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 ± 2° 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-hydroxyacetophenone 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-dibenzoylethane (prepared by the *in situ* bromination of 1,2-dibenzoylethylene) 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 (~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 of 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.

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[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.

[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′-Thenil[1]

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

Contribution from Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Masschusetts, and the Department of Chemistry, Iowa State University, Ames, Iowa.

Received December 30, 1965

Abstract: The preparation of semidiones (RC(O·)═C(O⁻)R) with R = 2-thenyl, 3-thenyl, and 2-furyl is described and their esr spectra reported. Resonance stabilization of 2-thenyl- and 2-furylcarbinyl 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

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

1

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[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).

radical anion has been thoroughly investigated by a number of techniques.[4]

We have examined the semidiones, **1**, Ar = 2-furyl and 2-thenyl, obtained by oxidation of the acyloins in ethanolic solutions of potassium hydroxide. The semidiones were also obtained in high yield when equimolar amounts of the acylil and acyloin are treated with base in ethanol in the absence of oxygen or in lower yield by the disproportionation of the acyloin in strongly basic solutions. Mixtures of furil–furoin gave ~36 times as

$$\mathrm{RCOCHOHR} \overset{B^-}{\rightleftharpoons} \mathrm{RC(O^-){=}C(O^-)R}$$

$$\mathrm{RCOCOR} + \mathrm{RC(O^-){=}C(O^-)R} \rightleftharpoons \mathrm{2RC(O\cdot){=}C(O^-)R}$$

$$\mathrm{2RCOCHOHR} \xrightarrow{B^-} \mathrm{RCOCOR} + \mathrm{RCHOHCHOHR}$$

much semidione as mixtures of benzil–benzoin under identical conditions. It is reported that under these conditions furoin is oxidized ~44 times as readily as benzoin.[5]

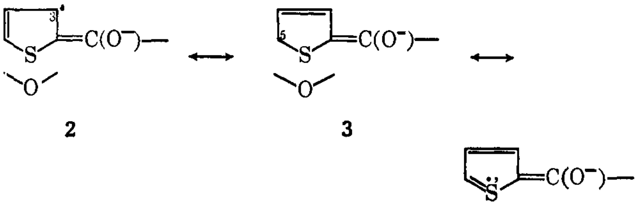
At moderate resolution the esr spectra of **1**, Ar = 2-thenyl and **1**, Ar = 2-furyl were similar and consisted of 19 lines. At low radical-anion concentration the spectrum of **1**, Ar = 2-furyl, could be resolved into 27 lines (Figure 1) but the 2,2′-thenil spectrum could not be resolved further. Analysis of the spectra yielded the hyperfine splitting constants listed in Table I.

Table I. Splitting Constants (gauss) of I, Ar = 2-Thenyl and 2-Furyl

Ar	Solvent	a^H (triplet)	$a^{C\,a}$
2-Furyl	Ethanol	2.37, 1.82, 0.38	6.30
2-Furyl	DMSO-*t*-BuOH^b	2.10, 1.54, 0.34	5.94
2-Thenyl	Ethanol	2.27, 1.84, 0.42	6.12
2-Thenyl	DMSO-*t*-BuOH^b	2.07, 1.66, 0.42	5.74

^{a} From C^{13} in natural abundance, presumably at the carbonyl carbon atoms. ^{b} Dimethyl sulfoxide (80 vol. %)-*t*-butyl alcohol (20%).

From a consideration of the valence bond partial structures **2** and **3** it seems likely that the major splitting involves hydrogen atoms at C-3 and C-5. If one



2 **3** **3a**

regards the 3 position as *ortho*-like and the 5 position as *para*-like, then by analogy with the benzil radical anion,[4a] the largest hfsc can be assigned to C-5 and the intermediate hfsc assigned to C-3. However, this assignment is only tentative.[6]

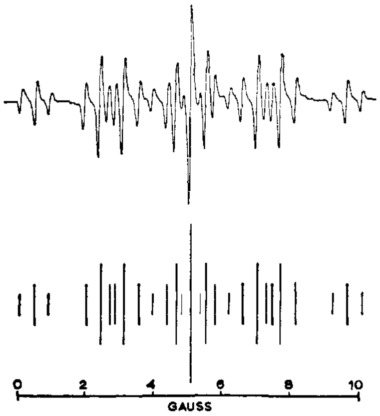
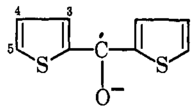


Figure 1. First-derivative esr spectrum (×9.5 Gcps) of 2,2′-furil radical anion prepared by disproportionation of furil (5×10^{-4} *M*) and furoin (5×10^{-4} *M*) in dimethyl sulfoxide (80 vol. %)-*t*-butyl alcohol (20 vol. %) containing 0.02 *M* potassium *t*-butoxide at 25–28°.

Oxidation of 2,2′-dithenylmethane in basic solution produces the corresponding ketone.[7] When 2,2′-dithenylmethane is treated with a deficiency of oxygen in a solution of potassium *t*-butoxide in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) a paramagnetic intermediate is formed which we believe to be the 2,2′-dithenyl ketyl (**4**). The spectrum was consistent with



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a^H = 4.1, 3.7, and 0.9 gauss triplet splittings which we tentatively assign to hydrogen atoms at C-5, C-3, and C-4, respectively. Ketyls can be detected in the analogous oxidation of fluorene, xanthene, and thiaxanthene.[8]

The 3,3′-dithenylsemidione (**1**, Ar = 3-thenyl) was prepared by reduction of 3,3′-thenil[9] by the anion of propiophenone in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution.[10] The 21-line spectrum (Figure 2) can be analyzed in terms of triplet splittings with a^H = 1.88, 0.44, and 0.22 gauss.[11] Since only the valence bond structures **5** and **5a** should be important in delocalizing the electron in the ring, the largest hfsc is assigned to the hydrogen atoms at C-2.

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(4) (a) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963); (b) B. Venkataraman and G. K. Fraenkel, *J. Am. Chem. Soc.*, 77, 2707 (1955); J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956); G. R. Luckhurst and L. E. Orgel, *Mol. Phys.*, 7, 297 (1963); C. Corvaja, P. L. Nordio, M. V. Pavan, and G. Rigatti, *Ric. Sci.*, [2] **34**, 297 (1964).

(5) A. Weissberger, E. Strasser, H. Mainz, and W. Schwarze, *Ann.*, **478**, 112 (1930).

(6) Preliminary McLachlan-type molecular orbital calculation (A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960)) indicate that there is a negative spin density at C-4 in the 2,2′-furil and 2,2′-thenil radical anions. Calculations for 2,2′-thenil radical anion indicate $\rho_{C\text{-}5} > \rho_{C\text{-}3}$. Conflicting results were obtained in calculations for 2,2′-furil radical anion. Furanyl oxygen parameters of Orgel (L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951)) predict $\rho_{C\text{-}3} > \rho_{C\text{-}5}$ while the opposite result is obtained using the parameters suggested by Streitwieser (A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5). The carbonyl parameters given in ref 4a were used for all calculations.

(7) See also T. L. Cairns, B. C. Mukusick, and V. Weinmayr, *J. Am. Chem. Soc.*, **73**, 1270 (1951).

(8) Unpublished results of Dr. E. G. Janzen.

(9) We wish to thank Professor E. E. Campaigne and Dr. E. Neiss for a sample of 3,3′-thenil.

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

(11) In Figure 2 the seven-line submultiplets have approximately a 1:2:3:4:3:2:1 intensity ratio. This excludes the possibility that the spectrum is due to some radical with six equivalent hydrogen atoms which would yield a 1:6:15:20:15:6:1 intensity pattern for the submultiplet.

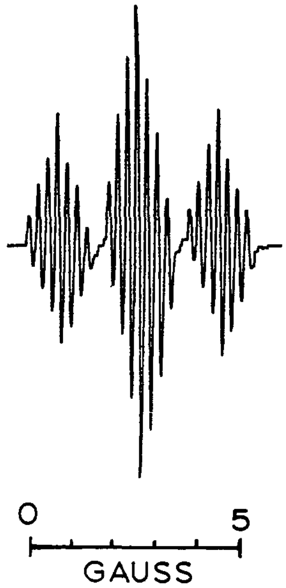
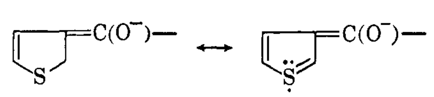


Figure 2. First-derivative esr spectrum of 3,3′-thenil radical anion prepared by the reaction of 3,3′-thenil (0.016 *M*) and propiophenone (0.05 *M*) in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing 0.10 *M* potassium *t*-butoxide at 25–28°.

From the observed hyperfine splitting constants, it is apparent that the 2-thenyl substituent is much more efficient than the 3-thenyl substituent in delocalization of the odd electron.[12] Such behavior is consistent with



5 **5a**

the reactivity of methyl-substituted thiophenes, furans, benzothiophenes, and benzofurans toward hydrogen abstraction by the phenyl radical. By application of a

$$ArCH_3 + C_6H_5\cdot \longrightarrow C_6H_6 + ArCH_2\cdot$$

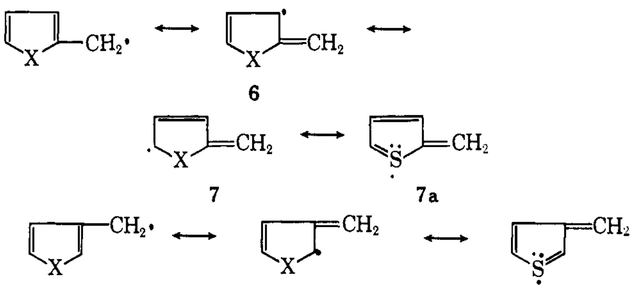
previously developed technique[13] we have measured the reactivities of the compounds in Table II relative to carbon tetrachloride.

Table II. Relative Reactivities of Methylfurans and Methylthiophenes toward Phenyl Radicals at 60°

Substrate	$(k_{\alpha\text{-H}}/k_{CCl_4}) \times 100^a$
Toluene	9.0^b
2-Methylthiophene	14.7^b
3-Methylthiophene	8.0^b
2-Methylbenzothiophene	13.7
3-Methylbenzothiophene	7.9
2-Methylfuran	8.6
3-Methylfuran	2.5
2-Methylbenzofuran	19.3
3-Methylbenzofuran	$\sim 1.7^c$

[a] Reactivity per α-hydrogen atom. [b] See ref 13. [c] 3-Methylbenzofuran adds phenyl radicals very easily.

The higher reactivity observed for the 2-methyl derivatives is consistent with a greater stabilization in the transition state for hydrogen abstraction from structures **6**, **7**, and **7a** than from **8** and **8a**. The data of both



6

7 **7a**

8 **8a**

Tables I and II emphasize the similarity of the furan and thiophene nucleus at stabilizing a free radical site at the 2α position.

Experimental Section

Reagents. Commercial dimethyl sulfoxide was distilled from calcium hydride at reduced pressure. Commercial 2,2′-furil and 2,2′-furoin were used without further purification. 2,2′-Thenil and 2,2′-thenoin were synthesized.[2c]

3-Methylfuran was synthesized.[14] It was twice distilled to give a product, bp 65–66°, that was >99% pure as measured by gas-liquid partition chromatography (glpc).

2-Methylbenzofuran[15] was thrice vacuum distilled at bp 93–94° (20 mm). The purity was estimated at >99% by glpc.

3-Methylbenzofuran[16] was distilled, bp 195–197°, to give material >99% pure by glpc.

2-Methylbenzothiophene[17] was first purified by vacuum distillation at bp 135–150° (80 mm), and fractionally crystallized to give material, mp 51–52°.

3-Methylbenzothiophene[18] was purified by several vacuum distillations at bp 125–127° (25 mm). The last fractional distillation gave material that did not turn yellow upon standing and which was >99% pure by glpc. Thiophenol or phenylthiopropanone could not be detected by glpc.

Esr Spectra. The spectra were obtained with a Varian V-4502 spectrometer equipped with a 9-in. magnet with 100-kcps field

Table III. Products from the Decomposition of Phenylazotriphenylmethane (0.1 *M*) at 60°

Substrate	CCl_4/ substrate	Yield of $C_6H_6{}^{a,b}$	Yield of $C_6H_5Cl^a$	Total reactivity^c
3-Methylfuran	0.548	0.0146	0.0895	0.089
3-Methylfuran	0.548	0.0118	0.0906	0.071
3-Methylfuran	0.548	0.0108	0.956	0.062
2-Methylbenzofuran	0.987	0.191	0.320	0.59
2-Methylbenzofuran	0.987	0.191	0.318	0.58
3-Methylbenzofuran	0.963	0.0063	0.1205	0.048
3-Methylbenzofuran	0.963	0.0065	0.1150	0.054
2-Methylbenzothiophene	1.41	0.106	0.350	0.43
2-Methylbenzothiophene	1.96	0.088	0.438	0.39
3-Methylbenzothiophene	0.87	0.064	0.246	0.23
3-Methylbenzothiophene	0.87	0.065	0.246	0.23

[a] Moles/mole of PAT. [b] Corrected for benzene formed from PAT in pure CCl_4.[13] [c] Total reactivity of substrate in hydrogen abstraction relative to carbon tetrachloride in chlorine abstraction.

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(12) Structures **2** and **3** ($\Sigma a^H = 3.7$ gauss) are more important in stabilizing 2,2′-thenil semidione than **5** ($a^H = 1.88$ gauss) in stabilizing 3,3′-thenil semidione. It is presumed that the importance of structures **3a** and **5a** are proportional to the spin density on C-5 and C-2, respectively.

(13) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(14) D. M. Burness, *J. Org. Chem.*, 21, 102 (1956).

(15) R. Adams and R. E. Rindfusz, *J. Am. Chem. Soc.*, **41**, 648 (1919).

(16) W. R. Boehme, *Org. Syn.*, **33**, 43 (1953).

(17) D. A. Shirley and M. D. Cameron, *J. Am. Chem. Soc.*, **74**, 664 (1952).

(18) E. G. G. Werner, *Rec. Trav. Chem.*, **68**, 509 (1949).

modulation. The special cells and technique for deoxygenation, electron transfer, and oxidation have been described previously.[19]

Phenyl Radical Reactivities. The general technique has been described.[13] Table III lists the experimental conditions and the observed yields of benzene and chlorobenzene.

Oxidation of 2,2′-Dithenylmethane in Basic Solution. A solution of 3 mmoles of 2,2′-dithenylmethane and 6.3 mmoles of potassium *t*-butoxide in 30 ml of DMSO (17 vol %)–*t*-butyl alcohol (83%) was vigorously stirred in an oxygen atmosphere for 30 min during which 6 mmoles of oxygen was absorbed. The oxidate was added to ice water and the precipitate was removed by filtration and vacuum sublimed to give 2.43 mmoles (81%) of 2,2′-dithenyl ketone, mp 85–86° (lit.[20] mp 87–88°), which gave a phenylhydrazone, mp 137° (lit.[20] mp 137°), and which showed only thiophene-type protons by proton magnetic resonance.

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(19) E. T. Strom, G. A. Russell, and R. D. Stephens, *J. Phys. Chem.*, **69**, 2131 (1965); G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964); E. R. Talaty and G. A. Russell, *ibid.*, **87**, 4867 (1965).

(20) L. Gattermann, A. Kaiser, and V. Meyer, *Ber.*, **18**, 3013 (1885).

Semidiones. III. Radical Ions Derived from Ninhydrin and Alloxan[1]

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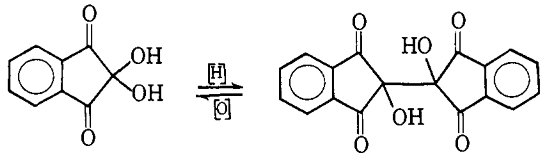
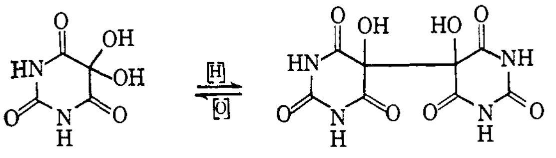
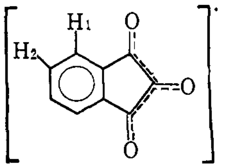
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received January 19, 1966*

Abstract: Radical anions are easily formed by reduction of ninhydrin and alloxan. These radical anions are also formed by the dissociation of hydrindantin and alloxantin in basic solution. In aqueous solution two different radical anions derived from triketohydrindan can be observed. Reaction of a number of 1,3-indandione derivatives in sulfuric acid under reductive ($Na_2S_2O_4$) or oxidative ($K_2S_2O_8$) conditions yields a radical cation believed to be a derivative of 1,1′,3,3′-tetrahydroxy-$\Delta^{2,2'}$-biisoindene.

The facile and reversible reductive dimerization of ninhydrin and alloxan suggested to us the possible existence of intermediate semitriones **1** and **2**.


ninhydrin hydrindantin


alloxan hydrate alloxantin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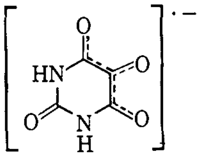
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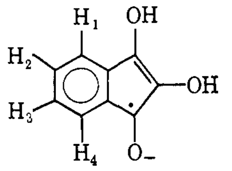
We have found that **1** and **2** can be readily detected by esr spectroscopy in dimethyl sulfoxide (DMSO) under a variety of conditions. In aqueous solution **2** can be detected but the reduction of ninhydrin gives rise to two radical anions. At high pH an unsymmetrical radical anion containing two hydroxyl groups is detected. We attribute the observed esr spectrum to **3**. At low pH the reduction of ninhydrin in aqueous solution yields a symmetrical radical anion to which we assign structure **1** or the rapidly time-averaged structure **4**.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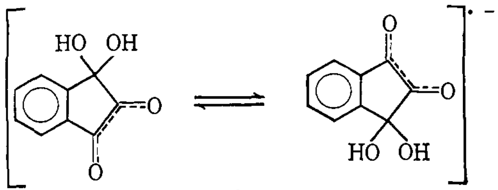
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In the course of this investigation we were led to consider radical anions and cations derived from 2,2′-biindan-1,1′,3,3′-tetraone (**5**)[2] and the isomeric 6,11-dihydroxynaphthacenequinone (**6**). Radical ions **7–9** have been observed.

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

(2) Evidence for the dienolic structure was presented by J. C. Eck and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 1898 (1935).