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.

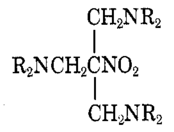
Reactions of Amines with 1,3-Dibromo-2-(bromomethyl)-2-nitropropane

David A. Klein[1] and J. E. Fernandez*

Chemistry Department, University of South Florida, Tampa, Florida 33620

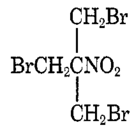
Received August 11, 1972

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.



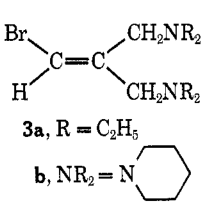
$$R_2NCH_2\underset{CH_2NR_2}{\overset{CH_2NR_2}{C}}NO_2$$

1



$$BrCH_2\underset{CH_2Br}{\overset{CH_2Br}{C}}NO_2$$

2



3a, R = C_2H_5

b, NR_2 = N

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 were no protons β to the bromine atom.

The loss of HNO_2 has been observed previously in

---

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

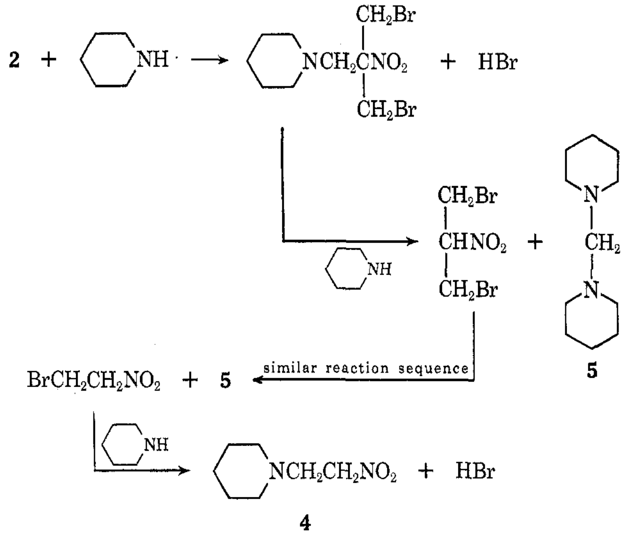
[7] J. C. Conner, U. S. Patent 2,661,375 (1953); *Chem. Abstr.*, **49**, 375*i* (1955).

[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).

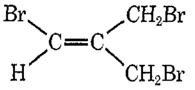
[3] The test used for the detection of nitrite ion is described by G. Charlot, "Rapid Detection of Cations and Anions," translated by R. E. Oesper, Chemical Publishing Co., New York, N. Y., 1965, p 80.

Scheme I



similar reactions of 2 with sodium amalgam[4] and with KOH in alcohol.[5]

The major products of these reactions, **3a** and **3b**, were probably formed in two steps: first the denitration similar to that observed by Kleinfeller, *et al.*, to form **6**, followed by substitution of amine groups for



6

the allylic bromine atoms. The vinyl bromine atom is so unreactive that it is not replaced by the amine group.

Thus in general the denitration of tertiary nitro alkanes containing vicinal halides can be brought about by amines with a basicity at least as weak as *tert*-butylamine (K_b = 2.8 × 10^{-4}) as well as by strong bases such as KOH and sodium amalgam as observed previously.[4,5]

Experimental Section

Boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 nmr spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer. Molecular weights were determined by titrating the products with standard HCl, following the titration with a pH meter.

Reaction of Diethylamine with $(CH_2Br)_3CNO_2$.—A solution of 2 (25 g, 0.0735 mol) in methanol (300 ml) was placed in a flask fitted with a reflux condenser protected with a drying tube and an addition funnel. The mixture was heated to reflux, and diethylamine (16.2 g, 0.221 mol) was added dropwise. The mixture was refluxed for 1 week and cooled, and then the solvent was evaporated leaving an oily solid, which was mixed with 50 ml of 10% HCl. The resulting mixture was filtered, leaving 21.5 g of the starting bromide. The filtered solution was saturated with K_2CO_3 and extracted with ether. The ether extract was dried ($MgSO_4$), concentrated, and distilled, giving 2.3 g (79%) of **4**: bp 68–69° (0.25 mm); ir (film) 3030, 1630 cm^{-1} (CH=C); nmr (neat) δ 0.93 (t, 12), 2.44 (q, 8), 3.05 (s, 2), 3.17 (s, 2), 6.24 (s, 1). The product decolorized Br_2 in CCl_4 and gave a positive Beilstein test but did not react with alcoholic $AgNO_3$.

Anal. Calcd for $C_{12}H_{25}BrN_2$: C, 51.98; H, 9.09; Br, 28.82; N, 10.11; mol wt, 277.26. Found: C, 51.52; H, 8.96; Br, 29.49; N, 9.77; mol wt (titration), 278.

Similar results were obtained when this reaction was carried out without a solvent.

Reaction of Piperidine with $(CH_2Br)_3CNO_2$ (2).—A mixture of 2 (10 g, 0.0294 mol) and piperidine (30 ml) was refluxed for 12 hr, cooled, and diluted with acetone (100 ml). This solution was filtered, yielding 10.8 g of piperidine hydrobromide. The filtered solution was concentrated and distilled into two fractions. The lower boiling fraction [bp 42–44° (0.25 mm)] was shown to be a mixture of **5** and **6** in a ratio of 3:1 by nmr analysis. This fraction weighed 4.0 g; no attempt was made to separate the mixture into its components. The higher boiling fraction, **7**, weighed 9.5 g: bp 104–108° (0.25 mm); ir (film) 3050, 1630 cm^{-1} (CH=C); nmr (neat) δ 1.42 (m, 12), 2.30 (m, 8), 2.92 (s, 2), 3.06 (s, 2), 6.25 (s, 1). This product decolorized Br_2 in CCl_4, and gave a positive Beilstein test, but did not react with alcoholic $AgNO_3$.

Anal. Calcd for $C_{14}H_{25}BrN_2$: C, 55.81; H, 8.36; Br, 26.53; N, 9.30; mol wt, 301.28. Found: C, 56.01; H, 8.49; Br, 26.34; N, 9.18; mol wt (titration), 297.

Similar results were obtained when methanol was used as a solvent.

Registry No.—**2**, 36809-38-8; **3a**, 36809-39-9; **3b**, 36809-40-2.

---

[4] H. Kleinfeller, A. Kirsch, and F. Eckert, *Ber.*, **62B**, 1582 (1929).

[5] H. Kleinfeller and H. Stahmer, *ibid.*, **66B**, 1127 (1933).

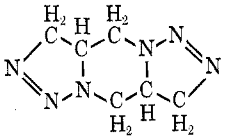
The Crystal and Molecular Structure of Dimeric Allyl Azide[1]

J. C. Pezzullo and E. R. Boyko*

Chemistry Department, Providence College, Providence, Rhode Island 02918

Received February 28, 1972

The dimer of allyl azide was first synthesized by Forster and Fierz[2] from the spontaneous dimerization of the monomer, $C_3H_5N_3$. The resulting prismatic crystals melted with decomposition at 150° but were found to be stable at room temperature. The conclusion that a dimer was present was based on boiling point elevation measurements of chloroform solutions of the compound. Forster and Fierz[2] considered several possible molecular structures and, a number of years later, Boyer and Canter[3] proposed the following as being more consistent with the known chemistry of olefinic azides.



The subsequent X-ray diffraction analysis of the compound shows this molecular structure to be the correct one.

Experimental Section

Preliminary diffraction photographs showed the crystals to be orthorhombic with systematic absences uniquely determining the space group as *Pbca*. The cell parameters were determined from calibrated photographs to be a = 7.803, b = 10.821, and c = 8.819 Å with standard deviations of 0.006 Å. The density measured by the flotation method was 1.45 g cm^{-3}; the density calculated on the basis of four dimer units per unit cell is 1.44 g cm^{-3}.

---

[1] Based on a thesis submitted by J. C. Pezzullo in Feb 1969 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 1178 (1908).

[3] J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).