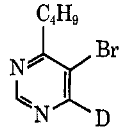
experiment showed that naphthalene undergoes more extensive D–H exchange than quinoline. This result is understandable in terms of deactivation due to adduct formation. We suggest that such a competition experiment may serve as a simple chemical method of detecting σ complexes in other heterocyclic systems.

Such deactivation due to σ complex formation probably accounts for the observation that 4-*tert*-butyl-5-bromopyrimidine-*6-d* (V) does not undergo significant exchange in KNH_2–NH_3.[12] In the absence of the addition of amide ion the pyrimidine is expected to be more reactive than deuterated pyridine in an H–D exchange reaction;[11] yet it is less reactive.

The present results along with those given in our earlier report dealing with the formation of complexes VI–VIII from diazines[13] show that σ complex formation between amide ion and hetarenes is extensive. Clearly an area awaits further profitable investigation. It promises to provide a wealth of new information, especially about complexes of simple heteroaromatic compounds which do not react in the more widely employed solvent–base systems.[2]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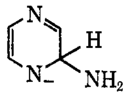
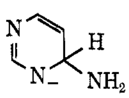
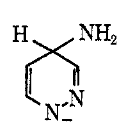

VI


VII


VIII

Experimental Section

Quinoline-*2-d* was prepared by heating equal volumes of quinoline and D_2O at 225° for 2 days in a bomb.[14] Nmr analysis indicated >95% deuteration. Naphthalene-d_8 (>95% D) was obtained from Merck Sharpe and Dohme of Canada.

The general procedure for obtaining nmr spectra of ammonia-amide ion reaction mixtures has been presented.[15] Trimethylamine (τ 7.87) or benzene (τ 2.60) served as a shift standard. A Varian A-60A spectrometer having a V-6040 variable temperature controller was employed.

Competitive Hydrogen–Deuterium Exchange of Quinoline-*2-d* and Naphthalene-d_8 in Ammonia.—Potassium amide (0.3 *M*) was generated by the method indicated above. To a precooled Parr metal bomb, flushed with nitrogen, was added 60 ml of amide solution. This was followed by the addition of 0.0074 *m* of naphthalene-d_8 and 0.0051 *m* of quinoline-*2-d*. The sealed bomb was heated in running tap water for 45 min, cooled in acetone–Dry Ice, and opened; the reaction was quenched by the addition of 3.2 g of NH_4Cl. After evaporation of the solvent, the residue was treated with 50 ml of 18% KOH to remove salts and then dissolved in ether. The aqueous solution was extracted with 2 × 30 ml of ether. The combined ether phases were exposed to 2 × 30 ml of 1 *M* HCl. Evaporation of the ether gave naphthalene which was sublimed. The nmr spectra of a mixture of purified naphthalene and *tert*-butyl alcohol (area standard) indicated that 74% dedeuteration had resulted.

Quinoline was recovered from the HCl following neutralization with Na_2CO_3 and extraction with ether (2 × 25 ml). Nmr analysis of the ether solution showed that 20% dedeuteration had taken place.

Registry No.—II, 38896-70-7; III, 38896-68-3; IV, 38896-69-4; isoquinoline, 119-65-3; quinoline, 91-22-5; 4-methylthioisoquinoline, 38896-71-8; amide ion, 17655-31-1.

Acknowledgment.—This work was kindly supported by the National Science Foundation (GP 25500 and RPCT-AYE).

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[12] H. C. van der Plas, P. Smit, and A. Koudijs, *Tetrahedron Lett.*, 9 (1968).

[13] J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **94**, 682 (1972).

[14] J. A. Zoltewicz and C. L. Smith, *J. Amer. Chem. Soc.*, **89**, 3358 (1967); U. Bressel, A. R. Katritzky, and J. R. Lea, *J. Chem. Soc. B*, 4 (1971).

[15] J. A. Zoltewicz and L. S. Helmick, *J. Org. Chem.*, **38**, 658 (1973).

Covalent Amination of Heteroaromatic Compounds[1]

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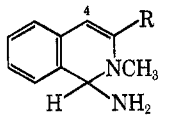
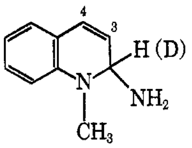
Received December 7, 1972

The discovery that heteroaromatic molecules may be transformed into their covalent hydrates in aqueous solution is of great importance. In the hydration process a water molecule or hydroxide ion serving as a nucleophile adds to a ring carbon atom to give a hydroxy derivative. This brings about major changes in the physical and chemical properties of the original substance.[2,3]

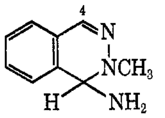
We wish to call attention by this report to analogous structural transformations involving heteroaromatic molecules in ammonia solvent. Covalent amination results.[4] Examples reported here include quaternized isoquinoline, quinoline, phthalazine, triazanaphthalene, 3-substituted pyridines and quinoxaline. These cations are converted in liquid ammonia, *free of added amide ion*, into aminodihydro structures I–IX. The amination reactions are remarkable in that they are complete in minutes below 0°. No starting material could be detected by nmr at equilibrium.



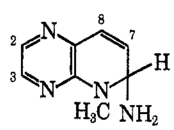
I, R = H
II, R = CH_3



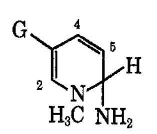
III



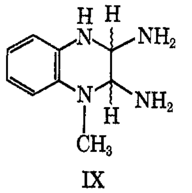
IV



V



VI, G = NO_2
VII, G = SO_2CH_3
VIII, G = $COCH_3$



IX

The present study complements our other investigations which show that uncharged heteroaromatic molecules such as the diazines, isoquinoline, and quinoline react rapidly and completely with amide ion in am-

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[1] Presented in part at the Gordon Conference on Heterocyclic Chemistry, New Hampton, N. H., June 26–30, 1972.

[2] W. L. F. Armarego, *Advan. Heterocycl. Chem.*, **1**, 253 (1963); A. Albert and W. L. F. Armarego, *ibid.*, **4**, 1 (1965); D. D. Perrin, *ibid.*, **4**, 43 (1965); A. Albert, *Angew. Chem., Int. Ed. Engl.*, **6**, 919 (1967); D. Beke, *Advan. Heterocycl. Chem.*, **1**, 167 (1963).

[3] J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, **50**, 919 (1972).

[4] Amino complexes of the type reported here have been isolated. For example, N-substituted isoquinolinium and quinolinium ions give crystalline solids with piperidine.[5]

[5] F. Kröhnke and J. Vogt, *Justus Liebigs Ann. Chem.*, **600**, 211 (1956).

Table I

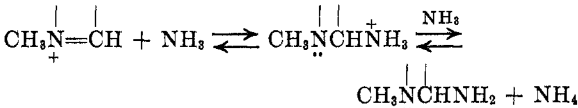
Chemical Shifts (τ) and Coupling Constants of Aminodihydro Compounds[a]

Compd	H-1	H-2	H-3	H-4	Other	J, Hz
I	4.85		3.63	4.55	H-5–H-8, 2.7–3.0 NCH_3, 6.90	$J_{3,4} = 7$ $J_{1,3} = 1.2$
II	4.97			4.67	H-5–H-8, 2.7–3.0 NCH_3, 7.02 CCH_3, 8.06	
III		5.21	4.14		H-4–H-8, 2.6–3.4 NCH_3, 6.97	$J_{3,4} = 9.8$ $J_{2,3} = 5.5$
IV	4.87			2.45	H-5–H-8, 2.4–2.7 NCH_3, 6.78	
V		2.17^b	1.93^b		H-6, 4.82; H-7, 3.60; H-8, 3.27 NCH_3, 6.84	$J_{6,7} = 4.5$ $J_{7,8} = 10$ $J_{2,3} = 3$
VI		1.51		3.15	H-5, 4.62; H-6, 4.94 NCH_3, 6.52	$J_{5,6} = 4$ $J_{4,5} = 10$ $J_{2,4} = 2.5$
VII		2.75		3.71	H-5, 4.72; H-6, 5.10 NCH_3,^{b} 6.74 SO_2CH_3,^{b} 7.03	$J_{5,6} = 4.5$ $J_{4,5} = 10$ $J_{2,4} = 2$
VIII		2.38		3.35	H-5, 4.75; H-6, 5.12 NCH_3, 6.74 $COCH_3$, 7.87	$J_{5,6} = 4.5$ $J_{4,5} = 10$ $J_{2,4} = 2$
IX		5.93^b	6.04^b		H-5–H-8, 3.41 NCH_3, 7.10	$J_{2,3} = 2.5$

[a] Nmr spectra of covalent amination products I, III, V, VIII, and IX appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JOC-73-1949. Remit check for $3.00 for photocopy or $2.00 for microfiche. [b] Assignments may be interchanged.

monia to give anionic covalent amination products.[6] Clearly, aminations must be taken into consideration when dealing with the chemistry of heteroaromatic compounds in ammonia[7] because major changes in physical and chemical properties are expected to result. The amination phenomenon is not limited to heterocyclic compounds.[8]

Structural assignments I–IX are based on the nmr data listed in Table I and on the well-established principle that the nucleophile will add to a carbon center so as to neutralize the charge on the quaternized nitrogen atom. This center generally will be located α or γ to the nitrogen atom. Product signals are at higher fields than those of the precursor cations. For example, reaction of 2-methylisoquinolinium ion[10] with ammonia gives a single product showing up-field shifts for H-1, H-3, and H-4 of about 4.4, 2, and 3 ppm, respectively. Such large shielding factors are similar to those known to result when nucleophiles add to aromatic rings.[11] Chemical shifts and coupling constants are consistent with those of known dihydro structures.[3,12,13] No spin coupling between the amino group and the proton of the newly formed tetrahedral carbon is found and none is expected. The probable stoichiometry of the addition reaction is given in eq 1. The ammonium ion product is expected to catalyze proton exchange between solvent and the amino group, leading to spin decoupling.[15] In agreement with this, the solvent shows a singlet rather than its usual triplet spectrum.



$$\mathrm{CH_3\overset{|}{\underset{+}{N}}{=}\overset{|}{C}H + NH_3 \rightleftharpoons CH_3\overset{|}{\underset{\cdot\cdot}{N}}\overset{|}{C}H\overset{+}{N}H_3 \overset{NH_3}{\rightleftharpoons} CH_3\overset{|}{\underset{\cdot\cdot}{N}}\overset{|}{C}HNH_2 + NH_4^+} \quad (1)$$

It is most likely that 2-methyl- and 2,3-dimethylisoquinolinium ions react with ammonia at C-1 to give aminodihydro compounds I and II. Of all the ring proton signals, that for H-1, easily recognized by the absence of large spin coupling, is found at the highest field (Table I). This is consistent with the formation of a tetrahedral center at C-1 by an addition reaction. Addition to C-3 or to a carbon atom of the carbocyclic ring can be ruled out if it is assumed that the proton at the tetrahedral center will resonate at high field. Such a proton is not expected to show a single, small (1.2 Hz) coupling as is found in the present case. Comparison of the spectra for I and II indicates that this 1.2-Hz coupling is likely to involve H-1 and H-3 of I. Note that the coupling constant involving the vinyl center

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(6) J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **94**, 682 (1972); J. A. Zoltewicz, L. S. Helmick, T. M. Oestreich, R. W. King, and P. E. Kandetzki, *J. Org. Chem.*, **38**, 1947 (1973).

(7) H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, Part 2, Interscience, New York, N. Y., 1963; H. J. den Hertog and H. C. van der Plas in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 17; T. Kauffmann and R. Wirthwein, *Angew. Chem. Int. Ed. Engl.*, **10**, 20 (1971).

(8) Polynitrobenzenes also have been reported to react with ammonia to give amino complexes.[9]

(9) R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 161 (1962).

(10) Iodide and perchlorate salts show identical spectra, thus eliminating the possibility that iodide ion rather than ammonia served as the nucleophile.

(11) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(12) R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1372 (1965); C. J. Cooksey and M. D. Johnson, *J. Chem. Soc. B*, 191 (1968); J. W. Bunting and W. G. Meathrel, *Tetrahedron Lett.*, 133 (1971); H. Albrecht and F. Kröhnke, *Justus Liebigs Ann. Chem.*, **717**, 96 (1968); T. Severin, H. Lerche, and D. Bätz, *Chem. Ber.*, **102**, 2163 (1969); **103**, 1 (1970).

(13) Ring-opened structures can easily be eliminated as possibilities. No aldimine signals are found at low fields. Coupling constants, *e.g.*, 2–5 Hz, for products from pyridinium ions are too small to be consistent with such structures.[14]

(14) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 191 and Chapter 4; R. Kuhn and E. Teller, *Justus Liebigs Ann. Chem.*, **715**, 106 (1968).

(15) R. A. Ogg, Jr., *Discuss Faraday Soc.*, **No. 17**, 215 (1954); D. R. Clutter and T. J. Swift, *J. Amer. Chem. Soc.*, **90**, 601 (1968).

directly bonded to the annular nitrogen atom is 7 Hz. In the case of II a new spectrum is observed at room temperature, corresponding to methylamine and 3-methylisoquinoline.

Although ammonia could add to the C-2 and C-4 positions of 1-methylquinolinium ion to give mixed monoaddition products, varying the temperature from −50 to 25° had no influence on the nature of the spectrum. Hence, only a single structure is detectable. That ammonia added to C-2 and not to C-4 follows from the spectrum of the adduct having deuterium at C-2. The doublet at τ 5.21 which is expected to be associated with the newly formed tetrahedral center disappeared on deuteration, showing that ammonia added to C-2 to give III. The large coupling constant (9.8 Hz) found for the vinyl protons in the nonaromatic ring provides additional evidence for the proposed structure. The C-4 adduct is expected to have a smaller coupling constant.[3,12]

1-Amino-2-methyl-1,2-dihydrophthalazine (IV) results from the amination of 2-methylphthalazinium ion. The chemical shift of the proton at the tetrahedral center (C-1) is nearly the same as those for H-1 of the analogous isoquinoline compounds I and II (Table I).

5-Methyl-1,4,5-triazanaphthalinium ion also readily undergoes amination. Ammonia could add to several positions of this cation. Only one structure was detected by nmr over the temperature range −43 to +30°. A structure may be designated by a consideration of the magnitude (10 Hz) of the coupling constant for the protons of the pyridine ring. The large value indicates that vinyl protons are present and the vinyl center is not bonded directly to nitrogen. Hence, addition takes place α to the quaternized nitrogen atom to give V.

In the case of 1-methyl 3-substituted pyridinium ions, three different amination products are likely, involving addition to positions C-2, C-4, and C-6. Only one isomer was detected between −50 and +30° (−23 and +30° in the case of the nitro compound). This isomer appears to be the same for ions having a nitro, a methylsulfonyl, or an acetyl substituent, as evidenced by similar coupling constants. Structures VI–VIII may be assigned. Amino adducts are formed by addition to C-6. The 10-Hz coupling constant rules out a C-4 adduct and the low-field position of H-2 eliminates a C-2 amination product. At room temperature another reaction occurs. Methylamine and a 3-substituted pyridine are formed; the order of increasing reactivity is acetyl, methylsulfonyl, and nitro substrate. Some 3-acetylpyridine imine forms as well.

It is interesting that 1-methylpyridinium ion, the parent compound, does not react with neutral ammonia to give covalent amination product in amounts detectable by nmr. Clearly, the effect of the 3 substituent is important. In the present cases, the electron-withdrawing effects of the substituents destabilize the precursor pyridinium ions, but the groups stabilize the amino adducts, especially when there is significant conjugation between the annular nitrogen atom and the substituent.

An especially interesting result is obtained with 1-methylquinoxalinium ion. Diaddition product IX is observed over the temperature range −30 to +30°. Evidence for this unusual structure is found in the high-field chemical shifts (τ 5.93 and 6.04) of the two protons bonded to the heterocyclic ring. A monoadduct, would, of course, show one of these protons at considerably lower field. Diaddition to the 1-methylquinoxalinium ion is not unprecedented. Most recently, di- as well as monoadduct formation in water and methanol were demonstrated.[3]

Ammonia and not amide ion formed from the dissociation of ammonia must be the nucleophile. The amide ion concentration resulting from the ionization of pure ammonia is $10^{-13.8}$ (pK = 27.7 at 25°),[16] but in the presence of 1 M NH_4I this is reduced to $10^{-27.7}$. In the case of 2-methylisoquinolinium ion adduct formation was complete in the presence or absence of NH_4I by the time the first spectrum was taken, about 30 min after mixing. If the heterocyclic cation had reacted with amide ion at a diffusion controlled rate, the half-life for the reaction involving NH_4I would be in excess of 10^{10} years.

Finally, a comparison of the extent of covalent amination and hydration reveals that for the cations considered here amination in neutral ammonia is complete but hydration in neutral water[2,3] is insignificant. This marked difference is readily understandable, however. In the reactions under consideration a cationic heterocycle is changed to a polar covalent molecule while a solvated proton is formed. Now, moderately polar ammonia is a better solvent for polar covalent molecules than for ions but the reverse is true for highly polar water.[17] Hence, the covalent adduct is stabilized in ammonia. Moreover, the solvated proton is considerably more stable in ammonia than in water.[18]

On the basis of our survey it seems that covalent amination of heteroaromatic compounds in ammonia is extensive.

Experimental Section

All compounds (perchlorate and/or iodide salts) were available from other studies. A Varian A-60A spectrometer equipped with a V-6040 variable temperature controller was employed. Quinoline-*2-d* was prepared by H–D exchange using D_2O.[19]

General Method of Amination.—Ammonia was added to quaternized compound in an ordinary nmr tube cooled in an acetone–Dry Ice bath. Vapor was passed into the tube through a glass capillary until about 0.5 ml of solvent condensed. Then 2 ml of trimethylamine (τ 7.87) vapor was added through a needle inside the tube in a region cooled by the bath. In a few instances benzene (τ 2.60) was employed as an internal standard. The tube, sealed with a torch, was alternately shaken and cooled so as to induce mixing without unduly warming the contents. The tube then was placed into the cooled (generally −50°) nmr probe. In some instances samples were not sufficiently soluble to give spectra at −50°; the most extreme case was 2-methylphthalazinium iodide which required about 0° to give a suitable spectrum. Substrate concentrations were 0.4 M. In some cases higher concentrations give rise to oil formation. Before spectra are recorded at ambient temperatures, it is wise to check the seal of the nmr tube to avoid damage to the spectrometer. A water bath heated 10–20° above that of the probe was used for this purpose.

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(16) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Amer. Chem. Soc.*, **81**, 2986 (1959).

(17) J. J. Lagowski, *Pure Appl. Chem.*, **25**, 429 (1971).

(18) W. L. Jolly, *J. Phys. Chem.*, **58**, 250 (1954); P. Kebarle in "Ions and Ion Pairs in Organic Reactions," M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 2.

(19) J. A. Zoltewicz and C. L. Smith, *J. Amer. Chem. Soc.*, **89**, 3358 (1967); U. Bressel, A. R. Katritzky, and J. R. Lea, *J. Chem. Soc. B*, 4 (1971).

Registry No.—I, 38896-59-2; II, 38896-60-5; III, 38896-61-6; IV, 38896-62-7; V, 38896-63-8; VI, 38896-64-9; VII, 38896-65-0; VIII, 38896-66-1; IX, 38896-67-2.

Acknowledgment.—This project was kindly supported by the National Science Foundation (GP 25500).

The Oxidation of Benzylamines with Nitrosobenzene

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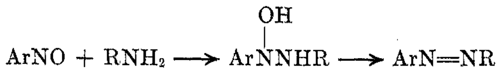
Received January 24, 1973

Aromatic amines react readily with nitrosobenzene to afford azobenzenes,[2] presumably through elimination of water from intermediate *N*-hydroxyhydrazines[3] (**1**, R = Ar). In view of this, we envisioned that the analogous reaction of nitrosobenzene with aliphatic amines might provide a convenient source of phenylazoalkanes (**2**, R = alkyl).[4] In fact, an early report is



$$\mathrm{ArNO + RNH_2 \longrightarrow Ar\overset{OH}{N}NHR \longrightarrow ArN{=}NR}$$

1 2

available which describes the formation of toluene-α-azobenzene (**2**, R = benzyl) from nitrosobenzene and benzylamine in alcohol solvent.[5] However, a subsequent study of this reaction with a variety of benzylamines reported instead the production of aldehydes or ketones, azoxybenzene, and ammonia with no evidence for azo formation.[6] The mechanism postulated for this reaction involved transfer of an oxygen from a molecule of nitrosobenzene to the benzyl carbon with concurrent loss of ammonia and generation of azoxybenzene.[6]

In order to shed light on the above discrepancies and hopefully to divert the reaction to give phenylazoalkanes, the reaction was reinvestigated in a variety of solvents, including diethyl ether, benzene, and dimethyl sulfoxide (DMSO); the results are presented in Table I. In all cases the product profiles were nearly identical as determined by glpc and consisted of *N*-benzylbenzaldimine (**3**) and azoxybenzene, identified by nmr and mass spectral comparisons with authentic samples. In addition, structure **3** was confirmed by chemical methods (see Experimental Section). Repetition of the exact experimental conditions employed by previous workers[6] using a 2:1 mole ratio of nitrosobenzene to benzylamine in refluxing benzene gave glpc-determined yields of 78% azoxybenzene and 76% **3** in 9 hr (Table I). Conceivably, **3** may arise by condensation of initially produced benzaldehyde with remaining benzylamine. However, in no case was benzaldehyde detected by glpc under conditions where its presence would have been evident.[7] In addition, **3** reacts readily with 2,4-dinitrophenylhydrazine by an amine–imine exchange reaction to liberate benzylamine along with the corresponding 2,4-dinitrophenylhydrazone of benzaldehyde. This latter reaction would account for the identification of carbonyl compounds as primary products.[6] As an alternative, the mechanistic sequence depicted in Scheme I is suggested in which initial attack of benzylamine on nitrosobenzene occurs to furnish the hydroxylhydrazine species **4**. Elimination of phenylhydroxylamine (**5**), possibly *via* a Cope-type elimination (as in **6**),[8] affords benzaldimine[9] (**7**), which gives the observed imine **3** and ammonia upon exchange with benzylamine.[13] The azoxybenzene most probably arises by the well-known condensation of phenylhydroxylamine with nitrosobenzene.[10]

To provide evidence for the production and intermediacy of unsubstituted imines, the reaction of diphenylmethylamine with nitrosobenzene was investigated in hopes of detecting the fairly stable imine **8**[15] before exchange with starting amine. Indeed, in benzene at 70°, **8** was observed to be produced concomitantly with azoxybenzene. The imine **8** further reacted with benzylamine to afford *N*-benzyldiphenylmethyleneimine (**9**), which had been previously observed.[6] The production of various products was monitored by glpc and plotted in Figure 1. Furthermore, benzophenone was observed to be unreactive toward

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[1] National Science Foundation Undergraduate Research Participant, 1971.

[2] (a) P. Ruggli and J. Rohner, *Helv. Chim. Acta*, **25**, 1523 (1952); (b) W. Borsche and I. Exss, *Ber.*, **56**, 2353 (1923); see also (c) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, pp 319–321, and references cited therein.

[3] P. Y. Sollenberger and R. B. Martin in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 395.

[4] Phenylazoalkanes may be prepared by oxidation of the corresponding hydrazines; see, for example, A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 2788 (1965). The reaction of alkylzinc compounds with diazonium salts gives phenylazoalkanes, but the method is often unreliable; see D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956). See also ref 2c, p 219, for a review of preparative methods for azo compounds.

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[6] (a) K. Suzuki and E. K. Weisburger, *Tetrahedron Lett.*, 5409 (1966); (b) *J. Chem. Soc. C*, 199 (1968).

[7] Benzaldehyde reacts with benzylamine to give the observed product *N*-benzylbenzaldimine under the reaction conditions, but sufficient amounts of benzaldehyde remain to be detectable by glpc. In addition, the reaction of nitrosobenzene with benzylamine at room temperature was followed by nmr (220 MHz). Even under such mild conditions benzaldehyde was not detected, only benzylbenzaldimine.

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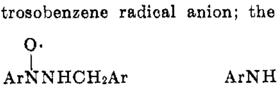
[9] Alternately, the breakdown of the first condensation intermediate **4** could involve an electron transfer to nitrosobenzene to afford an amino nitroxide (i) and nitrosobenzene radical anion; the latter species couple



$\mathrm{Ar\overset{O\cdot}{N}NHCH_2Ar}$ $\mathrm{ArNH\cdot}$

i ii

readily to azoxybenzene (ref 10). The amino nitroxide i may fragment to furnish benzylamino radical ii [in analogy to the behavior of alkoxy nitroxides (ref 11)], which could disproportionate to benzylamine and benzaldimine (**7**) (ref 12). While nitrosobenzene has been documented as an electron acceptor (ref 13, 14), other experiments in our laboratory using such easily oxidized amines as *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine do not indicate this to be the general case in the presence of amines. In addition, the reaction of phenylhydroxylamine and nitrosobenzene generates a small concentration of monophenyl nitroxide as detected by esr. An examination of the reaction of nitrosobenzene with benzylamine demonstrated the same occurrence. The somewhat analogous reaction of benzyl alcohols with nitrosobenzene in the presence of base to yield benzaldehyde and azoxybenzene is also thought to proceed by an ionic mechanism; see J. Hutton and W. A. Waters, *J. Chem. Soc. B*, 191 (1968).

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