Notes

The Reaction of Trityldifluoramine with Sulfuric Acid. A Simple Method of Preparation of Difluoramine

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Difluoramine has been prepared by the reaction between tetrafluorohydrazine and thiophenol[1] and by methods involving the direct fluorination of urea.[2,3]

We have obtained difluoramine of high purity in almost quantitative yield by the reaction of trityldifluoramine with concentrated sulfuric acid. This method has utility as a convenient laboratory source of difluoramine from a stable, solid starting material. Trityldifluoramine is readily available by the reaction of tetrafluorohydrazine with the triphenylmethyl free radical.[4]

Protonation of the weakly basic nitrogen of trityldifluoramine in concentrated sulfuric acid yields difluoramine and the triphenylmethyl carbonium ion, identified by its visible spectrum.[5]

$$(C_6H_5)_3CNF_2 \xrightarrow{H^{\oplus}} (C_6H_5)_3C^{\oplus} + HNF_2$$

Triphenylcarbinol was obtained upon dilution of the acid solution with water.

Experimental

Preparation of Trityldifluoramine.—Into a solution of 7.0 g. (0.025 mole) of trityl chloride dissolved in 400 ml. chlorobenzene, contained in an evacuated, 1-l. three-necked flask fitted with a manometer, dropping funnel, gas-inlet tube, and magnetic stirring bar, was expanded tetrafluorohydrazine[6,7] until the pressure reached 675 mm. Upon addition of a few drops of mercury the pressure decreased at a rate of ~ 5 mm./min. for 15 min. More tetrafluorohydrazine and mercury were introduced portionwise as the pressure decreased. A total of 1 l. of tetrafluorohydrazine (0.045 mole) and approximately 50 g. of mercury were used. Stirring was continued for 1 hr. after no pressure decrease was observed upon addition of fresh mercury. Excess tetrafluorohydrazine was removed under vacuum. (Caution: tetrafluorohydrazine, air, and organic materials can form explosive mixtures.) The mixture was filtered free of mercury and its salts and was concentrated on the vacuum line. The residue was taken up in pentane and filtered to remove a small amount of insoluble material. After removal of the pentane, 6.5 g. (88%) of white solid, m.p. 75–77° was obtained. Recrystallization from methanol afforded 6.0 g. of trityldifluoroamine, m.p. 82–83°.

Anal. Calcd. for $C_{19}H_{15}NF_2$: C, 77.28; H, 5.12; N, 4.74; F, 12.87. Found: C, 77.70; H, 5.94; N, 4.58; F, 12.9.

Preparation of Difluoramine.—Into a 50-ml. evacuated three-necked flask fitted with a monometer, dropping funnel, and magnetic stirrer and containing 0.30 g. (0.001 mole) trityldifluoramine was added slowly 10 ml. of concentrated sulfuric acid. The solution immediately became yellow and there was a brisk evolution of gas. Difluoroamine is only slightly soluble in concentrated sulfuric acid at subatmospheric pressure. After the pressure became steady, the gaseous product was condensed into a U-tube surrounded by a −128° (methylcyclohexane) slush bath. The yield of difluoramine (99% purity as indicated by the mass spectrum[2]) was nearly quantitative, 22.0 cc. (STP).

The visible spectrum of the sulfuric acid solution indicated the presence of the triphenylmethyl carbonium ion.[5] This solution was poured over ice and yielded triphenylcarbinol, m.p. 160°, identified by mixed melting point and comparison of its infrared spectrum with that of an authentic sample.

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(7) Tetrafluorohydrazine is supplied commercially by Air Products and Du Pont.

A Convenient Preparation of Monolithioferrocene[1]

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Discovery of the ability of ferrocene to undergo direct lithiation upon treatment with *n*-butyllithium[3,4] provided an important means of obtaining mono- and heteroannularly[5] disubstituted ferrocenes. Subsequent modification[6] of the procedure strengthened its usefulness by allowing much higher yields[7] of the lithiated ferrocenes.

A serious drawback of the direct lithiation procedure, however, lies in the fact that the presence of both mono- and dilithiated ferrocene may, in some cases, present undesirable complications, particularly when one wishes to obtain a monosubstituted ferrocene. We have found this to be especially troublesome in treatment of the lithioferrocenes with keto esters. It was, therefore, highly desirable to develop a convenient lithiation pro-

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(2) National Science Foundation Research Participant under the College Chemistry Teachers Program held at the University of South Carolina during the summer of 1961.

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(7) In all cases cited in this discussion, including the present work, yields of lithiated ferrocenes are actually those of the corresponding carboxylic acids obtained *via* carbonation.