ADDITION REACTIONS OF HALOOLEFINS. XII.*
THE REACTION OF TRIFLUOROCHLOROETHYLENE WITH MONOFLUOROCHLOROMETHANES IN THE PRESENCE OF ALUMINIUM CHLORIDE

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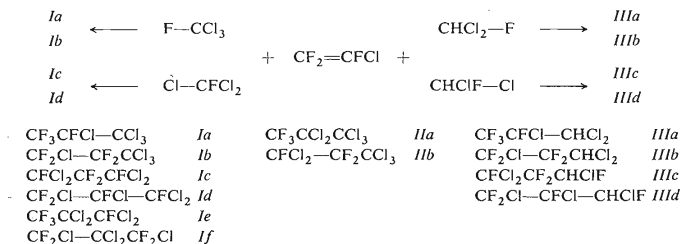Czechoslovak Academy of Sciences, Brno

The reaction of trifluorochloroethylene with fluorotrichloromethane in the presence of aluminium chloride afforded a mixture of five isomeres of tetrafluorotetrachloropropane among which 1,1,1,2-tetrafluoro- (Ia) and 1,1,2,2-tetrafluorotetrachloropropane (Ib) prevail, their relative amounts in the mixture being 49 and 36%. An analogous reaction of trifluorochloroethylene with fluorodichloromethane gave a mixture of five isomers of tetrafluorotrichloropropane in which 1-hydryl-1,1,3-trichlorotetrafluoropropane (IIIb) (67% rel.) prevailed. The addition of fluorotrichloromethane takes place in a 57% yield in agreement with the polarisation of the double bond of trifluorochloroethylene. On the other hand the addition of fluorodichloromethane takes place in 85% yield contrary to the direction of the polarisation. Relative reactivities of the C—F and C—Cl bonds in halomethanes during the addition are in a 88 : 11 ratio in the case of fluorotrichloromethane and in a 76 : 24 ratio in the case of fluorodichloromethane.

The addition reactions of trifluorochloroethylene with monofluorochloromethanes in the presence of aluminium chloride were carried out earlier[1,2]. The products of these additions have not been identified and their structure is only tentative. In the light of our investigations[3,4] of the additions of Freons to haloethylenes it followed that the conclusions drawn earlier[1] are not correct. In this paper we investigate the mentioned addition reactions with the aim of correcting the earlier inaccurate conclusions.

We carried out the ionic addition of fluorotrichloromethane to trifluorochloroethylene (cf.[2]) at atmospheric pressure, in which case the conversion was almost complete. In addition to tetrafluorotetrachloropropane (I) the reaction product contained trifluoropentachloropropane (II) in small yield (3—6%). An analogous addition of fluorodichloromethane, carried out under pressure and at room temperature, gave tetrafluorotrichloropropane in a 93% preparative yield.

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The composition of the addition products I and III, which are mixtures of isomers, agrees well with the knowledge[3,4] on the reactivity of the C—F and C—Cl bonds in halomethanes. In both cases the mixtures of I and III contain four isomers ($Ia-Id$; $IIIa-IIId$) which can be formed as primary addition products (Scheme 1), and an additional, "surplus" isomer (Ie; $IIIe$). The presence of "surplus" isomers was observed earlier[4,5] in analogous additions. Fraction I contained 1,1,1,2-tetrafluoro- (Ia), 1,1,2,2-tetrafluoro- (Ib), 1,2,2,3-tetrafluoro- (Ic), 1,1,2,3-tetrafluoro- (Id), and 1,1,1,3-tetrafluorotetrachloropropane (Ie) in relative amounts 49, 36, 5·5, 4·5, and 5%. Fraction III contained 1-hydryl-1,1,2-trichloro- ($IIIa$), 1-hydryl-1,1,3-trichloro-($IIIb$), 1-hydryl-1,3,3-trichloro-($IIIc$), 1-hydryl-1,2,3-trichloro-($IIId$), and the unidentified isomer $IIIe$ in relative amounts 8, 62, 16, 6, and 8%.

$$
\begin{array}{ccccccc}
Ia & & & & & & IIIa \\
Ib & \longleftarrow & \text{F---CCl}_3 & & \text{CHCl}_2\text{---F} & \longrightarrow & IIIb \\
 & & & + \quad \text{CF}_2\text{=CFCl} \quad + & & & \\
Ic & \longleftarrow & \text{Cl---CFCl}_2 & & \text{CHClF---Cl} & \longrightarrow & IIIc \\
Id & & & & & & IIId \\
\end{array}
$$

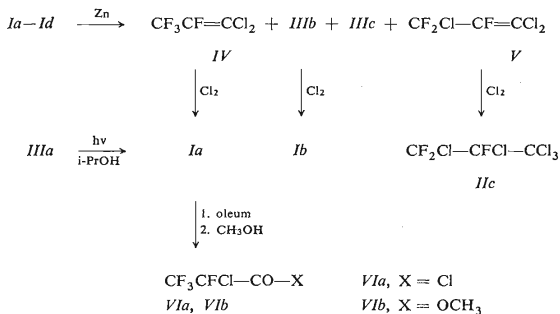|					
$\text{CF}_3\text{CFCl---CCl}_3$	Ia	$\text{CF}_3\text{CCl}_2\text{CCl}_3$	IIa	$\text{CF}_3\text{CFCl---CHCl}_2$	$IIIa$
$\text{CF}_2\text{Cl---CF}_2\text{CCl}_3$	Ib	$\text{CFCl}_2\text{---CF}_2\text{CCl}_3$	IIb	$\text{CF}_2\text{Cl---CF}_2\text{CHCl}_2$	$IIIb$
$\text{CFCl}_2\text{CF}_2\text{CFCl}_2$	Ic			$\text{CFCl}_2\text{CF}_2\text{CHClF}$	$IIIc$
$\text{CF}_2\text{Cl---CFCl---CFCl}_2$	Id			$\text{CF}_2\text{Cl---CFCl---CHClF}$	$IIId$
$\text{CF}_3\text{CCl}_2\text{CFCl}_2$	Ie				
$\text{CF}_2\text{Cl---CCl}_2\text{CF}_2\text{Cl}$	If				

SCHEME 1

We proved the structure of the addition products by gas chromatography, spectral analysis, and elemental analyses. The identity and the purity of isomers $Ia-If$ was checked under conditions[6] when all six isomers were separated.

For chromatographic analysis we prepared by independent procedures the isomers $Ic-If$ (Tables I and IV). For the preparation of Ic we took 1-hydryl-2,2,3-trifluoro-tetrachloropropane[5] as starting material. This was chlorinated to perhalogenated derivative IIb which gave on fluorination[7] substance Ic. The isomer Id was prepared on fluorination[7] of the addition product of fluorotrichloromethane to 1,2-difluoro-dichloroethylene[4]. The addition product of the mentioned reaction contains 90% of a mixture of IIc and 1,2,3-trifluoropentachloropropane, and both substances give on fluorination tetrafluoro derivative Id. The isomer Ie was prepared on fluorination[7] of halopropane IIa which was obtained[3] from the addition reaction of fluoro-trichloromethane with 1,1-difluorodichloroethylene via 3,3,3-trifluorotrichloro-propene. The latter can also be prepared[8] on fluorination of hexachloropropene. The isomer If was prepared on fluorination[7] od 1,1-difluorohexachloropropane which is

accessible[8] by a multistep synthesis from chloroform and perchloroethylene. The structure of isomers $Ic-If$ follows from the chemical procedure, from the regularities[7] inherent to the mentioned fluorinations, and from the infrared spectra (Table II).

Making use of a chemical procedure we isolated isomers Ia, Ib from the addition products I (Scheme 2). Under the influence of zinc in alcohol the isomers in the mixture I containing vicinal atoms of chlorine (Ia, Id, Ie) undergo dechlorination. The isomer Ia gave 1,1-dichlorotetrafluoropropene (IV; Table III) in which we were unable to prove the presence of dichlorotetrafluoropropene which would be formed on dechlorination of substance Id or Ie. The remaining two isomers, Ib and Ic, containing two fluorine atoms only on the central carbon atom undergo reduction[9] under these conditions, giving rise to corresponding hydro derivatives $IIIb$ and $IIIc$. The CCl_3 group is reduced much more rapidly in isomer Ib than the CCl_2F group in isomer Ic. It is interesting to note that the isomer Ib undergoes dehalogenation

$Ia-Id$ $\xrightarrow{Zn}$ $CF_3CF=CCl_2$ + $IIIb$ + $IIIc$ + $CF_2Cl-CF=CCl_2$

IV V

$\downarrow Cl_2$ $\downarrow Cl_2$ $\downarrow Cl_2$

$IIIa$ $\xrightarrow[\text{i-PrOH}]{hv}$ Ia Ib $CF_2Cl-CFCl-CCl_3$

IIc

$\downarrow$ 1. oleum
 2. CH_3OH

$CF_3CFCl-CO-X$ VIa, X = Cl
VIa, VIb VIb, X = OCH_3

Scheme 2

to a great extent, giving rise to 1,1,3-trichlorotrifluoropropene (V) after the splitting off of fluorine and chlorine atoms.

Fluoroalkanes of the R-CF_2CCl_3 type give on reaction with zinc[9,10] in aprotic solvent organozinc derivatives of the composition R-CF_2CCl_2ZnCl. (solv.). On reaction with water the organometallic derivatives decompose to hydrohaloalkanes, on heating at an elevated temperature they give olefins. This is probably the way substances $IIIb$, $IIIc$, and V are formed on reaction of mixture I with zinc in dioxan, diethylene glycol diethyl ether, and tetrahydrofuran after the decomposition of the reaction mixture. We attempted to prove the presence of organoderivative $CF_2Cl-CF_2CCl_2ZnCl$. (solv.) (VII) in the reaction mixture during the reaction in tetra-

hydrofuran. A part of the dehalogenation mixture was evaporated to dryness after the elimination of zinc, and the crystalline compound was decomposed with water. From the oily product we isolated hydro derivative *IIIb* in low yield (Table III), which demonstrates the low stability of organometallic derivative *VII*.

TABLE I

Preparation of Tetrafluorotetrachloropropanes *Ic*—*If* by Fluorination Methods

Starting compound[a]	Product, g (%)		Isomers, % rel.	Fraction $C_3Cl_3F_5$ % rel.
$CFCl_2CF_2CCl_3$[b]	*Ic* 13·2	(32·8)	3·5 *If*; 4·5 *Ie*	30·6
$CF_2Cl-CFCl-CCl_3$[c] $CFCl_2CFCl-CFCl_2$ }	*Id* 106·9	(49·4)	2·5 *Ic*; 2 *Ie*; 16 *If*	28·9
$CF_3CCl_2CCl_3$[d]	*Ie* 15·1	(25·3)	0	46·1
$CF_2Cl-CCl_2CCl_3$[e]	*If* 29·2	(83·3)	0	2·3

[a]For the weights of the strating compounds and for the conditions of fluorination see[7]; [b]see[5]; [c]see[4]; [d]see[8]; [e]see[3,8].

TABLE II

Absorption Maxima (cm^{-1}) in the IR Spectra of the Substance *Ia*—*Ie*, *IIIa*—*IIIc* (carbon disulfide, tetrachloromethane)

Compound	Absorption maxima
Ia	704 m, 775 m, 800 m, 848 m, 1 042 w; 1 123 m ν(CF); 1 212 s, 1 226 s, 1 269 m ν(CF$_3$)
Ib	677 w, 715 m, 850 s; 1 104 s a 1 179 s ν(CF$_2$)
Ic	719 s, 784 m, 893 s, 904 s, (sh), 951 m; 1 099 ν(CF); 1 182 s a 1 215 m ν(CF$_2$)
Id	720 s, 779 s, 832 mw, 859 m, 888 s, 903 m, 933 m, 992 s, 1 071 s; 1 103 s a 1 116 s (CF); 1 147 s a 1 171 s ν(CF$_2$)
Ie	697 m, 835 m, 906 m; 1 100 m ν(CF); 1 213 vs a 1 232 s ν(CF$_3$)
If	720 m, 777 s, 814 mw, 856 m, 903 m, 1 040 ms, 1 055 m; 1 147 m (sh) a 1 184 s ν(CF$_2$)
IIIa	715 ms, 824 m, 948 m, 1 065 m; 1 113 m ν(CF); 1 198 s, 1 219 s, 1 266 m a 1 292 m ν(CF$_3$); 2 995 w ν(C—H)
IIIb	722 m, 773 m, 832 s, 921 m, 950 s, 1 060 m, 1 089 s; 1 136 s, 1 162 s, 1 170 s (sh) a 1 216 m ν(CF$_2$); 3 001 w ν(C—H)
IIIc	716 s, 753 w, 790 m, 891 s, 910 s, 1 071 m; 1 100 s ν(CF); 1 150 s, 1 184 m, 1 239 m ν(CF$_2$); 3 001 w ν(C—H)

TABLE III
Reaction of Mixture *I* (49% *Ia*, 36% *Ib*, 5·5% *Ic*, 4·5% *Id*, 5% *Ie*) with Zinc in Various Solvents, and the Yields of Products *IV*, *IIIb*, *IIIc*, and *V*

Solvent	*I* g (mol)	Zinc g (gat)	Time, h (Temp., °C)	*IV*[a] g (%)	*IIIb*[a] g (%)	*IIIc*[a] g (%)	*V*[a] g (%)
Ethanol	300 (1·18)	116 (1·78)	12 (80—85)	98 (94)	38·3 (41·3)	4·9 (34·4)	26·4 (31·1)
Dioxan	150 (0·591)	60 (0·236)	7 (100—105)	38·3 (72·5)	19·3 (41·4)	2·4 (33·8)	17·6 (37·7)
Tetrahydrofuran	50 (0·197)	16·3 (0·249)	11 (65—70)	—	1·9 (12·2)	—	—

[a] Calculated from the chromatographic analysis of fractions obtained on rectification; the calculation is based on the content of corresponding isomers in the mixture *I*.

TABLE IV
Elemental Analyses and Boiling Points of Fluorochloropropanes *Ia—If*, *IIIa—IIIc*

Compound	B.p. °C	Literature b.p., °C	Ref.	Purity[a] % rel.	Found				Remarks
					% C	% H	% Cl	% F	
Ia	112 — 112·5	112·4—112·6	18	99·5	14·16	—	55·94	29·67	[b]
Ib	112 — 113	113·9	19	99	14·15	—	55·39	29·15	[b]
Ic	112·5—113·5	114·8	20	98·7	14·24	—	56·28	29·76	[b]
Id	110 — 112	112·2—113·8	19, 21	99·5	14·16	—	55·92	29·48	[b]
Ie	111 — 112	112 — 114	18	99	14·24	—	56·16	29·56	[b]
If	111·5	112·3	19	99	14·30	—	55·79	29·34	[b]
IIIa	91 — 92[c]	—	—	99·5	16·09	0·63	48·27	34·50	[d, e]
IIIa	92 — 92·5			92	16·69	0·57	47·95	34·65	[d, f]
IIIb	91 — 92[c]	91·7— 91·9	22	99·5	16·91	0·69	48·46	34·00	[d, e]
IIIb	90 — 91			99	16·52	0·65	48·37	34·07	[d, g]
IIIc	91 — 92[c]	—	—	97·5	16·14	0·53	48·51	34·48	[d, e]
IIIc	90 — 92			98·5	16·46	0·55	49·27	34·91	[d, g]

[a] For the conditions of analysis see Experimental; the isomers are not included among impurities; [b] for $C_3Cl_4F_4$ (253·9) calculated: 14·19% C, 55·87% Cl, 29·94% F; [c] boiling point of the mixture of isomers *IIIa—IIIc*; [d] for $C_3HCl_3F_4$ (219·4) calculated: 16·41% C, 0·46% H, 48·52% Cl, 34·61% F; [e] substance obtained by preparation from the mixture after addition; [f] prepared by photoreduction of compound *Ia*; [g] obtained from the reaction of the mixture *I* with zinc.

On reaction with chlorine halopropene IV gave the isomer Ia. Photochemical reduction[11,12] of this compound in isopropyl alcohol gave rise to hydro derivative $IIIa$. Acid hydrolysis of the isomer Ia with oleum takes place less rapidly than that of trifluoropentachloropropanes[3,4,8,9]. The formed chloride of 2-chlorotetrafluoropropionic acid (VIa) was transformed on reaction with methanol to its methyl ester VIb. The hydro derivative $IIIb$ was transformed by photochemical chlorination back to the isomer Ib. Halopropene V gave on addition of chlorine 1,1,2-trifluoropentachloropropane IIc known earlier[4].

After their isolation the isomers $IIIa$, $IIIb$ were identified by preparative gas chromatography taking as standards identical substances prepared from tetrafluorotetrachloropropanes Ia, Ib. The structure of the isomer $IIIc$ was proposed on the basis of its mass spectrum, but we were unable to identify substance $IIIe$. The PMR spectrum of substance $IIIa$ contains a doublet characteristic of a —CF—CH-grouping, the spectrum of compound $IIIb$ a triplet due to a —CF$_2$—CH-grouping. In the PMR spectrum of compound $IIIc$ the expected doublet of triplets was not present, but a doublet of a doublet of doublets was present instead $(J^2_{HF}$ 47·6; 15·2 and 2·2 c/s). This peculiarity was also observed[7,13,14] in other substances containing the —CF$_2$CHClF grouping (see Experimental). In the mass spectra of compounds $IIIa$ to $IIId$ characteristic fragments are present. In the IR spectra of compounds $Ia—If$ and $IIIa—IIIc$ vibrations of C—F bonds or also C—H bonds are present (Table II). The assignment of the absorption bands to the vibrations of the C—F bonds in the CF, CF$_2$ and CF$_3$ groups was carried out on the basis of empirical rules which we deduced earlier[7].

Ionic additions of fluorochloromethanes to halo olefins take place[4,15] very probably *via* the stage of a transition complex of the olefin with the ionized fluorochloromethane and aluminium chloride. The linking of the particles F$^-$, CCl$_3^+$, and Cl$^-$, CFCl$_2^+$ takes place inside this complex, and in the case of asymmetric olefins[3,5] it takes place in both directions of the polarisation of the double bond. In the case of trifluorochloroethylene we calculated[15] the magnitude of the π-charges on carbon atoms earlier: for the C-atom in CF$_2$ it was −16, in the CFCl group it was −74 thousandths of a charge unit. The relative amount of isomers formed on addition of the mentioned particles in agreement with the polarisation of the double bond $(Ia, Id; IIIa, IIId)$ to those which are formed on addition in the opposite direction $(Ib, Ic; IIIb, IIIc)$ can be regarded as a measure of the specificity of the addition. For the addition of fluorotrichloromethane the ratio of isomers $(Ia + Id) : (Ib + Ic)$ is 57 : 43, for the addition of fluorodichloromethane the ratio $(IIIa + IIId) : (IIIb + IIIc)$ is 15 : 85. From these data it follows that the addition of fluorotrichloromethane takes place predominantly in the direction of the polarisation of trifluorochloroethylene, while the addition of fluorodichloromethane takes place exclusively in the opposite direction.

The relative reactivity of C—F and C—Cl bonds in fluorochloromethanes is

dependent[7] both on fluoromethanes and on olefins. During the reaction of fluoro-trichloromethane with trifluorochloroethylene isomers Ia, Ib are formed on addition of F^- and CCl_3^+ particles. The ratio of the isomers $(Ia + Ib) : (Ic + Id) = 89 : 11$ indicates the relative reactivity of the C—F and C—Cl bonds during the addition of fluorotrichlormethane. The analogous relation $(IIIa + IIIb) : (IIIc + IIId) = 76 : 24$ gives the relative reactivity of the C—F and C—Cl bonds in fluorodichloro-methane during the reaction with trifluorochloroethylene.

EXPERIMENTAL

Temperature data were not corrected. Gas chromatography was carried out on a Chrom 3 apparatus (Laboratorní přístroje, Prague; thermal conductivity and flame ionisation detector, column of 0·6 cm diameter, carrier of the stationary phase Celite 545). The separation of the isomers of tetrafluorotetrachloropropane (I) was carried out on a Perkin-Elmer F 11 apparatus (polyamide capillary column 10000 cm, diameter 0.028 cm, squalane 0°C; for quantitative evaluation the same signal intensity was supposed for all isomers. The areas were determined by the multiplication of wave height by its width at half the height). IR spectra were measured on Zeiss UR 10 and Perkin-Elmer 325 (Bodenseewerk) spectrographs, PMR spectra on a BSS 477 (Tesla Brno) apparatus, and mass spectra on a Gas Chromatograph-Mass Spectrometer LKB 9000 (LKB-Produkter, AB Stockholm).

Reaction of Fluorotrichloromethane with Trifluorochloroethylene

Trifluorochloroethylene (100 g; 0·86 mol) was introduced with stirring over 3 hours into a mixture of fluorotrichloromethane (255 g; 1·85 mol), aluminium chloride (12 g; 0·09 mol), and carbon tetrachloride (100) kept at 5—30°C in a vessel provided with a low-temperature reflux condenser. When trifluorochloroethylene reacted completely the mixture was decomposed with dilute hydrochloric acid, washed with a sodium hydrogen carbonate solution and water, and dried over anhydrous calcium chloride. On rectification tetrafluorotetrachloropropane (I) distilled over between 111—112°C (177·2 g; 81·2%), purity 99·8% (gas chromatography: 20% silicone elastomer E 301, column 240 cm, 90 and 130°C, hydrogen, TC detection). Distillation of the residue (16·4 g) gave 7·6 g (3·3%) of trifluoropentachloropropane (II), b.p. 150—154°C, purity 99%. Determination of isomers: mixture I: 49% Ia, 36% Ib, 5·5% Ic, 4·5% Id, and 5% Ie; mixture II (for conditions see[6]): 70% IIa, 30% IIb. For $C_3Cl_4F_4$ (253·9) calculated: 14·19% C, 55·87% Cl, 29·94% F; found: 14·09% C, 55·80% Cl, 29·78% F. For $C_3Cl_5F_3$ (270·3) calculated 13·33% C, 65·59% Cl, 21·08% F; found: 13·49% C, 65·11% Cl, 20·86% F.

Reaction of Fluorodichloromethane with Trifluorochloroethylene

A mixture of fluorodichloromethane (72 g; 0·70 mol), trifluorochloroethylene (59 g; 0·36 mol), aluminium chloride (5·0 g; 37 mmol) and carbon tetrachloride (50 ml) was shaken in an autoclave at 0°C for 3 hours and at 15°C for 4 hours. The reaction mixture was worked up similarly as in the preceding reaction. On rectification trichlorotetrafluoropropane (III) distilled over between 90·5 and 92°C (73·2 g; 93·1%), purity 99·3% (for gas chromatography see the preceding reaction). Determination of isomers in mixture III: 8% $IIIa$, 62% $IIIb$, 16% $IIIc$, 6% $IIId$, and 8% $IIIe$ (gas chromatography: stainless steel capillary 5000 cm long, dinonyl phthalate, 25°C). For analytical purposes the isomers $IIIa$—$IIIc$ were isolated on an analytical column (20% poly(ethylene glycol) 400, column length 360 cm, 80°C, hydrogen); purity: $IIIa$ 85% (15% $IIId$,), $IIIb$ 99%, and $IIIc$ 99%. PMR spectra (deuteriochloroform): substance $IIIa$: d 3·90τ, J_{H-F}^3 5·2 Hz; substance $IIIb$: t 3·92τ, J_{H-F}^3 9·2 Hz; substance $IIIc$: ddd 3·35τ, J_{H-F}^2 47·6 Hz, J_{H-F}^3 15·2 and 2·2 Hz. Mass spectra (fragment, rel. intensity): substance $IIIa$: $(M)^+$ 0·14, $(CHCl_2)^+$ 100, $(CF_3)^+$ 39; substance $IIIb$:

$(CF_2Cl)^+$ 100, $(CHCl_2)^+$ 76; substance *IIIc*: $(CFCl_2)^+$ 100, $(CHClF)^+$ 95; substance *IIId*: $(CF_2Cl)^+$ 17, $(CHClF)^+$ 100; substance *IIIe*: $(C_3Cl_3F_4)^+$ 34, $(CF_2Cl)^+$ 100, $(CF_3)^+$ 46. For $C_3HCl_3F_4$ (219·4) calculated: 16·41% C, 0·46% H, 48·52% Cl, 34·61% F; found: 16·84% C, 0·55% H, 48·76% Cl, 34·61% F.

Reaction of Tetrafluorotetrachloropropane (*I*) with Zinc

A. *Reaction in ethanol.* To a mixture of ethanol (600 ml), powdered zinc (240 g; 3·67 gat), and mercuric chloride (1 g) the fraction of halopropanes *I* (585 g; 2·31 mol; *i.e. Ia* 287 g, 1·13 mol; *Ib* 210 g, 0·827 mol; *Ic* 32·2 g, 0·127 mol) was added at 80°C over 3 hours under stirring and the mixture was heated at 90°C for 6 hours. During the reaction a fraction was distilled over through a rectification column, b.p. 45—50°C (231 g). Its rectification gave 185·6 g (90·2%) of 1,1-dichlorotetrafluoropropene (*IV*), b.p. 45—46·5°C (literature[16,17] 46—46·4°C) purity 99% (gas chromatography: stainless steel capillary 5000 cm, dinonyl phthalate, 24°C). The distillation residue was worked up together with other fractions. The residual reaction mixture was steam distilled and the oily distillate was washed with water, conc. sulfuric acid, and then dried over anhydrous calcium chloride (193 g). On rectification the fraction of b.p. 85—92°C (84·7 g) was collected which contained 52% of hydro derivative *IIIb*, 6·4% of isomer *IIIc*, and 36% of 1,1,3-trichlorotrifluoropropene (*V*) (gas chromatography: 20% poly(ethylene glycol) 400, column 360 cm length, 80°C, hydrogen, TCD). For analytical purposes substances *IIIb*, *IIIc*, and *V* were isolated on an analytical column. For the IR spectrum of compound *V* see[4]. IR spectrum of the olefin *IV* (carbon disulfide, carbon tetrachloride; cm^{-1}): 711 s, 865 m, 979 m; 1162 s, 1217 s ν (CF$_3$); 1144 ms; 1139 vs ν(=CF), 1658 w ν(C=C). For $C_3Cl_3F_3$ (199·4) calculated: 18·13% C, 53·35% Cl, 28·52% F; found: 18·34% C, 52·53% Cl, 27·70% F.

The reactions in dioxan, diethylene glycol diethyl ether, and tetrahydrofuran, which gave mutually identicla results, were carried out in a manner analogous to that used for ethanol.

B. *Reaction in tetrahydrofuran*: Mixture I (50 g; 0·197 mol) was added under stirring over 2 hours to a mixture of powdered zinc (16·3 g; 0·249 gat) and tetrahydrofuran (80 ml) and the mixture was refluxed for 10 hours. The liquid fraction of the reaction mixture was filtered at 40°C and evaporated to dryness *in vacuo*. Sulfuric acid was added to the crystalline residue and the oily layer was mixed with Freon 113 (20 ml), washed with water and dried over anhydrous magnesium sulfate. On distillation a fraction b.p. 80—92°C (3·3 g) was obtained which contained hydro derivative *IIIb* (for gas chromatography see *A*). For analytical purposes substance *IIIb* was isolated on an analytical column for gas–liquid chromatography.

1,1,1,2-Tetrafluorotetrachloropropane (*Ia*)

Chlorine gas was introduced into refluxing 1,1-dichlorotetrafluoropropene (*IV*) (79 g; 0·432 mol) for 20 hours (low temperature reflux condenser). The crude product (92·2 g) was washed with a potassium hydroxide solution, water, and dried over phosphorus pentoxide. The mixture was rectified and the product, *Ia*, boiling at 111—112°C was obtained in a 79·2% yield (86·2 g), purity 99·5% (gas chromatography: silicone elastomer E 301, column 360 cm, 80°C, hydrogen, TCD), content of isomers: 96% *Ia*, 1% *Id*, 3% *If*.

1,1,2-Trifluoropentachloropropane (*IIc*) and 1-Hydryl-1,1,3-trichlorotetrafluoropropane (*IIIb*)

Chlorine gas was introduced into a flask fitted with a low temperature reflux condenser, containing a mixture of hydropropane *IIIb* and halopropene *V* (obtained on reaction of fraction *I* with zinc — see above; 36 g; *i.e.* 61% *IIIb*, 21·9 g, 0·101 mol; 7% *IIIc*, 2·52 g, 11·5 mmol; 32% *V*, 11·5 g,

59 mmol), for 16 hours at 40—60°C until all olefin V reacted. The reaction mixture was washed with a potassium hydroxide solution and water, and dried over anhydrous magnesium sulfate. Rectification of the mixture gave a mixture of $IIIb$ and $IIIc$ boiling at 90—92°C (17·9 g; 76·3%) in rel. amounts 92 and 8%, and compound IIc, b.p. 150—153°C (see[4]), yield 9·5 g (61%), purity 98·5%. The intermediate fraction b.p. 93—150°C (12·3 g) contained one third of tetrafluorotetrachloropropane (gas chromatography: 20% silicone elastomer E 301 and poly(ethylene glycol) 400, column 360 cm, 125° and 80°C, hydrogen, TCD). For the IR spectrum of compound IIc see[4]. For $C_3Cl_5F_3$ (270·3) calculated: 13·33% C, 65·59% Cl, 21·08% F; found: 13·50% C, 65·53% Cl, 20·86% F.

1,1,2,2-Tetrafluorotetrachloropropane (Ib)

Chlorine gas was introduced into a mixture of hydroalkane $IIIb$ (18·2 g; 83 mmol; 7% of isomer $IIIc$) and carbon tetrachloride (20 ml) kept in a vessel provided with a low temperature reflux condenser and the mixture was refluxed for 15 hours until 30% of the starting material reacted. After filtration off of the formed white precipitate the mixture was rectified and haplopropane Ib was collected at 110—111°C (2·93 g; 14·1%), purity 99·5% (gas chromatography) see the preparation of substance Ia) composition: 2% of isomer Ia, 87% of isomer Ib, 11% of isomer Ic).

1-Hydryl-1,1,2-trichlorotetrafluoropropane ($IIIa$)

A solution of halopropane Ia (14·1 g; 56 mmol) in 2-propanol (16·5 g; 458 mmol) was irradiated from close proximity with a UV lamp (80 W, Tesla) at 25°C for 6·5 hours until 51% of the starting Ia reacted. The reaction mixture was washed with water and a concentrated solution of calcium chloride and dried over phosphorus pentoxide. For analytical purposes the product $IIIa$ was isolated on an analytical gas–liquid chromatographic column (silicone elastomer, column 360 cm).

Methyl 2-Chlorotetrafluoropropionate (VIb)

A mixture of halopropane Ia (21·5 g; 85 mmol), 65% oleum (15 ml), mercuric oxide (O. 5 g), and silver acetate (0·1 g) was heated at 100—130°C for 18 hours and then submitted to distillation. The fraction distilling at 48—50°C was added over 15 minutes at 10—20°C to methanol (8·2 g; 0·256 mol). The mixture was mixed with Freon 113 (20 ml), washed with water, dried over anhydrous magnesium sulfate, and rectified. Fraction b.p. 84·5—85°C (5·41 g; 30·8%) was collected, purity 97% (for gas chromatography see compound $IIIa$). IR spectrum (carbon disulfide, carbon tetrachloride; cm^{-1}): 694 w, 802 w, 954 m, 1015 m, 1036 m, 1141 m v(C—F), 1204 s and 1220 s v(CF$_3$), 1269 a v(C—O), 1779 s and 1787 s v(C=O), 2957 w v(CH$_3$). For $C_4H_3ClF_3O_2$ (194·5) calculated: 24·72% C, 1·55% H, 39·12% F; found: 24·58% C, 1·45% H, 38·70% F.

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