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Abstract

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HOMOLYTIC ISOMERIZATION OF 1,1,1-TRICHLORO-2-BROMOPROPENE

Until recently the question of the possibility of rearrangement of free radicals in solutions was controversial (cf., for example, ([1–3])). By the present time a number of rearrangements in radicals due to aryl migration have been described in detail ([4–10]).

In work by two of the authors of the present article and L. I. Zakharkin ([11]), a rearrangement was found in a radical of the structure $CCl_3\dot{C}HCH_2X$ due to chlorine migration according to the scheme:

$$CCl_3\dot{C}HCH_2X \rightarrow \dot{C}Cl_2CHClCH_2X, \text{ where } X = Br,\ CCl_3 \qquad (1)$$

The indicated rearrangement occurred in the homolytic addition of hydrogen bromide or bromotrichloromethane to 1,1,1-trichloropropene.

In the present article we report on the homolytic isomerization of 1,1,1-trichloro-3-bromopropene into 1,1,2-trichloro-3-bromopropene-1 according to the scheme:

$$CCl_3CBr = CH_2 \rightarrow CCl_2 = CCl - CH_2Br \qquad (2)$$

1,1,1-Trichloro-2-bromopropene has the following constants: b.p. 57—58°/15 mm, n_D^{20} 1.5323, d_4^{20} 1.8493.

On standing, after a certain induction period (for 1-2 days), or upon illumination with a mercury lamp for several minutes without heating, a sample of this compound is completely isomerized into 1,1,2-trichloro-3-bromopropene-1 with b.p. 78—79°/19 mm, n_D^{20} 1.5550, d_4^{20} 1.8835. This isomerization is conveniently followed by the change in the refractive index. Addition of hydroquinone or dimethylaniline to 1,1,1-trichloro-2-bromopropene prevents isomerization, and samples containing an inhibitor were stored without change for more than a month.

We suppose that the isomerization proceeds according to the following scheme:

a) $C_3H_2Cl_3Br \rightarrow Br^{\cdot} + C_3H_2Cl_3^{\cdot}$

b) $CCl_3CBr = CH_2 + Br^{\cdot} \rightarrow CCl_3\dot{C}BrCH_2Br$

c) $CCl_3\dot{C}Br - CH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CClBrCH_2Br$

d) $\dot{C}Cl_2CClBrCH_2Br + CCl_3CBr = CH_2 \rightarrow CCl_2 = CClCH_2Br + CCl_3\dot{C}BrCH_2Br$ (3)

Thus, here, apparently, a rearrangement in the radical takes place, quite analogous to the rearrangement already mentioned (cf. schemes (1) and (3c)).

The case of homolytic isomerization of $CCl_3CBr = CH_2$ found by us is interesting in that this isomerization differs in direction from the anionotropic allylic rearrangement of the same compound. We have shown that 1,1,1-trichloro-2-bromopropene undergoes allylic rearrangement

under the action of antimony pentachloride or aluminum chloride, with formation, in 90% yield, of 1,1,3-trichloro-2-bromopropene-1, b.p. 81-82°/21 mm, n_D^{20} 1.5522, d_4^{20} 1.8954. The two rearrangements are compared in the scheme:

$$CCl_3{-}CBr{=}CH_2 \begin{array}{l} \xrightarrow{h\nu} CCl_2{=}CCl{-}CH_2Br \\ \xrightarrow[SbCl_5]{} CCl_2{=}CBr{-}CH_2Cl \end{array} \quad (4)$$

The methods of preparation of the compounds studied and the evidence for their structures may be summarized briefly as follows.

The starting material for the preparation of 1,1,1-trichloro-2-bromopropene was 1,1,1-trichloro-2,3-dibromopropane, obtained by the action of bromine on 1,1,1-trichloropropene in acetic acid without illumination, in a yield of 80% of theory.

When 1,1,1-trichloro-2,3-dibromopropane was treated with caustic potash in ethyl cellosolve with cooling, the sole reaction product obtained was 1,1,1-trichloro-2-bromopropene (yield 71% of theory), according to the scheme:

$$\underset{(I)}{CCl_3CHBrCH_2Br} \xrightarrow{KOH} \underset{(II)}{CCl_3CBr{=}CH_2} \quad (5)$$

The allylic isomer of this compound—1,1,3-trichloro-2-bromopropene-1—was obtained according to the scheme:

$$CCl_2{=}CHCH_2Cl + Br_2 \rightarrow \underset{(III)}{CCl_2BrCHBrCH_2Cl} \xrightarrow{KOH} \underset{(IV)}{CCl_2{=}CBrCH_2Cl} \quad (6)$$

The structure of substance III was confirmed by hydrolysis with nitric acid (sp. gr. 1.52), giving, in good yield, α-bromo-β-chloropropionic acid; the latter, under the action of alcoholic alkali, gave α-bromoacrylic acid.

The isomerization of substance II into substance IV under the action of $SbCl_5$ (scheme (4)) confirms structure II, since the reverse isomerization of substances of type IV into substances of type II is unknown.

1,1,2-Trichloro-3-bromopropene-1, the product of the homolytic isomerization of substance II (scheme (2)), was synthesized by an independent route according to the scheme:

$$CCl_2{=}CClCH_2Cl \xrightarrow[(CH_3)_2CO]{NaBr} \underset{(V)}{CCl_2{=}CClCH_2Br} \tag{7}$$

All three trichlorobromopropenes II, IV, and V, obtained both by isomerization according to scheme (4) and by independent routes according to schemes (6) and (7), were identified as the solid hydrochlorides of their diethylamino derivatives, obtained according to schemes (8) and (9), with yields above 80% of theory.

$$\begin{aligned} &\underset{(II)}{CCl_3CBr{=}CH_2} + (C_2H_5)_2NH \rightarrow \underset{(VI)}{CCl_2{=}CBrCH_2N(C_2H_5)_2}\cdot HCl \uparrow \\ &\underset{(IV)}{CCl_2{=}CBrCH_2Cl} + (C_2H_5)_2NH \end{aligned} \tag{8}$$

$$\underset{(V)}{CCl_2{=}CCl{-}CH_2Br} + 2\,(C_2H_5)_2NH \rightarrow CCl_2{=}CClCH_2N(C_2H_5)_2 \xrightarrow{HCl} \underset{(VII)}{CCl_2{=}CClCH_2N(C_2H_5)_2}\cdot HCl \tag{9}$$

Hydrochloride (VII) showed no depression of the melting point in a mixed sample with an authentic specimen obtained earlier ([12]).

Among other observations made in the course of this work, the following should be noted.

Upon treatment of 1,1,3-trichloro-1,2-dibromopropane with a solution of potassium hydroxide in ethyl cellosolve under cooling, after the usual work-up, a mixture of products was obtained, from which, by distillation on a column in vacuo, the already mentioned (scheme (6)) 1,1,3-trichloro-2-bromopropene-1 (IV) was isolated, b.p. 81–82°/21 mm; n_D^{20} 1.5522; d_4^{20} 1.8955, identical in all properties with the substance obtained by allylic isomerization of 1,1,1-trichloro-2-bromopropene, and a dibromide of composition $C_3H_2Cl_2Br_2$. This dibromide, on reaction with diethylamine in methanol, gave a diethylamino derivative identical with the previously described 1,1-dichloro-2-bromo-3-diethylaminopropene-1. The formation of this diethylamino derivative indicates that the dibromide may have the structure $CCl_2Br{-}CBr = CH_2$ or $CCl_2 = CBrCH_2Br$.

1,1,1-Trichloro-2-bromopropene (II) and its allylic isomer IV, obtained both by isomerization and according to scheme (6), in reaction with benzene in the presence of $AlCl_3$, give in good yield one and the same compound of the structure

$$C_6H_5CH_2CBr = CCl_2.$$

It should also be noted that when the reaction between 1,1,1-trichloropropene and bromine is carried out in chloroform under illumination with an incandescent lamp (150 W), 1,1,1-trichloro-2,3-dibromopropane is formed, contaminated with an admixture of an isomeric dibromotrichloropropane (cf. with ([13])).

The latter compound could not be isolated in pure form. Judging from the fact that, on heating this mixture with nitric acid (sp. gr. 1.52), α-chloro-β-bromopropionic acid was isolated in approximately 20% yield,

Table 1

Formula	B.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	C, %, found	C, %, calc.	H, %, found	H, %, calc.
$CCl_3CHBrCH_2Cl$	69/2	1.5630	2.1751	45.58	46.18	11.60	11.80	0.98	0.99
$CCl_2BrCHBrCH_2Cl$	66–67/1	1.5678	2.1874	45.64	46.18	11.71	11.80	0.96	0.99
$CCl_3CBr_2-CH_3$	57–58/15	1.5323	1.8493	37.52	37.95	15.82	16.06	0.88	0.89
$CCl_2 = CBr-CH_2Cl$	81–82/21	1.5521	1.8955	37.83	37.95	16.00	16.06	0.77	0.89
$CCl_2 = CBr-CH_2Cl$	78–79/19	1.5550	1.8835	38.23	37.95	15.80	16.06	0.85	0.82
$CCl_2 = CBrCH_2N(C_2H_5)_2$	69/1	1.5070	1.4060	55.33	55.50	32.35	32.21	4.78	4.63
$CCl_2 = CBrCH_2N(C_2H_5)_2 \cdot HCl$						32.39	32.21	4.81	4.63
$CCl_2 = CBrCH_2N(C_2H_5)_2 \cdot HCl$						28.64	28.26	4.65	4.58
$CCl_2 = CBrCH_2N(C_2H_5)_2 \cdot HCl$						28.58	28.26	4.45	4.58
$C_6H_5CH_2CBr = CCl_2$	97–98/2	1.5841	1.5566	57.19	57.19	40.80	40.64	2.56	2.65
$C_6H_5CH_2CBr = CCl_2$						40.93	40.64	2.64	2.65
$C_3H_2Cl_2Br_2$	97–98/21	1.5845	2.1957	41.00	40.85	13.28	13.40	0.73	0.75
$C_3H_2Cl_2Br_2$						13.49	13.40	0.75	0.75

* Found %: N 5.43; 5.26. Calculated %: N 5.36.
** M.p. 144-145°.
*** Obtained by the action of potassium hydroxide on $CCl_2BrCHBrCH_2Cl$.

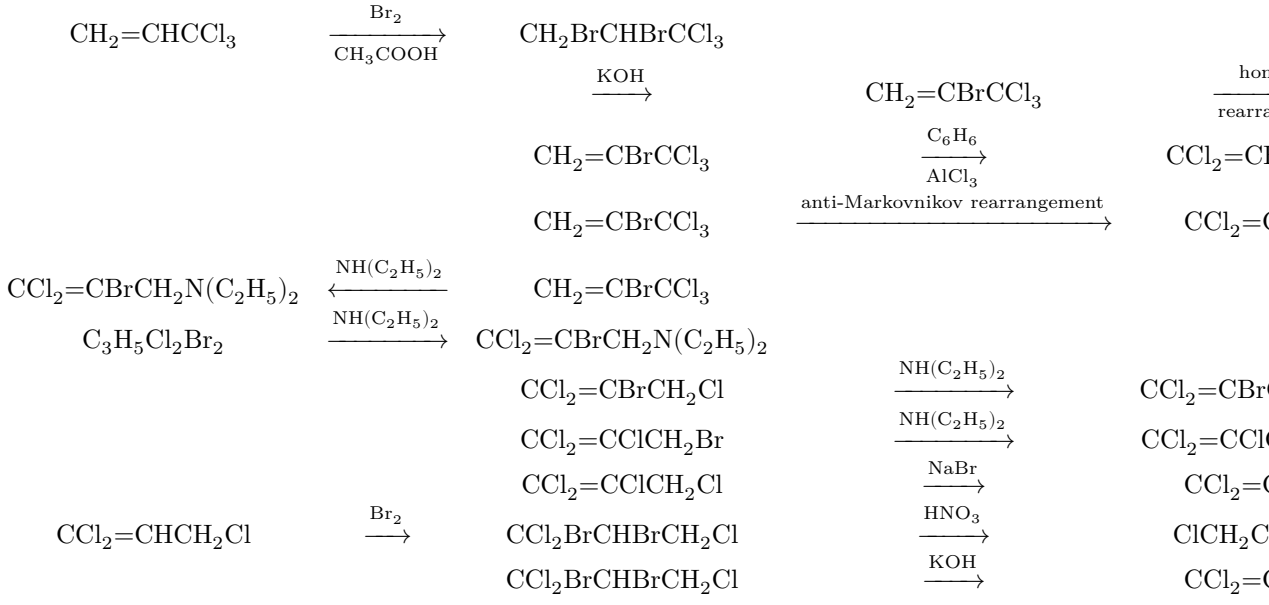
it may be assumed that the mixture contains, as an impurity, 1,1,2-trichloro-1,3-dibromopropane (pure 1,1,1-trichloro-2,3-dibromopropane, on heating with

nitric acid (sp. gr. 1.52), gives only neutral nitrogen-containing products). This conclusion is in agreement with the fact that, on treatment of a mixture of dibromotrichloropropanes with potassium hydroxide, a mixture of bromotrichloropropenes was obtained, which could be separated in the form of diethylamino derivatives of the structures

$$CCl_2 = CBrCH_2N(C_2H_5)_2 \quad \text{and} \quad CCl_2 = CClCH_2N(C_2H_5)_2.$$

The formation of 1,1,2-trichloro-1,3-dibromopropane can be explained by the fact that, under the described conditions, in contrast to the reaction in acetic acid without illumination, bromination also proceeds by a homolytic mechanism, accompanied by rearrangement in the radical according to the scheme:

$$\begin{gathered} CCl_3\text{—}CH = CH_2 + Br \rightarrow CCl_3\dot{C}HCH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CHClCH_2Br \\ \dot{C}Cl_2CHClCH_2Br + Br_2 \rightarrow BrCCl_2CHClCH_2Br + \dot{B}r \end{gathered} \tag{10}$$



The reactions carried out in the present work are shown in the scheme.* Some constants and analyses of the compounds obtained are collected in Table 1.

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* The amines obtained by different routes were identified through their chlorohydrates.

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