

NOTES

Trimethylamine Oxide Boron Fluoride

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Direct evidence of the strong electron-donor character of trimethylamine oxide was found in the recent study of its reaction with sulfur dioxide.² The compound $(\text{CH}_3)_3\text{NO}\cdot\text{SO}_2$ is not measurably dissociated below the char-point (*ca.* 120°), and it is best interpreted as a case of strong attachment of the oxide to the sulfur atom. Since sulfur dioxide usually forms only rather weak bonds to electron donors, the external dative bonding power of the amine oxide appears especially strong.

We have now found that boron fluoride adds directly to anhydrous trimethylamine oxide to form the very stable compound $(\text{CH}_3)_3\text{NOBF}_3$, thus affording further evidence of the strong electron-donor character of this oxide.

Preparation of $(\text{CH}_3)_3\text{NOBF}_3$.—Hydrated trimethylamine oxide, prepared by the action of hydrogen peroxide upon trimethylamine and purified by recrystallization from alcohol, was pumped for some hours at 90–100° and then sublimed several times in high-vacuum to remove the last trace of water. The effectiveness of this procedure had been demonstrated earlier.³ The anhydrous trimethylamine oxide was dissolved in dry chloroform, which appears to be almost unique among solvents in that it makes possible a convenient concentration of the anhydrous amine oxide, and yet does not damage it by irreversible reaction. Pure boron trifluoride³ was then bubbled in. The resulting white precipitate was washed by fresh chloroform, collected upon a suction-filter stick and dried.

Analysis of $(\text{CH}_3)_3\text{NOBF}_3$.—The new compound was analyzed for boron as boric acid by titration (0.1 *N* NaOH, phenolphthalein) in the presence of mannite. The boric acid was first set free by digestion of the original compound with 10% calcium chloride solution at 100° (one-half hour); this procedure also eliminated fluoride interference, by precipitation of calcium fluoride. The resulting hydrochloric acid was neutralized to the methyl red endpoint before mannite was added. This procedure was first tested and found quite satisfactory for recrystallized potassium fluoborate, and then used for analysis of the amine oxide boron fluoride, with results shown in Table I.

TABLE I

TITRATION OF BORON FROM $(\text{CH}_3)_3\text{NOBF}_3$

Sample, mg.	Boron found, mg.	Boron calcd., mg.	% Error
57.8	4.37	4.38	-0.2
66.8	5.01	5.06	-1.0
102.0	9.61	9.72	-1.1

Properties of $(\text{CH}_3)_3\text{NOBF}_3$.—This substance is quite stable in the open air. It melts at 89°. At 100° it turns tan-colored, and gives off white fumes (probably BF_3), accompanied by a little sublimate. At 175° it becomes

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(2) Burg, *This Journal*, **65**, 1633 (1943).

(3) Booth and Willson, *ibid.*, **57**, 2273 (1935).

dark brown and begins to effervesce against the atmosphere at 200°. Charring is complete at 227°.

The compound is soluble in water, but less so than trimethylamine oxide. After evaporation of the water under reduced pressure at 60°, the original weight of solid material is regained, and there is no change in appearance. Evidently the hydrolysis of the boron fluoride is wholly prevented by attachment to the amine oxide, except at temperatures at which discoloration begins.

Other Addition Products.—Using dry chloroform as a solvent it was possible to make some preliminary studies of the addition of silicon tetrachloride and phosphorus trichloride to trimethylamine oxide. Either of these attaches itself rather firmly, but the formulas of the addition compounds have not yet been established to complete satisfaction. It appears that numerous electron-receptors, too weak to react with a tertiary amine, may form stable compounds by addition to the amine oxide. Further studies in this field will be undertaken.

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New 2,5-Dimethylpyrrole Derivatives

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In connection with a research project in these Laboratories a number of 2,5-dimethylpyrrole derivatives have been prepared. Previous investigators^{1a,b} prepared such derivatives by refluxing the required diamine with acetyl acetone in alcohol for several hours, pouring the reaction product into water, separating and then purifying by fractionation or crystallization. We have carried on these reactions very satisfactorily in benzene by azeotropic distillation whereby the water is continuously removed.

Procedure.—The general procedure can be illustrated by the preparation of 1,1'-ethylene-bis-2,5-dimethylpyrrole: 0.5 mole of ethylenediamine (68%), 0.25 mole of acetylacetone and sufficient benzene (or toluene) are placed in a 500-cc. round-bottom flask which has a 24/40 standard-taper neck and a 10/30 S. T. joint as a side arm through which is inserted a S. T. J. thermometer. Bumping of the boiling mixture is prevented by the addition of a small piece of porous plate. The flask is connected to a Barrett water trap (having a stopcock at the bottom), and the trap to a water condenser. All-glass joints are preferred. The reaction flask is encased in a Glascol heating mantle, regulated by a variac.

The water collected in the trap indicates the rate and completeness of the reaction. At the end, by elevating the temperature of the mantle the benzene may be distilled. Finally, it may be found desirable to apply a vacuum, regulated by a screw clamp, to the top of the condenser to remove any excess acetyl acetone and amine.

The dipyrrole is then poured into an open dish and powdered; m. p. 132–133°; color, light-brown; yield 96–100%. After two crystallizations from alcohol, the product is nearly colorless; m. p. 136.5°, yield 80%. A melting point of 125–126° has been reported by Paal.²

The ethylene dipyrrole may be reduced in a bomb over

(1) (a) Barton, U. S. Patent 2,234,056; (b) Hazlewood, *et al.*, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 92 (1937).

(2) Paal and Schneider, *Ber.*, **19**, 3157 (1886).