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.

cedure to provide monolithioferrocene in the absence of dilithioferrocene. While the work for which this lithiation procedure was needed is still incomplete, we wish to report our monolithiation technique at this time because of its potential general utility.

It was found that treatment of ferrocene in diethyl ether solution with an equimolar amount of *n*-butyllithium—instead of the usual large excess[3,4,6]—at room temperature during 5–6 hours gives rise to a reaction mixture containing monolithioferrocene in the absence of the dilithiated species. We have found the 5–6 hour reaction period to be optimum, and that the desired material is produced under these conditions in 25–26% yield. The convenience of this procedure is enhanced by the fact that commercially-available *n*-butyllithium[8] works equally as well as the freshly prepared material.

Recently, Seyferth, and co-workers[9] reported procedures which also provide only monolithioferrocene. Treatment of chloromercuriferrocene with ethyllithium, *n*-butyllithium or phenyllithium gives rise to monolithioferrocene in yields of 64, 50, and 58%, respectively. Monolithioferrocene is also generated in 43% yield by reaction between *n*-butyllithium and diferrocenylmercury[9]; with the use of a large excess of *n*-butyllithium, yields in the neighborhood of 75% have been reported.[10] While these procedures give rise to high yields when calculated on the basis of the reacting mercury compounds, the over-all yields from ferrocene are, however, low. Chloromercuriferrocene is obtained in yields of about 50%[4,11] from ferrocene, and diferrocenylmercury is obtained in only about 35% yield[11] from ferrocene. Conversion of ferrocene to monolithioferrocene *via* these mercury compounds, therefore, gives the latter in about 25–28% yield. Thus, the presently described procedure provides the over-all conversion in comparable yield, but it does so with a great deal more experimental ease and economy.

Experimental

In an oven-dried flask fitted with stirrer, condenser, and gas-inlet tube was placed a solution of ferrocene (10.0 g.; 0.054 mole) in 150 ml. of anhydrous ether. After the system was thoroughly flushed with dry nitrogen—and while it was kept in an atmosphere of nitrogen—*n*-butyllithium[8] (0.056 mole, from 35 ml. of a 1.59 *M*[12] hexane solution) was added from a hypodermic syringe. While maintained under a slight head of nitrogen, the reaction mixture was stirred at room temperature during 6 hr. At that time a 5.00-ml. aliquot was withdrawn and added jet-wise to a slush of absolute ether and Dry Ice. After the excess Dry Ice had been allowed to evaporate and the basic ethereal residue washed with several portions of water, the combined aqueous extracts were acidified with 6 *N* hydrochloric acid. The mass of yellow precipitate was collected, washed with water, and dried. This material was found to be totally soluble in ether, giving no indication of the presence of the ether-insoluble ferrocenedicarboxylic acid. The ethereal solution was dried and evaporated, yielding 103 mg. (25% yield) of ferrocenecarboxylic acid which was identified by means of its infrared spectrum. In other runs, carbonation was carried out after 4, 5, and 8 hr. of lithiation. In each case only monoferrocenecarboxylic acid was obtained in yields of, 20, 26, and 21%, respectively.

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[8] *n*-Butyllithium in hexane solution, obtained from the Foote Mineral Co., West Chester, Pa., was used.

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[10] M. D. Rausch, *ibid.*, **1**, 414 (1962).

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[12] Determined according to the procedure described by R. G. Jones and H. Gilman [*Org. Reactions*, **VI**, 353 (1951)].

An Improved Synthesis of Phenyl(trichloromethyl)mercury from Sodium Methoxide and Ethyl Trichloroacetate

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Recently, Seyferth[2] and co-workers have reported a novel synthesis of dihalocarbon adducts under neutral conditions. The dichlorocarbon intermediate was phenyl(trichloromethyl)mercury prepared from phenylmercuric chloride (or bromide), with potassium *tert*-butylate and chloroform as the trichloromethyl anion precursor. However, our attempts to prepare the dichlorocarbon precursor, phenyl(trichloromethyl)mercury, from commercial grade potassium *tert*-butylate, using the method first described by Russian workers,[3] was quite unsuccessful. In order to avoid the tedious preparation of pure potassium *tert*-butylate, ethyl trichloroacetate and commercial sodium methoxide[4] were employed as the source of the needed trichloromethyl anion to give high yields (62%) of phenyl(trichloromethyl)mercury.

This new synthesis affords a convenient, rapid method for the preparation of the unique, neutral dichlorocarbon precursor and it may be used to prepare small or moderately large quantities (10 to 60 g.) with equal ease.

Experimental

Materials.—The powdered sodium methoxide, obtained from the Matheson Co., Inc., was always transferred in a drybox under an atmosphere of dry nitrogen to a dry erlenmeyer flask.

The phenylmercuric bromide, obtained from Wood Ridge Chemical Corporation, was pulverized prior to weighing.

The ethyl trichloroacetate, obtained from Eastman Kodak Co., was distilled prior to use.

Phenyl(trichloromethyl)mercury.—In a 500-ml. three-necked, round bottom flask equipped with a reflux condenser and an efficient mechanical stirrer were placed 200 ml. of anhydrous, thiophene-free benzene, 24 g. (0.18 mole) of ethyl trichloroacetate and 13.2 g. (0.037 mole) of phenylmercuric bromide. The mixture was stirred and cooled in an ice–water bath for 15 min. Sodium methoxide (8.4 g., 0.154 mole) was added all at once from an erlenmeyer flask attached to the round bottomed flask by a flexible tube. The mixture was stirred for 1.5 hr. with cooling then quenched with an equal volume of water. After thorough mixing, the benzene layer was decanted and filtered. The aqueous mixture was extracted with three 100-ml. portions of benzene. The organic layers were combined and evaporated to dryness under a stream of air. Phenyl(trichloromethyl)mercury (10.5 g., 71% yield), a white solid, m.p. 110–112°,

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[1] This work was supported by a grant from the University of Delaware Research Fund.

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