benzene, and pyridine.[13] Solvent shifts reported in this paper are perhaps not so widely applicable to spectrum simplification as those owing to solvent magnetic anisotropy, but do have the important advantages of being relatively large and more predictable in direction and magnitude. A solvent-shift study similar to that reported here has recently been reported.[14] Deuteriochloroform, acetic acid, and trifluoroacetic acid solvents were used in a study of N-methyl group chemical shifts. Several oxygen-containing functional groups were included, however. Relatively small $\Delta\delta$ values were observed (*e.g.*, $\Delta\delta$ for acetone, on changing from deuteriochloroform to trifluoroacetic acid, was 0.17), possibly as a result of the hydrogen-bonding properties of chloroform.

[13] (a) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1965); (b) R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

[14] J. C. N. Ma and E. W. Warnhoff, *Can. J. Chem.*, **43**, 1848 (1965).

The Formation of Radical Intermediates in Formazan–Tetrazolium Salt Systems[1]

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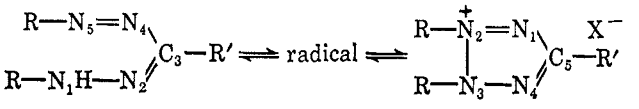
Oxidation of formazans or reduction of tetrazolium salts gives rise to a paramagnetic product stable to oxygen at 25°. Particularly high yields of the radical are formed by the reduction of tetrazolium salts by the propiophenone enolate anion. Possible structures of the radical are considered.

There are distinct resemblances between the formazan–tetrazolium salt oxidation-reduction system and the following thermodynamically reversible systems: hydroquinones–quinones,[2] benzoin–benzil,[3] and hydrazo compounds–azo compounds.[4] These processes, which involve the over-all transfer of two electrons per molecule, can proceed by the stepwise addition of individual electrons.[4] We have conducted electron spin resonance studies on several formazan–tetrazolium salt systems which indicate a facile, one-electron oxidation of the formazan anion or reduction of the tetrazolium salt.



formazan

tetrazolium salt

formazan

1, $R = R' = C_6H_5$
3, $R = C_6H_5$; $R' = p\text{-}CH_3OC_6H_4$
5, $R = C_6H_5$; $R' = p\text{-}NO_2C_6H_4$
7, $R = C_6H_5$,' $R' = CO_2C_2H_5$
9, $R = C_6H_5$; $R' = CH_3$

tetrozolium salt

2, $R = R' = C_6H_5$; $X^- = Br^-$
4, $R = C_6H_5$; $R' = p\text{-}CH_3OC_6H_4$; $X^- = NO_3^-$
6, $R = C_6H_5$; $R' = p\text{-}NO_2C_6H_4$; $X^- = Br^-$
8, $R = C_6H_5$; $R' = CO_2C_2H_5$; $X^- = Br^-$
10, $R = C_6H_5$; $R' = CH_3$; $X^- = Br^-$

The quinone–hydroquinone disproportionation is one of many that fit the generalized sequence[5]

$$\pi + \pi H_2 \xrightleftharpoons{B^-} 2\pi^-$$

Other examples are known, particularly in the area of dihydropyridines, that illustrate the analogous disproportionation[6]

$$\pi^{+2} + \pi \rightleftharpoons 2\pi^+$$

The formazan–tetrazolium salt disproportionation is an interesting variation fitting the generalized scheme

$$\pi^+ + \pi H \xrightleftharpoons{B^-} 2\pi$$

Results

Formazans in the presence of potassium *t*-butoxide and a trace of oxygen, generate free radicals in a variety of solvents. In the absence of oxygen, crimson solutions of the anion are formed, but no e.s.r. signal is detected. The corresponding tetrazolium salts in the presence of potassium *t*-butoxide, in the absence or presence of oxygen, produce the same radical species. Propiophenone, base, and tetrazolium salts, in the absence of oxygen, produced higher free-radical concentrations (Table I) than was observed for tetrazolium salts in the absence of a reducing agent or from mixtures of formazans and tetrazolium salts. This suggests considerable electron transfer in the propiophenone experiments and designates tetrazolium salts as good electron acceptors.[7] Formazan anions are only fair donors, judging by the extent of electron transfer observed for formazan–tetrazolium salt mixtures.

Figure 1 shows the 15-line e.s.r. spectrum observed either by oxidation of 1 or reduction of 2. This spectrum, with only minor modification of hyperfine splitting constants (h.f.s.c.), was also observed from 1 and 2 in *t*-butyl alcohol solutions containing potassium *t*-butoxide as well as in a solvent composed of 80% *t*-butyl alcohol and 20% water. The same spectrum was observed in dimethyl sulfoxide with sodium hydride

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[1] Electron Transfer Processes. III. For part II, see E. T. Strom and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 3326 (1965). This work was supported by a grant from the National Science Foundation.

[2] T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, **60**, 98 (1938); L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *ibid.*, **60**, 1678 (1938); J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1433 (1953); H. Diebler, M. Eigen, and P. Mattheis, *Z. Naturforsch.*, **B16**, 629 (1961).

[3] A. Weissberger, H. Mainz, and E. Strasser, *Ber.*, **62**, 1942 (1929); A. Weissberger, *ibid.*, **65**, 1815 (1932); L. Michaelis and E. S. Fletcher, *J. Am. Chem. Soc.*, **59**, 1246 (1937); J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956).

[4] L. Michaelis and M. P. Schubert, *Chem. Rev.*, **22**, 437 (1938).

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

[6] R. M. Elafson, D. H. Anderson, H. S. Gutowsky, R. B. Sandin, and K. F. Schulz, *ibid.*, **85**, 2622 (1963); H. Hart, J. S. Fleming, and J. L. Dye, *ibid.*, **86**, 2079 (1964); A. T. Nielsen, D. W. Moore, G. M. Muha, and K. H. Berry, *J. Org. Chem.*, **29**, 2175 (1964).

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

TABLE I

FREE RADICALS OF FORMAZANS AND TETRAZOLIUM SALTS IN DIMETHYL SULFOXIDE (80%)–*t*-BUTYL ALCOHOL (20%) AT 25 ± 3°

Concentration (M) of		Concentration (M) of potassium butoxide	Radical Concn.,[a] %	E.s.r. spectrum	
Donor	Acceptor			No. of obsd. lines	Hyperfine structure, a^N (gauss)
1 (0.005)	*b*	0.005	8	15	7.52, 13.08
	2 (0.0083)	0.033	8[c]	15	7.52, 13.08
d	**2** (0.0083)	0.033	40	15	7.52, 13.08
1 (0.0033)	**2** (0.0033)	0.0033	8[e]	15	7.52, 13.08
1 (0.005)	**2** (0.005)		8[e]	15	7.52, 13.08
3 (0.005)	*b*	0.005	10	15	7.75, 13.41
	4 (0.0083)	0.033	18[c]	15	7.75, 13.41
d	**4** (0.0083)	0.033	30	15	7.75, 13.41
3 (0.0033)	**4** (0.0033)	0.0033	16[e]	15	7.75, 13.41
3 (0.005)	**4** (9.005)		16[e]	15	7.75, 13.41
5 (0.005)	*b*	0.005	30	56	Complex
	6 (0.0083)	0.033	30[c]	56	Complex
d	**6** (0.0083)	0.033	80	56	Complex
5 (0.0033)	**6** (0.0033)	0.0033	30[e]	56	Complex
5 (0.005)	**6** (0.005)		30[e]	56	Complex
7 (0.005)	*b*	0.005	5	9	6.54
	8 (0.0083)	0.033	5[c]	9	6.54
d	**8** (0.0083)	0.033	26	9	6.54
7 (0.0033)	**8** (0.0033)	0.0033	15[e]	9	6.54
7 (0.005)	**8** (0.005)		10[e]	9	6.54

[a] Per cent radical concentration, based on starting formazan and tetrazolium salt, was determined by comparison with a diphenylpicrylhydrazyl standard solution. [b] Experiment was conducted in the presence of a trace of oxygen. [c] Identical results were obtained both in the absence and presence of a trace of oxygen. [d] Propiophenone (0.15 M) was present as a donor. [e] Experiments conducted in the absence of oxygen.

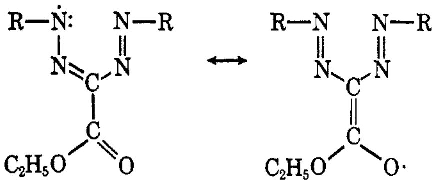
as base or in dimethylformamide solution with sodium methoxide as base. Signals were not observed in methanol or methanol–water as solvents. Formazan **1** formed a crimson solution in all solvents in the presence of bases while the tetrazolium salt either gave rise to a crimson or a yellow solution. There appeared to be no relationship between the color of the solutions and the strength of the e.s.r. signal observed. The radical formed from **1** or **2** was very stable to oxygen and showed no change in concentration for prolonged exposure to air (up to 24 hr.). The e.s.r. spectrum of Figure 1 shows only hyperfine splitting by nitrogen atoms, $a^N = 7.52, 7.52, 13.08, 13.08$ gauss.

Figures 2, 3, and 4 give the spectra observed for the radical intermediates produced from **3** or **4**, **5** or **6**, and **7** or **8**, respectively. Formazan **9** or tetrazolium salt **10** generated only a weak e.s.r. signal which was poorly resolved.

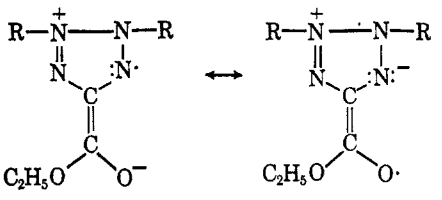
Discussion

As shown in Figures 1 and 2, the e.s.r. spectra of the formazan–tetrazolium salt systems **1**–**2** and **3**–**4** are almost identical. They are explained by assuming interaction of the unpaired electron with two pairs of equivalent nitrogen atoms. The h.f.s.c., which are a function of the spin densities, are somewhat larger for the radical of formazan **3** and tetrazolium salt **4** ($a^N = 7.75, 13.41$ gauss) than for the radical derived from **1** or **2** ($a^N = 7.52, 13.08$ gauss.) This is readily explained by the electron-donating or -repelling character of the *p*-methoxy substituent which results in an increase in the spin density on the heterocyclic portion of the molecule for the radical containing the *p*-methoxyphenyl substituent when compared with the radical containing only the phenyl substituent. The complexity of the e.s.r. spectrum observed for the formazan **5**–tetrazolium salt **6** system, prevented the determination of the hyperfine structure. However, predominant triplet splitting of the spectrum is suggestive of interaction of the unpaired electron with the nitrogen atoms of the *p*-nitro group.

Formazan **7** and tetrazolium salt **8** gave an e.s.r. spectrum (Figure 4) indicative of the unpaired electron interacting with four magnetically equivalent nitrogen atoms. The hyperfine splitting constant, $a^N = 6.54$ gauss, represents a considerable reduction from the splitting constants observed for the systems involving phenyl and *p*-methoxyphenyl groups in the 3- and 5-positions of the respective formazans and tetrazolium salts. We believe that a considerable contribution by a ketyl-type radical intermediate explains the depletion of spin density associated with the nitrogen atoms. The radical intermediate can be represented as either an open-chain (**11a**) or cyclic (**11b**) structure (R = C_6H_5).



11a



11b

A substantial reduction of the h.f.s.c. upon carbonyl substitution has also been observed in the 1,2,4,5-tetrazine system. A splitting constant of $a^N = 4.91$

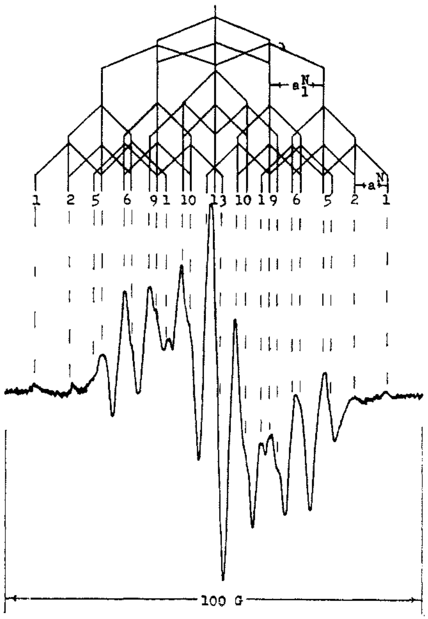


Figure 1.—First-derivative e.s.r. spectrum and correlation diagram observed for the radical produced from 1,3,5-triphenylformazan or 2,3,5-triphenyltetrazolium bromide under conditions specified in Table I.

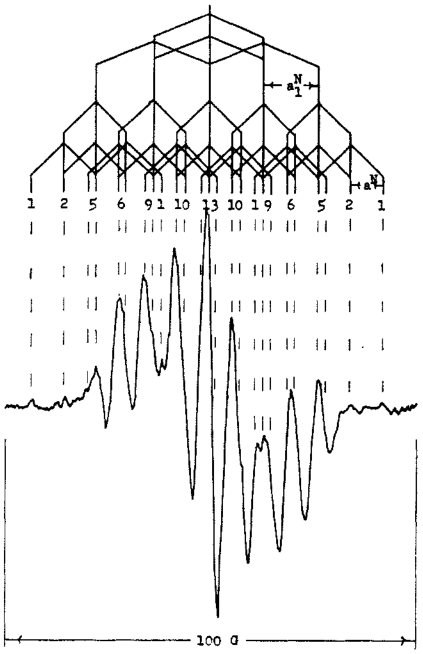


Figure 2.—First-derivative e.s.r. spectrum and correlation diagram observed for the radical produced from 1,5-diphenyl-3-*p*-methoxyphenylformazan or 2,3-diphenyl-5-*p*-methoxyphenyltetrazolium nitrate under conditions specified in Table I.

gauss was observed for the 3,6-diphenyl-1,2,4,5-tetrazine radical anion in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution.[8] For 3,6-dimesitoyl-1,2,4,5-tetrazine radical anion a value of $a^N = 2.44$ gauss was observed. Apparently the ketyl-type free radical is again responsible for the reduction in spin density in the 1,2,4,5-tetrazine system **12** and lends support to resonance forms **11**.

Free radical **13a** was proposed by Ashley, *et al.*,[9] as a likely intermediate in formazan oxidation or

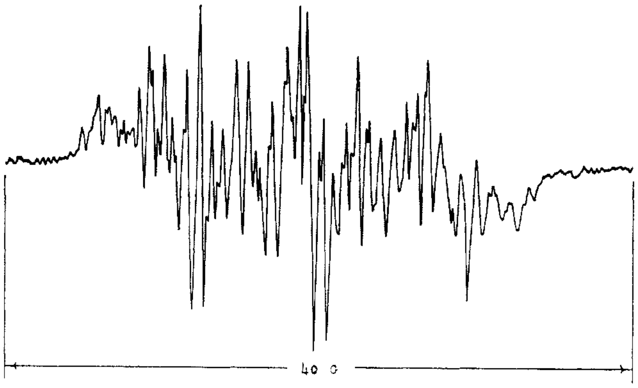


Figure 3.—First-derivative e.s.r. spectrum observed for the radical produced from 1,5-diphenyl-3-*p*-nitrophenylformazan or 2,3-diphenyl-5-*p*-nitrophenyltetrazolium bromide under conditions specified in Table I.

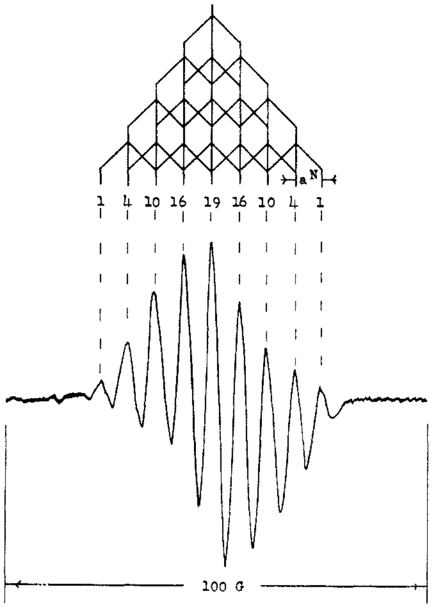
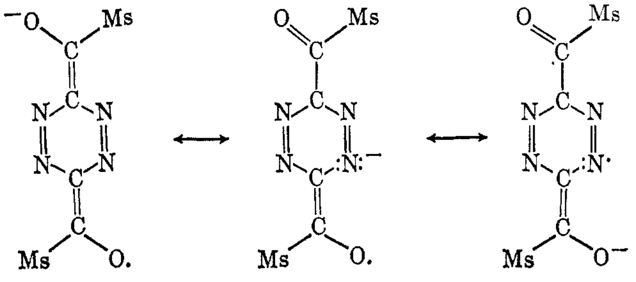


Figure 4.—First-derivative e.s.r. spectrum and correlation diagram observed for the radical produced from 3-carboethoxy-1,5-diphenylformazan or 5-carboethoxy-2,3-diphenyltetrazolium bromide under the conditions specified in Table I.



12, Ms = 2,4,6-trimethylphenyl

tetrazolium salt reduction. However, **13b** should also be considered for the intermediate free radical. From e.s.r. evidence compiled to date, it is not possible to distinguish unequivocally between the two structures. It is entirely possible that a rapidly time averaged mixture of radicals **13a** and **13b** actually is observed. Since evidence exists for cyclic, oxygen-stable free radicals derived from formazans and tetrazolium salts,[10]

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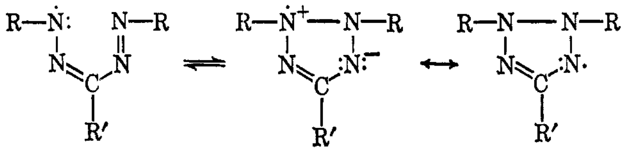
[8] Unpublished results of Dr. R. Konaka.

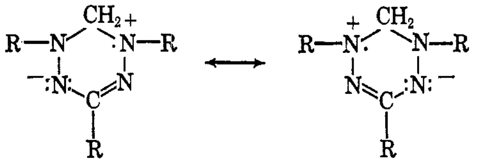
[9] J. N. Ashley, B. M. Davis, A. W. Nineham, and R. Slack, *J. Chem. Soc.*, 3881 (1953).

[10] (a) R. Kuhn and D. Jerchel, *Ann.*, **578**, 1 (1952); (b) R. Kuhn and H. Trischmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 155 (1963); (c) D. Jerchel and H. Fischer, *Ann.*, **590**, 216 (1954).



13a **13b**

the cyclic structure **13b** warrants serious consideration. We have repeated the preparation of **14** by the air oxidation of 1-methyl-1,3,5-triphenylformazan[10b] and found a nine-line spectrum, $a^N = 5.82$ gauss in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%). The magnetic equivalence of the four nitrogen atoms in **14** and **11** suggests that in **11**, as in **14**, there is not a formal bond between N-1 and N-5, *i.e.*, structure **11a**.[11] This approach leads to the conclusion that the radicals formed from **1-4** are cyclic (**13b**) with decidedly different h.f.s.c. for N-1, N-5 and N-2, N-4. This conclusion also demands that **11a** is a π radical (electron pair on N-1, N-5 in a σ orbital) and not a σ radical (electron pair N-1 in a *p*-orbital).



14

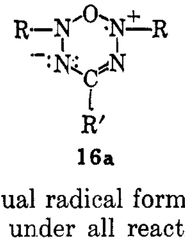
The formation of **13** from the formazan in the presence of oxygen and base appears to be a straight forward example of electron transfer. The formation

$$[\mathrm{R{-}N{=}N{-}C(R'){=}N{-}\ddot{N}{-}R}]^- + O_2 \longrightarrow O_2\cdot^- + \mathbf{13}$$
$$4O_2\cdot^- + 2H_2O \longrightarrow 3O_2 + 4OH^-$$

of **13** by reduction of tetrazolium salts by the propiophenone enolate anion also appears reasonable. However, the formation of **13** spontaneously from

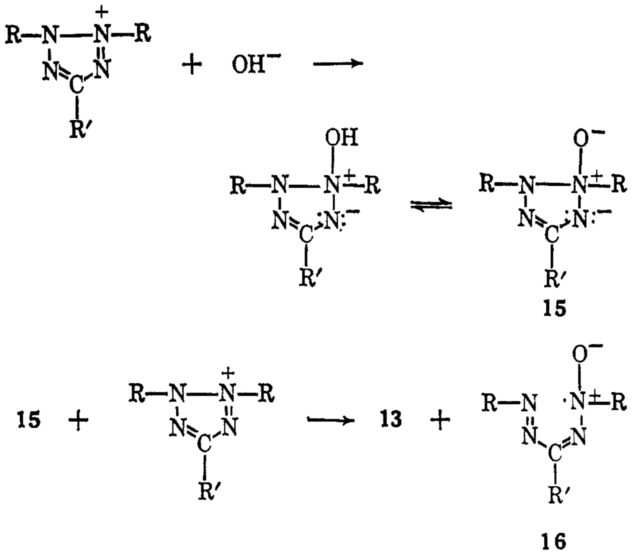
$$\mathbf{2} + C_6H_5COCHCH_3^- \longrightarrow \mathbf{13} + C_6H_5CO\dot{C}HCH_3$$
$$C_6H_5CO\dot{C}HCH_3 \longrightarrow \text{nonradical products}$$

tetrazolium salts in basic solution is surprising. Electron transfer from the alkoxide ion is not particularly appealing. Possibly reaction with hydroxide ion gives rise to some intermediate which can function as a reducing agent. For example, see Scheme I. The symmetry of the observed radicals apparently excludes **16** as the actual paramagnetic species. However, a cyclic structure, for example **16a** deserves consideration as the actual radical formed from formazans or tetrazolium salts under all reaction conditions and particularly as an alternative to structure **11a**.

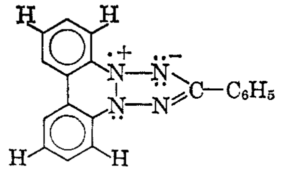


16a

SCHEME I



In one experiment a sample of 2,3,5-triphenyltetrazolium nitrate was exposed to diffuse sunlight in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) for a 2-week period. Upon treatment with base a 15-line e.s.r. spectrum of evenly spaced lines with intensities of approximately 1:2:5:8:12:16:18:20:18:16:12:8:5:2:1 was observed. This spectrum is consistent with a^N = 6.32, 6.32, a^H = 6.32, 6.32, 3.16, 3.16 gauss. This new radical is possibly **17**. It has been reported that **17** is formed from the corresponding tetrazolium salt by careful reduction.[10a] Moreover, Kuhn and Jerchel prepared the parent salt, 2,3-biphenylene-(2,2')-5-phenyltetrazolium nitrate, by the photolysis of 2,3,5-triphenyltetrazolium nitrate. The h.f.s.c. for **17** suggest that the unpaired spin is restricted to the benzo[*c*]cinnoline ring system rather than to the tetrazolium ring. There is a possibility that the observed radical is the benzo[*c*]cinnoline radical anion.[12] The reported spectrum of 13 multiplets with a^N = 5.38, 5.38, a^H = 2.72, 2.72, 2.72, 2.72 gauss for benzo[*c*]cinnoline radical anion in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%)[13] is not different enough from the spectrum observed to allow a differentiation between **17** and benzo[*c*]cinnoline radical anion. It is pertinent that benzo[*c*]cinnoline is a known reduction product of 2,3-biphenylene-(2,2')-5-phenyltetrazolium nitrate.[14]



17

Experimental Section[15]

Apparatus and Procedure.—All e.s.r. experiments were performed using a Varian V-4500 E.P.R. spectrometer, equipped with 100 kc./sec. field modulation and a 9-in. magnet with Fieldial control. The apparatus used for all experiments consisted of an inverted U-cell joined with a flat fused silica cell

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(11) The h.f.s.c. of nitrogen atoms is a complex function of spin density, not only of the nitrogen atom under consideration but also of atoms adjacent to the nitrogen atom. For pertinent references see ref. 12a.

(12) (a) E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965); (b) D. H. Geske and G. R. Padmanabham, *J. Am. Chem. Soc.*, **87**, 1651 (1965).

(13) Ref. 12b reports a^N = 5.27, 5.27, a^H = 3.58, 3.58, 2.83, 2.83, 0.77, 0.77, 0.28, 0.28 gauss in dimethylformamide solution.

(14) F. Weygand and I. Frank, *Z. Naturforsch.*, **B3**, 377 (1948).

(15) All compounds except the 2,3-diphenyl-5-*p*-methoxyphenyltetrazolium nitrate are known. Their infrared spectra and corrected melting points are in full agreement with literature values.

(Varian V-4548 aqueous solution sample cell).[7] After flushing the U-cell with prepurified nitrogen, a solution of the base was added to one leg by a syringe through a rubber septum. A solution of the formazan (donor), and/or tetrazolium salt (acceptor), was added to the other leg of the U-cell. Both solutions were deoxygenated by introducing prepurified nitrogen through two hypodermic needles extending below the surface of each solution (the nitrogen escaped through the open end of the e.s.r. cell). When purging was complete (20 min.) the exit was closed and the hypodermic needles were withdrawn. For experiments requiring a trace of oxygen (*e.g.*, formazan and base) a 5-min. purging left sufficient oxygen to generate an e.s.r. signal. After mixing the solutions, the mixture was forced into the e.s.r. cell by shaking. Initial e.s.r. spectra were recorded about 1 min. after mixing. Extreme precautions were required in deoxygenating since most of the formazans (donors), reacted with oxygen to give the free-radical species.

Estimates of the radical concentrations were made by comparing the peak-to-peak distance, from the maximum to the minimum, of the over-modulated first derivative curves of the radical and a standard solution of diphenylpicrylhydrazyl, at the same instrument settings and in the same solvents.[16]

Materials.—Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride. Dimethylformamide was purified by shaking with potassium hydroxide, followed by distillation at atmospheric pressure. Commercial *t*-butyl alcohol was distilled from calcium hydride. Potassium *t*-butoxide and sodium methoxide (Mine Safety Appliances Research Corp.) were commercial material. Sodium hydride (Metal Hydrides Inc.) consisted of a 50% oil suspension which was used directly.

1,3,5-Triphenylformazan (**1**) was synthesized by the method of Kuhn and Jerchel,[17] m.p. 173° (lit.[17] m.p. 173.5°).

2,3,5-Triphenyltetrazolium bromide (**2**) was prepared by the procedure of Pechmann and Runge,[18] m.p. 255° (lit.[18] m.p. 255°).

1,5-Diphenyl-3-*p*-methoxyphenylformazan (**3**) was prepared by the method of Jerchel and Fischer,[19] m.p. 156–157° (lit.[19] m.p. 156–158°).

2,3-Diphenyl-5-*p*-methoxyphenyltetrazolium nitrate (**4**) was prepared in 41% yield by oxidizing a methanolic solution of **3** (0.01 mole) with 0.01 mole of silver nitrate. A quantitative precipitation of silver metal resulted over a 1-hr. period at room temperature. After filtering, the product was precipitated from the methanol by adding a large excess of anhydrous ether. The pale yellow, water-soluble product was recrystallized to yield pale yellow needles from a minimum amount of methanol, m.p. 248–249°. The infrared spectrum (potassium bromide pellet) was consistent with the proposed structure. The asymmetric and symmetric C–O–C stretching frequencies were 1250 and 1026 cm.$^{-1}$. The broad asymmetric stretching vibration of NO_3^- came at 1360 cm.$^{-1}$. The 829 cm.$^{-1}$ of O–N–O bending was evident.

Anal. Calcd. for $C_{20}H_{17}N_5O_4$: C, 61.40; H, 4.35; N, 17.90. Found: C, 61.37; H, 4.44; N, 17.89.

The tetrazolium nitrate was prepared from 1,3,5-triphenylformazan in a yield of 66% of recrystallized material, m.p. 228–229°. Addition of 2,3,5-triphenyltetrazolium nitrate in methanol solution to a saturated methanolic solution of sodium bromide yielded a precipitate which was removed by filtration and recrystallized from methanol to give 2,3,5-triphenyltetrazolium bromide, m.p. 254–255°. This material had an identical infrared spectrum and did not depress the melting point of an authentic sample of 2,3,5-triphenyltetrazolium bromide.

1,5-diphenyl-3-*p*-nitrophenylformazan (**5**) was made by the method of Ashley, *et al.*,[9] m.p. 209–210° (lit.[9] m.p. 204°).

2,3-diphenyl-5-*p*-nitrophenyltetrazolium bromide (**6**) was synthesized by the method of Nineham,[20] m.p. 264–265° (lit.[20] m.p. 266°).

3-Carboethoxy-1,5-diphenylformazan (**7**) was prepared by the procedure of Pechmann,[21] m.p. 116–117° (lit.[21] m.p. 117°).

5-Carboethoxy-2,3-diphenyltetrazolium chloride was prepared by the method of Kuhn and Jerchel,[17] m.p. 173–174° (lit.[17] m.p. 173–174°). The bromide **8** was attained by adding a saturated solution of sodium bromide in methanol to the dissolved chloride, m.p. 198–200° dec. The infrared spectrum (potassium bromide pellet) of the bromide was identical with that of the chloride.

1,5-Diphenyl-3-methylformazan (**9**) was synthesized according to the method of Wedekind,[22] m.p. 125° (lit.[22] m.p. 125°).

2,3-Diphenyl-5-methyltetrazolium bromide (**10**) was prepared by the method of Ashley, *et al.*,[9] m.p. 263–264° (lit.[9] m.p. 263–264°).

3,5-Diphenyl-1-*p*-nitrophenylformazan was also prepared, m.p. 199–200°, by coupling the benzaldehyde *p*-nitrophenylhydrazone with the diazonium salt of aniline. Care was taken to maintain a pH of 8. The original formazan solution, red-brown color in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%), failed to generate an e.s.r. signal in the presence of base. However, on standing for 1 day the solution changed to a green color. This green solution failed to give an e.s.r. signal, but when mixed with a trace of potassium *t*-butoxide, in the presence of oxygen, an e.s.r. signal was observed which was consistent with $a^N = 5.21, 5.21, 5.21$, $a_{NH}^H = 23.85$ gauss. The e.s.r. spectrum appeared as two overlapping heptets. The nature of the free radical was not immediately evident.

3,6-Dimesitoyl-1,2-dihydro-1,2,4,5-tetrazine, m.p. 279–280° (lit.[23] m.p. 280°), was prepared according to the method of Morrison.[23] On allowing a concentrated methanol solution of mesitoyldiazomethane to react with sodium methoxide, the above tetrazine precipitated. Morrison prepared the mesitoyldiazomethane by first oxidizing acetylmesitylene to mesitylglyoxal with selenium dioxide. The hydrazone of mesitylglyoxal was prepared by condensing hydrazine sulfate, in the presence of sodium acetate, with the glyoxal. The hydrazone was then oxidized with activated manganese dioxide to mesitoyldiazomethane.

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