Dibutylacetoxychlorotin was prepared[15] by heating 3.5 g of dibutyltin diacetate and 3.0 g of dibutyltin dichloride at 80–90° for 5 min. Recrystallization from pentane gave 5 g of the acetoxytin chloride, mp 59–62° (lit.[15] mp 63–65°), ir (CCl_4) 1590 cm^{-1} (C═O).

PMHS Reduction with DBATO.—A solution of the organic substrate (1 mol) and 12 g of DBATO (0.02 mol) in 700 ml of 95% ethanol was heated to reflux (80°).[25] PMHS,[5] 70 g (1.1 equiv), was added dropwise slowly enough to maintain gentle reflux.[26] In most cases, reduction was complete when all the PMHS was added. Completion of reduction was determined by disappearance of carbonyl absorption using ir analysis. Water, 800 ml, was added and the reaction mixture was stirred at 80° until a granular methylsilsesquioxane gel was obtained (about 1 hr). The gel was filtered and the filtrate and gel were extracted with chloroform. The combined chloroform extracts were distilled, recrystallized, or analyzed by glc with addition of toluene or xylene as an internal standard. Products on which glc yields are reported were identified by tandem glc–mass spectroscopy. Isolated products were characterized by melting point or boiling point, and ir spectroscopy. Isomeric purity of *trans*-4-*tert*-butylcyclohexanol was determined by ir spectroscopy.[27] *p*-Hydroquinone was isolated as the quinhydrone.[17] Reductions that failed were carried out similarly, using 700 ml of 2-ethylhexanol as solvent in the 130° runs. The reductions of nitro compounds and nitriles at 130° gave traces of amines (or ammonia) as evidenced by alkalinity during attempted distillation. In addition, approximately 2% yields of aniline and toluene were obtained, by glc mass spectroscopy, in reductions of nitrobenzene and benzyl chloride, respectively.

Reaction of Polymethylhydrosiloxane and Bis(dibutylacetoxytin) Oxide.—A solution of 0.19 g of PMHS (3 mequiv) and 1.8 g of DBATO (3 mequiv) in 25 ml of dry cyclohexane was prepared under dry N_2. An ir spectrum, obtained immediately, showed a band at 1830 cm^{-1} attributable to ν(SnH) of dibutyltin dihydride [lit.[12] ν(SnH) 1832 cm^{-1}]. After storage overnight, a band appeared at 1550 cm^{-1} attributable to 1,1,2,2-tetrabutyl-1,2-diacetoxyditin [lit.[12] ν(C═O) 1553 cm^{-1}], which is a decomposition product of dibutylacetoxytin hydride.[12]

A solution of 0.20 g of PMHS and 1.8 g of DBATO in 20 ml of CCl_4 was refluxed for 2 hr. Infrared analysis during the reaction showed the disappearance of silyl hydride [ν(SiH) 2160 cm^{-1}] and the formation of chloroform [δ(CH) 1210 cm^{-1}] and dibutylacetoxychlorotin [ν(C═O) 1590 cm^{-1}].

PMHS Reductions with Pd on Charcoal. A 10% excess of PMHS was added to a mixture of the organic substrate (0.1 mol) and 0.05 g of 5% Pd on charcoal in 40 ml of 95% ethanol containing 1 drop of concentrated HCl.[28] For reduction of olefins, benzaldehyde, and nitrobenzene, 0.11, 0.22, and 0.33 equiv respectively of PMHS were used. The reaction mixture was swirled occasionally, and the temperature was maintained at 40–60° by cooling or heating, depending on substrate reactivity. Methyl vinyl ketone, which did not exotherm, was heated at 40–60° for 2 hr. Other substrates were heated for about 30 min after the exotherm, which required cooling, had subsided. The catalyst was removed by filtration, 80 ml of water was added, and the product was extracted from the aqueous mixture with pentane. The pentane extract was dried ($CaCl_2$) and products were identified by tandem glc–mass spectrometry. Yields were determined by addition of toluene or xylene as a glc internal standard to the pentane extract. Distillation of the 1-octene reduction product gave *n*-octane, bp 125°, containing 7% isomerized olefins. Isomerized olefins were also detected by glc in the 2-nonene reduction product.

Registry No.—**1**, 9004-73-3; **2**, 5967-09-9; Pd, 7440-05-3.

Acknowledgment.—We thank John Coutant and Ron Robinson for glc–mass spectroscopy analyses and Jerry Garner for glc analyses of isomerized olefins.

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[25] The rate of reduction can be increased by increasing DBATO concentration or by increasing reaction temperature by use of a higher boiling alcohol.

[26] Premature gelation before completion of reduction may occur if PMHS concentration is allowed to build up by too rapid addition.

[27] R. S. Ro, Ph.D. Thesis, University of Notre Dame, 1957; E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5992 (1957).

[28] *Caution.* PMHS should be added in small portions to reactions run on an appreciably larger scale to control the exotherm.

Carbonyl Compounds and Secondary Amines from Diarylhydroxylamines *via* Nitroxides

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Received August 7, 1972

In previous work we have described the preparation of *N*-phenyl-*N*-fluorenylhydroxylamines by the reaction of nitrofluorenes with phenylmagnesium bromide in a nitrogen atmosphere.[1] In the presence of air the hydroxylamines were transformed to products that have now been identified. The work presented here shows that *N*-phenyl-*N*-fluoren-2-ylhydroxylamine in the presence of air gives rise to 2-anilinofluoren-9-one and *N*-phenylfluoren-2-amine and that a nitroxide is the intermediate, as shown in Scheme I. Similarly, *N*-phenyl-*N*-fluoren-3-ylhydroxylamine yielded the corresponding diaryl ketone and diarylamine. 1-Anilinofluoren-9-one and *N*-phenylfluoren-1-amine, isolated from the reaction of 1-nitrofluorene and phenyl Grignard in air, undoubtedly arose from the intermediate *N*-phenyl-*N*-fluoren-1-ylhydroxylamine. The course of these reactions may be rationalized by a mechanism similar to that proposed by Calder and Forrester.[2] According to these workers, *N*,*N*-alkylarylhydroxylamines disproportionate to carbonyl compounds and arylamines *via* intermediate nitroxides. The applicability of this mechanism to diarylhydroxylamines was supported by the oxidation of *N*-phenyl-*N*-biphenyl-4-ylhydroxylamine to a stable nitroxides and by the conversion of the nitroxide to *p*-benzoquinone biphenyl-4-ylimine *N*-oxide and *N*-phenylbiphenyl-4-ylamine.

Another reaction which yields fluoren-9-ones from fluorenes is the oxidation of the methylene group involving intermediate peroxides.[3] This pathway may have contributed to the formation of fluorenones, since 2- and 3-anilinofluoren-9-one were obtained in minor amounts by air oxidation of the respective secondary amines.

Experimental Section

Melting points were taken with a Fisher-Johns apparatus. Ir spectra were recorded with a Beckman IR-10 spectrophotometer. The uv spectra were taken with a Beckman DK-2 spectrophotometer and the absorbancies at λ_{max} were read with a Gilford digital absorbance meter on a DR Beckman monochromator. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6 spectrometer. Silica gel GF_{254} for tlc was obtained from Brinkman Instruments, Inc., Westbury, N. Y.

2-Anilinofluoren-9-one.—*N*-Fluoren-2-yl-*N*-phenylhydroxyamine[1] (1.50 g, 5.50 mmol) in ethanol (60 ml) and 2.5 *N* NaOH (2.5 ml) were stirred in an open flask for 12 hr at 40°. The colorless mixture turned red, then yellow, and finally green. A red precipitate was dissolved by addition of dimethylformamide (25 ml). The solution was treated with gaseous ammonia (9 min) and hydrogen sulfide (20 min) and stirred at room temperature for 1 hr. The volume of the solution was reduced by 50%. Ice–water was added and the resulting red precipitate was collected and washed with water (1.22 g). A portion (80 mg) was chromatographed (tlc) on silica gel with benzene. The

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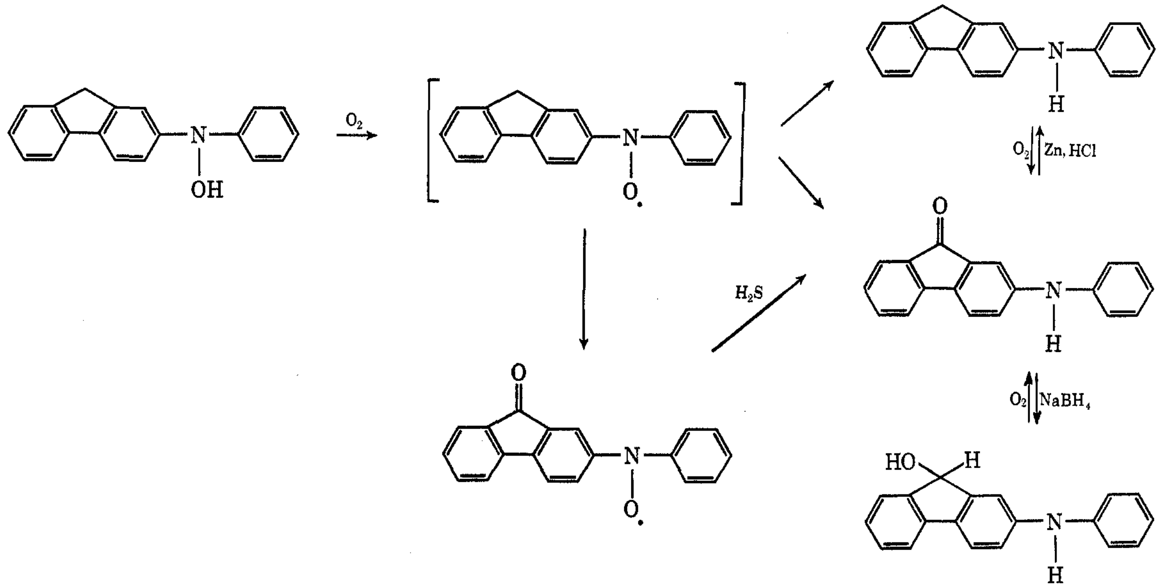
[1] Y. Yost, H. R. Gutmann, and C. Muscoplat, *J. Chem. Soc.*, 2119 (1971).

[2] A. Calder and A. R. Forrester, *J. Chem. Soc. C*, 1459 (1969); A. R. Forrester and S. P. Hepburn, *ibid.*, 1277 (1971).

[3] Y. Sprinzak, *J. Amer. Chem. Soc.*, **80**, 5449 (1958); E. F. Pratt and L. E. Trapasso, *ibid.*, **82**, 6405 (1960).

SCHEME I



band, R_f 0.7, yielded *N*-phenylfluoren-2-amine (27%) identified by the uv spectrum.[1] The red band, R_f 0.6, yielded the title compound (53%), as a red powder from benzene–*n*-heptane: mp 201–203°; uv max (EtOH) 245 nm (log ε 4.34), 250^i (4.29), 293 (4.59), 343 (4.28), and 506 (3.04); ir max (KBr) 3370 (NH) and 1710 cm^{-1} (C=O); *m/e* 271 (M^+). (Superscript i denotes inflection point.)

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.10; H, 4.83; N, 5.16. Found: C, 83.91; H, 4.91; N, 5.16.

In another experiment *N*-phenylfluoren-2-amine (5 mg) in ethanol (2 ml) was exposed to air at room temperature for 6 days. 2-Anilinofluoren-9-one was isolated by tlc and estimated spectrophotometrically (6%).

The ketone in a mixture of acetic acid and HCl was reduced with zinc to the *N*-phenylfluoren-2-amine.[1] The ketone was also reduced to the alcohol as follows. A mixture of 2-anilinofluoren-9-one (80 mg), sodium borohydride (50 mg) in methanol (25 ml), and 0.1 *N* sodium hydroxide (1 ml) were stirred until the red solution was colorless (~15 min). 2-Anilino-9-hydroxyfluorene was isolated (75%) by extraction with ether and crystallized from ethanol–water: mp 149–150°; uv max (EtOH) 328 nm (log ε 4.48); ir max (KBr) 3505 (OH) and 3310 cm^{-1} (NH); *m/e* 273 (M^+).

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.26; H, 5.50; N, 5.43.

The ethanolic solution used for the measurement of the uv spectrum was exposed to sunlight and the uv absorption spectrum was recorded at 10-min intervals. After 1 hr, the solution had turned pale red and the spectrum resembled that of 2-anilinofluoren-9-one. Oxidations of hydroxymethylene groups adjacent to aromatic systems have already been reported.[3]

Phenyl(9-oxofluoren-2-yl) Nitroxide.—*N*-Fluoren-2-yl-*N*-phenylhydroxylamine[1] (700 mg, 2.57 mmol) in ethanol (75 ml) and aqueous 2.5 *N* sodium hydroxide (5 ml) was stirred in an open flask for 30 min. A white precipitate (sodium carbonate, 200 mg) was removed by filtration. The red filtrate was stirred for 90 min. A maroon precipitate was collected and washed with water and ethanol (0.27 g), mp 160–170° dec. The material was suspended in hot benzene (10 ml) and the mixture was filtered (gravity). The product crystallized as dark needles after dilution with hot *n*-heptane (110 mg): mp 162° dec; uv max ($CHCl_3$) 250 nm (log ε 4.59), 304 (4.26), 312 (4.27), 338 (4.20), 380^i (3.72), 405^i (3.52), 470 (3.08), 500 (3.04), and 670^i (2.08); ir max (KBr) NH, OH none, 1715 cm^{-1} (C=O); *m/e* 286 (M^+); esr, a triplet with a_N 9.3 G, characteristic of diaryl nitroxides.[4]

Anal. Calcd for $C_{19}H_{12}NO_2$: C, 79.70; H, 4.23; N, 4.89 O, 11.18. Found: C, 79.56; H, 4.46; N, 4.98; O, 11.29.

The filtrate from which the crude product had been obtained was cooled in an open flask and a precipitate was collected every 24 hr over a period of four days. Each precipitate consisted essentially of 2-anilinofluoren-9-one and *N*-phenylfluoren-2-amine. The separations were effected by tlc and the compounds were identified spectrophotometrically. In another experiment in which air was excluded neither nitroxide nor ketone were obtained.

The title compound (10 mg) in dimethylformamide (2 ml) and ethanol (1 ml) was treated successively with NH_3 (5 min) and with H_2S (5 min). After 15 min, the mixture was diluted with water and chloroform. 2-Anilinofluoren-9-one, identified spectrophotometrically, was isolated from the organic phase.

3-Anilinofluoren-9-one.—A stream of air was passed for 2 hr through a solution of *N*-fluoren-3-yl-*N*-phenylhydroxylamine[1] (500 mg, 1.85 mmol) and 2.5 *N* sodium hydroxide (2 ml) in ethanol (5 ml). The mixture was kept at room temperature for 2 days. It was then treated with Na_2S (1 g) and NH_4Cl (1 g) and stirred for another 3 hr. The solvents were removed and the residue was triturated with water and chloroform. The organic phase was chromatographed on tlc with benzene–*n*-hexane (2:1). The first band, R_f 0.8, gave *N*-phenylfluoren-3-amine (60 mg): mp 145–147°; uv max (EtOH) 264 nm (log ε 4.45) and 298 (4.25); ir max (KBr) 3380 cm^{-1} (sharp, NH); *m/e* 257 (M^+). *Anal.* Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.96; H, 6.13; N, 5.17. The purple band, R_f 0.7, gave a crimson substance (40 mg) that could not be crystallized and remains unidentified. The orange band, R_f 0.3, gave the title compound (110 mg): mp 201–203°; uv max (EtOH) 252 nm (log ε 4.59), 267 i (4.22), 322 (4.24), 388 (3.80), and 444 (3.92); ir max (KBr) 3300 (NH) and 1690 cm^{-1} (C=O); *m/e* 271 (M^+).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.10; H, 4.83; N, 5.16. Found: C, 84.14; H, 4.89; N, 5.35.

In another experiment *N*-phenylfluoren-3-amine (5 mg) in ethanol (2 ml) was exposed to air at room temperature for 6 days. 3-Anilinofluoren-9-one was isolated by tlc and quantified spectrophotometrically (18% yield).

1-Anilinofluoren-9-one.—1-Nitrofluorene[5] (100 mg, 0.4 mmol) in anhydrous tetrahydrofuran (4 ml) was treated with phenylmagnesium bromide as previously described.[1] After addition of water, the organic phase was concentrated to 1 ml and diluted with ethanol (10 ml) and 8 *N* ammonium hydroxide (0.5 ml). The red mixture was stirred at room temperature for 24 hr. Sodium sulfide (0.1 g) and NH_4Cl (0.1 g) were then added and stirring was continued for 4 hr. The mixture was concentrated at reduced pressure, diluted with H_2O (20 ml), and then extracted with chloroform (2 × 3 ml). The extract was chromatographed (tlc) with benzene–*n*-hexane (1:1). The following compounds were isolated: biphenyl, R_f 0.9; *n*-phenylfluoren-1-amine, R_f

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(4) H. Lemaire, A. Rassat, and A. Ravet, *Bull. Soc. Chim. Fr.*, 1980 (1963). Esr spectra of the nitroxide will 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 St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-165. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(5) Y. Yost and H. R. Gutmann, *J. Chem. Soc. C*, 345 (1969).

0.7, mp 130–132°, uv max (EtOH) 266 nm (log ε 4.34), ir max (KBr) 3400 cm^{-1} (NH), m/e 257 (M$^+$). The red band, R_f 0.4, yielded 1-anilinofluoren-9-one. Prior to analysis the product was rechromatographed (tlc) with benzene and recrystallized from methylene chloride–n-hexane: 54 mg (46%); mp 187–188°; uv max (EtOH) 257 nm (log ε 4.68), 296 (4.04), and 500 (3.88); ir max (KBr) 3322 (NH), 1705 cm^{-1} (C═O); m/e 271 (M$^+$).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.10; H, 4.83; N, 5.16. Found: C, 83.98; H, 4.87; N, 5.38.

Biphenyl-4-ylphenyl Nitroxide. A. By Oxidation of *N*-Biphenyl-4-yl-*N*-phenylhydroxylamine with Ferric Chloride.—A 0.93 *M* ethanolic solution of ferric chloride (4.1 ml, 3.8 mmol) was added to *N*-biphenyl-4-yl-*N*-phenylhydroxylamine (1.00 g, 3.82 mmol) in ethanol–benzene (1:1) (40 ml). The red mixture was stirred for 5 min and was then diluted with water (40 ml). The organic phase was washed with water and dried ($MgSO_4$), and the solvent was removed. One crystallization from dichloromethane–n-hexane and two crystallizations from benzene–n-heptane gave the title compound: 0.25 g; mp 127–130° dec; uv max (n-hexane) 243 nm (log ε 4.00), 294 (4.02), 329 (4.29), and 400 i; uv max (EtOH) 243 nm (log 3.96), 294 (3.96), and 332 (4.27); ir max (KBr) 1477 cm^{-1} (NO); m/e 260 (M$^+$); esr, a triplet with a_N 9.5 G, characteristic of diaryl nitroxides.[4]

Anal. Calcd for $C_{18}H_{14}NO$: C, 83.05; H, 5.42; N, 5.38; O, 6.15. Found: C, 83.17; H, 5.38; N, 5.44; O, 6.30.

The nitroxide in dimethylformamide and ethanol was treated with gaseous NH_3 and H_2S for 10 min. The resulting colorless solution was diluted with water and washed with diethyl ether. The organic phase yielded *N*-phenylbiphenyl-4-ylamine.[1]

B. By Air Oxidation of *N*-Biphenyl-4-yl-*N*-phenylhydroxylamine.—To an ethanolic solution of *N*-biphenyl-4-yl-*N*-phenylhydroxylamine (54 mg, 0.21 mmol) was added KOH (5 mg) and the solution was flushed with air for 10 min. The yellow color of the solution turned red as soon as the air was admitted, and the red nitroxide precipitated. The compound was collected and washed with water (30 mg, 55%), mp 132–134°. Additional product (19 mg) was obtained from the filtrate by tlc; total yield, 90%. An alkaline ethanolic solution of the hydroxylamine that was flushed with nitrogen remained colorless. This indicated that no nitroxide was formed in the absence of air.

***p*-Benzoquinone Biphenyl-4-ylimine *N*-Oxide.**—Biphenyl-4-ylphenyl nitroxide (30 mg) in $CHCl_3$ was applied to a plate coated with silica gel (1 mm) and developed after 30 min with benzene–ethyl acetate (1:1). The band, R_f 0.8, gave *N*-phenylbiphenyl-4-ylamine (10%); the red band, R_f 0.6, yielded starting material (41%). The orange band, R_f 0.3, gave the *N*-oxide (7 mg, 22%): mp 200°; uv max (EtOH) 250 nm (log ε 4.21) and 378 (4.36); ir max (KBr) NH, OH none, 1623 cm^{-1} (C═O); m/e 275 (M$^+$). The tlc was intended to purify the nitroxide. In addition, the nitroxide was converted in part to the *N*-oxide on the chromatogram as indicated by the fact that additional bands containing *N*-oxide and amine, respectively, appeared when the chromatogram was developed a second time. The strong absorption bands of the *N*-oxide at 250 and 378 nm are evidence for the biphenyl system and for the *p*-benzoquinone imine *N*-oxide, respectively.[2,6] The structural assignment of the compound was confirmed by reduction to 4-hydroxy-4′-phenyldiphenylamine.[7] An ethanolic solution of the *N*-oxide was treated with ammonium chloride and sodium sulfide (hydrated). The mixture was stirred for 15 min and the solvent was removed. The residue was dissolved in a mixture of water and chloroform. The organic phase was chromatographed on silica gel with benzene–ethyl acetate (4:1). The major band, R_f 0.2, gave 4-hydroxy-4′-phenyldiphenylamine as pale tan needles from benzene–n-heptane: mp 149–150° (reported[7] mp 148–149°); ir max (KBr) 3420 (sharp, NH), 3300 (broad, OH), 815 (4 × 2 adjacent H), and 750 and 680 cm^{-1} (phenyl); m/e 261 (M$^+$).

Registry No.—2-Anilinofluoren-9-one, 36982-44-2; 2-anilino-9-hydroxyfluorene, 36982-45-3; phenyl(9-oxofluoren-2-yl) nitroxide, 36982-46-4; 3-anilinofluoren-9-one, 36982-47-5; *N*-phenylfluoren-3-amine, 36982-48-6; 1-anilinofluoren-9-one, 36982-49-7; *N*-phenylfluoren-1-amine, 36982-50-0; biphenyl-4-ylphenyl nitroxide, 36982-51-1; *p*-benzoquinone biphenyl-4-ylimine *N*-oxide, 36982-52-2; 4-hydroxy-4′-phenyldiphenylamine, 36982-53-3.

Acknowledgment.—The authors are indebted to Professor S. W. Fenton for comments, to Professor R. Barnett for interpretation of the esr spectra, and to Mrs. O. Hamerston and Mr. J. McMahon for recording the spectra. This work was supported by Grant CA02571 from the National Cancer Institute, NIH.

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[6] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 101.

[7] J. C. Conner, U. S. Patent 2,661,375 (1953); *Chem. Abstr.*, **49**, 375*i* (1955).

Reactions of Amines with 1,3-Dibromo-2-(bromomethyl)-2-nitropropane

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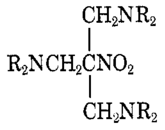
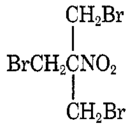
Received August 11, 1972

The object of this research was to prepare compounds of type **1** utilizing the appropriate secondary amines and the tribromide **2**. We find that these reactions do not lead to the desired compound **1**. Instead, compounds of structure **3** result.



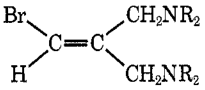
$$\begin{array}{c} CH_2NR_2 \\ | \\ R_2NCH_2CNO_2 \\ | \\ CH_2NR_2 \end{array}$$

1



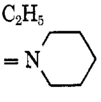
$$\begin{array}{c} CH_2Br \\ | \\ BrCH_2CNO_2 \\ | \\ CH_2Br \end{array}$$

2



3a, R = C_2H_5

b, NR_2 =



The reaction of **2** with diethylamine gave only one product, **3a**. The reaction with *tert*-butylamine did not give a pure product, and *N*-methylaniline did not react at all. Three products were obtained from the reaction of piperidine with **2**: *N*-(2-nitroethyl)piperidine (**4**), di(*N*-piperidino)methane (**5**), and **3b**. The formation of **4** and **5** in this reaction suggests that the desired triamine, **1**, was formed and then converted to **4** and **5** *via* two reverse Mannich reactions according to the mechanism of Spoerri, *et al.*[2] On the other hand, **2** could alternately have undergone aminomethylation and the reverse Mannich reaction to form the same products in a stepwise manner (Scheme I) without ever having formed the triamine **1**. Thus no conclusion can be drawn as to whether or not the desired compound **1** was ever formed.

Each of the reaction mixtures in which compound **3** was formed gave a positive test for the nitrite ion.[3] Dehydrobromination of **3** did not occur in any of these denitrations because there weie no protons β to the bromine atom.

The loss of HNO_2 has been observed previously in

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[1] Taken in part from the M.S. Thesis of David A. Klein, University of South Florida, 1971.

[2] D. Taber, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **76**, 776 (1954).

[3] The test used for the detection of nitrite ion is described by G. Charlot, "Rapid Detection of Cations and Anions," translated by R. E. Oesper, Chemical Publishing Co., New York, N. Y., 1965, p 80.