PREPARATION OF PERHALOGENATED CHLOROFLUOROPROPANES BY HALOGEN EXCHANGE IN THE LIQUID AND VAPOUR PHASES AND THEIR ISOMER ANALYSES BY ^{19}F NMR SPECTROSCOPY

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SUMMARY

The liquid-phase fluorination of pentachlorotrifluoro-propane (1) and tetrachlorotetrafluoropropane (2) of defined isomer composition at atmospheric or autogenous pressure by means of the Henne-Swarts reagent yielded from 60% to 70% of tetrachlorotetrafluoropropane (2) and trichloropentafluoro-propane (3). The vapour-phase fluorination of chlorofluoro-propanes 1-3 with hydrogen fluoride catalysed by ferric salts on a charcoal support afforded chlorofluoropropanes 2 and 3 in addition to dichlorohexafluoropropane (4) in a yield of 13.5% to 79%. Simultaneously an isomerisation reaction took place in some cases. The isomer compositions of the starting substances and products were determined by means of ^{19}F NMR spectroscopy. The NMR data of the isomers are given and compared with the chemical shifts calculated using the published empirical method [1].

INTRODUCTION

The Henne-Swarts reactions, i.e. the fluorination with antimony halogenides, and the fluorination with gaseous hydrogen fluoride in the presence of a catalyst [2] (most frequently salts of transition metals such as iron, manganese or chromium on a charcoal support [3,4]) are the
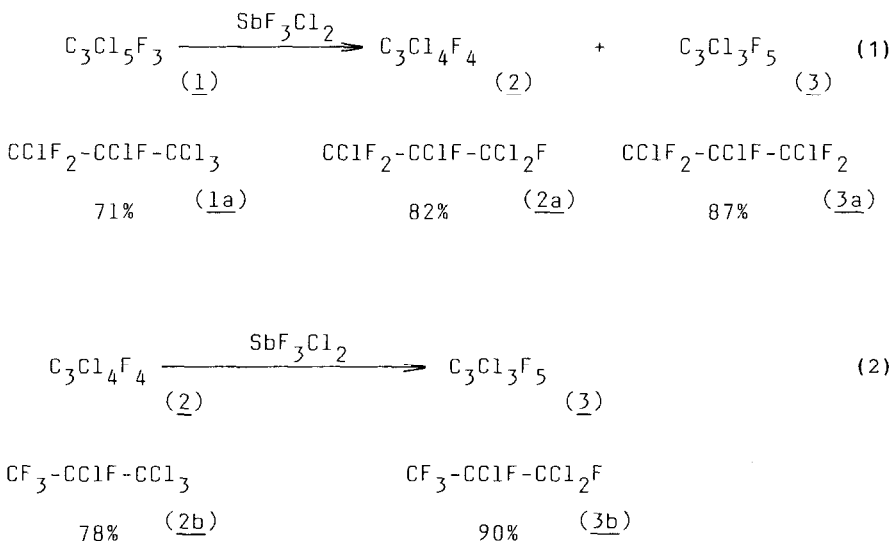
most common fluorination methods used for the preparation of chlorofluoroalkanes. The Henne-Swarts fluorination is characterised by milder reaction conditions compared with other methods, e.g. with catalytic fluorination by means of hydrogen fluoride at higher temperatures, which is widely used in technological processes.

The most important chlorofluoroalkanes are the C_1- and C_2- alkanes owing to their easy production and considerable industrial utilisation. However, perhalogenated chlorofluoropropanes were synthesized for the first time in 1939 by fluorination of chloropropanes [5]. Lately, analogous preparations starting from halogenated propanes with a low fluorine content were accomplished, using either the Henne-Swarts reaction [6], or reaction with potassium fluoride in dipolar aprotic solvents [7]. Relatively advantageous synthetic methods for the preparation of medium-fluorinated chlorofluoropropanes are the additions of halogenomethanes to fluorinated ethylenes [8], e.g. tetrafluoroethylene [9] and chlorotrifluoroethylene [10, 11]. The products of such reactions, however, are mostly mixtures of structural isomers with one predominating [8], as has been verified by means of gas-liquid chromatography [12]. Mixtures of isomeric products are prepared from these substances using some of the fluorination methods discussed above [13]. From some communications [4-7,14,15] it is not clear to what extent their authors were concerned with the isomer purity of the prepared chlorofluoropropanes.

FLUORINATION OF CHLOROFLUOROPROPANES

To obtain higher-fluorinated halogenopropanes, the starting materials used were the chlorofluoropropanes prepared earlier [10,11], viz. pentachlorotrifluoropropane (1), containing 71% of 1,1,1,2,3-pentachlorotrifluoropropane (1a), and tetrachlorotetrafluoropropane (2), containing 78% of 1,1,1,2-tetrachlorotetrafluoropropane (2b). The Henne-Swarts fluorination of these two compounds in a glass apparatus at atmospheric pressure yielded higher-fluorinated chlorofluoropropanes according to Scheme 1 (the reaction conditions and

yields are given in Table 1 and the composition of the initial substances and products are listed in Table 2; run numbers correspond to equation numbers, i.e. (1), (2), in the Schemes).

$$C_3Cl_5F_3 \xrightarrow{SbF_3Cl_2} C_3Cl_4F_4 \quad + \quad C_3Cl_3F_5 \quad (1)$$

(1)   (2)   (3)

$CClF_2-CClF-CCl_3$ $CClF_2-CClF-CCl_2F$ $CClF_2-CClF-CClF_2$

71%   (1a)   82%   (2a)   87%   (3a)

$$C_3Cl_4F_4 \xrightarrow{SbF_3Cl_2} C_3Cl_3F_5 \quad\quad\quad\quad (2)$$

(2)   (3)

$CF_3-CClF-CCl_3$ $CF_3-CClF-CCl_2F$

78%   (2b)   90%   (3b)

Scheme 1

The reduced ability of the $-CClF_2$ group to undergo further fluorination under the given reaction conditions led in both cases to chlorofluoropropanes of higher isomeric purity (from 71% 1a to 82% 2a and thence to 87% 3a; from 78% 2b to 90% 3b).
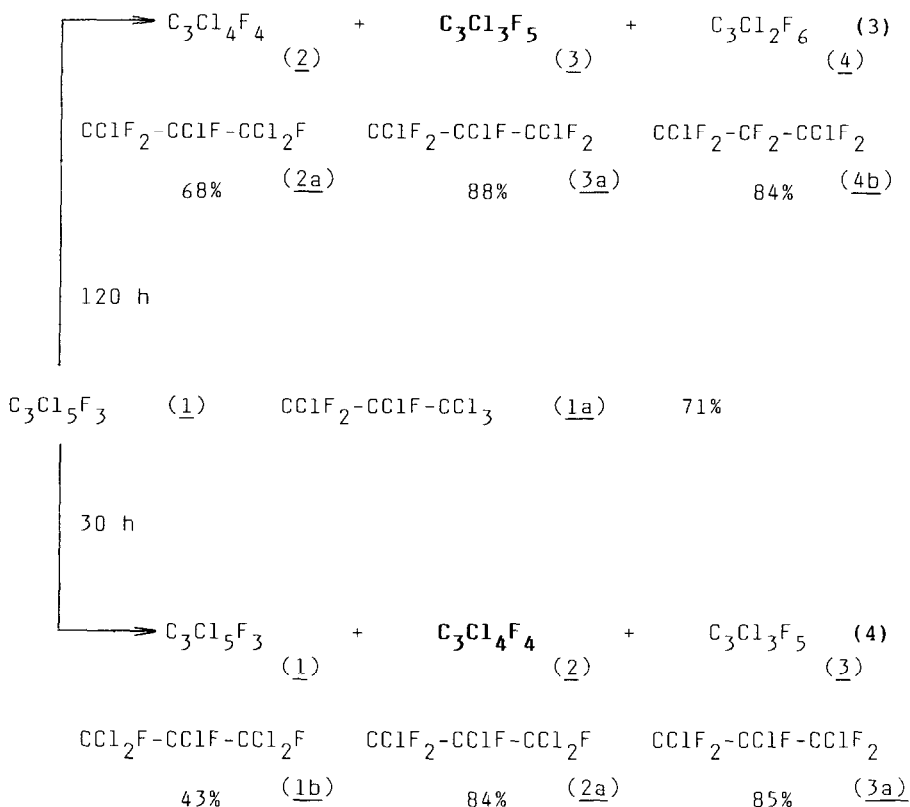
Chlorofluoropropane 2b gave chlorofluoropropane 3b in a high yield. The fluorination of chlorofluoropropane 1a, however, could not be performed to complete conversion to chlorofluoropropane 3a at atmospheric pressure, yielding only

its $\underline{ca}$. 2:3 mixture with chlorofluoropropane $\underline{2a}$. The resistance to further fluorination was probably caused both by the reduced reactivity of the $-CCl_2F$ group compared with the $-CCl_3$ group, and by the decrease in the reaction-mixture boiling point.

Because of the significance of chlorofluoropropane $\underline{3a}$ as a precursor of 3-chloropentafluoro-1-propene, 'perfluoro-allyl chloride', we turned our attention to preparative fluorination under autogenous pressure. A prolonged reaction time was achieved by using a non-stirred steel bomb as a reaction vessel. The conversion of the starting compound was checked by GLC. Depending on the reaction time, chlorofluoro-propane $\underline{2a}$ or chlorofluoropropane $\underline{3a}$ were obtained as the main reaction products according to Scheme 2 (the experimental conditions and isomer composition of the fractions are listed in Tables 1 and 2, respectively).

In run 3, the increase in the isomer purity of the trichloropentafluoropropane fraction $\underline{3}$ (88% $\underline{3a}$) compared with the starting compound $\underline{1}$ (71% $\underline{1a}$) was caused again by the different reactivities of the terminal trihalogenomethyl groups. The isomers containing a $-CCl_2-$ group (27%), less reactive than $-CCl_2F$ and $-CCl_3$ groups, tended to accumulate in the tetrachlorotetrafluoropropane fraction $\underline{2}$. Simultaneously, the isomers containing a $-CF_2-$ group were largely converted by fluorination to the dichlorohexafluoropropane fraction $\underline{4}$ (content 84% $\underline{4b}$).
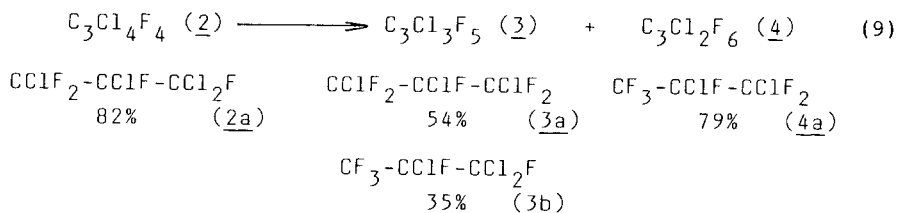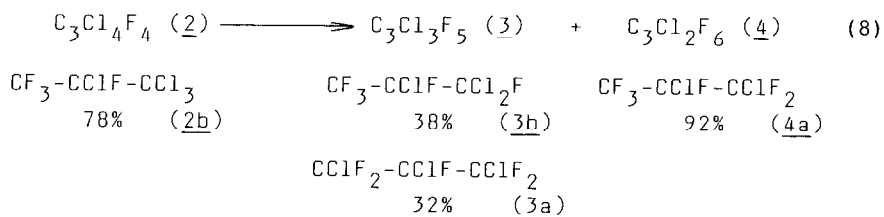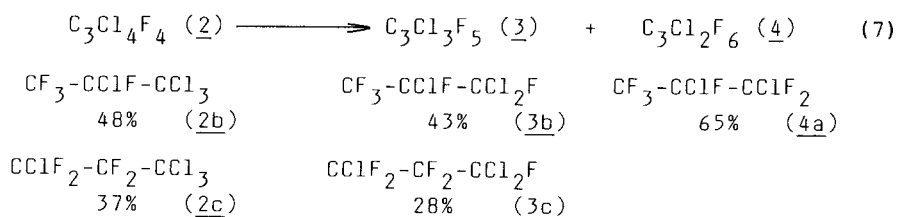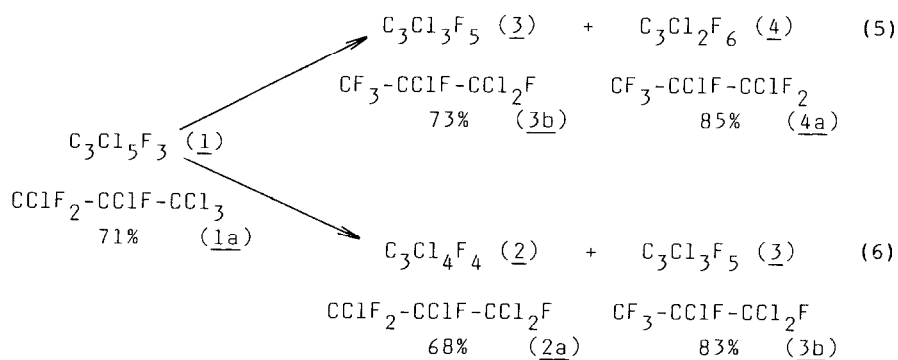
The second method we used in the present work was fluorination in the vapour phase with hydrogen fluoride under the catalysis of ferric salts on a charcoal support. Six initial chlorofluoropropanes, viz. pentachlorotrifluoropropane ($\underline{1}$, 71% $\underline{1a}$) and tetrachlorotetrafluoropropane ($\underline{2}$, 78% $\underline{2b}$), prepared after Refs. [10,11], tetrachlorotetrafluoropropane ($\underline{2}$, 82% $\underline{2a}$) and two trichloropentafluoropropanes ($\underline{3}$, 87% $\underline{3a}$, and 90% $\underline{3b}$), prepared by the above described fluorination (see Scheme 1), and tetrachlorotetrafluoropropane ($\underline{2}$, 48% $\underline{2a}$, 37% 1,1,1,3-tetrachlorotetrafluoropropane, $\underline{2c}$), prepared earlier after Ref. [11], were subjected to this fluorination method. The yields, distributions and isomer compositions for this

$$C_3Cl_4F_4 \quad + \quad C_3Cl_3F_5 \quad + \quad C_3Cl_2F_6 \quad (3)$$
$$\qquad (\underline{2}) \qquad\qquad\qquad (\underline{3}) \qquad\qquad\qquad (\underline{4})$$

$$CClF_2-CClF-CCl_2F \qquad CClF_2-CClF-CClF_2 \qquad CClF_2-CF_2-CClF_2$$
$$68\% \quad (\underline{2a}) \qquad\qquad 88\% \quad (\underline{3a}) \qquad\qquad 84\% \quad (\underline{4b})$$

120 h

$$C_3Cl_5F_3 \quad (\underline{1}) \qquad CClF_2-CClF-CCl_3 \qquad (\underline{1a}) \qquad 71\%$$

30 h

$$C_3Cl_5F_3 \quad + \quad C_3Cl_4F_4 \quad + \quad C_3Cl_3F_5 \quad (4)$$
$$\qquad (\underline{1}) \qquad\qquad\qquad (\underline{2}) \qquad\qquad\qquad (\underline{3})$$

$$CCl_2F-CClF-CCl_2F \qquad CClF_2-CClF-CCl_2F \qquad CClF_2-CClF-CClF_2$$
$$43\% \quad (\underline{1b}) \qquad\qquad 84\% \quad (\underline{2a}) \qquad\qquad 85\% \quad (\underline{3a})$$
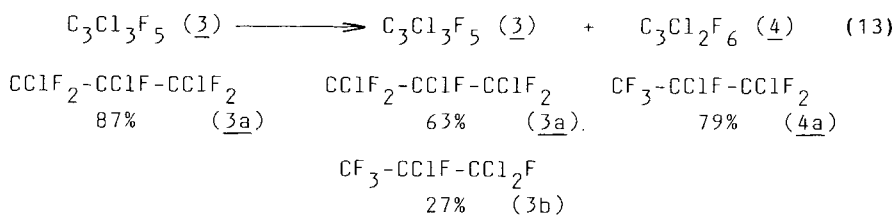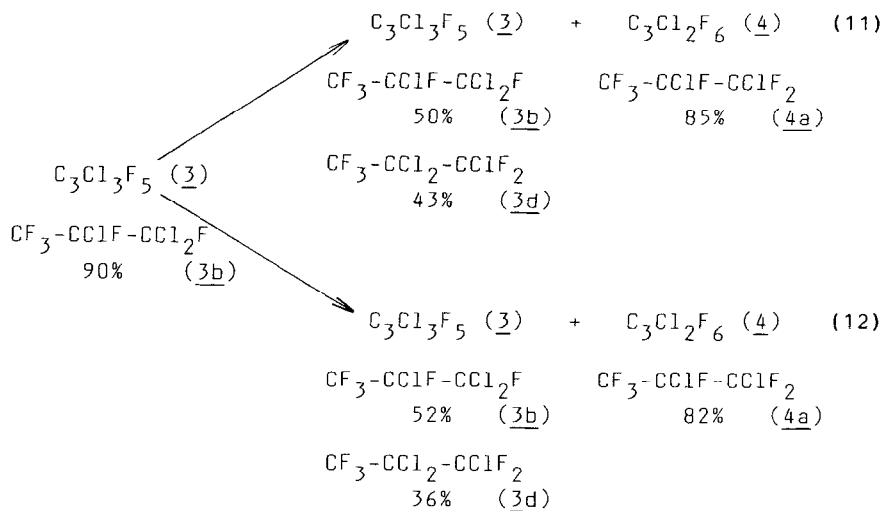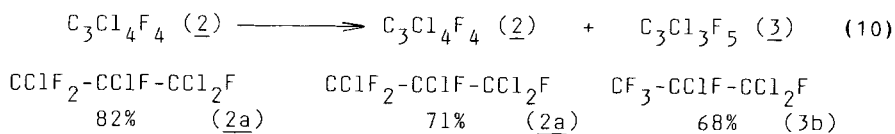
Scheme 2

reaction depended considerably on the reaction temperature, the chlorofluoropropane flow rate and the content of fluorine in its molecule, as shown in Scheme 3. The conditions and results of reactions are listed in Tables 1 and 2, respectively.

 Fluorination of pentachlorotrifluoropropane (reactions (5) and (6)) was performed in two ways. The fluorination at higher temperature and lower flow rate (reaction (5) yielded higher-fluorinated products, but at a cost of a substantial decrease in the yield and product purity, while the same

$$C_3Cl_3F_5 \; (\underline{3}) \quad + \quad C_3Cl_2F_6 \; (\underline{4}) \qquad (5)$$

$$CF_3\text{-}CClF\text{-}CCl_2F \qquad CF_3\text{-}CClF\text{-}CClF_2$$
$$73\% \quad (\underline{3b}) \qquad 85\% \quad (\underline{4a})$$

$$C_3Cl_5F_3 \; (\underline{1})$$

$$CClF_2\text{-}CClF\text{-}CCl_3$$
$$71\% \qquad (\underline{1a})$$

$$C_3Cl_4F_4 \; (\underline{2}) \quad + \quad C_3Cl_3F_5 \; (\underline{3}) \qquad (6)$$

$$CClF_2\text{-}CClF\text{-}CCl_2F \qquad CF_3\text{-}CClF\text{-}CCl_2F$$
$$68\% \quad (\underline{2a}) \qquad 83\% \quad (\underline{3b})$$

$$C_3Cl_4F_4 \; (\underline{2}) \longrightarrow C_3Cl_3F_5 \; (\underline{3}) \quad + \quad C_3Cl_2F_6 \; (\underline{4}) \qquad (7)$$

$$CF_3\text{-}CClF\text{-}CCl_3 \qquad CF_3\text{-}CClF\text{-}CCl_2F \qquad CF_3\text{-}CClF\text{-}CClF_2$$
$$48\% \quad (\underline{2b}) \qquad 43\% \quad (\underline{3b}) \qquad 65\% \quad (\underline{4a})$$

$$CClF_2\text{-}CF_2\text{-}CCl_3 \qquad CClF_2\text{-}CF_2\text{-}CCl_2F$$
$$37\% \quad (\underline{2c}) \qquad 28\% \quad (\underline{3c})$$

$$C_3Cl_4F_4 \; (\underline{2}) \longrightarrow C_3Cl_3F_5 \; (\underline{3}) \quad + \quad C_3Cl_2F_6 \; (\underline{4}) \qquad (8)$$

$$CF_3\text{-}CClF\text{-}CCl_3 \qquad CF_3\text{-}CClF\text{-}CCl_2F \qquad CF_3\text{-}CClF\text{-}CClF_2$$
$$78\% \quad (\underline{2b}) \qquad 38\% \quad (\underline{3h}) \qquad 92\% \quad (\underline{4a})$$

$$CClF_2\text{-}CClF\text{-}CClF_2$$
$$32\% \quad (\underline{3a})$$

$$C_3Cl_4F_4 \; (\underline{2}) \longrightarrow C_3Cl_3F_5 \; (\underline{3}) \quad + \quad C_3Cl_2F_6 \; (\underline{4}) \qquad (9)$$

$$CClF_2\text{-}CClF\text{-}CCl_2F \qquad CClF_2\text{-}CClF\text{-}CClF_2 \qquad CF_3\text{-}CClF\text{-}CClF_2$$
$$82\% \quad (\underline{2a}) \qquad 54\% \quad (\underline{3a}) \qquad 79\% \quad (\underline{4a})$$

$$CF_3\text{-}CClF\text{-}CCl_2F$$
$$35\% \quad (\underline{3b})$$

Scheme 3

$$C_3Cl_4F_4 \ (\underline{2}) \longrightarrow C_3Cl_4F_4 \ (\underline{2}) \quad + \quad C_3Cl_3F_5 \ (\underline{3}) \qquad (10)$$

$$\begin{array}{ccc}
CClF_2\text{-}CClF\text{-}CCl_2F & CClF_2\text{-}CClF\text{-}CCl_2F & CF_3\text{-}CClF\text{-}CCl_2F \\
82\% \quad (\underline{2a}) & 71\% \quad (\underline{2a}) & 68\% \quad (\underline{3b})
\end{array}$$

$$C_3Cl_3F_5 \ (\underline{3}) \quad + \quad C_3Cl_2F_6 \ (\underline{4}) \qquad (11)$$

$$\begin{array}{cc}
CF_3\text{-}CClF\text{-}CCl_2F & CF_3\text{-}CClF\text{-}CClF_2 \\
50\% \quad (\underline{3b}) & 85\% \quad (\underline{4a})
\end{array}$$

$$\begin{array}{c}
CF_3\text{-}CCl_2\text{-}CClF_2 \\
43\% \quad (\underline{3d})
\end{array}$$

$$C_3Cl_3F_5 \ (\underline{3})$$

$$\begin{array}{cc}
CF_3\text{-}CClF\text{-}CCl_2F \\
90\% \quad (\underline{3b})
\end{array}$$

$$C_3Cl_3F_5 \ (\underline{3}) \quad + \quad C_3Cl_2F_6 \ (\underline{4}) \qquad (12)$$

$$\begin{array}{cc}
CF_3\text{-}CClF\text{-}CCl_2F & CF_3\text{-}CClF\text{-}CClF_2 \\
52\% \quad (\underline{3b}) & 82\% \quad (\underline{4a})
\end{array}$$

$$\begin{array}{c}
CF_3\text{-}CCl_2\text{-}CClF_2 \\
36\% \quad (\underline{3d})
\end{array}$$

$$C_3Cl_3F_5 \ (\underline{3}) \longrightarrow C_3Cl_3F_5 \ (\underline{3}) \quad + \quad C_3Cl_2F_6 \ (\underline{4}) \qquad (13)$$

$$\begin{array}{ccc}
CClF_2\text{-}CClF\text{-}CClF_2 & CClF_2\text{-}CClF\text{-}CClF_2 & CF_3\text{-}CClF\text{-}CClF_2 \\
87\% \quad (\underline{3a}) & 63\% \quad (\underline{3a}). & 79\% \quad (\underline{4a})
\end{array}$$

$$\begin{array}{c}
CF_3\text{-}CClF\text{-}CCl_2F \\
27\% \quad (\underline{3b})
\end{array}$$

Scheme 3 (Cont.)

fluorination at a higher flow rate and lower temperature
(reaction (6)) afforded a reasonable yield of medium-
fluorinated substances. The same influence upon the yield

TABLE 1

Fluorinations. Reaction conditions and results

Run	Starting subst.		Reaction		Yield	Products Composition (% rel.)				
	Formula	(g)	temperature (°C)	time (h)	(%)	$C_3Cl_5F_3$	$C_3Cl_4F_4$	$C_3Cl_3F_5$	$C_3Cl_2F_6$	By-products
Fluorinations in the liquid phase (atmospheric pressure)										
1	$C_3Cl_5F_3$	900	120	9	75	0	60	40	0	0
2	$C_3Cl_4F_4$	850	180	21	72	0	0	100	0	0
Fluorinations in the liquid phase (autogenous pressure)										
3	$C_3Cl_5F_3$	351	200	120	71	0	27	67	5	1
4	$C_3Cl_5F_3$	433	200	30	76	10	82	8	0	0
Fluorinations in the vapour phase										
5	$C_3Cl_5F_3$	171	370	2	13.5	0	0	28	28.5	43.5
6	$C_3Cl_5F_3$	1417	360	5	54.5	0	35.5	57.5	1	6
7	$C_3Cl_4F_4$	165	365	2	28	0	0	56.5	17.5	22
8	$C_3Cl_4F_4$	154	360	1	53.5	0	0	71	21	8
9	$C_3Cl_4F_4$	166	370	2	38	0	0	43.5	24.5	32
10	$C_3Cl_4F_4$	252	360	0.7	79	0	71	27	0	2
11	$C_3Cl_3F_5$	182	390	4	48	0	0	13	71.5	15.5
12	$C_3Cl_3F_5$	161	380	1.7	31.5	0	0	60	30.5	9.5
13	$C_3Cl_3F_5$	161	370	3	61	0	0	57	23	20

TABLE 2

Isomeric composition of chlorofluoropropanes obtained

Chloro-fluoro-propane	Isomer	Content of isomers (% rel.); a = starting compound, b = product													
	Run	1		2		3		4		5		6		7	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
$C_3Cl_5F_3$	$CF_3CCl_2CCl_3$	7				7		7	2	7		7			
	$CClF_2CClFCCl_3$	71				71		71	30	71		71			
	$CCl_2FCF_2CCl_3$	3				3		3	4	3		3			
	$CClF_2CCl_2CCl_2F$	5				5		5	21	5		5			
	$CCl_2FCClFCCl_2F$	14				14		14	43	14		14			
$C_3Cl_4F_4$	$CF_3CClFCCl_3$		0	78	0		0		0				4	48	0
	$CClF_2CF_2CCl_3$		0	0	0		0		0				0	37	43
	$CF_3CCl_2CCl_2F$		6	15	2		2		6				20	8	28
	$CClF_2CClFCCl_2F$		82	7	68		68		84				68	2	7
	$CCl_2FCF_2CCl_2F$		5	0	5		5		5				6	5	22
	$CClF_2CCl_2CClF_2$		7	0	25		25		5				2	0	
$C_3Cl_3F_5$	$CF_3CF_2CCl_3$		0		0		0		0		0		0		0
	$CF_3CClFCCl_2F$		0		90		0		1		73		83		43
	$CClF_2CF_2CCl_2F$		3		0		3		3		2		1		28
	$CF_3CCl_2CClF_2$		10		8		9		11		15		8		7
	$CClF_2CClFCClF_2$		87		2		88		85		10		8		22
$C_3Cl_2F_6$	$CF_3CF_2CCl_2F$										0				0
	$CF_3CClFCClF_2$										87				65
	$CClF_2CF_2CClF_2$										0				13
	$CF_3CCl_2CF_3$										13				22

(Continued)

TABLE 2 (cont.)

Content of isomers (% rel.); a = starting compound, b = product

Chloro-fluoro-propane / Isomer	Run 8 a	8 b	9 a	9 b	10 a	10 b	11 a	11 b	12 a	12 b	13 a	13 b
$C_3Cl_4F_4$												
$CF_3CClFCCl_3$	78	0	0	0	0	5						
$CClF_2CF_2CCl_3$	0	38	0	35	0	0						
$CF_3CCl_2CCl_2F$	15	4	6	4	6	12						
$CClF_2CClFCCl_2F$	7	24	82	7	82	71						
$CCl_2FCF_2CCl_2F$	0	32	5	54	5	7						
$CClF_2CCl_2CClF_2$	0	2	7	0	7	5						
$C_3Cl_3F_5$												
$CF_3CF_2CCl_3$							0	0	0	0	0	0
$CF_3CClFCCl_2F$							90	50	90	52	90	27
$CClF_2CF_2CCl_2F$							0	0	0	0	0	1
$CF_3CCl_2CClF_2$							8	43	8	36	8	9
$CClF_2CClFCClF_2$							2	7	2	12	2	63
$C_3Cl_2F_6$												
$CF_3CF_2CCl_2F$							0	0	0	0	0	0
$CF_3CClFCClF_2$							3	85	3	82	3	79
$CClF_2CF_2CCl_2F$							10	0	10	0	10	2
$CF_3CCl_2CF_3$							87	15	87	18	87	19

(less pronounced) and product distribution was observed in the fluorination of tetrachlorotetrafluoropropane (reactions (9) and (10)). The fluorination of trichloropentafluoropropane ($\underline{3}$) at higher temperature and lower flow rate did not result in a substantial total yield decrease and the higher temperature was necessary for a sufficient fluorination rate (reactions (11) - (13)). As by-products of all these vapour-phase fluorination reactions, chlorofluoropropenes were obtained in most cases.

The isomer composition of the halogenopropanes prepared by the gas-phase fluorination was considerably affected by isomerisation analogous to the isomerisation of chlorofluoro-alkanes caused by aluminium trichloride [16], or aluminium trifluoride [17]. The isomerisation was probably catalysed by ferric salts, which, like aluminium halogenides, are Lewis acids. The isomerisation resulted in a double shift of the fluorine atoms in the propane skeleton, _i.e._ a migration from one terminal carbon atom towards the other one resulting in cumulation of the fluorine atoms at this end of the molecule (e.g. isomerisation of $CClF_2$-$CClF$-$CClF_2$ to CF_3-$CClF$-CCl_2F in reaction (13)), and a migration from the central carbon atom towards the terminal atoms (e.g. isomerisation of CF_3-$CClF$-CCl_2F to CF_3-CCl_2CClF_2 in reactions (11) and (12). Owing to the extensive isomerisation this fluorination method is not suitable for the preparation of 1,2,3-trichloropentafluoro-propane ($\underline{3a}$), which is an advantageous precursor of "perfluoro-allyl chloride". 1,2-Dichlorohexafluoropropane ($\underline{4a}$), the precursor of hexafluoropropene, prepared by this fluorination method, contained 10% - 20% of isomeric 2,2-dichlorohexa-fluoropropane (see Table 2).

^{19}F NMR SPECTRA OF CHLOROFLUOROPROPANES

As has been stated above, both the chlorofluoropropanes prepared by the addition of trichlorofluoromethane to chloro-fluoroethenes [10,11] and the chlorofluoropropanes prepared from them by some of the fluorination modifications are isomeric mixtures. Their precise identification by means of capillary gas chromatography, performed earlier [12,13], is

elaborate and requires careful comparison with authentic standards. We tried to develop another analytical method using ^{19}F NMR spectroscopy, useful for the determination of the composition of more complex mixtures of isomers. A second reason for studying ^{19}F NMR spectroscopy was that the ^{19}F NMR spectra of few chlorofluoropropanes have been published [1].

The starting point for assigning the individual signals to the corresponding halogenomethyl and halogenomethylene groups were published chemical shifts in earlier communications [1,18,19]. In the reaction products eighteen isomers of the four above mentioned chlorofluoropropanes were stepwise identified, i.e. all except two, viz. 1,1,1-trichloropenta-fluoropropane and 1,1-dichlorohexafluoropropane. Owing to the method of preparation used their absence in the reaction products was not surprising. The collected NMR data, i.e. the chemical shifts and coupling constants, are listed in Tables 3 and 4. A typical example of a studied spectrum is that in Fig. 1. All coupling constants are omitted for simplification and the spectrum is transformed to a line form. The Fig. 1 shows a spectrum of a mixture of four isomers of trichloro-pentafluoropropane fraction (3), prepared by fluorination of tetrachlorotetrafluoropropane (2, 48% 2b, 37% 2c; reactions (7), Table 2) with hydrogen fluoride in the vapour phase. The percentage content of the individual isomers was calculated from the integral intensities of the individual signals. In some cases, especially when low intensity signals were included, a manual correction of the zero line in the NMR spectra proved necessary.

The obtained NMR data indicate (Table 3) that the absolute values of the chemical shifts are increased with increasing fluorine content in the chlorofluoropropane molecule. This enhancement lies in the range from ca. 2.5 ppm/fluorine for the $-CF_3$ group to ca. 7 ppm/fluorine for the -CClF- group. The graphic illustration of these relationships, in which the band width represents the maximum shift differences for a given group, is shown in Fig. 2.

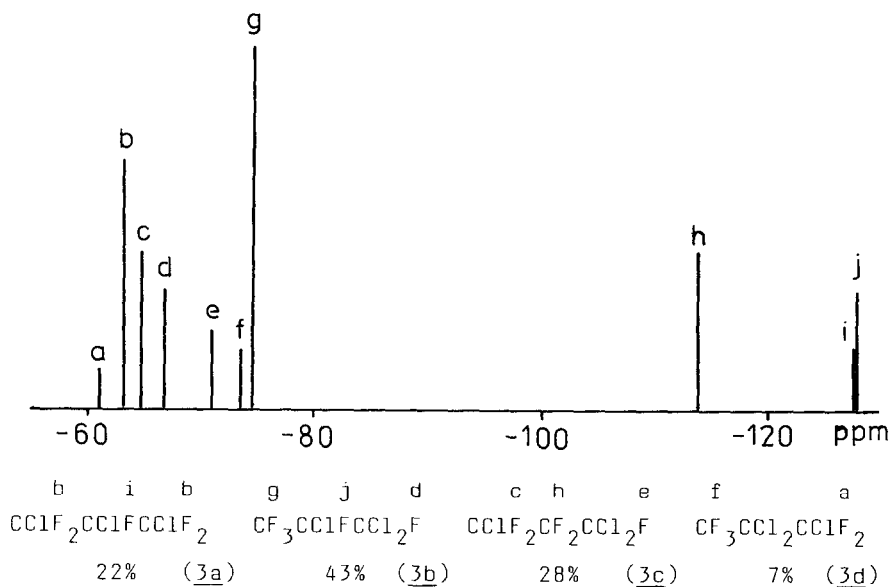When expressing the shift as a linear function of fluorine content the measured signals can be divided into two

b   i   b   g   j   d   c   h   e   f   a
$CClF_2CClFCClF_2$ $CF_3CClFCCl_2F$ $CClF_2CF_2CCl_2F$ $CF_3CCl_2CClF_2$

22%   (3a)   43%   (3b)   28%   (3c)   7%   (3d)

Fig. 1. ^{19}F NMR spectrum of trichloropentafluoropropane
        fraction 3 from fluorination (7) ($CFCl_3$ as internal
        standard).

groups: first, for signals of the $-CF_3$, $-CF_2-$ and $-CClF-$
groups the shift divergences in terms of the above dependence
are relatively small and do not exceed 2 ppm; second, these
divergences for signals of the $-CClF_2$ and CCl_2F groups are
considerably higher and amount from 4 to 6 ppm.

In the recently published paper [1] the empirical relations
for calculating the chemical shifts in fluorinated alkanes have
been derived. Using this method we made a calculation of the
chemical shifts in the ^{19}F NMR spectra of halogenopropanes we
prepared and compared these with the NMR data measured. The
differences between these data lay in the range from 2.5 to 4.5
ppm on the average for the individual groups and attained the
maximum value of 11 ppm. These differences are listed in Table
5. In Fig. 2 the dependences of the calculated shifts on the
fluorine content in the chlorofluoropropane are shown.
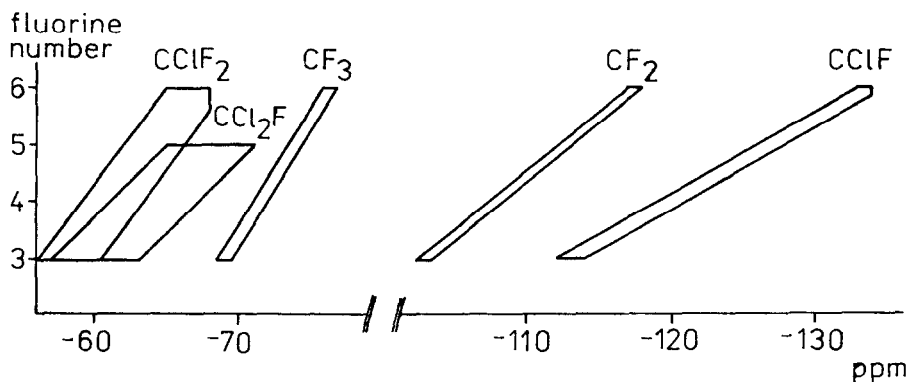
The measured spectra
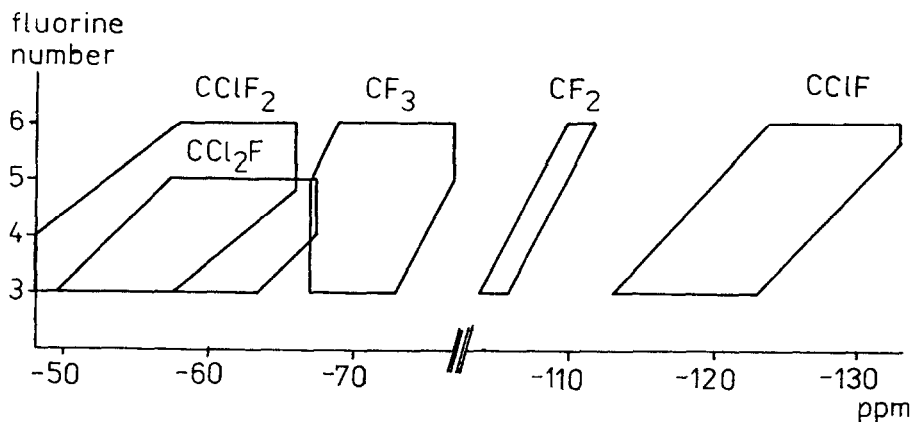
The calculated spectra

Fig. 2. Dependence of individual group shifts in chlorofluoro-
propanes based on the fluorine atoms present.

When applying the same linear function as above, the
divergences in calculated shifts excluding the $-CF_2-$ group
(2 ppm) were considerably higher and amounted from ca. 10 to

TABLE 3

^{19}F NMR data of chlorofluoropropanes obtained. Shifts and character of signals

Chloro-fluoro-propane	Isomer	Group: character of signal*; shift in ppm ($CFCl_3$ as internal standard)				
		$-CF_3$	$-CClF_2$	$-CCl_2F$	$-CF_2-$	$-CClF-$
$C_3Cl_5F_3$	$CF_3CCl_2CCl_3$	s -68.7				
	$CClF_2CClFCCl_3$		d -56.4 dd -58.7			d -113.8
	$CCl_2FCF_2CCl_3$			t -63.8	d -103.0	
	$CClF_2CCl_2CCl_2F$		d -55.9	t -57.8		
	$CCl_2FCClFCCl_2F$			d -60.3		t -115.9
$C_3Cl_4F_4$	$CF_3CClFCCl_3$	d -71.9				q -120.9
	$CClF_2CF_2CCl_3$		s -61.3		s -108.0	
	$CF_3CCl_2CCl_2F$	d -71.0		q -60.5		
	$CClF_2CClFCCl_2F$		ddd -59.2 ddd -61.2	ddd -64.1		ddd -121.1
	$CCl_2FCF_2CCl_2F$			t -66.6	t -108.7	
	$CClF_2CCl_2CClF_2$		s -58.6			
$C_3Cl_3F_5$	$CF_3CClFCCl_2F$	dd -74.5		dq -66.6		dq -127.9
	$CClF_2CF_2CCl_2F$		d -64.6	tt -70.9	d -113.8	
	$CF_3CCl_2CClF_2$	t -73.5	q -61.0			
	$CClF_2CClFCClF_2$		dt -62.6 ddd -63.6 dm -62.6 dm -63.6			m -127.6
$C_3Cl_2F_6$	$CF_3CClFCClF_2$	dt -77.0	ddq -64.7 ddq -65.9			ddq -135.0
	$CClF_2CF_2CClF_2$		s -67.8		s -119.2	
	$CF_3CCl_2CF_3$	s -75.8				

*s – singlet, d – doublet, t – triplet, q – quadruplet, m – multiplet

TABLE 4
^{19}F NMR data of chlorofluoropropanes obtained. Coupling constants (Hz).

Chloro-fluoro-propane	Isomer	Coupling constants for groups							
		-CF3			-CClF2			-CCl2F	
		-CClF2	-CCl2F	-CClF-	-CCl2F	-CF2-	-CClF-	-CF2-	-CClF-
C3Cl5F3	CF3CCl2CCl3	---							
	CClF2CClFCCl3				162		12 / 0		
	CCl2FCF2CCl3								
	CClF2CCl2CCl2F				14			5	
	CCl2FCClFCCl2F								15
C3Cl4F4	CF3CClFCCl3			5					
	CClF2CF2CCl3		13		163	21 / 10	11 / 5		
	CF3CCl2CCl2F								
	CClF2CClFCCl2F					0			7
	CCl2FCF2CCl2F				182 / 160		---	7	16
	CClF2CCl2CClF2	12							
C3Cl3F5	CF3CClFCCl2F		12	6					
	CClF2CF2CCl2F				173	13	0	7	17
	CF3CCl2CClF2	11 / 10	9						
	CClF2CClFCClF2						6		
C3Cl2F6	CF3CClFCClF2			7					
	CClF2CF2CClF2					0			
	CF3CCl2CF3		---						

TABLE 5

Differences between measured and calculated shifts in ^{19}F NMR of chlorofluoropropanes

Chlorofluoropropane	Isomer	Group				
		$-CF_3$	$-CClF_2$	$-CCl_2F$	$-CF_2-$	$-CClF-$
$C_3Cl_5F_3$	$CF_3CCl_2CCl_3$	-0.8				
	$CClF_2CClFCCl_3$		-3.4			1.5
	$CCl_2FCF_2CCl_3$			-0.5	1.5	
	$CClF_2CCl_2CCl_2F$		-3.6	-8.4		
	$CCl_2FCClFCCl_2F$			-0.9		1.1
$C_3Cl_4F_4$	$CF_3CClFCCl_3$	1.3				6.5
	$CClF_2CF_2CCl_3$		0.2		-1.4	
	$CF_3CCl_2CCl_2F$	0.3		-2.1		
	$CClF_2CClFCCl_2F$		-2.6	-9.4		-2.1
	$CCl_2FCF_2CCl_2F$			0.1	-0.5	
	$CCl_2FCCl_2CClF_2$		-11.0			
$C_3Cl_3F_5$	$CF_3CClFCCl_2F$	2.1		-2.8		-6.6
	$CClF_2CF_2CCl_2F$		0.3	-8.8	3.1	
	$CF_3CCl_2CClF_2$	-6.9	-4.2			
	$CClF_2CClFCClF_2$		-10.2		-3.6	
$C_3Cl_2F_6$	$CF_3CClFCClF_2$	-5.7	-2.3			-2.0
	$CClF_2CF_2CClF_2$		-7.6		-7.0	
	$CF_3CCl_2CF_3$	-0.1				

14 ppm. With exception of signals of the $-CClF_2$ and $-CCl_2F$ groups, however, there was virtually no overlapping of shifts and therefore the predictability for the other groups can be considered as relatively good, especially for the medium fluorinated chlorofluoropropanes. Thus, for the chlorofluoropropanes with a higher fluorine content (3,4), the empirical method after Ref. [1] provided systematically lower absolute values of shifts.

EXPERIMENTAL

The temperature data were uncorrected. GLC analyses were performed on a Chrom 41 (Laboratorní přístroje, Prague) instrument (FID, column diameter 0.3 cm, column length 380 cm carrier gas nitrogen, stationary phase silicon elastomer SE 301 on support Chromaton N-AW-DMCS (Lachema, Brno), grading 0.100 - 0.125 mm, concentration 10%, temperature 100°C). The NMR spectra were taken in deuteriochloroform on a Varian XL-100/15 (100 MHz, CW) and a Bruker 400 AM (400 MHz, FT) instruments.

Chemicals used

Antimony trifluoride was melted and finely ground before use. The catalyst for vapour-phase fluorinations (ferric chloride on charcoal support) was prepared after Ref. [20]. Pentachlorotrifluoropropane was prepared after Ref. [10], tetrachlorotetrafluoropropane and a separation of its isomers containing no $-CF_2-$ group after Ref. [11].

Liquid-phase fluorination at atmospheric pressure

Chlorine gas was introduced into antimony trifluoride in a reaction flask while stirring at ca. 100°C until it was absorbed (about 6 hrs.). After adding chlorofluoropropane dropwise to the resultant fluorination mixture, the reaction flask was heated in the range 120 - 150°C and crude

product was distilled off continuously through a Vigreux
column (60 cm).

Liquid-phase fluorination at autogenous pressure

Chlorine gas was introduced into antimony trifluoride in
a steel bomb fitted with a reflux condenser at ca. $100^{O}C$
until it was absorbed (about 24 hrs.). The bomb was charged
with starting chlorofluoropropane and then heated to ca.
$200^{O}C$. The composition of the chlorofluoropropane reaction
mixture was checked periodically by GLC and by measurement of
autogenous pressure. The crude product was obtained after
cooling the bomb by pouring off the upper organic layer.

Vapour-phase fluorination

A fluorination mixture containing hydrogen fluoride
(90% vol.) and chlorine (10% vol.) was introduced at the rate
of 25 - 50 l/h to a tubular reactor (length 80 cm, inner
diameter 12 cm) containing a catalyst packing consisting of
ferric chloride on a charcoal support. Simultaneously the
starting liquid chlorofluoropropane was added to the reactor
at a rate of 30 - 220 ml/h. The reactor was electrically
heated to 350 - $400^{O}C$. The crude product was collected in a
trap containing a concentrated aqueous solution of sodium
hydroxide cooled to 0 - $5^{O}C$.

Treatment of crude product

In the case of fluorination with antimony halogenides
the crude product was first washed twice with a two-fold
volume of dilute hydrochloric acid, then, like the crude
product from the vapour-phase fluorination, washed twice with
a two-fold volume of conc. aqueous solution of sodium
hydrogen carbonate, twice with water, dried with anhydrous
magnesium sulphate and fractionated.

REFERENCES

1   A. Battais, G. Baudvien, B. Boutevin and Y. Pietrasanta,
    J. Fluorine Chem., 31 (1986) 197.
2   A.M. Lovelace, D.A. Rausch and W. Postelnek, Aliphatic
    Fluorine Compounds, Reinhold Publ. Corp., New York,
    1958, pp. 7, 15.
3   H.W. Daudt and M.A. Youker, U.S. Pat. 2 005 707 (1935);
    Chem. Abstr., 29 (1935) 5123.
4   E.T. McBee and R.M. Robb, U.S. Pat. 2 578 721 (1951);
    Chem. Abstr., 46 (1952) 6156.
5   A.L. Henne and M.W. Renoll, J. Am. Chem. Soc., 61
    (1939) 2489.
6   J.D. Weaver, U.S. Pat. 4 438 088 (1984); Chem. Abstr.,
    101 (1984) 22972.
7   J.T. Maynard, J. Org. Chem., 28 (1963) 112.
8   O. Paleta in P. Tarrant (Ed.), 'Fluorine Chemistry Reviews'
    Vol. 8, Marcel Dekker, New York, 1977, p. 39.
9   D.D. Coffman, R. Cramer and G.W. Rigby, J. Am. Chem. Soc.,
    71 (1949) 979.
10 O. Paleta and A. Pošta, Collect. Czech. Chem. Commun.,
    32 (1967) 1427.
11 O. Paleta, A. Pošta and K. Tesařík, Collect. Czech. Chem.
    Commun., 36 (1971) 2257.
12 K. Tesařík, A. Pošta and O. Paleta, Collect. Czech. Chem.
    Commun., 33 (1968) 596.
13 O.K. Guha, K. Tesařík, O. Paleta and A. Pošta,
    Chromatographia, 4 (1971) 119.
14 R.P. Ruh and R.A. Davis, U.S. Pat. 2 745 886 (1956);
    Chem. Abstr., 51 (1957) 1245.

15 R.F. Sweeney and C. Woolf, Ger. Pat. DE 1 237 084 (1967);
    Chem. Abstr., 67 (1967) 53630.

16 W.T. Miller, E.J. Fager and P.H. Griswald, J. Am. Chem.
    Soc., 72 (1950) 705.

17 M. Vecchio, G. Gropelli and J.C. Tatlow, J. Fluorine Chem.,
    4 (1974) 117.

18 R.E. Banks, 'Fluorocarbon and Their Derivatives', MacDonald,
    London, 1970, p. 234.

19 O. Paleta, J. Kvíčala, J. Günter and V. Dědek, Bull. Soc.
    Chim. France, (1986) 920.

20 J. Kvíčala, O. Paleta and V. Dědek, Czechoslov. Pat. Appl.
    9475-86 (1986).