substrate. The analytical error would have been excessively large for lesser deuterium content. The aliquots were worked up in the manner described for 9-phenylxanthene. The recovered material was recrystallized from 1 ml of ethanol. The weighed sample, *ca.* 25 mg, was dissolved in 0.100 ml of bromoform and analyzed by the infrared method.

2-(N,N-Dimethylcarboxamido)-9-methylfluorene Exchange and Racemization Runs. The following experiment measured the ratio of first-order rate constants for exchange and racemization of the protio substrate (runs 22 and 23). In 10.00 ml of 3:1 (by volume) methanol-O-*d*–dimethyl-d_6 sulfoxide, which was approximately 0.0026 *N* in potassium methoxide, was dissolved 0.2124 g of protio substrate with $[\alpha]^{26}{}_{546}$ +34.0° (*c* 6.00, dioxane).[17] Nine 1.00-ml aliquots were placed in clean 3-ml test tubes, sealed with rubber septum caps, placed in the 24.80° bath, and quenched at timed intervals as follows. A Hamilton syringe equipped with a Chaney adaptor delivered a highly reproducible volume (±0.5% precision) of about 0.25 ml of 9:1 (by volume) methanol–12 *N* hydrochloric acid into each test tube. The quenched aliquots were then used as such to determine the optical rotation at 25° and 436 mμ. Each aliquot was retrieved from the polarimeter cell and worked up for isotopic content. The aliquot was poured into 25 ml each of water and ether, washed twice with water, dried, and evaporated. The residue was chromatographed on silica gel in a small tube of 15-cm length and 0.7-cm inner diameter. About 20 ml of ether was used as the eluent. The eluent was evaporated and residual ether was pumped off under vacuum. The purified material was analyzed according to an established procedure.[17]

The following experiment measured the first-order rate constants for racemization of optically active protio and deuterio substrates (runs 24 and 25). In 1.00 ml of 3:1 by volume methanol-O-*d*–dimethyl-d_6 sulfoxide, which was *ca.* 0.0067 *N* in potassium methoxide, was dissolved 21.1 mg of the optically active protio substrate. This solution was placed in a polarimeter cell and removed from the drybox. The optical rotation was observed at 24.80° and 436 mμ. An identical experiment was performed with 19.3 mg of optically active deuterio substrate dissolved in 1.00 ml of the same solvent.

Control on Isotopic Fractionation during Crystallization of Partially Deuterated 9-Phenylxanthene. A sample of 22.7 mg of 9-phenylxanthene and 127.2 mg of 9-deuterio-9-phenylxanthene (77.7% of one atom of deuterium per molecule) was dissolved in carbon tetrachloride, divided into two equal aliquots, and evaporated to dryness. One aliquot was recrystallized from ethanol. Both samples were weighed and dissolved in 0.200 ml of bromoform. The infrared absorbance was measured at 985 cm^{-1}. The two samples, recrystallized and untreated, gave values of 1.79 and 1.80, respectively, for (absorbance × 10^3/mg of sample). Estimated errors of ±0.2 mg in sample weights and ±0.5% in absorbances indicate that the two values are identical within experimental error.

Intramolecular Nucleophilic Participation. V. The Role of the *ortho* Substituent in the Solvolysis of *o*-Nitrobenzhydryl Bromide and *o*-Nitrobenzyl Tosylate

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Abstract: The capacity of the *o*-nitro group to serve as an internal nucleophile in the hydrolysis of *o*-nitrobenzhydryl bromide and of *o*-nitrobenzyl tosylate has been investigated. Two experimental observations lead to the conclusion that it is a highly effective participant in the reaction of the former compound: (a) *o*-nitrobenzhydryl bromide solvolyzes considerably more rapidly in 90% aqueous acetone than does its *para* isomer; (b) its hydrolysis product is *o*-nitrosobenzophenone. *o*-Nitrobenzyl tosylate hydrolyzes somewhat less rapidly than its *para* isomer, and the evidence is strong that the *o*-nitro group participates much less extensively in reactions of benzyl than of benzhydryl systems. Good yields of *o*-nitrobenzhydryl bromide are obtained from the reaction of *o*-nitrodiphenylmethane and N-bromosuccinimide in carbon tetrachloride only if the temperature of the reaction is controlled. Otherwise a mixed product is obtained, from which 5-bromo-3-phenyl-2,1-benzisoxazole can be isolated. The reaction paths for production of the benzisoxazole and for formation of *o*-nitrosobenzophenone by hydrolysis of *o*-nitrobenzhydryl bromide are considered to have certain features in common.

There is a considerable accumulation of evidence, varying in credibility from mildly suggestive[1,2] to virtually conclusive, that *o*-nitro groups may function as internal nucleophiles in polar reactions at aromatic side chains. The fact that in acetic acid *o*-nitroiodobenzene dichloride dissociates to the component iodo compound and chlorine much faster than does its *para* isomer[3] is of particular significance in this regard. Also of fundamental importance in the same connection is the observation that *o*-nitrobenzhydrol is converted to *o*-nitrosobenzophenone when it reacts with formic acid or with *o*-toluenesulfonyl chloride in pyridine and yields 5-chloro-3-phenyl-2,1-benzisoxazole on treatment with thionyl chloride in chloroform.[4]

An attempt has been made previously to explore the possibility that the nitro group may participate in solvolysis reactions of *o*-nitrobenzhydryl bromide.[5] Until the present investigation a crystalline sample of this bromide has not successfully been prepared. In the earlier study[5] the crude oily product of the reaction of N-bromosuccinimide with *o*-nitrodiphenylmethane was employed (as the *ortho*-substituted isomer) in comparing the hydrolysis rates of *o*- and *p*-nitrobenzhydryl bromides. On the basis of the results of those measure-

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[1] J. B. Hyne and R. Wills, *J. Am. Chem. Soc.*, **85**, 3650 (1963).

[2] W. C. Hamilton and S. J. LaPlaca, *ibid.*, **86**, 2289 (1964).

[3] E. A. Jeffery, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **30**, 617 (1965).

[4] W. B. Dickinson, *J. Am. Chem. Soc.*, **86**, 3580 (1964).

[5] E. A. Jeffery, R. K. Bansal, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **29**, 3365 (1964).

ments it was concluded tentatively that the isomeric bromides were of comparable reactivity.

Because of the strong indications, mentioned above, that an *o*-nitro substituent is a highly effective nucleophilic participant in closely related processes, a careful reexamination of the solvolytic reactivity of *o*-nitrobenzhydryl bromide has been conducted. Proper conditions for producing the pure bromide from the reaction of *o*-nitrodiphenylmethane and N-bromosuccinimide have been discovered. The results of a study of the products as well as the kinetics of hydrolysis of this bromide in aqueous acetone lead to the decision that the nitro group does indeed participate in the reaction.

The possibility that an *o*-nitro substituent may also serve as an internal nucleophile in polar reactions of benzyl systems has been explored by means of a comparative rate study of the hydrolysis of *o*- and *p*-nitrobenzyl tosylate in aqueous acetone. The results are not definitive.

Experimental Section

***o*-Nitrodiphenylmethane.** *o*-Nitrobenzyl bromide was prepared through the benzoyl peroxide induced reaction of equimolar quantities of N-bromosuccinimide and *o*-nitrotoluene in carbon tetrachloride.[6] A solution of 10 g (0.046 mol) of *o*-nitrobenzyl bromide and 5.7 g (0.043 mol) of anhydrous aluminum chloride in benzene was stirred for 17 hr and heated gently in the initial stages of reaction. After it was water extracted to remove inorganic matter, the product mixture was distilled to provide 6.55 g (67% yield) of *o*-nitrodiphenylmethane, bp 156–157° (1.3 mm) (lit.[7] bp 183–140° (10 mm)).

The Reaction of *o*-Nitrodiphenylmethane with N-Bromosuccinimide. A. To Provide 5-Bromo-3-phenyl-2,1-benzisoxazole. A solution of 2.3 g (0.0108 mol) of *o*-nitrodiphenylmethane in 75 ml of carbon tetrachloride was treated with 1.9 g (0.0107 mol) of N-bromosuccinimide and a small amount of benzoyl peroxide. The mixture was irradiated with ultraviolet light and allowed to reflux for a total reaction time of 15 min. It was then filtered to remove succinimide and stripped of solvent by using a rotary film evaporator. The remaining yellow-brown oil was extracted with petroleum ether (bp 30–60°). Some tarry material was left undissolved. By chilling the petroleum ether extract, yellow crystals of melting range 98–104° were obtained. These were recrystallized three times from methanol to yield 0.24 g (8%) of 5-bromo-3-phenyl-2,1-benzisoxazole; melting point and mixture melting point with an authentic sample,[8] 114–115°.

Anal. Calcd for $C_{13}H_8NOBr$: C, 56.96; H, 2.94; N, 5.11; Br, 29.15. Found: C, 56.94; H, 3.05; N, 5.09; Br, 29.44.

The anthranil was found not to undergo reaction with hot alcoholic silver nitrate solution. Its nmr spectrum (carbon tetrachloride solvent) showed only a complex multiplet in the region τ 1.80–2.90. The ultraviolet spectrum of the anthranil displayed absorption peaks similar to those reported[4] for 5-chloro-3-phenyl-2,1-benzisoxazole; $\lambda_{\max}^{95\%\,\mathrm{EtOH}}$ mμ (ϵ): 354 (21,200), 257 (22,300), 249 (19,100), and 218 (30,000).

B. To Provide *o*-Nitrobenzhydryl Bromide. A mixture of 2.09 g (0.0098 mol) of *o*-nitrodiphenylmethane in 75 ml of carbon tetrachloride, 1.7 g (0.0096 mol) of N-bromosuccinimide, and a small amount of benzoyl peroxide was irradiated with ultraviolet light and stirred over a 45-min period. While the bromination progressed, the solvent was kept from refluxing by cooling the reaction flask in an ice bath. The accumulated succinimide was filtered from the product mixture and the carbon tetrachloride removed from the filtrate by using a rotary film evaporator. The remaining oil was dissolved in petroleum ether, and the solution was refrigerated. Light yellow crystals of *o*-nitrobenzhydryl bromide, mp 52.5–53°, separated from the chilled mixture (2.42 g, 86% yield).

Anal. Calcd for $C_{13}H_{10}NO_2Br$: C, 53.45; H, 3.45; N, 4.80; Br, 27.53. Found: C, 53.86; H, 3.42; N, 4.88; Br, 26.82.

The bromide reacts readily with alcoholic silver nitrate solution to precipitate silver bromide. It decomposes with reasonable rapidity at room temperature with the evolution of hydrogen bromide. It can be retained for relatively long periods of time by storage in a vacuum desiccator at 10°. The nmr spectrum of the bromide (carbon tetrachloride solvent) shows a complex multiplet in the region τ 2.00–2.90 and a singlet at τ 3.00.

***o*-Nitrosobenzophenone.** Attempts to isolate the solid nitroso ketone in good yield from the products of hydrolysis of *o*-nitrobenzhydryl bromide were unsuccessful due largely to recovery problems in recrystallizing the crude material. As indicated below in the discussion of the spectrophotometric methods of investigating the kinetics of hydrolysis of the bromide, the evidence that the ketone is the only organic reaction product formed in significant quantity is good. Small samples of the nitroso ketone were isolated from the combined green solutions of products remaining from rate runs and test runs in which the kinetics of hydrolysis of *o*-nitrobenzhydryl bromide were investigated by the application of nmr techniques. The acetone was removed from the product solution using a rotary film evaporator. The organic matter was extracted from the wet concentrate with petroleum ether. The solvent was evaporated from the extract, and *o*-nitrosobenzophenone, mp 127–128° (lit.[4] mp 128–130°), was obtained by recrystallization of the residue from ethyl acetate.

Anal. Calcd for $C_{13}H_9NO_2$: N, 6.63. Found: N, 6.90.

The ultraviolet spectrum of this product is closely comparable to that reported previously for the nitroso ketone; $\lambda_{\max}^{95\%\,\mathrm{EtOH}}$ mμ (ϵ): 242 (15,000), 279 (infl 8100), and 306 (infl 6350). In 90% aqueous acetone the compound has an absorption peak in the visible region at 765 mμ (ϵ 44.9). The extinction coefficient reported for the ultraviolet peaks for the nitroso ketone and also (see above) for *o*-nitrobenzhydryl bromide are accurate to no more than two significant figures, since they are calculated from automatically recorded percentage transmission values which are likewise accurate to no more than two significant figures. The extinction coefficient at 765 mμ was calculated from a reading made with the manually operated Beckman DU spectrophotometer and is considered to be accurate within 1%.

***o*- and *p*-Nitrobenzyl Tosylates.** These tosylates were prepared from the corresponding nitrobenzyl alcohol by the procedure used previously[9] in synthesizing *p*-nitrobenzyl tosylate. The melting point obtained for the *para* isomer was 100–102° (lit.[9] mp 103–104°).

The crude product from the reaction of 7.4 g (0.048 mol) of *o*-nitrobenzyl alcohol and 10.0 g (0.052 mol) of *p*-toluenesulfonyl chloride was recrystallized from mixed hexanes. To avoid polymerization, the temperature was kept below 50° during the recrystallization process. A 3.0-g yield (21%) of *o*-nitrobenzyl tosylate was obtained as colorless needles, mp 80–90° dec.

Anal. Calcd for $C_{14}H_{13}O_5NS$: C, 54.70; H, 4.26; N, 4.56; S, 10.43. Found: C, 54.65; H, 4.13; N, 4.86; S, 10.18.

***o*- and *p*-Bromobenzyl Tosylates.** These tosylates were prepared from the corresponding bromobenzyl alcohols by the procedure described previously for preparing *p*-bromobenzyl tosylate.[9] The *p*-bromobenzyl alcohol was obtained by reduction of methyl *p*-bromobenzoate with lithium aluminum hydride in tetrahydrofuran; mp 76–77° (lit.[9] mp 77°). The ester was prepared from *p*-bromobenzoic acid using methanol and an acid catalyst; mp 78.5–79.5° (lit.[10] mp 79.5°). The *o*-bromobenzyl alcohol was prepared through lithium aluminum hydride reduction of *o*-bromobenzoic acid in tetrahydrofuran; mp 77–78° (lit.[10] mp 80°).

From 3.97 g (0.021 mol) of *o*-bromobenzyl alcohol a 4.39-g yield (61%) of *o*-bromobenzyl tosylate was obtained; mp 80.5–81.5°.

Anal. Calcd for $C_{14}H_{13}BrO_3S$: C, 49.28; H, 3.84; Br, 23.42; S, 9.40. Found: C, 49.45; H, 4.02; Br, 23.52; S, 9.26.

The melting point of the sample of *p*-bromobenzyl tosylate which was prepared was 73.5–74° (lit.[9] mp 76.8–77.5°).

Rate Studies of the Hydrolysis of *o*-Nitrobenzhydryl Bromide. A. The Nmr Method. The rate of production of hydrogen bromide during the solvolysis of an organic bromide in a water–organic mixed solvent can be determined by observing the accompanying shifts in position of that nmr peak which is characteristic of the water (actually H_2O–H_3O^+) in the medium. This method has been used successfully in investigating the kinetics of hydrolysis of various

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[6] N. Kornblum and D. C. Iffland, *J. Am. Chem. Soc.*, 71, 2137 (1949).

[7] J. R. A. Pollock and R. Stevens, Ed., "Dictionary of Organic Compounds," Eyre and Spottiswood Publishers, Ltd., London, 1965, p 2495.

[8] R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, 25, 1884 (1960).

[9] J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, 75, 3443, 3447 (1953).

[10] Reference 7, pp 421–422.

substituted benzyl bromides in aqueous dioxane[11] and has now been applied to the study of the reaction of *o*-nitrobenzhydryl bromide in 90% aqueous acetone (a mixture of 90 volumes of acetone and 10 volumes of water). The rate sample was prepared by diluting a weighed portion of the bromide to a known volume with 90% aqueous acetone which had previously been equilibrated to the temperature of the nmr probe. About 0.5 ml of this solution was transferred to an nmr sample tube containing a water-filled capillary which served as a reference standard. The nmr tube was then inserted in the temperature-controlled nmr probe, and from time to time (after temperature equilibration) the spectrum was recorded until the reaction was at least two-thirds complete.

The absorption peak of water in the capillary standard was observed to appear at τ 5.26. The H_2O-H_3O^+ peak of the reaction mixture was located at higher values of τ but shifted downfield toward τ 5.26 as the hydrogen bromide content of the medium increased. In a run in which the initial organic bromide concentration was approximately 0.2 *M*, the two peaks were about 54 cps apart at completion of reaction, and the H_2O-H_3O^+ peak shifted by approximately 38 cps from the first measurement to completion of reaction.

Assuming that the change in position of the latter peak is directly proportional to HBr concentration, it can readily be shown that the rate constant for *o*-nitrobenzhydryl bromide solvolysis is defined by eq 1. The terms δ_t and δ_∞ are the differences in chemical shifts

$$2.303 \log (\delta_t - \delta_\infty) = k_s t + \text{constant} \qquad (1)$$

for the H_2O-H_3O^+ peak of the medium and the pure water peak at times *t* and infinity, respectively. The rate constant was evaluated from a plot of $\log (\delta_t - \delta_\infty)$ *vs.* time.

B. The Spectrophotometric Method. As *o*-nitrobenzhydryl bromide solvolyzes in 90% aqueous acetone, the solutions turn green because of the production of *o*-nitrosobenzophenone. It therefore proved feasible to investigate the rate of reaction by a spectrophotometric procedure in which the change in optical density of the reaction mixture at 765 mμ, the absorption peak of the nitroso ketone, was recorded as a function of time. The rate samples and solvent blank were contained in 1-cm absorption cells which were left in the temperature-controlled housing of the Beckman DU spectrophotometer during the course of reaction. In one run in which the initial *o*-nitrobenzhydryl bromide concentration was 0.0109 *M* the optical density (765 mμ) at completion of reaction was 0.483. If it is assumed that *o*-nitrosobenzophenone was produced quantitatively in the reaction, a value of $\epsilon_{765\ \mathrm{m}\mu}$ 44.3 can be calculated using these figures. This is in good agreement with the extinction coefficient evaluated from the results of measurements on solutions prepared from a solid sample of the nitroso ketone (see above).

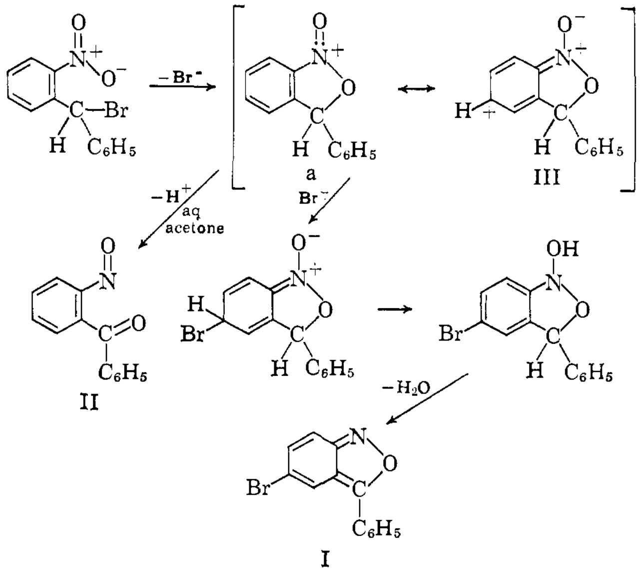
The reactions were followed to completion. First-order solvolysis rate constants were calculated from the spectrophotometric data by the method of Guggenheim.[12] Absorbance values at the required times were obtained from a plot of absorbance *vs.* time.

Rate Studies of the Benzyl Tosylate Solvolyses. Solutions of known initial concentration of the tosylate in 90% aqueous acetone were sampled by pipet from time to time. The samples were quenched in a chilled mixture of 10 ml of distilled water and 10 ml of acetone. Time was recorded when addition to the quenching mixture was half complete. Eight drops of an indicator[9] prepared by mixing 100 ml of a 0.1% solution of bromocresol green in acetone with 100 ml of a 0.2% solution of methyl red in 80 vol % aqueous acetone were added, and the solutions were titrated with standard sodium hydroxide to the greenish end point. The reactions were followed to at least two-thirds completion. Rate constants were calculated from slopes of plots of values of log $[RC_6H_4CH_2OTs]$ *vs.* time.

Results

o-Nitrobenzhydryl bromide can be prepared in crystalline form in good yield through the reaction of *o*-nitrodiphenylmethane and N-bromosuccinimide in carbon tetrachloride, provided the reactants are chilled during the course of the bromination process. If the reaction is allowed to take place at solvent reflux temperature, as is customary in conducting brominations by this general procedure, the crude product is tar-like in character. From this intractable material a single solid product, 5-bromo-3-phenyl-2,1-benzisoxazole (I), has been isolated. Even at room temperature *o*-nitrobenzhydryl bromide is rather unstable, and presumably it decomposes readily to form I, among other products, when it is generated at the boiling point of carbon tetrachloride.

The organic product of hydrolysis of *o*-nitrobenzhydryl bromide in aqueous acetone has been found to be *o*-nitrosobenzophenone (II). As mentioned in the introductory section, II and the chlorine analog of I are formed in certain reactions of *o*-nitrobenzhydrol which are related to those under consideration. The reaction paths proposed by Dickinson[4] in discussing the results of the studies of *o*-nitrobenzhydrol can be applied with slight modification in accounting for the generation of I and II from *o*-nitrobenzhydryl bromide as described.



It is suggested that both in its conversion to I and in its hydrolysis to II the first step in the reaction of *o*-nitrobenzhydryl bromide is one in which the nitro group in effect displaces bromide ion with the formation of the intermediate III. The solvent used for hydrolysis, 90% aqueous acetone, is sufficiently basic so that proton abstraction at site a in III occurs readily and leads to the formation of the nitroso ketone. The medium used in the preparation of *o*-nitrobenzhydryl bromide from *o*-nitrodiphenylmethane and N-bromosuccinimide (carbon tetrachloride) is probably sufficiently polar in character, because of contamination with HBr and traces of water, to induce ionization as shown in the first step of the above reaction scheme. Under such conditions, however, III is very likely a tight ion pair which is less subject to proton loss than to recombination of bromide ion at the ring position as shown.

The Kinetics of Hydrolysis of *o*-Nitrobenzhydryl Bromide. It is conceivable that the formation of *o*-nitrosobenzophenone from *o*-nitrobenzhydryl bromide might occur through formation of *o*-nitrobenzhydrol as an intermediate rather than as proposed above, *i.e.*

$$C_6H_5CH(Br)C_6H_4NO_2 \xrightarrow[-\mathrm{HBr}]{H_2O} C_6H_5CH(OH)C_6H_4NO_2 \xrightarrow{-H_2O} \mathrm{II} \qquad (2)$$

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(11) M. J. Strauss, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, in press.

(12) E. A. Guggenheim and J. E. Prue, "Physicochemical Calculations," 2nd ed, North Holland Publishing Co., Amsterdam, 1956, p 442.

If, in fact, the alcohol is a reaction intermediate, it must be very short lived since the solvolysis rate constants for the bromide which were determined alternately by investigating the rate of HBr production (nmr method) and the rate of *o*-nitrosobenzophenone formation (spectrophotometric method) are closely similar—see Table I for the results of runs at 39°.

Table I. Rate Constants for Solvolysis of *o*-Nitrobenzhydryl Bromide in 90 Vol % Aqueous Acetone

$[RBr]_i$, mol/l.	Method	Temp, °C	10^5k_s, sec^{-1}
0.0133	Spectrophotometric	45.0 ± 1.0	26.7
0.0109	Spectrophotometric	45.0 ± 1.0	29.3
0.0046	Spectrophotometric	45.0 ± 1.0	28.8
	Av	45	28.3 ± 1.0
0.222	Nmr	39.0 ± 1.0	20.6
0.005	Spectrophotometric	39.0 ± 1.0	18.0
	Av	39	19.3 ± 1.3
0.0198	Spectrophotometric	25.0 ± 1.0	4.22
0.0151	Spectrophotometric	25.0 ± 1.0	4.69
0.0092	Spectrophotometric	25.0 ± 1.0	4.79
	Av	25	4.57

In Table I an average rate constant of 28.3 × 10^{-5} sec^{-1} is reported for reaction of the bromide in 90 vol % aqueous acetone at 45°. The corresponding figure for reaction of *p*-nitrobenzhydryl bromide[5] is 0.34 × 10^{-5} sec^{-1}. That is, under comparable reaction conditions the *ortho* isomer is approximately 83 times more reactive than the *para*. In cases in which the *ortho* substituents are functionally incapable of participation, the hydrolysis rates of *ortho*-substituted benzhydryl halides are substantially lower (roughly speaking by a factor of 10–100) than those of their *para* isomers.[13] The evidence, from the standpoint of the reaction kinetics as well as reaction products, is therefore strong that the nitro group functions as an internal nucleophile in polar reactions of *o*-nitrobenzhydryl bromide.

The ratio of solvolysis rate constants for the *o*- and *p*-carbophenoxybenzhydryl bromides[13] at 45° in 90% aqueous acetone is 59. It appears, therefore, that o-NO_2 and o-$COOC_6H_5$ are comparable in their capacities to promote a polar reaction at an adjacent side chain. Much the same conclusion has been reached[3] concerning the relative effectiveness of o-NO_2 and o-$COOCH_3$ in promoting iodobenzene dichloride dissociation.

An activation energy of 17.2 kcal/mol for *o*-nitrobenzhydryl bromide solvolysis in 90 vol % aqueous acetone has been calculated from the slope of a plot of the logarithms of the average k_s values reported in Table I *vs.* the reciprocals of the corresponding absolute temperatures. The value of $\Delta S^{\neq}$ for the reaction is −22.6 eu. Values of E_a (18.7 kcal/mol) and $\Delta S^{\neq}$ (−22.9 eu) for solvolysis of *p*-nitrobenzhydryl bromide in 80% aqueous acetone have been reported previously.[5] If anything the value of E_a for the *para*-substituted bromide should increase as the solvent is changed from 80 to 90% aqueous acetone. It appears, therefore, the energy barrier for reaction of the *ortho* isomer is significantly less than the *para*, and this is presumed to reflect the contribution of the *o*-nitro group as a participating substituent.

The Relative Hydrolysis Rates of the Nitrobenzyl Tosylates. Generally *ortho*-substituted benzyl halides solvolyze somewhat more slowly than their *para* isomers, although the reactivity differences are not large.[14] In aqueous ethanol *o*-nitrobenzyl chloride is slightly more reactive than *p*-nitrobenzyl chloride, but the difference is not sufficient so that it can be ascribed with any assurance to *o*-nitro group participation. Tosylate is a better leaving group than chloride,[15] and it is reasoned that benzyl tosylates should solvolyze with greater charge development on the exocyclic carbon at the transition state than should the corresponding benzyl chlorides. Conceivably, because of the difference in the degree of polarization during the course of the reactions, the *o*-nitro group might contribute more as an internal nucleophile to the solvolysis of a substituted benzyl tosylate than to the reaction of a substituted benzyl chloride. In Table II hydrolysis rate constants for the *o*- and *p*-nitrobenzyl tosylates are compared with those of the *o*- and *p*-bromobenzyl tosylates. The ratio of k_s values for the *o*- and *p*-bromo-substituted tosylates is only about one-third as large as that for the nitro-substituted compounds. The difference is not large enough, however, so that in contrast to *o*-Br the o-NO_2 group can be said to participate extensively in the benzyl tosylate reaction. Like the *o*-COOR group the o-NO_2 group provides internal assistance in displacement reactions of benzyl systems much less readily (if at all) than it does in similar reactions of benzhydryl systems. The difference in sensitivity of the two types of reactions to the influence of *o*-COOR groups has been explained on geometric grounds,[13] and that argument can be extended to the o-NO_2 group.

Table II. Rate Constants for Solvolysis of $RC_6H_4CH_2OTs$ (90 Vol % Aqueous Acetone, 32.5°)

R	$[RC_6H_4CH_2OTs]_i$, mol/l.	10^5k_s, sec^{-1}	$k_s(ortho)/k_s(para)$
o-NO_2	0.106	0.051	
	0.039	0.051	
	0.027	0.056	
		Av 0.053	0.88
p-NO_2	0.067	0.059	
	0.042	0.061	
		Av 0.060	
o-Br	0.084	0.124	
	0.048	0.131	
	0.026	0.122	
		Av 0.126	
			0.32
p-Br	0.076	0.393	
	0.048	0.394	
	0.031	0.397	
		Av 0.395	

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(13) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

(14) See ref 13 for specific examples and also see J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 850 (1956).

(15) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 184.

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Mechanisms of Oxidation of Aniline and Related Compounds in Basic Solution

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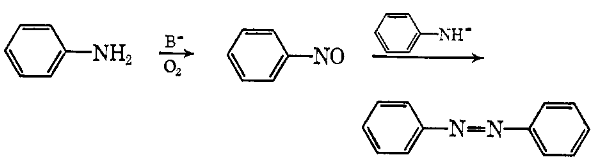
Abstract: The formation of azobenzene by oxidation of aniline in basic solution is explicable in terms of condensation involving nitrosobenzene rather than coupling of anilino radicals. This view is supported by the experimental results of a study of the oxidation of hydrazobenzene and condensation of nitrosobenzene with aniline. In the condensation reaction, the different results observed in the presence and in the absence of oxygen depend on the behavior of nitrosobenzene radical anion. In the oxidation of nitrosobenzene itself, azoxybenzene is possibly formed from the condensation of nitrosobenzene radical anion with nitrosobenzene rather than coupling of nitrosobenzene radical anions; this view is supported by the experimental rate of decay of the nitrosobenzene radical anion by esr as compared to the oxygen absorption rate and by the comparison of the behavior of nitrosobenzene in the presence of excess base with deficient base.

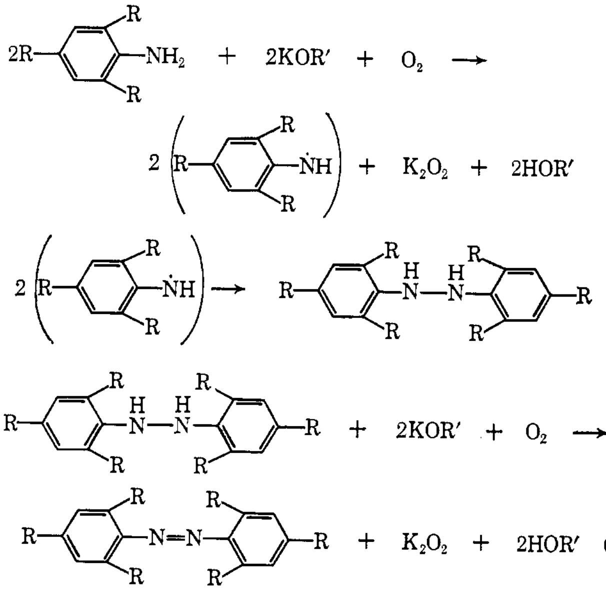
It is well known that primary arylamines react with molecular oxygen to yield azobenzene derivatives in the presence of base.[1–4] Russell[5a,6] suggested that azobenzene is formed from a base-catalyzed condensation involving the nitroso compound as shown in eq 1.



(1)

Alternatively, Horner[4] proposed that azobenzene derivatives may result from the dehydrogenation of the hydrazobenzenes arising from the coupling of anilino radicals as shown in eq 2–4.

In the present paper, we discuss these mechanisms in view of results of a study of a base-catalyzed oxidation of hydrazobenzene and a base-catalyzed condensation of nitrosobenzene with aniline in the presence of molecular oxygen or nitrogen. This condensation reaction sequence accompanying the azoxybenzene formation is also discussed based on its reaction rate and esr spectroscopy.



(2)

(3)

(4)

$R = CH_3, R' = C(CH_3)_3$

Reactions 2–4 relate to the base-catalyzed oxidation of nitrosobenzene, which produces mainly azoxybenzene and nitrobenzene.[7] However, the effect of oxygen and the oxidation mechanism have not been investigated yet. Consequently, the base-catalyzed oxidation of nitrosobenzene was examined by product analysis, oxygen absorption rate, and esr spectroscopy. A novel mechanism of azoxybenzene formation has been proposed.

Experimental Section

Reagents. Dimethyl sulfoxide (Crown Zellerbach Corp.) was distilled under reduced pressure from molecular sieves. Commercial *t*-butyl alcohol was distilled from calcium hydride. Potassium *t*-butoxide was commercial material (K & K Laboratories, Inc.). Aniline was purified as follows. Commercial aniline was

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(1) R. Anschütz and G. Schulz, *Ber.*, **10**, 1803 (1877).

(2) A. Bacovescu, *ibid.*, **42**, 2938 (1909).

(3) G. A. Russell, E. G. Janzen, H-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

(4) L. Horner and J. Dehnert, *Ber.*, **96**, 786 (1963).

(5) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965: (a) p 150; (b) p 120.

(6) After this manuscript was submitted, Russell reported the mechanism of oxidation of aniline in basic solution (G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Am. Chem. Soc.*, **89**, 3821 (1967)).

(7) E. Bamberger, *Ber.*, **33**, 1939 (1900); **35**, 732 (1902).