Aliphatic Semidiones. V. Radical Anions Derived from Vicinal Triketones[1]

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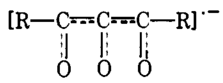
Abstract: Preparation and detection by esr spectroscopy of radical anions (semitriones) derived from C_6H_5CO-$COCOC_6H_5$, $CH_3COCOCOOR$, and ROCOCOCOOR are described. In basic solution vicinal tri- or tetraketones have a great tendency to undergo decarbonylation to yield the α-diketone or its radical anion. These semitriones can be prepared only in the absence of strong base. The same degradation was observed for $C_6H_5COCOCOOR$ but it was possible to prepare semitriones in the series $CH_3COCOCOOR$ and ROCOCOCOOR in basic solution. A variety of reactions of α-substituted β-diketones and α-substituted β-keto esters with base are discussed.

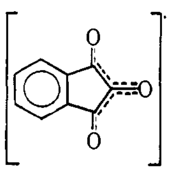
Semidione radical anions (RC(O·)=C(O⁻)R′) have been shown to have considerable stability even when R and R′ are alkyl groups or the hydrogen atom.[3] Since the stability of the semidione is greater than the corresponding ketyl ($R_2\dot{C}$–O^-), it appears logical that the semitriones (**1**) should be even more readily formed.



$$[\mathrm{R{-}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{-}R}]^{\cdot-}$$

1

In fact, the semitrione radical anions from ninhydrin (**2**),[4] alloxan (**3**),[4] reductic acid (**4**),[5] and triose reductions (**5**)[5] have been reported. (It is pertinent that decarbonylation of **2** or **4** would be unlikely since this would lead to a cyclobutene or cyclobutadiene derivative.)



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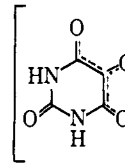

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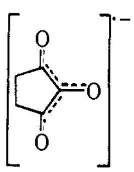

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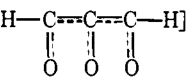

$$[\mathrm{H{-}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{-}H}]^{\cdot-}$$

5

Hückel molecular orbital calculations and experimental reduction potentials support this premise. In Table I, the calculated energy of the lowest unoccupied molecular orbital and the first reduction potential of the substrate in dimethyl sulfoxide solution are tabulated. In Figure 1, a correlation between reduction potential and calculated energy of the unoccupied molecular orbital is demonstrated.

In view of these results we decided to attempt to detect a series of semidione radical anions, particularly in acyclic systems, by reduction of tricarbonyl compounds or oxidation of hydroxy-substituted dicarbonyl compounds.

Table I. Reduction Potentials and Calculated Energies of Polycarbonyl Compounds

Compound	$-E_{1/2}$[a]	E_{calcd}[b]
1,4-Diphenyl-1,2,3,4-butanetetraone	0.78, 2.04	0.2443
1,3-Diphenyl-1,2,3-propanetrione	0.76, 2.25	0.1613
Benzil	1.16	0.0000
Benzophenone	...	−0.2939
Ethyl benzoylglyoxylate	...	0.1220
Ethyl benzoylformate	1.48	−0.1024
Ethyl formylglyoxylate	...	0.1341
Ethyl pyruvate	1.51	−0.1285
Ethyl mesoxalate	0.84	0.0646
Ethyl oxalate	1.85	−0.2904
Biacetyl	1.27	−0.1221[c]
Glyoxal	...	−0.1456
1,3-Butadiene	...	−0.625

[a] In 0.1 *M* solutions of tetra-*n*-propylammonium perchlorate in dimethyl sulfoxide *vs.* a saturated calomel electrode. [b] Energy of lowest unoccupied orbital in units of β. The carbonyl parameters suggested by A. Streitwieser ("Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961) were used: $\alpha_{\mathrm{O}} = \alpha_{\mathrm{C}} + \beta_{\mathrm{CC}}$, $\beta_{\mathrm{CO}} = \beta_{\mathrm{CC}}$. The ester oxygen was treated as an ether substituent (OR); $\alpha_{\mathrm{OR}} = \alpha_{\mathrm{C}} + 1.65\beta_{\mathrm{CC}}$, $\beta_{\mathrm{COR}} = \beta_{\mathrm{CC}}$. [c] Methyl groups treated as heteroatoms with $\alpha_{\mathrm{CH_3}} = \alpha_{\mathrm{C}} + 2.0\beta_{\mathrm{CC}}$, $\beta_{\mathrm{CCH_3}} = \beta_{\mathrm{CC}}$.

Results

Paramagnetic Products Obtained from Vicinal Triketones. 1,3-Diphenyl-1,2,3-propanetrione (DPPT) was subjected to a variety of reaction conditions known to convert benzil to the benzil radical anion. In particular benzil is converted to the radical anion by the reaction with the alkali metal salts of methanol, ethanol, isopropyl alcohol, or *t*-butyl alcohol in dimethyl sulfoxide (DMSO) or alcoholic solutions.[6]

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

(2) National Aeronautics and Space Administration Predoctoral Fellow, 1964–1965.

(3) G. A. Russell, E. T. Strom, E. R. Talaty, K.-Y. Chang, R. D. Stephens, and M. C. Young, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 3 (1966).

(4) G. A. Russell and M. C. Young, *J. Am. Chem. Soc.*, **88**, 2007 (1966).

(5) I. Yamazaki, H. S. Mason, and L. Piette, *J. Biol. Chem.*, **235**, 2444 (1960).

(6) The conversion of benzil to the radical anion by methoxide, ethoxide, or isopropoxide anions can be formulated to occur by hydride transfer.

$$C_6H_5COCOC_6H_5 + R_2CHO^- \longrightarrow R_2CO + C_6H_5C(O)CH(O^-)C_6H_5 \rightleftarrows C_6H_5C(O^-){=}C(O^-)C_6H_5$$

$$C_6H_5COCOC_6H_5 + C_6H_5C(O^-){=}C(O^-)C_6H_5 \leftrightarrows 2C_6H_5C(O\cdot){=}C(O^-)C_6H_5$$

The reaction with *t*-butoxide ion cannot be explained in this manner. Perhaps a reducing species can be derived *via* the benzilic acid rearrangement.

$$C_6H_5COCOC_6H_5 + OR^- \longrightarrow (C_6H_5)_2C(O^-)CO_2R \xrightarrow{OR^-} (C_6H_5)_2CO^{2-} + ROC(O)OR$$

$$(C_6H_5)_2CO^{2-} + 2C_6H_5COCOC_6H_5 \longrightarrow 2C_6H_5C(O\cdot){=}C(O^-)C_6H_5 + (C_6H_5)_2CO$$

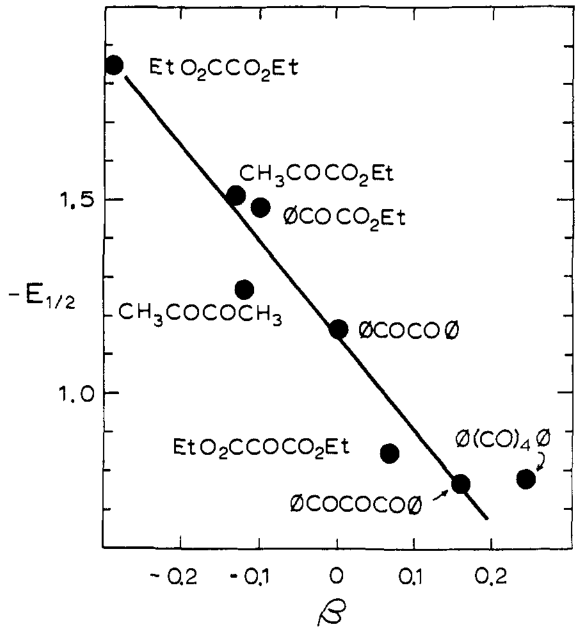


Figure 1. Relationship between half-wave reduction potentials (in volts) of polyketones and keto esters in dimethyl sulfoxide solution (*vs.* sce) and the calculated Hückel energy of the LUMO of the polyketone in units of β. The data give the equation, $E_{1/2} = -1.15 - 2.5\beta$. For similar relationships see R. E. Sioda and W. S. Koshi, *J. Am. Chem. Soc.*, **89**, 475 (1967); A. Rembaum, A. Eisenberg, R. Haack, and R. F. Landel, *ibid.*, **89**, 1062 (1967), and references cited therein. The slope of the plot is indicative of a one-electron reduction.

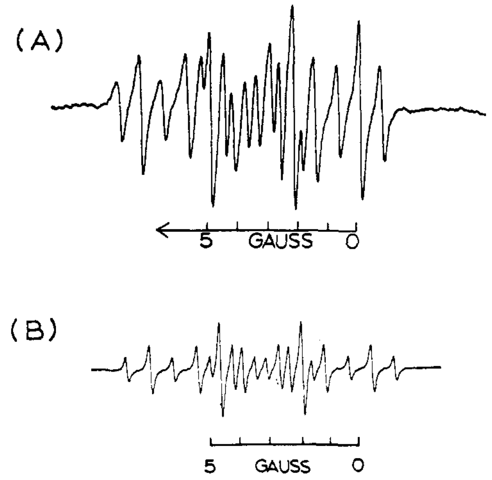


Figure 2. (a) First derivative esr spectrum of potassium salt of radical anion of *t*-butyl ester of benzoylformic acid in dimethyl sulfoxide at 23°. (b) Calculated spectrum with a Lorentzian line width of 0.2 gauss and a^{H} = 2.90, 2.45, 2.45, 0.80, and 0.80 gauss.

Treatment of DPPT (0.05 *M*) with potassium *t*-butoxide (0.5 *M*) in DMSO yielded a paramagnetic solution whose esr spectrum is given in Figure 2. This spectrum had been previously assigned to the radical anion of *t*-butyl benzoylformate ($C_6H_5C(O\cdot){=}(O^-)OC(CH_3)_3$).[7] The hyperfine splitting constants (hfsc) are consistent with a^{H} = 2.90, 2.45, 2.45, 0.80, and 0.80 gauss. With sodium methoxide in DMSO the triketone was converted to the same radical anion formed by disproportionation of methyl mandelate and methyl benzoylformate in basic solution. The hfsc of a^{H} = 2.80, 2.46, 2.46, 0.83, 0.83, 0.83, 0.74, and 0.74 gauss are consistent with $C_6H_5C(O\cdot){=}C(O^-)CH_3$. Similarly potassium isopropoxide yielded $C_6H_5C(O\cdot){=}C(O^-)CH(CH_3)_2$, a^{H} = 2.67, 2.25, 2.25, 0.76, 0.76, and 0.49 gauss. However, the calculated spectrum gives a good fit with the experimental intensities only if the 2.25-gauss triplet splitting is assigned an intensity ratio of 1:1:1 rather than 1:2:1 (Figure 3). This suggests line broadening of the center peak of this triplet because of restricted rotation about the phenyl–carbonyl bond. At a lower temperature magnetic nonequivalence of the *o*-hydrogen atoms may occur, as has been observed for several ketyls.[8]

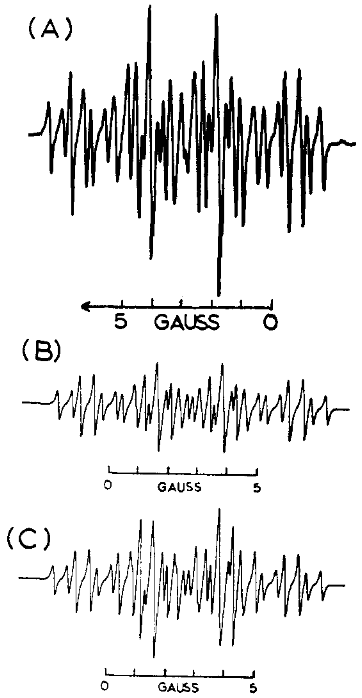
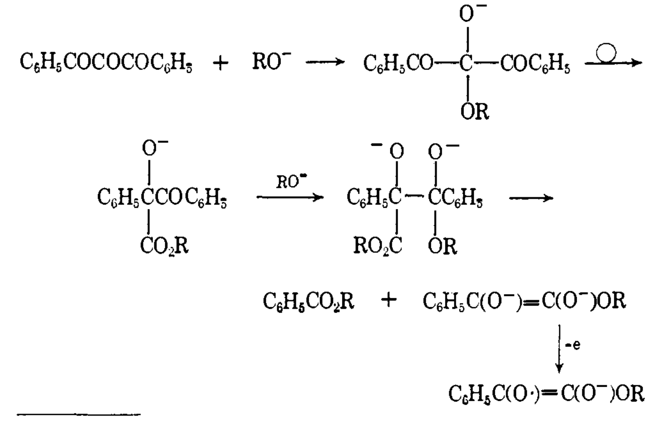


Figure 3. (a) First derivative esr spectrum of potassium salt of radical anion of isopropyl ester of benzoylformic acid in dimethyl sulfoxide at 23°. (b) Calculated spectrum for Lorentzian line widths of 0.2 gauss and hyperfine splittings of 2.67 (doublet), 2.25 (1:1:1 triplet), 0.76 (1:2:1 triplet), and 0.49 (doublet) gauss. (c) Calculated spectrum except with 2.25-gauss triplet given 1:2:1 intensity ratio.

Apparently in DMSO solution DPPT is undergoing nucleophilic attack by the alkoxide ion. A possible reaction scheme is shown below. It has been noted



$$C_6H_5COCOCOC_6H_5 + RO^- \longrightarrow C_6H_5CO{-}\overset{\displaystyle O^-}{\underset{\displaystyle OR}{C}}{-}COC_6H_5 \xrightarrow{\bigcirc}$$

$$C_6H_5\overset{\displaystyle O^-}{\underset{\displaystyle CO_2R}{C}}COC_6H_5 \xrightarrow{RO^-} C_6H_5\overset{\displaystyle {}^-O}{\underset{\displaystyle RO_2C}{C}}{-}\overset{\displaystyle O^-}{\underset{\displaystyle OR}{C}}C_6H_5 \longrightarrow$$

$$C_6H_5CO_2R + C_6H_5C(O^-){=}C(O^-)OR \xrightarrow{-e} C_6H_5C(O\cdot){=}C(O^-)OR$$

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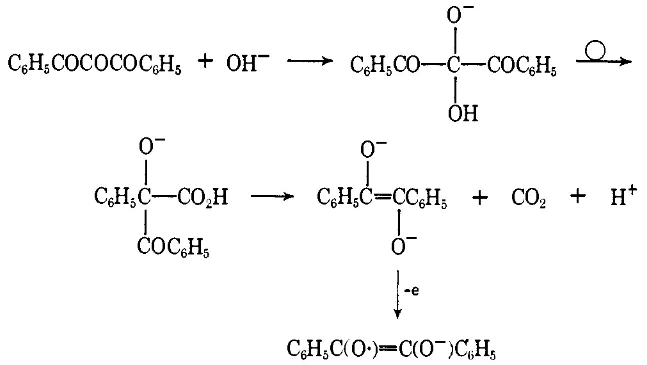
(7) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Am. Chem. Soc.*, **88**, 1998 (1966).

(8) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

that DPPT treated with aqueous hydroxide ion formed benzoin, carbon dioxide, benzoic acid, and mandelic acid.[9]

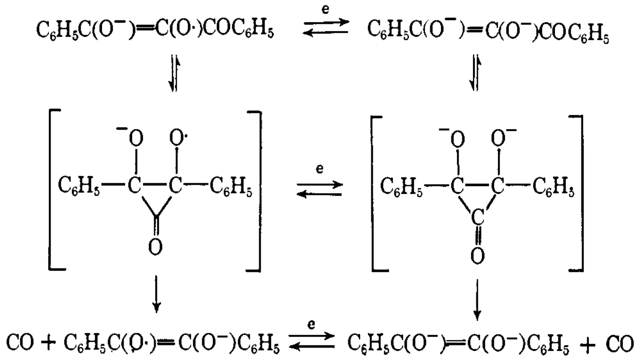
Reaction of DPPT with potassium isopropoxide in DMSO containing >5% of isopropyl alcohol (or in 100% isopropyl alcohol), or of sodium methoxide in methanol–DMSO (25:75), yielded the benzil radical anion (Figure 4a) which was observed 5 min after mixing. Benzil radical anion is also produced when DPPT is treated with potassium *t*-butoxide in N,N-dimethylformamide. It is possible that traces of moisture may have been involved in these reactions. This could lead to an intermediate that would readily decarboxylate after the benzilic acid rearrangement.



$$C_6H_5COCOCOC_6H_5 + OH^- \longrightarrow C_6H_5CO{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}COC_6H_5 \xrightarrow{\circlearrowleft}$$

$$C_6H_5\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle COC_6H_5}{|}}{C}}{-}CO_2H \longrightarrow C_6H_5\overset{\overset{\displaystyle O^-}{|}}{C}{=}\underset{\underset{\displaystyle O^-}{|}}{C}C_6H_5 + CO_2 + H^+ \xrightarrow{-e} C_6H_5C(O\cdot){=}C(O^-)C_6H_5$$

However, since Roberts has shown that the action of base on DPPT labeled with ^{14}C at C-1 and C-3 yields carbon dioxide devoid of radioactivity,[10] the formation of benzil radical anion in the present experiments appears to us to most likely arise *via* a decomposition reaction of DPPT radical anion or dianion.



Treatment of DPPT (0.05) with propiophenone (0.05 *M*) and base (0.5 *M*) (an excellent one-electron reducing agent for α-diketones) in DMSO yields benzil radical anion. A mixture of DPPT (0.05 *M*) and 0.05 *M* 2-hydroxy-1,3-diphenyl-1,3-propanedione (**6**) in DMSO in the presence of potassium *t*-butoxide (0.5 *M*) also yields only the benzil radical anion. It seems likely that methoxide or isopropoxide anions in DMF or DMSO–alcohol solutions can reduce DPPT by hydride transfer to yield **6**. It is known that sodium methoxide in methanol will convert benzil to benzoin in up to 10% yield while sodium isopropoxide in isopropyl alcohol gives a high yield of benzoin.[11] Moreover, it has been observed that the sodium salt of diethyl malonate in benzene solution converts DPPT to benzoin.[12]

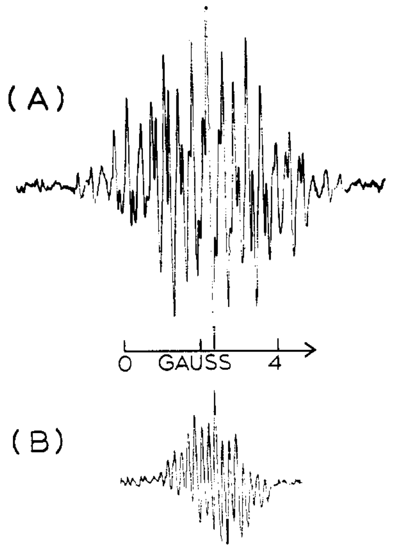


Figure 4. First derivative esr spectra of potassium salts of (a) benzil radical anion and (b) 1,3-diphenyl-1,2,3-propanetrione radical anion in dimethyl sulfoxide solution at 23°.

The semitrione radical anion of DPPT (Figure 4b) was obtained by the addition of an excess of DPPT (0.025 *M*) to a solution of benzil radical anion (Figure 4a) in DMSO prepared from 0.005 benzil and 0.005 *M* base. It can also be formed by electron transfer between the sodium salt of thiophenol and the triketone in DMSO solution. When formed in these manners, $DPPT\cdot^-$ is fairly stable and a resolved spectrum can be obtained for periods up to 30 min. Formation of $DPPT\cdot^-$ from benzil radical anion supports the electrochemical data and indicates that the equilibrium $C_6H_5C(O\cdot){=}C(O^-)C_6H_5 + C_6H_5COCOCOC_6H_5 \rightleftarrows C_6H_5COCOC_6H_5 + C_6H_5(O\cdot){=}C(O^-)COC_6H_5$ lies far to the right ($\Delta F_{25°} = 9.2$ kcal/mole).

The failure to observed $DPPT\cdot^-$ in the other experiments must mean that the DPPT had been extensively decomposed before the esr spectra were recorded. Moreover, it appears that production of benzil radical anion in these experiments probably results from the decarbonylation of the dianion (or from the attack of hydroxide ion), since the radical ion actually has some stability when formed.

The esr spectrum of $DPPT\cdot^-$ shows equivalent *o*- and *p*-hydrogen atoms, $a^H = 0.54$ gauss. The *m*-hydrogen atoms have a hfsc of 0.17 gauss. The benzil radical anion in the presence of excess benzil (exchange broadening) shows four hydrogen atoms (*meta*) $a^H = 0.34$ gauss and six hydrogen atoms (*ortho* and *para*) $a^H = 1.04$ gauss. The ratio of a^H $(DPPT\cdot^-)/a^H$ $(benzil\cdot^-)$ is $\sim$0.5 for all positions. A McLachlan calculation[13] predicts the ratios of 0.4, 0.5, and 0.35 for the *ortho*, *meta*, and *para* positions.

Reaction of DPPT with potassium in hexamethylphosphoramide also yields the benzil radical anion as does the electrolytic reduction of DPPT in DMSO at 2.5 v relative to a saturated calomel electrode. However, at a potential of 1.8 v a mixture of benzil and DPPT radical anions is formed. We conclude that

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(9) R. de Neufville and H. von Pechman, *Ber.*, 23, 3375 (1890).

(10) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, 73, 618 (1951); see also H. Kwart, R. W. Spayd, E. N. Givens, and C. J. Collins, *Chem. Commun.*, 530 (1967).

(11) W. von E. Doering and R. S. Urban, *J. Am. Chem. Soc.*, 78, 5938 (1956).

(12) D. B. Sharp and H. A. Hoffman, *ibid.*, 72, 4311 (1950).

(13) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

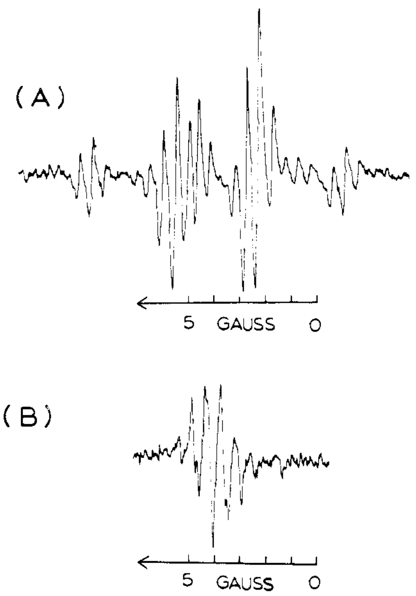


Figure 5. (a) First derivative esr spectrum of mixture of radical anions **9a** and **10** observed initially upon treatment of ethyl 2-hydroxy-3-ketobutanoate with potassium *t*-butoxide in dimethyl sulfoxide solution. (b) Esr spectrum assigned to **10** observed after a reaction period of 20 hr.

DPPT is rapidly destroyed at the electrode surface and that the concentration of DPPT above the mercury pool electrode is very low because of diffusion.[14]

In view of the foregoing results it was not surprising to observe that 1,4-diphenyl-1,2,3,4-butanetetraone (partially hydrated), 1,2,3-phenalenetrione, and 2,3,4-pentanetrione are converted by reaction with potassium *t*-butoxide in DMSO solution to give benzil, acenaphthenequinone, and biacetyl radical anions, respectively. It is recognized that treatment of 1,4-dimesityl-1,2,3,4-butanetetraone with base leads to the formation of the trione.[15]

Paramagnetic Products from Oxidation of α-Substituted β-Diketones. Reaction of deoxybenzoin or a wide variety of other monoketones with traces of oxygen in the presence of potassium *t*-butoxide yields the expected semidiones.[16] However, similar treatment of dibenzoylmethane, benzoylacetone, 2,4-pentanedione, or 5,5-dimethylcyclohexane-1,3-dione with base and oxygen failed to produce a paramagnetic product. These diketones do not absorb appreciable amounts of oxygen in basic solution, presumably due to the resonance stabilization of the enolate anion.[17]

α-Hydroxy ketones, such as benzoin or acetoin, undergo spontaneous disproportionation in basic solution to yield significant quantities of the corresponding semidiones.[7] It was thus of interest to examine the reaction of **7a–f** with potassium *t*-butoxide or tetramethylammonium hydroxide in DMSO solution. Treatment of **7a** yielded the benzil radical anion as the only paramagnetic product, presumably *via* decarbonylation. Treatment of **7b** with potassium *t*-butoxide yielded the phenylglyoxal radical anion ($C_6H_5C(O\cdot){=}C(O^-)H$). It is known that the hydrolysis of **7b** ($NaHCO_3$) yields α-hydroxyacetophenone[18] and that the acetol disproportionates in basic solution to yield the semidione.[7]

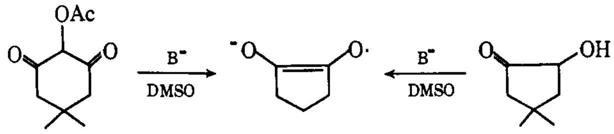
RCOCH(OR″)COR′
7a, R = R′ = C_6H_5; R″ = H
b, R = R′ = C_6H_5; R″ = $COCH_3$
c, R = C_6H_5; R′ = CH_3; R″ = H
d, R = C_6H_5; R′ = CH_3; R″ = $COCH_3$
e, R = R′ = CH_3; R″ = H
f, R = R′ = CH_3; R″ = $COCH_3$

$$\mathbf{7a} \rightleftarrows C_6H_5C(OH){=}C(O^-)COC_6H_5 \rightleftarrows C_6H_5C(O^-){=}C(O^-)COC_6H_5 \longrightarrow C_6H_5C(O^-){=}C(O^-)C_6H_5 + CO$$

$$C_6H_5COCH(O_2CCH_3)COC_6H_5 + OR^- \longrightarrow C_6H_5C(O^-){=}CHO_2CCH_3 \xrightarrow{OR^-} C_6H_5C(O^-){=}C(O^-)H + CH_3CO_2R$$

In a similar fashion **7c** yielded the semidione of 1-phenylpropane-1,2-dione while **7d** yielded phenylglyoxal semidione. Both **7e** and **7f** yielded the biacetyl radical anion[19] upon treatment with base.

Reaction of 2-acetoxy-5,5-dimethylcyclohexane-1,3-dione or 4,4-dimethyl-2-hydroxycyclopentanone with potassium *t*-butoxide in DMSO yielded a five-line sextet consistent with four equivalent hydrogen atoms, a^H = 12.8 gauss. Treatment of reductic acid (2,3-dihydroxycyclopentenone) with potassium *t*-butoxide in DMSO gave only a broad singlet although a quintet has been observed at pH 4.8 in water.[5,20]



Paramagnetic Products from Oxidation of α-Substituted β-Keto Esters. Paramagnetic oxidation products could not be detected in the reaction of ethyl acetoacetate or ethyl benzoylacetate with potassium *t*-butoxide in DMSO solution in the presence of oxygen. We therefore examined compounds **8a–e**. Treatment of **8a** or **8b** with potassium *t*-butoxide in DMSO yielded the decarbonylation product, the previously described radical anion of ethyl benzoylformate.[7] Similar treatment of **8c** and **8d** yielded initially the spectrum of Figure 5 (top). Upon standing 20 hr the spectrum of

$RCOCH(OR'')CO_2R'$
8a, R = C_6H_5; R′ = CH_3CH_2; R″ = H
b, R = C_6H_5; R′ = CH_3CH_2; R″ = $COCH_3$
c, R = CH_3; R′ = CH_3CH_2; R″ = H
d, R = CH_3; R′ = CH_3CH_2; R″ = $COCH_3$
e, R = CH_3; R′ = CH_3; R″ = H

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[14] Electrolytic reductions at a mercury cathode in acetonitrile solution or DMSO solution give reaction products characteristic of a strongly basic solution, particularly at the higher potentials. Electrolytic generation of semidiones from diketones occurs without complication where base-catalyzed side reactions are not encountered, *e.g.*, the reduction of cyclohexane-1,2-dione to the semidione. However, all attempts to reduce biacetyl to the semidione electrolytically have produced 2,5-dimethyl-*p*-benzosemiquinone, the recognized product of the actions on strong base in biacetyl: M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

[15] A. R. Gray and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 1367 (1934).

[16] G. A. Russell and E. T. Strom, *ibid.*, **86**, 744 (1964).

[17] G. A. Russell, A. J. Moye, and K. L. Nagpal, *ibid.*, **84**, 4154 (1962).

[18] A. H. Blatt and W. L. Hawkins, *ibid.*, **58**, 81 (1936); P. Karrer, J. Kebrle, and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).

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

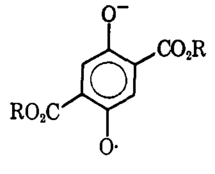
[20] Similarly Lagercrantz[21] reported he was unable to obtain an esr signal from $HC(OH){=}C(OH){=}C(OH)CHO$ upon treatment with 6 *N* potassium hydroxide even though $HC(O^-){=}C(O\cdot)CHO$ has been detected at pH 4.8.

[21] C. Lagercrantz, *Acta Chim. Scand.*, **18**, 1321 (1964).

Figure 5 (bottom) was observed. We interpret these spectra as being due to a mixture of **9** and **10**. Semidione **9a** has hfsc $a_{CH_3}{}^{H}$ = 3.2 gauss and $a_{CH_2}{}^{H}$ = 0.5 gauss and **10** (R = CH_3CH_2) a^H = 0.65 (2) and 0.48 (4) gauss. Evidence for hfs by the ester alkyl group is

$CH_3C(O^-){=}C(O\cdot)CO_2R$

9a, R = CH_2CH_3
b, R = CH_3



10

furnished by the observation that **8e** yielded **9b** (in addition to **10**) and that **9b** contained two methyl splittings, $a_{CH_3}{}^{H}$ = 3.2 and 0.5 gauss. Decarbonylation did not occur for **8c–e** since the pyruvic ester radical anion has a larger hfsc than those of Figure 5. Treatment of a mixture of ethyl pyruvate and ethyl lactate with potassium *t*-butoxide in DMSO yields a single radical anion with $a_{CH_3}{}^{H}$ = 5.6, $a_{CH_2}{}^{H}$ = 0.8 gauss. The triplet splitting of 0.65 gauss appears reasonable for **10**. The hfsc of 2,5-dihydroxy-*p*-benzosemiquinone is a^H = 0.81 gauss (water).[21] The formation of **10** is reasonable since biacetyl upon electrolysis in DMSO (1.5 v), or upon treatment with potassium *t*-butoxide in DMSO, forms the analogous 2,5-dimethyl-*p*-benzosemiquinone as the only paramagnetic substance.

The difference in behavior between benzoyl derivatives (**8a** and **8b**) and the acetyl derivatives (**8c–e**) may be connected with a more facile formation of dianion (leading to decarbonylation) for the benzoyl compounds. Another example of this behavior is the observation that the methyl, ethyl, or isopropyl esters of mandelic acid are oxidized in DMSO–potassium *t*-butoxide to yield the semidione of the benzoylformic esters, possibly *via* an enolate dianion intermediate. However, under similar conditions methyl, ethyl, or isopropyl lactates yield only the biacetyl radical anion. We can only presume that methylation by the methylsulfinylcarbanion ($CH_3SOCH_2^-$) has occurred.[22] Apparently, the mandelate esters are converted to dianions and hence to semidiones too readily for the methylation reaction to compete.

$$CH_3CH(O^-)CO_2R + CH_3SOCH_2^- \longrightarrow$$

$$CH_3CH(O^-)COCH_2SOCH_3 + OR^- \rightleftarrows$$

$$CH_3C(O^-){=}C(OH)CH_2SOCH_3 \longrightarrow$$

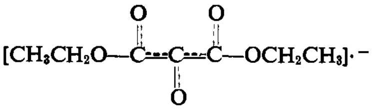
$$CH_3COC(OH){=}CH_2 + CH_3SO^- \longrightarrow$$

$$CH_3COCOCH_3 \xrightarrow{e} CH_3C(O\cdot){=}C(O^-)CH_3$$

Radical Anions of Mesoxalate Esters. The reduction of ethyl mesoxalate (**11**), electrolytically in dimethylformamide or acetonitrile, with potassium in hexamethylphosphoramide, or by the actions of potassium *t*-butoxide in DMSO leads to a single radical believed to be **12**. The esr spectrum is a 1:4:6:4:1 quintet with a^H = 0.66 gauss. There is no detectable solvent effect on the hfsc. The same radical anion is also produced by oxidation of **13a**, or by reduction of ethyl oxalate by potassium in hexamethylphosphoramide.

$$CH_3CH_2OCOCOCO_2CH_2CH_3 \longrightarrow$$

11



$$[CH_3CH_2O{-}\overset{\overset{O}{\|}}{C}{\cdots}\underset{\underset{O}{\|}}{C}{\cdots}\overset{\overset{O}{\|}}{C}{-}OCH_2CH_3]\cdot^-$$

12

$RO_2CC(OH){=}C(OH)CO_2R$

13a, R = CH_3CH_2
b, R = CH_3

Repetition of these experiments with the methyl ester of **11**, **13b**, or methyl oxalate yields a radical anion with hfs by six equivalent protons, a^H = 0.66 gauss. Reaction of isopropyl oxalate with potassium produces a radical anion with a 1:2:1 triplet splitting, a^H = 0.44 gauss. The structure of **12** has been assigned mainly by consideration of the observed hfsc, the known chemistry of oxalic esters and dihydroxymaleic acid, and the low reduction potential observed for mesoxalate esters (Table I). In Table II are summarized methyl, methylene, and methine hfsc of a series of semidione radical anions of esters.

Table II. Alkoxy Hyperfine Splitting Constants in $[RCO_2CH_3]\cdot^-$, $[RCO_2CH_2CH_3]\cdot^-$, and $[RCO_2CH(CH_3)_2]\cdot^-$

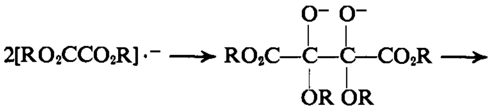
R	$a_{CH_3}{}^{H}$	$a_{CH_2}{}^{H}$	$a_{CH}{}^{H}$
CH_3CO		0.8	
CH_3COCO	0.5	0.5	
C_6H_5CO	0.83	0.78	0.49
ROCOCO[a]	0.66	0.66	0.42

[a] Symmetrical species, R = CH_3, CH_3CH_2, and $(CH_3)_2CH$, respectively.

From the hyperfine splitting constants for the methylene hydrogen in $RCOCO_2CH_2CH_3$ (R = CH_3, C_6H_5) we can make a lower estimate of the expected value of $a_{CH_2}{}^{H}$ in the radical anion of ethyl oxalate. Since the carbonyl group is more electron attracting than the ester group, it follows that $a_{CH_2}{}^{H}$ in the radical anion of ethyl oxalate would be greater than 0.8 gauss. The observed value of $a_{CH_2}{}^{H}$ of 0.66 gauss excludes the ethyl oxalate structure. We can also estimate in the same fashion the minimum value of $a_{CH_2}{}^{H}$ for the ethyl mesoxylate radical anion. From $[CH_3COCOCO_2Et]\cdot^-$, $a_{CH_2}{}^{H}$ = 0.5 gauss, we estimate $a_{CH_2}{}^{H}$ in **12** should be greater than 0.50 gauss.

Conclusive proof that the observed radical anion is not a single one-electron reduction product of the oxalic ester is furnished by the following observations. Reduction of diethyl oxalate by potassium in hexamethylphosphoramide yielded a spectrum that was unaffected by the addition of diisopropyl oxalate. Reduction of diisopropyl oxalate gave a spectrum that was not effected by the addition of ethyl oxalate. Reduction of a mixture of diethyloxalate and diisopropyl oxalate yielded mainly a radical anion with $a_{CH}{}^{H}$ = 0.3, $a_{CH_2}{}^{H}$ = 0.75 gauss, presumably the semitrione $[(CH_3)_2CHO_2CCOCO_2CH_2CH_3]\cdot^-$. These results are readily rationalized by the following mechanisms.

$$RO_2CCO_2R + e \longrightarrow [RO_2CCO_2R]\cdot^-$$



$$2[RO_2CCO_2R]\cdot^- \longrightarrow RO_2C{-}\overset{\overset{O^-}{|}}{\underset{\underset{OR}{|}}{C}}{-}\overset{\overset{O^-}{|}}{\underset{\underset{OR}{|}}{C}}{-}CO_2R \longrightarrow$$

$$RO_2CCOCOCO_2R + 2RO^-$$

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(22) G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

$$RO_2CCOCOCO_2R \xrightarrow{2e} [RO_2CCOCOCO_2R]^{2-} \longrightarrow [RO_2CCOCO_2R]^{2-} + CO$$

$$[RO_2CCOCO_2R]^{2-} \xrightarrow{-e} \mathbf{12}$$

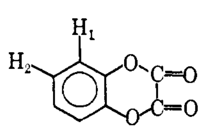
It is known that the reduction of ethyl oxalate by sodium amalgan in ethanol yields ethyl mesoxalate and ethyl tartrate.[23] Mesoxalic acid is produced in the oxidation of tartaric acid by hydrogen peroxide[24] and in the ferric ion oxidation of dihydroxymaleic acid.[25] Heating an alkaline solution of tartaric acid produces tartronic acid.[26]

We have observed the treatment of ethyl tartronate acetate (**14**) with potassium *t*-butoxide in DMSO also produces radical anion **12**.

$$CH_3CO_2CH(CO_2CH_2CH_3)_2$$

14

We were unable to obtain resolved esr signals for the reduction product of phenyl or benzyl oxalate with potassium in hexamethylphosphoramide. No signal was detected from the electroreduction of ethylene oxalate. However, 1,2-benzoxalate (**15**) upon reduction in dimethylformamide yielded an esr signal with four equivalent hydrogen atoms, $a^H = 0.18$ gauss. A McLachlan calculation predicts $a_1^H = 0.74$ and $a_2^H = 0.05$ (assuming $a^H = 23\rho_C$) for the resulting cyclic semidione.



15

Experimental Section

Polarography and Electrolytic Reductions. All polarograms (0.001 *M* in substrate) were obtained by use of a Sargent Model XXI Polarograph utilizing DMSO distilled from alumina under vacuum and stored over molecular sieves. Potentials were measured relative to an aqueous saturated calomel electrode. Tetra-*n*-propylammonium perchlorate[27] (0.1 M) was used as the electrolyte. The electrolytic generation of radical anions was performed at a mercury pool cathode using a modified Varian Associates electrolytic accessory. Potentials were measured relative to a nonaqueous silver | silver perchlorate electrode which has a potential of −0.14 v relative to an aqueous saturated calomel electrode in acetonitrile.

Electron Spin Resonance Spectra. The spectra were obtained with a Varian V-4502 spectrometer equipped with a 9-in. magnet with 100 Kcps field modulation. Reactions were performed in the inverted U-type cell described previously.[28] All solutions were deoxygenated prior to mixing. Reactions with potassium *t*-butoxide in DMSO involved the mixing of solution about 0.1 *M* in substrate with an equal volume of a solution about 1.0 *M* in potassium *t*-butoxide. Reactions between dihydro and dehydro pairs involved solution 0.1 *M* in each reactant and 1 *M* in base.

Reagents.[29] Acetonitrile (spectrographic grade; Matheson Coleman and Bell) was stored over molecular sieves. DMF and HMPA were distilled from calcium hydride under vacuum and stored over calcium hydride and molecular sieves.

1,3-Diphenyl-1,2,3-propanetrione and ethyl α,β-dihydroxycinnamate were prepared as described earlier.[7] 2-Hydroxy-1,3-diphenyl-1,3-propanedione, mp 106–110°, 2-hydroxy-1-phenyl-1,3-butanedione, mp 82–95°, 2-acetoxy-1-phenyl-1,3-butanedione, bp 120–122° (0.4 mm), and 2-acetoxy-1,3-diphenyl-1,3-propanedione, mp 90–95°, were prepared according to Böhme and Schneider.[30] 1,4-Diphenyl-1,2,3,4-butanetetraone and its dihydro derivative were prepared by the method of Blatt.[31] 2,3,4-Pentanetrione was prepared according to Sachs.[32] 1,2,3-Phenalenetrione was prepared by selenium dioxide oxidation of 1,3-phenalenedione.[33] 3-Hydroxy-2,4-pentanedione, bp 60–70° (8 mm), was prepared by hydrolysis of the chloride.[34]

3-Acetoxy-2,4-pentanedione,[35] bp 112–118° (33 mm), ethyl 2-acetoxyacetoacetate,[36] by 120–124° (15 mm), and ethyl 2-acetoxybenzoyl,[37] bp 125–130° (0.5 mm), were prepared by reaction of 2,4-pentanedione, ethyl acetoacetate, and ethyl benzoylacetate with lead tetraacetate. 2-Acetoxy-4,4-dimethylcyclohexane-1,3-dione, mp 155–160°, was prepared by the procedure of Eistert.[37] 4,4-Dimethyl-2-hydroxycyclopentan-1-one, bp 67° (2.3 mm), was prepared by the acyloin condensation.[38] 2-Ethyl-2-hydroxyacetoacetate, bp 95–98° (15 mm), and the methyl ester, bp 79–85° (15 mm), were prepared by oxidation of ethyl and methyl acetoacetate with *m*-chloroperbenzoic acid.[39] Diphenyl oxalate, mp 132–134°, was obtained from oxalyl chloride.[40] Oxalic acid, ethylene ester, was obtained by the method of Carothers, *et al.*[41] The dimethyl ester of dihydroxymaleic acid, mp 178–181°, and diethyl ester, mp 54–58°, were obtained according to Hartree.[42] 1,2-Benzoxalate and dibenzyl oxalate were kindly supplied by Dr. W. S. Trahanovsky and Miss C. C. Ong.

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