

with sodium chloride, and filtered. Anhydrous magnesium sulfate was added to the crude aldehyde **6**, and the mixture was sublimed under reduced pressure at room temperature. Cold water (*ca.* 5°) was introduced into the cold finger of the sublimator. The sublimed aldehyde was a colorless, waxy solid which had mp 84.5–88°; $[\alpha]_D^{25} -6.8^\circ$ (*c* 5.08, benzene); infrared spectrum (CCl₄) 3.58, 3.70, 5.85 (formyl group), and 7.21, 7.30 μ (*gem*-dimethyl group); nmr spectrum (CCl₄) 0.92 (singlet, 3 H), 1.06 (doublet, *J* = 7.5 cps, 1 H), 1.28 (singlet, 3H), 1.77 (multiplet, 4 H), 2.08 (multiplet, 1 H), 2.33 (broad, 1 H), and 9.67 (singlet, 1 H).

A sample of the sublimed material in carbon tetrachloride was found to be homogeneous by vpc (temperature programmed from 125 to 250°, 5-ft column packed with 20% silicone Ge-SF-96 on 60–80 mesh firebrick). The crude material was also homogeneous by vpc analysis. An attempt to prepare the *p*-nitrobenzoate of any alcoholic product in the filtrate from the crude aldehyde yielded negative results.

Semicarbazone of Aldehyde 6. The aldehyde **6** was prepared from the amino alcohol **5** (0.500 g, 0.00322 mole) as described previously using sodium nitrite (5 ml of a 4 *m* solution, 0.0181 mole) and acetic acid (15 ml of a 50% solution). Ethanol (15 ml) was added to the reaction medium.³² The solution was shaken vigorously after addition of semicarbazide hydrochloride (0.520 g, 0.00465 mole) and sodium acetate trihydrate (0.800 g, 0.00588 mole). A white, powdery solid appeared within 2 min. The semicarbazone (0.480 g, mp 189–191° dec) was obtained in 76% yield based on the amino alcohol **5**. An analytical sample was prepared after three recrystallizations from ethanol–water, yielding colorless needles, mp 192–193.2° dec.

Anal. Calcd for C₁₀H₁₇N₃O: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.69; H, 8.80; N, 21.58.

5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxylic acid (14). The crude aldehyde **6** (prepared in the manner described previously using 1.00 g of amino alcohol **5**, 9 ml of a 4 *m* sodium nitrite solution, and 25 ml of a 50% acetic acid solution) was added gradually to a solution of sodium hydroxide (8 ml of a 5% solution) and hydrogen peroxide (4 ml of a 30% solution) which had been heated to 65–70°

in a water bath.³² The mixture was shaken and kept at 65–70° for 20 min. Another 3 ml of 30% hydrogen peroxide was added during the reaction. The solution was acidified to congo red, and the white solid which precipitated was removed by filtration. The acid **14** (0.287 g, mp 115–119°) was obtained in 29% yield based on the amino alcohol **5**. After sublimation under reduced pressure at 50–60°, the acid exhibited mp 120.2–122.2°; $[\alpha]_D^{25} +11.2^\circ$ (*c* 5.03, benzene); infrared spectrum (CCl₄) 3.0–4.2, 5.90 (carboxyl group), and 7.21, 7.29 μ (*gem*-dimethyl group); nmr spectrum (CCl₄) 0.91 (singlet, 3 H), 1.14 (doublet, *J* = 7.5 cps, 1 H), 1.28 (singlet, 3 H), 1.80 (multiplet, *ca.* 4 H), 2.02 (multiplet, *ca.* 1 H), 2.29 (broad, 1 H), and 12.15 (singlet, 1 H).

Anal. Calcd for C₉H₁₄O₂: C, 70.10; H, 9.15; O, 20.75. Found: C, 70.15; H, 9.20; O, 20.72; neut equiv, 155.

Dimedone Derivative of Aldehyde 6. The crude aldehyde **6** (prepared as described previously using 0.500 g of amino alcohol **5**, 5 ml of a 4 *m* sodium nitrite solution, and 15 ml of a 50% acetic acid solution) was dissolved in 10 ml of 70% ethanol.³² The solution was added gradually to a hot solution of dimedone (0.398 g, 0.00284 mole), ethanol (15 ml of a 70% solution), and piperidine (2 drops). The resulting solution was heated at *ca.* 75° for 8 min. One milliliter of water was added, and the solution was left to stand at room temperature overnight and white crystals appeared. The dimedone derivative (0.198 g, mp 170–173.5°) was obtained in 15% yield based on the amino alcohol **5**. An analytical sample was prepared after four recrystallizations from 70% ethanol, mp 176–178°.

Anal. Calcd for C₂₅H₃₆O₄: C, 74.96; H, 9.06; O, 15.98. Found: C, 74.91; H, 9.03; O, 16.01.

Octahydroxanthene Derivative of Aldehyde 6. Concentrated hydrochloric acid (2 drops) was added to a solution of the dimedone derivative of **6** (0.157 g) in 13 ml of 80% ethanol.³² The mixture was heated at *ca.* 80° for 10 min. One milliliter of 80% ethanol and another drop of hydrochloric acid were added during the reaction. Water was added to the cloud point, and the mixture was kept in the cold. The white octahydroxanthene derivative (0.125 g, 83%, mp 222.4–223.2° dec) was recovered by filtration. After four recrystallizations from methanol–water, the derivative exhibited mp 224.7–225.7° dec.

Anal. Calcd for C₂₅H₃₄O₈: C, 78.49; H, 8.96; O, 12.55. Found: C, 78.75; H, 8.98; O, 12.52.

(32) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956.

Semidiones. I. Acyclic Semidione Radical Anions and Cations Containing a Single Aryl Substituent¹

Glen A. Russell, E. Thomas Strom,^{2a} Erach R. Talaty, and Steven A. Weiner^{2b}

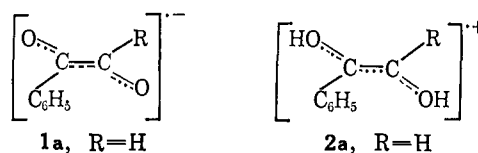
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa. Received December 20, 1965

Abstract. The preparation of a number of semidione radical anions (ArC(O⁻)=C(O[·])R) and the analysis of their well-resolved esr spectra are reported. Less highly resolved spectra are reported for some of the corresponding diprotonated derivatives (ArC(OH)—C⁺(OH)R).

Acyclic semidione radical anions (RC(O[·])=C(O⁻)R) or radical cations (RC(OH)—C⁺(OH)R) can be detected by electron spin resonance (esr) spectroscopy under a variety of reaction conditions. We now report details on the preparation, detection, and esr spectral analysis of a series of radical anions (**1**) and cations (**2**) with 1-aryl substituents.

(1) Reactions of Resonance Stabilized Anions. XXI. This work was supported by grants from the Petroleum Research Fund and the National Science Foundation.

(2) (a) National Institutes of Health Predoctoral Fellow, 1962–1963; (b) National Aeronautics and Space Administration Predoctoral Fellow, 1964–1965.



The parent molecules (R = H) of series **1** and **2** have both been prepared. Reduction of anhydrous phenylglyoxal in 98% sulfuric acid by sodium dithionite gives rise to a radical cation presumed to be **2a**. The esr spectrum (Figure 1) shows a doublet splitting of $a^H = 3.14$ gauss. The *p*-bromo, *p*-methyl, and *p*-methoxy

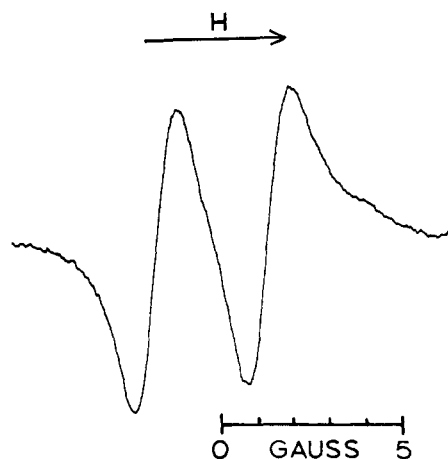
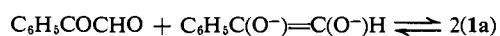


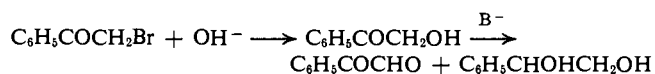
Figure 1. First-derivative esr spectrum (~ 9.5 Gcps) of radical cation prepared by sodium dithionite reduction of phenylglyoxal in 98% sulfuric acid at $25 \pm 2^\circ$.

derivatives of **2a** also give doublet splittings with $a^H = 3.07, 3.24,$ and 3.29 gauss, respectively. The lack of resolved splitting by the aromatic hydrogens and hydroxyl hydrogens may be due to the intrinsic line widths under the reaction conditions as well as due to the small values expected for a_{aromatic}^H and the rapid exchange of the hydroxylic protons.³ In deuterio-sulfuric acid only a singlet is observed for the phenylglyoxal radical cation. Apparently the aldehydic hydrogen exchanges readily. Treatment of 1-phenylpropane-1,2-dione with sodium dithionite in 98% sulfuric acid yields the radical cation **2**, $R = \text{CH}_3$. The quartet splitting from the methyl group, $a_{\text{CH}_3}^H = 2.05$ gauss, is shown in Figure 2.⁴

Reduction of phenylglyoxal by the enolate anion of propiophenone in dimethyl sulfoxide (DMSO) solutions containing potassium *t*-butoxide produces **1a** immediately. In the absence of propiophenone alkylation by the methylsulfinyl carbanion eventually yielding 1-phenylpropane-1,2-semidione occurs slowly.⁵ Formation of phenylglyoxal in the presence of the enediol dianion formed from ω -hydroxyacetophenone also gives rise to **1a**. Thus **1a** is readily formed from the



spontaneous disproportionation of ω -hydroxyacetophenone in basic DMSO solutions or by treatment of phenacyl bromide with DMSO containing potassium *t*-butoxide and a trace of moisture.^{5,6}



(3) Hyperfine splitting is routinely observed for hydroxylic hydrogen atoms of *p*-benzosemiquinone radical cations: J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161, (1962); *Proc. Chem. Soc.*, 174, 385 (1961); J. R. Bolton, A. Carrington, and J. dos Santos Veiga, *Mol. Phys.*, **5**, 465 (1962).

(4) Our assignment of the spectra of Figures 1 and 2 to the radical cations is supported by the observation of the expected splitting patterns for a wide variety of aliphatic analogs of **2** [G. A. Russell, E. R. Talaty, and M. C. Young, *J. Phys. Chem.*, **70**, 1321 (1966)].

(5) G. A. Russell, R. D. Stephens, and E. R. Talaty, *Tetrahedron Letters*, 1139 (1965); see also G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

(6) The spectrum of **1a** has been reported previously and in pure DMSO is consistent with $a_{\text{CHO}}^H = 6.88$ $a_p^H = 1.70$, $a_o^H = 1.50$, and $a_m^H = 0.52$ gauss.

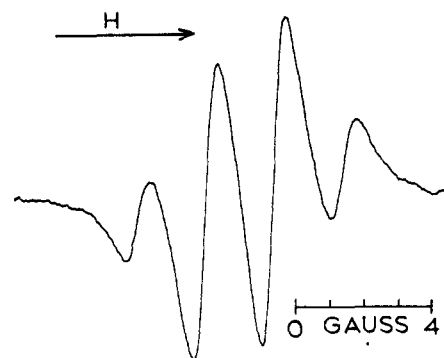
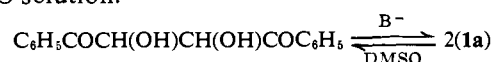
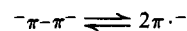


Figure 2. First-derivative esr spectrum of radical cation prepared by sodium dithionite reduction of 1-phenylpropane-1,2-dione in 98% sulfuric acid at $25 \pm 2^\circ$.

Phenylglyoxal radical anions can also be prepared from the pinacol by treatment with an excess of base in DMSO solution.



This reaction apparently involves the dissociation of a dianion

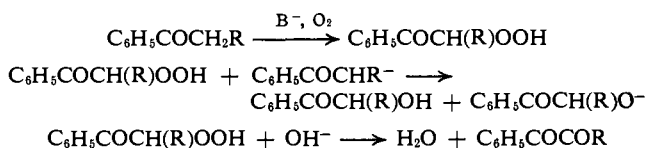


and is characteristic of many pinacols.⁷ Treatment of 1,2-dibromo-1,2-dibenzoylthane with base in DMSO solution also produces **1a**, presumably by formation of the intermediate pinacol.

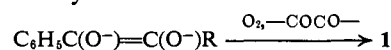


Semidiones **1** with $R = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, n\text{-C}_3\text{H}_7, t\text{-C}_4\text{H}_9,$ and $i\text{-C}_4\text{H}_9$ are readily prepared by oxidation of the corresponding phenones by a deficiency of molecular oxygen (~ 10 mole %) in DMSO solutions containing potassium *t*-butoxide. Yields of **1** are about 1% based on oxygen or 0.1% based on ketone. Under these reaction condition acetophenone does not form detectable amounts of **1a**.

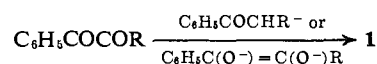
Formation of semidione radical anions by autoxidation of ketones in basic solution undoubtedly involves an intermediate hydroperoxide.⁸ The hydroperoxide can be converted to the acyloin or acylil by further reactions. Among the subsequent reactions that can



form the semidione radical anions are oxidation of the dianion of the acyloin



or reduction of the acylil by electron transfer. Mix-



(7) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

(8) Evidence for the intermediacy of hydroperoxides in carbanion oxygenations has been presented by G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, *Advances in Chemistry Series*, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

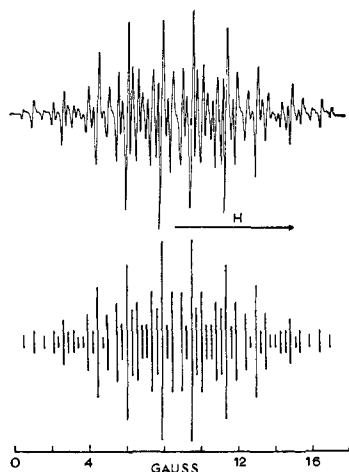


Figure 3. First-derivative esr spectrum of radical anion of 1-phenylpropane-1,2-dione prepared by oxidation of propiophenone or spontaneous disproportionation of 1-phenylpropane-1,2-dione in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) solutions of potassium *t*-butoxide at $25 \pm 2^\circ$.

tures of the preformed acylil and acyloin give especially high yields ($\sim 5\%$) of the semidiones. Moreover, the acylils with α -hydrogen atoms, such as 1-phenylpropane-1,2-dione, spontaneously form semidiones in DMSO in the presence of potassium *t*-butoxide, presumably *via*



The acyloins ($\text{RCOCH}(\text{OH})\text{R}$) will also undergo spontaneous disproportionation yielding the semidione in strongly basic solution (potassium *t*-butoxide in DMSO). However in a solvent composed of 80% DMSO and 20% *t*-butyl alcohol this disproportionation is slow and the semidione is best prepared from the acyloin by reaction with a trace of oxygen. Yields of semidione in the oxidation of an acyloin are generally much higher than in the oxidation of a monoketone and are usually in the range of 5% based on acyloin.

In Figure 3, the esr spectrum of 1-phenylpropane-1,2-semidione radical anion is given.⁹ The correlation diagram in Figure 3 has been constructed with $a_{\text{CH}_3}^{\text{H}} = 3.43$, $a_p^{\text{H}} = 1.84$, $a_o^{\text{H}} = 1.59$, and $a_m^{\text{H}} = 0.53$.

The electrolytic reduction of benzaldehyde and acetophenone to yield the ketyls has been studied.¹¹ The original report^{11a} of reduction in dimethylformamide described radical anions now known^{11b} not to be the simple ketyls. Amazingly, the spectrum originally attributed to acetophenone ketyl is identical in all details with that of 1-phenylpropane-1,2-semidione (Figure 3).^{11c} The values of the hyperfine splitting

(9) The existence of *cis* and *trans* structures for 1, and possibly 2, seems likely since these structures are recognized for the completely aliphatic analogs of 1.¹⁰ However, we have so far recognized only a single stereoisomer of 1 in DMSO solution, presumably the *trans* structure. The presence of a few per cent of the isomeric *cis* radical anion may well have been obscured by the complexity of the esr spectra of semidiones with a 1-aryl substituent.

(10) (a) G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **70**, 1320 (1966). (b) J. R. Steven and J. C. Ward, *Chem. Commun.* (London), 273 (1965).

(11) (a) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962); (b) N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964); (c) The similarity of the hfsc was first pointed out to us by Dr. P. H. Rieger.

constants (hfsc) reported by Rieger and Fraenkel are $a_{\text{CH}_3}^{\text{H}} = 3.30$, $a_p^{\text{H}} = 1.84$, $a_o^{\text{H}} = 1.58$, and $a_m^{\text{H}} = 0.52$ gauss.¹²

The conversion of acetophenone ketyl to 1-phenylpropane-1,2-semidione has apparently been observed *only* in dimethylformamide solution. It is formed only at high reduction potentials and by an irreversible electrode process.^{11b} It is tempting to speculate that the additional carbonyl group comes from the dimethylformamide.¹³

The spectrum originally attributed to benzaldehyde ketyl may well be phenylglyoxal semidione. The hfsc reported^{11a} were $a_{\text{CHO}}^{\text{H}} = 5.53$, $a_p^{\text{H}} = 1.56$, $a_o^{\text{H}} = 1.36$, and $a_m^{\text{H}} = 0.45$. The ring-hydrogen splittings found in DMSO solution for phenylglyoxal semidione are 9–15% higher than those reported by Rieger and Fraenkel in dimethylformamide solution while the aldehydic hydrogen splitting is 24% greater in the present work. However, it appears most likely that Rieger and Fraenkel did actually observe the phenylglyoxal radical anion.¹⁴

The *p*-chlorophenyl and *p*-methoxyphenyl derivatives of 1, $\text{R} = \text{CH}_3$, have also been prepared in DMSO (80%)–*t*-butyl alcohol (20%) by oxidation of the ketones. The *p*-chloro derivative gives $a_{\text{CH}_3}^{\text{H}} = 3.22$, $a_o^{\text{H}} = 1.73$, and $a_m^{\text{H}} = 0.59$ gauss. The *p*-methoxyphenyl derivative gives $a_{\text{CH}_3}^{\text{H}} = 3.88$ and 0.15 gauss. The 0.15 gauss splitting is assigned to the methoxy group. Other hyperfine splittings are due to $a_o^{\text{H}} = 1.54$ and $a_m^{\text{H}} = 0.51$ gauss.

The hfsc observed for 1 containing a variety of alkyl substituents are listed in Table I.

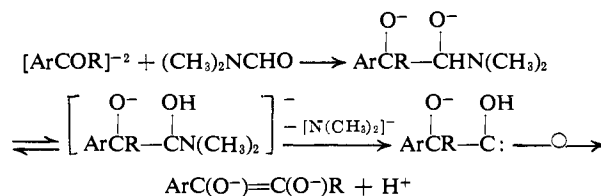
Table I. Hyperfine Splitting Constants of Semidione Radical Anions ($\text{C}_6\text{H}_5\text{C}(\text{O}^-)=\text{C}(\text{O}^-)\text{R}$) in Dimethyl Sulfoxide (80%)–*t*-Butyl Alcohol (20%) at 25°

R	$a_\alpha^{\text{H}^a}$	$a_\beta^{\text{H}^a}$	a_p^{H}	a_o^{H}	a_m^{H}
CH_3	3.43	...	1.84	1.59	0.53
CH_2CH_3	3.38	<i>b</i>	1.82	1.61	0.54
$\text{CH}_2\text{CH}_2\text{CH}_3$	3.12	0.11	1.85	1.62	0.55
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	3.15	<i>c</i>	1.82	1.59	0.54
$\text{CH}(\text{CH}_3)_2$	1.45	<i>b</i>	1.84	1.60	0.53
$\text{C}(\text{CH}_3)_3$...	0.18	1.84	1.58	0.54
$\text{CH}_2\text{CH}(\text{CH}_3)_2$	3.05	0.14	1.85	1.61	0.53
$\text{OCH}_2\text{CH}_3^d$...	0.78 ^e	2.75	2.32	0.78
$\text{OC}(\text{CH}_3)_3^d$	2.90	2.45	0.80

^a Hydrogen atoms α or β to the dicarbonyl system. ^b Not observed. ^c No attempt made to resolve splitting. ^d In DMSO. ^e $a_{\text{CH}_2}^{\text{H}}$.

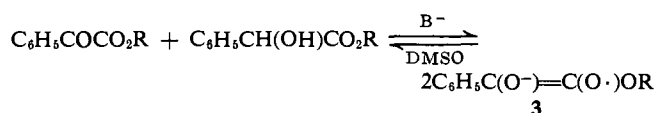
(12) Restricted rotation in the aromatic semidiones has not been detected. For the aromatic ketyls rotation of the aromatic ring is restricted. Thus, Steinberger and Fraenkel report^{11b} for acetophenone ketyl that $a_{\text{CH}_3}^{\text{H}} = 6.74$, $a_p^{\text{H}} = 6.60$, $a_o^{\text{H}} = 4.25$, 3.71, and $a_m^{\text{H}} = 1.07$, 0.88 gauss in dimethylformamide solution.

(13) We are currently testing the postulate that the following reaction sequence is involved.

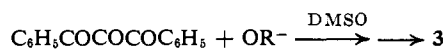


(14) Benzaldehyde ketyl^{11b} has restricted rotation, $a_{\text{CHO}}^{\text{H}} = 8.51$, $a_p^{\text{H}} = 6.47$, $a_o^{\text{H}} = 4.69$, 3.39, and $a_m^{\text{H}} = 1.31$, 0.75 gauss in dimethylformamide solution.

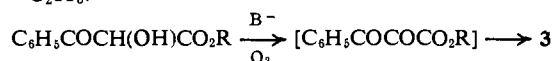
Radical anions can be prepared by the disproportionation of the esters of benzoylformic and mandelic acids in DMSO solution containing potassium alkoxides. In Figure 4 the esr spectrum of **3**, R =



C_2H_5 , is given together with a spectrum calculated from the hfsc given in Table I. Radical anions **3** can also be prepared by the reaction of 1,3-diphenyl-1,2,3-propanetrione with alkali alkoxides in DMSO solution.

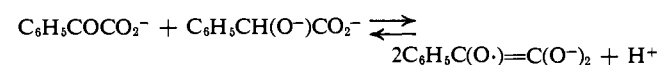


In this manner **3**, R = *t*-butyl, can be readily prepared. Oxidation of the ethyl ester of α,β -dihydroxycinnamic acid in DMSO or DMF solution also provides **3**, R = C_2H_5 .



The spectra for **3**, R = CH_3 , $(\text{CH}_3)_2\text{CH}$, will be reported at a later date. Because of the high spin density in the aromatic ring there may be restricted rotation of the aromatic ring in these radical anions with magnetically nonequivalent *ortho* and *meta* hydrogen atoms.¹² Such restricted rotation is not demanded by the spectrum of **3**, R = C_2H_5 (Figure 4), but it is not necessarily excluded.

Disproportionation of the salts of mandelic and benzoylformic acids could form the radical dianion. A similar process has been observed for pyruvate and



lactate salts.¹⁰ However, disproportionation of mandelate and benzoylformate salts in DMSO solution have led only to a low concentration of radical anions which do show hyperfine splitting but which cannot be uniquely assigned to the benzoylformate radical dianion. Reduction of benzoylformic acid by potassium in hexamethylphosphoramide solution yielded a spectrum consistent with the biphenylradical anion.

Discussion

A consideration of the hfsc observed for semidione radical anions and cations is illuminating. Carbonyl carbon spin densities (ρ_{C}) can be empirically estimated in these radical ions since it is likely that these carbon atoms have sp^2 hybridization. It thus appears feasible to apply equations of the types employed by McConnell,¹⁵ McLachlan,^{16a} Bersohn,^{16b} Symons,¹⁷ and Heller and McConnell¹⁸ for aromatic radical ions and trigonal radicals.

$$a_{\text{CH}^{\text{H}}} = Q_{\text{CH}^{\text{H}}}\rho_{\text{C}\pi} \quad (1)^{18}$$

$$a_{\text{CH}_3^{\text{H}}} = Q_{\text{CH}_3^{\text{H}}}\rho_{\text{CCH}_3} \quad (2)^{16}$$

$$a_{\alpha^{\text{H}}} = B\rho_{\text{CCH}} < \cos^2 \theta \quad (3)^{17, 18}$$

(15) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(16) (a) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); (b) R. Bersohn, "Determination of Organic Structures by Physical Methods," Vol. II, E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1962, Chapter 9.

(17) M. C. R. Symons, *J. Chem. Soc.*, 277 (1959).

(18) H. C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960), suggested the equation

$$a_{\alpha^{\text{H}}} = (B \cos^2 \theta + B')\rho_{\text{CCH}} <$$

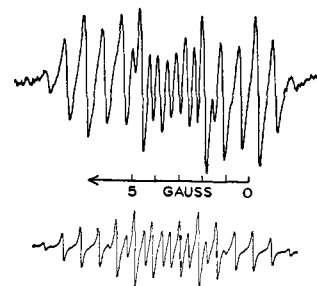


Figure 4. First-derivative esr spectrum of ethyl benzoylformate radical anion (top) in dimethyl sulfoxide solution; calculated spectrum for Lorentzian line width (bottom) of 0.2 gauss and hfsc from Table I performed by Japan Electron Optics Laboratory Co. JNM-RA-1 spectrum accumulator.

Equation 1 can be applied to **1a** and **2a** and to the aromatic hydrogen atoms of **1**. Equation 2 can be used for spin density estimation only for methyl substituted centers because of conformational effects inherent in any alkyl substituent other than methyl. Equation 3 reduces to (2) with $Q_{\text{CCH}_3^{\text{H}}} = B/2$ when the substituent is methyl since the time-averaged dihedral angle (θ) between the carbonyl carbon p_z orbital and the α -carbon-hydrogen bond is 45° in the absence of any conformational preference.¹⁹

From ρ_{CCH_3} one can obtain ρ_{C} by use of eq 4 and 5.

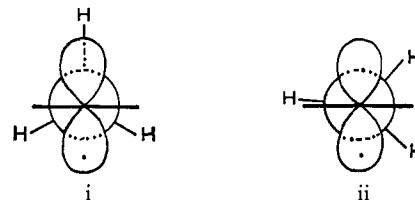
$$\rho_{\text{CCH}_3} = \rho_{\text{C}} + \rho_{\text{CH}_3} \quad (4)$$

$$\rho_{\text{CH}_3} = 3a_{\text{CH}_3^{\text{H}}}/508 \quad (5)$$

Values of $Q_{\text{CH}^{\text{H}}}$ in the range of -22 to -27 are used for aromatic radical anions.²⁰ Values of $Q_{\text{CH}^{\text{H}}}$ as low as -30 have been suggested²¹ for radical cations which generally show larger hfsc than the corresponding radical anions.²² We will use $Q_{\text{CH}^{\text{H}}} = -22.5$ for **1** and $Q_{\text{CH}^{\text{H}}} = -30$ for **2**. Values of $Q_{\text{CCH}_3^{\text{H}}}$ ($B/2$) have been

Recent results (G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965)) concerning bridged bicyclic semidiones indicate that B' must be quite small (<1 gauss) if the Heller and McConnell equation applies in these systems. K. Morokuma and K. Fukui (*Bull. Chem. Soc. Japan*, **36**, 534 (1964)) have concluded that the $\cos^2 \theta$ relationship applies in a time-averaged situation only when time averaging involves a rotational movement. They conclude that $a_{\alpha^{\text{H}}}$ varies more rapidly with a change in θ when rocking motion is involved. Other estimates of B' have been 1.1 gauss (calculated) (J. P. Colpa and E. deBoer, *Mol. Phys.*, **7**, 333 (1963)), 3–4 gauss (A. Horsfield, J. R. Morton, and D. H. Whiffen, *ibid.*, **5**, 115 (1962)), and 4.5 gauss (S. Ogawa and R. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964)). Since B is in the range of 40 gauss the contribution of B' to $a_{\alpha^{\text{H}}}$ will be small except when θ approaches 90° .

(19) The time-averaged value of θ for the three equally populated conformations similar to i is 40° while for the three equally populated conformations similar to ii θ is 50° .



(20) The value of $Q_{\text{CH}^{\text{H}}} = -22.5$ is the experimental parameter for benzene radical anion at -80° : T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958). Values of $Q_{\text{CH}^{\text{H}}}$ of -24.2 (A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960)) and -27.0 gauss (J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964)) have been used for polynuclear aromatic radical anions. The methyl radical yields a value of $Q_{\text{CH}^{\text{H}}}$ extrapolated to 25° of -22.7 gauss (I. A. Zlochower, W. R. Miller, and G. K. Fraenkel, *ibid.*, **42**, 3339 (1965)).

(21) B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 1455 (1964).

(22) E. deBoer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958).

Table II. Empirical Estimates of Carbonyl Carbon Spin Densities in Semidione Ions at 25 °a

System	Anion, DMSO ^b			Cation, 98% H ₂ SO ₄ ^c		
	$a_{\text{CH}_3^{\text{H}}}$	$a_{\text{CHO}^{\text{H}}}$	ρ_{C}	$a_{\text{CH}_3^{\text{H}}}$	$a_{\text{CHO}^{\text{H}}}$	ρ_{C}
C ₆ H ₅ COCOH		6.88	0.31		3.14	0.10
C ₆ H ₅ COCOCH ₃	3.43		0.15	2.05		0.04
HCOCOH		7.7	0.34		2.76	0.09
CH ₃ COCOH	7.46	8.72	0.39, ^d 0.33 ^e			
<i>trans</i> -CH ₃ COCOCH ₃	5.6		0.27	2.17		0.04
<i>cis</i> -CH ₃ COCOCH ₃	7.0		0.35			
4- <i>t</i> -butylcyclohexane-1,2-dione	13.02, 6.64 ^f		0.28 ^g	4.04, 2.02 ^f		0.03 ^g

^a At carbonyl carbon containing alkyl or hydrogen substituent. ^b Using $Q_{\text{CH}^{\text{H}}} = -22.5$, $Q_{\text{CCH}_3^{\text{H}}} = 20$. ^c Using $Q_{\text{CH}^{\text{H}}} = -30$, $Q_{\text{CCH}_3^{\text{H}}} = 40$. ^d Aldehydic carbonyl. ^e Acetyl carbonyl. ^f $a_{\alpha\text{-H}^{\text{H}}}$. ^g Solution of simultaneous equations for axial and equatorial hfs yields $\theta_{\text{axial}} \cong 15^\circ$: G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

suggested as 27 (ethyl radical)^{23a} and 20 gauss (*m*-xylene radical anion at -70° ,^{24,25} and cyclohexyl radical^{23b}). Values of $Q_{\text{CCH}_3^{\text{H}}}$ also appear to be larger for cations than for anions. Values suggested have been 21.9 gauss for methyl-substituted dihydropyrazine radical cations²¹ and 38.7 gauss for hexamethylbenzene radical cation.²⁶ There perhaps is a linear relationship between $Q_{\text{CCH}_3^{\text{H}}}$ and charge density of the carbon atom bearing the methyl group.^{26b} For many methyl- or methylene-substituted aromatics the values of a_{CH_3} or a_{CH_2} for the radical cations are approximately twice those of the radical anions (9-methylanthracene,^{27a} 9,10-dimethylanthracene,^{27a} pyracene,^{27b} acenaphthene^{27b}). We will use a value of $Q_{\text{CCH}_3^{\text{H}}}$ (uncorrected for delocalization of the electron onto the methyl group²⁸) of 20 gauss for 1 and 40 gauss for 2.²⁹

Table II lists the carbonyl carbon spin densities estimated for the carbon atom containing a hydrogen or methyl substituent. Data from Table I as well as data to be published elsewhere are included in Table II.

Inspection of Table II shows that ρ_{C} is much greater for the anions than the cations. Spin densities as summarized in Table II can be interpreted in terms of resonance structures and contributions to the hybrid ion. For the biacetyl radical ions delocalization involving α -hydrogen atoms can be evaluated as $6a_{\text{CH}_3^{\text{H}}}/508$. This leads to 7% contribution from hyperconjugation radical structures for the *trans* radical anion and 2% for the cation. The value of ρ_{O} can now be evaluated as $(1.00 - 2\rho_{\text{C}} - 6\rho_{\text{H}})/2$ since $\rho_{\alpha\text{-C}}$ is presumably zero.³⁰ This yields $\rho_{\text{O}} = 0.195$ for the anion and 0.45 for the cation.

The contributions to the resonance hybrids are as shown. In the hybrid structures 4 and 5, the partial

(23) (a) R. W. Fessenden and R. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) S. Ogawa and R. W. Fessenden, *ibid.*, **41**, 994 (1964).

(24) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1963).

(25) E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965).

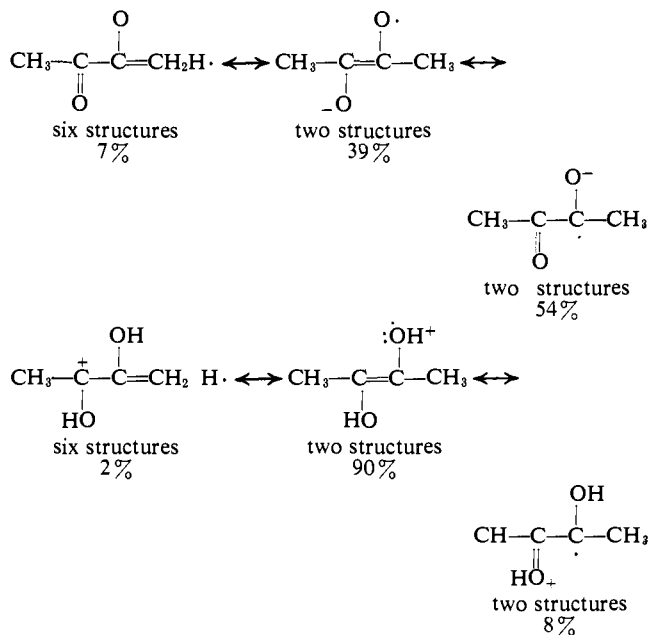
(26) (a) R. Hulme and M. C. R. Symons, *Proc. Chem. Soc.*, 241 (1963); (b) *J. Chem. Soc.*, 1120 (1965).

(27) (a) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962); (b) J. P. Colpa and E. de Boer, footnote 18.

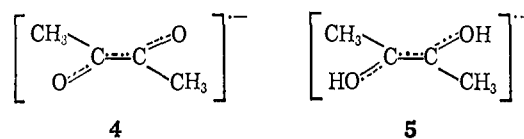
(28) M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962); E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965).

(29) The values of $Q_{\text{CH}^{\text{H}}}$ and $Q_{\text{CCH}_3^{\text{H}}}$ for 1 are based on benzene and *m*-xylene radical anions at -80 and -70° , respectively. R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964), have reported that for benzene radical anion $a_{\text{CH}^{\text{H}}}$ is temperature dependent. Presumably this is also true for *m*-xylene radical anion. The application of these values of $Q_{\text{CH}^{\text{H}}}$ and $Q_{\text{CCH}_3^{\text{H}}}$ to semidione radical anions at 23–25° is only approximate.

(30) In the radical anions a single C¹³ hfs is detected and this has been assigned to the carbonyl carbon atom: E. T. Strom and G. A. Russell, *J. Chem. Phys.*, **41**, 1514 (1964).

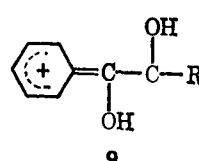
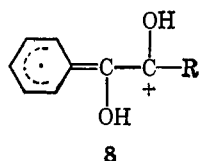
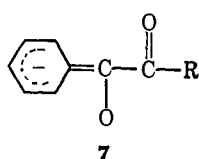
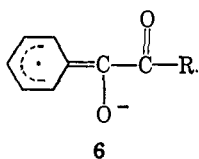
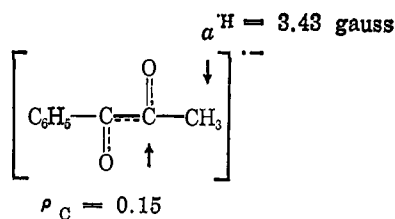
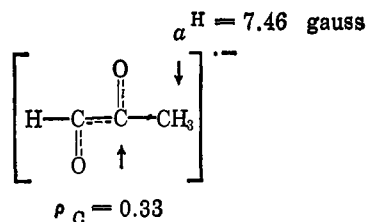


double bond between the carbonyl carbon atoms thus



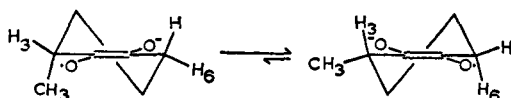
involves roughly 39 and 90% of the overlap of a normal olefinic double bond. The per cent double bond character in 5 clearly shows that the independent existence of *cis* and *trans* isomers is probable. The large positive charge on oxygen, however, must demand a considerably greater stability of the *trans* configuration from electrostatic considerations.

The presence of a phenyl group at C-1 causes a considerable decrease in spin density at C-2 for the semidione radical anions. Thus, we observe the following decrease in ρ_{C} . This reflects the delocalization by the aromatic ring (structures 6 and 7). On the other hand there is little change in carbonyl carbon spin density at C-2 in the radical cations upon substitution of a phenyl group for hydrogen or methyl at C-1 (Table II). This indicates that 8 and 9 contribute roughly to the same degree for the radical cations. A *p*-methoxy substituent increases $\rho_{\text{C}-2}$ in both the radical anion and cation. In the radical anion of 1-phenylpropane-1,2-dione a_{CH_3} increases from 3.43 to 3.88 when a *p*-methoxy substituent is introduced. The



substituent would be unfavorable to structure 7. In the radical cation a_{CH_3} increases from 3.14 to 3.29 when the *p*-methoxy group is substituted possibly indicating an increased importance of structure 9. A more thorough investigation of the effects of substituents in these systems may lead to the definition of new sets of σ constants, σ^- and σ^+ .

The data of Table I indicate a considerable conformational effect in the series **1**, R = CH₃, CH₃CH₂, and (CH₃)₂CH. The hfsc for hydrogen atoms α to the dicarbonyl system decreases from 3.43 for R = methyl, to 3.38 for R = ethyl, to 1.45 gauss for R = isopropyl. The effect of alkyl substitution at the α carbon atom in the absence of serious conformational effects is best estimated from the hfsc observed for 3-methylcyclohexane-1,2-semidione.³¹ Two hydrogen

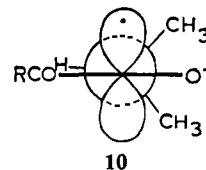


atoms (H-3 and H-6) spend most of their time in a quasiaxial conformation. The hfsc assigned to H-3 (10.29 gauss) and to H-6 (11.15 gauss) indicates a small reduction (<10%) in a_{α}^{H} upon substitution of a methyl group for an α hydrogen atom. This may result from a combination of polar and magnetic effects or may result from the fact that $\langle \theta \rangle$ for H-3 and H-6 are not exactly equal.

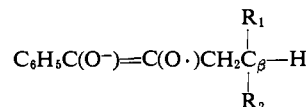
The decrease of a_{α}^{H} from **1**, R = CH₃ to **1**, R = CH₃CH₂ is not outstanding but the decrease in a_{α}^{H} in going from R = CH₃CH₂ to R = CH(CH₃)₂ is quite significant and must represent a decrease in $\langle \cos^2 \theta \rangle$ (eq 3) from 0.5 expected for a freely rotating alkyl

(31) E. R. Talaty and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 4867 (1965).

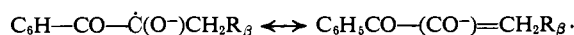
group.³² Assuming that B (eq 3) is independent of alkyl substitution a time-average value of $\theta = 63^\circ$ is calculated for the α -hydrogen atom of **1**, R = isopropyl. This indicates that **10** ($\theta = 90^\circ$) is a highly populated conformation.³³



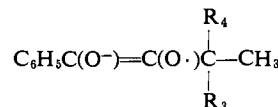
Another structural effect apparent from Table I concerns the value of a_{β}^{H} .



Hyperfine splitting due to a_{β}^{H} could not be resolved when R₁ = R₂ = H. The value of a_{β}^{H} is 0.11 gauss for R₁ = methyl, R₂ = H and increases to 0.14 gauss for R₁ = R₂ = methyl. This trend is consistent with β splitting via hyperconjugation



The importance of this delocalization increases as R_β is altered from methyl to ethyl to isopropyl. Of course such an interaction should be dependent upon dihedral angle and conformational effects may also be involved.³⁴ When the series



is considered we find $a_{\text{CH}_3}^{\text{H}}$ is not observed when R₃ = R₄ = H or when R₃ = CH₃, R₄ = H. However, when R₄ = R₃ = CH₃ the value of $a_{\text{CH}_3}^{\text{H}}$ is 0.18 gauss. This suggests a steric driving force for methyl group hyperconjugation.

Experimental Section

1-Aryl-2-alkyl-1,2-semidione Radical Anions. Radical anions were formed by the base-catalyzed oxidation of the acyl aromatic compounds with the exception of 1-phenyl-2-*t*-butylglyoxal radical anion which was prepared by oxidation of phenylpivalylcarbinol,³⁵ mp 44.5–45.0° (lit.³⁵ mp 46–47°), in basic solution. The phenones were commercially available except for 1-phenyl-4-methyl-1-pentanone, which was prepared by Friedel-Crafts acylation of benzene.³⁶

(32) The constancy of a_{α}^{H} in **1**, R = methyl to *t*-butyl, indicates that the carbonyl carbon and other spin densities are quite independent of the nature of R. Since J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962), have shown that the spin-repelling power of alkyl groups is in the order, methyl > ethyl ~ isopropyl > *t*-butyl, the spin density at the carbonyl carbon atoms may increase slightly in **1** as R is varied from methyl to ethyl to *t*-butyl.

(33) Similar explanations have been advanced to explain a large decrease in a_{α}^{H} in going from butane-2,3-semidione to hexane-3,4-semidione radical anions [E. T. Strom, G. A. Russell, and R. D. Stephens, *J. Phys. Chem.*, **69**, 2131 (1965)] and in the methyl- and ethylcyclooctatetraene radical anions (A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 533 (1964); **8**, 299 (1964)).

(34) A C¹³ hfs should be observable for C_β. Such hfs has been reported for several ketyl radical anions (N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960); R. L. Ward, *J. Chem. Phys.*, **36**, 2230 (1962)) and *t*-butyl-*p*-semiquinone anion (L. M. Stock and J. Suzuki, *Proc. Chem. Soc.*, 136 (1962)).

(35) R. C. Fuson, H. Gray, and J. J. Gouza, *J. Am. Chem. Soc.*, **61**, 1937 (1939).

(36) H. Pines and J. T. Arrigo, *ibid.*, **79**, 4958 (1957).

In a typical experiment 1 ml of a 0.025–0.10 *M* solution of a ketone in DMSO or DMSO (80%)–*t*-butyl alcohol (20%) was mixed with 1 ml of 0.2 *M* potassium *t*-butoxide in the same solvent. The reactions are conveniently carried out using the inverted U-type mixing cell previously described.³⁷ The source of oxygen was the air normally present in the solvent. The mixing chamber was flushed with nitrogen but the solutions were not deoxygenated by bubbling nitrogen through them. The solutions became yellow immediately after mixing and thence slowly deepened in color. The oxidates were shaken down into a flat-fused silica "aqueous" sample cell supplied by Varian Associates. The esr spectra were recorded 1–10 min after mixing at $25 \pm 2^\circ$ using a Varian V-4500 epr spectrometer operating at ~ 9500 Mcps with a 9-in. magnet with Fieldial control and 100-kcps modulation. A single cavity was used with sweep rates calibrated to 1% by the spectrum of *p*-benzosemiquinone in aqueous ethanol.³⁸ The radical anions were stable for hours after preparation. Deoxygenation of the reactants before mixing by a stream of prepurified nitrogen introduced through a hypodermic needle for 20 min yielded solutions in which paramagnetic materials could not be detected after mixing. The best resolution was obtained by introduction of about 10 mole % of oxygen (based on ketone) by a hypodermic needle into such a solution containing ketone at a final concentration of about 0.01 *M* and potassium *t*-butoxide at 0.02 *M*.

Arylglyoxal Radical Anions. Phenylglyoxal radical anion has been prepared from ω -bromoacetophenone by treatment with potassium *t*-butoxide in DMSO solution. The radical anion is also formed spontaneously from ω -hydroxyacetophenone (mp 85–86°)³⁹ in the presence of potassium *t*-butoxide in DMSO solution. In a typical experiment 5 ml of 0.10 *M* solutions of ω -bromo- or ω -hy-

(37) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(38) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

(39) Prepared by Mr. G. Mikol: (a) ω -hydroxyacetophenones are readily prepared in good yield by the reduction of phenylglyoxal hemimercaptals (H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963)) by sodium formaldehydesulfoxylate; (b) the hemimercaptals are readily converted to phenylglyoxals by refluxing in acidic solution; (c) symmetrical pinacols of the glyoxals (mixtures of diastereoisomers) are prepared in low yield from the hemimercaptals by treatment with Raney nickel or in good yield from the glyoxals by reduction with sodium formaldehydesulfoxylate in the presence of traces of cupric ion.

droxyacetophenone in deoxygenated DMSO solution was mixed with an equal volume of a 0.2 *M* solution of potassium *t*-butoxide in deoxygenated DMSO under a nitrogen atmosphere utilizing the inverted U-type mixing cell. Phenylglyoxal radical anions were also formed from the pinacol of phenylglyoxal ($C_6H_5COCH(OH)CH(OH)COC_6H_5$),^{39c,40} mp 119.3–120.8° (lit.⁴⁰ mp 118–119°), or from 2,3-dibromo-1,2-dibenzoylthane (prepared by the *in situ* bromination of 1,2-dibenzoylthylene) by treatment with an excess of potassium *t*-butoxide in deoxygenated DMSO solution. The radical anions were detected immediately upon mixing solutions 0.01 *M* in pinacol or dibromide and 1 *M* in potassium *t*-butoxide.

Arylglyoxal Radical Cations. Phenylglyoxal, *para*-substituted phenylglyoxals,^{39b} or 1-phenylpropane-1,2-dione are converted to radical cations by treatment with sodium dithionite in 98% sulfuric acid. In a typical experiment a mixture of 0.1 mmole of diketone, and 0.2 mmole of sodium dithionite in one leg of an inverted U-type mixing cell, was dissolved in 2 ml of 98% sulfuric acid and the resulting solution was introduced into a flat-fused silica esr cell. The esr signal could be detected immediately. Deoxygenation was not necessary since the radical cations are stable to oxygen. However, the solutions were routinely deoxygenated to avoid oxygen broadening of the esr spectra.

Radical Anions of Benzoylformate Esters. These radical anions are formed in low concentration ($\sim 10^{-5}$ *M*) when solutions of a benzoylformate ester and the corresponding mandelic acid ester, at concentrations of about 0.1 *M* each, are treated with an equal volume of 0.2 *M* potassium *t*-butoxide in deoxygenated DMSO solution. Attempts to reduce benzoylformate esters with carbanions, such as the enolate anion of propiophenone, did not give the radical anions. Appreciable concentrations of radical anions were formed by the reaction of 1,3-phenyl-1,2,3-propanetrione,⁴¹ mp 67–69°, with an excess of solid potassium *t*-butoxide or sodium methoxide in DMSO. The radical anion of ethyl benzoylformate was also detected in significant quantity by the exposure of a DMSO solution (0.1 *M*) of ethyl α,β -dihydroxycinnamate,⁴² bp 119–123° (0.1 mm), and excess potassium *t*-butoxide to a trace of oxygen.

(40) Also prepared by treatment of *trans*-1,4-diphenyl-2-butene-1,4-dione with aqueous potassium permanganate: R. C. Fuson, C. H. McBurney, and W. E. Holland, *J. Am. Chem. Soc.*, **61**, 3246 (1939).

(41) J. D. Roberts, D. R. Smith, and C. C. Lee, *ibid.*, **73**, 618 (1951).

(42) P. Karrer, J. Kebrle, and R. M. Thakkar, *Helv. Chim. Acta*, **33**, 1711 (1950).

Semidiones. II. Radical Anions of 2,2'-Furil, 2,2'-Thenil, and 3,3'-Thenil¹

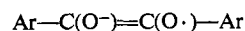
E. Thomas Strom, G. A. Russell, and Joseph H. Schoeb

Contribution from Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Massachusetts, and the Department of Chemistry, Iowa State University, Ames, Iowa. Received December 30, 1965

Abstract: The preparation of semidiones ($RC(O\cdot)=C(O^-)R$) with R = 2-thenyl, 3-thenyl, and 2-furil is described and their esr spectra reported. Resonance stabilization of 2-thenyl- and 2-furilcarbinyl radicals has been estimated from the reactivity of the methylthiophenes, methylfurans, methylbenzothiophenes, and methylbenzofurans toward phenyl radicals. These results compare favorably with the delocalization indicated by the esr spectra of the heteroaromatic semidiones.

Aromatic acyloins, $ArCH(OH)COAr$, give colored solutions when treated with base and deficient quantities of oxygen in ethanol solution. Benzoin,^{2a} 2,2'-furoin,^{2b} and 2,2'-thenoin^{2c} give purple, blue, and

green solutions, respectively. Michaelis and Fetcher proposed that the colored intermediate formed from benzoin possessed structure **1**, $Ar = C_6H_5$.³ This



1

(1) This work was supported by grants from the National Science Foundation and the Petroleum Research Fund.

(2) (a) A. Hantzsch and W. H. Glower, *Ber.*, **40**, 1520 (1907); (b) E. Fischer, *Ann.*, **211**, 214 (1882); (c) S. Z. Cardon and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 4248 (1948).

(3) L. Michaelis and E. S. Fetcher, Jr., *ibid.*, **59**, 1246 (1937).