CHEMISTRY

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1961

SovietRxiv

Abstract

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CHEMISTRY

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HOMOLYTIC ISOMERIZATION OF 2-BROMO-3,3-DICHLOROBUTENE-1

(Presented by Academician A. N. Nesmeyanov, 23 XI 1960)

As was shown earlier, 2-bromo-3,3,3-trichloropropene, after a certain induction period or upon irradiation with ultraviolet light, isomerizes to 3-bromo-1,1,2-trichloropropene-1. This transformation was interpreted as the result of a homolytic rearrangement (^{1}).

In the present work, the ability of 2-bromo-3,3-dichlorobutene-1 to isomerize was investigated; it was obtained according to the scheme

$$\mathrm{CH_3CCl_2{—}CH_2CH_2Br} \xrightarrow{\mathrm{KOH}} \mathrm{CH_3CCl_2CH = CH_2},$$

$$\mathrm{CH_3CCl_2{—}CH = CH_2} \xrightarrow[\mathrm{(CH_3COOH)}]{\mathrm{Br_2}} \mathrm{CH_3CCl_2CHBr{—}CH_2Br},$$

$$\mathrm{CH_3CCl_2{—}CBrH{—}CH_2Br} \xrightarrow{\mathrm{KOH}} \mathrm{CH_3CCl_2CBr = CH_2}.$$

On standing or upon irradiation with ultraviolet light, a sample of the compound $\mathrm{CH_3CCl_2CBr = CH_2}$ isomerizes to $\mathrm{CH_3CCl = CCl{—}CH_2Br}$, which with thiourea forms a bromine-free derivative isolated in the form of a picrate. This isomerization may be described by scheme (A), entirely analogous to the rearrangement scheme for 2-bromo-3,3,3-trichloropropene (^{1}):

$$\mathrm{CH_3CCl_2{—}CBr = CH_2} \xrightarrow{\mathrm{Br}} \mathrm{CH_3CCl_2{—}\dot{C}Br{—}CH_2Br},$$

$$\mathrm{CH_3CCl_2\dot{C}Br{—}CH_2Br} \xrightarrow{\text{rearrangement}} \mathrm{CH_3\dot{C}Cl{—}CClBr{—}CH_2Br}, \quad \text{(A)}$$

$$\mathrm{CH_3\dot{C}Cl{—}CClBr{—}CH_2Br} \rightarrow \mathrm{CH_3CCl = CCl{—}CH_2Br + Br} \text{ etc.}$$

Addition of hydroquinone prevents this isomerization. Under the action of $SbCl_5$, $CH_3CCl_2CBr = CH_2$ undergoes an anionotropic allylic rearrangement according to the scheme

$$CH_3CCl_2CBr = CH_2 \xrightarrow{SbCl_5} CH_3CCl = CBr—CH_2Cl.$$

2-Bromo-1,3-dichlorobutene-2 was isolated in the form of the picrate of an isothiuronium derivative.

The structure of $CH_3CCl_2CBr = CH_2$ was confirmed by obtaining the dimethylamine derivative $CH_3CCl = CBr—CH_2N(CH_3)_2$, identified in the form of its picrate. The same amine $CH_3CCl = CBr—CH_2N(CH_3)_2$ was obtained by two routes: by the interaction of an excess of dimethylamine with 1,2-dibromo-3,3-dichlorobutane according to the scheme

$$CH_3CCl_2CHBr—CH_2Br \rightarrow CH_3CCl = CBr—CH_2N(CH_3)_2$$

and by the interaction of 2,3-dibromo-1,3-dichlorobutane, obtained by bromination of $CH_3CCl = CH—CH_2Cl$, with dimethylamine.

Next, the interaction of hydrogen bromide with $CH_3CCl_2CBr = CH_2$ in the presence of benzoyl peroxide was studied. As the sole reaction product, in 90% yield, a mixture of isomers of structure was obtained

$CH_3CCl{=}CCl{-}CH_2Br$. The indicated reaction probably proceeds according to a scheme analogous to (A). In the present case hydrogen bromide is the source of bromine atoms initiating the process of homolytic isomerization.

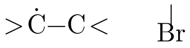
From a mixture of $CH_3CCl{=}CCl{-}CH_2Br$, by reaction with dimethylamine, the amines $CH_3CCl{=}CCl{-}CH_2N(CH_3)_2$ were obtained, isolated as picrates, which contain no bromine; this confirms the indicated structure of the dichlorobromobutene. In all the reactions cited above, in which unsaturated compounds of the structure $CH_3CCl{=}CX{-}CH_2Y$ are formed, where $X = Cl$ or Br, $Y = Br$ or $N(CH_3)_2$, the appearance of cis-trans isomers was noted. However, in the present work the stereochemistry of these reactions was not studied in detail.

Thus, substances of the structure $XCCl_2{-}CBr{=}CH_2$, where $X{-}Cl$ (1), CH_3, under the influence of radical agents undergo homolytic isomerization to $XCCl{=}CCl{-}CH_2Br$, accompanied by 1,2-migration of chlorine in the radicals formed as intermediates:

$$XCCl_2{-}\dot{C}Br{-}CH_2Br \rightarrow X\dot{C}Cl{-}CClBr{-}CH_2Br.$$

1 2

Radicals of structure 2 are stabilized with formation of the unsaturated $XCCl{=}CCl{-}CH_2Br$, which, apparently, is associated with the ease of elimination of a Br atom from a system of the type



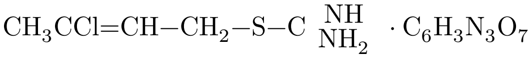
$$>\dot{C}{-}\underset{Br}{C}<$$

Experimental Part

1. Preparation of 3,3-dichlorobutene-1. 135 g of 1-bromo-3,3-dichlorobutane was dehydrobrominated with 45.9 g of KOH in ethyl cellosolve with stirring at 0°. After the usual work-up, distillation on a column gave 35.5 g of 3,3-dichlorobutene-1 (43% of theory); b.p. 45° at 105 mm; n_D^{20} 1.4460; d_4^{20} 1.1043; found MR 30.16, calculated 29.94.

Found %: C 38.25; 38.44; H 4.96; 4.76
$C_4H_6Cl_2$. Calculated %: C 38.43; H 4.84

On heating with thiourea for several minutes in alcoholic solution, the thiourea derivative was isolated as the picrate



$$CH_3CCl{=}CH{-}CH_2{-}S{-}C\begin{matrix}NH\\NH_2\end{matrix}\cdot C_6H_3N_3O_7$$

with m.p. 168.5-170° (from alcohol).

Found %: C 33.33; 33.56; H 3.19; 3.14; N 17.74; 17.60
$C_{11}H_{12}ClN_5O_7S$. Calculated %: C 33.55; H 3.07; N 17.78

A mixed sample with the picrate of the isothiourea derivative obtained from $CH_3CCl{=}CH{-}CH_2Cl$ gave no depression of the melting point.

2. Bromination of 3,3-dichlorobutene-1. To 90 g of $CH_3CCl_2CH{=}CH_2$ in 100 ml of glacial acetic acid, 34.2 ml of bromine was added dropwise. After the usual work-up, 1,2-dibromo-3,3-dichlorobutane was distilled on a column in the range 79-80° at 4 mm, weight 158 g (77% of theory); n_D^{20} 1.5435; d_4^{20} 1.9810; found MR 45.35, calculated 45.94.

Found %: C 16.77; 17.00; H 2.08; 2.18
$C_4H_6Br_2Cl_2$. Calculated %: C 16.52; H 2.12

On treatment with an excess of dimethylamine, an unsaturated amine, $CH_3CCl = CBr{-}CH_2N(CH_3)_2$, was obtained, distilling in the range 82-87° at 20 mm, n_D^{20} 1.4996-1.5006. Picrates with m.p. 153-154° (from alcohol) were isolated. Found %: N 12.62; 12.68. Found m.p. 160-161°.

Found %: N 12.62; 12.82

$C_{12}H_{14}BrClN_4O_7$. Calculated %: N 12.68 (cf. experiment 4)

3. **Preparation of 2-bromo-3,3-dichlorobutene-1 and its properties.** 127 g of 1,2-dibromo-3,3-dichlorobutane was dehydrobrominated with 34.2 g of KOH in ethylene glycol, analogously to experiment 1. Distillation through a column gave 58 g (59% of theory) of 2-bromo-3,3-dichlorobutene-1 with b.p. 61–62° at 25 mm; n_D^{20} 1.5120; d_4^{20} 1.6363; found MR 37.88, calculated 37.70.

Found %: C 24.00; 23.82; H 2.53; 2.44

$C_4H_5BrCl_2$. Calculated %: C 23.56; H 2.47

On standing without the addition of hydroquinone, the substance becomes tear-producing, n_D^{20} 1.5300; with hydroquinone it does not isomerize. 2-Bromo-3,3-dichlorobutene-1, previously distilled (n_D^{20} 1.5130), was subjected to UV irradiation. After 10 min n_D^{20} 1.5280; after another 20 min n_D^{20} 1.5320. The substance was distilled in the range 77–80° at 25 mm; n_D^{20} 1.5340; d_4^{20} 1.6674; found MR 38.01, calculated 37.70.

The picrate of the isothiourea derivative melted at 194.5–195° (from alcohol).

Found %: C 30.47; 30.73; H 2.55; 2.77; N 16.54; 16.54

$C_{11}H_{11}Cl_2N_5O_7S$. Calculated %: C 30.85; H 2.59; N 16.35

On treatment of 2-bromo-3,3-dichlorobutene-1 with $SbCl_5$, an isomer was obtained which distilled in the range 75–80° at 24 mm; n_D^{20} 1.5380, from which, by reaction with thiourea, the isothiourea derivative was obtained as the picrate with m.p. 185° with decomposition (from alcohol).

Found %: C 28.44; 28.55; H 2.33; 2.52

$C_{11}H_{11}ClBrN_5O_7S$. Calculated %: C 27.95; H 2.35

4. **Reaction of 2-bromo-3,3-dichlorobutene-1 with dimethylamine.** a) A solution of 7.9 g of 2-bromo-3,3-dichlorobutene-1, obtained as described in experiment 3, in 20 ml of alcohol was heated in a sealed ampoule with an excess of dimethylamine for several hours at 100°. After the usual workup, dimethyl-2-bromo-3-chlorobuten-2-ylamine was distilled at 81–83° at 20 mm, 5.6 g (68% of theory); n_D^{20} 1.4994; d_4^{20} 1.3507; found MR 46.23, calculated 46.01. Picrate m.p. 153–154° (from alcohol).

Found %: C 32.60; 32.84; H 3.13; 3.19; N 12.81; 13.00

$C_{12}H_{14}BrClN_4O_7$. Calculated %: C 32.66; H 3.19; N 12.68

A mixed sample of this picrate with a sample of the corresponding compound from experiment 2 showed no depression of the melting point.

b) The picrate of an amine of structure $CH_3CCl = CBr{-}CH_2N(CH_3)_2$, stereoisomeric with that described above, was obtained by reaction of an excess of dimethylamine with 1,3-dichloro-2,3-dibromobutane, which in turn had been obtained by bromination of 1,3-dichlorobutene-2. Constants of $CH_3CClBr{-}CHBr{-}CH_2Cl$: b.p. 88° at 8 mm; n_D^{20} 1.5502; d_4^{20} 1.9910; found MR 45.59, calculated 45.94.

Found %: C 16.98; 16.90; H 2.03; 2.01; Cl 25.08; Br 55.76
$C_4H_6Br_2Cl_2$. Calculated %: C 16.52; H 2.12; Cl 24.89; Br 56.11

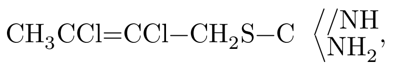
The amine obtained was distilled at 58-60° at 4 mm; n_D^{20} 1.5030; m.p. of the picrate 166-167° (from alcohol).

Found, %: C 32.66; 32.68; H 3.11; 3.18; N 13.08; 13.07
$C_{12}H_{14}BrClN_4O_7$. Calculated, %: C 32.63; H 3.19; N 12.68

Reaction of HBr with $CH_3CCl_2CBr{=}CH_2$ in the presence of benzoyl peroxide. A solution of 36.5 g of 2-bromo-3,3-dichlorobutene-1 and 0.5 g of benzoyl peroxide in 112 g of carbon tetrachloride was saturated with hydrogen bromide for 30 min. The reaction product was washed with soda solution and with water, and dried over $CaCl_2$. After removal of the solvent and distillation on a column, 31.4 g (90% of theory) of 1-bromo-2,3-dichlorobutene-2 (a mixture of cis-trans isomers) was obtained, with b.p. 64-70° at 15 mm; n_D^{20} 1.5310-1.5323; d_4^{20} 1.6519-1.6775; found MR 38.20-37.88, calculated 37.70.

Found, %: C 23.60; 23.76; H 2.32; 2.42
$C_4H_5BrCl_2$. Calculated, %: C 23.56; H 2.47

By reaction with thiourea there was obtained



$$CH_3CCl{=}CCl{-}CH_2S{-}C\left\langle\begin{matrix}/\!\!/NH\\ NH_2\end{matrix}\right.,$$

isolated in the form of the picrate with m.p. 197° (from alcohol).

Found, %: N 16.56; 16.50; Cl 16.48; 16.33
$C_{11}H_{11}Cl_2N_5O_7S$. Calculated, %: N 16.35; Cl 16.56

On treating a mixture of 1-bromo-2,3-dichlorobutene-2 with dimethylamine in alcohol, a mixture of stereoisomeric amines of structure $CH_3CCl{=}CCl{-}CH_2N(CH_3)_2$

was obtained in good yield; from this a fraction was isolated with b.p. 65-68° at 20 mm; n_D^{20} 1.4720; m.p. of the picrate 144-145° (from alcohol).

Found, %: C 36.25; 36.25; H 3.30; 3.37; N 14.39; 14.29, and a fraction with b.p. 75-77° at 20 mm; n_D^{20} 1.4750; m.p. of the picrate 160-161° (from alcohol).

Found, %:	C 35.90; 35.89;	H 3.68; 3.54;	N 14.17; 14.19
$C_{12}H_{14}Cl_2N_4O_7$. Calculated, %:	C 36.28;	H 3.55;	N 14.11

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Received
10 XI 1960

CITED LITERATURE

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