

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

A New Method of Synthesizing Aliphatic Difluorides

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The present work originated from the observation that the reaction of anhydrous hydrogen fluoride with 2-chloro-1-pentene gave almost exclusively $\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$, referred to in this paper as the "substitution product," rather than the expected addition product, $\text{CH}_3\text{CClFCH}_2\text{C}_2\text{H}_5$. This observation has proved the starting point for a new method of synthesizing aliphatic difluorides from monochloroolefins of general structure, $\text{CH}_2=\text{CClR}$ or $\text{RCH}=\text{CClR}$. The method has been applied to the preparation of a number of difluorides (from butane to octane).

The reaction of anhydrous hydrogen fluoride with these monochloroolefins gives mainly (59–70%) the "substitution product," with very small amounts of the addition product and small amounts (up to 25%) of the corresponding dichloride. Despite careful fractionation it was not found possible to isolate the addition compound in pure state. The presence of the dichloride in the reaction product can be attributed to addition to the original olefin of part of the hydrogen chloride liberated. When the reaction is carried out in such a way that the hydrogen chloride is not removed from the reaction as it is evolved, a larger amount of dichloride is formed than when provision for removal of hydrogen chloride is made. This fact indicates that the formation of the "substitution product" is probably a case of combined addition and substitution rather than disproportionation.

The addition of anhydrous hydrogen fluoride to a dichloroolefin, $\text{CH}_2=\text{CClCH}_2\text{Cl}$, has been reported by Henne and Haackl¹ to give a 74% yield of addition product, $\text{CH}_3\text{CClFCH}_2\text{Cl}$, and a 4% yield of "substitution product," $\text{CH}_3\text{CF}_2\text{CH}_2\text{Cl}$. In this case the presence of an additional chlorine atom apparently stabilizes the molecule and prevents formation of any appreciable quantity of "substitution product." The difference in procedure between that of these authors and the present work has not been found to affect the yield of addition product, $\text{CH}_3\text{CClFCH}_2\text{Cl}$.

The important features of the new method are: (1) its smoothness and ease of execution; (2) economical requirement of hydrogen fluoride;

(3) high yields of difluorides obtained; and (4) absence of tarry by-products. Especially with respect to the first two points, it possesses advantages over another method, reported by Grosse and Linn,² which consists in adding hydrogen fluoride to acetylenic compounds to yield difluoro paraffins. In practice, the present method consists in reaction of the chloroolefin (1 mole) with anhydrous hydrogen fluoride (2 moles) under pressure at moderate temperature. Most of the hydrogen chloride liberated is permitted to escape through a dephlegmator cooled with solid carbon dioxide, while holding the entire system under a pressure of 4 to 11 atmospheres. The loss of hydrogen fluoride during this operation is negligible. The reaction can be carried out in a closed system without removal of hydrogen chloride but the yield of difluoride is considerably lower and the amount of dichloride formed is increased. It is essential that both the hydrogen fluoride and the chloroolefin be cooled to -78° (verified by actual measurement) before mixing, in order to prevent spontaneous reaction. The permissible rate of warming from -78° depends on the observed rate of pressure increase, which varies with the nature and quantity of the chloroolefin used. Adequate temperature control must be maintained throughout and it is advisable to have ready a liquid bath containing excess "dry-ice" for cooling the reaction vessel in case of a sudden pressure increase. In the present work, the final temperature attained ranged from 35° in the case of chlorobutene, to 46° in the case of chlorooctene.

The monochloroolefins used were prepared by reaction of phosphorus pentachloride with the appropriate ketone.³ This reaction, which should give only the dichloride, produces an appreciable amount of chloroolefin as by-product. By carrying out the reaction at 20 to 30° the chloroolefin becomes the main product and is obtained in generally high yields. The chloroolefins prepared were purified by distillation before use.

The experimental results are summarized in Table I. All yields listed in Table I were ob-

(2) Grosse and Linn, paper presented before the Organic Division at the Baltimore meeting of the American Chemical Society, April, 1939.

(3) Henne, Renoll and Leicester, *THIS JOURNAL*, **61**, 938 (1939).

(1) Henne and Haackl, *THIS JOURNAL*, **63**, 2692 (1941).

TABLE I

Chloroolefin	Difluoride	Yield of difluoride, %
$\text{CH}_2=\text{CClC}_2\text{H}_5$	$\text{CH}_3\text{CF}_2\text{C}_2\text{H}_5$	67.0
$\text{CH}_3\text{CH}=\text{CClCH}_3$	$\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$	64.1
$\text{CH}_2=\text{CClCH}_2\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{CF}_2\text{C}_2\text{H}_5$	59.7
$\text{CH}_3\text{CH}=\text{CClC}_2\text{H}_5$	$\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	70.5
$\text{CH}_2=\text{CClCH}_2\text{CH}(\text{CH}_3)_2$	$\text{CH}_3\text{CF}_2(\text{CH}_2)_3\text{CH}_3$	58.9

previously tested to withstand a pressure of 30 atmospheres. The temperature was raised slowly to 30° by means of a water-bath, at which time a pressure of about 4 atmospheres was reached and the withdrawal of hydrogen chloride was started. The final temperature of 43° was reached in a total heating time of two hours and the temperature maintained at this point for two hours longer. The escape of hydrogen chloride was so regulated that the pressure did not exceed about 6 atmospheres. After removing the source of heat, the vessel was allowed to stand

TABLE II

Compound	F. p., °C.	B. p., °C.	τ	d_4^20	n_D^{20}	MR_D	AR_F	% Fluorine	
								Calcd.	Found
$\text{C}_2\text{H}_5\text{CF}_2\text{C}_2\text{H}_5$	-94.0	60.8	20	0.9106	1.3390	24.83	0.87	35.1	35.1
$\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	-112.7	78.2	20	0.8882	1.3515	29.71	1.00	31.1	31.4
$\text{CH}_3\text{CF}_2(\text{CH}_2)_3\text{CH}_3$	-50.0	136.3-136.6 ^a 66.2-66.6 (60 mm.)	20	0.8867	1.3766	38.92	0.99	25.3	25.2
$\text{CH}_3\text{CF}_2\text{C}_2\text{H}_5^b$	-114.0	31.0	10	0.9170	1.3189	20.29	0.91		
$\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5^b$	-98.1	60.1	20	0.8987	1.3360	24.95	0.93		

^a Very slight decomposition. ^b See reference 3.

tained by the procedure involving removal of hydrogen chloride during reaction. The physical properties, with analyses of the new compounds, are reported in Table II. The molecular refractions, MR_D , were calculated by means of the Lorentz-Lorenz formula. The atomic refraction for fluorine, AR_F , was obtained by subtracting from the molecular refraction the increments for C (2.418) and H (1.100). The freezing points are accurate to $\pm 0.5^\circ$. The two known compounds, $\text{CH}_3\text{CF}_2\text{C}_2\text{H}_5$ and $\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$, were identical with those prepared from $\text{CH}_3\text{CCl}_2\text{C}_2\text{H}_5$ and $\text{CH}_3\text{CCl}_2\text{CH}_2\text{C}_2\text{H}_5$, respectively, by fluorination with antimony fluoride.³

Experimental

All the difluorides listed in Table I were prepared by a procedure analogous to the following.

Preparation of $\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$.—Liquid anhydrous hydrogen fluoride (75 g. or 3.75 moles), cooled to -78° , was mixed with $\text{CH}_2=\text{CClCH}_2\text{C}_2\text{H}_5$ (189 g. or 1.81 moles), also cooled to -78° , in a stainless steel vessel surmounted by a 45-cm. length of pipe. The latter was provided with pressure gage, needle valve, and a 30-cm. cooling jacket filled with solid carbon dioxide. The equipment had been

in the water-bath for eighteen hours (room temperature was reached in several hours). After cooling in ice, the reaction mixture was poured into an ice-water mixture, shaken well and exactly neutralized. Steam distillation separated the organic material which was then dried and distilled. A yield of 125.5 g. or 64.1% of $\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$, boiling at 60.1° was obtained, together with 27.5 g. of intermediate boiling from 95 to 115° and 35.5 g. (13.9%) of $\text{CH}_3\text{CCl}_2\text{CH}_2\text{C}_2\text{H}_5$.

When the above reaction was repeated without removal of hydrogen chloride during reaction, there was obtained a 53.4% yield of $\text{CH}_3\text{CF}_2\text{CH}_2\text{C}_2\text{H}_5$, an amount of intermediate similar to that of the first run, and 24% of $\text{CH}_3\text{CCl}_2\text{CH}_2\text{C}_2\text{H}_5$.

Summary

A method of preparing aliphatic difluorides is described which consists in treatment of monochloroolefins with anhydrous hydrogen fluoride under pressure at moderate temperature. Practical directions are given for carrying out the method which has been applied to the preparation of five difluorides from butane to octane. Physical properties have been tabulated for the three new compounds, $\text{C}_2\text{H}_5\text{CF}_2\text{C}_2\text{H}_5$, $\text{CH}_3\text{CF}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$, and $\text{CH}_3\text{CF}_2(\text{CH}_2)_3\text{CH}_3$.

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