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1960

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Abstract

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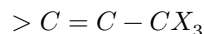
CHEMISTRY

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HOMOLYTIC ADDITION OF HYDROGEN BROMIDE

TO 1-FLUORO-1,1-DICHLOROPROPENE

It is known that the presence of fluorine in polyhalomethyl groups makes the C–Hal bond in them more inert toward heterolytic, as well as toward homolytic, cleavage. In particular, the influence of fluorine has a substantial effect on the ability of compounds of the structure

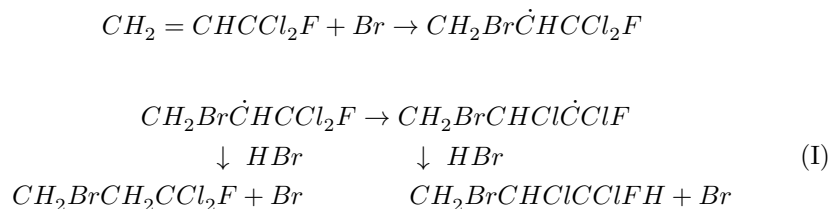


(where $X = Cl, F$) to undergo an anionotropic allylic rearrangement, sometimes directing it in the direction opposite to that observed in polychloro derivatives. An example is the formation of $CHCl = CCl - CF_3$ (1) from $CHCl_2CCl = CCl_2$ (2) (1), in the course of the reaction of the latter with antimony trifluoride, whereas in a series of polychloro derivatives isomerization of substances of type 1 into substances of type 2 is usually observed. In works (2,3) we studied allylic rearrangements of a series of polyhalopropenes of the structure $CH_2 = CRCX_3$, where $R = H, Cl$, and $CX_3 = CCl_3, CCl_2F, CClF_2$. It was shown that the ability to undergo allylic rearrangement upon successive replacement of chlorine in the trichloromethyl group of polyhalopropenes by fluorine decreases sharply (3).

In the present work we have also found a definite difference in the behavior of 1-fluoro-1,1-dichloropropene in the reaction of homolytic addition in comparison with 1,1,1-trichloropropene. As a result of the reaction of 1-fluoro-1,1-dichloropropene with hydrogen bromide under ultraviolet irradiation, two fluorodichlorobromopropanes were obtained: 1-fluoro-1,1-dichloro-3-bromopropane and 1-fluoro-1,2-dichloro-3-bromopropane in a ratio of 2 : 1. The reaction proceeded by a free-radical chain mechanism, as indicated by the reaction conditions (the need for ultraviolet irradiation), as well as by inhibition of the addition by small additions of hydroquinone or acetone. Addition of hydrogen bromide to 1,1,1-trichloropropene under these conditions leads to the sole addition product,

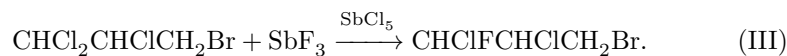
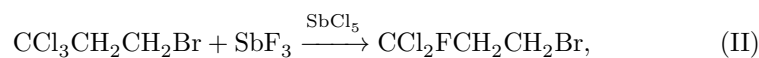
1,1,2-trichloro-3-bromopropane, i.e., it proceeds with rearrangement in the intermediately formed free radical, analogously to what was described earlier (4) in the case of initiation of the reaction by benzoyl peroxide.

The reaction of fluorodichloropropene with hydrogen bromide may be represented by scheme 1:



Thus, apparently, as a result of the stabilizing effect of fluorine in the radical $CH_2Br\dot{C}HCl_2F$, the rate of rearrangement of the latter decreases substantially and becomes comparable with the rate of its reaction with hydrogen bromide. It should be noted that such dual reactivity of a free radical (with and without rearrangement) in the polyhaloalkyl series is observed for the first time (compare with (4-9)).

The structure of the fluorodichlorobromopropanes obtained was proved as follows. First, these compounds were synthesized by an independent route according to schemes II and III:



The yield of the fluoride in reaction III is very small. The corresponding fluorodichlorobromopropanes, obtained both according to scheme I and according to schemes II and III, were identified in the form of crystalline picrates of their isothiuronium derivatives. In addition, dehydrobromination of 1-fluoro-1,1-dichloro-3-bromopropane gave the starting 1-fluoro-1,1-dichloropropene. Dehydrobromination of 1-fluoro-1,2-dichloro-3-bromopropane gave 1-fluoro-1,2-dichloropropene-2, the structure of which was established by ozonization with formation (after hydrolysis of the ozonide) of formaldehyde and fluorochloroacetic acid. The starting 1-fluoro-1,1-dichloropropene was synthesized in two stages from 1,1,1,3-tetrachloropropane by several modified procedures (3).

Experimental Part

Synthesis of 1-fluoro-1,1,3-trichloropropane and 1-fluoro-1,1-dichloropropane. 1-Fluoro-1,1,3-trichloropropane was obtained as described⁽³⁾. In order to promote preferential formation of the monofluoride, the ratio of reagents was changed. For 1 mole of 1,1,1,3-tetrachloropropane, 0.5 mole of antimony trifluoride and 3 ml of antimony pentachloride were taken. The yield of 1-fluoro-1,1,3-trichloropropane was 45% of theory.

Dehydrochlorination of 1-fluoro-1,1,3-trichloropropane was carried out by the described procedure⁽³⁾, but in ethyl cellosolve medium. This made it possible, besides 1-fluoro-1,1-dichloropropane, which was obtained in 59% yield, to isolate 1-fluoro-1,3-dichloropropene-1 in 10% yield of theory, with b.p. 89–90°, n_D^{20} 1.4350; d_4^{20} 1.3219. Literature data⁽³⁾: b.p. 88.5–89.5°; n_D^{20} 1.4310; d_4^{20} 1.3186. Picrate of the isothiuronium derivative, m.p. 176–177° (from aqueous alcohol).



Found, %: N 17.31; 17.51
Calculated, %: N 17.30

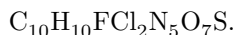
Addition of hydrogen bromide to 1-fluoro-1,1-dichloropropane. A stream of hydrogen bromide was passed for 10 h, under irradiation with a PRK-4 lamp, through 50 g of fluorodichloropropene placed in a quartz tube. The reaction product was washed with soda solution and water and dried over calcium chloride. Distillation gave two addition products.

First product: 1-fluoro-1,1-dichloro-3-bromopropane (32 g) with b.p. 69–70°/70 mm; 136°/760 mm; n_D^{20} 1.4630; d_4^{20} 1.7307; *MR* found 33.43, calculated 33.45.



Found, %: C 17.29; 17.16; H 1.94, 1.93; F 9.76; 9.81
Calculated, %: C 17.16; H 1.92; F 9.05

Picrate of the isothiuronium derivative, m.p. 164° (from alcohol).



Found, %: C 27.36; 27.35; H 2.28; 2.24; N 16.06
Calculated, %: C 27.66; H 2.32; N 16.13

On dehydrobromination of this fluorodichlorobromopropane with alkali in ethyl cellosolve at 0°, the starting 1-fluoro-1,1-dichloropropene is formed in 60% yield. 1-Fluoro-1,1-dichloro-3-bromopropane, synthesized by an independent route from the reaction of 1,1,1-trichloro-3-bromopropane with antimony trifluoride,* has b.p. 136°; n_D^{20} 1.4630; d_4^{20} 1.7295. Picrate

* During the fluorination process, 1,1,3-trichloropropene-1 is also formed. To isolate 1-fluoro-1,1-dichloro-3-bromopropane, the mixture was treated with bromine, after which separation of the products by fractionation was readily achieved.

of its isothiuronium derivative melts at 164°. A mixed sample of both picrates shows no depression of the melting point.

The second product: 1-fluoro-1,2-dichloro-3-bromopropane (15 g) with b.p. 72–73°/40 mm; 161°/760 mm; n_D^{20} 1.4870; d_4^{20} 1.8200; *MR* found 33.17, calculated 33.45.

Found, %: C 17.18; 17.04; H 1.87; 1.82; F 8.99; 9.20
 $C_3H_4FCl_2Br$. Calculated, %: C 17.16; H 1.92; F 9.05

Picrate of the isothiuronium derivative, m.p. 171° (from alcohol).

Found, %: C 27.34; 27.39; H 2.29; 2.19; N 15.98
 $C_{10}H_{10}FCl_2N_5O_7S$. Calculated, %: C 27.66; H 2.32; N 16.13

On dehydrobromination of this fluorodichlorobromopropane with alkali in ethyl cellosolve at 0°, 1-fluoro-1,2-dichloropropene-2 was obtained in 54% yield, with b.p. 84°; n_D^{20} 1.4290; d_4^{20} 1.3214; *MR* found 25.10, calculated 25.22.

Found, %: C 28.31; 28.25; H 2.42; 2.50
 $C_3H_3FCl_2$. Calculated, %: C 27.93; H 2.34

Picrate of the isothiuronium derivative, m.p. 160–161° (darkens at 149°).

Found, %: C 29.86; 29.95; H 2.49; 2.47; F 4.57; 4.56
 $C_{10}H_9FCIN_5O_7S$. Calculated, %: C 30.19; H 2.28; F 4.77

On ozonization of this fluorodichloropropene, followed by decomposition of the ozonide with water, the following were isolated: formaldehyde in the form of its dimedone derivative, m.p. 189°, literature data (10): m.p. 189°; fluoro-chloroacetic acid with b.p. 162°, n_D^{20} 1.4090, literature data (11): b.p. 162°, n_D^{25} 1.4085, which was converted through the acid chloride into the anilide of the acid, m.p. 86–87° (from heptane).

Found, %: C 51.31; 51.32; H 3.89; 3.87; F 10.18; 10.17
 C_8H_7FCINO . Calculated, %: C 51.22; H 3.76; F 10.13

A mixed sample with anilide obtained from authentic fluoro-chloroacetic acid showed no depression of the melting point. 1-Fluoro-1,2-dichloro-3-bromopropane, although in very low yield, was also obtained by an authentic route—the reaction of 1,1,2-trichloro-3-bromopropane with antimony trifluoride—and had b.p. 161–162°; n_D^{20} 1.4860; d_4^{20} 1.8194. The picrate of its isothiuronium derivative melts at 169°. A mixed sample of both picrates shows no depression of the melting point.

Addition of hydrogen bromide to 1,1,1-trichloropropene. The experiment was carried out in the same way as in the case of 1-fluoro-1,1-

dichloropropene-2. Thus, from 50 g of trichloropropene, on saturation with hydrogen bromide for 2.5 h and after the corresponding work-up and distillation, 68 g of 3-bromo-1,1,2-trichloropropane were obtained, with b.p. 84–85°/16 mm; n_D^{20} 1.5295; d_4^{20} 1.8390. Literature data (4): b.p. 75–75.5°/9 mm; n_D^{20} 1.5290; d_4^{20} 1.8322.

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Received
24 II 1960

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