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HOMOLYTIC ISOMERISATION OF 1,1,1-TRICHLORO-2-BROMOPROPENE*

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Abstract—(1) 1,1,1-trichloro-2-bromopropene has been shown to isomerise homolytically when exposed to ultra-violet light to form 1,1,2-trichloro-3-bromopropene and heterolytically under the action of antimony pentachloride to yield 1,1,3-trichloro-2-bromopropene.

(2) The bromination of 1,1,1-trichloropropene has been investigated under various conditions. It has been found, that the reaction runs unambiguously to give a normal addition product of 1,1,1-trichloro-2,3-dibromopropene only in strongly polarised media. When the reaction is being carried out in non-polarised media or in the presence of benzoyl peroxide, 1,1,2-trichloro-1,3-dibromopropane is obtained together with 1,1,1-trichloro-2,3-dibromopropane, the former being due to the homolytic isomerisation of the intermediate radical.

UNTIL recently the question whether free radicals can rearrange in solutions was subject to controversy.[1,2,3] At present a number of such rearrangements has been unambiguously proved, several cases of rearrangement by the migration of phenyl (or tolyl) according to scheme 1 being known:[4–8]

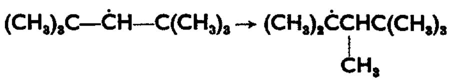
$$C_6H_5CR_2\dot{C}H_2 \rightarrow R_2\dot{C}{-}CH_2C_6H_5 \quad \text{where} \quad R = \text{alkyl, aryl} \qquad (1)$$

Two of the present authors and Zakharkin[9] have discovered a rearrangement in the radical by the migration of chlorine, scheme 2:

$$CCl_3\dot{C}HCH_2X \rightarrow \dot{C}Cl_2CHClCH_2X \quad \text{where} \quad X = Br,\ CCl_3 \qquad (2)$$

This rearrangement has been observed when investigating the reaction of bromotrichloromethane or hydrogen bromide addition to 1,1,1-trichloropropene in the presence of benzoyl peroxide.

In the literature there are contradictory statements about the possibility of rearrangements in radicals due to the migration of the methyl group. Some authors[8,10,11] have found that the neopentyl radical does not undergo isomerisation. Kharasch *et al.*[12] are of the opinion that they did observe this type of rearrangement when brominating 2,2,4,4-tetramethylpentane, at 200°, according to scheme 3:



$$(CH_3)_3C{-}\dot{C}H{-}C(CH_3)_3 \rightarrow (CH_3)_2\dot{C}\underset{\displaystyle CH_3}{\underset{|}{C}}HC(CH_3)_3 \qquad (3)$$

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*Translated by A. L. PUMPIANSKY, Moscow.

[1] H. Clazebrook and T. Pearson *J. Chem. Soc.* 1777 (1936).

[2] M. Kharasch, S. Kane, and H. Brown *J. Amer. Chem. Soc.* **63**, 526 (1941).

[3] M. Dewar *The Electronic Theory of Org. Chem.* p. 263. Oxford (1950).

[4] W. Urry and M. Kharasch *J. Amer. Chem. Soc.* **66**, 1438 (1944).

[5] S. Winstein and F. Seubold *J. Amer. Chem. Soc.* **69**, 2916 (1947).

[6] F. Seubold *J. Amer. Chem. Soc.* **75**, 2532 (1953).

[7] D. Curtin and M. Hurwitz *J. Amer. Chem. Soc.* **74**, 5381 (1952).

[8] W. Urry and N. Nicolaides *J. Amer. Chem. Soc.* **74**, 5163 (1952).

[9] A. N. Nesmeyanov, R. Kh. Freidlina, and L. J. Zakharkin *Dokl. Akad. Nauk SSSR* **81**, 199 (1951); *Quart. Rev.* **10**, No. 3, 330 (1956).

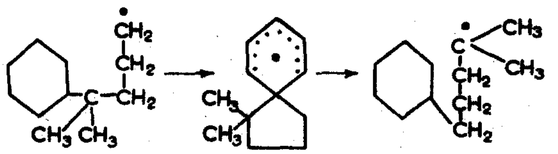
[10] F. Whitmore, A. Popkin, H. Bernstein, and J. Wilkins *J. Amer. Chem. Soc.* **63**, 124 (1941).

[11] E. Reid and R. Fortenbaugh *J. Org. Chem.* **16**, 33 (1951).

[12] M. Kharasch, Yu Cheng Lin, and W. Nudenberg *J. Org. Chem.* **19**, 1150 (1954).

Using different procedures,[13-16] it has been shown, that rearrangements in radicals by the migration of hydrogen from the adjacent carbon atom are impossible, whilst those due to the migration of hydrogen from carbon atoms situated at a great distance appear to take place.[13]

Decarbonylation of 5-methyl-5-phenyl hexanal results in a rearrangement,[17] which is represented by scheme 4:



(4)

As far as we know, there have up to now been no detailed reports on the homolytic conversion of any compound into an isomeric one, that is on homolytic isomerisation.

We are now reporting on the homolytic isomerisation of 1,1,1-trichloro-2-bromopropene into 1,1,2-trichloro-3-bromopropene-1, according to scheme 5:

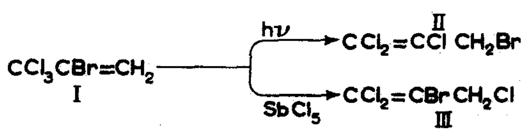
$$\underset{\text{I}}{CCl_3CBr{=}CH_2} \rightarrow \underset{\text{II}}{CCl_2{=}CCl{-}CH_2Br} \qquad (5)$$

When a sample of this compound is allowed to stand, it isomerises fully into 1,1,2-trichloro-3-bromopropene-1 after an induction period (1 or 2 days) or when exposed to ultra-violet light for several minutes, without heating. Addition of hydroquinone or dimethylaniline to 1,1,1-trichloro-2-bromopropene inhibits isomerisation, samples containing the inhibitor undergoing no change for over a month.

The isomerisation must have proceeded along the following scheme:

$$\begin{aligned}
&\text{a. } CCl_3CBr{=}CH_2 \rightarrow C_3H_2Cl_3^{\cdot} + Br \\
&\text{b. } CCl_3CBr{=}CH_2 + Br \rightarrow CCl_3\dot{C}BrCH_2Br \\
&\text{c. } CCl_3\dot{C}Br{-}CH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CBrClCH_2Br \\
&\text{d. } \dot{C}Cl_2CClBrCH_2Br + CCl_3CBr{=}CH_2 \rightarrow CCl_2{=}CClCH_2Br + CCl_3\dot{C}BrCH_2Br
\end{aligned} \qquad (6)$$

The homolytic isomerisation of $CCl_3C\ Br{=}CH_2$, is of interest in that its direction differs from that of the anionotropic allylic rearrangement of the same compound. We have shown 1,1,1-trichloro-2-bromopropene to undergo allylic rearrangement under the action of antimony pentachloride or aluminium chloride to form 1,1,3-trichloro-2-bromopropene-1. The two rearrangements are compared in scheme 7:



(7)

The procedures employed to obtain the substances under investigation and to prove their structures are, briefly, as follows.

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[13] R. E. Mardaleishvili Report at Lomonosov Readings, edited by Moscow State University (1953). D. N. Kursanov and V. V. Voyevodski *Uspekhi Khimii* **23**, No. 6, 641 (1954).

[14] H. Brown and G. Russel *J. Amer. Chem. Soc.* **74**, 3995 (1952).

[15] N. Kornblum and E. Olivels *J. Amer. Chem. Soc.* **71**, 226 (1949).

[16] N. Kornblum and H. De La Mare *J. Amer. Chem. Soc.* **72**, 3079 (1952).

[17] S. Winstein, R. Heck, S. Lapporte, and R. Baird *Experientia* **12**, 138 (1956).

As starting compound for 1,1,1-trichloro-2-bromopropene we used 1,1,1-trichloro-2,3-dibromopropane, obtained by the action of bromine on 1,1,1-trichloropropene in acetic acid medium in the dark.

1,1,1-trichloro-2,3-dibromopropane being acted upon by potassium hydroxide in ethylcellosolve gave 1,1,1-trichloro-2-bromopropene, as a sole product, according to the following scheme:

$$CCl_3CHBrCH_2Br \xrightarrow{KOH} CCl_3CBr{=}CH_2$$

The allylic isomer of this compound—1,1,3-trichloro-2-bromopropene-1 was obtained following scheme 8:

$$CCl_2{=}CHCH_2Cl + Br_2 \rightarrow \underset{IV}{CCl_2BrCHBrCH_2Cl} \xrightarrow{KOH} \underset{III}{CCl_2{=}CBrCH_2Cl} \qquad (8)$$

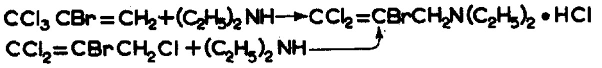
The structure of compound IV was ascertained by the hydrolysis with nitric acid (sp. gr. 1·52), which resulted in a high yield of α-bromo-β-chloropropionic acid, the latter yielding, when treated with alcoholic alkali, α-bromoacrylic acid.

The isomerisation of I into III under the action of $SbCl_5$ (scheme 7) suggests the structure of the former compound, for the reverse isomerisation of III into I is unknown.

1,1,2-Trichloro-3-bromopropene-1 resulting from the homolytic isomerisation of substance I (scheme 5) has been synthesised independently according to scheme 9:

$$CCl_2{=}CClCH_2Cl \xrightarrow[(CH_3)_2CO]{NaBr} CCl_2{=}CClCH_2Br \qquad (9)$$

The three trichlorobromopropenes I, II and III, produced by isomerisation according to scheme 7 as well as independently according to schemes 8 and 9, were identified as crystalline hydrochlorides of their diethylamine derivatives, obtained by schemes 10 and 11:



$$\begin{aligned} &CCl_3CBr{=}CH_2 + (C_2H_5)_2NH \rightarrow CCl_2{=}CBrCH_2N(C_2H_5)_2 \cdot HCl \\ &CCl_2{=}CBrCH_2Cl + (C_2H_5)_2NH \nearrow \end{aligned} \qquad (10)$$

$$CCl_2{=}CClCH_2Br + (C_2H_5)_2NH \rightarrow CCl_2{=}CClCH_2N(C_2H_5)_2 \xrightarrow{HCl} \underset{VI}{CCl_2{=}CClCH_2N(C_2H_5)_2.HCl} \qquad (11)$$

Hydrochloride VI did not reveal any depression of the melting point on mixing with the authentic sample, obtained previously.[18] 1,1,1-trichloro-2-bromopropene (I) and its allylic isomer (III), obtained by isomerisation as well as following scheme 8, reacting with benzene in the presence of aluminium chloride, yield the same compound $C_6H_5CH_2CBr{=}CCl_2$.

One is also to mention the following observations made in the course of this work.

Two of the present authors and V. I. Firstov[19] have reported on the bromination of 1,1,1-trichloropropene, and by analogy the trichlorodibromopropane formed has been assigned the structure of 1,1,1-trichloro-2,3-dibromopropane.

The rearrangement mentioned above having been discovered[9] (see scheme 2), we

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[18] R. Kh. Freidlina, V. N. Kost, and A. N. Nesmeyanov *Izv. Akad. Nauk SSSR. Otdel. khim. Nauk* 233 (1955).

[19] A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov *Izv. Akad. Nauk SSSR. Otdel. khim. Nauk* 505 (1951).

were led to suggest that depending on the reaction conditions, bromination of 1,1,1-trichloropropene could proceed both without rearrangement (electrophilic addition) and with rearrangement (homolytic addition).

$$CCl_3CH{=}CH_2 + Br \rightarrow CCl_3\dot{C}HCH_2Br \rightarrow \dot{C}Cl_2CHClCH_2Br$$

$$\dot{C}Cl_2CHClCH_2Br + Br_2 \rightarrow CCl_2BrCHClCH_2Br + Br$$

The elucidation of this point seemed to be of particular importance as the reaction of bromine addition to unsaturated compounds is frequently used for ascertaining the structure and identification of unsaturated compounds.

Keeping this in mind we have undertaken the investigation of the bromination of 1,1,1-trichloropropene, the following results having been obtained.

In media, favouring ionic addition, e.g. in acetic acid or ether in the presence of HBr, the reaction between 1,1,1-trichloropropene and bromine runs unambiguously to form 1,1,1-trichloro-2,3-dibromopropane. When acting with nitric acid on pure, 1,1,1-trichloro-2,3-dibromopropane we obtained only a neutral substance containing nitrogen, whose analysis showed it to correspond to a nitrate of the composition $C_3H_3Cl_3BrNO_3$.

With potassium hydroxide in ethylcellosolve 1,1,1-trichloro-2,3-dibromopropane forms, as already mentioned, 1,1,1-trichloro-2-bromopropene, which in turn, reacts with diethylamine, yielding, as a sole product $CCl_2{=}CBrCH_2N(C_2H_5)_2$.

When the reaction is carried out in chloroform, the reaction mixture being exposed to electric light (150 W), a mixture is formed which cannot be separated by distillation, which seems to consist of 1,1,1-trichloro-2,3-dibromopropane and 1,1,2-trichloro-1,3-dibromopropane. This mixture having been hydrolysed with nitric acid (sp. gr. 1·52) we isolated α-chloro-β-bromopropionic acid in 20 per cent yield. On treating the mixture with potassium hydroxide in ethylcellosolve a mixture of bromotrichloropropenes was obtained, which we succeeded in separating into their diethylamine derivatives.

$$\left.\begin{array}{l} CCl_3CHBrCH_2Br \\ CCl_2BrCHClCH_2Br \end{array}\right\} \xrightarrow{KOH} \left\{\begin{array}{l} CCl_3CBr{=}CH_2 \\ CCl_2BrCCl{=}CH_2 \end{array}\right\} \xrightarrow{HN(C_2H_5)_2}$$

$$\rightarrow CCl_2{=}CBrCH_2N(C_2H_5)_2 + CCl_2{=}CClCH_2N(C_2H_5)_2$$

The yield of 1,1,2-trichloro-1,3-dibromopropane is still higher, when bromination is carried out in carbon tetrachloride solution, and heating in the presence of benzoyl peroxide.

EXPERIMENTAL

1,1,1-*Trichloro-2,3-dibromopropane* To a solution of 1,1,1-trichloropropene (21 g) in glacial acetic acid (20 cc), a solution of bromine (24 g) in 30 ml of acetic acid was added in small portions. After the reaction was complete, the mixture was diluted with water. The dibromide, which separated was extracted, washed with water, then with aqueous sodium carbonate, again with water and dried (calcium chloride).

Distillation gave 1,1,1-trichloro-2,3-dibromopropane. Yield 36 g (80 per cent of theory), b.p. 69°/2 mm; n_D^{20} 1·5630; d_4^{20} 2·1751 (Found: MR, 45·58. Calc. MR, 46·18).

A solution of 1,1,1-trichloro-2,3-dibromopropane (15 g) in 35 cc of nitric acid (sp. gr. 1·52) was refluxed for 20 min. The reaction gave only traces of acidic material and a neutral substance (12 g) containing nitrogen, b.p. 79–80°/2 mm; n_D^{20} 1·5240;

d_4^{20} 1,9115 (Found: C 12·63; 12·57; H 1·11; 0·89; N 4·33, 4·44. $C_3H_3Cl_3BrNO_3$ requires C 12·54, H 1·05, N 4·09 per cent).

1,1,1-*Trichloro-2-bromopropene* To 1,1,1-trichloro-2,3-dibromopropane (48 g) with cooling and stirring a solution of potassium hydroxide (10 g) in 75 cc of ethylcellosolve was added dropwise with stirring for 3 hr. After diluting with water the oil which separated was extracted, washed with water and dried over sodium sulphate. Distillation gave 1,1,1-trichloro-2-bromopropene. Yield 25 g (71 per cent of theory), b.p, 57–58°/15 mm; n_D^{20} 1·5323; d_4^{20} 1·8493 (Found: MR, 37·52. Calc. MR, 37·95).

Heating trichlorobromopropene (10 g) with diethylamine (8·5 g) in methyl alcohol (50 cc) on the water-bath for 4 hr gave $CCl_2 = CBrCH_2\,N/C_2H_5/_2$. Yield 9 g (77 per cent of theory); b.p. 59°/1 mm; n_D^{20} 1·5079, d_4^{20} 1·4060 (Found: MR, 55·33. Calc. for MR, 55·50).

(Found: C, 32·35, 32·39; H, 4·79, 4·81; N, 5·43, 5·26. $C_7H_{12}Cl_2BrN$ requires C, 32·21; H, 4·63; N, 5·36 per cent.) Hydrochloride: m.p. 144–145° (from benzene and chloroform).

(Found: C, 28·64, 28·58; H, 4·65, 4·58. $C_7H_{13}Cl_3BrN$ requires C, 28·26; H, 4·45 per cent.)

Heating 1,1,1-trichloro-2-bromopropene (15 g) with 50 cc of benzene in presence of aluminiumchloride (0·5 g) gave $C_6H_5CH_2CBr = CCl_2$. Yield 14 g (78 per cent of theory); b.p. 97–98°/2 mm; n_D^{20} 1·5840; d_4^{20} 1·5566; (Found: MR, 57·19. Calc. MR, 57·19). (Found: C, 40·80, 40·93; H, 2·56, 2·64. $C_9H_7Cl_2Br$ requires C, 40·64; H, 2·65.)

Isomerisation of 1,1,1-*Trichloro-2-bromopropene*

(a) *Allylic rearrangement in the presence of* $SbCl_5$. To 1,1,1-trichloro-2-bromopropene (10 g) $SbCl_5$ (0·2 g) was added with cooling. After two hours at room temperature the mixture was washed with dilute hydrochloric acid, then with water and dried over calcium chloride. Distillation gave 1,1,3-trichloro-2-bromopropene-1. Yield 7,5 g b.p. 81–82°/21 mm; n_D^{20} 1·5522; d_4^{20} 1·8954 (Found: MR, 37·83. Calc. MR, 37·95) with properties identical to those of trichlorobromopropene, produced by dehydrobromination of $CCl_2BrCHBrCH_2Cl$ (see below).

With benzene in the presence of aluminium chloride 1,1,3-trichloride-2-bromopropene-1 gives 1,1-dichloro-2-bromo-3-phenylpropene-1 in good yield, b.p. 97–98°/2 mm; n_D^{20} 1·5840; d_4^{20} 1·5566, identical to dichlorobromophenylpropene obtained by condensation of 1,1,1-trichloro-2-bromopropene with benzene (see above).

With diethylamine in methyl alcohol solution $CCl_2 = CBrCH_2N/C_2H_5/_2$ was obtained, b.p. 61–62°/1·5 mm; n_D^{20} 1·5085; d_4^{20} 1·4068; hydrochloride: m.p. 144–145°. The mixed melting point with the hydrochloride produced by treating 1,1,1-trichloro-2-bromopropene with diethylamine (see above) and following the scheme: $CCl_2BrCHBr{-}CH_2Cl \xrightarrow{KOH} CCl_2{=}CBr{-}CH_2Cl \xrightarrow{N(C_2H_5)_2} CCl_2{=}CBrCH_2N(C_2H_5)_2$. HCl (see above) showed no depression.

(b) *Homolytic isomerisation.* When exposed to ultra-violet light, 1,1,1-trichloro-2-bromopropene, isomerises completely into 1,1,2-trichloro-3-bromopropene-1, b.p. 78–79°/19 mm; n_D^{20} 1·5550; d_4^{20} 1·8835; (Found: MR, 38·23. Calc. MR, 37·95).

(Found: C, 15·80, 15·72; H, 0·85, 0·82 $C_3H_2Cl_3Br$ requires C, 16·06; H, 0·89 per cent.)

The structure of 1,1,2-trichloro-3-bromopropene-1 was ascertained by converting it on treatment with diethylamine into 1,1,2-trichloro-3-diethylaminopropene-1, b.p.

68°/2·5 mm, n_D^{20} 1·4885; d_4^{20} 1·1910; lit.[19] b.p. 72°/3 mm, n_D^{20} 1·4888; d_4^{20} 1·1922. The mixed melting point of the hydrochloride of this amine with the hydrochloride of an authentic specimen of 1,1,2-trichloro-3-diethylaminopropene-1 showed no depression.

1,1,2-trichloro-3-bromopropene-1 was also obtained by treating sodium bromide in acetone with 1,1,2,3-tetrachloropropene-1 and had the following constants: b.p. 79–80°/20 mm; n_D^{20} 1·5550; d_4^{20} 1·8820.

1,1,3-*Trichloro*-1,2-*dibromopropane*

To a solution of 1,1,3-trichloropropene-1 (43 g) in chloroform (50 cc) a solution of bromine (48 g) in chloroform (50 cc) was added gradually. After the reaction was complete, chloroform was removed and the residue distilled in a vacuum. 1,1,3-trichloro-1,2-dibromopropane was obtained. Yield 85 g (94 per cent of theory) n_D^{20} 1·5678; d_4^{20} 2·1874 (Found: MR, 45·64. Calc. MR, 46·18).
(Found: C, 11·71, 11·60; H, 0·98, 0·96. $C_3H_3Cl_3Br_2$ requires C, 11·80; H, 0·99 per cent.)

A solution of trichlorodibromopropane (15 g) in nitric acid (30 cc, sp. gr. 1·52) was first heated gently until the violent reaction had subsided, and then refluxed for 30 min. After dilution with water the mixture was repeatedly extracted with chloroform. The chloroform extracts were washed with aqueous sodium carbonate to remove acidic products.

After acidification of the sodium carbonate washings, the acid obtained was extracted with chloroform and dried (calcium chloride). Distillation gave α-bromo-β-chloropropionic acid. Yield 7·2 g (76 per cent of theory); b.p. 125–126°/15 mm; m.p. 43–44° lit.[20] m.p. 43°.

When treated with alcoholic solution of potassium hydroxide it gave α-bromoacrylic acid, m.p. 68–69° lit.[20] m.p. 69°.

1,1,3-*Trichloro*-2-*bromopropene*-1 was prepared by dehydrobromination of 1,1,3-trichloro-1,2-dibromopropane (70 g) carried out similarly to the dehydrobromination of 1,1,1-trichloro-2,3-dibromopropane. Purification through a column, gave 1,1,3-trichloro-2-bromopropene-1. Yield 22 g, b.p. 81–82°/21 mm; n_D^{20} 1·5522; d_4^{20} 1·8955 (Found: MR, 37·83. Calc. MR, 37·95). (Found: C, 15·82, 16·00; H, 0·88, 0·77. $C_3H_2Cl_3Br$ requires C, 16·06; H, 0·89 per cent.)

In addition dichlorodibromopropene was also obtained. Yield 13 g; b.p. 97–98°/21 mm; n_D^{20} 1·5845; d_4^{20} 2·1957 (Found; MR, 41·00. Calc. MR, 40·85).
(Found: C, 13·28, 13·40; H, 0·73, 0·75. $C_3H_2Cl_2Br_2$ requires C, 13·40; H, 0·75 per cent.)

Treatment of trichlorobromopropene as well as of dichlorodibromopropene with diethylamine in methyl alcohol solution resulted in 1,1-dichloro-2-bromo-3-diethylaminopropene-1, b.p. 65–66°/1 mm; n_D^{20} 1·5079; d_4^{20} 1·4060 (Found MR, 55·33. Calc. MR, 55·50); hydrochloride: m.p. 144–145° (from benzene and chloroform).

Reaction of 1,1,1-*trichloropropene with bromine in chloroform.*

To a solution of trichloropropene (36 g) in chloroform (50 cc) a solution of bromine (40 g) in chloroform (30 cc) was added in portions, with stirring and exposure to electric light (150 w). After removal of the solvent, the residue was distilled in a vacuum, yielding a mixture of dibromides of the structureCCl_3·CHBr—CH_2Br and

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[20] L. Henry *Ber. Dtsch. Chem. Ges.* 7, 757 (1874).

$CCl_2BrCHCl—CH_2Br$, b.p. 61–62°/1 mm; n_D^{20} 1·5637; d_4^{20} 2·1756. Yield 65 g (85 per cent of theory).

Treatment of trichlorodibromopropenes produced (15 g) with nitric acid (35 cc, sp. gr. 1·52) as described above for 1,1,3-trichloro-1,2-dibromopropane gave α-chloro-β-bromopropionic acid. Yield 2 g; b.p. 134–136°/21 mm. Dehydrobromination of the latter with potassium hydroxide gave rise to α-chloroacrylic acid, m.p. 64–65°, in a good yield, lit.[20] m.p. 65°.

Neutral products. Yield 6·5 g, b.p. 79–80°/2 mm; n_D^{20} 1·5260.

Dehydrobromination of dibromotrichloropropanes (48 g) with potassium hydroxide (10 g) in ethylcellosolve (75 cc) yielded a mixture of trichlorobromopropenes. When distilled it gave the following fractions:*

(I) 48–49°/9 mm; n_D^{20} 1·5340; d_4^{20} 1·8517. Yield 19 g
(II) 49–60°/9 mm; Yield 6 g
Residue: Yield 9 g

Fraction 1 appears to be a mixture of $CCl_3CBr = CH_2$ and $CCl_2BrCCl = CH_2$, as being treated with diethylamine in methyl alcohol solution, it gave rise to $CCl_2 = CCl — CH_2N(C_2H_5)_2$, yield 3·8 g; b.p. 61–62°/2 mm; n_D^{20} 1·4890; d_4^{20} 1·1980; hydrochloride: m.p. 168–169°, lit[19] 168–169° as well as to $CCl_2 = CBrCH_2N(C_2H_5)_2$, b.p. 68–69°/2 mm; n_D^{20} 1·5080; d_4^{20} 1·4060; hydrochloride: m.p. 144°.

Fraction 11 gave $CCl_2 = CCl—CH_2Br$. Yield 2 g, b.p. 78–79°/19 mm; n_D^{20} 1·5550; d_4^{20} 1·8834.

Bromination of 1,1,1-*trichloropropene with bromine in carbon tetrachloride in the presence of benzoyl peroxide.* To the boiling solution of 1,1,1-trichloropropene (45 g) in carbon tetrachloride (50 cc) a solution of bromine (48 g) and benzoyl peroxide (0·5 g) in carbon tetrachloride (50 cc) was added dropwise. After distillation of the solvent, the residue was distilled in a vacuum. The reaction product distilled almost entirely at 75°/3 mm; n_D^{20} 1·5640; d_4^{20} 2·1710.

Treatment of the product (15 g) with concentrated nitric acid (35 cc, sp. gr. 1·52) gave rise to α-chloro-β-bromopropionic acid, yield 3·5 g and to a neutral substance, yield 3·8 g; b.p. 79–80°/2 mm; n_D^{20} 1·5245.

Dehydrobromination of trichlorodibromopropenes (45 g), following the procedure described above, resulted in trichlorobromopropenes, yield 16 g, b.p. 49–50°/10 mm; and in 1,1,2-trichloro-3-bromopropene, yield 3·5 g, b.p. 78–79°/19 mm; n_D^{20} 1·5550; d_4^{20} 1·8834. The mixture of trichlorobromopropenes, b.p. 49–50°/10 mm was separated and the following derivatives obtained:
$CCl_2 = CCl —CH_2N(C_2H_5)_2$, yield 7 g, b.p. 61–62°/2 mm; n_D^{20} 1·4891; d_4^{20} 1·1985; hydrochloride: m.p. 168–169° and $CCl_2 = CBrCH_2N(C_2H_5)_2$, yield 3 g, b.p. 68–69°/2 mm; n_D^{20} 1·5080; d_4^{20} 1·4057; hydrochloride: m.p. 144°.

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* To stabilise trichlorobromopropenes during distillation hydroquinone was added both into the still and the receivers.