[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Halogeno Methyl Ethers. I. Fluorination of Trichlorodimethyl Ether

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This paper describes an investigation of the fluorination of, and the fluorinated products of, trichlorodimethyl ether.

Experimental

Monochlorodimethyl ether was prepared essentially as described by C. Friedel.[2] Continuous streams of chlorine and dimethyl ether were introduced into a reaction tube, in which a sufficient excess of dimethyl ether necessary to prevent flashing was maintained. Monochlorodimethyl ether was further chlorinated according to the method of A. de Sonay,[3] with the formation of dichloro-, trichloro-, and tetrachlorodimethyl ethers. The chlorinated products were readily separated by fractional distillation.

Fluorination of Trichlorodimethyl Ether

One-half mole (75 g.) of trichlorodimethyl ether (b. p. 130.6 corr., 748 mm.) was refluxed for two hours with 100 g. (excess) of sublimed anhydrous antimony fluoride only. There was obtained, after washing with water and drying with barium oxide, 50 g. of a mixture boiling between 30 and 55.3°. The components of the fluorinated mixture were separated by fractional distillation in a modified Dufton column and the mixture was shown to consist of two volatile liquids, difluoromonochloro- and trifluorodimethyl ether.

Analyses

Difluoromonochlorodimethyl ether: Calcd. for $C_2F_2ClH_3O$: mol. wt., 116.4; C, 20.6; H, 2.59; Cl, 30.5. Found: mol. wt. (Victor Meyer), 119.0; C, 20.47; H, 2.46; Cl (Carius), 30.7.

Trifluorodimethyl ether: Calcd. for $C_2F_3H_3O$: mol. wt., 100.0; C, 23.9; H, 3.0. Found: mol. wt. (Victor Meyer), 102.7; C, 23.85; H, 2.96.

Qualitative tests revealed the presence of fluorine in each of the above compounds.

Physical Properties

The physical properties of the compounds reported in this paper were determined as described by Booth, Elsey and Burchfield,[4] and are found in Table I.

TABLE I

PHYSICAL PROPERTIES OF $C_2F_2ClH_3O$ AND $C_2F_3H_3O$

Compound	B. p., °C. (corr.)	M. p., °C.	ΔH at b. p. Calcd.	Sp. gr. 25°C.
$C_2F_2ClH_3O$	55.3	−105.1	7650	1.370
$C_2F_3H_3O$	30.1	− 96.2	6990	1.328

Constants of the Rankine Equation

	A	B	C	Av. deviation of calcd. values from obsd. values—mm.
$C_2F_2ClH_3O$	−1649	0.1686	7.479	±1.6
$C_2F_3H_3O$	−2405	−6.661	27.344	±1.2

These compounds have a very faint odor somewhat resembling chloroform. They do not fume in air, but slowly hydrolyze in water.

Attempted Preparation of Monofluorodichlorodimethyl Ether

Rapid reaction of trichlorodimethyl ether with antimony fluoride and calcium fluoride, respectively, gave no indication of a fluorinated compound boiling above 55.3° in either case. In this fact, that a monofluoro compound could not be made and that antimony fluoride would fluorinate it without a catalyst, trichlorodimethyl ether resembles benzotrichloride, which until now has been the only organic chloride in the literature with this behavior. It would be interesting to see whether trichloromethyl phenyl ether would behave in the same way.

Summary

The fluorination of trichlorodimethyl ether by anhydrous sublimed antimony fluoride without a catalyst yields a mixture of difluoromonochlorodimethyl ether, m. p. −105.1° and b. p. +55.3°, and trifluorodimethyl ether, m. p. −96.2° and b. p. +30.1°. These compounds are only slowly hydrolyzed in water.

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(2) Friedel, *Compt. rend.*, **84**, 247 (1877).

(3) A. de Sonay, *Bull. Acad. Roy. Belg.*, **26**, 629 (1893).

(4) Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2066 (1935).