mμ (log ε 4.24), 446 sh (4.12), 429 (4.29), 406 (4.07), 366 (4.02), 270 (4.47).

Anal. Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.68; H, 3.62.

Compound **3** is insoluble in water and most organic solvents; it can be recrystallized from acetic acid but large volumes (4000/1) are needed. The hydrochloride of **3**, 1,4,7-trihydroxyphenalenium chloride, was obtained by stirring a mixture of **3** (0.686 g) and 5% hydrochloric acid (37 ml) for 1 day at room temperature, followed by filtration and drying (100° (0.3 mm), 12 hr). The resulting salt (0.798 g, 99%) decomposed without melting between 300 and 350° and regenerated **3** when stirred in water for 3 days at room temperature.

Visible and ultraviolet maxima for the various ions of **3** are as follows: *monoanion* (95% C_2H_5OH saturated with Na_2CO_3) 478 mμ (log ε 4.35), 452 (4.26), 380 (4.01), 368 sh (3.98), 280 (4.41), 236 (4.13); dianion **5** (95% C_2H_5OH, 0.02 *N* NaOH) 457 (4.41), 432 (4.43), 277 (4.41), 259 (4.39); cation **4** (95% C_2H_5OH containing 5% CH_3SO_3H) 424 (4.51), 412 sh (4.42), 245 (4.37).

4,7-Dimethoxyphenalenone (from **3** and methyl sulfate in aqueous alkali) showed the following characteristics: mp 176–178° (benzene–petroleum ether); visible and uv_{max} (95% C_2H_5OH) 455 mμ (log ε 4.06), 432 (4.23), 410 (4.10), 366 (4.00), 270 (4.51); nmr ($CDCl_3$) τ 5.95 (s, 3), 5.91 (s, 3), 3.37 (d, J = 10.1 Hz, 1), 3.08 (d, J = 8.4, 1), 2.86 (d, J = 9.2, 1), 1.86 (d, J = 10.1, 1), 1.68 (d, J = 9.2, 1), 1.41 (d, J = 8.4, 1); ir ($CDCl_3$) 1635 cm^{-1} ($\nu_{C=O}$).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.05; H, 5.07.

4,7-Diacetoxyphenalenone (from **3** and acetic anhydride containing a catalytic amount of sulfuric acid) showed the following characteristics: mp 180–182° (benzene); uv_{max} (95% C_2H_5OH) 380 mμ (log ε 4.07), 323 (3.71), 257 (4.45); nmr ($CDCl_3$), τ 7.55 (s, 3), 7.52 (s, 3), 3.37 (d, J = 9.9 Hz, 1), 2.72 (d, J = 9.1, 1), 2.55 (d, J = 8.1, 1), 2.22 (d, J = 9.9, 1), 2.00 (d, J = 9.1, 1), 1.47 (d, J = 8.1, 1); ir ($CHCl_3$) 1646 and 1777 cm^{-1} ($\nu_{C=O}$).

Anal. Calcd for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08. Found: C, 69.30; H, 4.30.

Acknowledgment. The author is indebted to Professor Charles F. Koelsch for useful discussions related to this research and to the Esso Education Foundation for financial support.

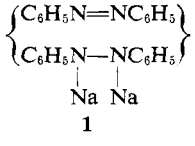
Formation of Azo Radical Anions and Their Vinylogs[1]

Glen A. Russell, R. Konaka, E. Thomas Strom, Wayne C. Danen,[2] Kuo-Yuan Chang, and Gerd Kaupp

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received November 27, 1967*

Abstract: Several types of reactions leading to azo-type radical anions have been investigated. Disproportion between RN=NR and RNHNHR can be readily observed in basic solutions for R = C_6H_5 or $CO_2C_2H_5$ and for the phenazine–dihydrophenazine, 2,3-diphenylquinoxaline–dihydro-2,3-diphenylquinoxaline, and diphenyltetrazine–dihydrodiphenyltetrazine systems. Oxidation–reduction of the type, 2π-CH_3 + 2π-CH_2^- → 2π-$CH_3\cdot^-$ + π-CH_2CH_2-π, can be observed for 3,6-dimethyltetrazine, 3-benzyllumiflavin, and 1,4,5,8-bis(trimethylene)pyridazino[4,5-*d*]pyridazine (**3**) but not for the simple methylpyrazines. A wide variety of unsaturated compounds can be reduced to the radical anions by the propiophenone enolate anion. These compounds include azobenzene and ring-substituted derivatives, benzo[*c*]cinnaline, tetrazines, phenazine, 2,3-diphenylquinoxaline, and benzoxadiazole. Reaction with traces of oxygen in basic dimethyl sulfoxide solutions forms the radical anions from hydrazobenzene, dihydrophenazine, dihydro-2,3-diphenylquinoxaline, *o*- and *p*-phenylenediamines, benzidine, and N,N′-diphenylbenzidine.

Schlenk in his classical studies of the addition of sodium to unsaturated compounds recognized the existence of a 1:1 adduct with azobenzene.[3] However, he formulated this adduct as **1** rather than the "ketyl-type" radical anion **2**. The intermediacy of



1

$[C_6H_5N\dot{-}NC_6H_5]^-Na^+$

2

radical anions could be inferred from later work that showed that the "di-Grignard" reagent of hydrazobenzene readily reduced benzil to benzoin[4] and that azobenzene oxidized many organometallic compounds.[5] For example, azobenzene converts phenyllithium or phenylmagnesium bromide to biphenyl in good yield.[5] The later process is consistent with reaction 1. Wittig

$$C_6H_5M + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5\cdot + \mathbf{2} \qquad (1)$$

described a crystalline salt of a radical anion prepared by the reaction of azobenzene with the dilithium salt of hydrazobenzene,[6] although it is now known that in solution and in the presence of lithium cations that the equilibruim of eq 2 lies far to the left.[7] Wittig also

$$C_6H_5N{=}NC_6H_5 + [C_6H_5\bar{N}{-}\bar{N}C_6H_5]^{2-} \rightleftharpoons 2[C_6H_5N{=}NC_6H_5]\cdot^- \qquad (2)$$

showed that the solid reaction product from benzo[*c*]cinnoline and its disodium salt was extensively paramagnetic (eq 3).[8]

(1) Electron-Transfer Reactions. Part IX. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

(2) National Institutes of Health Predoctoral Fellow, 1965–1966.

(3) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914).

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(6) G. Wittig, *Angew. Chem.*, **53**, 241 (1940).

(7) G. N. Aylward, J. L. Garnett, and J. H. Sharp, *Chem. Commun.*, 173 (1966).

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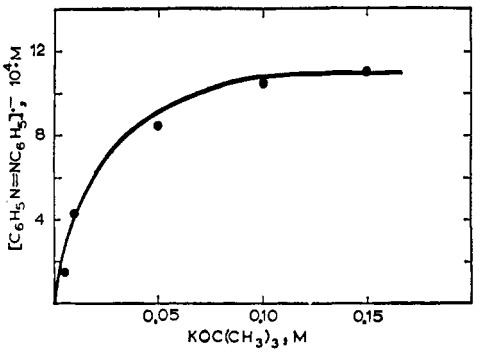
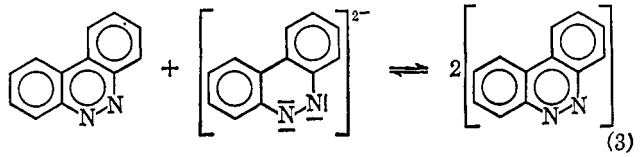


Figure 1. Formation of azobenzene radical anions from a solution initially 0.001 M in azobenzene and hydrazobenzene in dimethyl sulfoxide–t-butyl alcohol (80:20).

In solution we have shown that the azobenzene radical anion can be prepared by a variety of techniques.[9-11] Reduction of azobenzene by a variety



(3)

of carbanions, such as the enolate ion of propiophenone, occurs readily particularly in dimethyl sulfoxide (DMSO) solution. In fact, in 100% DMSO azobenzene spontaneously forms the radical anion in the presence of potassium t-butoxide. The radical anion is also formed by autoxidation of hydrazobenzene in basic solution[12,13] and is the sole paramagnetic product detected when aniline is exposed to air in DMSO solution containing potassium t-butoxide. Electrolytic reduction of azobenzene in dimethylformamide[7] or dimethoxyethane solution[14] also yields the radical anion.

In basic solutions mixtures of azobenzene and hydrazobenzene disproportionate to the radical anion (eq 1).[9] This process is complicated by acid–base reactions as well as ion-pairing phenomena.[7] In Figure 1 a value of K_e of ~6 at 25° (potassium cation, DMSO–t-butyl alcohol (80:20)) is indicated for the equilibrium ($K_e = [R\cdot^-]^2/[R][R^{2-}]$). As shown in Figure 1 the acid–base equilibria in the ionization of hydrazobenzene can be forced completely to the side of the dianion. Further increase in the concentration of base (above 0.05 M in Figure 1) does not affect the concentration of dianion or radical anion.

In Figure 2 are given experimental and calculated spectra for azobenzene radical anion in DMSO–t-butyl alcohol (80:20) at 25° in the presence of 0.2 M potassium t-butoxide. The esr spectrum is consistent with two equivalent nitrogen atoms, $a^N = 4.84$ G; four equivalent hydrogens, $a^H = 2.90$ G; two equivalent

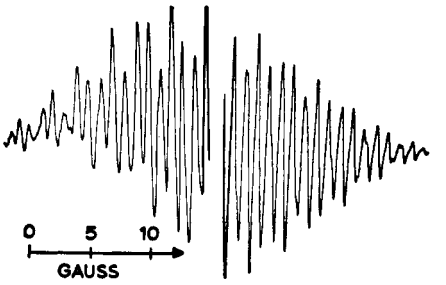
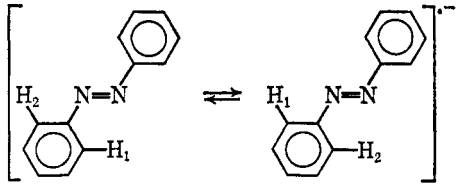


Figure 2. First derivative esr spectrum of azobenzene radical anion: left, experimental low-field half spectrum in dimethyl sulfoxide–t-butyl alcohol (80:20); right, calculated spectrum with hyperfine splitting constants given in text.

hydrogens, $a^H = 2.00$ G; four equivalent hydrogens with $a^H = 0.86$ G, and a line width of 0.125 G. The smaller hyperfine splitting is obviously connected with the m-hydrogen atoms.[15] A spectrum of azobenzene-o,o,o',o',p,p'-d_6 radical gave a 1:2:3:2:1 quintet with $a^N = 4.84$ G. At first glance one might suspect that the two hfsc of 2.00 G are associated with the p-hydrogen atoms. However, this is not the case. Preparation of azobenzene-o,o,o',o',m,m,m'-d_8 radical anion gave a spectrum consistent with $a^N = 4.84$ and a^H (two equivalent) = 2.81 G. Thus we concluded that (a) the o-hydrogen atoms of azobenzene radical anion are not magnetically equivalent, and (b) one o- and the p-hydrogen atoms of each ring have the same hfsc.[16,17] This can occur only if there is restricted rotation about the bond between the aromatic ring and the azo group.[16] Moreover, to resolve the difference in hfsc between the two o-hydrogen atoms of 0.8 G must mean that precession of the electron magnetic moment around the nuclear magnetic moments is fast compared to conformation interconversions.



This corresponds to a conformational lifetime of greater than $1/\nu$ where $\nu = 2.8\Delta a^H$ in megacycles per second (Mcps). Using 0.8 for Δa^H yields $\nu < 2.2 \times 10^6$ cps and $1/\nu < 5 \times 10^{-5}$ sec.

The reduction of *cis*-azobenzene was also examined. The esr spectrum observed initially was exactly the same as observed from *trans*-azobenzene. However, in DMSO containing potassium t-butoxide, it was observed by spectroscopy that *cis*-azobenzene quite rapidly isomerized to the *trans* isomer and it cannot be concluded that *cis*- and *trans*-azobenzene radical anions do not have independent existence. However, it is quite likely that the *cis*-radical anion would isomerize to the *trans* structure quite rapidly.[14]

(9) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).
(10) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).
(11) E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1967).
(12) G. A. Russell, E. G. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Am. Chem. Soc.*, **89**, 3821 (1967).
(13) For a discussion of this process see G. Kaupp and G. A. Russell, *Chem. Ber.*, **101**, 1729 (1968), and references cited therein.
(14) C. S. Johnson, Jr., and R. Chang, *J. Chem. Phys.*, **43**, 3183 (1965).
(15) For MO calculations using Hückel orbitals and the McLachlan approximate self-consistent-field method, see N. M. Atherton, F. Gerson, and J. N. Ockwell, *J. Chem. Soc., A*, 109 (1966).
(16) E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, 13, (1965).
(17) At −40° in dimethoxyethane solution the five aromatic hydrogen atoms are all magnetically different. A similar situation is encountered in *trans*-stilbene radical anion.[14]

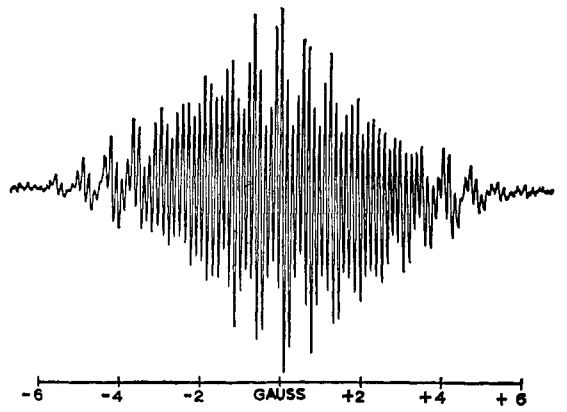


Figure 3. First derivative esr spectrum of indigo radical ion formed by reduction of indigo with hydrazobenzene in methanol containing sodium methoxide. Under the reaction conditions there was no signal without the hydrazobenzene. The spectrum is similar to that reported by F. Bruin, F. W. Heineken, and M. Bruin, *J. Org. Chem.*, **28**, 562 (1963). Although too complex to be uniquely analyzed, it appears to give good agreement with the relative intensities of lines expected for a^N = 1.22, 1.22, a^H = 2.30, 2.30, 0.68, 0.68, 0.68, 0.68, 0.14, 0.14 G. Perhaps the NH hydrogen atoms are exchanging readily under the reaction conditions.

Azobenzene is reduced to the radical anion by a variety of organometallic reagents in ethereal solvents.[10] Under these conditions phenyllithium or phenylmagnesium bromide undergo coupling to biphenyl and the azobenzene is reduced to a salt of hydrazobenzene. Gilman and Adam showed that the formation of bi-

$$2C_6H_5MgBr + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5{-}C_6H_5 + [C_6H_5N{=}NC_6H_5]^{2-}Mg^{2+} \quad (4)$$

phenyl in the reaction of phenylmagnesium bromide with azobenzene did not involve triphenylhydrazine anion as an intermediate.[18] We have shown that no symmetrical intermediate can be involved by examining the reaction with a ^{14}C label. Table I summarizes results of the reaction of a 20 mol % excess of phenylmagnesium bromide with azobenzene in ether solution. The results of Table I point to reaction 1 as a likely possibility. However, ether is a good trap for phenyl radicals and biphenyl cannot be formed in significant yield by the coupling of phenyl radicals in this solvent.[19] A similar phenomenon has been recently encountered in the photolysis of phenyllithium in tetrahydrofuran solu-

$$2C_6H_5Li \xrightarrow[THF]{h\nu} C_6H_5{-}C_6H_5 + 2Li \quad (5)$$

tion (reaction 5).[20] It seems likely to us that the organometallic reagent may be a superior trap for phenyl radicals (reaction 6), in part due to the stability of biphenyl radical anion. Unequivocal evidence for trapping of radicals by nitro-substituted carbanions has been presented.[21]

$$C_6H_5\cdot + C_6H_5{}^-M^+ \longrightarrow [C_6H_5{-}C_6H_5]\cdot{}^-M^+ \quad (6)$$

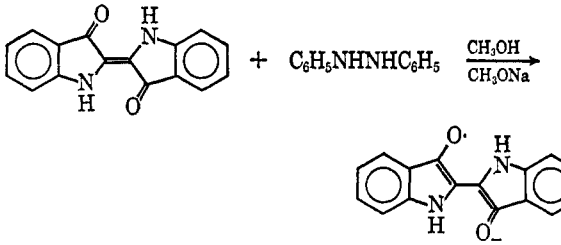
The azobenzene radical anion is not stable in basic alcohol solution. Because of this hydrazobenzene has some value as a reducing agent in esr spectroscopy.

Table I. Material Balance for Radioactive Label in the Reaction of Phenylmagnesium Bromide with Azobenzene[a]

Reactants		Products	
C_6H_5MgBr[b]	$C_6H_5N{=}NC_6H_5$[b]	$C_6H_5C_6H_5$ (%)[b,c]	$C_6H_5NHNHC_6H_5$ (%)[b,c]
0	9.43	0 (60)	9.41 (77)
32.8	0	67.5 (60)	0 (77)

[a] 2.4 equiv of phenylmagnesium bromide per equivalent of azobenzene (~0.1 *M*) in ether solution at 25°. [b] Disintegrations per min per mmol × 10^5. [c] Isolated yield in parentheses.

In methanol containing sodium methoxide, propiophenone is not highly ionized and is not an effective reductant. Sodium dithionite has a low solubility and is of little value. However, hydrazobenzene is an effective reductant and does not complicate the spectrum by formation of a stable radical anion. Figure 3 illustrates the application of this technique to indigo. Using pure methanol and sodium methoxide no esr



(7)

signal could be detected in the absence of hydrazobenzene.

A variety of azobenzene derivatives can be reduced to radical anions readily detected by esr spectroscopy in DMSO solution. Thus, *p,p'*-azobenzophenone in DMSO–*t*-butyl alcohol (80:20) when treated with propiophenone enolate anion yields the radical anion. The spectrum could be well resolved to give a^N (two equivalent) = 3.61, a^H (two equivalent) = 3.61, a^H (six equivalent) = 1.51 G. Preparation of *p,p'*-azobenzophenone with four deuterium atoms α to the azo group gave a quintet with a^N = 3.61 G. The difference between the two *o*-hydrogen atoms in this molecule is 2.1 G and again free rotation is restricted.

o,o'- and *p,p'*-Dichloroazobenzenes readily formed stable radical anions under the reaction conditions but the spectra have not been analyzed. *p*-(Phenylazo)-azobenzene gave a strong esr signal in the presence of propiophenone enolate anion but the spectrum could not be resolved.

Cyclization of azobenzene through the *o,o'* positions yields benzo[*c*]cinnoline. This heteroaromatic can be reduced to the radical anion by the propiophenone enolate anion. However, reduction is not as facile as for azobenzene itself (see Figure 4, ref 10). The spectrum of the radical anion is reported elsewhere[22] and is consistent with the product of reduction of benzo[*c*]cinnoline by potassium in tetrahydrofuran and electrolytically in acetonitrile.[23,24] Appreciable quantities of the benzo[*c*]cinnoline radical anion could be formed by reduction with the anions formed from 9,10-

(18) H. Gilman and C. E. Adams, *J. Am. Chem. Soc.*, **48**, 2004 (1926).
(19) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).
(20) E. E. van Tamelen, J. I. Bauman, and L. E. Ellis, *ibid.*, **87**, 4964 (1965).
(21) G. A. Russell and W. C. Danen, *ibid.*, **90**, 347 (1968).
(22) E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965).
(23) T.-L. Kuo and K'-O. Hsueh, *Tung Chi Ta Hsueh Hsueh Pao*, 55 (1963).
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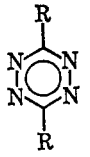
dihydroanthracene in DMSO–*t*-butyl alcohol (80:20) solution. Since the anthracene radical anion was not seen, apparently benzo[*c*]cinnoline is more easily converted to the radical anion than anthracene.

sym-Tetrazines (**3**) are readily reduced by alkali metals to give radical anions.[25] Moreover, some dihydrotetrazines can be prepared. We have examined 3,6-dimethyl-, 3,6-diphenyl-, and 3,6-diaminotetrazine.



3a, R = CH_3
b, R = C_6H_5
c, R = NH_2

We found that 3,6-dimethyltetrazine spontaneously disproportionated in basic solution to yield the radical anion. The process is apparently quite similar to that described previously for *p*-nitrotoluene and fits the generalized scheme shown below.[26]

$$\pi\text{-}CH_3 + B^- \rightleftharpoons \pi\text{-}CH_2^- + HB$$

$$\pi\text{-}CH_2^- + \pi\text{-}CH_3 \longrightarrow \pi\text{-}CH_3\cdot^- + \pi\text{-}CH_2\cdot$$

$$\pi\text{-}CH_2\cdot \longrightarrow \text{dimers, etc.}$$

As is typical of some *p*-nitrotoluene derivatives,[24] a higher concentration of the 3,6-dimethyltetrazine radical anion was found at intermediate concentrations of base in accord with the supposition that electron transfer requires the presence of the ionized and un-ionized forms of π-CH_3. The 3,6-dimethyltetrazine radical anion was quite stable and its spectrum has been described elsewhere.[20] Table II summarizes data on the maximum yield of radical anions observed a few minutes after adding dimethyltetrazine to the basic solution. The solutions of the radical were orange to orange brown.

Table II. Spontaneous Disproportionation of 3,6-Dimethyltetrazine at 25 ± 1°

Concn of 3,6-dimethyltetrazine, *M*	Solvent	Concn of potassium *t*-butoxide, *M*	Concn of radical anions, *M*	% conversion of tetrazine to radical anion
0.005	DMSO–*t*-BuOH (80:20)	0.05	0.003	60
0.002	DMSO–*t*-BuOH (80:20)	0.05	0.0006	30
0.003	DMSO–*t*-BuOH (80:20)	0.25	0.0005	17
0.007	*t*-BuOH	0.07	0.002	30
0.007	*t*-BuOH	0.14	0.0016	23
0.004	*t*-BuOH	0.04	0.0015	40

Spontaneous disproportion was not observed for the methyl-substituted pyrazines or *sym*-triazines under the conditions found to be successful to 3,6-dimethyltetrazine. Negative results were obtained for 2-methyl-4,6-diphenyltriazine, 2-methylpyrazine, and 2,5-dimethylpyrazine even in the presence of propiophenone anion. The pyrazine nucleus has been reduced by alkali metals to give the radical anions upon numerous occasions.[23,27] However, 1,4,5,8-bis(trimethylene)pyridazino[4,5-*d*]pyridazine (**4**)[28] underwent spontaneous disproportionation in basic solution to give a brown radical anion with nine main peaks (intensities 1:3.4:11:15:18.4:15:11:3.4:1) consistent with a^N = 3.44 G. Under higher resolution each peak was split further into nine lines due to the eight α-hydrogen atoms, $a^H \cong 0.2$ G.

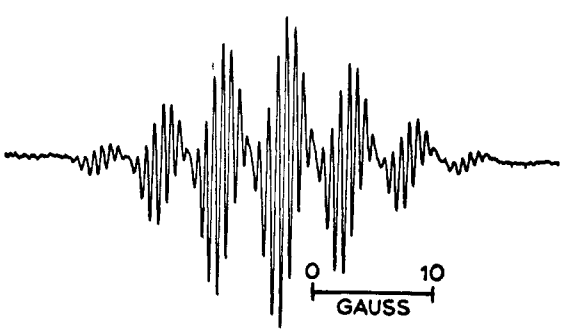
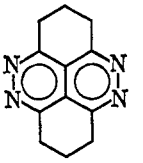


Figure 4. First derivative esr spectrum of 2,5-diaminotetrazine radical anion formed by reduction of 2,5-dimethyltetrazine (0.0025 *M*) by 0.025 *M* propiophenone, 0.1 *M* potassium *t*-butoxide in dimethyl sulfoxide–*t*-butyl alcohol (80:20) solution.



4

3,6-Diaminotetrazine failed to undergo the spontaneous disproportionation reaction in DMSO–*t*-butyl alcohol (80:20) solutions of potassium *t*-butoxide. However, the tetrazine could be reduced slowly with propiophenone enolate anion, or the anions formed from 9,10-dihydroanthracene, to yield a few per cent of the radical anions shown in Figure 4. The spectrum in Figure 4 is consistent with the 3,6-diaminotetrazine radical anion with a_{ring}^N = 5.07, $a_{NH_2}^N$ = 0.72, and a_{NH}^N = 0.72 G.

3,6-Diphenyltetrazine very slowly formed a few per cent of radical anion in DMSO–*t*-butyl alcohol (80:20) solutions of potassium *t*-butoxide. The esr spectrum had the proper intensities (nine lines) for four equivalent nitrogen atoms, a^N = 4.91 G, and no further hfs was detected. The lines were quite sharp. Mixtures of 3,6-diphenyltetrazine and 3,6-diphenyldihydrotetrazine gave very high concentrations of the radical anion (~50%) and the system is very similar to azobenzene–hydrazobenzene. Table III summarizes some pertinent experiments.

Preparation of Aliphatic or Vinylogous Analogs of the Azobenzene Radical Anion. Mixtures of phenylazomethane and the hydrazine in DMSO–*t*-butyl alcohol

(25) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).
(26) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962); **89**, 300 (1967).
(27) (a) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962); (b) R. L. Ward, *J. Am. Chem. Soc.*, **84**, 332 (1962); N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, **5**, 509 (1962); J. C. M. Henning and C. de Waard, *Phys. Letters*, **3**, 139 (1962).
(28) J. K. Stille and R. Ertz, *J. Am. Chem. Soc.*, **86**, 661 (1964).

Table III. Formation of 3,6-Diphenyltetrazine Radical Anion

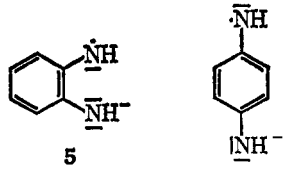
Concn of 3,6-diphenyl-tetrazine, *M*	Concn of 3,6-diphenyldihydro-tetrazine, *M*	Solvent	Concn of $KOC(CH_3)_3$, *M*	Concn of $R\cdot^-$, *M*	Color
0.005	...	DMSO–*t*-BuOH (80:20)	0.1	0.00012	Yellow
	0.005	DMSO–*t*-BuOH (80:20)	0.25	0.001[a]	Purple
	0.005	DMSO–*t*-BuOH (80:20)	0.25	0.0005[b]	Purple
0.0025	0.0025	DMSO–*t*-BuOH (80:20)	0.25	0.003	Yellow-orange
...	0.003	*t*-BuOH	0.15	0.00001	None
0.002	0.002	*t*-BuOH	0.20	0.001	Orange

[a] Solutions deoxygenated for 5 min with prepurified nitrogen before mixing. [b] Solutions deoxygenated or 20 min before mixing.

(80:20) containing potassium *t*-butoxide failed to give an esr signal and only a trace of an apparently seven-line radical was found when phenylazomethane was treated with the propiophenone enolate anion. Similar experiments with phenylazotriphenylmethane and phenylazodiphenylmethane failed to yield detectable esr signals. Whether radicals are not formed, or if formed are unstable, could not be determined. It appears that two phenyl rings are required for the formation of an acyclic azo radical anion stable at 25° in DMSO solution. Negative results were also obtained in attempted reduction of azoisobutane and tetramethyltetrazene by propiophenone enolate anion in DMSO.

Mixtures of dibenzoyldiimide and 1,2-dibenzoylhydrazine in the presence of base gave a barely detectable esr signal which decayed rapidly. However mixtures of diethyl azodiformate and diethyl dicarbamate gave a well-resolved spectrum of the expected radical anion, a^N = 6.31 and a^H (four equivalent) = 1.07 G.[29]

It is possible to prepare certain vinylogs of the azo radical anion and even some vinylogs of the parent diimide radical anion ($[NH{=}NH]\cdot^-$). Thus, the *o*- and *p*-phenylene derivatives, **5** and **6**, can be detected. However, the simple vinylogs of azo compounds **7** are not readily converted to radical anions. Compound **7**, R = C_6H_5, in basic DMSO solutions yields only the benzil radical anion, apparently *via* hydrolysis of the anil. The osazone of cyclohexane-1,2-dione gives rise



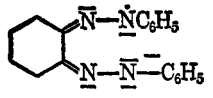
5

6

RN=CRCR=NR

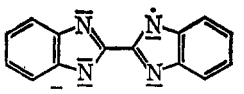
7

to a high concentration of radical anion when exposed to oxygen in basic solution of DMSO–*t*-butyl alcohol (80:20). It appears that the complicated esr pattern, some 36 G in width, is due to **8** in which the odd electron is distributed over four nitrogen and two carbon atoms. Reduction of $\Delta^{2,2'}$-bibenzimidazolylidene has

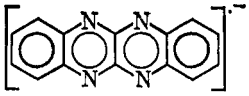


8

been reported to yield **9**,[24,30] which can be considered



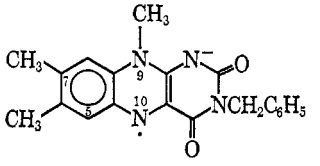
9



10

to be a vinylog of an azobenzene. However, the bibenzimidazolylidene is difficult to purify and usually contains traces of 5,6,11,12-tetraazanaphthacene.[31] Indeed, the spectrum attributed to **9** is readily obtained from the tetraazanaphthacene and is thus due to **10**. Pure $\Delta^{2,2'}$-bibenzimidazolidene fails to yield an esr signal under the conditions reported to yield **9**.

The radical anion of 3-benzyllumiflavin (**12**) is a



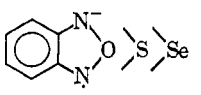
12

vinylog of an azo radical anion. Radical anion **12** is readily obtained by the spontaneous disproportionation of 3-benzyllumiflavin in basic solution. Hemmerisch has shown that in basic solution the lumiflavin couples through the C-7 methyl group to give dimers.[32] We are apparently dealing with an oxidation–reduction system similar to *p*-nitrotoluene and 3,6-dimethyltetrazine that can be generalized as

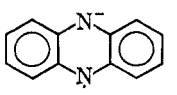
$$2\pi\text{-}CH_2^- + 2\pi\text{-}CH_3 \longrightarrow \pi\text{-}CH_2CH_2\text{-}\pi + 2CH_3\text{-}\pi\cdot^-$$

The esr spectrum obtained for **12** contained 14 lines and is similar to the spectrum reported by Guzzo.[33] Table IV summarizes some experiments in which the concentration of **12** was measured.

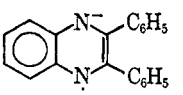
***o*-Phenylene Derivatives of Azo Radicals.** Radical anions **5** and **13**–**15** have been examined. *o*-Phenylenediamine gives a weak esr signal in DMSO–*t*-butyl



13



14



15

(29) A. Zweig and A. K. Hoffman, *J. Am. Chem. Soc.*, **85**, 2736 (1963), report the preparation of this radical anion by reduction with potassium metal in dimethoxyethane solutions, a^N = 5.9, a^H = 0.9 G.

(30) G. A. Russell and R. Konaka, *J. Org. Chem.*, **32**, 234 (1967).

(31) We wish to thank Professor S. Hünig for highly purified samples of the imidazolylidene and tetraazanaphthacene and for pointing out that the assignment of structure **10** might be in error; see also R. Kuhn, P. Skrabal, and P. H. H. Fischer, *Tetrahedron*, **24**, 1843 (1968).

(32) P. Hemmerisch, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **42**, 2164 (1959).

(33) A. V. Guzzo, *Arch. Biochem. Biophys.*, **105**, 380 (1964), reports a_9^V = 3.28, a_{10}^N = 6.56, $a_{C-7}^{CH_3}$ = 3.28, $a_{NCH_3}^{CH_3}$ = 3.28, and a_{C-5}^H = 3.28 G.

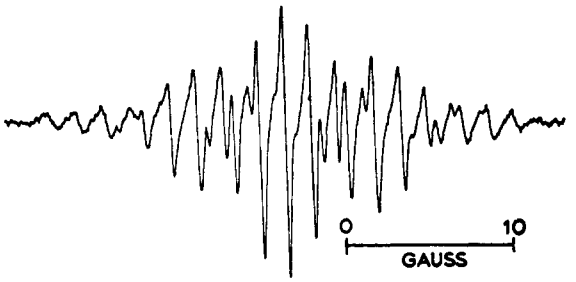


Figure 5. First derivative esr spectrum of phenazine radical anion in dimethyl sulfoxide–*t*-butyl alcohol (80:20) solution.

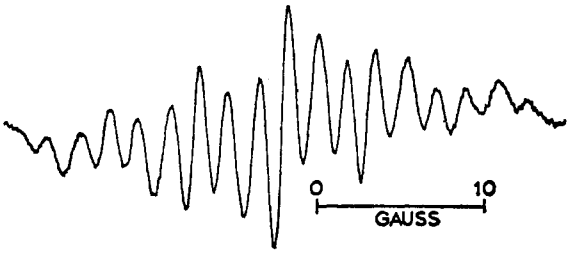


Figure 6. First derivative esr spectrum of 2,3-diphenylquinoxaline radical anion generated by electron transfer from 1,2-dihydro-2,3-diphenylquinoxaline to 2,3-diphenylquinoxaline in dimethyl sulfoxide–*t*-butyl alcohol (80:20).

alcohol (80:20) in the presence of potassium *t*-butoxide and a trace of oxygen. Under these conditions in 100% DMSO a strong signal of 19 lines is obtained. The signal is tentatively assigned to **5**. Cyclization of *o*-phenylenediamine by means of an oxygen, sulfur, or selenium atom yields the benzoxadiazole, benzothiadiazole, and benzoselenadiazoles. These substances

Table IV. Formation of Radical Anion of 3-Benzyllumiflavin at 25 ± 1° [a]

Solvent	Concn of $KOC(CH_3)_3$, *M*	Color	Concn of **12**, *M*
DMSO–*t*-BuOH (80:20)	0.1	Green-brown	0.00035, 40–210 min[b]
DMSO–*t*-BuOH (80:20)	0.1	Green-brown	0.0002, 12–55 min
t-BuOH	0.1	Yellow-green	0.0002, 15–60 min
DMF	0.001[c]	Yellow	$<1 \times 10^{-6}$

[a] 0.0025 *M* 3-benzyllumiflavin. [b] 0.025 *M* propiophenone. [c] K_2CO_3.

are readily reduced by the enolate anion of propiophenone in DMSO–*t*-butyl alcohol (80:20) solution to yield **13** whose spectra have been reported separately.[34]

Phenazine has been reduced to the radical anion **14** by alkali metals.[27a] Appreciable quantities of **14** are readily formed when phenazine and 9,10-dihydrophenazine are mixed in a DMSO–*t*-butyl alcohol (80:20) solution containing potassium *t*-butoxide. Dihydrophenazine is very easily oxidized in basic solution and is possibly dehydrogenated by DMSO in the presence of base. In any event, blank experiments involving solutions of dihydrophenazine in DMSO containing potassium *t*-butoxide yielded appreciable quantities of **14**. Table V summarizes some pertinent results.

The esr spectrum of **14** is given in Figure 5. The spectrum yields a^N (two equivalent) = 5.15, a^H (four equivalent) = 2.03, 1.56 G.[31] Electrolytic reduction of phenazine in DMSO has been reported to give the radical anion with a^N = 5.15, a^H = 1.80, 1.57 G.[25] Ward[27b] and Carrington and dos Santos-Viega[27a] prepared **14** by alkali metal reduction in dimethoxyethane and report (respectively) a^N = 5.0, a^H = 2.0, 16, and a^N = 5.14, a^H = 1.93, 1.61 G.

2,3-Diphenylquinoxaline reacts with 1,2-dihydro-2,3-diphenylquinoxaline in basic solutions of DMSO–*t*-butyl alcohol (80:20) to yield high concentrations of

(34) E. T. Strom and G. A. Russell, *J. Am. Chem. Soc.*, 87, 3326 (1965).

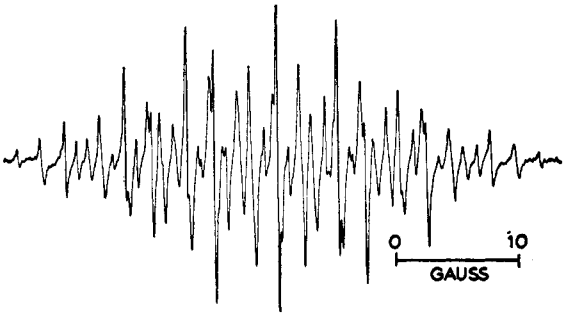


Figure 7. First derivative esr spectrum of radical anion generated by treatment of *p*-phenylenediamine with a trace of air in dimethyl sulfoxide solution containing excess potassium *t*-butoxide.

15. Radical anion **15** can also be prepared by reaction of a trace of oxygen with 1,2-dihydro-2,3-diphenylquinoxaline or by the reductions of 2,3-diphenylquinoxaline with the enolate anion of propiophenone. In all cases, a 17-line spectrum (Figure 6) with peak heights of 1:3.2:4.4:3.6:5.8:10.8:7.6:10.4:18.4:9.8:7.0:10.0:6.0:3.0:3.6:2.6:1 was observed. The spectrum is consistent with a^N (two equivalent) = 5.30 and a^H (four nearly equivalent) = 1.87 G. In dimethoxyethane it has been reported that for the quinoxaline radical anion that a^N = 5.64, a^H = 2.32 (four equivalent) and 1.00 (two equivalent), G.[27a]

Table V. Formation of Phenazine Radical Anions at 25 ± 1° in Dimethyl Sulfoxide–*t*-Butyl Alcohol Solutions[a]

Dihydrophenazine, *M*	Phenazine, *M*	Color	Concn of **14**, *M*	Yield of **14**, %
0.00125	0.00125	Purple	0.00068	27
0.0025	0.0025	Purple	0.0012 (7 min)	24
			0.0018 (10 hr)	36
0.0025	...	Purple-brown	0.001	44[b]
0.0025	...	Dark brown	0.0005	20[c]
0.0025	...	Dark brown	0.0005	20[d]

[a] 0.1 *M* $KOC(CH_3)_3$. [b] Solutions deoxygenated 5 min with prepurified nitrogen. [c] Deoxygenated 10 min. [d] Deoxygenated 30 min.

***p*-Phenylene Derivatives of Azo Radical Anions.** Radical anions **6** and **16** are readily prepared by autoxidation of *p*-phenyldiamine in 100% DMSO and of N,N′-diphenyl-*p*-phenylenediamine in DMSO–*t*-butyl alcohol (80:20). The spectrum of **6** is given in Figure 7.

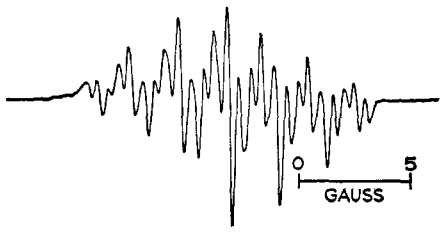
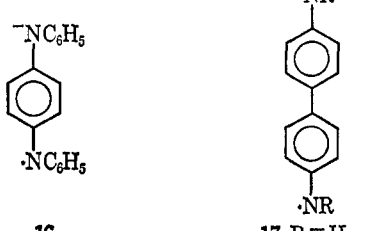


Figure 8. First derivative esr spectrum of 2,5-bis(*t*-butylamino)-*p*-benzosemiquinone in dimethyl sulfoxide–*t*-butyl alcohol (80:20) solution.

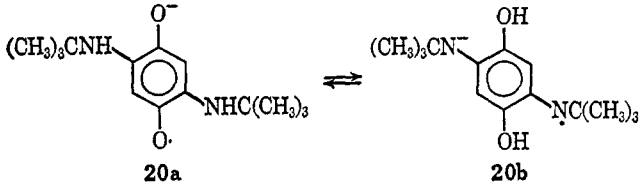
Figure 7 is consistent with a^N (two equivalent) = 5.10, $a_{CH}{}^H$ (four equivalent) = 1.96 and $a_{NH}{}^H$ (two equivalent) = 7.35 G. The assignment was confirmed by observing the spectra of the completely ring deuterated and the N,N′-dideuterio derivatives of **6**. As would be expected **16** gave a very complex spectrum. A main quintet due to a^N = 5.36 is readily discernable.



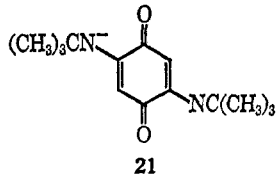
16 **17**, R = H; **18**, R = C_6H_5

Benzidine and N,N′-diphenylbenzidine are apparently converted to **17** and **18** by exposure to traces of oxygen in DMSO–*t*-butyl alcohol (80:20). The esr signals decayed rapidly; the hfs pattern appeared fairly complex, and no attempt was made to analyze the spectra.

2,5-Bis(*t*-butylamino)-*p*-benzoquinone and the corresponding hydroquinone were examined to ascertain if the radical preferred structure **20a** or **20b** and if the quinone could be further oxidized to **21**. Only one



20a **20b**



21

cherry red radical anion was observed under oxidative conditions (Figure 8), and we attribute it to the semiquinone **20a**. The hfsc observed were a^N (two equivalent) = 2.06, $a_{NH}{}^H$ (two equivalent) = 1.54, and $a_{CH}{}^H$ = 0.52 G (two equivalent). Table VI presents some typical data.

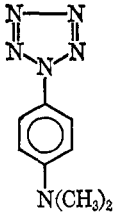
From the data of Table VI, it is seen that the quinone is not readily reduced in basic solution but that the hydroquinone is very easily oxidized.

Table VI. Formation of Radical Anion **20a** from 2,5-Bis(*t*-butylamino)-*p*-benzoquinone and 2,5-Bis(*t*-butylamino)-*p*-hydroquinone in Dimethyl Sulfoxide–*t*-Butyl Alcohol (80:20) at 25 ± 1° [a]

2,5-Bis(*t*-butylamino)-*p*-benzoquinone, *M*	2,5-Bis(*t*-butylamino)-*p*-hydroquinone, *M*	Concn of **20a**, *M*	Yield of **20a**, %
0.003	0.003	0.0044 (5 or 23 min)	88
	0.005[b]	0.0007	34[c]
0.0025	...	$<1 \times 10^{-6}$	0
0.0025	*d*	0.00006	2.5

[a] 0.1 *M* $KOC(CH_3)_3$. [b] Added as hydrochloride salt. [c] Solution deoxygenated 5 min before mixing. [d] 0.0025 *M* propiophenone.

Other Systems Investigated. Attempted reductions of *p*-dimethylaminophenylpentazole (**22**),[35] *p*-quinonedioximedimethyl ether, diphenylcarbodiimide, N-methylpyrazole, and γ,γ′-dipyridyl by propiophenone enolate anions or the anions derived from 9,10-dihydroanthracene gave traces of radical anions at most. The dipyridylethylenes and salts of N,N′-dibenzylviologin can be reduced to the radical anion and radical by the propiophenone enolate anion. These reactions will be considered at a later date.



22

Experimental Section

Esr Spectra. First derivative esr spectra were obtained at ~9.5 cps with a Varian V-4500 epr spectrometer and 6-in. magnet with 100-kcps field modulation. Solutions of donor, acceptor, and base were deoxygenated in an inverted U-type cell described previously[4] and then mixed and shaken down into a flat fused silica esr cell. Experiments were performed in a room thermostated at 23 ± 1°. However temperatures in the magnet gap were routinely 25 ± 1°.

Preparation of Azobenzenes. Aniline hydrochloride was converted to 2,4,6-trideuterioaniline by the procedure of Best and Wilson.[36] Analysis by nmr indicated the sample to contain 1.6% of undeuterated azobenzene. 2,3,5,6-Tetradeuterio-*p*-phenylenediamine was prepared by the procedure of Banthorpe and Hughes.[37] After five deuterium exchanges aromatic protons could not be detected by nmr. 2,3,5,6-Tetradeuterio-*p*-phenylenediamine was deaminated by hypophosphorous acid at 2–3° over a period of 70 hr to give 2,3,5,6-tetradeuterioaniline. The ratio of aromatic hydrogen to amino hydrogen was 1:2.03.

3,5-Dideuterioaniline was prepared by treatment of 2,3,5,6-tetradeuterioaniline (1.4 g) in 10 ml of ethanol with 50 ml of water and 1.3 ml of concentrated hydrochloric acid. Solvent was removed by distillation and the residue placed in a Carius tube containing 80 ml of water and heated at 100° for 24 hr. The aniline isolated analyzed by nmr as 62% 3,5-dideuterioaniline and 38% 2,3,5,6-tetradeuterioaniline. The procedure was repeated to give material that analyzed 88% 3,5-dideuterioaniline and 12% 2,3,5,6-tetradeuterioaniline.

Azobenzene-*o,o,o′,o′,p,p′*-d_6, azobenzene-*o,o,o′,o′,m,m,m′,m′*-d_8, and azobenzene-*m,m,m′,m′*-d_4 were prepared by coupling of the

(35) I. Ugi, H. Perlinger, and L. Behringer, *Chem. Ber.*, **91**, 2324 (1958)
(36) A. P. Best and C. D. Wilson, *J. Chem. Soc.*, 29 (1938).
(37) D. V. Banthorpe and E. D. Hughes, *ibid.*, 3308 (1962).

appropriate anilines with active manganese dioxide[38] by the method of Barakat and El-Sadr.[39] The hydrazobenzenes were prepared from the azo compounds by reduction with hydrogen using a palladium-on-charcoal catalyst in alcohol (ten parts)–water (two parts) solution.[40] The hydrazobenzene-*o,o,o',o',p,p'*-d_6 contained 2.1% undeuterated azobenzene by nmr.

***o,o,p*-Trideuterioazobenzene** was prepared by the condensation of nitrosobenzene and aniline in DMSO–*t*-butyl alcohol (80:20) solution.[41] Under a nitrogen atmosphere 190 mg (1.8 mmol) of nitrosobenzene, 170 mg (1.8 mmol) of *o,o,p*-trideuterioaniline in 5 ml of the solvent was added to 450 mg (4 mmol) of potassium *t*-butoxide in 20 ml of the solvent mixture. After shaking for 5 min the reaction products were poured into 50 ml of water. The precipitate was dissolved in ether and after evaporation of the ether yielded 130 mg of azobenzene-d_3, mp 65–66°, after recrystallization from methanol. Another 90 mg of azobenzene was obtained from the filtrate of the recrystallization. The total yields of azobenzene in two experiments were 67 and 77%. A standard solution of azobenzene-d_3 in dimethylsulfolane was prepared so that the ratio of azobenzene protons to dimethylsulfolane protons was expected to be 0.866. The experimental ratio was 0.868. The hydrazo compound and the radical anion were prepared. The radical anions confirmed the structural assignment given azobenzene radical anion since a^N = 4.84, a^H (two equivalent) = 2.81, a^H (single hydrogen) = 2.03 G. The hfs by *m*-hydrogen atoms was not resolved.

***cis*-Azobenzene** was prepared according to the procedure of Cook.[42] The product had mp 68° (mmp 40–41° with *trans*-azobenzene), λ_{max} at 294 mμ in ethanol (λ_{max} for *trans*-azobenzene is 315 mμ in ethanol) and gave nmr multiplets at τ 2.92 and 3.22 (τ values for *trans*-azobenzene multiplets are 2.17 and 2.60).

4-Aminobenzophenone was prepared[43] from the reaction of benzoyl chloride with aniline. The intermediate 4-benzoylaminobenzophenone had mp 152–153° (lit.[44] 150°) and the final product mp 122–123° (lit.[42] 123°). Oxidation of 4-aminobenzophenone with activated manganese dioxide yielded ***p*-azobenzophenone**, mp 219–220° (lit.[45] 217°). Repetition of the above experiment using *o,o,p*-trideuterioaniline yielded ***o,o,o',o'*-tetradeuterioazobenzophenone**, mp 220–221°.

Preparation of Tetrazines. 3,6-Dimethyltetrazine was prepared according to the procedure of Curtius.[46] By sublimations at 1 atm, red needles, mp 70–71°, were obtained. 2,5-Dimethyl-N-aminotriazole (mp 197–198°) was obtained as a by-product. ***sym*-Diaminotetrazine** was prepared according to Lin[47] from 5-methylthiosemicarbazide hydriodide[48] by oxidation at a pH of 8 to give red crystals that could be sublimed at 200° (2 mm), mp >300°.

3,6-Diphenyltetrazine was prepared from the reaction of benzonitrile with 96% hydrazine.[49] The reaction product was a mixture of colorless, yellow, and red crystals. The red and yellow crystals were dissolved by acetone. The residue from the acetone solution was dissolved in methanol to which 10% aqueous sodium nitrite solution was added. Addition of acetic acid caused blue-red crystals to precipitate, mp 195–196° (lit. 191°[49] and 195°[50]). 3,6-Diphenyltetrazine was reduced with zinc powder and acetic acid whence the red tetrazine was converted to a yellow substance. Cooling gave rise to a precipitate that was recrystallized from ethanol to give yellow crystals, mp 195–196° (on heating the yellow color changed to orange at 170–180° and to red above 190°). Treatment of a solution of the yellow crystals with sodium nitrite and acetic acid caused the yellow solution to become red. According to Pimner this compound is **diphenyldihydrotetrazine.**[51] From ir and nmr analysis it follows that the compound is either 1,2- or 1,4-dihydro-3,6-diphenyltetrazine.

Preparation of Other Reagents. Dihydrophenazine was prepared according to Morley[52] from catechol and *o*-phenylenediamine. Sublimation under vacuum at 200° yielded slightly green crystals, mp 280° dec (lit.[52] mp 280° dec).

2,5-Bis(*t*-butylamino)benzoquinone[53] was recrystallized from ethanol and sublimed at 150° under vacuum. The orange material melted at 242.5–243.5°, showed no hydroxyl bond in the ir, and had a sharp NH bond at 3330 cm^{-1}. The nmr spectrum showed NH, CH, or CH_3 protons in the ratio of 1:1:9. Reduction of the quinone with stannous chloride (1.5 g of stannous chloride, 1.5 ml of concentrated hydrochloric acid in 3 ml of water added to 0.25 g of quinone in 20 ml of warm ethanol). The colorless solution contained a white precipitate that was removed by filtration. The solution was concentrated on a steam bath to yield white crystals that gradually changed color to black upon heating (150–300°). The ir spectrum showed no carbonyl peak and had absorptions at 2400 and 3500 cm^{-1} (OH and NH_2^+). It was concluded that the compound is a hydrochloride of **bis(*t*-butylamino)benzohydroquinone.**

***o,o*-Dimethyl-*p*-quinonedioxime** was prepared from the dioxime (mp 249–250°) by reaction with methyl sulfate in aqueous basic solution at −10° followed by heating for 1 hr on a steam bath. Upon cooling white crystals were deposited which could be steam distilled to give white crystals, mp 95–96° upon crystallization from methanol. The ir and nmr spectra were consistent with the O-methyl ether structure and not with the N-methyl-N-oxide structure.

2,3-Diphenylquinoxaline[54] was prepared, mp 124.0–124.5° (lit. 126°[54] and 124°[55]). **1,2,-Dihydro-2,3-diphenylquinoxaline** was prepared according to the procedure of Hinsberg and König,[55] mp 143–145° (lit.[56] 148–149°). **Benzo[*c*]cinnoline** was prepared[56] and had mp 157–158° (lit.[56] mp 156°).

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