676. *Fluoro-olefins. Part II.* Synthesis and Reactions of Some 3 : 3 : 3-Trihalogenopropenes.*

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The synthesis of the olefins $\mathrm{CX_3\cdot CY{:}CH_2}$ ($\mathrm{CX_3 = CClF_2}$ or $\mathrm{CF_3}$; Y = H, Cl, or Br) from 3-bromo-1 : 1 : 1-trichloropropane, 1 : 1 : 1 : 3-tetrachloropropane, or 3 : 3 : 3-trichloropropene, is described. Reaction of the compounds $\mathrm{CX_3\cdot CH_2\cdot CH_2Y}$ or $\mathrm{CX_3\cdot CHY'\cdot CH_2Y}$ ($\mathrm{CX_3 = CCl_3}$ or $\mathrm{CBrCl_2}$; Y and Y′ = Cl or Br) with antimony trifluoride yields $\mathrm{CF_3\cdot CH_2\cdot CH_2Y}$ or $\mathrm{CF_3\cdot CHY'\cdot CH_2Y}$.

The allylic rearrangement of $\mathrm{CCl_3\cdot CH{:}CH_2}$ and $\mathrm{CCl_3\cdot CCl{:}CH_2}$ to $\mathrm{CCl_2{:}CH\cdot CH_2Cl}$ or $\mathrm{CCl_2{:}CCl\cdot CH_2Cl}$ takes place on heating, or in presence of strong acids or Friedel–Crafts catalysts. $\mathrm{CClF_2\cdot CH{:}CH_2}$ probably rearranges to $\mathrm{CF_2{:}CH\cdot CH_2Cl}$.

This communication describes the synthesis of compounds of the type $\mathrm{CX_3\cdot CY{:}CH_2}$ ($\mathrm{CX_3 = CClF_2}$ or $\mathrm{CF_3}$; Y = H, Cl, or Br) required for experiments involving 3 : 3 : 3-trifluoro-propene and -propyne reported in other series (*J.*, 1951, 2495; 1952, 2504).

The starting compounds were 1 : 1 : 1 : 3-tetrachloropropane and 3-bromo-1 : 1 : 1-trichloropropane, prepared by the benzoyl peroxide-initiated reaction of carbon tetrachloride or bromotrichloromethane with ethylene (Joyce, Hanford, and Harmon, *J. Amer. Chem. Soc.*, 1948, **70**, 2529; Kharasch, Reinmuth, and Urry, *ibid.*, 1947, **69**, 1105).

The tetrachloropropane was converted into 3-chloro-1 : 1 : 1-trifluoropropane in high yield on treatment with antimony trifluoride activated by quinquevalent antimony, with benzotrifluoride or ethylene dichloride as diluent (cf. Henne and Nager, *ibid.*, 1951, **73**, 1042, Stewart and Henne, unpublished); small amounts of 1 : 3-dichloro-1 : 1-difluoropropane were also isolated.

Dehydrochlorination of 1 : 1 : 1 : 3-tetrachloropropane gave three products (I)—(III):

$$\mathrm{CCl_3\cdot CH_2\cdot CH_2Cl} \xrightarrow{\text{KOH-EtOH}} \underset{\text{(I)}}{\mathrm{CCl_3\cdot CH{:}CH_2}} + \underset{\text{(II)}}{\mathrm{CCl_2{:}CH\cdot CH_2Cl}} + \underset{\text{(III)}}{\mathrm{CCl_2{:}CH\cdot CH_2\cdot OEt}}$$

Compound (I), b. p. 100·5°, was prepared by Ladd and Slunkle (U.S.P. 2,561,516/1951) and by Nesmeyanov, Freidlina, and Firstov (*Doklady Akad. Nauk. S.S.S.R.*, 1951, **78**, 717; *Chem. Abs.*, 1952, **46**, 1957), and compound (II), b. p. 130·5°, was prepared by Kirrman and Kremer (*Bull. Soc. chim.*, 1948, **15**, 166). The constitution of (I) is proved below, and the boiling points of the known trichloropropenes now fall into the expected order: $\mathrm{CH_2Cl\cdot CCl{:}CHCl}$, 142°; $\mathrm{CH_2Cl\cdot CH{:}CCl_2}$, 131°; $\mathrm{CH_3\cdot CCl{:}CCl_2}$, 116°; $\mathrm{CCl_3\cdot CH{:}CH_2}$, 101°. The ether (III) has also been prepared by reaction of sodium ethoxide with (II). In

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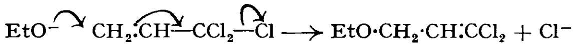
3 : 3 : 3-trichloropropene nucleophilic attack on the :CH$_2$ group is facilitated by the inductive effect of the CCl$_3$ group :



$$\mathrm{EtO^-\ CH_2{:}CH{-}CCl_2{-}Cl \longrightarrow EtO{\cdot}CH_2{\cdot}CH{:}CCl_2 + Cl^-}$$

The ready replacement of allylic chlorine by fluorine (Swarts, *Bull. Acad. roy. Belg.*, 1898, **35**, 375; 1920, **78**, 389) is further exemplified by the conversion of 3 : 3 : 3-trichloropropene into 3 : 3 : 3-trifluoropropene. Completely anhydrous conditions must be employed, however, since moisture liberates acid which converts (I) into (II). Anhydrous antimony trifluoride catalyses this allylic rearrangement only slowly. The change (I) ⟶ (II) is brought about by concentrated acids, by ferric or aluminium chloride, or by heat (see also Nesmeyanov *et al., loc. cit.*). Ethanolic potassium hydroxide has little effect in absence of chloride, and hydrogen fluoride gives mainly tar, although some halogen replacement occurs. Reaction of (II) with antimony trifluoride gave only complex products. Henne and Whaley (*J. Amer. Chem. Soc.*, 1942, **64**, 1157) reported that 3 : 3 : 3-trichloropropene failed to react with antimony trifluoride, but their starting material was probably 1 : 1 : 2-trichloropropene. Whaley and Davis (*ibid.*, 1948, **70**, 1026) observed allylic rearrangement on treatment of 1 : 1 : 2 : 3 : 3-pentachloropropene with antimony trifluoride, $\mathrm{CHCl_2{\cdot}CCl{:}CCl_2 \longrightarrow CHF_2{\cdot}CCl{:}CCl_2 + CF_3{\cdot}CCl{:}CHCl + CF_2Cl{\cdot}CCl{:}CHCl}$, although the compound $\mathrm{CCl_3{\cdot}CCl{:}CHCl}$ apparently yielded only $\mathrm{CF_3{\cdot}CCl{:}CHCl}$. It is to be noted that other compounds reported to undergo replacement of allylic halogen by fluorine with high yields would give the same product even if rearrangement had occurred (*e.g.*, $\mathrm{CCl_3{\cdot}CCl{:}CCl_2}$, $\mathrm{CF_2Cl{\cdot}CCl{:}CF_2}$, $\mathrm{CCl_3{\cdot}CH{:}CCl_2}$).

The following reactions have been applied to 3 : 3 : 3-trichloropropene :

$$\mathrm{CCl_3{\cdot}CH{:}CH_2 \xrightarrow{Cl_2} \underset{(IV)}{CCl_3{\cdot}CHCl{\cdot}CH_2Cl} \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CHCl{\cdot}CH_2Cl \xrightarrow{Zn\text{-}EtOH} CF_3{\cdot}CH{:}CH_2}$$

$$\mathrm{(IV) \xrightarrow{KOH\text{-}EtOH} \underset{(VI)}{CCl_3{\cdot}CCl{:}CH_2} + \underset{(VII)}{CCl_2{:}CCl{\cdot}CH_2Cl}}$$

$$\mathrm{CCl_3{\cdot}CH{:}CH_2 \xrightarrow{Br_2} \underset{(V)}{CCl_3{\cdot}CHBr{\cdot}CH_2Br} \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CHBr{\cdot}CH_2Br}$$

$$\mathrm{(V) \xrightarrow{KOH\text{-}EtOH} CCl_3{\cdot}CBr{:}CH_2}$$

$$\mathrm{CCl_3{\cdot}CX{:}CH_2 \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CX{:}CH_2 \quad (X = Cl\ or\ Br)}$$

The trichloropropenes (I) and (II) react with chlorine (Nesmeyanov *et al., loc. cit.*) to give the same pentachloro-compound (IV), which with antimony trifluoride yields the known 2 : 3-dichloro-1 : 1 : 1-trifluoropropane; the constitution of (IV) is thus proved. The markedly more rapid reaction of chlorine with (I) than with (II) is in accord with the proposed constitutions of (I) and (II).

The constitution of (V) follows from its conversion into the known 2 : 3-dibromo-1 : 1 : 1-trifluoropropane. The trichloropropene (II) gives, less readily, a different liquid dibromide, which in turn yields 2-bromo-3-chloro-1 : 1 : 1-trifluoropropane; this is different from the known 3-bromo-3-chloro-1 : 1 : 1-trifluoropropane. Since one bromine atom in the dibromide of (II) has been replaced by fluorine, the following reactions must have occurred :

$$\mathrm{CCl_2{:}CH{\cdot}CH_2Cl \xrightarrow{Br_2} CBrCl_2{\cdot}CHBr{\cdot}CH_2Cl \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CHBr{\cdot}CH_2Cl}$$

and the relation between (I) and (II) is proved.

With ethanolic potassium hydroxide the pentachloropropane (IV) gives two isomeric products (VI) and (VII). That the major product (VI) is 2 : 3 : 3 : 3-tetrachloropropene follows from its conversion by antimony trifluoride into the known 2-chloro-3 : 3 : 3-trifluoropropene; (VII) is 1 : 1 : 2 : 3-tetrachloropropene, since by reaction with chlorine it gives the same compound as (VI) :

$$\mathrm{CCl_3{\cdot}CCl{:}CH_2\ or\ CCl_2{:}CCl{\cdot}CH_2Cl \xrightarrow{Cl_2} CCl_3{\cdot}CCl_2{\cdot}CH_2Cl}$$

Allylic rearrangement of 2 : 3 : 3 : 3-tetrachloropropene into (VII) can be brought about by heat or by addition of aluminium chloride [cf. (I) ⟶ (II), above].

The allylic chlorine atoms in 2-bromo-3 : 3 : 3-trichloropropene were similarly readily replaced by fluorine.

When 3-bromo-1 : 1 : 1-trichloropropane was treated with antimony trifluoride activated by chlorine, 3-bromo-1 : 1 : 1-trifluoropropane, 3-bromo-1-chloro-1 : 1-difluoropropane, and a compound *A* were produced. The first of these is known; the constitution of the second follows from the reactions

$$\mathrm{CClF_2{\cdot}CH_2{\cdot}CH_2Br \xrightarrow{KOH-EtOH} CClF_2{\cdot}CH{:}CH_2\ (VIII) \xrightarrow{SbF_3Cl_2} CF_3{\cdot}CH{:}CH_2}$$

1 : 3-Dichloro-1 : 1-difluoropropane is similarly converted into (VIII).

Compound *A*, $C_3H_3BrCl_2F_2$, is formed in much lower yield when bromine is used to activate the antimony trifluoride. It boils in the region expected for a compound of this formula, and infra-red spectroscopic examination shows that it is not olefinic. Its constitution is shown by the following reactions which, since they take place in high yield, show that *A* is not a mixture of isomers. Zinc and ethanol removed equimolar amounts of bromine and chlorine, to give 3-chloro-3 : 3-difluoropropene (VIII) and 1 : 1-difluoroprop-1-ene (IX); zinc and acetic acid gave the same compounds but with increased yields of the difluoropropene. The mechanism of formation of (IX) is discussed below; its constitution is proved by its boiling point, by formation of a dichloride, b. p. 70° [cf. $CH_3{\cdot}CHCl{\cdot}CClF_2$, b. p. 69·8°; $CClF_2{\cdot}CH_2{\cdot}CH_2Cl$, 80·8°; $CH_3{\cdot}CF_2{\cdot}CHCl_2$, 79°; $CH_2Cl{\cdot}CF_2{\cdot}CH_2Cl$, 96·1°], and by its infra-red spectrum which shows the characteristic $CH{:}CF_2$ double bond stretching vibration at 5·67 μ.

Reaction of *A* with ethanolic potassium hydroxide gave an olefin $C_3H_2BrClF_2$ by removal of the elements of hydrogen chloride; bromide was not liberated. This olefin (X) reacted with antimony trifluoride to yield the known 2-bromo-3 : 3 : 3-trifluoropropene (XI). *A* is thus 2-bromo-1 : 3-dichloro-1 : 1-difluoropropane (XII):

$$\underset{\mathrm{(IX)}}{\mathrm{CF_2{:}CH{\cdot}CH_3}} \qquad \underset{\mathrm{(XII)}}{\mathrm{CClF_2{\cdot}CHBr{\cdot}CH_2Cl}} \xrightarrow{\mathrm{KOH-EtOH}} \underset{\mathrm{(X)}}{\mathrm{CClF_2{\cdot}CBr{:}CH_2}} \xrightarrow{\mathrm{SbF_3Cl_2}} \underset{\mathrm{(XI)}}{\mathrm{CF_3{\cdot}CBr{:}CH_2}}$$

A is also isolated as a by-product from the reaction of 1 : 2-dibromo-1 : 1 : 3-trichloropropane with antimony trifluoride.

The olefin (X) may also be obtained as follows:

$$\mathrm{(VIII) \xrightarrow{Br_2} CClF_2{\cdot}CHBr{\cdot}CH_2Br \xrightarrow{KOH-EtOH} CClF_2{\cdot}CBr{:}CH_2}$$

3-Chloro-3 : 3-difluoropropene combined with chlorine to give a trichloride which, with ethanolic potassium hydroxide, yielded 2 : 3-dichloro-3 : 3-difluoropropene; the last compound was readily converted into the known 2-chloro-3 : 3 : 3-trifluoropropene. Exchange of allylic chlorine for fluorine is thus easy with $CCl_3{\cdot}CX{:}CH_2$ and $CClF_2{\cdot}CX{:}CH_2$ (X = H, Cl, or Br) provided that allylic rearrangement is not dominant.

The unexpected formation of (XII) from 3-bromo-1 : 1 : 1-trichloropropane must involve a complex reaction [*e.g.*, $CCl_3{\cdot}CH_2{\cdot}CH_2Br \longrightarrow CClF_2{\cdot}CH_2{\cdot}CH_2Br \longrightarrow CClF_2{\cdot}CH{:}CH_2 \longrightarrow CClF_2{\cdot}CHBr{\cdot}CH_2Br \longrightarrow$ (XI)].

The rearrangements, $CCl_3{\cdot}CH{:}CH_2 \longrightarrow CCl_2{:}CH{\cdot}CH_2Cl$; $CCl_3{\cdot}CCl{:}CH_2 \longrightarrow CCl_2{:}CCl{\cdot}CH_2Cl$, have been established as above, and the rearrangement $CClF_2{\cdot}CH{:}CH_2 \longrightarrow CF_2{:}CH{\cdot}CH_2Cl$ seems probable (see below). They can be brought about by a variety of reagents and various mechanisms are possible (for a review with references to kinetic work see Braude *Ann. Reports*, 1949, **46**, 114).

The formation of 1 : 1-difluoroprop-1-ene (IX) on treatment of (XII) with zinc and ethanol also involves allylic rearrangement. It is well established that removal of halogen from adjacent carbon atoms which are also attached to hydrogen is easier than when the carbon atoms are attached to fluorine. The initial product from (XII) will thus be $CClF_2{\cdot}CH{:}CH_2$ and not $CF_2{:}CH{\cdot}CH_2Cl$, and rearrangement followed by reduction must occur when zinc chloride is present:

$$\mathrm{CClF_2{\cdot}CH{:}CH_2 \xrightarrow{ZnCl_2-EtOH} CF_2{:}CH{\cdot}CH_2Cl \xrightarrow{Zn-EtOH} CF_2{:}CH{\cdot}CH_3\ (IX)}$$

Acetic acid as solvent facilitates the rearrangement and thus increases the yield of (IX). That replacement of allylic chlorine by hydrogen can occur is shown by the reactions

$$CCl_2{:}CH{\cdot}CH_2Cl \xrightarrow{\text{Zn-EtOH}} CCl_2{:}CH{\cdot}CH_3; \quad CCl_2{:}CCl{\cdot}CH_2Cl \xrightarrow{\text{Zn-EtOH}} CCl_2{:}CCl{\cdot}CH_3$$

A second example of allylic rearrangement followed by reduction (zinc–alcohol) is probably $CCl_3{\cdot}CHCl{\cdot}CH_2Cl \longrightarrow CCl_2{:}CCl{\cdot}CH_3$ although here the possibility of the reaction $CCl_3{\cdot}CHCl{\cdot}CH_2Cl \longrightarrow CCl_2{:}CH{\cdot}CH_2Cl$ (without rearrangement), followed by reduction, cannot be excluded with as much certainty as for (XI).

EXPERIMENTAL

Reaction of Carbon Tetrachloride with Ethylene.—The procedure of Joyce *et al.* (*loc. cit.*) was followed, with carbon tetrachloride (100 ml.), ethylene (50 atm.), and benzoyl peroxide (0·9 g.) in a 300-ml. autoclave. The temperature was slowly increased to 100° during 24 hr., and as the pressure dropped more ethylene was added. Distillation gave 1 : 1 : 1 : 3-tetrachloropropane (25%), b. p. 65°/30 mm., 158—159°/760 mm., n_D^{20} 1·482.

Reactions of 1 : 1 : 1 : 3-*Tetrachloropropane.*—(a) *With antimony trifluoride* (cf. Henne and Nager, *loc. cit.*). A flanged cylindrical steel vessel (4 l.) was fitted with large steel paddles and scrapers which could be rotated by a powerful motor and were capable of stirring and mixing efficiently a dense semi-solid mass. To antimony trifluoride (100 g.) and antimony trifluorodichloride (100 g.), stirred for 1 hr., was added benzotrifluoride (50 ml.), then 1 : 1 : 1 : 3-tetrachloropropane (75 g.) added dropwise during 3 hr. The temperature, which had been kept at 20—25°, was then raised to give a reflux in the steel condenser, which was attached to the flanged lid of the apparatus and led *via* rubber tubing to a trap cooled in liquid oxygen. Efficient stirring was essential for good yields. After 1 hr. the volatile contents were pumped out, collected in the liquid-oxygen trap, and distilled, to give 3-chloro-1 : 1 : 1-trifluoropropane (61%), b. p. 45—46°, n_D^{25} 1·334, and 1 : 3-dichloro-1 : 1-difluoropropane (10%), b. p. 81—81·5°, n_D^{25} 1·325 (*J.*, 1951, 2495). Ethylene dichloride may be used instead of benzotrifluoride if only 3-chloro-1 : 1 : 1-trifluoropropane is required. In other experiments the products were isolated in slightly increased yield by steam-distillation of the acidified (HCl) reaction mixture.

(b) *Dehydrochlorination* (cf. Nesmeyanov *et al.*, *loc. cit.*). To 1 : 1 : 1 : 3-tetrachloropropane (50 g.) in ethanol (25 ml.), stirred and cooled to −10°, was slowly added 10% ethanolic potassium hydroxide (10% excess). An immediate precipitate of potassium chloride was observed, and after 1 hour's stirring at $\not>$0° an excess of water was added, and the lower layer was washed with water, dried ($CaCl_2$), and distilled, to give 3 : 3 : 3-trichloropropene (57%), b. p. 60—60·5°/175 mm., 100·5—101·0°/760 mm., n_D^{20} 1·468 (Found: C, 24·8; H, 2·2. Calc. for $C_3H_3Cl_3$: C, 24·8; H, 2·1%), 1 : 1 : 3-trichloroprop-1-ene (30%), b. p. 90—91°/175 mm., 130·0—131·5°/760 mm., n_D^{20} 1·497 (Found: C, 24·6; H, 2·5. Calc. for $C_3H_3Cl_3$: C, 24·8; H, 2·1%), starting material (2%), 1 : 1-*dichloro*-3-*ethoxyprop*-1-*ene* (5%), b. p. 110—111°/205 mm., n_D^{20} 1·453 (Found: C, 38·7; H, 5·0. $C_5H_8OCl_2$ requires C, 38·7; H, 5·2%), and unidentified material of higher b. p. (5%). Kirrman and Kremer (*loc. cit.*) report b. p. 130—131°, n_D^{18} 1·4960, for 1 : 1 : 3-trichloroprop-1-ene. Reaction of this compound (2·0 g.) with an ethanolic solution containing 5% of sodium ethoxide and 5% of potassium hydroxide gave 1 : 1-dichloro-3-ethoxyprop-1-ene in 58% yield.

Reactions of 3 : 3 : 3-*Trichloropropene.*—(a) *Conversion into* 3 : 3 : 3-*trifluoropropene.* Resublimed anhydrous antimony trifluoride (30 g.) was vigorously stirred and treated with chlorine until the ratio of $SbF_3 : SbF_3Cl_2$ was 9 : 1. Dried ethylene dichloride (20 ml.) was then added dropwise (2 hr.) at −10° to −5° to a solution of 3 : 3 : 3-trichloropropene (10·0 g.) in ethylene dichloride (5 ml.). The reaction, which is smooth and easily controlled only if efficient stirring is maintained, was completed by heating to 60°. Distillation of the volatile product in a vacuum system gave 3 : 3 : 3-trifluoropropene (51%), b. p. −22° (Found: *M*, 96. Calc. for $C_3H_3F_3$: *M*, 96), identified spectroscopically.

(b) *Isomerisation.* 3 : 3 : 3-Trichloropropene (3·0 g.) was converted into 1 : 1 : 3-trichloroprop-1-ene as tabulated. 1 : 1 : 3-Trichloroprop-1-ene was not converted into 3 : 3 : 3-trichloropropene by the reagents listed. Nesmeyanov *et al.* (*loc. cit.*) report the isomerisation of 3 : 3 : 3-trichloropropene by aluminium chloride at 0° or by heat at 150°.

(c) *With chlorine and bromine.* Chlorine (5% excess) and 3 : 3 : 3-trichloropropene (3·0 g.), sealed in glass at 0°, readily gave 1 : 1 : 1 : 2 : 3-pentachloropropane (94%), b. p. 84—85°/20 mm.,

n_D^{20} 1·513 (Found: C, 16·4; H, 1·0. Calc. for $C_3H_3Cl_5$: C, 16·6; H, 1·4%). Nesmeyanov *et al.* report b. p. 64—65°/8 mm., n_D^{20} 1·5105.

Reagent	Amount	Temp.	Time (hr.)	Yield of $CCl_2{:}CH{\cdot}CH_2Cl$ (%)
SbF_3	0·5 g.	0°	12	12
Conc. HCl	2 drops	20	36	71
Conc. H_2SO_4	2 drops	20	36	75
$AlCl_3$	0·05 g.	−10	1	65
Heat	—	100 (glass tube)	5	31
		140	5	74
$FeCl_3$	0·1 g.	30	3	52
KOH–EtOH	2 ml. of 10%	0	5	<5
Anhyd. HF	5 ml.	0	2	10 *

* $CF_3{\cdot}CH{:}CH_2$ and tar were also found.

The compound reported as 1 : 1 : 1 : 2 : 3-pentachloropropane (Huntress, "Organic Chlorine Compounds," Wiley, New York, 1948, p. 430) has m. p. 179°. Since this solid product was derived from what is now known to be 1 : 1 : 2-trichloroprop-1-ene, it is actually 1 : 1 : 1 : 2 : 2-pentachloropropane; the high m. p. is in accord with a molecule of this type, where the halogen atoms are concentrated on the minimum number of carbon atoms. The other known pentachloropropane is $CHCl_2{\cdot}CHCl{\cdot}CHCl_2$, b. p. 198—200°, $n_D^{16\cdot5}$ 1·5131 (*op. cit.*, p. 849).

Bromine was similarly absorbed by 3 : 3 : 3-trichloropropene (5·0 g.) at 20°, to give 1 : 2-dibromo-3 : 3 : 3-trichloropropane (95%), b. p. 100—101°/10 mm., n_D^{20} 1·562 (Found: C, 12·1; H, 0·9. Calc. for $C_3H_3Br_2Cl_3$: C, 11·8; H, 1·0%). Nesmeyanov *et al.* (*loc. cit.*) report b. p. 76—77°/3 mm., n_D^{20} 1·5640.

The compound reported as 1 : 2-dibromo-3 : 3 : 3-trichloropropane is a solid, m. p.. 210° (*op. cit.*, p. 663), but, since it was obtained from what is now known to be 1 : 1 : 2-trichloropropene, this solid is actually 1 : 2-dibromo-1 : 1 : 2-trichloropropane; a specimen prepared from authentic 1 : 1 : 2-trichloropropene had m. p. 216°.

Treatment of 1 : 2-dibromo-3 : 3 : 3-trichloropropane (4·0 g.) with a 50% excess of antimony trifluoride containing 40% of antimony trifluorodichloride at 90° for 12 hr. in a vigorously shaken steel autoclave gave 1 : 2-dibromo-3 : 3 : 3-trifluoropropane (53%), b. p. 116°, n_D^{25} 1·426 (Found: *M*, 254) (*J.*, 1951, 2495), identified spectroscopically and readily debrominated to 3 : 3 : 3-trifluoropropene (90%).

The pentachloropropane (3·1 g.) and antimony trifluoride similarly gave 1 : 2-dichloro-3 : 3 : 3-trifluoropropane (47%), b. p. 76—77° (Found: *M*, 167), identified spectroscopically and dechlorinated to 3 : 3 : 3-trifluoropropene (92%).

Ice-cold 10% ethanolic potassium hydroxide (5% excess) was added to 1 : 1 : 1 : 2 : 3-pentachloropropane (3·7 g.) at 0—5°, to give 2 : 3 : 3 : 3-tetrachloropropene (65%), b. p. 76—77°/70 mm., n_D^{20} 1·504 (Found: C, 20·2; H, 0·9. Calc. for $C_3H_2Cl_4$: C, 20·0; H, 1·1%), 1 : 1 : 2 : 3-tetrachloroprop-1-ene (10%), b. p. 92°/70 mm., n_D^{20} 1·518 (Found: C, 20·2; H, 1·1. Calc. for $C_3H_2Cl_4$: C, 20·0; H, 1·1%), and a middle fraction (15%). Hatch and McDonald (*J. Amer. Chem. Soc.*, 1952, **74**, 3328) report b. p. 59°/17 mm., 162°/743 mm., for 1 : 1 : 2 : 3-tetrachloroprop-1-ene.

1 : 2-Dibromo-3 : 3 : 3-trichloropropane (4·1 g.) similarly yielded 2-bromo-3 : 3 : 3-trichloropropene (61%), b. p. 81—82°/30 mm., n_D^{20} 1·535 (Found: C, 16·3; H, 1·0. Calc. for $C_3H_2BrCl_3$: C, 16·0; H, 0·9%), and a residue which decomposed on attempted distillation.

Reactions of 1 : 1 : 3-*Trichloroprop*-1-*ene*.—Unlike 3 : 3 : 3-trichloropropene, 1 : 1 : 3-trichloroprop-1-ene (3·7 g.) failed to react appreciably with bromine at 10° (2 hr.). After its exposure to ultra-violet light (1 hr.) in a Pyrex vessel, 1 : 2-*dibromo*-1 : 1 : 3-*trichloropropane* (66%), b. p. 105—6°/11 mm. (Found: C, 12·1; H, 1·0. $C_3H_3Br_2Cl_3$ requires C, 11·8; H, 1·0%), and unchanged olefin were isolated.

The dibromide (4·1 g.) was treated with antimony trifluoride as described above for its isomer, and gave 2-*bromo*-1-*chloro*-3 : 3 : 3-*trifluoropropane* (58%), b. p. 94—96° (Found: C, 17·0; H, 1·0%; *M*, 210. $C_3H_3BrClF_3$ requires C, 17·0; H, 1·4%; *M*, 211·5). The isomeric 1-bromo-1-chloro-3 : 3 : 3-trifluoropropane has been described (*J.*, 1951, 2495). Reaction at 50° gave as by-product 2-bromo-1 : 3-dichloro-1 : 1-difluoropropane (15%), shown by spectroscopic examination to be identical with compound *A* (see below).

Reaction of chlorine with 1 : 1 : 3-trichloroprop-1-ene (3·3 g.) was very slow in absence of light, but on exposure to radiation of wave-length >3000 Å yielded 1 : 1 : 1 : 2 : 3-pentachloropropane (85%), b. p. 80—81°/18 mm., shown to be identical with the compound prepared as above from 3 : 3 : 3-trichloropropene.

Reactions of 2 : 3 : 3 : 3-*Tetrachloropropene and* 2-*Bromo*-3 : 3 : 3-*trichloropropene*.—(a) *With antimony trifluoride*. Antimony trifluoride (20 g., containing 10% of SbF_3Cl_2) was slowly heated from −5° to 55° with 2 : 3 : 3 : 3-tetrachloropropene (4·1 g.) and ethylene dichloride (10 ml.), to give 2-chloro-3 : 3 : 3-trifluoropropene (59%), b. p. 15·5° (Found : *M*, 130. Calc. for $C_3H_2ClF_3$: *M*, 130·5), identical with the material prepared earlier (*J.*, 1951, 2495). 2-Bromo-3 : 3 : 3-trichloropropene (2·2 g.) similarly yielded 2-bromo-3 : 3 : 3-trifluoropropene (64%), b. p. 33—34° (Found : *M*, 175. Calc. for $C_3H_2BrF_3$: *M*, 175).

(b) *Isomerisation*. Aluminium chloride (0·1 g.) and 2 : 3 : 3 : 3-tetrachloropropene (2·0 g.), sealed at 0° for 4 hr., gave 1 : 1 : 2 : 3-tetrachloroprop-1-ene (51%), b. p. 89—90°/67 mm., n_D^{22} 1·517. This was also obtained (45%) by heating 2 : 3 : 3 : 3-tetrachloropropene (2·3 g.) at 180° for 5 hr. in a glass tube.

(c) *With chlorine*. A slight excess of chlorine combined readily with 2 : 3 : 3 : 3-tetrachloropropene (1·1 g.) at 0°, to give 1 : 1 : 1 : 2 : 2 : 3-hexachloropropane, b. p. 124—125°/40 mm. (Found : C, 14·2; H, 0·9. Calc. for $C_3H_2Cl_6$: C, 14·3; H, 0·8%). The same compound, b. p. 133—135°/60 mm., was prepared from 1 : 1 : 2 : 3-tetrachloroprop-1-ene (0·5 g.) and chlorine on exposure in a Pyrex tube to ultra-violet light (1 hr.).

Reactions of 1-*Bromo*-3 : 3 : 3-*trichloropropane*.—1-Bromo-3 : 3 : 3-trichloropropane, b. p. 97—98°/50 mm., n_D^{20} 1·513, was prepared in 60% yield from bromotrichloromethane (105 g.), ethylene (50 atm. in a 300-ml. autoclave) and benzoyl peroxide (0·8 g.), heated from 0° to 70° during 5 hr., then kept at 70° for 4 hr. before being heated to 90° for 1 hr.

(a) *Dehydrobromination*. Ice-cold ethanolic potassium hydroxide (5% excess of 10%) was added (2 hr.) to 1-bromo-3 : 3 : 3-trichloropropane (26·7 g.) in ethanol (10 ml.), with vigorous stirring at 0°. After a further hour an excess of water was added rapidly and the organic layer separated, dried ($CaCl_2$), and distilled, to give 3 : 3 : 3-trichloropropene (67%), b. p. 50—50·5°/125 mm., n_D^{20} 1·468, identical with the material described above, and a small amount of a product with higher b. p.

(b) *Reaction with antimony dichlorotrifluoride*. The apparatus described for 1 : 1 : 1 : 3-tetrachloropropane (above) was used. Antimony trifluoride (70 g.) and antimony dichlorotrifluoride (80 g.) were thoroughly mixed at 60°, then cooled to 20°. A solution of 1-bromo-3 : 3 : 3-trichloropropane (52 g.) in benzotrifluoride (20 ml.) was added (3 hr.) at 20—25° and the temperature was then raised to 60° for 30 min. Steam-distillation, etc., gave (i) 1-bromo-3 : 3 : 3-trifluoropropane (51%), b. p. 62—64°, n_D^{20} 1·360 (*J.*, 1951, 2495), identified spectroscopically, (ii) a fraction, b. p. 98—107°, which contained benzotrifluoride, (iii) 1-bromo-3-chloro-3 : 3-difluoropropane [*ca.* 15% determined by treatment of the mixture with alcoholic potassium hydroxide and separation of the olefin by distillation (see below)], and (iv) a compound *A*, (20%), b. p. 133—134°, n_D^{18} 1·448 (see below).

In a second experiment, antimony trifluoride (150 g.) was converted into dichlorotrifluoride (50%), and to it was added 1-bromo-3 : 3 : 3-trichloropropane (43·5 g.) in the absence of a solvent. Efficient stirring was essential to prevent extensive decomposition. After 3 hr. at 25°, the temperature was raised to 75° for 30 min. The products were 1-bromo-3 : 3 : 3-trifluoropropane (42%), b. p. 63—64°, 1-*bromo*-3-*chloro*-3 : 3-*difluoropropane* (11%), b. p. 99—102°, on redistillation 100—100·5°, n_D^{20} 1·362 (Found : C, 18·7; H, 2·0. $C_3H_4BrClF_2$ requires C, 18·6; H, 2·1%), and compound *A* (30%), b. p. 130—134°.

At 40°, bromotrichloropropane (46·2 g.) gave 1-bromo-3 : 3 : 3-trifluoropropane (19%), b. p. 63—65°, 1-bromo-3-chloro-3 : 3-difluoropropane (39%), b. p. 100—103°, compound *A* (10%), b. p. 132—135°, and starting material (15%). 1-Bromo-3 : 3-dichloro-3-fluoropropane was not detected.

(c) *Reaction with antimony dibromotrifluoride*. The last two experiments of (b) above were repeated, with bromine instead of chlorine to produce Sb^V salts. Treating 1-bromo-3 : 3 : 3-trichloropropane (45 g.) at $\ngtr$75°, and removing the products by pumping, gave 1-bromo-3 : 3 : 3-trifluoropropane (53%), b. p. 63—64°, 1-bromo-3-chloro-3 : 3-difluoropropane (27%), b. p. 99—102°, and compound *A* (7%), b. p. 132—135°. With a maximum reaction temperature of 40°, the bromotrichloropropane (45 g.) gave 1-bromo-3 : 3 : 3-trifluoropropane (26%), 1-bromo-3-chloro-3 : 3-difluoropropane (42%), and starting material (17%); compound *A* was not formed.

Dehydrobromination of 1-*Bromo*-3-*chloro*-3 : 3-*difluoropropane*.—To the compound (5·6 g.), in ethanol (5 ml.), cooled to 10°, was added dropwise (1 hr.) a 10% excess of ice-cold 10% ethanolic potassium hydroxide. Dilute hydrochloric acid was then added in excess, and air was blown through the solution. The combined volatile products were fractionated in a vacuum-system, to give 3-*chloro*-3 : 3-*difluoropropene* (78%), b. p. 18° (isoteniscope) (Found : C, 31·8; H, 2·5%; *M*, 113. $C_3H_3ClF_2$ requires C, 32·0; H, 2·7%; *M*, 112·5).

Dehydrochlorination of 1 : 3-*Dichloro*-1 : 1-*difluoropropane*.—The compound (3·1 g.), treated as in the last experiment, gave 3-chloro-3 : 3-trifluoropropene (84%), b. p. 17·5° (Found : *M*, 112. Calc. for $C_3H_3ClF_2$: *M*, 112·5), identical with the compound obtained above.

Constitution and Reactions of Compound A.—*A* was shown to be 2-*bromo*-1 : 3-*dichloro*-1 : 1-*difluoropropane*, b. p. 133·5—134·0°, n_D^{25} 1·444 (Found : C, 15·6; H, 1·5; Cl + Br, 51·0. $C_3H_3BrCl_2F_2$ requires C, 15·8; H, 1·3; Cl + Br, 50·6%), by the following reactions :

(a) *Dehydrochlorination.* The technique described above for 1-bromo-3-chloro-3 : 3-difluoropropane was applied to *A* (8·2 g.), to give 2-*bromo*-3-*chloro*-3 : 3-*difluoropropene* (89%), b. p. 78·5—79·0°, n_D^{20} 1·415 (Found : C, 18·7; H, 1·3%; *M*, 191. $C_3H_2BrClF_2$ requires C, 18·8; H, 1·1%; *M*, 191·5), and unchanged *A* (5%).

The olefin (4·3 g.) was added dropwise to a stirred suspension of antimony dichlorotrifluoride (10 g.) and antimony fluoride (5 g.) in ethylene dichloride (10 ml.) at 20°, to give 2-bromo-3 : 3 : 3-trifluoropropene (85%), b. p. 33° (isoteniscope) (Found : C, 20·7; H, 1·4%; *M*, 175. Calc. for $C_3H_2BrF_3$: C, 20·6; H, 1·4%; *M*, 175), identified by its infra-red spectrum.

(b) *Dehalogenation.* (i) *In ethanol. A* (10·7 g.) in ethanol (20 ml.) was added dropwise (1·5 hr.) to zinc (30 g.) and refluxing ethanol (30 ml.) in a flask fitted with reflux condenser at 25°. At the end of the reaction an excess of water was added, and the flask was swept out with nitrogen. Chloride and bromide had been formed in equimolar amounts. The combined volatile products were fractionated to give (*a*) 3-chloro-3 : 3-difluoropropene (72%), b. p. 17° (Found : *M*, 112. Calc. for $C_3H_3ClF_2$: *M*, 112·5), shown by its infra-red spectrum to be identical with the material obtained above from 1-bromo-3-chloro-3 : 3-difluoropropane and 1 : 3-dichloro-3 : 3-difluoropropane, and (*b*) 1 : 1-difluoroprop-1-ene (21%), b. p. −29° (isoteniscope) (Found : C, 46·2; H, 5·2%; *M*, 78. Calc. for $C_3H_4F_2$: C, 46·2; H, 5·1%; *M*, 78). Henne and Waalkes (*J. Amer. Chem. Soc.*, 1946, **68**, 496) report b. p. −29° for 1 : 1-difluoroprop-1-ene.

Chlorine (5% excess) combined readily with 1 : 1-difluoroprop-1-ene (1·1 g.) at 0°, giving 1 : 2-dichloro-1 : 1-difluoropropane (90%), b. p. 70—70·5° (Found : *M*, 149. Calc. for $C_3H_4Cl_2F_2$: *M*, 149). Robbins (*J. Pharmacol.*, 1946, **86**, 197) reports b. p. 69·8°.

(ii) *In acetic acid.* The experiment was repeated with glacial acetic acid in place of ethanol. *A* (6·3 g.) gave 3-chloro-3 : 3-difluoropropene (41%) and 1 : 1-difluoroprop-1-ene (52%), separated in the vacuum-system and identified spectroscopically.

(c) *Reactions of* 3-*chloro*-3 : 3-*difluoropropene.* The compound (2·0 g.), treated with a slight excess of bromine in a Pyrex vessel exposed to ultra-violet light, yielded 1 : 2-*dibromo*-3-*chloro*-3 : 3-*difluoropropane* quantitatively (Found : C, 13·0; H, 1·0. $C_3H_3Br_2ClF_2$ requires C, 13·2; H, 1·1%), b. p. 151—152°, n_D^{21} 1·474. The dibromide (3·1 g.) with ethanolic potassium hydroxide at 0° gave 2-bromo-3-chloro-3 : 3-difluoropropene (89%), b. p. 78·5°, n_D^{20} 1·415 (Found : *M*, 190. Calc. for $C_3H_2BrClF_2$: *M*, 191·5), shown by infra-red spectroscopic examination to be identical with the compound obtained by dehydrochlorination of *A*.

Chlorine (slight excess) combined with 3-chloro-3 : 3-difluoropropene (3·1 g.) at 0° on exposure to ultra-violet light and gave 1 : 2 : 3-*trichloro*-1 : 1-*difluoropropane* (98%), b. p. 113°, n_D^{20} 1·415 (Found : C, 19·8; H, 1·6%; *M*, 185. $C_3H_3Cl_3F_2$ requires C, 19·6; H, 1·6%; *M*, 183·5). The trichloride (4·1 g.), treated with ethanolic potassium hydroxide at 0°, gave 2 : 3-*dichloro*-3 : 3-*difluoropropene* (91%), b. p. 57—58°, n_D^{22} 1·378 (Found : C, 24·7; H, 1·5%; *M*, 147. $C_3H_2Cl_2F_2$ requires C, 24·5; H, 1·4%; *M*, 147).

The last compound (1·75 g.) was sealed with a 1 : 1 mixture of SbF_3 and SbF_3Cl_2 and set aside at 30° for 1 hr. Fractionation *in vacuo* then gave 2-chloro-3 : 3 : 3-trifluoropropene (81%), b. p. 15° (Found : *M*, 131. Calc. for $C_3H_2ClF_3$: *M*, 130·5), identical with the material described earlier (*J.*, 1951, 2495).

Reaction of Chloro-compounds with Zinc and Ethanol.—(a) 1 : 1 : 3-*Trichloroprop*-1-*ene.* The compound (5·1 g.) was added (1 hr.) to stirred zinc (10 g.) and 95% ethanol (20 ml.) at 65°. Filtration and addition of an excess of water gave an organic layer which, dried ($CaCl_2$) and distilled, gave 1 : 1-dichloroprop-1-ene (51%), b. p. 76—77°, n_D^{20} 1·445. Kirrman and Oestermann (*loc. cit.*) report b. p. 76·5°, n_D^{18} 1·4465. The olefin was identified by its infra-red spectrum, and by formation at 0° of a dichloride, b. p. 95°/120 mm., 155° (micro), n_D^{20} 1·487. Huntress (*op. cit.*, p. 757) records b. p. 153°.

(b) 1 : 1 : 2 : 3-*Tetrachloroprop*-1-*ene.* This compound (4·6 g.) was treated as above and yielded 1 : 1 : 2-trichloroprop-1-ene (53%), b. p. 116°, n_D^{20} 1·481. Kirrman and Oestermann report b. p. 41°/52 mm. The olefin and bromine gave 1 : 2-dibromo-1 : 1 : 2-trichloropropane m. p. 216°.

(c) 1 : 1 : 1 : 2 : 3-*Pentachloropropane*. Treatment of this compound (2·1 g.) with zinc and 95% ethanol at 65° gave 1 : 1-dichloroprop-1-ene (58%), b. p. 75—77°, identified spectroscopically, and unidentified material of higher b. p.

Infra-red Spectra.—The spectra of certain of the compounds mentioned above will be presented and discussed in another series.

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