Chemistry

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1961

SovietRxiv

Abstract

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Rearrangements in the Homolytic Addition of Hydrogen Bromide to Polyhaloalkenes

It was found earlier ($^{1-5}$) that radicals $CCl_3\dot{C}X—CH_2Y$, where $X = H, Cl, Br, CH_3$; $Y = Cl, Br, CCl_3, SC_6H_5$, isomerize into radicals of the structure $\dot{C}Cl_2—CXCl—CH_2Y$. An analogous rearrangement was noted by us (^{6}) also in the case of the radical with a dichloromethyl group $CHCl_2—\dot{C}H—CH_2Br$, which isomerizes into the more stable radical $\dot{C}HCl—CHCl—CH_2Br$.

In the present work we investigated the capacity for such rearrangement of radicals of the structure $RCCl_2\dot{C}R'(CH_2Br)$ ($R = H, CH_3$; $R' = H, CH_3$), containing dichloromethyl and dichloromethylene groups in the α-position to the radical center; the radicals were generated in the course of the homolytic addition of hydrogen bromide to the corresponding unsaturated compounds $RCCl_2CR' = CH_2$

$$RCl_2—\dot{C}R' = CH_2 \xrightarrow[(C_6H_5CO_2)_2]{HBr} RCCl_2—\dot{C}R'—CH_2Br. \tag{1}$$

It could be expected that radicals 1 in the reactions studied would react according to scheme A:

$$\underset{1}{\mathrm{RCCl_2{-}CR'{-}\dot{C}H_2Br}} \xrightarrow[\text{a) HBr}]{} \underset{\mathrm{I}}{\mathrm{RCCl_2{-}CR'H{-}CH_2Br}} + \mathrm{Br}$$

$$\mathrm{RCCl_2{-}CR'{-}\dot{C}H_2Br} \xrightarrow[\text{b)}]{} \underset{\mathrm{II}}{\mathrm{RCCl{-}CR'{-}CH_2Br}} + \mathrm{Cl}$$

$$\mathrm{RCCl_2{-}CR'{-}\dot{C}H_2Br} \xrightarrow[\text{c)}]{} \mathrm{R\dot{C}Cl{-}CR'Cl{-}CH_2Br} \qquad \text{(A)}$$

$$\mathrm{R\dot{C}Cl{-}CR'Cl{-}CH_2Br} \xrightarrow[\text{d) HBr}]{} \underset{\mathrm{III}}{\mathrm{RCClH{-}CR'Cl{-}CH_2Br}} + \mathrm{Br}$$

$$\mathrm{RCCl_2{-}CR' = CH_2 + Cl} \xrightarrow[\text{e)}]{} \underset{2}{\mathrm{RCCl_2{-}\dot{C}R'{-}CH_2Cl}} \text{ etc.,}$$

where $R, R' = \mathrm{H, CH_3}$; radical 2 undergoes the same transformations as radical 1.

In the present case it was of interest to compare the stability of the initial radicals and the radicals that may be formed upon rearrangement, namely: the secondary radical $\mathrm{CH_3CCl_2{-}\dot{C}H{-}CH_2Br}$ with the formally secondary radical, but one bonded to chlorine, $\mathrm{CH_3\dot{C}Cl{-}CHCl{-}CH_2Br}$, then the secondary and tertiary radicals $\mathrm{CHCl_2{-}CR'{-}CH_2Br}$ ($R' = \mathrm{H}$ or $\mathrm{CH_3}$) with the primary radical with chlorine at the carbon bearing the free valence, $\mathrm{CHCl{-}CClR'{-}CH_2Br}$.

Addition of hydrogen bromide to 3,3-dichlorobutene-1 led to the formation only of the rearranged reaction product–2,3-dichloro-1-bromobutane (see scheme A, directions c, d; $R = CH_3$, $R' = H$).

The reaction of hydrogen bromide with 1,1-dichloropropene-2, as we showed earlier, proceeds with formation of the rearranged reaction product, 1,2-dichloro-3-bromopropane. Carrying out the experiment in a solvent and working with a large amount of material made it possible in this case to isolate, together with 1,2-dichloro-3-bromopropane, the unrearranged reaction product, 1,1-dichloro-3-bromopropane (see scheme A, directions a, c, d; $R, R' = H$).

1,1-Dichloro-2-methylpropene-2 reacts with hydrogen bromide to form a mixture of reaction products consisting of rearranged 1,2-dichloro-3-bromo-2-methylpropane (III), unrearranged 1,1-dichloro-3-bromo-2-methylpropane (I), trichloroisobutane, and 1-chloro-3-bromo-2-methylpropene-1 (II). The formation of these substances may be represented by a scheme analogous to scheme A ($R = H$, $R' = CH_3$).

Table 1

Olefin	Yield of total products of HBr addition, % of theory	Rearrangement, %
$CH_3CCl_2—CH = CH_2$	73	100
$CHCl_2—CH = CH_2$	53	90
$CHCl_2—C(CH_3) = CH_2$	61	50–55
$CHCl_2—CCl = CH_2$	22	0

To exclude the assumption that the rearranged reaction products were obtained by allylic isomerization of the initial unsaturated compounds followed by addition of hydrogen bromide to them and have the structures $CH_3CHCl—CHBr—CH_2Cl$ and $CH_2ClC(CH_3)Br—CH_2Cl$, respectively, blank experiments were carried out on the addition of hydrogen bromide in the presence of benzoyl peroxide to $CH_3CCl = CH—CH_2Cl$ and $CHCl = C(CH_3)—CH_2Cl$ (allylic isomers of the initial unsaturated compounds), which gave negative results.

The yields of the addition products and the dependence of rearrangement on the structure of the initial olefins are shown in Table 1.

On the basis of these data the studied radicals may be arranged according to their stability as follows:
$CHCl_2—\dot{C}ClCH_2Br > CHClCCl_2CH_2Br$;
$CH_3\dot{C}ClCHClCH_2Br > CH_3CCl_2\dot{C}HCH_2Br$;
$\dot{C}HClCHClCH_2Br > CHCl_2\dot{C}HCH_2Br$;
$CHCl_2\dot{C}(CH_3)CH_2Br \simeq \dot{C}HClCCl(CH_3)CH_2Br$.

Experimental Part

Addition of hydrogen bromide to $CH_3CCl_2—CH = CH_2$. A solution of 16 g of $CH_3CCl_2CH = CH_2$* and 0.5 g of benzoyl peroxide in 48 g of carbon tetrachloride was saturated with hydrogen bromide at 70–75°. After washing with soda solution and water, drying over $CaCl_2$, and distilling off the solvent, 18.5 g (73% of theory) of 2,3-dichloro-1-bromobutane was obtained, b.p. 67–67.5° at 12 mm, n_D^{20} 1.5042; d_4^{20} 1.5985; found MR 38.15; calculated 38.17.

$C_4H_7Cl_2Br$.	Found %:	C 23.06; 23.30;	H 3.52; 3.32
	Calculated %:	C 23.33;	H 3.43

Picrate $CH_3CHCl—CHCl—CH_2S—C = NH(NH_2)$, m.p. 165–165.5° (from alcohol).

$C_{11}H_{13}Cl_2N_5O_7S$.	Found %:	C 30.91; 31.09;	H 3.23; 3.28;	N 16.80; 16.76
	Calculated %:	C 30.71;	H 3.05;	N 16.28

* Constants of $CH_3CCl_2CH = CH_2$: b.p. 95°, n_D^{20} 1.4460; d_4^{20} 1.1043.

On dehydrobromination of 13.6 g of $CH_3CHClCHClCH_2Br$ with 4.1 g of KOH in ethyl cellosolve, 4.1 g (60% of theory) of 2,3-dichlorobutene-1 was obtained, b.p. 111-112°, n_D^{20} 1.4580; d_4^{20} 1.1340 (literature data ([7]): b.p. 111.8°, n_D^{20} 1.4571; d_4^{20} 1.1411). As a result of ozonolysis of $CH_3CHClCCl = CH_2$, formaldehyde was isolated, with m.p. of the dimedone derivative 185-186° (literature data ([8]): 188-189°), and α-chloropropionic acid*, identified as the anilide, m.p. 88° (literature data ([9]): m.p. 92°).

$C_9H_{10}ClNO$. Found, %: C 58.72; 58.53; H 5.44; 5.46; Cl 20.20; 20.06
Calculated, %: C 58.83; H 5.49; Cl 19.31

Addition of HBr to $CHCl_2CH = CH_2$. A solution of 143 g of $CHCl_2CH = CH_2$ and 1.5 g of benzoyl peroxide in 240 g of heptane was saturated with hydrogen bromide at 80°. After the work-up described in the preceding experiment and distillation on a column at 34 mm, 131 g of a mixture of dichlorobromopropanes was obtained (53% of theory), from which the following fractions were isolated: I, b.p. 71-77°, n_D^{20} 1.5034-1.5080, 12 g (9% of the total products); II, b.p. 81°, n_D^{20} 1.5170, d_4^{20} 1.7504, 113.7 g (86% of the total products).

From fraction I, after a second distillation, 1,1-dichloro-3-bromopropane was isolated, b.p. 74-74.5° at 34 mm, n_D^{20} 1.5045; d_4^{20} 1.7084; found MR 33.29; calculated 33.55**.

Picrate of $CHCl_2CH_2{-}CH_2S{-}C = NH(NH_2)$, m.p. 147-148° (from alcohol).

$C_{10}H_{11}Cl_2N_5O_7S$. Found, %: C 28.82; 28.56; H 2.56; 2.61
Calculated, %: C 28.86; H 2.67

A mixed sample with the picrate obtained from known $CHCl_2{-}CH_2CH_2Br$ melted at 147-148°; with the picrate of $CH_2Cl{-}CHCl{-}CH_2S{-}C{=}NH(NH_2)$, 139°. For the structure of the substance of fraction II, see ([6]).

Addition of hydrogen bromide to $CHCl_2C(CH_3){=}CH_2$. A solution of 45 g of $CHCl_2C(CH_3) = CH_2$ and 0.5 g of benzoyl peroxide in 110 g of carbon tetrachloride was saturated with hydrogen bromide at 80° until the refractive index ceased to change. After the usual work-up and distillation of the reaction products on a column at 17 mm, the following fractions were obtained: I, 52-60°, n_D^{20} 1.4929, 7.4 g; II, 60-66°, n_D^{20} 1.4886, 2.7 g; III, 69.5-71°, n_D^{20} 1.5025, d_4^{20} 1.6098; found MR 37.78; calculated for $C_4H_7Cl_2Br$ 38.17; 46.2 g (61% of theory).

Fractions I and II contained a mixture of $CHCl{=}C(CH_3){-}CH_2Br$ and trichloroisobutane. The former was removed by treating the mixture with thiourea under mild conditions to give $CHCl{=}C(CH_3){-}CH_2S{-}C{=}NH(NH_2)$, picrate m.p. 193° (from alcohol). A mixed sample with a known specimen gave no depression of the melting point.

$C_{11}H_{12}ClN_5O_7S$. Found, %: C 33.58; 33.86; H 3.17; 3.20; N 17.37; 17.38
Calculated, %: C 33.55; H 3.07; N 17.78

On distillation of the residue, trichloroisobutane was isolated, b.p. 160°, n_D^{20} 1.4765; d_4^{20} 1.2918; found *MR* 35.29; calculated 35.27. (Constants of 1,2,3-trichloro-2-methylpropane, obtained by an independent route ([10]): b.p. 163°, n_D^{20} 1.4770; d_4^{20} 1.3010.)

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* α-Chloropropionic acid was obtained from the ozonolysis products without additional oxidation.

** Constants of $CHCl_2{-}CH_2{-}CH_2Br$, obtained by an independent route: b.p. 72° at 30 mm, n_D^{20} 1.5030; d_4^{20} 1.7093. Found *MR* 33.19.

$C_4H_7Cl_2Br$. Found, %: C 18.88; 18.91; H 2.58; 2.53
Calculated, %: C 18.77; H 2.63

Fraction III is a mixture of 3,3-dichloro-1-bromo-2-methylpropane and 2,3-dichloro-1-bromo-2-methylpropane.

Found, %: C 23.27; 23.43; H 3.33; 3.28
$C_4H_7Cl_2Br$. Calculated, %: C 23.33; H 3.43

As a result of heating 8.4 g of the mixture (fraction III) with 3.1 g of thiourea in alcohol in a sealed ampoule for 20 h and of the corresponding work-up, the following were isolated: 1) 6.4 g of a dry residue consisting of unreacted thiourea and the isothiouronium derivative $CHCl_2C(CH_3)H{-}CH_2SC{=}NH(NH_2)$ (yield 40% of theory); m.p. of the picrate 164–165° (from alcohol).

Found, %: C 31.01; 30.90; H 3.07; 3.15; N 15.84; 15.95
$C_{11}H_{13}Cl_2N_5O_7S$. Calculated, %: C 30.71; H 3.05; N 16.24

2) 3.6 g (42% of theory) of an oil, from which, after distillation, 1,2-dichloro-3-bromo-2-methylpropane was isolated, b.p. 67–68° at 16 mm, n_D^{20} 1.5040; d_4^{20} 1.6154; found *MR* 37.71, calculated 38.18*.

On dehydrobromination of 45 g of the dichlorobromoisobutane fraction with 15 g of KOH in ethyl cellosolve at 0°, the following were obtained: 1) 8.5 g of $CHCl_2$—$C(CH_3)$=CH_2, b.p. 49-50° at 105 mm, n_D^{20} 1.4560; d_4^{20} 1.1346 (constants of $CHCl_2C(CH_3)$=CH_2, obtained by the method of (11): b.p. 48-49° at 100 mm; n_D^{20} 1.4582; d_4^{20} 1.1344).

On ozonolysis of $CHCl_2$—$C(CH_3)$=CH_2, formaldehyde was isolated in the form of the dimedone derivative.

2) 20.4 g of 1,2-dichloro-3-bromo-2-methylpropane, which under these conditions does not react with KOH, b.p. 112–113° at 100 mm; n_D^{20} 1.5038; d_4^{20} 1.6124; found MR 37.75; calculated 38.18; it does not react with thiourea under severe conditions; on treatment with Zn in alcohol, CH_2Cl—$C(CH_3)$=CH_2 was isolated, identified as the picrate of the isothiouronium derivative, m.p. 168–169°.

From authentic CH_2Cl—$C(CH_3)Cl$—CH_2Br, the isothiouronium derivative was obtained in an analogous manner (Zn, then thiourea), m.p. of the picrate 168-169.5° (from alcohol).

Found, %:	C 36.42; 36.59;	H 3.63; 3.44;	N 20.01; 20.23
$C_{11}H_{13}N_5O_7S$. Calculated, %:	C 36.76;	H 3.66;	N 19.49

A mixed sample of the two picrates melted at 168–169°.

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Received
23 XI 1960

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* 1,2-Dichloro-3-bromo-2-methylpropane obtained by chlorination of $CH_2{=}C(CH_3){—}CH_2Br$ in an acid medium had the following constants: b.p. 75° at 21 mm; n_D^{20} 1.5071; d_4^{20} 1.6110.

Found, %:	C 23.50; 23.62;	H 3.47; 3.57
$C_4H_7Cl_2Br$. Calculated, %:	C 23.33;	H 3.43

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

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