Experimental Section[5]

2,2′-(Phenylphosphinylidene)diacetic Acid (1).—Through a solution of 5.16 g (0.025 mol) of diallylphenylphosphine oxide[6] in 40 ml of methanol was passed ozonized oxygen at −78° until a blue color appeared (about 4 hr). The solvent was evaporated to give a clear, glassy, viscous material which was treated at −78° with 35 ml of 97% formic acid and 17 ml of 30% hydrogen peroxide and was stirred at room temperature overnight. The mixture was then heated to the reflux temperature for 2 hr, the solvents were evaporated, and the residue was triturated with ether to give a total of 5.0 g (83%) of **1**: mp 148–151° (lit.[7] 152–154°); nmr (D_2O) δ 7.6 (m, 5), 4.7 (HDO), 3.48 (d, 4, J = 14.5 Hz); ir (KBr) 3000, 1730 (C═O), 1440 (C_6H_5P), 1250 (P→O), 1120, 895, 748, 691, 662 cm^{-1}. *Anal.* Calcd for $C_{10}H_{11}O_5P$: C, 49.59; H, 4.59. Found: C, 49.44; H, 4.45.

The nmr of **1** in strong base (sodium hydroxide–deuterium oxide) showed a singlet in the methylene region. A multiplet of low intensity surrounded the base of this signal. When **1** was heated to 145° for 1.5 hr, bubbling occurred; the nmr spectrum of the resulting material had a doublet at 1.72 (J = 13.5 Hz), characteristic of the P–CH_3 group.

Dimethyl-2,2′-(phenylphosphinylidene)diacetic Acid (2).—To a mixture of 90 ml of 40% potassium hydroxide and 400 ml of ether at 0° was added 53.5 g (0.248 mol) of *N*-methyl-*N*-nitrosourea. The resulting yellow ether solution was decanted and the solids were washed five times with ether. To the combined ether fractions at 0° was added 30.0 g (0.1238 mol) of 2,2′-(phenylphosphinylidene)diacetic acid (**1**) in small portions. Considerable gas evolution occurred during addition. The resulting mixture was stirred for 2 hr at 0° and for 8 hr at room temperature. The white solid was filtered, recrystallized from ether, and dried to give 9.6 g (30%) of **2**: mp 102–103° (lit.[7] 102–104.5°); nmr ($CDCl_3$) δ 7.65 (m, 5), 3.67 (s, 6), 3.43 (d, 4, J = 15.4 Hz); ir (KBr) 2950, 1740 (C═O), 1440 (C_6H_5P), 1270 (P→O), 1180, 1105, 913, 738, 690 cm^{-1}. *Anal.* Calcd for $C_{12}H_{15}O_5P$: C, 53.37; H, 5.57. Found: C, 53.38; H, 5.23.

Attempts to esterify **1** with methanol in the presence of sulfuric acid with methyl iodide (on the salt of **1**) and by treatment of the acid with thionyl chloride followed by methanol did not yield the desired ester. The products of these reactions were not identified.

Phenylethynyldiphenylphosphine Oxide (4).—A mixture of 47 g (0.184 mol) of 2-chloro-2-phenylvinylphosphonic dichloride (**3**)[8,9] in 250 ml of dry ether was added to a solution of 0.552 mol of phenylmagnesium bromide in 700 ml of dry ether over a period of 1 hr. The mixture was then hydrolyzed with 10% sulfuric acid, washed with 10% sodium bicarbonate solution, dried, and distilled to give an orange, viscous material, bp 240° (0.1 mm). The distillate was recrystallized from ethanol and ether and washed successively with ether to afford **4**: mp 102° (lit.[10] 102°); ir (KBr) 3050, 2170 (C≡C), 1490, 1440 (C_6H_5P), 1195 (P→O), 1120, 998, 848, 756, 724, 704, 690 cm^{-1}. The nmr spectrum showed only aromatic and no vinyl signals. A melting point of a mixture of **4** and an authentic sample of **4**[10] was not depressed. *Anal.* Calcd for $C_{20}H_{15}OP$: C, 79.40; H, 4.97. Found: C, 79.34; H, 4.82.

Ozonization of Phenylethynyldiphenylphosphine Oxide (4).—Ozone was bubbled for 6.5 hr through a solution of 5 g (0.016 mol) of **4** in 200 ml of dry carbon tetrachloride at 0°. The resulting blue solution was combined with 150 ml of water and stirred overnight. A white solid precipitated and was filtered and dried to give 3.1 g (90%) of product. The melting point (189–192°) and infrared spectrum matched those of diphenylphosphinic acid.[11] The filtrate was reduced by evaporation to afford more solid. Filtration gave a small amount of material, mp 120–122°; a melting point of material mixed (50:50) with benzoic acid was 120–122°.

Ozonization of 1,2,3,4,5-Pentaphenylphosphacyclopentadiene Oxide.—Ozone was bubbled for 4 hr through a solution of 3 g (0.00624 mol) of 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide and 200 ml of dry chloroform at 0°. After 1 hr the yellow color had disappeared, but it returned by the end of the reaction. While the solution was still cold, 250 ml of water was added. The mixture was then stirred at room temperature overnight, the layers were separated, and the water layer was washed with chloroform. The organic portions were combined, and the chloroform was removed at reduced pressure. Sublimation of the residue gave >2.8 g (93%) of benzoic acid which was identified by its melting point (122°) and comparative infrared spectroscopy. The water layer was partially evaporated, filtered, and then evaporated to dryness to give 0.756 g (86%) of a solid. An infrared spectrum of this material was identical with that of phenylphosphonic acid.[11]

Registry No.—**1**, 17166-71-1; **2**, 17166-66-4; **4**, 7608-18-6; 1,2,3,4,5-pentaphenylphosphacyclopentadiene oxide, 1641-63-0.

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[5] Nmr spectra were taken on a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin-Elmer Model 21 double beam recording spectrophotometer. Melting points were taken on a Mel-Temp melting point block which was calibrated with known standards. Elemental analyses were performed by the University of Iowa Chemistry Department and by Micro-Tech Laboratories, Inc. Ozone was generated by a Welsbach, Model T-23 ozonator.

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[11] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

The Synthesis of *N*-Alkylanilines *via* Aryne Reaction in Primary Aliphatic Amine Solvent[1a]

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Dehydrobenzene has so far found its widest area of synthetic application in the addition of ammonia and secondary amines.[2] Surprisingly, no detailed investigation concerning the addition of primary aliphatic, acyclic amines to aryne has been reported. One would expect that this reaction would yield readily isolable *N*-alkylanilines in a convenient one-step synthesis. This note reports the results (Table I) of the addition of various primary aliphatic amines to benzyne generated by the action of sodamide on bromobenzene.

TABLE I

REACTION OF BROMOBENZENE AND SODAMIDE IN VARIOUS PRIMARY ALIPHATIC AMINE SOLVENTS

Solvent, RNH_2, R	I, C_6H_5NHR, yield, %
n-C_3H_7	74
i-C_3H_7	71
n-C_4H_9	78
i-C_4H_9	72
sec-C_4H_9	72
tert-C_4H_9	72

$$C_6H_5Br + NaNH_2 + RNH_2 \longrightarrow \underset{\text{I}}{C_6H_5NHR}$$

It was found that this reaction is general and that good yields (71–78%) of corresponding *N*-alkylaniline I are obtained using a reaction time of 6 hr at room temperature and a sodamide–bromobenzene mole ratio

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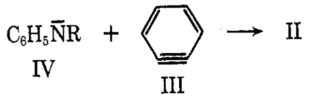
[1] (a) Supported in part by Grant N-118 of the Robert A. Welch Foundation, Houston, Texas. (b) To whom correspondence should be addressed. (c) Robert A. Welch Undergraduate Fellow.

[2] For a comprehensive listing, see R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 115.

of 3:1. Production of I in greater yields was precluded by the formation of higher phenylated *N*-alkylanilines II (*ca.* 20–25%).[3]

The formation of I most likely occurs by the addition of the neutral solvent molecule to benzyne (III). Lyate anion addition to III is unlikely because of the relative low acidity of primary aliphatic amines toward sodamide. However, I is converted readily to its conjugate base $C_6H_5\bar{N}R$ (IV) due to phenyl substitution. The increased reactivity of IV as compared to that of the solvent molecules results in the formation of appreciable quantities of II by the addition of IV to III.



This method provides a convenient means of preparing pure *N*-alkylanilines and is the method of choice for preparation when the *N*-alkyl group is sterically hindered or subject to isomerization. For example, *N*-*tert*-butylaniline (V) (72% in this study) is produced in only a 12% yield *via* alkylation at atmospheric pressure.[4] A higher yield (60%) of V has been obtained in a patented process utilizing high-pressure alkylation techniques.[5] In addition, the yields of *N*-isobutylaniline (72%) and *N*-*sec*-butylaniline (72%) obtained in this study are vastly superior to those previously reported.[6,7]

Experimental Section

Sodamide was obtained from Fisher Scientific Co. and was used as received. All manipulations of sodamide were carried out in a drybox. Amine solvents, obtained from Eastman Kodak, were dried over anhydrous calcium hydride for 24 hr and then distilled directly into a thoroughly dried reaction flask. Bromobenzene was dried over calcium chloride and distilled before use.

General Procedure.—All reactions were carried out under a nitrogen atmosphere. To a stirred mixture containing 300 ml of amine solvent and 11.7 g (0.3 mol) of sodamide was added 15.7 g (0.1 mol) of bromobenzene. The reaction mixture was then stirred for 6 hr (a color change to orange occurs after 1–3 hr of stirring) and then quenched by the addition of 18.4 g (0.35 mol) of ammonium chloride. The solvent was removed by distillation and collected. The residue was combined with ether and stirred, and the solids were removed by filtration. The product was extracted from the ether layer with 10% HCl. The aqueous extracts were made basic with $NaHCO_3$ and 10% NaOH and extracted with ether. Drying of the ether layer by anhydrous $MgSO_4$ followed by vacuum distillation yielded the desired products.

The physical properties of the products are: *N*-*n*-propylaniline, bp 119–121° (31 mm) [lit.[8] bp 98.5–100° (11 mm)], n^{25}D 1.5420 (lit.[8] n^{22}D 1.5406); *N*-isopropylaniline, bp 111–113° (36 mm) [lit.[9] bp 198–206° (760 mm)], n^{25}D 1.5355 (lit.[9] n^{25}D 1.5380); *N*-*n*-butylaniline, bp 105–107° (6.5 mm) [lit.[6a] 124–126° (25 mm)], n^{25}D 1.5331 (lit.[6a] n^{25}D 1.5298); *N*-isobutylaniline, bp 119–120° (25 mm) [lit.[6a] 90° (7 mm)], n^{27}D 1.5281 (lit.[6a] n^{20}D 1.5328); *N*-*tert*-butylaniline, bp 112–114° (36 mm) [lit.[5] bp 208–211° (760 mm)], n^{25}D 1.5260 (lit.[5] n^{20}D 1.5270); *N*-*sec*-butylaniline, bp 113–114° (24 mm) [lit.[7] 96–98° (10 mm)], n^{25}D 1.5319 (lit.[7] n^{20}D 1.5333).

Mass spectral, nmr, and ir analyses of all the products were consistent with the proposed structures.

Registry No.—Bromobenzene, 108-86-1; sodamide, 7782-92-5.

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[3] Nmr and mass spectral analyses indicate that these higher phenylated products were essentially the corresponding *N*-alkyldiphenylamines together with smaller amounts of the *N*-alkylbiphenylamines.

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2,3-Dihydroquinoxaline 1,4-Dioxides as Intermediates in the Reaction between Benzofurazan 1-Oxide and Enamines

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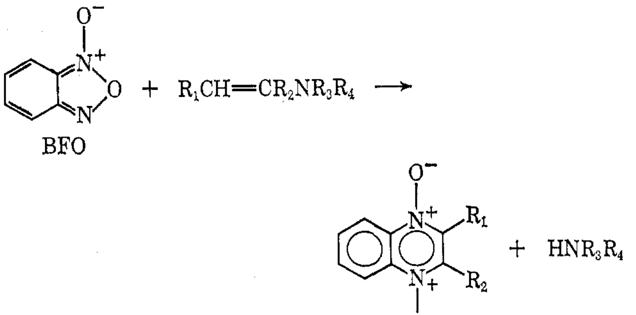
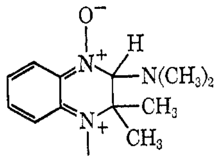
A one-step preparation of quinoxaline 1,4-dioxides from benzofurazan 1-oxide (BFO) and enamines was reported by Haddadin and Issidorides in 1965.[1] During the course of a typical reaction, deep red colors are observed; these eventually disappear during work-up, and the products generally consist of yellow crystals. In an effort to trap an intermediate, BFO was allowed to react with *N*,*N*-dimethylisobutenylamine,[2] an enamine which cannot undergo a β elimination of dimethylamine. There was obtained from this reaction deep-red crystals of a compound, mp 135–137°. Analysis of the substance and the determination of its nmr, uv, and mass spectra suggested that it was 2-dimethylamino-2,3-dihydro-3,3-dimethylquinoxaline 1,4-dioxide (**1**), a nonaromatic cyclic polyene system.





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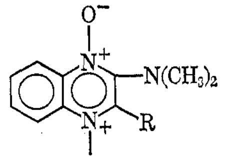

2, R = H
3, R = CH_3

In order to establish the nonaromatic character of **1**, the fully aromatic and closely analogous 2-dimethylaminoquinoxaline 1,4-dioxides **2** and **3** were prepared for comparison. The uv spectrum of **1** has as its longest wavelength absorption maximum a peak at 482 nm. The corresponding maxima for **2** and **3** occur at some

[1] M. J. Haddadin and C. H. Issidorides, *Tetrahedron Lett.*, 3253 (1965).

[2] A gift from Eastman Chemical Products, Inc., Kingsport, Tenn. 37662.