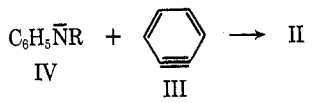
of 3:1. Production of I in greater yields was precluded by the formation of higher phenylated *N*-alkylanilines II (*ca.* 20–25%).[3]

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.

(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.

(4) E. G. Rozantseu and F. M. Egidis, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 932 (1967); N. S. Lobanova and M. A. Popov, *Zh. Prikl. Khim.*, **43**(4), 938 (1970).

(5) A. Bell and N. B. Knowles, U. S. Patent 2,692,287 (1954).

(6) (a) R. G. Rice and E. J. Kohn, *J. Amer. Chem. Soc.*, **77**, 4052(1955); (b) W. J. Hickinbottom, *J. Chem. Soc.*, 992 (1930).

(7) R. Stroh, J. Ebensberger, H. Haberland, and W. Hahn, *Angew. Chem.*, **69**, 124 (1951).

(8) V. Wolf and D. Ramie, *Justus Liebigs Ann. Chem.*, **626**, 47 (1969).

(9) C. Ainsworth, *J. Amer. Chem. Soc.*, **78**, 1635 (1956).

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

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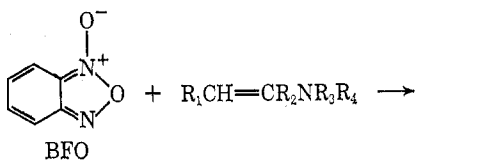
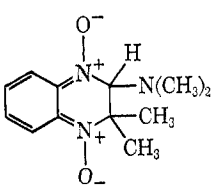
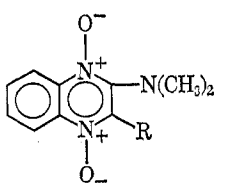
A one-step preparation of quinoxaline 1,4-dioxides from benzofurazan 1-oxide (BFO) and enamines was reported by Haddadin and Issidorides in 1965.[1] Dur-



ing 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.





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.

60–70 nm shorter wavelength. In the nmr spectra, protons on the carbocyclic ring of **1** absorbed energy at a higher magnetic field than do the corresponding protons on **2** and **3**. The absorption due to the proton at C-2 on **1** is shifted 4.0 ppm upfield with respect to that of the proton at C-3 on **2**. All these facts speak for the nonaromatic character of **1** and for the assigned structure.

The compound **1** was synthesized under conditions comparable to those reported earlier for the preparation of quinoxaline 1,4-dioxides from BFO.[1] Further, the color of **1** in solution approximates that observed during the course of more typical reactions which lead to fully aromatic compounds. It follows that 2,3-dihydroquinoxaline 1,4-dioxides are likely intermediates in the reaction between BFO and enamines; also, this same possibility cannot be ignored in considering intermediates in the reaction between BFO and carbanions.[3]

Experimental Section

2-Dimethylamino-2,3-dihydro-3,3-dimethylquinoxaline 1,4-Dioxide (1).—A stirred solution of 13.6 g (0.1 mol) of BFO in 100 ml of $CHCl_3$ was treated dropwise over a period of 30 min with a solution of 9.9 g (0.1 mol) of *N,N*-dimethylisobutenylamine[2] in 50 ml of $CHCl_3$. During the addition the temperature rose spontaneously but slowly to 37° and the reaction solution turned deep red. The temperature remained at 37° for 15 min and then dropped slowly to room temperature. The reaction mixture was allowed to stand overnight. The $CHCl_3$ was evaporated under reduced pressure, and the dark-red residue was eluted by C_6H_6–$CHCl_3$ (1:1) on a column of Florisil to afford 12 g of a dark crystalline substance which was recrystallized from Me_2CO–C_6H_{14} to give garnet-colored crystals, yield 4.5 g, mp 119–123°. Two further recrystallizations furnished an analytically pure sample of **1**: yield 3.5 g (15%); mp 135–137°; uv max (H_2O) 251 nm (ε 17,200), 482 (9320); nmr (CCl_4) δ 1.49 (s, 3, *trans*-3-CH_3), 1.52 (s, 3, *cis*-3-CH_3), 2.34 (s, 6, NCH_3), 4.20 (s, 1, 2 H), 6.6–6.9 (m, 2), 7.2–7.5 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 235 (6), 192 (11), 177 (14), 99 (100), 84 (83).

Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.3; H, 7.3; N, 17.9. Found: C, 61.2; H, 7.1; N, 18.0.

2-Dimethylaminoquinoxaline 1,4-Dioxide (2).—In a reaction vessel equipped with a reflux condenser, a stirred solution of 1.36 g (0.01 mol) of BFO in 50 ml of $CHCl_3$ was treated dropwise over a period of 2 min with 1.14 g (0.01 mol) of *N,N,N',N'*-tetramethyl-1,1-vinylidenediamine.[4] The temperature rose spontaneously to the boiling point of the mixture and after 5 min began to fall. When the reaction mixture was at room temperature a yellow crystalline precipitate formed. The crude product was recrystallized from $CHCl_3$–C_6H_{14} to give 1.1 g (54%) of **2**, mp 177–180°. One further recrystallization afforded the analytical sample: mp 178–180°; uv max (MeOH) 239 nm (sh, ε 10,300), 279 (24,800), 305 (sh, 9340), 354 (8500), 422 (6200); nmr ($CDCl_3$) δ 3.20 (s, 6, NCH_3), 7.84 (m, 2), 8.20 (s, 1), 8.40 (m, 2).

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.5; H, 5.4; N, 20.5. Found: C, 58.3; H, 5.2; N, 20.4.

2-Dimethylamino-3-methylquinoxaline 1,4-dioxide (3) was prepared from *N,N,N',N'*-tetramethyl-1,1-propenylidenediamine[4] in a manner similar to that described above: yield 39%; mp 124–127° (Me_2CO–C_6H_{14}); uv max (H_2O) 240 nm (ε 20,000), 276 (16,200), 310 (8500), 341 (sh, 9250), 352 (10,900), 411 (5000); nmr ($CDCl_3$) δ 2.70 (s, 3, CCH_3), 3.06 (s, 6, NCH_3), 7.72 (m, 2), 8.48 (m, 2).

Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.3; H, 6.0; N, 19.1. Found: C, 60.3; H, 5.9; N, 19.2.

Registry No.—**1**, 29086-42-8; **2**, 29086-43-9; **3**, 29086-44-0.

(3) (a) C. H. Issidorides and M. J. Haddadin, *J. Org. Chem.*, **31**, 4067 (1966); (b) K. Ley, F. Seng, U. Eholzer, R. Nast, and R. Schubart, *Angew. Chem., Int. Ed. Engl.*, **8**, 596 (1969).

(4) H. Bredereck, F. Effenberger, and H. P. Beyerlin, *Chem. Ber.*, **97**, 3081 (1964).

Acknowledgment.—The technical assistance of Mr. David A. Johnson was a valuable asset to the completion of this work. Also, I would like to express my appreciation to Professor Hans Muxfeldt for helpful advice.

Preparation of Substituted 1,2-Benzoisothiazolin-3-one 1,1-Dioxides (*o*-Benzoic Sulfimides)

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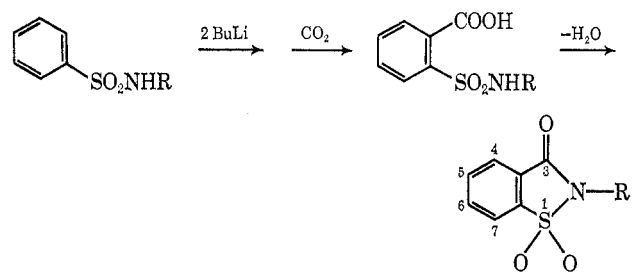
Ortho lithiation of *N*-methyl- and *N*-phenylbenzenesulfonamides followed by carbonation and cyclization has previously been reported[1] to produce *N*-methyl- and *N*-phenyl-1,2-benzoisothiazolin-3-one 1,1-dioxide (Ia,b), in 49 and 22% yields, respectively (Scheme I).

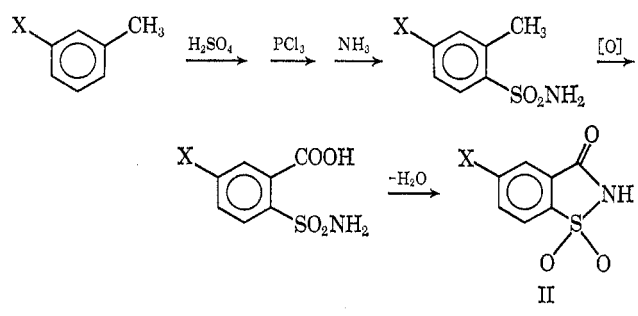
SCHEME I



Ia, R = CH_3
b, R = C_6H_5

In connection with another study, fairly large quantities of certain 5-substituted 2*H*-1,2-benzoisothiazolin-3-one 1,1-dioxides (*i.e.*, 5-substituted *o*-benzoic sulfimides) (II) were required. The multistep preparation of a few such compounds has been reported (Scheme II)

SCHEME II



II

utilizing vigorous oxidation of *o*-toluenesulfonamides. The latter compounds are obtained *via* sulfonation of a substituted toluene, and cyclodehydration of the *o*-sulfamoylbenzoic acid gives II. The reported procedures did not appear promising, however, since

(1) H. Watanabe, R. Gay, and C. R. Hauser, *J. Org. Chem.*, **33**, 900 (1968).