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ADDITION OF 1,2-DIBROMO-1-CHLOROTRIFLUOROETHANE TO CHLOROTRIFLUOROETHYLENE INDUCED BY UV-RADIATION. SYNTHESIS OF PERFLUORO-1,3-BUTADIENE AND PERFLUORO-1,3,5-HEXATRIENE

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SUMMARY

Photochemically initiated reaction of 1,2-dibromo-1-chlorotrifluoroethane (II) with chlorotrifluoroethylene (I) gave 38% 1,4-dibromo-2,3-dichlorohexafluorobutane (III) and 19% 1,6-dibromo-2,3,5-trichlorononafluorohexane (IV) in addition to the higher telomers. Dehalogenations of III and IV yielded perfluoro-1,3-butadiene (VI) and perfluoro-1,3,5-hexatriene (VIII) with 3-chlorononafluoro-1,5-hexadiene (VII), respectively. Photochemical reduction of butane III with 2-propanol resulted in a preferential reduction of C-Br bonds, and from 2,3-dichloro-1,1,2,3,4,4-hexafluorobutane (IX) thus formed, esters of difluoroacetic acid were prepared by dehalogenation of IX and subsequent oxidation and esterification of the product. The photochemical reduction of hexane IV gave a mixture of 79% trichlorononafluorohexane XII and 21% dichlorononafluorohexane XIII. The mechanism of formation of the unusual products of the title addition reaction is discussed.

INTRODUCTION

The additions of 1,2-dibromo-1-chlorotrifluoroethane (II) to alkenes [1,2] and fluoroalkenes [3] catalyzed by peroxides have been described, and it has been found that with, the increasing fluorine content in the fluoroalkene molecule the yield of low-molecular adducts decreases as the tendency to telomerization increases. A photochemically induced addition of II to I has been also described [4], stating that the prevalent telomers are $Br(CClFCF_2)_nBr$, where $n \geq 5$, without giving their structure.

RESULTS AND DISCUSSION

In this paper we describe the addition reaction of 1,2-dibromo-1-chlorotrifluoroethane (II) to chlorotrifluoroethylene (I) initiated by ultraviolet radiation giving low-molecular adducts in a satisfactory yield. The addition was performed under relatively intensive UV-irradiation of the reaction mixture and maintaining a low concentration of alkene I in the course of reaction [5,6]. We found that under these conditions 38% of a butane fraction, 19% of a hexane fraction and 43% of a higher telomers fraction are formed. The butane fraction is composed of more than 90% 1,4-dibromo-2,3-dichlorohexafluorobutane (III), the hexane fraction contains mainly 1,6-dibromo-2,3,5-trichlorononafluorohexane (IV), and a substantial part of the higher telomers fraction, b.p. 150-156°C/2.13 kPa, is represented by 1,8-dibromo-2,4,5,7-tetrachlorododecafluorooctane (V).

$$\underset{\mathrm{I}}{CClF{=}CF_2} + \underset{\mathrm{II}}{Br{-}CClFCF_2{-}Br} \xrightarrow{(UV)} Br{-}(CF_2CClF)_n(CClFCF_2)_m{-}Br$$

$$\begin{array}{l} \mathrm{III};\ n = m = 1 \\ \mathrm{IV};\ n = 1,\ m = 2 \\ \mathrm{V};\ n = m = 2 \end{array}$$

The addition reaction was also carried out with 1,4-dibromo-2,3-dichlorohexafluorobutane (III) under similar conditions, and we found that dibromotrichlorononafluorohexane IV as well as dibromotetrachlorododecafluorooctane V were formed.

$$\mathrm{I} + \mathrm{III} \xrightarrow{(UV)} \mathrm{IV} + \mathrm{V}$$

Structure of the addition products was proved by means of IR and ^{19}F-NMR spectra and by dehalogenation with zinc powder in alcohol. Dehalogenation of butane III yielded perfluoro-1,3-butadiene (VI) [7], and the procedure employed by us, using chlorotrifluoroethylene (I) and dibromoderivative II as the starting compounds, represents a new and relatively simple synthesis of this perfluorodiene [8].

$$\text{III} \xrightarrow{\text{Zn/EtOH}} \underset{\text{VI}}{CF_2{=}CFCF{=}CF_2}$$

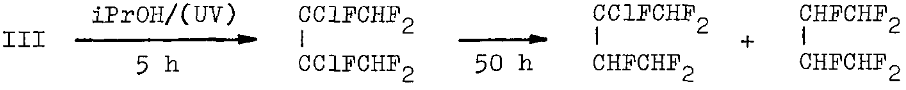
Dehalogenation of crude dibromotrichlorononafluorohexane IV gave rise to a mixture of 35% 3-chlorononafluoro-1,5-hexadiene (VII) and 65% perfluoro-1,3,5-hexatriene (VIII). Preparation of triene VIII has been described in the patent literature in a more complicated way [9].

$$\text{IV} \xrightarrow{\text{Zn/EtOH}} \underset{\text{VII}}{CF_2{=}CFCClFCF_2CF{=}CF_2} + \underset{\text{VIII}}{CF_2{=}CFCF{=}CFCF{=}CF_2}$$

Dehalogenation of dibromotetrachlorododecafluorooctane V in propanol yielded perfluoro-1,4,7-octatriene in a yield higher than 50%.

$$\text{V} \xrightarrow{\text{Zn/nPrOH}} CF_2{=}CFCF_2CF{=}CFCF_2CF{=}CF_2$$

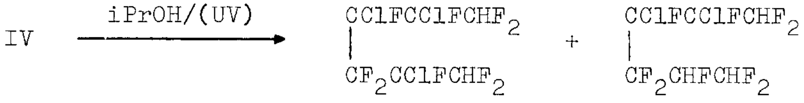
Further evidence of the structure of adducts III and IV was provided by a photochemical reduction with 2-propanol [10,11]. It proved possible to reduce selectively the C-Br bonds, and the reduction of the fraction containing butane III produced only 2,3-dichloro-1,1,2,3,4,4-hexafluorobutane (IX). The reduction of the C-Cl bonds in butane IX occured only after its isolation and a substantially longer reaction time, with the formation of a mixture of 2-chloro-1,1,2,3,4,4-hexafluorobutane (X) and 1,1,2,3,4,4-hexafluorobutane (XI) in the ratio 1 : 1.22.



$$\text{III} \xrightarrow[\text{5 h}]{\text{iPrOH/(UV)}} \begin{matrix} CClFCHF_2 \\ | \\ CClFCHF_2 \end{matrix} \xrightarrow{\text{50 h}} \begin{matrix} CClFCHF_2 \\ | \\ CHFCHF_2 \end{matrix} + \begin{matrix} CHFCHF_2 \\ | \\ CHFCHF_2 \end{matrix}$$

IX X XI

In the case of photochemical reduction of dibromotrichlorononafluorohexane IV under similar conditions as with III there also occured a preferential reduction of the C-Br bonds, but, in addition, one of the C-Cl bonds was reduced as well, and a mixture of 2,3,5-trichloro-1,1,2,3,4,4,5,6,6-nonafluorohexane (XII) with dichlorononafluorohexane XIII in the ratio 3.76 : 1 was formed. The exact constitution of the latter, however, failed to be reliably proved by ^{19}F-NMR spectra (Table 4); nevertheless we assume it to be 2,3-dichloro-1,1,2,3,4,4,5,6,6-nonafluorohexane (XIII).



$$\mathrm{IV} \xrightarrow{\mathrm{iPrOH/(UV)}} \begin{array}{l} \mathrm{CClFCClFCHF_2} \\ | \\ \mathrm{CF_2CClFCHF_2} \end{array} + \begin{array}{l} \mathrm{CClFCClFCHF_2} \\ | \\ \mathrm{CF_2CHFCHF_2} \end{array}$$

XII XIII

The selective photochemical reduction of dibromodichlorohexafluorobutane III to dichlorohexafluorobutane IX was employed for the synthesis of difluoroacetic acid. By dehalogenation of butane IX with zinc powder in ethanol we obtained a 85% yield of 1,1,2,3,4,4-hexafluoro-2-butene (XIV) as a mixture of 45% cis isomer and 55% trans isomer. The mixture was separated by means of preparative gas chromatography, and the spectral data for both isomers are listed in Tables 4 and 5. Butene XIV was oxidized according to Henne and Trott [12], and after extraction with ether the resultant difluoroacetic acid was esterified with diazomethane. As shown by the GLC, NMR and MS, there occurred also a partial esterification of the acid with the ether, and a mixture of methyl difluoroacetate (XVa) and ethyl difluoroacetate (XVb) in the ratio 1.22 : 1 was isolated.

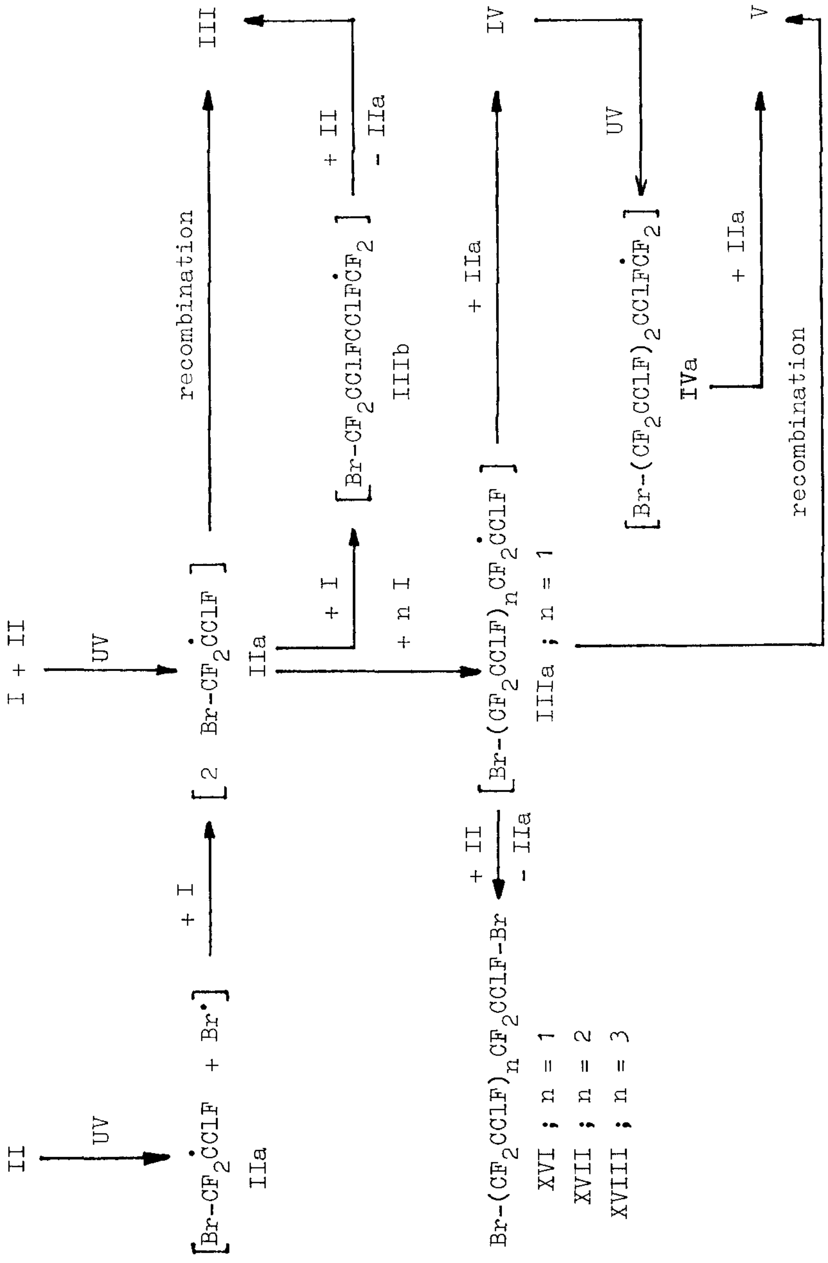
$$\mathrm{IX} \xrightarrow{\mathrm{Zn/EtOH}} \underset{\mathrm{XIV}}{\mathrm{CHF_2CF{=}CFCHF_2}} \xrightarrow[\mathrm{2.\ CH_2N_2/Et_2O}]{\mathrm{1.\ KMnO_4/KOH}} \mathrm{CHF_2COOR}$$

$$\mathrm{XVa;\ R = CH_3}$$

$$\mathrm{XVb;\ R = C_2H_5}$$

The confirmed structure of the major components of the 1:1 adducts III, 1:2 adducts IV and 1:3 telomers V is unusual and does not conform to the hitherto accepted findings [17,18] on the predominant orientation of addition in the reactions of haloalkanes with chlorotrifluoroethylene (I) under the conditions of the radical reactions. According to these [17] **the primarily** arising adduct radical IIIa should give 1,4-dibromo-1,3-dichlorohexafluorobutane (XVI) as a major 1 : 1 adduct, since the halogenoalkyl group of the haloalkane usually prefers bonding to the difluoromethylene group of chlorotrifluoroethylene (I). Analogously the derivative XVII, containing the chlorine atom on positions 1,2,5-, and the 1,3,5,7-tetrachloro derivative XVIII among the 1 : 2 adducts and 1 : 3 telomers respectively should predominate (Scheme 1).

We suppose that for the formation of the prevailing anomalous adducts III, IV and V the decisive intermediate is the 2-bromo-1-chloro-1,2,2-trifluoroethyl radical IIa arising by interaction of chlorotrifluoroethylene (I) with dibromoethane II under UV irradiation, and/or by photolysis of dibromoethane II and addition of a bromine atom to ethylene I as shown in Scheme 1. It is most probable that under the conditions of our experiments the 1 : 1 adduct III results from recombination of the radicals IIa, although the possibility of the formation of III via a less probable addition of the radical IIa to ethylene I generating the butyl radical IIIb, which is converted to the adduct III, cannot be ruled out, either. In another **report** [13] we have described the isomeric adduct XVI as a minor product in the butane fraction of this reaction. Its formation can be likewise accounted for by assuming that the decisive intermediate of the reaction is the chlorotrifluoroethyl radical IIa. The addition of IIa to I can give rise to the free radical IIIa as a precursor of the minor adduct XVI, and by its propagation the intermediates yielding the telomers XVII and XVIII can be formed. However, even the ascertained major components of the hexane and octane fraction can arise from the intermediate IIIa. Octane V can be a product of recombination of the adduct radicals IIIa, and hexane IV the product of recombination of the free radical IIIa with the primary intermediate IIa and/or of the reaction with ethane II giving hexane IV and the bromine atom.


II
UV
[Br-CF2ĊClF + Br•]
IIa
+ I
[2 Br-CF2ĊClF]
IIa
I + II
UV
recombination
III
+ I
[Br-CF2CClFCClFĊF2]
IIIb
+ II
- IIa
+ n I
[Br-(CF2CClF)nCF2ĊClF]
IIIa ; n = 1
+ IIa
IV
UV
[Br-(CF2CClF)2CClFĊF2]
IVa
+ IIa
V
recombination
+ II
- IIa
Br-(CF2CClF)nCF2CClF-Br
XVI ; n = 1
XVII ; n = 2
XVIII ; n = 3

Scheme 1

Since we have found the hexane derivative IV and the octane derivative V also as the major products of the addition of 1,4-dibromo-2,3-dichlorohexafluorobutane (III) to chlorotrifluoroethylene (I) it is to be assumed that by UV irradiation of dibromobutane III and ethylene I free radicals IIIb and IIa are formed, which by recombination will give the hexane derivative IV. Analogously the octane derivative V can arise from the hexane derivative IV, as shown in Scheme 1.

EXPERIMENTAL

General comments

All boiling points are uncorrected. Chromatographic analyses were performed on a Chrom 2 (Laboratorní přístroje, Prague) instrument (FID, stainless steel column 0.3 x 240 cm, support Chromaton N-AW-DMCS, Lachema Brno), carrier gas nitrogen, Preparative gas chromatography was performed on a modified Chrom 2 instrument (FID with by-pass, stainless steel column 1 x 500 cm). All new compounds were characterized by elemental analysis and by NMR (^{19}F and ^{1}H) and infrared spectroscopy. The analyses and physical measurements of the products are summarized in Tables 3, 4 and 5. NMR spectra were recorded in deuteriochloroform on Varian XL-100/15 and Tesla BS 567 spectrometers. ^{1}H chemical shifts are quoted in δ units using tetramethylsilane, and ^{19}F chemical shifts in ppm positive to high field of trichlorofluoromethane, both internal references. IR spectra were measured on a Perkin-Elmer 325 instrument. The mass spectra of methyl and ethyl difluoroacetate were measured on a gas chromatograph - mass spectrometer LKB 9000 (Stockholm); single focus, 70 eV, chromatographic inlet: Carbowax 20 M on Chromaton N-AW, glass column 0.23 x 250 cm, carrier gas helium.

Chemical used

Chlorotrifluoroethylene was of commercial grade quality (United Chemical and Metallurgical Works, Ústí n. L.). 1,2-Dibromo-1-chlorotrifluoroethylene (I) was prepared according to [7]. 2-Propanol (Lachema Brno) was of p.a. quality.

Addition of haloalkanes II and III to chlorotrifluoroethylene

The reactions were performed in a glass vessel with an inner high-pressure mercury vapour lamp (Tesla 400 W) placed in a water-cooled quartz double-jacket tube immersed in the reaction mixture. During the reactions gaseous chlorotrifluoroethylene (I) was introduced in the haloalkane II or III at a flow rate of 2 l per hour. Reaction products III, IV and V were separated by distillation, composition of the individual fractions was monitored by GLC analysis (15% Silicon elastomer SE-301 and Carbowax 6000 stationary phases).

TABLE 1

Conditions and results of the addition of haloalkanes II and III to chlorotrifluoroethylene (I)

Haloalkane		$CClF=CF_2$	Temperature	Time	Products (g)			
No.	g	g	^oC	h	III	IV	V	residue
II	1003	416	20 - 30	40	284	140	a	317
III	434	218	15 - 20	21	-	65	70	115

[a] not estimated

Dehalogenation of haloalkanes III, IV, V and IX

A three-necked flask fitted with a mechanical stirrer, dropping funnel and a Vigreaux column (40 cm) was charged with zinc powder activated with a trace amount of glacial acetic acid, and 150 ml of ethanol was added. The mixture was stirred and heated to reflux, and a solution of haloalkane III, IV, V or IX in 30 ml of ethanol was dropwise added for 6 hours, the reaction products being slowly withdrawn and collected.

(a) Perfluoro-1,3-butadiene (VI)

The reaction of butane derivative III (25.8 g) with zinc powder (40 g) gave a volatile product collected in a trap cooled with dry ice and ethanol, which was placed behind the apparatus. After washing the product with a mixture of water and ice, drying with a molecular sieve Potasit 3M, and redistilling trap-to-trap, 5.1 g (79.7%) of diene VI, b.p. 5.8 °C, was obtained, its identity being verified by comparing IR [14] and ^{19}F NMR spectra [15].

(b) Perfluoro-1,3,5-hexatriene (VIII) and 3-Chlorononafluoro-1,5-hexadiene (VII)

Fraction 65-78 °C from the reaction of hexane derivative IV (20 g) and zinc powder (60 g) was washed three times with 30 ml of water, dried over anhydrous calcium chloride, and rectified; 6.9 g of fraction 65-72 °C was obtained, which by GLC was proved to be a mixture of triene VIII (65%) and diene VII (35%). Authentic samples of both compounds were obtained by preparative GLC (Silicon elastomer 301 stationary phase).

(c) Perfluoro-1,4,7-octatriene

Fraction 77-78 °C (21.8 g) from the reaction of octane derivative V (80 g) and zinc powder (120 g) in propanol (250 ml) was dried over phosphorus pentoxide and rectified; 21 g of perfluoro-1,4,7-octatriene [19], b.p. 99-100 °C was obtained as a mixture of cis- and trans- isomer.
^{19}F NMR spectrum: /ppm/: 92.3 and 107.5 multiplets, 4F, $C\underline{F}_2$=; 104.7 (cis) and 108.4 (trans), singlet and multiplet, 4F + 4F, $C\underline{F}_2$, 138.7 (cis) and 158.3 (trans), singlets, 2F + 2F, $C\underline{F}=C\underline{F}$; 190.7 multiplet, 2F, $C\underline{F}=CF_2$.

(d) 1,1,2,3,4,4-Hexafluoro-2-butene (XIV)

Dehalogenation of dichlorohexafluorobutane IX (28.2 g) with zinc powder (40 g) yielded fraction 55-78 °C. After washing it three times with 30 ml of water, drying over anhydrous magnesium sulphate and rectifying, 16.7 g (85.6%) of butene XIV, b.p. 53-57 °C, was obtained, which by GLC (Carbowax 6000 stationary phase) was proved to be a mixture of 55% trans- and 45% cis-isomer. The isomers were separated by preparative GLC and trans-isomer of butene XIV became solid in the receiver chilled with dry ice and ethanol, whereas the cis-isomer remained liquid.

Photochemical reduction of haloalkanes III, IV and IX

The solution of haloalkane in 2-propanol was irradiated with a high-pressure mercury vapour lamp (Tesla, 400 W or 125 W in the third run) placed in water-cooled quartz double-jacket tube immersed in the reaction mixture agitated with a stream of nitrogen. Temperature of the reaction mixture was maintained at 20-30 °C by cooling of the mercury lamp. The course of the reaction was monitored by GLC analysis (Silicon elastomer SE-30 stationary phase). After achieving complete conversion of the starting material the crude reaction mixture was diluted with a 5-fold volume of water and the organic layer was dried over anhydrous calcium chloride. The products were then separated by rectification, or, in the case of reduction products X and XI, purified by preparative GLC (Carbowax 6000 stationary phase).

TABLE 2
Conditions and results of the photochemical reduction of haloalkanes III, IV and IX

Haloalkane		2-Propanol	Reaction time	Yield of products
No.	g	ml	h	No. (%)
III	110	427	2	IX (75.7)
IV	61	228	2	XII (52.4), XIII (15.5)
IX	10	100	50	X (25.6), XI (37.6)

Preparation of difluoroacetates XVa and XVb

To a mixture of potassium permanganate (13.4 g), potassium hydroxide (7.2 g) and water (100 ml) heated to 60 °C, while stirring, butene XIV (7 g) was added dropwise at moderate reflux. Afterwards the reaction mixture was decolorized with sulphur dioxide and on acidification with 25 ml of 50% sulphuric acid, the solution was extracted with 400 ml of diethyl ether in a continual extractor for 40 hours. The corresponding amount of diazomethane solution in ether was added

TABLE 3

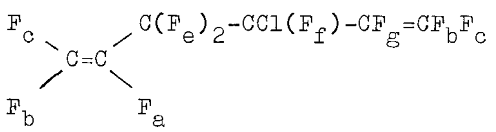
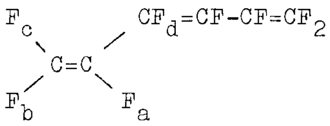
Elemental analyses and boiling points of compounds III-V and VII-XIV

Comp.	Formula	Mol.wt.	Calculated/Found					b.p. °C/torr
			% C	% H	% Br	% Cl	% F	
III[a]	$C_4Br_2Cl_2F_6$	392.8	12.3/12.4	-	40.7/40.7	18.1/18.5	29.0/28.8	55-57/14
IV	$C_6Br_2Cl_3F_9$	509.2	14.2/14.3	-	31.4/31.1	20.9/21.1	33.6/33.5	106-108/14
V	$C_8Br_2Cl_4F_{12}$	625.7	15.4/15.6	-	25.5/25.5	22.7/23.1	36.4/36.2	121-22/0.06
VII	C_6ClF_9	278.5	25.9/25.7	-	-	12.7/12.0	61.4/61.1	65-72
VIII[b]	C_6F_8	224.1	32.2/32.0	-	-	-	67.8/67.8	62-64
IX	$C_4H_2Cl_2F_6$	235.0	20.5/20.6	0.86/1.01	-	30.2/30.6	48.5/47.8	104-108
X	$C_4H_3ClF_6$	200.5	24.0/24.5	1.51/1.72	-	17.7/17.4	56.8/57.2	67-73
XI[c]	$C_4H_4F_6$	166.1	28.9/29.3	2.43/2.75	-	- /1.07	68.6/69.3	67-73
XII	$C_6H_2Cl_3F_9$	351.4	20.5/20.4	0.57/0.61	-	30.3/30.4	48.7/48.7	60/12
XIII	$C_6H_3Cl_2F_9$	317.0	22.7/23.0	0.95/1.00	-	22.4/22.1	53.9/53.8	127-29
XIV	$C_4H_2F_6$	164.1	29.3/28.7	1.23/1.27	-	-	69.5/69.6	53-57

[a] See Ref.[7]. [b] See Ref.[9]. [c] See Ref.[20]; IV, V, VII, IX, X, XII-XIV are new compounds.

TABLE 4

NMR spectra[a] of compounds III-V and VII-XIV

Comp.	Signals[b]
III	^{19}F: 56.1 (m, 4F, $-CBr\underline{F}_2$); 116.9 (m, 2F, $-CCl\underline{F}-$); 54.7 and 56.6 (dm, $^2J_{FF}=160$, 4F, $-CBr\underline{F}_2$); 116.9 (m, 2F, $-CCl\underline{F}-$).
IV	^{19}F: 55.7 and 58.1 (m,4F,$-CBr\underline{F}_2$); 99.0-109.6 (bm,2F,$-C\underline{F}_2-$); 117.1-126.6 (bm,3F,$-CCl\underline{F}-$).
V	^{19}F: 55.8 and 57.9 (m,4F,$-CBr\underline{F}_2$); 102.2-117.7 (bm,4F,$-C\underline{F}_2-$); 120.1-128.3 (bm,4F,$-CCl\underline{F}-$).
VII	^{19}F:  90.1 (m, 2F, $\underline{F}_b$); 105.2 (m, 2F, $\underline{F}_c$); 114.4 (dd, $^2J_{ee}=280$, 2F, $\underline{F}_e$); 135.0 (m,1F,$\underline{F}_f$); 178.5 (m, $^3J_{gc}=115$, 1F, $\underline{F}_g$); 186.6 (dm, $^3J_{ac}=120$, 1F, $\underline{F}_a$).
VIII	^{19}F:  91.1 (m, 2F, $\underline{F}_b$); 106.4 (dm, $^3J_{ac}=115$, 2F,$\underline{F}_c$); 134.1 (m, 2F,$\underline{F}_d$); 182.2 (dt, $^3J_{ad}=30$, 2F, $\underline{F}_a$).
IX	^{19}F: 127.2 and 131.3 (dm, $^2J_{FF}=300$, 4F, $-C\underline{F}_2H$); 134.0 (m, 2F, $-CCl\underline{F}-$); 127.3 and 130.0 (dm, $^2J_{FF}=300$, 4F, $-C\underline{F}_2H$); 135.1 (m, 2F, $-CCl\underline{F}-$). ^1H: 6.2 (dm, $^2J_{FH}=54$, 2H, $-CF_2\underline{H}$).

X	^{19}F: 114.0-143.8 (bm, 5F, -C$\underline{F}_2$H, -CCl$\underline{F}$-); 209.0-218.0 (bm, 1F, -1F, -C$\underline{F}$H-).
	^{1}H: 4.9 (dm, $^{2}J_{FH}$=42, 1H, -C$\underline{H}$F-); 6.0 (tm, $^{2}J_{FH}$=53, 2H, -C$\underline{H}F_2$).
XI	^{19}F: 132.2 and 132.7 (dm, 4F, -C$\underline{F}_2$H); 216.0 and 220.0 (dm, 2F, -C$\underline{F}$H-).
	^{1}H: 4.8 (m, $^{2}J_{FH}$=55 and 30, 2H, -C$\underline{H}$F-); 6.0 (tm, $^{2}J_{FH}$=53, 2H, -C$\underline{H}F_2$).
XII	^{19}F: 106.9 and 108.4 (m, 2F, -C$\underline{F}_2$-); 123.9-136.9 (bm, 7F, -C$\underline{F}_2$H, -CCl$\underline{F}$-).
	^{1}H: 6.2 (tm, $^{2}J_{FH}$=54, 2H, -C$\underline{H}F_2$).
XIII	^{19}F: 107.4-143.4 (bm, 8F, -C$\underline{F}_2$H, -C$\underline{F}_2$-); 199.6 and 203.3 (dm, 1F, -C$\underline{F}$H-).
	^{1}H: 5.1 (m, 1H, -C$\underline{H}$F-): 6.1 (tm, $^{2}J_{FH}$=54, 2H, -C$\underline{H}F_2$).
XIV	^{19}F: trans-isomer^{c}: 128.0 (dt, 4F, -C$\underline{F}_2$H); 173.6 (m, 2F, -C$\underline{F}$=);
	cis-isomer^{c}: 123.2 (dm, 4F, -C$\underline{F}_2$H); 150.0 (m, 2F, -C$\underline{F}$=).
	^{1}H: trans-isomer: 6.5 (tm, $^{2}J_{FH}$=51, $^{3}J_{FH}$=12, 2H, -C$\underline{H}F_2$);
	cis-isomer: 6.4 (tm, $^{2}J_{FH}$=52, $^{3}J_{FH}$=12, 2H, -C$\underline{H}F_2$).

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[a] internal standard $CFCl_3$ (^{19}F NMR) or TMS (^{1}H NMR)

[b] chemical shifts in ppm (m multiplet, bm broad multiplet, d dublet, t triplet; coupling constants J in Hz; relative signal intensities; assortment)

[c] the configuration was estimated on the base of analogy [16].

TABLE 5

Absorption maxima (cm^{-1}) in IR spectra of compounds III-V, VII-IX and XII-XIV in CS_2

Comp.	Absorption bands
III	608 vs, 627 ms, 658 ms, 700 vs, 737 s, 748 ms, 758 w, 772 w, 800 s, 820 s, 835 ms, 855 ms, 887 s, 916 ms, 940 s, 960 s, 975 s, 1015 vs, 1070 vs, 1095 s, 1112 s, 1135 si, 1160 vs, 1188 vs.
IV	604 s, 615 s, 629 ms, 660 s, 690 ms, 712 ms, 725 ms, 732 w, 749 w, 756 ms, 760 ms, 773 ms, 788 ms, 809 ms, 837 msi, 845 ms, 871 ms, 888 msi, 900 ms, 914 ms, 916 msi, 935 s, 955 s, 968 si, 973 si, 1010 s, 1053 s, 1092 s, 1110 vs, 1130 si, 1145 vsi, 1159 vssh, 1184 vs, 1208 si, 1223 s.
V	600 s, 611 ms, 620 mssh, 632 ms, 660 ms, 670 ms, 687 ms, 710 ms, 742 ms, 758 ms, 792 ms, 810 mssh, 856 ms, 968 vs, 1024 s, 1062 s, 1121 vs, 1157 vsi, 1161 vs, 1193 vs, 1242 s, 1260 msi, 1361 w, 1385 w.
VII	653 w, 688 w, 725 ms, 765 ms, 790 wi, 813 s, 859 ms, 877 msi, 892 s, 913 msi, 982 ms, 1007 s, 1020 wi, 1068 ms, 1092 s, 1145 si, 1161 vs, 1183 vs, 1220 wi, 1283 s, 1308 s, 1340 vs, 1351 si, 1660 w, 1773 vs, 1830 w,
VIII	641 w, 690 w, 725 ms, 760 vs, 783 vs, 805 w, 829 w, 840 w, 869 w, 883 s, 915 w, 941 w, 969 ms, 978 ms, 1001 vs, 1008 vsi, 1023 ms, 1068 ms, 1101 s, 1115 s, 1124 s, 1161 si, 1175 vs, 1184 vs, 1222 ms, 1258 ms, 1280 ms, 1292 si, 1315 vs, 1348 vs, 1365 msi, 1381ms.
IX	565 m, 618 w, 660 ms, 673 ms, 740 w, 760 ms, 780 ms, 807 ms, 840 ms, 872 w, 914 w, 927w, 950 ms, 974 ms, 1010 w, 1026 ms, 1034 ms, 1068 ms, 1092 ms, 1140 s, 1160 s, 1195 ms, 1224 ms, 1240 ms, 1270 wsh, 1290 wsh, 1320 wsh, 1350 ms, 1376 ms, 1385 msi, 1398 wi.

XII	600 w, 627 w, 660 s, 670 s, 697 ms, 715 ms, 722 s, 745 ms, 750 ms, 770 ms, 790 msi, 794 ms, 805 ms, 856 ms, 866 ms, 885 ms, 905 ms, 955 s, 970 s, 1025 ms, 1035 ms, 1065 s, 1075 s, 1130 vs, 1170 vs, 1231 s, 1350 s, 1375 s, 1395 wi, 1640-70 wsh, 2205 w, 3000 w.
XIII	630 w, 665 ms, 700 ms, 705 ms, 750 ms, 760 msi, 800 ms, 820 ms, 870 wi, 890 ms, 915 w, 960 ms, 970 ms, 1010 w, 1030 msi, 1050 msi, 1060 ms, 1190 msi, 1130 vs, 1170 vs, 1185 vsi, 1200 si, 1250 ms, 1255 msi, 1290 ms, 1350 ms, 1375 ms, 1395 ms, 3000 ms.
XIV	trans-isomer: 724 w, 729 wi, 750 ms, 773 vs, 792 wi, 805 wi, 841 w, 935 wi, 947 ms, 1018 msi, 1028 ms, 1069 vs, 1118 vs, 1128 msi, 1140 ms, 1150 msi, 1164 wi, 1198 ms, 1263 vs, 1302 ms, 1333 ms, 1370 ms, 1390 s, 1672 w, 1690 vw, 2990 w.
	cis-isomer: 690 wi, 719 msi, 742 ms, 756 msi, 763 msi, 780 ms, 784 msi, 800 w, 807 w, 826 wi, 842 s, 854 ms, 918 w, 1000 ms, 1007 msi, 1023 s, 1070 vs, 1101 vs, 1114 si, 1132 s, 1148 msi, 1160 ms, 1173 wi, 1213 w, 1733 msi, 1737 ms, 2968 w.

to the extract while stirring. After drying over anhydrous magnesium sulphate, diethyl ether was distilled off and subsequent distillation yielded 5.5 g of fraction 85-95 °C, which by GLC analysis (Silicone elastomer SE-30 stationary phase) was proved to be a mixture of two compounds identified by GLC/MS and NMR spectra as difluoroacetates XVa (55%) and XVb (45%).

Mass spectrum [mass/relative intensity, (ionic species)] for $C_3H_4F_2O_2$ (XVa): 109/4, $(M-1)^+$; 81/77, $(CH_3OCF_2)^+$; 79/6, $(CHF_2CO)^+$; 66/19, $(CF_2O)^+$; 59/100, $(CH_3OCO)^+$; 51/100, $(CHF_2)^+$; 31/54, $(CH_2OH)^+$; 29/43, $(CHO)^+$. For $C_4H_6F_2O_2$ (XVb): 122/2, $(M-2)^+$; 96/6, $(C_2H_5OCHF_2)^+$; 81/31, $(CH_3OCF_2)^+$; 79/2,$(CHF_2CO)^+$; 73/3, $(C_2H_5OCO)^+$; 51/70, $(CHF_2)^+$; 45/25, $(C_2H_5O)^+$; 29/100, $(C_2H_5)^+$; 28/28, $(C_2H_4)^+$, (CO)+; 27/28 $(C_2H_3)^+$.

^1H NMR spectrum: /ppm/: 1.4, triplet $^3J(HH)$= 7 Hz, $C\underline{H}_3$ in XVb; 3.9, singlet, $C\underline{H}_3$ in XVa; 4.4, quartet, $C\underline{H}_2$; 5.9, triplet, $^2J(HF)$ = 54 Hz, $C\underline{H}F_2$.

^{19}F NMR spectrum: 127.8, multiplet, $CH\underline{F}_2$.

IR spectrum (cm^{-1}): 1768 vs, 1778 vs, ν(C=O).

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