ALUMINIUM CHLORIDE INDUCED ISOMERISATION OF 1,1,2-TRICHLOROTRIFLUOROETHANE AND 1,2-DIFLUOROTETRACHLOROETHANE*

Oldřich PALETA, František LIŠKA, Antonín POŠTA and Václav DĚDEK

Department of Organic Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

Received December 12th, 1978

Under comparable conditions, the isomerisation of 1,1,2-trichlorotrifluoroethane (*I*) to 1,1,1-trichlorotrifluoroethane (*II*) is more difficult than the isomerisation of 1,2-difluorotetrachloroethane (*III*) to 1,1-difluorotetrachloroethane (*IV*). Advantageously, *III* was isomerised to *IV* in the presence of *I* or *II*. The degree of isomerisation of the starting compounds *I* and *III* was 95—99%, the preparative yield of *IV* being 65—74%. The C—F bond energies in *I*—*IV* were derived from correlation diagram and the physico-chemical aspects of the isomerisations are discussed.

The isomerisation of chlorofluoroalkanes with aluminium chloride was studied for the first time by Miller and collaborators[1-3] who discovered thus a reaction in which vicinal fluorine atoms are shifted to one carbon atom. This rearrangement is accompanied by side reactions consisting in replacement of the fluorine atoms by halogen atoms of the catalyst. This finding of Miller was utilized in many studies[4-11] concerning the preparation of various polyfluorohalogenoalkanes some of which found use in laboratory or in industry[8-12]. Yields of such isomerisations range from about 40% for polychloroethanes[1-3] to about 90% for bromofluoroethanes[4,5,11]. The hitherto obtained results show that there are no exact quantitative data on the reaction of chlorofluoroethanes with aluminium chloride. Therefore, we decided to study in more detail the reaction of 1,1,2-trichlorotrifluoroethane (*I*; Ledon 113) and 1,2-difluorotetrachloroethane (*III*; Ledon 112) with this reagent. The compounds *I* and *III* represent suitable models for finding optimum isomerisation conditions; they may also afford information about the relative reactivity of the trifluoromethyl, chlorodifluoromethyl and dichlorofluoromethyl groups towards aluminium chloride.

Previous investigations have shown[2,7] that the reaction of polyfluorohalogenoalkanes with aluminium chloride or bromide affords a wide spectrum of products. In addition to the already mentioned halogenation of starting compounds and intermediates, another side reaction has been observed, namely the disproportionation

---

[*] Part XXI in the series Organic Compounds of Fluorine; Part XX: This Journal *43*, 2932 (1978).

of halogenoethanes and halogenopropanes to perchloroethylene[2,7,13]. Three factors, operating in the isomerisation of 1-chloro-1,2,2-trifluorodibromoethane were observed[11]: induction period, temperature and the amount of catalyst. Operation of the two last factors is reflected markedly by the fact that below a certain temperature and with amounts of catalyst below a certain "limit" the reaction rate substantially drops and the induction period is unproportionally long. On the basis of these facts we have chosen standard conditions for the reactions of compounds *I* and *III* with aluminium chloride which, according to the mentioned data[2,7,11,13] proceed heterogeneously. Aluminium chloride for industrial purposes was employed (kind *A*, kind *B*).

Reaction of *I* with aluminium chloride was studied at 48°C, *i.e.* at the highest temperature at which the reaction mixture did not boil. The reaction led to 1,1,1-trichlorotrifluoroethane (*II*) and 1,1-difluorotetrachloroethane (*IV*) as principal products[2]. The reaction course is depicted in Fig. 1 which at the same time illustrates the dominant role of the catalyst quality on the length of the induction period. On the other hand, chlorination of the compound *I* takes place almost without any induction period and in the first reaction phase it predominates over the isomerisation. When the concentrations of *II* and *IV* in the reaction mixture become the same, there is no further increase in the concentration of *IV*. It follows also from Fig. 1 that the amount of the chlorinated side product *IV* (26 ± 2%) does not depend on the quality of the aluminium chloride employed. The formation of compound *IV* which practically does not contain the isomer *III* proves that the C—F bond in the CCl_2F group is more sensitive towards halogenation with aluminium chloride than the same bond in the $CClF_2$ group.

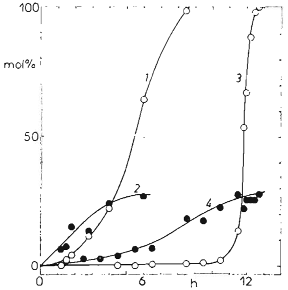


FIG. 1

Reaction of 1,1,2-Trichlorotrifluoroethane (*I*, Ledon 113) with Aluminium Chloride

1, *3* 1,1,1-Trichlorotrifluoroethane (*II*); *2*, *4* 1,1-Difluorotetrachloroethane (*IV*); *1*, *2* reaction with aluminium chloride *B*; *3*, *4* reaction with aluminium chloride *A*.

In order to find optimum conditions for the isomerisation of *III*, we studied the effect of temperature and of the amount of catalyst (Fig. 2). It is obviously possible to isomerise more than 90% of the starting compound *III* during 2–3 h at 45°C, using about 10% of aluminium chloride (related to the weight of *III*) (curve *1*). With 5% of the catalyst (curve *4*) only 32% of *III* were isomerised during the same time. Even when the reaction was carried out at 60°C (curve *3*), the reaction rate did not increase substantially. However, we have found that high yields can be obtained when the isomerisation is carried out in 1,1,1-trichlorotrifluoroethane (*II*; curve *2*), the extension of reaction time, as compared with an undiluted mixture (curve *1*), being proportional to the dilution.

Together with the isomerisation rate measurement we analysed the reaction mixture (Fig. 3) which, in addition to the product *IV*, contained fluoropentachloroethane (*V*), hexachloroethane (*VI*) and tetrachloroethylene (*VII*). Curve *1* shows a decrease in the content of *III* and *IV*, indicating side reactions, mainly chlorination. Curve *3*, describing the percentage of the side product *V*, corresponds in its initial phase to the decrease in the content of *III* and *IV*. However, as soon as the reaction mixture contains about 30% of *IV*, the amount of *V* reaches its maximum and then decreases, probably

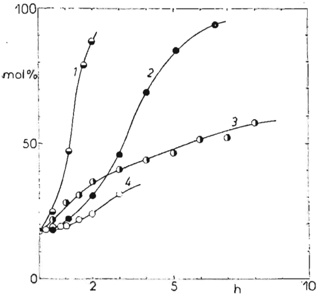


FIG. 2

Isomerisation of 1,2-Difluorotetrachloroethane (*III*, Ledon 112; 521 g, 2·56 mol)

1 45°C, 50 g (0·375 mol) of $AlCl_3$; *2* 45°C, 50 g (0·375 mol) of $AlCl_3$, 330 ml of 1,1,1-trichlorotrifluoroethane (*II*); *3* 60°C, 25 g (0·187 mol) of $AlCl_3$; *4* 45°C, 25 g (0·187 mol) of $AlCl_3$.

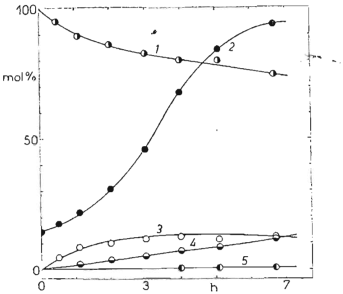
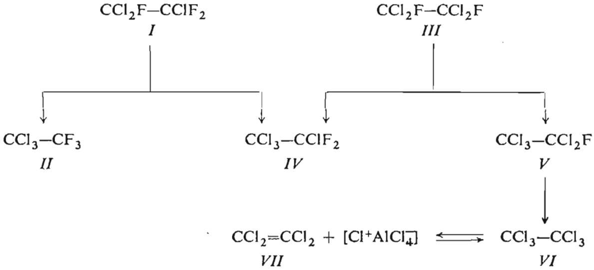


FIG. 3

Composition of Reaction Mixture Arising by Isomerisation of Compound *III* with Aluminium Chloride (conditions see Fig. 2, curve 2)

1 Sum of *III* + *IV* (g.l.c.); *2* *IV* (IR); *3* *V* (g.l.c.); *4* *VI* (g.l.c.); *5* *VII* (g.l.c.).

due to transformation of *V* to hexachloroethane. The percentage of the latter compound (curve *4*) linearly increases and in the end it is practically the same as that of *V*. The sum of the side products *V*–*VII* corresponds to the decrease in the amount of *III* and *IV*. In the same manner we followed other isomerisations represented by curves in Fig. 2. A temperature increase from 45°C to 60°C enhances both the isomerisation and the chlorination but results in substantially increased amount of the formed hexachloroethane.



An important conclusion is that the compound *III* can be isomerised in a suitable solvent[14]. The use of solvent is advantageous in many respects; *e.g.* the stirring in the end is facilitated, temperature can be easily controlled, *etc.* We therefore investigated isomerisation of the compound *III*, using *I* as solvent (Fig. 4). Curves *1* and *2* show that at 45°C and in the presence of 15% (wt) of aluminium chloride the starting compound *III* is practically completely converted to the isomer *IV* during 7–8 h whereas the conversion of *I* was about 50%. The shape of the curve *4* (corresponding to *II*) differs only slightly from that of the curve *3* (starting compound *I*) indicating that during the reaction almost no chlorination of *I* to *IV* takes place. The same situation was found for the isomerisation of *III* in a mixture of *I* and *II*.

Thus, of the possible transformations (*i.e.* isomerisation and chlorination), isomerisation of *III* at a given temperature is the fastest reaction whereas chlorination of *II* is the slowest one. Chlorination of *I* and *III* proceeds at a medium rate but faster than chlorination of the product *IV*. We can thus confirm that the overal reactivity of chlorofluoromethyl groups in halogenoethanes towards aluminium chloride decreases in the order $CCl_2F > CClF_2 > CF_3$. If halogenation can take place in addition to isomerisation, the latter is the principal reaction, probably due to a lower activation energy. The mentioned reactivity order for halogenomethyl groups is in accord with that derived previously[2] only for isomerisation reactions.

The isomerisation of the compounds *I* and *III* is exothermic. As far as we know, thermochemical data for the compounds *I–IV*, as well as the enthalpies of the isomerisations studied in this paper, have not been measured. In the series of fluorinated methanes the thermochemical measurements have shown[15] that the C–F bond energy increases with an increasing number of fluorine atoms in the molecule (Table I). On the other hand, it is remarkable that the C–Cl bond energy is constant within the limits of experimental error[15,16]. This property of C–F bonds is reflected by the exothermic course of disproportionation reactions of chlorofluoromethanes, catalysed with aluminium chloride, which are used also preparatively[16–19].

The compounds *I–IV* can be regarded upon as chlorofluoromethanes of the type R—CCl_mF_n, where $(m + n) = 3$ and $n = 0$, or 2, $m = 1$, 2 or 3, and the group R is CCl_3, CCl_2F or $CClF_2$. Chemical experience confirmed that compounds *I* and *III* undergo an exothermic isomerisation, resulting in cumulation of the fluorine atoms on one carbon atom; it can thus be assumed that the driving force of the isomerisation is also due to the energetic effect of C–F bonds. In order to assess the enthalpy of the isomerisation reactions of compounds *I* and *III* we tried to derive the missing data on the C—F bond energies in compounds *I–IV*. According to the experimental data given in Table I the bond length in halogenomethanes decreases with increasing bond energy. From the graphical representation (Fig. 5) it is obvious that, in spite of the relatively large scatter of the experimental data, the relation between the C—F

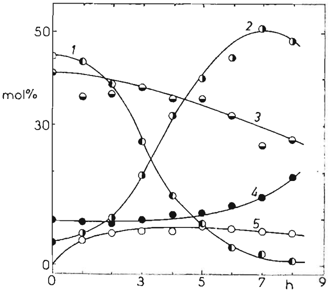


FIG. 4

Reaction of a Mixture of *I* and *III* with Aluminium Chloride

1 *III*; 2 *IV*; 3 *I*; 4 *II*; 5 *V*.

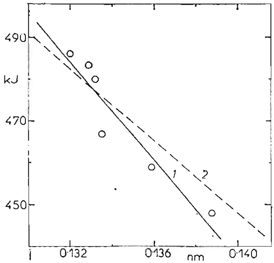


FIG. 5

Plot of Bond Length against Bond Energy for C—F Bonds in Fluorinated Methanes bond length and energy in halogenomethanes is approximately linear. The regression straight line *1* which does not include the data for CCl_3F, has a more significant

TABLE I

C—F Bond Lengths and Energies in Some Fluorinated Methanes and Ethanes

Compound	Bond length[a], nm	Bond energy		Ref.
		kJ . mol^{-1}	kcal . mol^{-1}	
CH_3F	0·1385			20
	0·1391	448	107	15
	(0·1388)[b]			
CH_2F_2	0·1358	459	109·6	15
	0·1360			21
	(0·1359)			
CHF_3	0·1328			20
	0·1332	480	114·6	15
	0·1334			21
	(0·1332)			
CF_4	0·1317	486	116	15
	0·1323			20
	(0·1320)			
CCl_3F	0·140[b]	458	109·3	15
CCl_2F_2	0·1335[b]			15
	0·135	467	111·5	20
$CCl F_3$	0·1328	483·5	115·5	15
	0·1330			21
	(0·1329)			
CH_3-CF_3	0·1335	475[c]	113[c]	20
	0·1346	469[c]	112[c]	21
CHF_2-CF_2-F	1·1336	474·5[c]	113[c]	21
CF_3-CF_3	0·132	484[c]	115·5[c]	20
	0·1326	480·5[c]	114·5[c]	21
$CClF_2$-$CClF_2$	0·133[d]	478[c]	114[c]	20
CCl_2F-CClF-F	0·1329	478·5[c]	114	20
CCl_2F-CCl_2F	0·138[e]	449·5[c]	107[c]	20

[a] The values are given without experimental error; [b] in parentheses are given mean values used in the linear correlation; [c] values taken from correlation line *1* (Fig. 5); [d] C—C bond length 0·154 ± 0·004; [e] C—C bond length 0·154 ± 0·006.

correlation coefficient (0·9464) than the regression line *2* (0·8834) in which these data are included. Apparently, the mentioned data for CCl_3F are not accurate enough to be included in the correlation and therefore in the final analysis they were omitted. For the mentioned series of fluorinated methanes, representing a practically identical hybridisation type, we assume on the basis of this correlation that a given bond length corresponds to a bond energy whose approximate value is given by the corresponding point on the regression line *1*.

In the perhalogenated ethanes of the type R'—CF_3 the substituent R' affects the C—F bond length (ref.[21] and Table I). Also in this case, a change in bond length will be accompanied by a change in bond energy. Since the perhalogenated ethanes of the mentioned structure R—CCl_mF_n represent, within acceptable limits, the same hybridisation type as fluorinated methanes, we assume that the correlation between the C—F bond length and its energy can be extended to chlorofluoroethanes *I*–*IV*. It further follows from Table I that composition of the trihalogenomethyl group R (compounds *I* and *III*) does not practically influence (within the experimental error) C–F bond lengths on the next carbon atom. Within the same experimental error the C–C bond lengths are independent of the number of fluorine atoms in perhalogenated fluoroethanes[21]. Table I lists the C–F bond energies in halogenoethanes, as taken from the regression line.

Using the derived C–F bond energies in *I*–*IV*, *i.e.* for R—CF_3 481 kJ . mol^{-1} (115 kcal . mol^{-1}), for R—$CClF_2$ 477 (114) and for R—CCl_2F 450 (107), we calculated approximate enthalpy values (Table II). Calculations show a greater enthalpy for the isomerisation *III* → *IV*, in accord with the qualitative observation.

The final distribution of the isomers *I* and *II*, *III* and *IV* in the reaction mixture after prolonged time (20–25 h) can be regarded to be close to the equilibrium composition (98·1% *II* and 1·9% *I*; 99·2% *IV* and 0·8% *III*). The approximate entropy

TABLE II

Enthalpy Differences for the Isomerisations *I* → *II* and *III* → *IV*

Reaction	Enthalpy, kJ . mol^{-1}
CCl_2F-$CClF_2$ → CCl_3-CF_3 *I* *II*	$450 + (2 . 477) - (3 . 481) = -39$
CCl_2F-CCl_2F → $CClF_2$-CCl_3 *III* *IV*	$(2 . 450) - (2 . 477) = -54$

changes, ΔS°, can be calculated from the relationship between the equilibrium constant of the reaction and the corresponding Gibbs free energy change, ΔG°, the enthalpy value being known. For the reaction *I* → *II* the ΔS° value amounts to -98 J . . grad^{-1} mol^{-1}, for the reaction *III* → *IV* -144 J grad^{-1} mol^{-1}. In the studied cases, the isomerisation represents a process reverse to the "statistical" formation of the compounds *I* and *III* by fluorination reaction (see the composition of the technical Ledon 113 and Ledon 112, given in the Experimental), so that it is obvious that the isomerisation entropy will be negative. The calculated absolute ΔS° values are very high, apparently as a consequence of the previous approximation, and it is likely that the real values are lower. The higher ΔS° value for the reaction *III* → *IV* than for *I* → *II* is in accord with the relatively larger symmetry change in going from *III* to *IV*, *i.e.* from a completely symmetric structure to a completely asymmetric one; on the other hand, in the transformation of *I* to *II*, already the starting compound is asymmetric and this asymmetry merely increases during the reaction.

EXPERIMENTAL

The temperature data are uncorrected. Gas–liquid chromatography was performed on a Chrom 3 chromatograph (Laboratorní přístroje, Prague) with flame-ionisation detector; support Chromaton N-AW-DMCS (Lachema, Brno). The IR spectra were taken on a Perkin–Elmer 325 instrument (Bodenseewerk), the NMR spectra were measured on a Varian XL-10015 (Palo Alto) instrument.

Chemicals

1,1,2-Trichlorotrifluoroethane (*I*, Ledon 113) was a technical product, containing about 2—4% of the isomer *II* (Spolek pro chemickou a hutní výrobu, Ústí n. Labem, Czechoslovakia). It was purified as described further. 1,2-Difluorotetrachloroethane (*III*, Ledon 112) was obtained by fractionation of the technical product which was washed with sodium hydrogen carbonate solution and water and dried over calcium chloride. After fractionation (b.p. 90—92°C) it contained 10—15% of the isomer *IV*.

Analytical Standards

1,1,2-*Trichlorotrifluoroethane* (I): The technical fractionated product was purified by photochemically initiated chlorination according to ref.[22]. The standard *I* was 99·95% pure according to gas–liquid chromatography (poly(butanediol succinate) and silicon elastomer E 301; 360 cm column, 30—60°C, carrier gas nitrogen) and ^{19}F-NMR spectra (Table III).

1,1,1-*Trichlorotrifluoroethane* (II): The standard compound was prepared by isomerisation of the fractionated technical product with aluminium chloride at 48°C for 20 h (for amounts, see Fig. 2). The reaction mixture was decomposed with water, the organic layer washed with water till the reaction was neutral and dried over anhydrous calcium chloride. Fractionation afforded *II*, b.p. 45—46°C, which was shown (^{19}F-NMR, Table III) to contain 1·9% of the isomer *I*.

TABLE III

^{19}F-NMR Spectra of Compounds *I*—*V*

Chemical shifts in ppm relative to CCl_3F; s singlet, d doublet, t triplet.

No	Compound	Solvent	Chemical shift	Character of the signal
I	$CCl_2F-CClF_2$	$CDCl_3$	72·0; 68·0	t (CF); d (CF_2)
II	CCl_3-CF_3	$CDCl_3$	82·6	s
III	CCl_2F-CCl_2F	$CDCl_3$; CCl_4	67·8; 67·9	s
IV	$CClF_2-CCl_3$	$CDCl_3$, CCl_4	65·1; 65·2	s
V	CCl_2F-CCl_3	$CDCl_3$; CCl_4		s

1,2-*Difluorotetrachloroethane* (III): Technical fractionated Ledon 112 (750 g; 3·68 mol), containing about 10% (molar) of the isomer *IV*, was heated for 70 h at 80—110°C under stirring with 60% oleum (500 ml) and catalysts (5 g of mercuric oxide; 5 g of lead dioxide). During the reaction the distillate boiling under 40°C was collected; low-boiling products were condensed in a trap immersed in dry ice. By this procedure the halogenoalkane *IV* was hydrolysed preferentially[10]. The unreacted compound *III* was separated by distillation, the distillate was washed with dilute sodium hydroxide, water and dried over anhydrous magnesium sulfate. The product was fractionated under nitrogen: after acidic components boiling below 91°C, the main fraction, b.p. 91—92°C, was collected (156 g). It represented the compound *III*, containing 0·05—0·06% (mol) of the isomer *IV* (^{19}F-NMR; Table III).

1,1-*Difluorotetrachloroethane* (IV): This analytical standard was prepared analogously as described for the compound *II*. Fractionation afforded *IV*, b.p. 90—92°C, containing 0·48% of the isomer *III* (^{19}F-NMR; Table III).

Isomerisation of 1,2-Difluorotetrachloroethane (*III*) and 1,1,2-Trichlorotrifluoroethane (*I*)

Prior the reaction, the starting compounds *I* and *III* were dried for 20 h over molecular sieve Potasit 3A (Lachema). Relative concentrations of the isomeric pairs *I*—*II*, *III*—*IV* were followed during the reaction using the non-overlapping IR-bands and the ^{19}F-NMR spectroscopy (Table III). Absorption maxima: compound *I* 1106 cm^{-1}; *II* 1247 cm^{-1}, *III* 1110 cm^{-1}, *IV* 1160 cm^{-1} (for the IR spectra of compounds *I*—*IV* see ref.[23]). The content of compounds *I*—*VII* in the reaction mixture was determined by ^{19}F-NMR spectra and gas–liquid chromatography (from the peak areas and calibration graphs).

The reaction samples were worked up in the following way: The withdrawn sample (2—3 ml) was added to tetrachloromethane (5 ml) and water (10 ml), shaken until the aluminium chloride dissolved, the oily layer was washed twice with water and dried over phosphorus pentoxide. After separation from the drying agent, the sample was analysed by gas–liquid chromatography (10% silicone elastomer E 301, 360 cm column, 40—120°C, nitrogen) or by NMR spectroscopy. The fraction 40—50°C was taken for measuring the compounds *I*—*II*, fraction 80—95°C for

III—*IV*. In the end of the isomerisation of *III* without solvent, the samples were sucked into a heated tube.

A) *Isomerisation of* III: A mixture of the compound *III* and aluminium chloride was stirred in a thermostated bath at 45°C (for the amounts see Figure 2). After the reaction had ended, Ledon 113 (250 ml) was added to the stirred mixture at 40°C, followed by stepwise addition of water (200 ml). The mixture was stirred till the aluminium chloride dissolved, another portion of Ledon 113 was added (250 ml), the oily layer was washed three times with water and dried over anhydrous calcium chloride. The product *IV* was obtained in 65—74% yield; isomer purity 95—99% (according to IR spectra).

B) *Isomerisation of the compound* III *in a solvent*: A mixture of *III* (1 111 g; 5·45 mol; content 9·9% mol of *IV*) trichlorotrifluoroethane (*I*, 1070 g, 5·71 mol; content 19% mol of *II*) and aluminium chloride (150 g; 1·12 mol) was stirred at 45°C for 9 h. The mixture was then worked up according to the procedure *A*. The preparative yield of *IV* was 70—74%, isomer purity 98·4—99·2% (^{19}F-NMR spectra).

Isomerisation and chlorination of compound I: The reaction was carried out and followed in an analogous manner as described under *A*, starting from 501 g (2·67 mol) of *I* and 47 g (0·352 mol) of aluminium chloride. The reaction mixture was worked up as described for the preparation of standards.

The spectral measurements were carried out in the Department of NMR *Spectroscopy (Dr P. Trška, Head) and in the Department of Absorption Spectrometry (Dr A. Muck, Head) of this Institute. This help is gratefully acknowledged.*

REFERENCES

1. Miller W. T.: J. Amer. Chem. Soc. *62*, 993 (1940).
2. Miller W. T., Fager E. W., Griswald P. H.: J. Amer. Chem. Soc. *72*, 705 (1950).
3. Miller W. T., Fager E. W.: U.S. 2,598,411 (1952); Chem. Abstr. *47*, 4357 (1953).
4. Calfee J. D., Florio P. A.: U.S. 2,469,290 (1949); Chem. Abstr. *43*, 5789 (1949).
5. Goerrig D.: Ger. Offen. 1,039,503 (1958); Chem. Abstr. *54*, 22358 (1960).
6. Goerrig D.: Ger Offen. 1,052,390 (1959); Chem. Abstr. *55*, 5347 (1961).
7. Burton D. J.: *Thesis.* Cornell University, 1961. Diss. Abstr. 22, 2190 (1962).
8. Madai H., Müller R.: J. Prakt. Chem. *19*, 83 (1962).
9. Hudlický M.: Czech. 114, 121 (1965); Chem. Abstr. *64*, 6495 (1966).
10. Pošta A., Paleta O., Hemer I.: This Journal *32*, 2301 (1967).
11. Paleta O., Liška F., Pošta A.: This Journal *35*, 1302 (1970).
12. Larsen E. R. in the book: *Fluorine Chemistry Reviews* (P. Tarrant, Ed.), Vol. 3, p. 1. M. Dekker, New York 1969.
13. Prins H. J.: J. Prakt. Chem. *89*, 414, 415 (1914).
14. Dědek V., Paleta O., Pošta A., Liška F., Lukáč J., Šimon J., Šimek S.: Czech. 171, 526 (1974).
15. Patrick C. R. in the book: *Advances in Fluorine Chemistry* (M. Stacey, J. C. Tatlow, A. G. Sharpe, Ed.), Vol. 2, p. 1. Butterworths, London 1961
16. Hine J.: J. Amer. Chem. Soc. *85*, 3239 (1969).
17. Murray W. S.: U.S. 2,426,637 (1947).
18. Murray W. S.: U.S. 2,426,638 (1947).

19. Pailthorp J. R.: U.S. 2,694,739 (1954).
20. Iwasaki M.: Bull. Chem. Soc. Jap. *32*, 205 (1959).
21. Yokozeki A., Bauer S. H. in the book: *Topics in Current Chemistry*, Vol. 53, p. 71. Springer, New York 1975.
22. Dědek V., Pošta A., Bárta M., Morštadt J., Roubal M., Šiler J., Vachta J.: Czech. Appl. PV 3847-74.
23. Nielsen J. R., Liang C. Y., Smith D. C.: J. Chem. Phys. *21*, 383 (1953).

Translated by M. Tichý.