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).

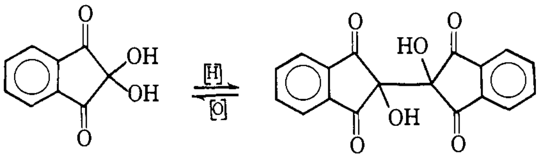
Semidiones. III. Radical Ions Derived from Ninhydrin and Alloxan[1]

Glen A. Russell and Maria C. Young

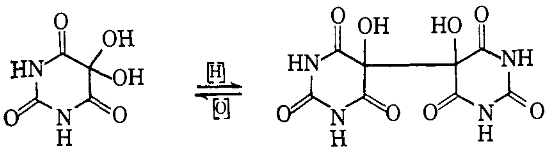
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received January 19, 1966*

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.

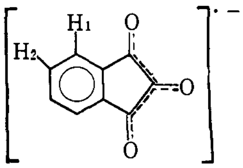
The facile and reversible reductive dimerization of ninhydrin and alloxan suggested to us the possible existence of intermediate semitriones **1** and **2**.



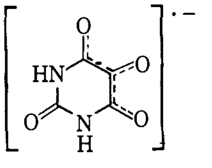
ninhydrin hydrindantin



alloxan hydrate alloxantin

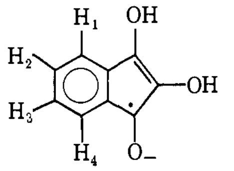


1



2

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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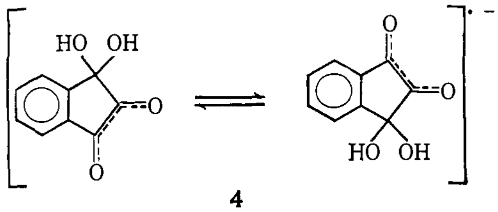

4

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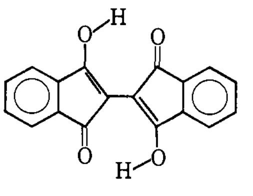
[1] This work was supported by grants from the National Science Foundation and the Petroleum Research Fund.

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



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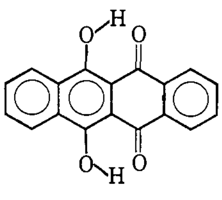

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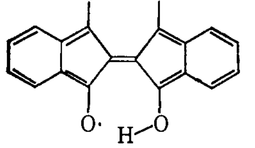
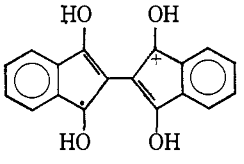
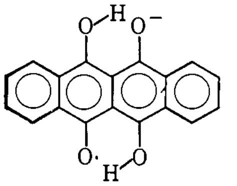


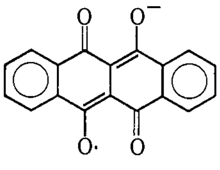
7a



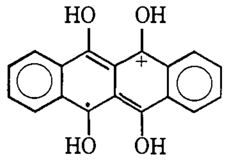
7b



8a



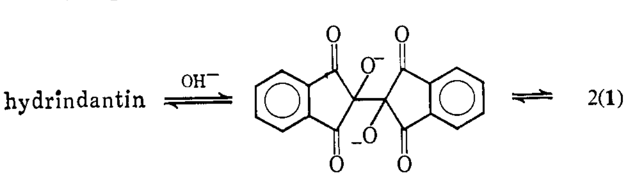
8b



9

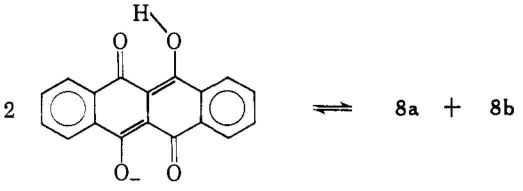
Results

Triketohydrindene Radical Anion (1). Radical anion 1 is easily prepared in high yield by a variety of techniques. Ninhydrin when dissolved in deoxygenated, anhydrous DMSO containing potassium *t*-butoxide forms 1 spontaneously with the development of little if any color. Reduction apparently involves the methylsulfinyl carbanion ($CH_3SOCH_2^-$) in some manner since in *t*-butyl alcohol ninhydrin is not converted to the radical anion by potassium *t*-butoxide. In *t*-butyl alcohol ninhydrin is reduced to 1 by the propiophenone enolate anion or by the anions derived from 9,10-dihydroanthracene and potassium *t*-butoxide.[3a] Hydrindantin in DMSO in the presence of an excess of potassium *t*-butoxide forms 1 in *essentially a quantitative yield*, possibly *via* dissociation.[3b]

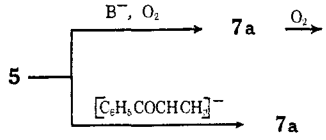


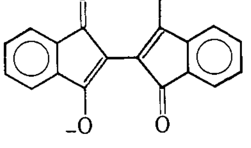
The esr spectrum of 1 in DMSO solution is given in Figure 1 and shows a 1:4:6:4:1 quintet, $a^{H} = 0.97$ gauss, attributed to the four aromatic hydrogen atoms which appear to be magnetically equivalent even though they exist in two chemically distinct sets.

Radical anion 1 can also be prepared by the action of potassium *t*-butoxide and air upon 2-bromo-1,3-indandione or 5 in DMSO solution. In both cases an intermediate radical anion whose esr spectrum shows a nine-line pattern (eight equivalent hydrogen atoms), $a^{H} = 0.423$ gauss, further split into triplets, $a^{H} = 0.292$ gauss, can be detected. We believe this new intermediate to be 7a and to involve hyperfine splitting by the hydroxyl hydrogen atoms. In d_6-DMSO and using the deuteroxy analog of 5 a broad singlet was observed. Since $a^{H}/a^{D} \cong 6.5$ splitting by deuterium atoms of the deuteroxy groups ($a^{D} \sim 0.04$ gauss) would not be experimentally observable. The same radical anion (7a) is formed by the action of propiophenone enolate anion with 5 in the absence of oxygen. Under these conditions the nine-line multiplet is stable and does not collapse into the quintet characteristic of 1. The rearranged structures 8a and b were eliminated as the intermediate since the parent hydroquinone 6 upon treatment in basic solution with propiophenone or oxygen produces paramagnetic products, presumably 8a and b, respectively, which show no hyperfine splitting. For 8b the half-width of the first derivative spectrum between maximum and minimum is 0.35 gauss and the *g* value is 0.0022 greater than for 7a. 6,11-Dihydroxynaphthacenequinone produced the same singlet absorption when dissolved in dimethyl sulfoxide containing potassium *t*-butoxide, perhaps due to proportionation.



The "oxidative" or reductive conversions of 5 to 7a can be achieved in DMSO solution only when the concentration of base is low relative to 5 and in the range of 0.5 mole of potassium *t*-butoxide per mole of 5. When the base is present in a large excess no paramagnetic products are detected. This suggests that 10 is neither easily oxidized or reduced. In independent experiments it was found that 5 does not absorb oxygen in the presence of excess base in DMSO (80%)-*t*-butyl alcohol (20%) at 25°.[4] The formation of 7a from





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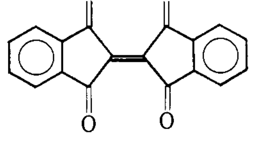

11

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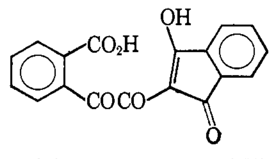
(3) For analogous reactions see (a) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, 86, 1807 (1964); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, 84, 4155 (1962).

(4) The action of base and hydrogen peroxide at elevated temperatures converts 5 to



(A. Schönberg, N. Latif, R. Moubasher, and W. I. Award, *J. Chem. Soc.*, 374 (1950)).

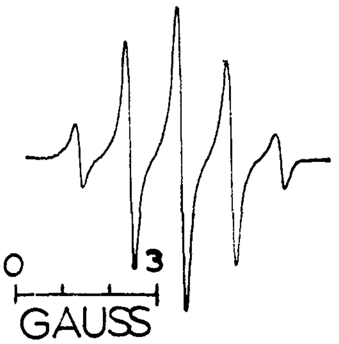
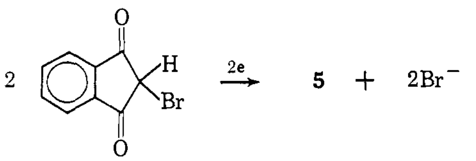


Figure 1. First-derivative esr spectrum (~9.5 Gcps) of radical anion formed spontaneously from hydrindantin or ninhydrin in dimethyl sulfoxide solutions of potassium *t*-butoxide at 25–28°.

2-bromo-1,3-indandione may involve **5** as an intermediate. Compound **11**, a possible intermediate, is



reported in the literature but we have been unable to repeat the preparation and unable to bring about the reductive coupling of 2,2-dichloro-1,3-indandione *via* a number of modifications of the reported synthesis.[5]

Ninhydrin Radical Anions in Aqueous Solution. Reduction of ninhydrin (~0.01 *M*) by zinc in basic aqueous solution forms paramagnetic products.[6] When the ratio [OH⁻]/ninhydrin is <3, the spectrum shown in Figure 2 is found for the pale yellow-green (at very low base concentration) or red-orange (at higher base concentration) solutions. Hyperfine splitting by two pairs of hydrogen atoms, a^H = 1.00 and 0.68 gauss, is observed. When hydroxyl-deuterated ninhydrin is reduced in deuterium oxide by zinc and sodium deuteroxide at low base concentration the spectrum shown in Figure 2 is unaltered.[7] Treatment of a solution giving the spectrum of Figure 2 with a large excess of base, or performing the zinc reduction at [OH⁻]/ninhydrin = 15–40, gives rise to a dark blue solution yielding a new esr spectrum (Figure 3). The hyperfine splittings required by Figure 3 are: a^H (1:3:3:1 quartet) = 3.08 gauss, a^H (doublet) = 2.66 gauss, and a^H (1:2:1 triplet) = 0.84 gauss. Ninhydrin in deuterium oxide–sodium deuteroxide solution gave a very complex spectrum upon reduction in the presence of a large excess of base. Although the spectrum could not be analyzed by trial and error approaches, excellent agreement with the experimental spectrum was achieved by a computed spectrum of Lorentzian absorption curves (0.15 gauss half-width) with a^H (doublet) = 3.08 gauss, a^H (doublet) = 2.80 gauss, a^H (triplet) = 0.776 gauss, and a^D (1:2:3:2:1 quintet) = 0.446 gauss. Thus the radical anion at high pH has hyperfine splittings by two hydroxyl hydrogen atoms, $a_{OH}{}^H$ = 3.08, $a_{OD}{}^D$ = 0.45 gauss, a^H/a^D = 6.85. At [OH⁻]/ninhydrin ratios of >200, a colorless solution is produced, but the esr spectrum of Figure 3 is still observed. Among the structures reasonable for the low pH radical or radical anion are **1**, **4**, **12**, or **13**. We discount **12** because of the

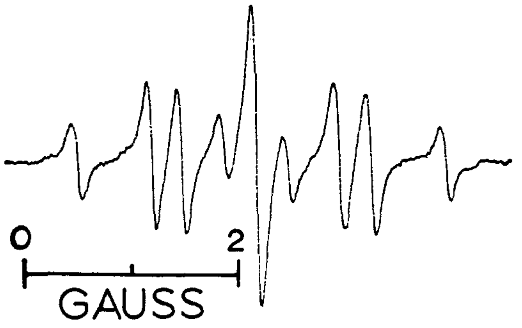


Figure 2. Esr spectrum of radical anion formed from hydrindantin in dilute aqueous potassium hydroxide at 25–28° ([OH⁻] < 0.05 *M*). The same radical anion is formed by reduction of ninhydrin with zinc in dilute aqueous base.

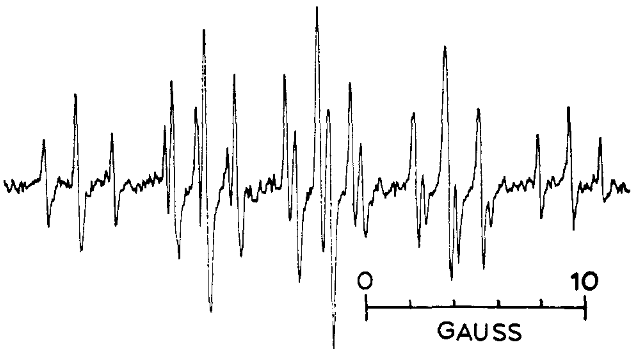
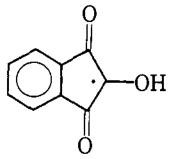
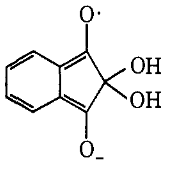


Figure 3. Esr spectrum of radical anion formed by reduction of ninhydrin or hydrindantin with zinc at [OH⁻] > 0.2 *M*. The same radical anion is formed by addition of hydroxide ion to a solution containing the radical anion whose spectrum is given in Figure 2.



12



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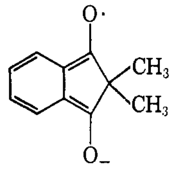

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expected acidity of **12** and of the stability observed for the radical anion. Structure **13** is discounted because **14** is difficult to produce and has little stability. Either **1** or a rapidly time-averaged structure **4** are consistent with the esr spectrum and the stability observed for the low pH radical anion.

In methanol containing potassium hydroxide ninhydrin spontaneously formed the low pH radical anion with triplet splittings of a^H = 0.98 and 0.81 gauss. There is apparently a gradual change in the ratio of the two hfsc in going from DMSO as solvent (ratio = 1), to methanol (ratio = 1.2), to methanol–water mixtures,[7] to water (ratio = 1.5).

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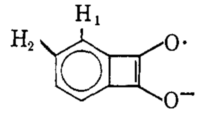
(5) A. Schonberg and R. Moubasher, *J. Chem. Soc.*, 212 (1949).

(6) M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958).

(7) (a) The esr spectrum of this radical anion has also been observed in aqueous solution by C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, 17, 277 (1963), and in methanol solution by J. C. Orr, *Nature*, 205, 1008 (1965). These authors report a^H (triplet) of 1.0, 0.75, and 0.94, 0.74 gauss, respectively. Lagercrantz and Yhland observed a poorly resolved spectrum which was unaltered when the solvent was changed to deuterium oxide. They assigned structure **13** to the radical anion. (b) Orr observed that the radical anion was also formed from hydrindantin at pH 9 and was destroyed by excess base to produce a blue solution. Lagercrantz and Yhland observed that the radical anion was unstable below a pH of 7.

In view of the hfs by two pairs of ring hydrogen atoms for the low pH radical anion it is of interest that the hfsc reported for **15** in acetonitrile solution are $a_1^H = 1.87$ gauss and $a_2^H = 3.74$ gauss.[8,9]



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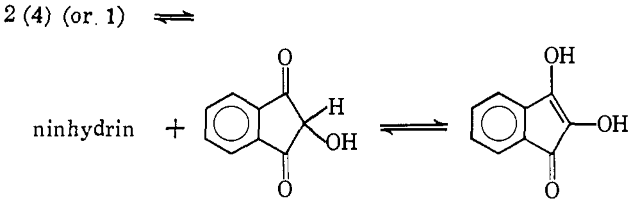
The esr spectra observed in aqueous solutions at high and low pH could possibly be explained by assuming that only **4** is formed and that time averaging with concurrent hydrogen exchange occurs at low pH but not at high pH. However, the hydroxyl hydrogen splitting observed at high pH is not particularly consistent with structure **4** and numerous qualitative observations completely eliminate this explanation.

The high pH radical anion cannot be transformed to the low pH radical anion even though the reverse process can be routinely observed by adjustment of pH. Neutralization of excess base in a solution containing the high pH anion simply destroys the esr signal. Moreover, at intermediate pH stable mixtures of the two radical anions are never observed.

When a 0.05 *M* solution of ninhydrin was reduced with an excess of zinc in the presence of hydroxide ion the following observations were made. At ratios of $[OH^-]$/ninhydrin less than 4 the low pH radical anion is formed rapidly. After the maximum concentration is formed the low pH radical anion decays at a rate barely detectable over a 5-min period. At $[OH^-]$/ninhydrin = 8–15 the low pH radical anion is initially formed but decays rapidly, particularly at the high concentrations of base. Following or concomittant with the decay of the low pH radical anion the high pH radical anion is formed at these base concentrations. The high pH radical is not particularly stable in 0.5 *M* sodium hydroxide solution and decays with loss of all paramagnetic character.[7b] Thus at $[OH^-]$/ninhydrin = 10–12 a low concentration of radical anions can be observed for only a few minutes at best. At $[OH^-]$/ninhydrin = 15–40, we have detected only the high pH radical anion although the possibility that the low pH radical anion is a precursor cannot be eliminated. The rate of formation of the high pH radical anion increases with hydroxide ion concentration. The net effect of these phenomena is that a high concentration of the low pH radical anion is achieved only at $[OH^-]$/ninhydrin < 4 while a high concentration of the high pH radical anion is found only when $[OH^-]$/ninhydrin > 20.

The above-mentioned qualitative observations can be explained in the following manner. The low pH radical anion is considered a one-electron reduction product of ninhydrin. It thus can be considered to be in equilibrium with ninhydrin and the two-electron reduction product of ninhydrin (**16**).[3b] The destruction of **4** (or **1**) at high pH may involve the cleavage of the triketo ring of ninhydrin by hydroxide ion. The action of a large excess of base on a mixture of ninhydrin and **4** (or **1**) should thus destroy **4** (or **1**) and give rise to **16**,



16

which to our knowledge has never been isolated. This interpretation suggests that the high pH radical anion is derived from **16**. In support of this, reduced ninhydrin solutions that are blue—a color previously ascribed to dianions derived from **16**[10]—always give the esr spectrum of the high pH radical anion (**3**).

Apparently **16** does not spontaneously form **3**. Evidence in regard to this point is available from observations made with hydrindantin in basic aqueous solutions. At low pH hydrindantin forms **4** (or **1**) in high yield in the absence of any reducing agent. At high pH blue solutions are formed but radical anions are detected only when a reducing agent (zinc) is present. The high pH radical anion formed under these conditions is the same as found in the reduction of ninhydrin.

The hfsc observed for the high pH radical anion are entirely consistent with **3**, including the presence of two hydroxyl hydrogen atoms with appreciable hfs. The major splitting by aromatic hydrogen atoms in **3** (a^H = 2.66, 3.08 gauss) is undoubtedly associated with H_4 and H_2 while the 0.84-gauss triplet splitting involves H_1 and H_3. It seems likely that $a_2^H > a_4^H$ since in benzil radical anion $a_p^H > a_o^H$.[11]

In dilute aqueous base in the presence of zinc **5** gave appreciable amounts of a paramagnetic product. However, we have been unable to obtain a resolved spectrum. At high concentration of base the sodium salt of **5** is insoluble in water.

Radical Anions Derived from Alloxan. Alloxantin in DMSO containing potassium *t*-butoxide produces a colorless solution containing a paramagnetic intermediate whose esr spectrum is a 15-line multiplet consistent with hyperfine splitting by two equivalent nitrogen atoms, $a^N = 0.587$ gauss, and two equivalent hydrogen atoms, $a^H = 0.48$ gauss (Figure 4). Alloxantin-d_6 gave a broadened five-line multiplet (approximately 1:2:3:2:1) consistent with the deuterated analog of **2** with $a^N = 0.579$ gauss. The same radical anion at approximately the same concentration was formed from anhydrous alloxantin and from alloxantin dihydrate. Amalic acid (tetramethylalloxantin) gave a spectrum consistent with two nitrogen atoms, $a^N = 0.500$ gauss, and two methyl groups, $a_{CH_3}^H = 0.300$ gauss (line width 0.15 gauss).

Radical anion **2** was not formed spontaneously from alloxan in DMSO containing potassium *t*-butoxide. However, **2** was formed from alloxan in the presence of the propiophenone anion or the anions derived from 9,10-dihydroanthracene.[3a] Radical anion **2** was formed in high concentration from an equimolar mixture of dialuric acid and alloxan in DMSO containing excess potassium *t*-butoxide.

The concentration of **2** formed from alloxantin was dependent upon the concentration of base suggesting

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[8] D. H. Geske and A. C. Balch, *J. Phys. Chem.*, **68**, 3423 (1964).

[9] On the basis of Hückel and McLachlan molecular orbital calculations [A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960)] we believe the hfsc have been incorrectly assigned by Geske and Balch.[8]

[10] D. A. Macfadyen and N. Fowler, *J. Biol. Chem.*, **186**, 13 (1950).

[11] R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

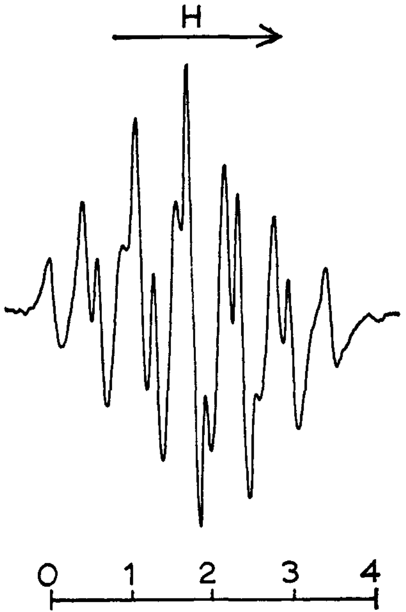
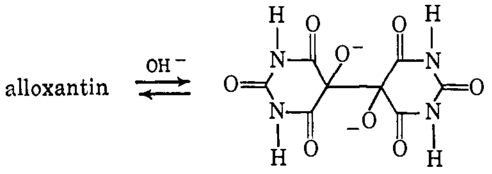


Figure 4. Esr spectrum of radical anion formed by disproportionation of dialuric acid and alloxan in dimethyl sulfoxide containing an excess of potassium *t*-butoxide.

that an acid–base equilibrium is involved in a reversible process leading to the formation of **2** from alloxantin. Figure 5 shows the effect of base concentration on the yield of **2** in DMSO solutions and indicates that at high base concentrations the yield of **2** becomes independent of the concentration of base. Such behavior is consistent with the following formulation.



17

$$\mathbf{17} \overset{K_e}{\rightleftharpoons} 2(\mathbf{2})$$

We have measured K_e using a variety of different initial alloxantin concentrations by increasing the concentration of base until the concentration of **2** became constant. Table I summarizes results that lead to a value of K_e of 2–3 × 10^{-4} mole/l. Values of K_e in Table I were calculated on the basis that [alloxantin]$_{\text{initial}}$ = 2[**2**] + [**17**].

Table I. Dissociation of Alloxantin in Dimethyl Sulfoxide Solution in the Presence of Potassium *t*-Butoxide at 25°

Initial alloxantin concn, mmoles/l.	$KOC(CH_3)_3$ concn, mmoles/l.[a]	Concn of **2**, mmoles/l.[b]	10^4K_e
7.8	45	1.28	2.27
8.8	45	1.60	3.20
7.0	22	1.34	2.84
3.9	22	0.87	2.18
3.9	12	0.67	1.85

[a] Concentration required to give a base-independent radical anion concentration. [b] Obtained by comparison of the height of the slightly overmodulated signal of **2** with the central peak of diphenylpicrylhydrazyl (DPPH) whose intensity was equated to ¹/₃ of the concentration of DPPH.

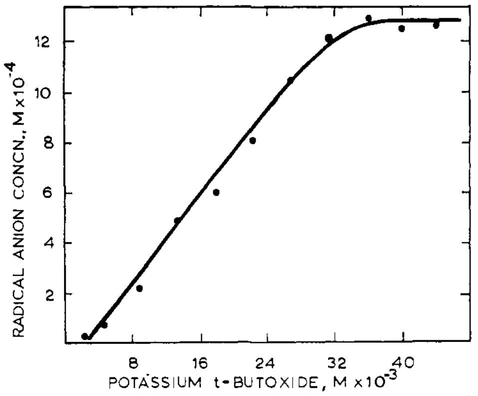
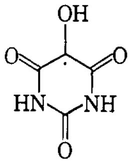
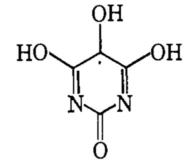


Figure 5. Radical anion formation from 7.8 × 10^{-3} *M* alloxantin in dimethyl sulfoxide solution at 25–28°.

Alloxan in aqueous base did not give an esr signal upon reduction with zinc. However, in aqueous basic solution alloxan (0.1 *M*) is readily reduced by sodium dithionite ($Na_2S_2O_4$). At ratios of [OH^-]/alloxan of <2.5 a seven-line multiplet was observed that was superimposable upon the low-resolution multiplet observed for **2** in DMSO solution (*i.e.*, seven lines with an intensity ratio of approximately 1:4:8:10:8:4:1 separated by about 0.51 gauss). However, in DMSO the multiplet could be completely resolved to give 15 lines while in water the spectrum could not be further resolved. At a ratio of [OH^-]/alloxan of 3:40 only a five-line pattern with intensity ratios of approximately 1:2:3:2:1 was observed. The value of a^N decreased with increasing [OH^-] up to a ratio of 20:1 after which it remained constant at a^N = 0.276 gauss. At [OH^-]/alloxan = 4 the value of a^N was 0.374 gauss.[12]



2a



2b

d_6-Alloxantin dissociated in deuterium oxide–sodium deuteroxide solution to give an appreciable concentration of radical anions but the resulting signal could not be resolved. Reduction of amalic acid or N,N′-dimethylalloxan with sodium dithionite in aqueous basic solution produced an esr signal of 0.96 gauss line width but the signal could not be resolved.

Radical Cations Derived from 5. The radical cation whose esr spectrum is shown in Figure 6 was obtained from a variety of 1,3-indandione derivatives. This

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(12) In aqueous solution this radical anion was previously observed by C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, **17**, 905, 1677 (1963), and in aqueous methanol by J. C. Orr, *Nature*, **201**, 816 (1964). Both groups prepared the paramagnetic species by the reduction of alloxan and the oxidation of dialuric acid. Lagercrantz and Yhland observed a seven-line multiplet with ~0.4-gauss separation over the pH range 4.6–8.6. These authors ascribed the spectrum to a species with two equivalent nitrogen and hydrogen atoms with $a^N = a^H$. In deuterium oxide they observed a five-line spectrum ascribed to two equivalent nitrogen atoms. Orr observed the seven-line spectrum at low pH (colorless solution), $a^N \cong a^H \cong$ 0.48 gauss, and ascribed it to **2a**. At higher pH (8 *M* potassium hydroxide) he observed a purple solution giving a five-line spectrum which he ascribed to **2b**, a^N = 0.24 gauss.

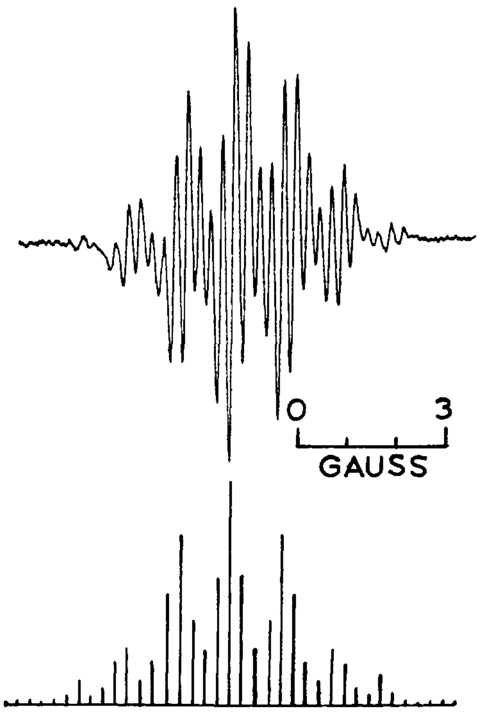


Figure 6. First-derivative esr spectrum of radical cation formed from reduction of ninhydrin by sodium dithionite in 98% sulfuric acid. The same radical cation is formed by the oxidation of 1,3-indandione by potassium persulfate in sulfuric acid solution. The correlation diagram was derived from the hfsc given in the text.

radical cation is assigned structure **7b** with a^{H} (eight equivalent hydrogen atoms) = 0.912 and a^{H} (four equivalent hydrogen atoms) = 0.228 gauss. Table II lists the methods by which **7b** has been formed.

Table II. Formation of Radical Cations from 1,3-Indandione Derivatives

	Reagents		
Substrate	98% H_2SO_4	98% H_2SO_4 + $Na_2S_2O_4$	98% H_2SO_4 + $K_2S_2O_8$
Ninhydrin	**7b**, slowly formed	**7b**	Poor spectrum
1,3-Indandione	No signal	No signal	**7b**
2-Bromo-1,3-Indandione	**7b**	**7b**	Poor spectrum
Hydrindantin	**7b**, slowly formed	**7b**	Poor spectrum
Bishydroxyindone (**5**)	**7b**	**7b**	Poor spectrum

Although the observed spectrum (Figure 6) is consistent with **7b**, it can also be easily rationalized with the rearranged cation **9**. In fact, in sulfuric acid **6** with a purity estimated at >95% gave rise to a radical cation whose esr spectrum was identical with that of Figure 5. However, on the basis of additional experimental results, we are forced to conclude that **5** yields radical cation **7b** and not **9**, and that **5** is not isomerized to **6** under the reaction conditions.

Compound **5** (mp 315–317°, dark purple) is readily distinguished from **6** (mp 345–347°) by ultraviolet spectroscopy. In ethanol **5** gives $\lambda_{\max}$ 220 and 288 mμ whereas **6** has $\lambda_{\max}$ 261 mμ. In sulfuric acid solution, wherein radical cations can be detected at higher substrate concentrations, compound **5** gives a purple solution, $\lambda_{\max}$ 216 and 309 mμ, while **6** gives a pink solution, $\lambda_{\max}$ 298 mμ. The sulfuric acid solution of **6** shows no change in the ultraviolet spectrum during a 2-week period whereas a solution of **5** deteriorates in a few hours with a shift in the 309-mμ peak to longer wavelength. On the other hand the esr spectrum of the radical cation generated from **5** shows no change in 2 weeks at 25° while the esr spectrum of the radical cations generated from **6** decays in a few hours.

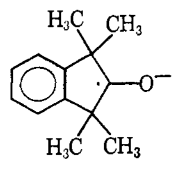
Examination of mixtures of **5** and **6** by ultraviolet absorption led to the conclusion that 5% of **5** could be detected in **6**. Samples of **5** and **6** were treated with 98% sulfuric acid and the buildup of radical cations followed. In 2 hr, a maximum concentration of radical cations had been formed. The signal from **5** grew very rapidly until about 50% of the starting material had been converted to a radical cation. Compound **6** formed radical cations more slowly and only 1–2% of the starting material was converted to a radical cation. After the 2-hr reaction period, the samples were diluted with water and a quantitative recovery (from weight of filtrate) of material was obtained. The infrared and ultraviolet spectra of the crude filtrates showed them to be identical with the respective starting compound. These observations exclude the rearrangement of **5** to **6** or **9** under the reaction conditions.

Oxidation of **6** in DMSO solutions containing potassium *t*-butoxide gave rise to a singlet esr absorption that we ascribe to **8b**. There was no indication of the formation of **7a** or **1**. Oxidation of basic solutions of **6** to which 5% of **5** had been purposefully added gave mainly **7a** which is readily distinguished from **8b** by hyperfine structure and *g* value. We conclude that **6**, whose oxidation gave no indication of the presence of **5**, must have contained <0.5% of **5**.

The radical cation prepared from **5** in deuteriosulfuric acid did not give a well-resolved spectrum, presumably due to the small value of a^{D} and line broadening due to the quadrapole of the deuterium nucleus.

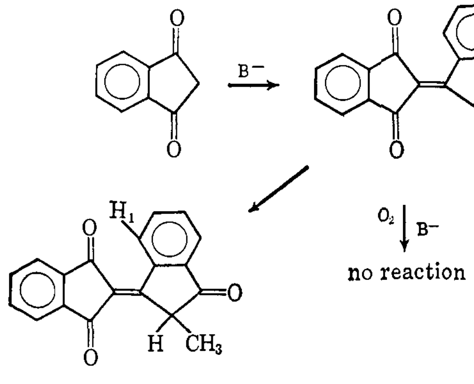
Attempts to prepare radical cations from alloxan and alloxantin in sulfuric acid gave only unresolved esr signals.

Attempted Synthesis of Other Radical Anions in the Indan System. 2,2-Dimethyl-1,3-indandione, 2-methyl-2-phenyl-1,3-indandione, and 1,1,3,3-tetramethyl-2-indanone were synthesized. None of these compounds were reduced to give detectable amounts of radical anions by the propiophenone enolate anion in DMSO solution. Reduction by potassium in tetrahydrofuran gave esr signals which were short lived at room temperature and showed poor resolution. We conclude that structures **14** and **18** are not unusually stable.



18

Exposure of 1,3-indandione to oxygen in basic solution failed to give an esr signal. Presumably the carbanion is stable to oxygen. In addition, condensation to bindone occurs readily. We have been unable to alkylate 1,3-indandione with methyl iodide in basic solution prior to condensation. The situation is analogous to cyclopentene-1,4-dione.[13] Methylated



19

bindone (**19**) shows unusual diamagnetic shielding of H_1 which absorbs (60 Mcps) 9.62 ppm downfield from tetramethylsilane. The other seven aromatic hydrogen atoms absorb at the expected ~7.0-ppm shift from tetramethylsilane.

Discussion

The spontaneous formation of **1** from ninhydrin in DMSO solutions containing potassium *t*-butoxide is somewhat surprising. A similar process has been observed with nitrobenzene, and other nitroaromatics, and has been ascribed to the methylsulfinyl carbanion first methylating the aromatic ring to give a benzylic carbanion that is the actual reducing agent.[14] A

$$\mathrm{ArH} + \mathrm{CH_3SOCH_2^-} \longrightarrow\longrightarrow \mathrm{ArCH_2^-} + \mathrm{CH_3SOH}$$

$$\mathrm{ArCH_2^-} + \mathrm{ArH} \longrightarrow \mathrm{ArH}\cdot^- + \mathrm{ArCH_2}\cdot$$

$$\mathrm{ArCH_2}\cdot \longrightarrow \text{nonradical products}$$

similar process with ArH = ninhydrin may occur. We presume that in DMSO ninhydrin is dehydrated to give the triketohydrindene radical anion.

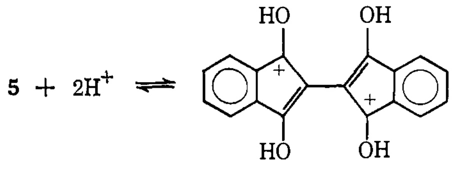
Much of the chemistry connected with **5** was unexpected. In DMSO solution in the presence of deficient quantities of potassium *t*-butoxide both reduction and oxygenation yielded the radical anion **7a**. The formation of **7a** by reduction is a straightforward example of electron transfer.[3a] However, the oxidative result is surprising. A possible explanation is that the reaction involves oxygenation followed by electron transfer to unreacted **5**. With small amounts of oxygen

$$\mathbf{5} + \mathrm{O_2} \xrightarrow{\mathrm{B^-}} \mathbf{1}$$

$$\mathbf{1} + \mathbf{5} \longrightarrow \mathrm{7a} + \text{ninhydrin}$$

the formation of **7a** might be favored by mass law effects. With higher extents of oxidation **1** is the observed product.

The formation of **7b** in high yield from **5** in 98% sulfuric acid in the absence of sodium dithionite is not easily explained. The reaction formally involves the addition of two protons and a one-electron reduction. The solvent system (98% sulfuric acid) is not usually considered to be a reducing agent. Moreover, upon dilution with water **5** can be recovered in nearly quantitative yield. The best explanation we can put forth is a series of oxidation–reduction steps. The reaction sequence could proceed by a series of bimolecular electron-transfer reactions which could be reversed by the addition of water.



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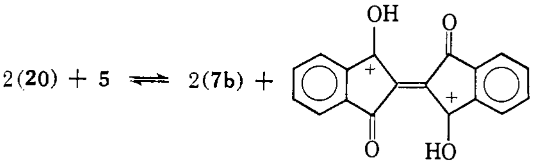
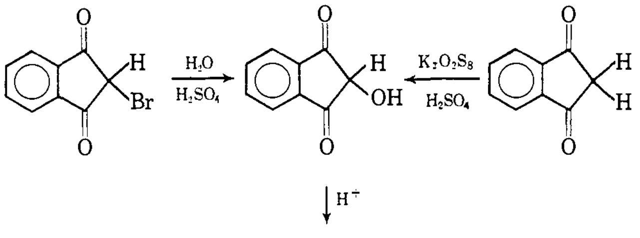


The formation of **7b** from the other indone derivatives (Table II) is very suggestive of reactions involving **5** as an intermediate. Ninhydrin is converted to **5** by sulfuric acid,[15] possibly involving **16** as an intermediate.

$$\text{ninhydrin} + 2\mathrm{H^+} + 2\mathrm{e} \longrightarrow \mathbf{16} + \mathrm{H_2O}$$

$$2(\mathbf{16}) \xrightarrow{\mathrm{H^+}} \mathbf{5} + \mathrm{H_2O_2}$$

The reaction should be greatly facilitated at the first step by a reducing agent ($Na_2S_2O_4$). The formation of **7b** from 2-bromo-1,3-indandione in 98% sulfuric acid follows logically. Oxidation of 1,3-indandione by persulfate can be formulated to involve similar intermediates. The formation of **7b** from hydrindantin in the presence of sodium dithionite undoubtedly involves **5** since **5** is commonly prepared by the reduction of hydrindantin by hydrogen sulfide.



5

We were originally drawn to a study of hydrindantin and alloxantin in basic solution by the report that both compounds gave rise to brilliant blue solutions in the presence of aqueous barium hydroxide.[16] In DMSO solution in the presence of potassium *t*-butoxide alloxantin or hydrindantin give little color. In aqueous solution we have seen no correlation between the blue color and the concentration of **1** or **2**. It is possible to detect **2** in aqueous basic solutions of alloxantin or alloxan that are nearly colorless. In aqueous solution hydrindantin gives the same color (green at low base, blue at high base concentration) in the presence or absence of zinc. Radical anion **3** can be detected only

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[13] C. H. DePuy and P. Wells, *J. Am. Chem. Soc.*, **82**, 2911 (1960).

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

[15] A. Schonberg and R. C. Azzam, *J. Chem. Soc.*, 1428 (1939).

[16] (a) S. Ruheman, *ibid.*, **99**, 792 (1911). (b) It was proposed that the blue color characteristic of hydrindantin in aqueous base was due to a ketyl structure: A. Hantzsch, *Ber.*, **54B**, 1267 (1921). However, magnetic susceptibility measurements of the blue barium salts in aqueous solution failed to support this conclusion: R. W. Asmussen and H. Soling, *Acta Chem. Scand.*, **8**, 558 (1954).

when zinc is present. At very high base concentrations the solutions become colorless but **3** can still be detected.

The equivalence of hfsc of H_1 and H_2 in **1** contrasts with the report of Geske and Balch that $a_2^{H} >> a_1^{H}$ in **15**.[8] This prompted us to examine the predicted spin densities of the aromatic carbon atoms ($\rho_{C}\pi$) in **1** and **15** by Hückel and McLachlan[9] calculations. Using $\alpha_O = \alpha_C + \beta_C$, $\beta_O = \beta_C$, $\lambda = -1.2$, and the equation $|a^{H}| = 22.5\rho_{C}\pi$[17] leads to the values given in Table III. We conclude that probably $a_2^{H} < a_1^{H}$ for **15**.

Table III. Predicted and Experimental Hyperfine Splitting Constants (gauss) for **1** and **15**

	1, a_1^{H}	**1**, a_2^{H}	**15**, a_1^{H}	**15**, a_2^{H}
Predicted, Hückel	0.42	0.50	1.52	1.06
Predicted, McLachlan	0.22	0.16	1.63	0.68
Found	0.95[a] 1.00[d]	0.95[a] 0.68[d]	3.74[b,c]	1.87[b,c]

[a] DMSO. [b] Our assignment. [c] CH_3CN, ref 8. [d] H_2O.

Although the magnitudes of the spin densities calculated are in poor agreement with experimental values they do predict the near equivalence of hfsc for the aromatic hydrogen atoms of **1** and a ratio of close to **2** for the two sets of aromatic hydrogen atoms in **15**.

Experimental Section

Reagents. **Dimethyl sulfoxide** was distilled (reduced pressure) at 100° from calcium hydride. The potassium *t*-butoxide used was commercial material (Mine Safety Appliance Corp.). **Ninhydrin** was commercial material. **Deuterated ninhydrin** was recrystallized from deuterium oxide until hydroxyl protons could not be detected by pmr. **Hydrindantin** (W. R. Grace and Co.) was recrystallized from water, mp 235–236° dec.

Commercial **2,2′-biindan-1,1′,3,3′-tetraone**, mp 295–315°, was sublimed at 292° under reduced pressure to give material melting sharply at 315–317°.

Anal. Calcd for $C_{18}H_{10}O_4$: C, 74.48; H, 3.47. Found (crude): C, 74.2; H, 3.55. Found (sublimed): C, 74.4; H, 3.47. In sulfuric acid λ_{max} occurred at 309 μ (ϵ 2.8 × 10^3) and 216 mμ (ϵ 1.82 × 10^3). In ethanol λ_{max} occurred at 288 mμ (ϵ 1.95 × 10^4) and 220 mμ (ϵ 4.65 × 10^4). The mass spectrum contained peaks at mass numbers 273, 262, 256, 233, 228, 216, 205, 187, 178, 150, and 145. **Dideuteroxy-2,2′-biindan-1,1′,3,3′-tetraone** was prepared by refluxing the ketone in a dilute solution of sodium deuteroxide in deuterium oxide for 2 days. Upon cooling 6,11-dideuteroxynaphthacenequinone was removed by filtration. The cold solution was neutralized with deuteriosulfuric acid to yield the deuterated tetraone.

6,11-Dihydroxynaphthacenequinone was prepared from 2,2′-biindan-1,1′,3,3′-tetraone by refluxing an ammoniacal solution according to the procedure of Vanag,[18] mp 347–349°. In sulfuric acid the quinone gave λ_{max} at 298 mμ (ϵ 6.7 × 10^3). In ethanol λ_{max} occurred at 261 mμ (ϵ 3.9 × 10^4). The mass spectrum gave peaks at mass numbers 262, 233, 205, 187, 178, 150, and 145. At high sensitivity, mass number 273, 272, 256, 228, and 216 could be detected, but these peaks were no more than 7.5% as intense as the corresponding peaks observed for 2,2′-biindan-1,1′,3,3′-tetraone.

2,2-Dimethyl-1,3-indandione was prepared from **2-methyl-1,3-indandione** (mp 132–133°) by the method of Koelsch,[19] mp 106–107°, pmr (60 Mcps) sharp singlet at 1.07 ppm. **2-Methyl-2-phenyl-1,3-indandione** (mp 155–157°) was prepared from **2-phenyl-1,3-indandione**,[20] pmr sharp singlet at 1.71 ppm. **1,1,3,3-Tetramethyl-2-indanone** was prepared,[21] mp 76–77°, pmr sharp singlet at 1.37 ppm. **2-Bromo-1,3-indandione** was prepared by the reaction of 5 g of pyridinium perbromide (0.0156 mole) with 3 g of 1,3-indandione (0.0206 mole) in 25 ml of acetic acid. Since the dibromo compound was also formed, the reaction product was extracted with 10% aqueous sodium hydroxide and acidified to obtain the monobromo product. The crude product was recrystallized from ether, mp 119–120° (lit.[22] mp 119°). **2,2-Dichloro-1,3-indandione** was prepared from ninhydrin by reaction with phosphorus pentachloride in phosphorus oxychloride solution.[5] The material melted at 123–125° (lit.[5] mp 125°).

2-Methyl-$\Delta^{1,2'}$-biindan-1′,3,3′-trione was prepared by adding an excess of methyl iodide to 1,3-indandione in methanolic potassium hydroxide solution. The material, mp 175–176° (lit.[23] mp 176°), gave a pmr showing a doublet (intensity 3.0) at 1.48 ppm (J = 6.96 cps), a quartet (intensity 1.0) at 4.42 ppm (J = 6.96 cps), a single deshielded aromatic proton at 9.62 ppm, and seven aromatic protons at approximately 7.8 ppm. **Bindone** ($\Delta^{1,2'}$-biindan-1′,3,3′-trione) also showed a single low-field proton at 9.62 ppm in deuteriochloroform.

Alloxan was commercial material. Commercial **alloxantin hydrate** was pyrolyzed under vacuum at 75° for 12 hr and recrystallized from dry DMSO until the pmr did not show any hydroxyl peak at about 3.5 ppm to give **alloxantin**, mp 226–228°. **d_6-Alloxantin** was prepared by refluxing the hydrate in deuterium oxide for 2 days. The product gave no proton peaks in pmr, mp 248° dec. **N,N′,N″,N‴-Tetramethylalloxantin** was prepared from caffeine by the method of Cope, *et al.*,[24] mp 215–217. **N,N′-Dimethylalloxan** was prepared from caffeine as an intermediate in the preparation of N,N′,N″,N‴-tetramethylalloxantin. The aqueous solution containing N,N′-dimethylalloxan was evaporated to dryness at 50°. The residue was repeatedly extracted by ether to give material mp 267° dec upon recrystallization from ether (lit.[25] mp 270–272°).

Esr Studies. The esr spectra were obtained using a Varian V-4500 spectrometer equipped with a 9-in. magnet with 100-kcps field modulation. Flat-fused silica cells and a temperature of 25–28° were used for all experiments. An inverted U-type reaction cell[3a] was used. All reactants were thoroughly deoxygenated by purging with prepurified nitrogen before mixing even though the radical cations were stable to oxygen.

Reactions involving reduction by zinc were performed by adding aqueous potassium hydroxide to a mixture of the compound and powdered zinc in one leg of the inverted U-type cell. For the preparation of radical cations sulfuric acid was added from one leg of the U-type cell to a mixture of the compound and sodium dithionite or potassium persulfate in the other leg of the cell.

Concentration measurements were obtained by comparison of a slightly overmodulated signal with the central peak of standard solutions of diphenylpicrylhydrazyl under the same instrumental conditions. In one experiment both signals were doubly integrated by hand. The concentration calculated was the same as found by the comparison of the peak heights of the derivative signals.

Simulated spectra were calculated with a Japanese Electron Optics Co. RA-1 electronic accumulator, or an IBM 7074 computer with IBM 1727 data plotter by plotting 4000 points of a first-derivative spectrum obtained by adding Lorentzian adsorption curves.

Acknowledgment. The mass spectra were obtained by Dr. Thomas Kinstle using an Atlas CH-4 spectrometer. Pmr spectra were obtained with Varian A-60 and HR-60 spectrometers by Dr. R. King and Mr. R. Thrift. We wish to thank Dr. L. L. Wood for a generous sample of hydrindantin.

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