energetically possible. Actually, one must take into consideration the differences in energy in the π-electronic system too, but in these compounds they are smaller than the differences between the σ-bond energies. We cannot explain why in some cases only radicals formed by a replacement reaction are observed, whereas in other cases predominantly, or only, radicals formed by hydrogen addition on unsubstituted carbons are observed. Structural indices, bond orders, and free valences are of little help in the explanation. We do not know whether some of the compounds are in the lactam (2,4-dioxy) or lactim (2,4-dihydroxy) form. Whatever the form assumed, the replaceable substituted groups were never attached to the carbons with the largest free valence. In all cases where hydrogen addition occurs, the preferable places are the unsubstituted carbons C_5 or C_6.

The observed uracil-like hydrogen-addition radicals can be attributed to hydrogen addition on either C_5 or C_6 after the replacement. In the lactam form, both electronic indices and localization energies favor hydrogen addition on C_5 of the uracil.[7] Our experiments on 5-iodouracil proved that the hydrogen addition does occur on C_5. For the lactim form there is no experimental evidence. The free valence is slightly larger for C_5 than for C_6, but the localization energies are in favor of addition on C_6—2.55β for C_6 and 2.58β for C_5. The bond orders, free valences, and localization energies for these compounds were calculated in Hückel's approximation of molecular orbital theory, outlined by Pullman and Pullman.[8]

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Electron-Transfer Processes. VII. Formation of Paramagnetic and Condensation Products from Nitrosobenzene in Basic Solution[1]

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Abstract: The formation of nitrosobenzene radical anions and nitroxide-type radicals from nitrosobenzene is considered. In the presence of strong base nitrosobenzene forms the radical anion. The radical anion can be detected in appreciable quantity from mixtures of nitrosobenzene and phenylhydroxylamine in basic solution, and it is argued that the radical anion is an intermediate in the condensation reaction yielding azoxybenzene. The oxidative coupling of aniline by base and oxygen to yield azobenzene is considered and data are presented to show that the coupling proceeds *via* nitrosobenzene as an intermediate. Reactions of nitrosobenzene and phenylhydroxylamine in the absence of added base are shown to involve the formation of phenyl nitroxide. It is suggested that nitrosobenzene can also give rise to a stable species, $C_6H_5N(O\cdot)ONHC_6H_5$, previously assigned the $C_6H_5\dot{N}OH$ structure.

Nitrosobenzene can be converted to a number of paramagnetic species. Photolysis in tetrahydrofuran solution,[2] or reaction with phenylmagnesium halides[3] produces diphenyl nitroxide ($(C_6H_5)_2NO\cdot$). The product of photolysis in tetrahydrofuran may be a result of photolysis of the nitroso dimer.[4a] In dimethyl sulfoxide (DMSO) solution photolysis yields a mixture of phenyl nitroxide and diphenyl nitroxide, perhaps as a result of photolysis of monomeric and dimeric species. Alkylphenyl nitroxides can be prepared by photolysis of mixtures of nitrosobenzene and alkylnitroso compounds with red light.[4b] Upon heating, nitrosobenzene is reported to react with 2,3-dimethyl-2-butene to yield a radical assigned the structure $C_6H_5N(O\cdot)C(CH_3)_2C(CH_3){=}CH_2$.[5]

Reduction of nitrosobenzene in strongly basic solutions,[6] or electrochemically,[7] produces the nitrosobenzene radical anion ($C_6H_5NO\cdot^-$) while reduction with titanous ion in aqueous acid yields phenyl nitroxide ($C_6H_5NHO\cdot$).[6] The nitrosobenzene radical anion is also produced by the action of strong bases with nitrosobenzene, particularly in DMSO solution,[8] by the reaction of traces of oxygen with phenylhydroxylamine in basic solution,[9] or by electron transfer between nitrosobenzene and phenylhydroxylamine in basic solution (Figure 1A).[9] In the absence of added base, mixtures of nitrosobenzene and phenylhydroxylamine yield phenyl nitroxide (Figure 1B).[10] Phenyl nitroxide is

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(1) Reactions of Resonance Stabilized Anions. XXIX. This work was supported by grants from the National Science Foundation, Petroleum Research Fund, and the Air Force Office of Scientific Research.

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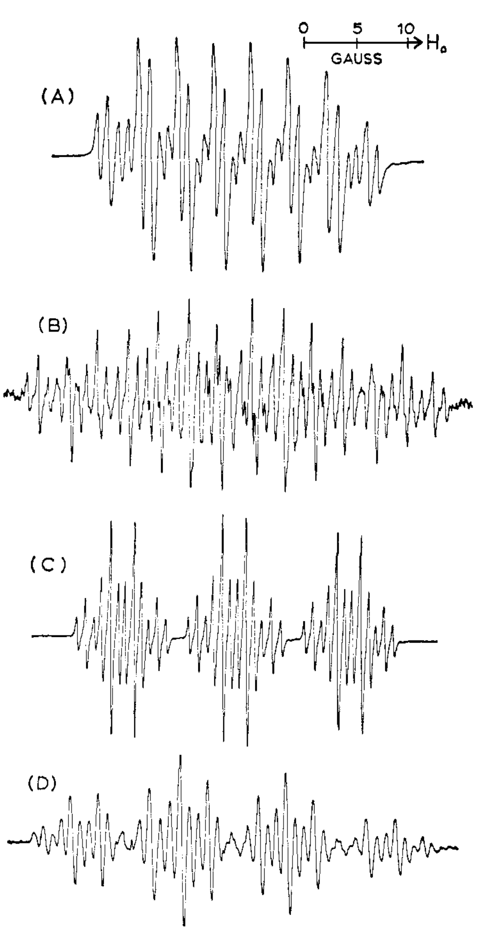
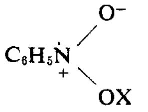


Figure 1. First-derivative esr spectra of paramagnetic intermediates formed from nitrosobenzene in dimethyl sulfoxide solution: (A) nitrosobenzene radical anion from disproportionation of nitrosobenzene and phenylhydroxylamine in presence of potassium *t*-butoxide; (B) phenyl nitroxide from disproportionation in absence of base; (C) radical formed by reduction of nitrosobenzene by sodium dithionite in presence of a trace of acetic acid; and (D) mixture of radicals responsible for spectra B and C observed (transitory) by treatment of nitrosobenzene with deficient quantities of potassium hydroxide.

also produced by the action of various inorganic oxidizing agents upon phenylhydroxylamine.[11] Both nitrosobenzene radical anion[10] and phenyl nitroxide[12] show restricted rotation about the bond between the aromatic ring and the nitrogen atom. Since one *ortho* and one *para* hydrogen are nearly magnetically equivalent, it has been a common error to assign the equivalent aromatic hydrogen atoms to the *ortho* positions.[6,8] In ammonia solution (−78°) it is possible to magnetically distinguish all five aromatic hydrogens in nitrosobenzene radical anion.[13]

Another paramagnetic reduction product of nitrosobenzene that is readily formed in DMSO and other solutions is shown in Figure 1C. This species is readily produced in moist DMSO or in DMSO containing acetic acid by dithionite reduction of nitrosobenzene and under these conditions is an extremely stable species. The species responsible for spectrum 1C was originally observed in the azobisisobutyronitrile-catalyzed oxidation of aniline.[14] It is also formed in the reaction of *t*-butyl hydroperoxide with phenylhydroxylamine or triphenylhydrazine[15,16] and in the reaction of nitrosobenzene with sodium methoxide in methanol.[7] The spectrum is very similar to that reported for $C_6H_5N(O\cdot)C(CH_3)_2C(CH_3){=}CH_2$ except that the latter radical shows an additional doublet splitting of 0.43 gauss in cyclohexane solution (for the *m*-Cl, *p*-Cl, *p*-CH_3, and *p*-CH_3O derivatives the doublet splitting is not reported).[17] Several authors have assigned the structure $C_6H_5\dot{N}OH$ to this species,[7,15,16] or to a time average between $C_6H_5\dot{N}OH$ and $C_6H_5NHO\cdot$.[14] However, the stability of this ubiquitous species, coupled with the fact that it can be detected in the presence of low concentrations of base, makes this structure appear unlikely to us.[18] Furthermore, there is no hydroxyl splitting apparent in spectrum 1C although such a splitting ($a^H = 0.38$ gauss) can be observed for $C_6H_5\dot{N}O_2H$ in tetrahydrofuran solution.[19] The spectrum of this species is rather similar to $C_6H_5N(O\cdot)OH$ and to $C_6H_5N(O\cdot)OC(CH_3)_3$,[20] and strongly suggests the general structure **1**. Structure **2** is a specific possibility.



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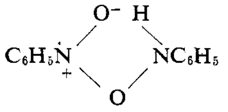

2

This radical is converted to nitrosobenzene radical anion by an excess of base, as is phenyl nitroxide. Mixtures of this radical with phenyl nitroxide can produce a fortuitous cancellation of peaks to yield a spectrum (Figure 1D) that can be misinterpreted as due to a single species. Such spectra are observed in DMSO solution upon reduction of nitrosobenzene with dithionite in the presence of traces of potassium *t*-butoxide, by the reaction of hydroxide ion with an excess of nitrosobenzene, or when phenyl nitroxide is treated with limited amounts of potassium *t*-butoxide.[21] In general spectrum 1D is transitory and eventually gives rise to spectrum 1C, perhaps due to the preferential destruction of phenyl nitroxide.

The formation of **2** can be readily envisioned as occurring by a reaction of nitrosobenzene radical anion with nitrosobenzene in the presence of a proton donor. The formation of **2** by dithionite reduction in the pres-

$$C_6H_5NO + SO_2\cdot^- \longrightarrow C_6H_5NO\cdot^- \overset{H^+}{\rightleftarrows} C_6H_5NHO\cdot$$

$$C_6H_5NO\cdot^- + C_6H_5NO \rightleftarrows [C_6H_5N(O\cdot)ONC_6H_5]^- \overset{H^+}{\rightleftarrows} \mathbf{2}$$

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(17) Note that a^N of 11.1 gauss for this radical is much less than the value of a^N reported for $C_6H_5N(O\cdot)C(CH_3)_3$ of 13.3 gauss: H. Lemaire, Y. Marechal, R. Ramesseul, and A. Rassat, *Bull. Soc. Chim. France*, 372 (1965).

(18) The species $C_6H_5\dot{N}OH$ has been invoked in the past as a reactive intermediate in the oxidation of phenylhydroxylamine: Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *J. Am. Chem. Soc.*, **86**, 3854 (1964); Y. Ogata and T. Morimoto, *J. Org. Chem.*, **30**, 597 (1965).

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(20) A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 385 (1967).

(21) Spectra similar to that in Figure 1D can also be obtained from mixtures of phenyl and diphenyl nitroxides wherein the triplet spectrum of diphenyl nitroxide "burns three holes" in the phenyl nitroxide spectrum. The spectrum reported for phenyl nitroxide prepared by the lithium aluminum hydride reduction of nitrobenzene [H. LeMaire, A. Rassat, and J.-P. Ravet, *Tetrahedron Letters*, 3507 (1964)] illustrates this behavior.

Table I. Hyperfine Splitting Constants of Stable Radical Produced by Sodium Dithionite Reduction of Nitrosobenzene[a]

Nitrosobenzene	Solvent	Hyperfine splitting constant, gauss a^N	$a^H_{triplet}$	$a^H_{quartet}$	Other
C_6H_5NO	DMSO	11.30	0.90	2.40	
C_6H_5NO	DMSO–HOAc (86:34)	11.46	0.90	2.40	
C_6H_5NO	DMSO–H_2O (40:60)	11.73	0.90	2.37	
C_6H_5NO	*t*-BuOH–H_2O (60:40)	11.84	0.91	2.46	
C_6H_5NO	C_2H_5OH	11.70	0.91	2.49	
C_6H_5NO	CH_3OH	11.69	0.90	2.49	
2,4,6-d_3-C_6H_5NO	DMSO	11.30	0.80	...	$a^D = 0.40$
p-$CH_3OC_6H_4NO$	DMSO	11.70	2.50, 0.80	0.30	
p-$CH_3CH_2OC_6H_4NO$	DMSO	11.73	2.44, 0.79, 0.30		
p-ClC_6H_4NO	DMSO	11.05	2.50, 0.90	...	$a^{Cl} \cong 0.18$
p-ClC_6H_4NO	C_2H_5OH	11.49	2.47, 0.90	...	$a^{Cl} \cong 0.21$

[a] 0.05 *M* nitrosobenzene or derivative in the presence of a saturated solution of sodium dithionite.

ence of acetic acid would undoubtedly be controlled by kinetic considerations.[22] Under other conditions, particularly at low concentrations of base, the formation of **2** may be controlled by other considerations; for example, it seems likely that **2** would be less acidic than phenyl nitroxide.

Table I summarizes hyperfine splitting constants observed for **2** in a number of solvents.

Reaction of Nitrosobenzene with Base. The reaction of nitrosobenzene under a nitrogen atmosphere in the presence of hydroxide or alkoxide ions in *t*-butyl alcohol, ethanol, or methanol gives rise to azoxybenzene in yields of 65–70%.[23] During the first 10–15 min of reaction, solutions that were originally 0.005–0.010 *M* in nitrosobenzene give rise to the nitrosobenzene radical anion in yields of about 1% based on starting nitrosobenzene. After reaction no trace of nitrobenzene could be detected in the product by glpc. Exposure of solutions to limited amounts of oxygen during the first few minutes of reaction yielded an esr spectrum of nitrobenzene radical after the nitrosobenzene had been consumed.

In aprotic solvents, such as DMSO, the nitrosobenzene radical anion is stable for hours and is not converted to azoxybenzene. Treatment of nitrosobenzene in DMSO with a large excess of potassium hydroxide or potassium *t*-butoxide gives rise to an appreciable concentration of nitrosobenzene radical anion. When an excess of base is not used, a variety of esr signals can be observed. Initially the nitrosobenzene radical anion is observed. Within a few minutes (C_6H_5NO = 0.02 *M*, KOH = 0.005 *M*) spectra similar to that of Figure 1D are obtained while after several hours the spectrum has changed to that of species **2** (*i.e.*, spectrum of Figure 1C). The reduction of nitrosobenzene apparently involves the formation of an adduct between hydroxide ion and nitrosobenzene that can donate an electron to another molecule of nitrosobenzene.[24]

$$C_6H_5NO + OH^- \longrightarrow [C_6H_5NO_2H]^- \rightleftarrows [C_6H_5NO_2]^{2-}$$

$$[C_6H_5NO_2]^{2-} + C_6H_5NO \longrightarrow C_6H_5NO\cdot^- + C_6H_5NO_2\cdot^-$$

$$C_6H_5NO_2\cdot^- + C_6H_5NO \rightleftarrows C_6H_5NO\cdot^- + C_6H_5NO_2$$

We have been unable to detect nitrobenzene as a reaction product. This suggests that the addition of hydroxide ion probably does not occur at the nitrogen atom of nitrosobenzene. Perhaps addition occurs to the aromatic ring, a process that would eventually yield a quinone type structure that could be destroyed by base. Nitrosobenzene is a better electron acceptor than nitrobenzene. This is obvious from the observation that addition of a slight stoichiometric excess of nitrosobenzene to nitrobenzene radical anion gives an esr spectrum showing only the nitrosobenzene radical anion.

Reaction of Nitrobenzene and Phenylhydroxylamine. In the absence of added base in DMSO, DMSO–*t*-butyl alcohol (80:20), DMSO–water (50:50), *t*-butyl alcohol, ethanol, or benzene the reaction of nitrosobenzene (5×10^{-3} *M*) and phenylhydroxylamine (5×10^{-3} *M*) gives rise to a low concentration ($\sim 10^{-4}$ *M*) of phenyl nitroxide. The concentration of radicals as measured by esr slowly decreases over a period of hours after which an essentially quantitative yield of azoxybenzene can be isolated.

The esr spectrum of phenyl nitroxide is quite sensitive to solvent although the actual hfsc as listed in Table II shows only a modest change with solvent.[25,26] The spectrum of phenyl nitroxide is unaffected by the addition of a large excess of nitrosobenzene, nitrobenzene, azobenzene, azoxybenzene, or phenylhydroxylamine. Addition of an excess of acetic acid gives rise to spectra similar to 1D with an over-all decrease in the total radical concentration.

Reaction of nitrosobenzene (5×10^{-3} *M*) and phenylhydroxylamine (5×10^{-3} *M*) in the presence of excess (5×10^{-2} *M*) potassium *t*-butoxide in deoxygenated DMSO–*t*-butyl alcohol (80:20) solution at 23 ± 1° produces essentially a quantitative yield of nitrosobenzene radical anion in <0.5 sec. The radical anion is undoubtedly produced by the following reaction sequence.

$$C_6H_5NHOH \overset{OH^-}{\rightleftarrows} \overset{OH^-}{\rightleftarrows} C_6H_5NO^{2-}$$

$$C_6H_5NO^{2-} + C_6H_5NO \rightleftarrows 2C_6H_5NO\cdot^-$$

The formation of nitrosobenzene radical anion (**3**) represents another example of the electronic dispro-

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(22) The possibility that this reduction involves electron transfer and protonation of the nitroso dimer cannot be overlooked. It is also possible that $C_6H_5\dot{N}OH$ might be a precursor to **2**.

(23) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Japan*, **36**, 728 (1963).

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

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(26) The solvent effects observed support the formulation of phenyl nitroxide as $C_6H_5\dot{N}H^+–O^-$.

Table II. Hyperfine Splitting Constants (gauss) of Phenyl Nitroxides in Various Solvents at 23 ± 1°

Solvent	Hyperfine splitting constants				
	a^N	$a_o^H \cong a_p^H$	a_m^H	a_{NH}^H	a^D
DMSO	8.89	3.01 (2) 2.80 (1)	0.97	11.75	
DMSO–*t*-BuOH (80:20)	9.10	3.00	1.04	11.90	
DMSO–*t*-BuOH (50:50)	9.10	3.10	1.05	12.40	
DMSO–*t*-BuOH[a] (50:50)	9.50	3.07	0.95	...	1.84
C_6H_6	9.02	2.88	1.00	11.87	
t-BuOH	8.65	2.96	1.00	11.08	
C_2H_5OH	8.80	3.08	1.02	12.00	
C_2H_5OH[b]	8.76	...	1.00	12.00	0.46
DMSO	8.90	2.98	1.00	11.70	
DMSO–*t*-BuOH[c] (80:20)	8.95	3.00	1.00	11.75	

[a] Reaction product of nitrosobenzene and O,N-dideuteriophenylhydroxylamine. [b] Reaction product of 2,4,6-trideuterionitrosobenzene and 2,4,6-trideuteriophenylhydroxylamine. [c] Reaction product of *p*-chloronitrosobenzene and *p*-chlorophenylhydroxylamine.

portionation between unsaturated molecules and their dianions ($\pi + \pi^{2-} \rightleftarrows 2\pi\cdot^-$).[27] In DMSO–*t*-butyl alcohol (80:20) **3** is very stable and decays only slowly over a period of days. We have been unable to form **3** from the reaction of hydroxide ion with azoxybenzene in this solvent at 23°. However, a solution of azoxybenzene (0.05 *M*) in pure DMSO 50% saturated with potassium hydroxide slowly forms the nitrosobenzene radical anion, presumably by the following reactions.

$$OH^- + C_6H_5N(O){=}NC_6H_5 \rightleftarrows C_6H_5N(O^-)N(OH)C_6H_5 \overset{OH^-}{\rightleftarrows}$$

$$H_2O + C_6H_5N(O^-)N(O^-)C_6H_5 \rightleftarrows 2C_6H_5NO\cdot^-$$

In ethanol containing sodium hydroxide, nitrosobenzene and phenylhydroxylamine rapidly react to yield up to 96% of azoxybenzene. Nitrosobenzene radical anions can be detected and identified under flow conditions but rapidly decay when the flow is stopped. In *t*-butyl alcohol containing potassium *t*-butoxide **3** can be detected but decays rapidly. A plot of the concentration of **3** as a function of time for the reaction in ethanol solution is given as Figure 2 in ref 9. Some typical concentrations of **3** detected in a flow system are listed in Table III. Under flow conditions the mixed solution underwent a blue to green to yellow color transformation in a matter of seconds, the blue and yellow representing the colors of nitrosobenzene and azoxybenzene, respectively. The decay curve for nitrosobenzene radical anion (Figure 2, ref 9) is second order in radical anion concentration from 5 × 10⁻³ *M* to 2.5 × 10⁻⁴ *M* with a rate constant of 1.40 × 10² l./mole sec. The kinetics and esr results suggest the occurrence of either process A or process B.

Table III. Detection of Nitrosobenzene Radical Anion from Reaction of Nitrosobenzene (0.005 *M*) and Phenylhydroxylamine (0.005 *M*) in Basic Solution at 23 ± 1°

Solvent	Base, 0.05 *M*	Flow time, sec	Concn of **3**,[a] mole/l.
EtOH	NaOH	0.38	0.0050
EtOH	NaOH	0.48	0.0049
t-BuOH	$KOC(CH_3)_3$	0.60	0.0086
DMSO–*t*-BuOH (80:20)	$KOC(CH_3)_3$	0.50	0.010

[a] Estimated experimental uncertainty, ±30%.

$$2C_6H_5NO\cdot^- \rightleftarrows C_6H_5N(O^-)N(O^-)C_6H_5 \xrightarrow{H^+,\ \text{slow}} \underset{\mathbf{4}}{C_6H_5N(O^-)N(OH)C_6H_5} \quad (A)$$

$$C_6H_5NO\cdot^- \overset{H^+}{\rightleftarrows} C_6H_5\dot{N}OH \xrightarrow{\mathbf{3},\ \text{slow}} \mathbf{4} \quad (B)$$

$$\mathbf{4} \xrightarrow{\text{irreversibly}} C_6H_5N(O){=}NC_6H_5 + OH^-$$

We cannot distinguish kinetically between processes A and B. Because of the concentrations of **3** observed, it must follow that any equilibrium involving **3** lies considerably toward the side of the free nitrosobenzene radical anion. Apparently in DMSO–*t*-butyl alcohol (80:20) containing potassium *t*-butoxide the low activity of protons, or a value of the equilibrium constant that greatly favors **3**, prevents the last step of the condensation from occurring. In Table IV are listed the observed hyperfine splitting constants for **3** and some of its deuterio derivatives in a variety of solvents.

Our results on the mechanism of the coupling of nitrosobenzene and phenylhydroxylamine provide a full explanation of a number of earlier results. Bamberger and Renauld in 1897[28] found that nitrosobenzene reacted with substituted phenylhydroxylamines to give both symmetrical azoxy compounds. These results have been confirmed[29] and in one case both cross-condensation products have been isolated.[30] One possible explanation advanced was that interconversion of the nitroso compound and phenylhydroxylamine had occurred prior to condensation.[31] A symmetrical intermediate of type $C_6H_5N(O^-)N(O^-)C_6H_5$ has been proposed on the basis of ^{15}N- and ^{18}O-labeling experiments.[23,32–34] In ethanol containing potassium hydroxide there is a statistical scrambling of ^{15}N in the isolated azoxybenzene,[32] and exactly 50% of the ^{18}O of labeled phenylhydroxylamine is lost.[33]

The Oxidation of Nitrosobenzene, Phenylhydroxylamine, and Aniline in Basic Solution. Exposure of solutions of the nitrosobenzene radical anion to oxygen destroyed the esr signal. Such solutions on standing usually developed slowly the esr signal of nitrobenzene radical anion. Reaction of oxygen with nitrosobenzene in *t*-butyl alcohol solution containing an excess of potassium *t*-butoxide occurs readily. In a typical experiment 1 mole of nitrosobenzene absorbed 0.88 mole of oxygen and was converted to nitrobenzene in

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Table IV. Hyperfine Splitting Constants of Nitrosobenzene Radical Anions (RNO·⁻) at 23 ± 1°

R =	Solvent	Splitting constants, gauss a^N	a_o^H	a_p^H	a_m^H	a^D
C_6H_5	DMSO-*t*-BuOH (80:20)	7.90	3.90, 2.83	3.90	1.01	...
C_6H_5	*t*-BuOH	9.30	4.00, 3.45	4.00	1.25	...
C_6H_5	C_2H_5OH	10.10	4.02, 3.65	4.02	1.29	...
p-DC_6H_4	DMSO-*t*-BuOH (80:20)	8.00	3.90, 2.90	...	1.00	0.59
p-DC_6H_4	*t*-BuOH	9.38	3.99, 3.40	...	1.28	0.60
p-DC_6H_4	C_2H_5OH	10.02	4.04, 3.52	...	1.23	0.61
p-ClC_6H_4	DMSO-*t*-BuOH (80:20)	7.57	3.82, 2.78	...	1.18	
p-ClC_6H_4	*t*-BuOH	9.28	3.90, 3.48	...	1.22	
p-ClC_6H_4	C_2H_5OH	9.68	4.05, 3.53	...	1.24	
2,4,6-$C_6H_2D_3$	DMSO-*t*-BuOH (80:20)	7.90				
2,4,6-$C_6H_2D_3$	*t*-BuOH	9.38				
2,4,6-$C_6H_2D_3$	C_2H_5OH	10.10				

63% yield. The only other reaction product detected was azoxybenzene.

The autoxidation of phenylhydroxylamine in methanol has been reported to give azoxybenzene as the only product.[18] In *t*-butyl alcohol solution containing excess potassium *t*-butoxide, phenylhydroxylamine oxidized very rapidly with the absorption of about 0.9 mole of oxygen/mole of phenylhydroxylamine. Analysis of the oxidation product by gas–liquid partition chromatography revealed that 46% of the phenylhydroxylamine had been converted to nitrobenzene and the remainder to azoxybenzene. The azoxybenzene formed in the oxidation of both nitrosobenzene and phenylhydroxylamine may result from the coupling of nitrosobenzene radical anions. If this is the case, the radical ion must not be immediately destroyed by oxygen under the normal reaction conditions in which the solutions are vigorously shaken in the presence of oxygen at 1-atm pressure.[35]

Aniline does not react readily with oxygen in *t*-butyl alcohol solution containing excess potassium *t*-butoxide at room temperature. However, in DMSO solution containing excess potassium *t*-butoxide, aniline is converted to azobenzene in 80–90% yield with the absorption of about 1 mole of oxygen/mole of aniline.[36] An esr signal could not be detected during the course of this oxidation or from interrupted oxidations.

Two mechanisms for the formation of azobenzene by the oxidation of aniline in basic solution appear reasonable. A coupling of anilino radicals may be involved,[36b] or the azobenzene may result from the base-catalyzed condensation of initially formed nitrosobenzene with unreacted aniline. We favor the later mechanism on the basis of experiments performed in which a small amount of radioactive nitrosobenzene was slowly added to the oxidizing solution of aniline. In a typical experiment 2.17% (based on starting aniline) of ^{14}C-nitrosobenzene was slowly added to the oxidizing solution at a rate proportional to the rate of oxygen absorption. Purified azobenzene was isolated from the reaction product in a yield of 45%. This sample of azobenzene was found to contain 34.3% of the activity of the nitrosobenzene added. It thus appears that nitrosobenzene when purposefully added to an oxidizing solution of aniline is converted to azobenzene in about the same yield as observed for aniline itself.[37]

The formation of azobenzene *via* the coupling of anilino radicals can also be eliminated by a consideration of the stoichiometry since this mechanism would require the intermediacy of hydrazobenzene. Under reaction conditions wherein aniline is converted to azobenzene with the absorption of 1 mole of oxygen/mole of aniline, the oxidation of hydrazobenzene to azobenzene itself requires 2 moles of oxygen/mole of hydrazobenzene. A mechanism involving hydrazobenzene as an intermediate would require *at least* 1.25 moles of oxygen/mole of aniline.

$$2C_6H_5NH_2 + 0.5O_2 \xrightarrow{B^-} 2C_6H_5NH\cdot + H_2O$$

$$2C_6H_5NH\cdot \longrightarrow C_6H_5NHNHC_6H_5$$

$$C_6H_5NHNHC_6H_5 + 2O_2 \xrightarrow{B^-} C_6H_5N{=}NC_6H_5 + 2O_2\cdot^-$$

The formation of superoxide ion was verified in the oxidation by analysis by the procedure of Seyb and Kleinberg.[38] In 10 ml of DMSO-*t*-butyl alcohol (80:20), 0.91 mmole of hydrazobenzene in the presence of 6.3 mmoles of potassium *t*-butoxide absorbed a total of 1.88 mmoles of oxygen at a pressure of 732 mm (complete reaction, 30 min, 26°) to yield 0.91 mmole of azobenzene and 1.73 mmoles of potassium superoxide (KO_2). In DMSO-*t*-butyl alcohol (50:50), the stoichiometry of hydrazobenzene oxidation was also observed to be 2 moles of oxygen/mole of hydrazobenzene (azobenzene yield = 100%). However, in *t*-butyl alcohol containing potassium *t*-butoxide or methanol containing sodium methoxide high yields of azobenzene were obtained after the absorption of 1 mole of oxygen/mole of hydrazobenzene.[39] Possibly in the latter solvents the oxidation of hydrazobenzene involves the sequence[40]

$$C_6H_5NHNHC_6H_5 \rightleftharpoons [C_6H_5NHNC_6H_5]^- \xrightarrow{O_2}$$

$$C_6H_5NHN(OO^-)C_6H_5 \xrightarrow{B^-} C_6H_5N{=}NC_6H_5 + O_2^{2-}$$

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(35) The mechanism of the formation of azoxybenzene in these oxidations will be considered in a future publication by R. Konaka, K. Kuruma, and S. Terabe of the Shionogi Research Laboratory.

(36) (a) G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962); (b) L. Horner and J. Dehnert, *Ber.*, **96**, 786 (1963); (c) R. Anschütz and G. Schulz, *ibid.*, **10**, 1802 (1877); A. Bacovescu, *ibid.*, **42**, 2938 (1909).

(37) The formation of dibenzo[*a,h*]phenazine from the oxidation of α- or β-naphthylamine reported by Horner and Dehnert does appear to require a radical coupling mechanism.[36b]

(38) E. Seyb and J. Kleinberg, *Anal. Chem.*, **23**, 115 (1951).

(39) W. Manchot and Y. Herzog, *Ann.*, **316**, 331 (1901), reported similar stoichiometries in ethanol containing sodium hydroxide. A. Étienne and J.-P. Zumbrunn, *Compt. Rend.*, **257**, 3624 (1963), report a peroxide of hydrazobenzene obtained by autoxidation of hydrazobenzene in tetrahydrofuran solution.

(40) See also D. A. Blackadder and C. Hinshelwood, *J. Chem. Soc.*, 2898 (1957).

In the more basic systems dianions and radical anions are apparently involved.

$$[C_6H_5N\text{-}NC_6H_5]^{2-} + O_2 \longrightarrow [C_6H_5N{=}NC_6H_5]\cdot^- + O_2\cdot^-$$

$$[C_6H_5N{=}NC_6H_5]\cdot^- + O_2 \longrightarrow C_6H_5N{=}NC_6H_5 + O_2\cdot^-$$

Exposure of a solution of azobenzene radical anion[41] to oxygen resulted in the consumption of 1 mole of oxygen/mole of radical anion and the formation of azobenzene and potassium superoxide.[42] In a solvent composed of 80% *t*-butyl alcohol and 20% dimethyl sulfoxide, hydrazobenzene gave a 100% yield of azobenzene after the absorption of 1.79 moles of oxygen/mole of hydrazobenzene (hydrazobenzene:potassium *t*-butoxide, 0.09 *M*:0.63 *M*). Apparently both mechanisms are occurring. In this solvent, or in *t*-butyl alcohol, the initially formed potassium peroxide (K_2O_2) slowly reacts with more oxygen to yield potassium superoxide so that the oxygen absorptions can be forced to approach 2 moles of oxygen/mole of hydrazobenzene under very long reaction periods.

The rates of oxidation of a number of substituted anilines are given in the Experimental Section. The rates apparently parallel the stability of the nitranions. Very stable nitranions such as derived from 2- or 4-nitroaniline or 4-cyanoaniline are oxidized very slowly. On the other hand electron-supplying groups such as the 4-oxy anion ($-O^-$), 4-amino, or 4-thiophenyl cause the anilino anion to undergo rapid oxidation. Similar rate effects were also observed in the oxidation of a series of diphenylamines in basic solution where the diaryl nitroxides are presumably an important reaction product.

The base-catalyzed condensation of nitrosobenzene and aniline in *t*-butyl alcohol or DMSO–*t*-butyl alcohol (80:20) is an excellent reaction for the preparation of azo compounds and particularly azobenzenes with unsymmetrical substitution. Only a single azo compound is formed and the reaction appears to be mainly ionic.

$$\left.\begin{array}{l} XC_6H_4NO + C_6H_5NH_2 \\ \\ C_6H_5NO + XC_6H_4NH_2 \end{array}\right] \xrightarrow{B^-} XC_6H_4N{=}NC_6H_5 + H_2O$$

Experimental Section

Esr Spectra. The esr spectra were recorded in a flat fused silica cell (Varian Associates aqueous sample cell) with a Varian V-4500 spectrometer with 100-kc/sec field modulation and a 9-in. magnet. Concentrations were estimated by comparison of peak heights for overmodulated spectra of diphenylpicrylhydrazyl and the radical being measured in the same solvent and at identical instrumental settings. Field scans were calibrated by use of *p*-benzosemiquinone.

Samples were prepared by use of an inverted U-type mixing cell or a flow system described previously.[24,43] Solutions of nitrosobenzene in the desired solvent were deoxygenated in one leg of the cell by a stream of prepurified nitrogen. Such solutions were mixed with deoxygenated solutions of reducing agent, base, phenylhydroxylamine, or base plus phenylhydroxylamine from the other leg of the mixing cell. Under certain conditions concentrated solutions of the reactants were added to deoxygenated solutions in the mixing cell *via* hypodermic syringe. No special precautions were taken to exclude the occurrence of photochemical electron-transfer reactions.[44]

Reagents. All nitrosobenzenes and phenylhydroxylamines had the correct melting point, nmr, and infrared spectra. Nitrosobenzene from a variety of sources was found to contain paramagnetic organic substances. Nitrosobenzene was recrystallized several times from ethanol and stored in the dark at 0°. Such material gave only a trace (<0.01%) of paramagnetic impurities for a period of several weeks.

Phenylhydroxylamine, *p*-chlorophenylhydroxylamine, and 2,4,6-trideuteriophenylhydroxylamine were prepared by reduction of the corresponding nitro compounds with zinc dust in aqueous ammonium chloride solution. *p*-Chloronitrosobenzene was prepared by the oxidation of *p*-chlorophenylhydroxylamine with aqueous potassium dichromate; *p*-deuterionitrosobenzene and 2,4,6-trideuterionitrosobenzene were prepared by the oxidation of the corresponding anilines with neutralized Caro's acid. Typical procedures are described for the 2,4,6-trideuterio derivative.

2,4,6-Trideuterioaniline was prepared by the reaction of 40 g of aniline hydrochloride and 27 g of deuterium oxide at 100° for 24 hr.[45] After repetition of the experiment five times the ratio of *o*- and *p*-hydrogen atoms to *m*-hydrogen atoms was determined to be 0.0215:1 by nmr spectroscopy. 2,4,6-Trideuterioaniline·DCl was dissolved in 50 ml of water and *immediately* basified with 10% aqueous sodium hydroxide, extracted with ether, washed with water, and dried over magnesium sulfate. Vacuum distillation yielded 5.8 g of 2,4,6-trideuterioaniline which showed by nmr the presence of 1.6% of *o*- and *p*-hydrogen atoms. A solution of 3.9 g of 2,4,6-trideuterioaniline·DCl was basified in 20 ml of water with 10% sodium carbonate solution. To this solution was added neutralized Caro's acid prepared by the careful grinding of 18 g of potassium persulfate and 15 ml of concentrated sulfuric acid in a mortar at 0°. After 1 hr this mixture was poured into 100 g of ice and neutralized to pH 6 by 30 g of sodium carbonate with cooling. Upon adding the aqueous aniline solutions to the neutralized Caro's acid a brown oil was produced that soon crystallized. The crystals were separated by filtration after 15 min and steam distilled to yield 0.9 g of pale yellow crystals. Recrystallization from ethanol yielded 0.5 g of 2,4,6-trideuterionitrosobenzene, mp 66.5–67.5°. Analysis by nmr indicated the presence of 3% of *o*- and *p*-hydrogen atoms.

O,N-Dideuteriophenylhydroxylamine was prepared by crystallization of phenylhydroxylamine from deuterium oxide. The absence of hydroxyl and amino hydrogen atoms was verified by nmr spectroscopy.

2,4,6-Trideuterioazobenzene was prepared by the condensation of 2,4,6-trideuterioaniline and nitrosobenzene. A 100-ml flask was equipped with a retort-shaped side arm, a capillary tube for deoxygenation, and a vacuum connection. A solution of 450 mg of potassium *t*-butoxide in 20 ml of DMSO–*t*-butyl alcohol (80:20) was deoxygenated by a stream of nitrogen. To this solution was added from the side arm a mixture of 190 mg of nitrosobenzene and 170 mg of 2,4,6-trideuterioaniline in 5 ml of the solvent. The mixture was shaken for 5 min and poured into 50 ml of water to give a colloidal suspension of an orange precipitate. Extraction with ether followed by recrystallization from methanol yielded 220 mg (67%) of trideuteriozobenzene, mp 65–66°. The integrated nmr spectra of this azobenzene in the presence of dimethyl sulfone in carbon tetrachloride was obtained. The expected ratio on the basis of 100% purity was azobenzene hydrogens:dimethyl sulfone hydrogens = 0.866. The observed ratio was 0.868.

2,4,6-Trideuterioaniline was converted to the acetanilide with acetyl chloride and oxidized to 2,4,6-trideuterionitrobenzene in acetic acid with 30% hydrogen peroxide. The yield of distilled 2,4,6-trideuterionitrobenzene was 5–10%.

^{14}C-Aniline hydrochloride was converted to ^{14}C-nitrosobenzene by the technique described above. The ^{14}C-nitrosobenzene had mp 67–68° and a radioactivity of 93,000 dpm/mg as determined by

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[41] Prepared from equal amounts of azobenzene and hydrazobenzene in DMSO–*t*-butyl alcohol (80:20) in the presence of a large excess of potassium *t*-butoxide. Under these conditions the value of K_e has

$$C_6H_5N{=}NC_6H_5 + [C_6H_5N\text{—}NC_6H_5]^{-2} \xrightleftharpoons{K_e} 2[C_6H_5N\text{-}NC_6H_5]\cdot^-$$

been estimated by esr spectroscopy [E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965)] to be 2.7 [E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, **1**, 13 (1965)].

[42] For a similar oxidation of radical anions of nitrobenzene, see G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

[43] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selected Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

[44] G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

[45] A. P. Best and C. D. Wilson, *J. Chem. Soc.*, 29, (1938).

liquid scintillation counting in a Packard Model 3002 scintillation spectrometer.

Oxidation of Aniline in Basic Solution. In the presence of 750-mm partial pressure of oxygen, 732 mg (6 mmoles) of sublimed potassium *t*-butoxide in 20 ml of DMSO–*t*-butyl alcohol (80:20) was vigorously stirred. From a retort-shaped side arm was added 276 mg (3 mmoles) of aniline in 3 ml of the solvent. Oxygen absorption was followed by a gas buret at constant pressure. During the reaction a solution of 6.96 mg (0.065 mmole) of ^{14}C-nitrosobenzene was added dropwise from a buret at a rate commensurate with the rate of oxygen absorption. A total of 2.97 mmoles of oxygen was absorbed during the 1-hr period. The reaction product was poured into 100 g of ice and water and the resulting mixture extracted with ether. Chromatography of the ethereal concentrate over 60 g of alumina and elution with petroleum ether (bp 30–60°) yielded 121 mg (45%) of azobenzene, mp 66–68°. Recrystallization from petroleum ether sharpened the melting point to 67–68°. The nitrosobenzene employed had a total radioactivity of 651,000 dpm. The azobenzene isolated (121 mg) had a radioactivity of 222,300 dpm with 34% of the radioactivity present in the nitrosobenzene added.

Table V. Oxidation of Aniline (6 mmoles) in the Presence of Potassium *t*-Butoxide (12 mmoles) at 25° in 50 ml of DMSO–*t*-Butyl Alcohol (80:20)

C_6H_5NO added, mmole	Oxygen adsorbed, mmole	Azobenzene, mmole	Polymer, mg
0.0	6.1	2.11	70
0.75	5.2	2.40	70
1.50	5.3	2.8	66
3.00	5.4	3.5	66

Table VI. Oxidation of 3 mmoles of Aniline ($XC_6H_4NH_2$) in the Presence of 8 mmoles of Potassium *t*-Butoxide in 25 ml of DMSO–*t*-Butyl Alcohol (80:20) at 25°

X =	Total oxygen absorbed, mmoles	Time, min	% $XC_6H_4N{=}NC_6H_4X$	Mp, °C	Lit. mp, °C
H	3.01	60	85	67–68	68
3-Cl	4.20	60	14	98–100	101[a]
4-Cl[b]	7.70	147	55	187–188	188[c]
4-Br[b]	8.10	104	51	204–205	205[a]
2-C_6H_5	3.90	54	41	145–146	144[d]
4-C_6H_4S	4.10	52	68	132–133	

[a] A. Laubenheimer, *Ber.*, **8**, 1621 (1875). [b] Nine mmoles of aniline, 24 mmoles of potassium *t*-butoxide, 75 ml of solvent. [c] J. Burns, H. McCombie, and H. L. Scarborough, *J. Chem. Soc.*, 2933 (1928). [d] F. Bell, *ibid.*, 2773 (1928).

Table V summarizes the formation of azobenzene from oxidation of aniline in the presence of massive amounts of nitrosobenzene. Again there is evidence that the azobenzene is formed by condensation of nitrosobenzene and aniline.

A variety of symmetrically substituted azobenzenes were prepared by oxidation of substituted anilines. In a typical experiment 2,2′-dichloroazobenzene was prepared in 66% yield by the reaction of oxygen with 3 mmoles of *o*-chloroaniline in 25 ml of DMSO–*t*-butyl alcohol (80:20) containing 8 mmoles of potassium *t*-butoxide at 25°. In 50 min a total of 4.0 mmoles of oxygen had been absorbed. The purple solution was poured into 50 ml of water and the orange precipitate filtered and washed with water until neutral to give 370 mg of material, mp 122–135°. This material was treated with chloroform to yield an insoluble fraction having mp 280°. The chloroform solution (5 ml) was chromatographed on a 70 × 2.75 cm column packed with 60 × 200 mesh Davison silica gel and eluted with hexane-benzene mixtures. Fractions 8–11 were eluted with a total of 2 l. of a solvent mixture containing 25% benzene and yielded 267 mg of 2,2′-dichloroazobenzene upon evaporation of solvent, mp 137–138° (lit.[46] mp 137°). Yields of other azobenzenes are gnive in Table VI.

o- or *p*-Nitroaniline failed to absorb oxygen under the reaction conditions of Table VI. Moreover, oxidation of aniline in the presence of *p*-nitroaniline yielded only azobenzene (63% yield). The condensation of nitrosobenzene with *p*-nitroaniline also proceeded slowly. *m*-Nitroaniline oxidized readily but the azo compounds could not be isolated.

A series of substituted anilines were oxidized under the conditions of Table VI (3 mmoles of aniline). The rate of oxygen absorption over the initial 5–10-min period was 2.20 ml/min for aniline itself. Relative rates observed for substituted anilines were: 4-oxy anion (30); 3-nitro (5.5); 2-fluoro (4.5); 4-amino (2.2); 3-methyl (1.5); 4-thiophenyl (1.3); 4-bromo (1.2); 2-chloro, 4-methyl, 2-phenyl (1.1); aniline, 2-trifluoromethyl, 4-carbomethoxy, 4-chloro, 3-chloro (1.0); 4-aminophenylsulfonyl, 2,6-dibromo (0.5); 4-phenylazo, 2,4,6-trichloro (0.45); 4-benzoyl (0.3); 4-cyano (0.2); 2-nitro-4-ethoxy, N-benzoyl, 2-nitro (0.03); N-carbethoxy (0.02); 4-nitro, 2,4-dinitro, 2,4,6-trinitro (0.005). On the same scale a series of N-methylanilines yielded the following relative rates: no substituent, 3-nitro, 4-methyl (1.7); 4-nitro (0.4). Monosubstituted diphenylamines gave the rate sequence: 4-amino (6); no substitutent (1.6); 4-phenylazo (0.2); 4-nitroso (0.1); 2-nitro (0.03). The oxidations occurred very slowly in pyridine solution and about 15 times as rapidly in the solvent employed as in pure *t*-butyl alcohol.

Oxidation of Nitrosobenzene in Basic Solution. A mixture of 1.07 g (10 mmoles) of nitrosobenzene and 0.56 g of potassium hydroxide in 25 ml of ethanol was stirred at 22° in the presence of oxygen (749 mm). A total of 4.2 mmoles of oxygen was absorbed in a few minutes. The oxidate was diluted with water and the aqueous solution extracted with ether. The ethereal solution was shown to contain 7.0 mmoles of nitrobenzene by glpc employing *p*-chloronitrobenzene as an internal standard.

Condensation of Nitrosobenzenes and Anilines in Basic Solution. Some pertinent results are summarized in Table VII.

Table VII. Coupling of Nitrosobenzenes and Anilines in the Presence of Potassium *t*-Butoxide at 28 ± 2°

Nitroso compd, mmoles	Aniline, mmoles	Base, mmoles	Time, min	Azo compd, yield, % (mp, °C)
C_6H_5NO, 1.5	$C_6H_5NH_2$, 1.5	0.5	15[a]	$C_6H_5N{=}NC_6H_5$, 73 (60–65)
C_6H_5NO, 1.75[b]	$C_6H_5NH_2$, 5.75	1.5	10	$C_6H_5N{=}NC_6H_5$,[b] 50 (67–68)
C_6H_5NO, 1.5	$C_6H_5NH_2$, 1.5	3	5	$C_6H_5N{=}NC_6H_5$, 90 (64–65)
C_6H_5NO, 30	*p*-$NH_2C_6H_4NH_2$, 10	6	20	*p*-$C_6H_5N{=}NC_6H_4N{=}NC_6H_5$, 38 (167–168) *p*-$NH_2C_6H_4N{=}NC_6H_5$, 26 (122–124)
C_6H_5NO, 1.8	2,4,6-$C_6H_2D_3NH_2$, 1.8	4	5	$C_6H_2D_3N{=}NC_6H_5$, 67–75 (65–66)
C_6H_5NO, 1.5	*p*-$ClC_6H_4NH_2$, 1.5	3	25	*p*-$ClC_6H_4N{=}NC_6H_5$, 90 (90–91)
C_6H_5NO, 1.5	*m*-$ClC_6H_4NH_2$, 1.5	3	15	*m*-$ClC_6H_4N{=}NC_6H_5$, 95 (65–66)

[a] *t*-Butyl alcohol solvent, all other experiments involved DMSO–*t*-butyl alcohol (80:20). [b] ^{14}C-Labeled, 9.4 ± 0.1 × 10^5 dpm/mmole.

Oxidation of Hydrazobenzene in Basic Solution. Solutions of base and hydrazobenzene were added by hypodermic syringe to a double-chambered flask containing an oxygen atmosphere. The solutions were mixed, and the oxygen absorption was followed by a

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(46) L. Zechmeister and P. Rom, *Ann.*, **468**, 117 (1929).

manually controlled gas buret. Potassium superoxide was analyzed[38] by the addition of diethyl phthalate (50 vol. %) followed by an equal volume of acetic acid at 0°. A vigorous evolution of oxygen occurred. The temperature was brought to room temperature and after shaking for 100 min the oxygen evolution was measured. The yield of potassium superoxide was calculated from the equation

$$2KO_2 + 2CH_3CO_2H \longrightarrow 2CH_3CO_2K + H_2O_2 + O_2$$

Azobenzene was isolated from the oxidates after acidification with hydrochloric acid by the addition of 300 ml of water for 20 ml of the initial oxidate. After standing for 24 hr, the precipitated azobenzene was removed by filtration. The crystals were dissolved in methylene chloride and transferred to a tared flask. The solvent was removed under vacuum and the azobenzene, mp 67–68°, evacuated for 4 hr before weighing. Recovery tests indicated a loss of 20 mg of azobenzene in this procedure, and this correction has been applied to yields given in the text.

Photochemical Transformations of Unsaturated Bicyclic Ketones. Verbenone and Its Photodynamic Products of Ultraviolet Irradiation[1]

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Abstract: Irradiation of verbenone (**1**) in cyclohexane or acetic acid with a light source with principal emission >300 $m\mu$ or a Pyrex filter afforded chrysanthenone (**2**) of high optical purity as the principal product (37–67 %). In contrast, irradiation of **1** in cyclohexane with a broad-spectrum mercury arc lamp using a quartz or Vycor filter afforded as many as six products: the two decarbonylation products **9** (1–2 %) and **10** (6–13 %) and the rearranged ketones **8** (9–20 %), **2** (6–16 %), **11a** (4–6 %), and **12** (2–3 %). Three other ketones, **13**, **14**, and **15**, were produced in small amounts. Each of the compounds **2**, **8**, and **12**, from the latter irradiation, though optically active, showed appreciable loss of activity depending upon the length and conditions of irradiation. When alcohols were employed as solvent for the irradiation of **1** using the broad-spectrum lamp, the major products were the ketone **2** (12–20 %) and the ester **3** (21 %). Irradiation of **2** or **8** with the broad-spectrum lamp led to a photostationary state in which the the ratio of **2** to **8** was approximately 1.5:1. The ketone **14** on exposure to ultraviolet light in methanol solution afforded the three acetals **19** (3 %), **20** (2%), and **21** (11 %) and the ester **3** (5 %). Irradiation of **14** in cyclohexane afforded the hydrocarbon **10** (12%) as the principal isolable product and only trace quantities of **2** (1.8 %) and **8** (2.1 %). The above results are discussed in terms of the dual mechanisms proposed by Hurst and Whitham for the formation of chrysanthenone (**2**) from verbenone (**1**).

The photochemical conversion of verbenone (**1**) to chrysanthenone (**2**)[2] is one of two recorded examples in which α,β-unsaturated ketones undergo photoinduced rearrangement resulting in an ultimate 1,3-alkyl shift.[3] Whitham and Hurst, in their investigation of this transformation, showed that ultraviolet irradiation of verbenone in cyclohexane afforded chrysanthenone with partial optical retention while irradiation in the presence of alcohol or amines yielded, besides ketone **2**, derivatives related to geranic acid (*e.g.*, the ester **3b** or **4b**[4] and the esters **5b** and **6b** resulted from irradiation of **1** in ethanol). They further showed that irradiation of chrysanthenone **2** in ethanol produced the same esters **3b**, **4b**, **5b**, and **6b**, while irradiation of optically active **2** for long periods in inert media afforded **2** with considerable loss of optical activity depending upon the period of irradiation.

All of these observations were consistent with a two-path mechanism for the formation of chrysanthenone (Chart I): path a, a fast process involving an ultimate 1,3-alkyl migration, and path b, cleavage of **1** to the ketene **7**, an optically inactive species, which undergoes an intramolecular thermal or photolytic cyclization to **2**. Photochemical racemization of chrysanthenone by cleavage to ketene **7** and recyclization to **2** (path c) would account for part of the loss in optical activity of **2** during the irradiation process.

In an over-all program directed toward the utilization of this reaction in sesquiterpene synthesis, we reinvestigated the photochemistry of verbenone with the hope of (1) effecting the rearrangement with minimal racemization, and (2) discovering other products of the irradiation (by varying reaction conditions) which might shed further light on the mechanism of product formation.

Results

(−)-Verbenone (**1**) was irradiated under a variety of conditions using light sources with broad spectrum emission in quartz or Vycor vessels, using light sources with limited emission in the 280–300-$m\mu$ region, and using filters which diminish transmission of light below 300 $m\mu$. The results of these experiments are listed in Table I.

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(1) Paper presented in part before the Division of Organic Chemistry, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p 29S.

(2) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960).

(3) A second example has been provided recently by Zimmerman and Sam, who reported the production of 2-(*cis*-styryl)-3-phenylcyclobutanone in 8–9 % yield from the ultraviolet irradiation of 4,5-diphenylcyclohexenone in *t*-butyl alcohol: H. E. Zimmerman and D. J. Sam, *J. Am. Chem. Soc.*, **88**, 4905 (1966).

(4) Although two geometric isomers of the β,γ-unsaturated ester, *i.e.*, 3 and 4, could be produced in this reaction, Hurst and Whitham did not separate the isomers or assign stereochemistry to the predominant isomer.