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Abstract

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HOMOLYTIC ISOMERIZATION OF 1-FLUORO-1,1-DICHLORO-2-BROMOPROPENE

As was shown earlier ([1]), 1,1,1-trichloro-2-bromopropene is readily isomerized by a chain radical mechanism into 1,1,2-trichloro-3-bromopropene-1. For this isomerization the following scheme was proposed:

$$\begin{aligned} &\mathrm{Br}\cdot + \mathrm{CH_2{=}CBrCCl_3} \longrightarrow \mathrm{BrCH_2\dot{C}BrCCl_3} \quad A \\ &\quad \xrightarrow[\text{rearr.}]{} \mathrm{BrCH_2CBrCl\dot{C}Cl_2} \quad A' \\ &A' \longrightarrow \mathrm{BrCH_2CCl{=}CCl_2} + \mathrm{Br}\cdot \end{aligned} \tag{I}$$

On irradiation of the substance with ultraviolet light this isomerization proceeds so rapidly that it is impossible to detect the intermediately formed radicals A and A', even with so effective a chain carrier as hydrogen bromide (i.e., the reactions $A + \mathrm{HBr} \rightarrow \mathrm{CH_2BrCHBrCCl_3} + \mathrm{Br}\cdot$ and $A' + \mathrm{HBr} \rightarrow \mathrm{CH_2BrCClBrCCl_2H} + \mathrm{Br}\cdot$ do not take place).

The introduction of fluorine into the trichloromethyl group, as we showed in a preceding work ([2]), considerably slows the rearrangement of the radical $\mathrm{CCl_2F\dot{C}HCH_2Br} \rightarrow \mathrm{\dot{C}ClFCHClCH_2Br}$, as a result of which, in the ultraviolet-light-catalyzed addition of hydrogen bromide to $\mathrm{CCl_2FCH{=}CH_2}$, two reaction products are formed: $\mathrm{CH_2BrCH_2CCl_2F}$ and $\mathrm{CH_2BrCHClCHFCl}$ (1,1,1-trichloropropene in this reaction gives only the rearranged $\mathrm{CHCl_2CClHCH_2Br}$).

In the present work we studied certain transformations of 1-fluoro-1,1-dichloro-2-bromopropene—an analog of 1,1,1-trichloro-2-bromopropene. On standing, 1-fluoro-1,1-dichloro-2-bromopropene undergoes dimerization (Table 1, experiment 5). The dimer consists mainly, as will be shown below, of

$$\begin{array}{l} \mathrm{BrCH_2CBrCH_2CCl{=}CClF} \\ \qquad\qquad\qquad\quad \vert \\ \qquad\qquad\qquad\quad \mathrm{CCl_2F} \end{array}$$

the formation of which can be explained by the following reactions:

$$
\begin{aligned}
&\mathrm{Br}\cdot + \mathrm{CH_2{=}CBrCCl_2F} \longrightarrow \mathrm{CH_2Br\dot{C}BrCCl_2F} \quad B \\
&B + \mathrm{CH_2{=}CBrCCl_2F} \longrightarrow \mathrm{BrCH_2CBrCH_2\dot{C}BrCCl_2F} \\
&\qquad\qquad \Big|_{\mathrm{CCl_2F}} \quad B \\
&B \xrightarrow[\text{rearr.}]{} \mathrm{BrCH_2CBr(CCl_2F)\dot{C}H_2CBrClCClF} \quad B' \\
&B' \longrightarrow \mathrm{BrCH_2CBr(CCl_2F)CH_2CCl{=}CClF + Br}\cdot
\end{aligned}
\qquad \text{(II)}
$$

On heating the initial fluorodichlorobromopropene (Table 1, experiments 1 and 2), together with synthesis of the dimer, isomerization takes place with formation of 1-fluoro-1,2-dichloro-3-bromopropene-1 according to a scheme analogous to (I). These transformations are accelerated by addition of small amounts of benzoyl peroxide and are suppressed by addition of hydroquinone (Table 1, experiments 3 and 6).

Carrying out this reaction under illumination with ultraviolet light in the presence of an excess of hydrogen bromide led to the formation of only small amounts of dimer; in addition, 1-fluoro-1,1-dichloro-2,3-dibromopropane (the main reaction product) and 1-fluoro-1,2-dichloro-3-bromopropene-1 were obtained (Table 1, experiment 7). Thus, the radical B formed in the reaction was trapped as the product of its interaction with hydrogen bromide, with regeneration of a bromine atom

$$
\mathrm{B} \xrightarrow{\mathrm{HBr}} \mathrm{CH_2BrCHBrCCl_2F + Br}\cdot .
$$

The absence from the reaction mixture of $\mathrm{CH_2BrCClBrCClFH}$—the product of interaction of the rearranged radical B′ with HBr according to scheme (III)—and the presence of $\mathrm{CH_2BrCCl{=}CClF}$, obtained according to scheme (IV),

$$
\begin{aligned}
\mathrm{B} \xrightarrow{\text{rearr.}} \mathrm{CH_2BrCClBr\dot{C}ClF} \xrightarrow{\mathrm{HBr}} &\mathrm{CH_2BrCClBrCClFH + Br} \quad \text{(III)} \\
\longrightarrow &\mathrm{CH_2BrCCl{=}CClF + Br} \quad \text{(IV)}
\end{aligned}
$$

indicate a considerably higher rate of the elimination reaction in this radical (equation (IV)) as compared with the substitution reaction with hydrogen bromide. This result gives grounds to believe that another possible path for formation of the dimer, namely through radical B′ according to scheme (V),

$$
\mathrm{BrCH_2CClBr\dot{C}ClF} \xrightarrow{+\mathrm{CH_2{=}CBrCCl_2F}} \mathrm{BrCH_2CBrClCClFCH_2\dot{C}BrCCl_2F} \qquad \text{(V)}
$$

and subsequently, as in (II), with formation of a dimer of normal structure $\mathrm{BrCH_2CBr\cdot ClCClFCH_2CCl{=}CClF}$, is unlikely, since the rate of this reaction

under the given conditions apparently should be lower than the rate of interaction

Table 1*

No.	Reaction conditions	Time, h	n_D^{20} of final mixture	Yield of $CFCl_2-CBr=CH_2$, g	Yield of $CFCl=CClCH_2Br$, g	Yield of $CFCl=CClCH_2Br$**, % of theoretical for reacted product	Dimer***, g
1	90°	6	1.4860	11.2	3.7	42	4.2
2	140°	6	1.5040	5	6.4	42	7.5
3	90° + Bz_2O_2	6	1.5000	6.9	6	46	6.4
4	Illumination with ultraviolet light	6	1.4870	13.2	2.4	34	4
5	Room temperature	5 days	1.5010	9	–	–	9.1
6	90°+ hydroquinone	6	1.4740	19.1	–	–	–
7	Addition of HBr under illumination with ultraviolet light (40–50°)****	7	–	10	0.9	3	2.7

* Experiments 1–6 were carried out with 20 g of fluorodichlorobromopropene;

experiment 7 was carried out with 40 g of fluorodichlorobromopropene.

** 1-Fluoro-1,2-dichloro-3-bromopropene, obtained in all experiments, has identical constants: b.p. 58° at 35 mm; n_D^{20} 1.5000; d_4^{20} 1.8461; MR 33.15; calculated MR 32.98.
Found, %: C 17.23; 17.14; H 0.96; 0.98; F 9.17; 9.26.
Calculated, %: C 17.33; H 0.97; F 9.14.
Diethylamine picrates derived from these fluorodichloropropenes have m.p. 101-102° and show no depression of the melting point of a mixed sample with picrate obtained by an independent route (see the following experiments).

*** The dimer obtained in all experiments also has identical constants: b.p. 110° at 3 mm; n_D^{20} 1.5410; d_4^{20} 2.0605; MR 63.80; calculated MR 64.23. Found mol. wt. 409.5; calculated 415.7 (cryoscopically in benzene).
Found, %: C 17.30; 17.39; H 1.03; 0.99; F 9.12; 9.24.
Calculated, %: C 17.33; H 0.97; F 9.14.
The IR spectrum of the dimer (recorded in the optical laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR, by N. V. Chumaevskii) contains an intense absorption band at 1670 ± 5 cm^{-1}, characteristic of compounds containing the CFCl=CCl group (4).

**** The main reaction product (32 g) is 1-fluoro-1,1-dichloro-2,3-dibromopropane with b.p. 80-81° at 17 mm; n_D^{20} 1.5175; d_4^{20} 2.1536. On dehydrobromination it gave the starting 1-fluoro-1,1-dichloro-2-bromopropene.

B′ with hydrogen bromide,* and therefore, still less the rate of elimination. Thus, under the conditions studied, radical B′ can give only 1-fluoro-1,2-dichloro-3-bromopropene-1.

The structure of the initial 1-fluoro-1,1-dichloro-2-bromopropene, obtained according to the scheme

$$CCl_2FCH{=}CH_2 + Br_2 \rightarrow CCl_2FCHBrCH_2Br \xrightarrow{KOH} CCl_2FCBr{=}CH_2 \quad (VI)$$

was proved by ozonization, with isolation of formaldehyde and fluorodichloroacetic acid.

The structure of the 1-fluoro-1,2-dichloro-3-bromopropene-1 obtained in the reactions was established by the following transformations:

$$CClF{=}CCl{-}CH_2Br \xrightarrow{NH(C_2H_5)_2} CClF{=}CCl{-}CH_2N(C_2H_5)_2 \xleftarrow{KOH}$$

$$CClF{=}CHCH_2Cl \rightarrow CClF{=}CHCH_2N(C_2H_5)_2 \xrightarrow{Cl_2} CCl_2FCHClCH_2N(C_2H_5)_2$$

The amines obtained by both routes were identified in the form of their picrates.

The 1-fluoro-1,1-dichloro-2,3-dibromopropane obtained in the reaction of addition of HBr to 1-fluoro-1,1-dichloro-2-bromopropene was identical in all properties to the dibromide from reaction (VI). Moreover, on dehydrobromination of it with alcoholic alkali, the initial fluorodichlorobromopropene was obtained.

$$CCl_2FCHBrCH_2Br \rightarrow CCl_2FCBr{=}CH_2.$$

A number of experimental confirmations were obtained for the structure of the dimer $BrCH_2CBr(CCl_2F)CH_2CCl{=}CClF$. Thus, according to the IR spectrum, this compound contains an FCCl=CCl group; furthermore, on treatment of it with Zn in alcohol a diene of composition $C_6H_4Cl_4F_2$ was obtained, which on mild ozonization gives formaldehyde and a carbonyl compound (the latter was not isolated in pure form). In reaction with zinc under more severe conditions (heating with a large excess of zinc for 8 h on a boiling water bath), along with the elimination of two bromine atoms, reduction occurs at the expense of one or two chlorine atoms, with formation of dienes of composition $C_6H_5Cl_3F_2$ and $C_6H_6Cl_2F_2$. On ozonolysis of these dienes, formaldehyde was likewise obtained.

Experimental Part

1-Fluoro-1,1-dichloro-2,3-dibromopropane was obtained in 80% yield by bromination of 1-fluoro-1,1-dichloropropene in glacial acetic acid; b.p. 80° at 17 mm; n_D^{20} 1.5175; d_4^{20} 2.1540, MR 40.60, calculated MR 41.21.

Found %:	C 12.48; 12.54;	H 1.17; 1.08
Calculated %:	C 12.47;	H 1.05

By reaction of it with diethylamine, 1-fluoro-1-chloro-2-bromo-3-diethylaminopropene-2 was obtained in 73% yield; b.p. 85–86° at 20 mm; n_D^{20} 1.4710; d_4^{20} 1.3591; MR 50.30; calculated MR 50.53.

Found %:	C 34.42; 34.48;	H 4.81; 5.06
Calculated %:	C 34.37;	H 4.94

The picrate of the diethylamine derivative has m.p. 121–122° (from alcohol).

1-Fluoro-1,1-dichloro-2-bromopropene was obtained in 65% yield by dehydrobromination of 1-fluoro-1,1-dichloro-2,3-dibromopropane with potassium hydroxide in ethyl cellosolve. After double distillation, b.p. 53° at 70 mm; n_D^{20} 1.4740; d_4^{20} 1.7905; MR 32.70; calculated MR 32.98.

Found %:	C 17.23; 17.18;	H 1.02; 1.08
Calculated %:	C 17.33;	H 0.97

* In the preceding work ([2]) it was shown that, under analogous conditions, a radical of similar structure $BrCH_2CHClCClF$ reacts almost exclusively by abstraction of hydrogen from HBr, and not by addition to the olefin (CH_2=$CHCCl_2F$).

On ozonization of this fluorodichlorobromopropene, followed by decomposition of the ozonide with water, there were isolated: formaldehyde in the form of its dimedone derivative, m.p. 189°, mixed-sample m.p. with an authentic specimen 189°, and fluorodichloroacetic acid, b.p. 162°; literature data ([3]) b.p. 162.5°. The anilide of fluorodichloroacetic acid has m.p. 75° (from heptane).

Found, %:	C 42.96; 43.00;	H 2.78; 2.83;	F 8.12; 8.56
Calculated, %:	C 43.27;	H 2.72;	F 8.56

Transformations of 1-fluoro-1,1-dichloro-2-bromopropene.
The data obtained for the transformations of fluorodichlorobromopropene are summarized in Table 1.

Preparation of the picrate of 1-fluoro-1,2-dichloro-3-diethylaminopropene-1.
a) 1-Fluoro-1-chloro-3-diethylaminopropene-1 was obtained analogously to that described in ([1]), in 73% yield, from 1-fluoro-1,3-dichloropropene-1. B.p. 87° at 100 mm; n_D^{20} 1.4320; d_4^{20} 1.0119; MR 42.46; calculated MR 42.76.

Found, %:	C 50.65; 50.70;	H 8.05; 7.90;	F 11.52; 10.83
Calculated, %:	C 50.75;	H 7.91;	F 11.47

Picrate m.p. 85–86° (from alcohol).

b) 1-Fluoro-1,1,2-trichloro-3-diethylaminopropane was obtained in 74% yield by chlorination of 1-fluoro-1-chloro-3-diethylaminopropene-1. B.p. 64–65° at 2 mm; n_D^{20} 1.4540; d_4^{20} 1.2200; MR 52.40; calculated MR 52.96.

Found, %:	C 35.65; 35.69;	H 5.67; 5.66;	F 8.23; 8.13
Calculated, %:	C 35.54;	H 5.54;	F 8.05

Picrate m.p. 152–153° (from alcohol).

c) 1-Fluoro-1,2-dichloro-3-diethylaminopropene-1 was obtained by dehydrochlorination of 1-fluoro-1,1,2-trichloro-3-diethylaminopropane with alcoholic caustic potash, in 91% yield, with b.p. 66–67° at 15 mm; n_D^{20} 1.4520; d_4^{20} 1.1400; MR 47.22; calculated MR 47.66.

Found, %:	C 41.83; 41.73;	H 6.19; 6.20;	F 8.97; 9.05
Calculated, %:	C 42.04;	H 6.05;	F 9.50

Picrate m.p. 101–102° (from alcohol).

Debromination of the dimer.
To 4 g of zinc dust in 10 ml of absolute ethyl alcohol, previously activated by heating with 0.1 ml of hydrobromic acid and 0.1 ml of acetic acid, there were added dropwise 22 g of the dimer in 40 ml of absolute ethyl alcohol, after which the reaction mixture was heated at 50° for 6 hours. The precipitate was filtered off and washed with chloroform. The filtrate was acidified with hydrochloric acid and extracted with chloroform. The chloroform extract was dried over $CaCl_2$, the chloroform was distilled off, and the residue was distilled in vacuo.

There were obtained 4.2 g of a bromine-free diene (31%), with b.p. 95° at 35 mm; n_D^{20} 1.4710; d_4^{20} 1.4844; MR 48.19; calculated MR 48.23.

Found, %:	C 28.42; 28.36; H 1.79; 1.80
Calculated, %:	C 28.16; H 1.86

Starting dimer: 11.5 g, with b.p. 110° at 3 mm; n_D^{20} 1.5410.

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Note: Figure translations are in progress. See original paper for figures.