[CONTRIBUTION NO. 77 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING COMPANY]

THE PREPARATION OF 1,1-DI-*H*-HEPTAFLUOROBUTYL IODIDE AND 1,1-DI-*H*-HEPTAFLUOROBUTYL BROMIDE AND THEIR INTERMEDIATES

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Received November 25, 1953

Three distinct methods of preparation of 1,1-di-*H*-perfluoroalkyl halides have been developed in this laboratory. We wish to report a brief account of two of these methods along with the chemistry of some of the intermediates. The third method has been published (1).

The first 1,1-di-*H*-heptafluorobutyl halide ever prepared was 1,1-di-*H*-heptafluorobutyl iodide. 1,1-Di-*H*-heptafluorobutyl amine, $C_3F_7CH_2NH_2$, was reacted with nitrous acid in aqueous solution to give 1-*H*-heptafluorodiazobutane, $C_3F_7CHN_2$, which was isolated by distillation in one run. Treatment of 1-*H*-heptafluorodiazobutane with an excess of hydrogen iodide in β,β'-dichlorodiethyl ether at room temperature gave 1,1-di-*H*-heptafluorobutyl iodide, $C_3F_7CH_2I$. No reaction occurred at Dry Ice temperature, $-78°$.

This method (2) was unsatisfactory for 1,1-di-*H*-heptafluorobutyl bromide which was prepared by a procedure similar to that used by Swarts (3) for 1,1,1-trifluoroisopropyl bromide, $CF_3CHBrCH_3$. Although Swarts obtained 1,1,1-trifluoroisopropyl dibromophosphite, $CF_3(CH_3)CHOPBr_2$, on treatment of trifluoroisopropyl alcohol with phosphorus tribromide, 1,1-di-*H*-heptafluorobutanol gave tris(1,1-di-*H*-heptafluorobutyl) phosphite, $(C_3F_7CH_2O)_3P$, when it was subjected to the action of either phosphorus tribromide or phosphorus trichloride. Treatment of the phosphite ester with one equivalent of bromine gave up to a 30% yield of 1,1-di-*H*-heptafluorobutyl bromide. Use of an excess of bromine did not improve the yield, indicating that only one of the di-*H*-heptafluorobutoxy groups was converted to the bromide.

Moreover, no iodide was obtained on treatment of the phosphite ester with iodine. Only traces of bromide were obtained when phosphorus pentabromide alone was used.

Trifluoroethanol behaved similarly when treated with phosphorus trichloride, tris(1,1-di-*H*-trifluoroethyl) phosphite, $(CF_3CH_2O)_3P$, being obtained in good yield. Treatment of the phosphite ester with one equivalent of bromine gave a low but measurable yield of 1,1-di-*H*-trifluoroethyl bromide, CF_3CH_2Br.

Similarly, trifluoroethanol reacted with phosphorus oxychloride in the presence of pyridine in benzene solution to give tris(1,1-di-*H*-trifluoroethyl) phosphate, $(CF_3CH_2O)_3PO$. Treatment of the phosphate ester with an excess of sodium iodide in pentaethylene glycol at high temperature gave a 28% yield of 1,1-di-*H*-trifluoroethyl iodide, CF_3CH_2I.

EXPERIMENTAL[1]

Preparation of 1,1-di-H-heptafluorobutyl iodide, $C_3F_7CH_2I$. In a 250-ml., 3-necked flask equipped with a stirrer and dropping-funnel were placed 20 g. (0.10 mole) of 1,1-di-*H*-

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[1] We wish to thank H. E. Freier for the analytical data and W. E. Keiser for the infrared spectra reported in this paper.

heptafluorobutylamine (4), 10 ml. of conc'd hydrochloric acid, 20 ml. of water, and 20 ml. of β,β'-dichlorodiethyl ether. The flask was cooled in an ice-salt bath, the stirrer was started, and a solution of 8 g. (0.114 mole) of sodium nitrite in 20 ml. of water was added drop-wise to the reaction mixture. Stirring was stopped after one hour and the layers were separated. The aqueous layer was washed twice with 5-ml. portions of dichlorodiethyl ether. The combined ether extracts were washed with 5 ml. of 5% sodium carbonate solution, then with 5 ml. of water, and were dried with calcium chloride.

The dichlorodiethyl ether solution of 1-*H*-heptafluorodiazobutane was placed in a 250-ml. flask cooled with Dry Ice and an excess of anhydrous hydrogen iodide was distilled directly into the flask. A condenser was attached and the reaction mixture was kept at Dry Ice temperature for two hours, then warmed to room temperature and kept there for an additional three hours. The product was distilled from the reaction mixture under reduced pressure and gave 26.5 g. (0.0855 moles) of crude 1,1-di-*H*-heptafluorobutyl iodide. The crude material was redistilled twice through an 11-inch helices-packed column to give 18 g. (0.058 mole, 58%) of a water-white liquid, b.p. 91–91.5° (740 mm.), n_D^{20} 1.3603.

Anal. Calc'd for $C_4H_2F_7I$: I, 40.9. Found: I, 40.8.

Tris(1,1-di-H-heptafluorobutyl) phosphite, $(C_3F_7CH_2O)_3P$. 1,1-Di-*H*-heptafluorobutyl alcohol (90 g., 0.45 mole) and 20.6 g. (0.15 mole) of phosphorus trichloride were placed in a 250-ml. flask equipped with a reflux condenser and thermometer. Hydrogen chloride was vigorously evolved at the start of the reaction. The flask was heated gently to 80–90° and kept at that temperature for four hours. The reaction mixture was then fractionally distilled through a Vigreux column to give a water-white liquid, b.p. 97.5–98° (16 mm.). Yield, 78.5 g. (0.125 mole, 83%), n_D^{20} 1.3143, d_4^{20} 1.6618.

Anal. Calc'd for $C_{12}H_6F_{21}O_3P$: C, 22.95; F, 63.52; P, 4.93.
Found: C, 22.9; F, 63.2; P, 4.75.

1,1-Di-H-heptafluorobutyl bromide, $C_3F_7CH_2Br$. Tris(1,1-di-*H*-heptafluorobutyl) phosphite (78 g., 0.125 mole) was placed in a 250-ml. flask equipped with a stirrer, dropping-funnel, and condenser. The material was stirred vigorously while 20 g. (0.125 mole) of bromine was added dropwise. The bromine was decolorized rapidly and some heat was evolved. When all the bromine had been added, the reaction mixture was distilled and the fraction boiling at 64–70° was collected. This fraction was washed twice with 5% sodium hydroxide, twice with water, and dried over Drierite. Fractionation of the material through a 10-inch column packed with "Helipak" gave a water-white liquid, b.p. 69° (732 mm.). Yield, 25.7 g. (0.098 mole, 26%) based on the phosphite ester, n_D^{20} 1.3182.

Anal. Calc'd for $C_4H_2BrF_7$: C, 18.27; Br, 30.39; F, 50.57.
Found: C, 18.3; Br, 30.4; F, 50.6.

Tris(1,1-di-H-trifluoroethyl) phosphite, $(CF_3CH_2O)_3P$. By the procedure described above, 46 g. (0.460 mole) of 1,1-di-*H*-trifluoroethanol was reacted with 21 g. (0.153 mole) of phosphorus trichloride to give 38.6 g. (0.118 mole) of tris(1,1-di-*H*-trifluoroethyl) phosphite. The yield of water-white liquid was 78%, b.p. 130–131° (743 mm.), n_D^{25} 1.3224, d_4^{25} 1.4866.

Anal. Calc'd for $C_6H_6F_9O_3P$: C, 21.95; P, 9.45.
Found: C, 22.2; P, 9.33.

1,1-Di-H-trifluoroethyl bromide, CF_3CH_2Br. Treatment of 37.8 g. (0.115 mole) of tris-(1,1-di-*H*-trifluoroethyl) phosphite with 18.4 g. (0.115 mole) of bromine at room temperature gave 2.0 g. (0.012 mole) of 1,1-di-*H*-trifluoroethyl bromide which was collected in a Dry Ice trap connected to the reaction vessel. The yield was 3.5% based on the phosphite ester. The identity of the trifluoroethyl bromide, CF_3CH_2Br, was established by comparison of its infrared absorption spectra with that of an authentic sample.[2]

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[2] The sample of trifluoroethyl bromide was prepared by Mr. Benji Oiye from trifluoroethanol, CF_3CH_2OH, and phosphorus pentabromide according to the method of Swarts, *Compt. rend.*, **197**, 1261 (1933), b.p. 26°; lit. b.p. 26.5°. The infrared absorption curve showed characteristic bands (λ in μ) at 3.33, vw; 6.96, m; 7.65, 7.84, 8.03, triplet, s; 8.76, s; 9.25 s; 11.87, w; 13.74, 13.81, 13.93, triplet, m. *Anal.* Calc'd for $C_2H_2BrF_3$: C, 14.74; Br, 49.04; F, 34.98. Found: C, 14.7; Br, 48.7; F, 34.8.

Tris(1,1-di-H-trifluoroethyl) phosphate, $(CF_3CH_2O)_3PO$. 1,1-Di-*H*-trifluoroethanol (100 g., 1 mole), 79.1 g. (1 mole) of pyridine, and 100 ml. of benzene were placed in a 1-l. flask equipped with a stirrer, condenser, and dropping-funnel. The flask was cooled in an ice-bath and stirred vigorously while 51.2 g. (0.33 mole) of phosphorus oxychloride was added dropwise. The reaction was quite exothermic and needed efficient cooling during the addition. Stirring was continued for 30 minutes longer and then pyridine hydrochloride was collected. The filtrate was distilled under reduced pressure and the fraction boiling at 78–83° (10 mm.) was collected. The crude product weighed 77.4 g. (0.225 mole, 68%). The sample was redistilled and a fraction boiling at 74–75° (9 mm.) was analyzed, n_D^{25} 1.3180.

Anal. Calc'd for $C_6H_6F_9O_4P$: C, 20.94; F, 49.70; P, 9.01.

Found: C, 20.9; F, 49.9; P, 8.75.

1,1-Di-H-trifluoroethyl iodide, CF_3CH_2I. A mixture of 17 g. (0.049 mole) of tris(1,1-di-*H*-trifluoroethyl) phosphate, 22.5 g. (0.15 mole) of sodium iodide, and 50 g. of pentaethylene glycol was placed in a distilling flask and heated strongly. 1,1-Di-*H*-trifluoroethyl iodide began distilling and the heating was continued until no more iodide was collected. The yield of crude material was 8.8 g. (0.041 mole or 28%). The crude product was redistilled, b.p. 54.5–55°, n_D^{25} 1.3981 (1).

SUMMARY

1,1-Di-*H*-heptafluorobutyl iodide, $C_3F_7CH_2I$, has been prepared from the corresponding amine. 1,1-Di-*H*-heptafluorobutyl bromide, $C_3F_7CH_2Br$, has been prepared from the corresponding alcohol, *via* the phosphite ester.

Four new compounds have been prepared and characterized. These are: 1-*H*-heptafluorodiazobutane, tris(1,1-di-*H*-heptafluorobutyl) phosphite, tris(1,1-di-*H*-trifluoroethyl) phosphite, and tris(1,1-di-*H*-trifluoroethyl) phosphate.

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(4) HUSTED AND AHLBRECHT, 116th American Chemical Society Meeting, Atlantic City, 1949, Paper No. 17, Abstract p. 10K.