation of a radical species containing six equivalent fluorines and two non-equivalent protons. One of the protons also showed significant variation of coupling constant depending on the temperature. At -80°C , the radical species gave a spectrum with a^F (6F) 21.77, a^H (1H) 2.79, and a^H (1H) 1.04 G. The corresponding values at -67°C are 21.48, 2.51, and 0.72 G, respectively. Similar observations were made using triethylamine. The e.s.r. results can be accounted for by the photochemical reactions (4) and (5). With trimethylamine, reaction (5) is unlikely to proceed *via* a hydrogen abstraction mechanism from the methyl groups of the amine and thus an electron transfer mechanism is more probable, giving the radical anion (D). The reversible temperature-dependent proton coupling constant for the proton between the two CO groups as observed in the experiment is consistent with the assignment of the radical anion (D). It should be pointed out that in the radical dianion (C), the single proton coupling constant value is independent of temperature.

To support the assignment of radical anion (D) and the mechanism of the reactions, $\text{CF}_3\text{COCD}_2\text{COCF}_3$ was prepared in CDCl_3 by exchange with CH_3OD . The full deuteration of the diketone was confirmed by n.m.r. The deuteriated diketone was then photoreduced by trimethyl- or triethyl-amine in CH_3OD or $[\text{D}_8]\text{THF}$. Again the e.s.r. spectrum of the deuteriated analogue of (D) was observed with six equivalent fluorine splittings, one non-temperature-dependent deuterium splitting, and one temperature-dependent deuterium splitting. The confirmation of structure (D) in these systems also

suggests that the ionization of the radical anion (D) to give a proton and an analogous radical dianion (C) is not observed at low temperatures. However, it would be interesting to see if radical anion (D) could be transformed into a radical dianion (C) by the addition of alkali-metal tetraphenylborate. An experiment was designed having a solution of sodium tetraphenylborate in a side-arm of the e.s.r. sample cell containing the radical anion (D). No effect was observed on the e.s.r. spectrum of (D) when the solution of sodium tetraphenylborate was introduced. This fact suggests that the hydrogen atom sitting between the two CO groups is strongly co-ordinated to the two oxygen atoms and it is not easily replaced by the metal ion. However, when the photochemical reactions (4) and (5) were carried out in the presence of sodium tetraphenylborate, again only the radical anion (D) was observed. This indicates that the electron-transfer process in (5) proceeds much faster than the molecular mechanism required initially to form (C).

(II) *Photoreduction of 2-Thienyl-COCH₂COCF₃ in THF.—1 Photolytic experiments.* Conventional alkali-metal reduction methods did not produce any e.s.r. observations of paramagnetic intermediates in the reaction systems containing sodium metal, excess of crown ether, and 2-thienyl-COCH₂COCF₃ at low temperatures. However, radical ions were generated and observed by e.s.r. when THF solutions containing the same diketone and alkali-metal tetraphenylborate (with or without the addition of crown ether) were photolysed at low temperatures. The results are summarized in Table 2. Again a control experiment confirmed that the photolysis of the diketone alone in THF produced no observable e.s.r. signals. This series of experiments establishes that the substitution of the 2-thienyl group for CF_3 , together with another strongly electron-withdrawing CF_3 group, is capable of inducing ionization from an intermediate radical 2-thienyl-C(OH)CH $\dot{\text{C}}$ (OH)CF₃ to yield the resultant radical dianion similar to (C) in the reaction (2). One difference between the $\text{CF}_3\text{COCH}_2\text{COCF}_3$ and the 2-thienyl-COCH₂COCF₃ systems is that the radical dianions can only be observed for the latter system when crown ether is present to reduce the interaction of the alkali-metal cation. This suggests that the ionic interaction is stronger with the latter diketone than with $\text{CF}_3\text{COCH}_2\text{COCF}_3$.

2 Photoreduction in the presence of amines. The photoreduction of 2-thienyl-COCH₂COCF₃ in THF at low temperatures by trimethyl- or triethyl-amine again led to the e.s.r. observation of a radical anion (D') similar to (D) in reactions (4) and (5). The additional proton coupling with a constant between 0.7 and 1.08 G, dependent upon temperature, is consistent with the assignment of the proton sitting between two CO groups in (D'). In the 2-thienyl-COCH₂COCF₃ system, not only did the addition of MBPh_4 have no effect upon the e.s.r. spectrum of (D') but the presence of amines in the photolysis of a THF solution containing the dike-

TABLE 2
E.s.r. parameters of radical dianion
2-thienyl-COCH₂COCF₃ in THF *

Crown ether	None	12-Crown-4	15-Crown-5	12-Crown-6
MBPh ₄	No signal	No signal		
LiBPh ₄	No signal	No signal		
NaBPh ₄	No signal		At -35 °C <i>a</i> ^F (3F) 15.97, 5.12 G <i>a</i> ^H (1H) 4.76, 2.04, 1.11 G <i>g</i> 2.0037	At -55 °C <i>a</i> ^F (3F) 15.96, 5.08 G <i>a</i> ^H (1H) 4.56, 2.06, 1.11 G
KBPh ₄	No signal			At -55 °C <i>a</i> ^F (3F) 16.04, 5.08 G <i>a</i> ^H (1H) 4.53, 2.08, 1.07 G <i>g</i> 2.0037
CsBPh ₄	No signal			At -55 °C <i>a</i> ^F (3F) 16.15, 5.19 G <i>a</i> ^H (1H) 4.33, 2.04, 1.00 G <i>g</i> 2.0037
NH ₄ BPh ₄	Very weak			At -50 °C <i>a</i> ^F (3F) 15.82, 5.17 G <i>a</i> ^H (1H) 4.62, 2.09, 1.11 G <i>g</i> 2.0036
Bu ⁿ ₄ NBPh ₄	At -36 °C <i>a</i> ^F (3F) 16.06, 5.16 G <i>a</i> ^H (1H) 4.58, 2.08, 1.13 G <i>g</i> 2.0037			At -36 °C <i>a</i> ^F (3F) 16.02, 5.05 G <i>a</i> ^H (1H) 4.53, 2.04, 1.11 G <i>g</i> 2.0036

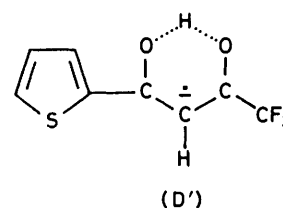
* Blanks in the Table indicate no experiments were attempted.

tone and metal tetraphenylborate actually suppressed the formation of the radical dianion and led to the observation of only the radical anion (D').

(III) *Some Group IVB Organometallic Radical Adducts of CF₃COCH₂COCF₃*.—The photolysis at -55 °C of a THF solution containing di-*t*-butyl peroxide, triethylsilane, and CF₃COCH₂COCF₃ led to the formation of the triethylsilyl radical adduct (E) of the parent diketone.

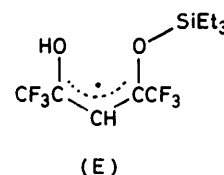
The structure is similar to the triethylsilyl radical adduct of acetylacetone reported by Cooper *et al.*³ This suggests that the silyl radical adds mainly to the enol form of the diketone, which is consistent with the observation¹ that the enol form is predominant for these

diketones. However, similar experiments using 2-thienyl-COCH₂COCF₃ failed to give the e.s.r. observation of the analogous radical adduct. The reason is not immediately obvious to us as to why the silyl adduct of 2-thienyl-COCH₂COCF₃ escaped detection.



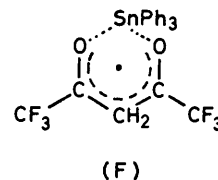
g 2.0040, *a*^F(3F) 15.04, *a*^H(1H) 4.76, *a*^H(1H) 4.48, *a*^H(1H) 2.42, *a*^H(1H) 1.07, *a*^H(1H) 0.7 - 1.08 G

The photolysis of a THF solution containing triphenyltin hydride Ph₃SnH and CF₃COCH₂COCF₃ alone at low temperatures did not lead to any observable e.s.r. signal. No e.s.r. spectrum was obtained upon the photolysis of either di-*t*-butyl peroxide with Ph₃SnH or the peroxide



g 2.0034, *a*^F(3F) 17.92, *a*^F(3F) 16.56, *a*^H(1H) 3.22, *a*^H(1H) 1.22 G

with CF₃COCH₂CF₃ separately. However, when di-*t*-butyl peroxide was added to the solution containing both Ph₃SnH and CF₃COCH₂COCF₃, the induced Ph₃Sn radical was 'trapped' by the ketone and the tin radical adduct of the diketone was observed at -60 °C. The e.s.r. parameters showing six equivalent fluorines and two equivalent protons support structure (F). Unlike



g 2.0030
a^H(6F) 19.7, *a*^H(2H) 2.1 G

radical anion (D), both protons, which are equivalent in (F), did not show any temperature dependence in their coupling constant value. It is generally recognized¹² that organotin radicals prefer to add across two CO groups or one CO and one OR group as the extra co-ordination due to two oxygen atoms appears to be most critical. In this case, such a preference means that the

organotin radicals would add mainly to the keto-form of the diketone, even though the enol form may be predominant. The results illustrate the role of chemical selectivity by different organometallic radicals towards the tautomers of diketones such as $\text{CF}_3\text{COCH}_2\text{COCF}_3$.

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