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

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The question of the possibility of rearrangement of free radicals in solution remained debatable until recently (see for example [1-3]). A number of such rearrangements have been firmly established at this time. Several cases of rearrangement in radicals, through migration of the aryl group, are known to follow the scheme (1) [4-9]:

\[
R' \\
\text{XCH}_2\text{H}_2\text{C} - \text{CH}_2 \rightarrow \text{iR'C} - \text{CH}_2\text{C}_2\text{H}_4\text{X}, \text{ where } R, R' = \text{alkyl, aryl}; X = \text{H, alkyl.} \tag{1}
\]

Two of the authors of the present paper and Zalharkin [10] found a rearrangement in a radical through migration of chlorine by scheme (2):

\[
\text{CCl}_3 - \text{CH} - \text{CH}_2\text{Y} \rightarrow \text{CCl}_2\text{CHClCH}_2\text{Y}, \text{ where } Y = \text{Br, CCl}_3 \tag{2}
\]

This rearrangement was observed during the study of the addition reaction of bromotrichloromethane or hydrogen bromide to 1,1,1-trichloropropene in the presence of benzoyl peroxide.

Contradictory data are found in the literature concerning the possibility of rearrangement in radicals through migration of a methyl group. It was shown in a number of papers [9, 11, 12] that the neopentyl radical does not isomerize. Kharasch and co-workers [13] consider that they did observe a rearrangement of this type in bromination of 2,2,4,4-tetramethylpentane at 200° according to scheme (3):

\[
(\text{CH}_3)\text{C} - \text{CH} - \text{C} (\text{CH}_3)\text{H} \rightarrow (\text{CH}_3)\text{C} - \text{CH} - \text{C} (\text{CH}_3)\text{H}. \tag{3}
\]

It was shown in several ways [14-17] that rearrangements in radicals through migration of hydrogen from a neighboring carbon atom are impossible; rearrangements through migration of a hydrogen from more remote carbon atoms do take place [14]. A rearrangement occurs during decarbonylation [18] of 5-methyl-5-phenyl-hexanal, this being represented by the authors by scheme (4):
As far as it is known to us, not a single case of homolytic transformation of any substance into an isomeric substance has been studied, i.e., a case of a homolytic isomerization is unknown.

In the present paper we report a homolytic isomerization of 1,1,1-trichloro-2-bromopropene into 1,1,2-trichloro-3-bromo-1-propene according to the scheme (5):

\[
\begin{align*}
\text{CCl}_3\text{CBr} &= \text{CH}_2 \rightarrow \text{CCl}_2 = \text{Cl} \rightarrow \text{CH}_2\text{Br}. \\
(\text{I}) & \quad (\text{II})
\end{align*}
\]

A sample of this compound on standing after a certain induction period (over 1-2 days) or under illumination with a mercury lamp for a few minutes, without heating, isomerizes completely into 1,1,2-trichloro-3-bromo-1-propene. Addition of hydroquinone or dimethylaniline to 1,1,1-trichloro-2-bromopropene hinders the isomerization and samples containing the inhibitors were kept for over a month without change.

We suppose that the isomerization proceeds by the following scheme:

a) \( \text{CCl}_3\text{CBr} = \text{CH}_2 \rightarrow \text{Br} + \text{C}_3\text{H}_2\text{Cl}_2 \)
b) \( \text{CCl}_3\text{CBr} = \text{CH}_2 + \text{Br} \rightarrow \text{CCl}_3\text{BrCH}_2\text{Br} \)
c) \( \text{CCl}_3\text{CBr} \rightarrow \text{CH}_2\text{Br} \) rearrangement \( \rightarrow \text{CCl}_3\text{CBrCH}_2\text{Br} \)
d) \( \text{CCl}_3\text{CBrCH}_2\text{Br} + \text{CCl}_3\text{CBr} \rightarrow \text{CCl}_3\text{CH}_2\text{Br} + \text{CCl}_3\text{CBrCH}_2\text{Br} \).

The case of homolytic isomerization of \( \text{CCl}_3\text{CBr} = \text{CH}_2 \) discovered by us is interesting in that this isomerization differs in direction from the anionotropic allylic rearrangement of the same compound. We showed that 1,1,1-trichloro-2-bromopropene undergoes the allylic rearrangement under the influence of antimony pentachloride or aluminum chloride, forming 1,1,3-trichloro-2-bromo-1-propene. Both rearrangements are compared in scheme (7):

\[
\begin{align*}
\text{CCl}_3\text{CBr} = \text{CH}_2 & \rightarrow \text{CCl}_2 = \text{Cl} \rightarrow \text{CH}_2\text{Br} \\
(\text{I}) & \rightarrow \text{CCl}_2 = \text{Br} \rightarrow \text{CH}_2\text{Cl} \\
(\text{III}) & \rightarrow \text{CCl}_2 = \text{Cl} \rightarrow \text{CH}_2\text{Br}
\end{align*}
\]

The methods of preparation of the substances under examination and the proof of their structure may be summarized as follows. The starting material for preparation of 1,1,1-trichloro-2-bromopropene was 1,1,1-trichloro-2,3-dibromopropane, formed by the action of bromine on 1,1,1-trichloropropene in acetic acid medium without illumination. 1,1,1-Trichloro-2-bromopropene was obtained by the action of potassium hydroxide in the Ethyl Cellosolve medium on 1,1,1-trichloro-2,3-dibromopropane, with cooling, with the above being the sole reaction product formed by the scheme:

\[
\begin{align*}
\text{CCl}_3\text{CBrCH}_2\text{Br} \rightarrow \text{KOH} \rightarrow \text{CCl}_3\text{CBr} = \text{CH}_2.
\end{align*}
\]

The allylic isomer of this compound - 1,1,3-trichloro-2-bromo-1-propene, was formed by scheme (9):

\[
\begin{align*}
\text{CCl}_2 = \text{CHCH}_2\text{Cl} + \text{Br}_2 & \rightarrow \text{CCl}_2\text{BrCHBrCH}_2\text{Cl} \rightarrow \text{KOH} \rightarrow \text{CCl}_2 = \text{BrCH}_2\text{Cl}. \\
(\text{IV}) & \rightarrow \text{CCl}_2 = \text{BrCH}_2\text{Cl}.
\end{align*}
\]

The structure of substance (IV) was confirmed by hydrolysis with nitric acid (s. g. 1.52) with formation of \( \alpha \)-bromo-\( \beta \)-chloropropionic acid in good yield. The latter yielded \( \alpha \)-bromoacrylic acid under the influence of alcoholic alkali. See [19] about the action of concentrated nitric acid on polychloroalkanes. Isomerization