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REACTIONS OF HEXAFLUOROPROPENE TRIMERS WITH THIOLS

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SUMMARY

Reactions of the hexafluoropropene (HFP) trimers - perfluoro-3-isopropyl-4-methyl-2-pentene (I) and perfluoro-3-isopropyl-2-methyl-2-pentene (II) with thiols have been studied. Trimer (I) was shown to give vinyl derivatives by substitution of fluorine atoms. Interaction of trimer (II) with thiols produces alkyl(aryl)perfluoroalkadienylsulfides. A mechanism for their formation, including nucleophilic attack of the thiolate-anion at a RS-group of intermediate alkyl(aryl)perfluoroalkenylsulfides is proposed. The first perfluoroalkylsubstituted thiete is obtained.

INTRODUCTION

Interaction of the HFP trimers with O-nucleophiles in the presence of Et_3N has been reported [1]. The reversible isomerisation of the trimers (I) $\rightleftharpoons$ (II) takes place in the conditions of these reactions [1]. In the reactions with alcohols, trimer (I) is more reactive than trimer (II) and gives ether substitution products of the vinylic and allylic fluorine atoms $C_9F_{17}OR$ (their proportion depends on the nature of nucleophile). Trimer (II) does not react with alcohols directly, but isomerises into trimer (I). The insomerisation rate is comparable with the rate of interaction between trimer (I) and alcohols and depends on the temperature and the solvent.

The reactions of the HFP trimers with S-nucleophiles were not investigated previously. It is likely that the rate of interactions of thiolate-anions with the HFP trimers will be substantially greater than the rate of

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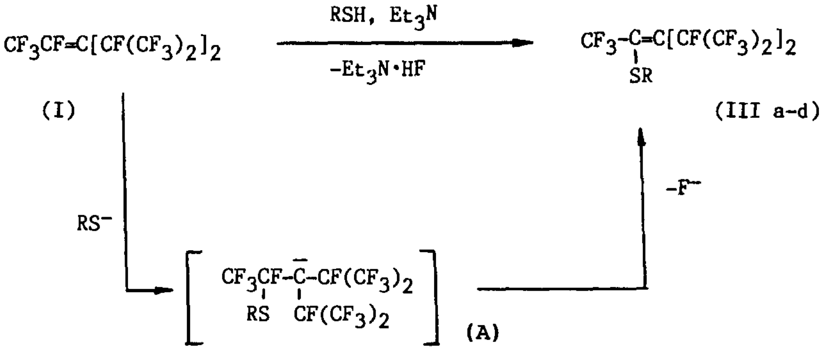
the above isomerisation, because of the high nucleophilicity of RS^- and thus the possibility of studying the reactivity of each trimer arises.

RESULTS AND DISCUSSION

The HFP trimers (I) and (II) react readily with thiols in the presence of Et_3N giving alkyl(aryl)perfluoro-3-isopropyl-4-methyl-2-pentenylsulfides (III a-d) and alkyl(aryl)perfluoro-3-isopropyl-2-methyl-1,3-pentadienylsulfides (IV a-e) respectively. The reactions were carried out in ether at temperature -20°C*.

The expected products of vinylic fluorine atom substitution (III a-d) are formed in the reaction of trimer (I) with equimolar amounts of thiols (Scheme 1).



R = Et (IIIa), n-Bu (IIIb), t-Bu(IIIc), Ph (IIId).
Scheme 1

The reaction of thiols with trimer (II) is a more complex process and results in the formation of 1,3-pentadiene derivatives (IV a-e) according to Scheme 2.

The direction of thiolate-anion initial attack appears to be determined by steric factors. The intermediate (B) is generated as a result of a substitution reaction S_N2'. The most important stage of Scheme 2 is the nucleophilic attack at the RS-group of intermediate (B) by a thiolate-anion resulting in dialkyl(aryl)disulfides and anion (C). This process is facilitated by the fact that the leaving group - an anion of allylic type (C) - is highly stabilised by the perfluoroalkyl groups.

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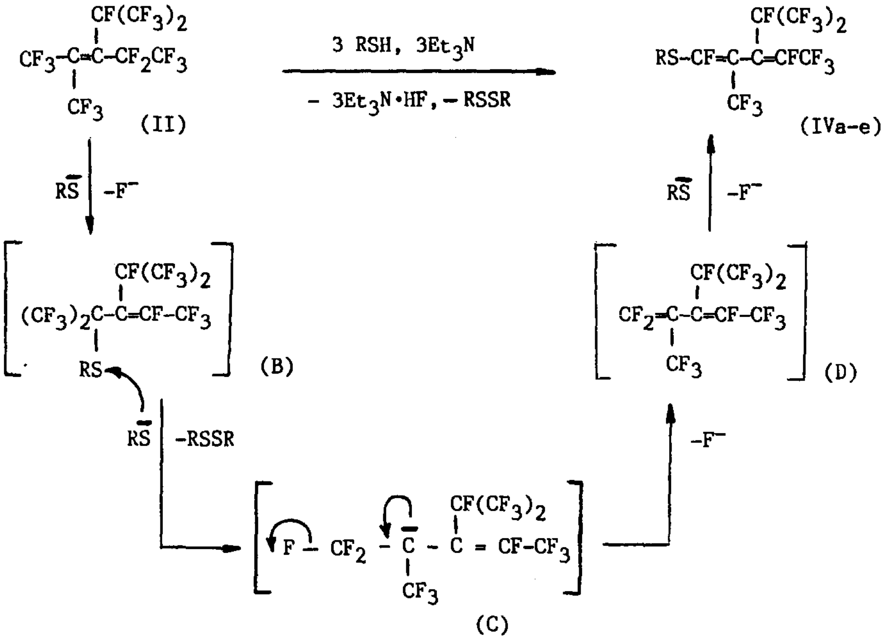
* The conditions of the reaction between the HFP trimers and t-BuSH are discussed below.

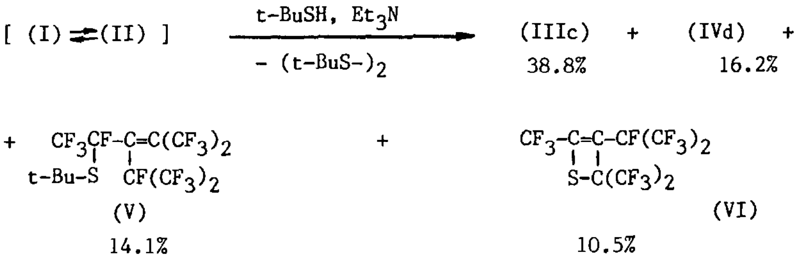


R = Et (IVa), n-Pr (IVb), n-Bu (IVc), t-Bu (IVd), Ph (IVe).
Scheme 2

Further fluoride-ion elimination from anion (C) gives a reactive diene (D) with a $=CF_2$terminal group, the latter reacts readily with thiolate-anions, forming the final product (IV). The proposed Scheme 2 is verified by the formation of equimolar amounts of the respective disulfides.

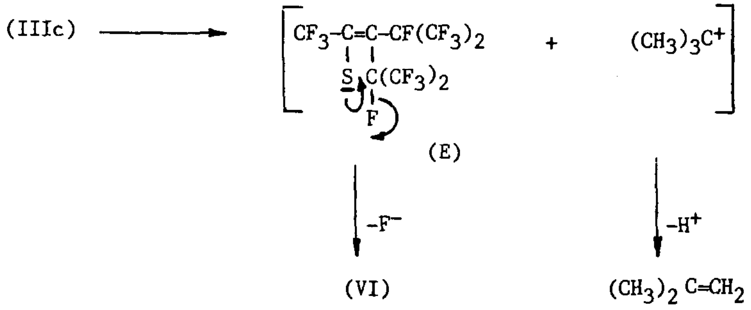
The cleavage of a C-S bond by nucleophilic attack of thiolate-anion at RS-group was reported for α-carbonylsulfides [2,3] and 4-thiosubstituted diazolinium salts [4]. Highly stabilised C-anions and corresponding disulfides were also formed in these cases. The same mechanism involving nucleophilic attack of RS-anion at sulfur atom of the fragment $(CF_3)_2C(SR)$-$\overset{|}{C}$=$\overset{|}{C}$- was suggested [5] to explain the formation of 1,3-pentadiene thio derivatives in the reaction of HFP dimers with thiols [6,7].

The interaction of HFP trimers with t-BuSH needs more rigid conditions. This reaction was carried out in ether at reflux (40-45°C) in the presence of Et_3N. During 30 h only 75% of the trimers reacted. Under these conditions, because of isomerisation as discussed above, we are dealing with a mixture of the trimers, but not with individual compounds (I) or (II). According to it the trimers (I) and (II) on reaction with t-BuSH give the same mixture of products, namely compounds (IIIc), (V), (IVd), perfluoro-3-isopropyl-2,4,4-trimethyl-2-thiete (VI) and $(t\text{-}BuS\text{-})_2$ (Scheme 3). Apart from compound (IIIc) product (V) is formed from the intermediate anion (A) (R = t-Bu) (Scheme 1).



Scheme 3

The formation of thiete (VI) was shown to proceed by decomposition of the originally generated product (IIIc). It is probable that dealkylation of compound (IIIc) takes place and the generated anion (E) undergoes intramolecular cyclisation forming thiete (VI) and that the t-Butyl-cation gives isobutylene (according to the PMR data) (Scheme 4). The process of thiete (VI) forming substantially accelerated with the temperature increase.



Scheme 4

Compound (VI) is the first perfluoroalkylsubstituted thiete [8]. It is a colourless liquid, b.p. 120-121°C, stable at 200°C. A preparative procedure for the thiete directly from the HFP trimers and excluding intermediate isolation of product (IIIc) has been proposed [9].

The new compounds obtained have been characterized by elemental analysis (Table 1). The molecular weights have been confirmed by mass-spectroscopy. The structures of the products were proved with NMR (^1H, ^{19}F, ^{13}C) and IR spectra. The NMR data of the compounds are given in Tables 2 and 3. PMR spectra of compounds (III), (IV), (V) are the signals of corresponding alkyl(aryl)groups (R-). Infrared spectroscopy has confirmed the presence of C=C bonds .

TABLE 1

Yields, physical properties and chemical analysis of new compounds

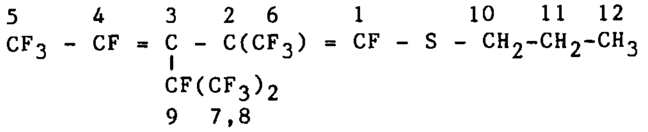
Compound	Yield [%]	bp [°C/Torr]	Found / Calculated [%]		
			C	H	F
IIIa	81.0	74-75/17	27.26 26.83	1.06 1.02	65.65 65.65
IIIb	82.0	76-77/12	30.06 30.00	1.66 1.74	62.26 62.04
IIIc	38.8*	85-86/11	30.15 30.00	1.68 1.74	62.56 62.04
IIId	78,8	94-95/6	32.77 33.32	0.95 0.93	59.25 59.74
IVa	77.0	69-70/12	29.08 29.09	1.05 1.10	62.85 62.75
IVb	71.8	64-65/8	30.47 30.78	1.32 1.51	61.15 60.86
IVc	72.8	77-78/8	32.31 32.37	1.56 1.88	58.61 59.10
IVd	16.2*	79-80/11	32.66 32.37	1.56 1.88	58.61 59.10
IVe	71.2	121-122/12	35.83 35.84	1 05 1.00	56.84 56.70
V	14.1*	77-78/8	30.06 30.00	1.81 1.74	62.27 62.04

*Taking into account conversion of the initial HFP trimers, equal to 75% .

Dienes (IVa-e) are formed as a mixture of two isomers in the ratio 3:2. The isomers of compound (IVb) - (IVb') and (IVb'') - were isolated by preparative GLC and characterized. The structure of product (IV) has been confirmed unambiguously from the ^{13}C NMR data (Table 2).

TABLE 2

^{13}C NMR spectrum data of n-propyl-perfluoro-3-isopropyl-2-methyl-1,3-pentadienylsulfide (IVb')



$$\overset{5}{CF_3} - \overset{4}{CF} = \overset{3}{\underset{\underset{9\ \ 7,8}{CF(CF_3)_2}}{C}} - \overset{2}{C}(\overset{6}{CF_3}) = \overset{1}{CF} - S - \overset{10}{CH_2}-\overset{11}{CH_2}-\overset{12}{CH_3}$$

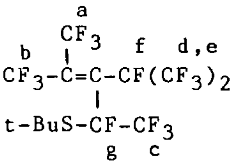
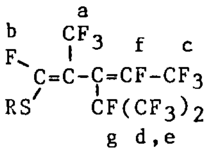
Nucleus C	Chemical shift [ppm]*	^1J [Hz]	^2J [Hz]
1	165.0	314.4 d	-
2	97.9	-	26.8 d, 38.0 q
3	103.8	-	15.7 d, 33.2 d
4	147.1	288.2 d	39.3 q
5	116.5	275.1 q	39.9 d
6**	118.3	271.1 q	-
7	116.0	287.1 q	28.0 d
8	115.5	286.8 q	27.0 d
9	81.7	204.2 d	35.8 hpt
10	28.5	-	-
11	19.4	-	-
12	7.5	-	-

*Chemical shifts are reported relative to TMS.

** $^3J = 12.1$ Hz.

The configurations (1-E, 3-E- and 1-Z, 3-E-) of isomers (IVb') and (IVb'') were deduced from the analysis of their ^{19}F NMR spectra (Table 3). The values of coupling constants J_{a-b}(12 and 15 Hz for 1-E,3-E- and 1-Z,3-E--isomers respectively)are in agreement with the literature values [10] for E- and Z-isomers of compounds containing $F-\overset{|}{C}=\overset{|}{C}-CF_3$ groups. The presence of the interaction between F^b and F^e in the first isomer (IV') (J_{b-e} 11Hz) and the absence of such an interaction in the second gives additional support to the configuration assigned. The forms of signals, the spectral parameters of the substituents in positions 3 and 4 are almost the same for both isomers. Interaction between groups $CF_3{}^a$ and $CF_3{}^c$ (J_{a-c} 2.4 Hz) is observed in both isomers. The coupling constants J_{b-f} are 6.4 and 7.0 Hz for isomers (IVb') and (IVb'') respectively. These facts point to the same 3-E-confi-

TABLE 3 (Cont.)

Compound	Chemical shift [ppm]*	Coupling constant J_{F-F} [Hz]
 $CF_3-C(CF_3)=C(CF(CF_3)_2)-CF(S\text{-}t\text{-}Bu)-CF_3$		
Vx**	-21.1 (a), -17.5 (b), -13.1 (c), -4.9 (d), -2.0 (e), 64.1 (f) 74.6 (g)	8.0(d-e), 52.0(a-f) 22.0(f-g), 40.0(d-g), 7.5 (e-g)
Vy**	-21.1(a), -21.1 (b), -12.6(c), -9.1 (d) -6.1 (e), 79.3(f), 52.4 (g)	7.5 (d-e), 58.0(a-f), 11.0(f-g), 32.0(d-g), 32.0(e-g)
 $F(RS)C=C(CF_3)-C(CF(CF_3)_2)=CF-CF_3$		
IVa' R = Et	-18.7 (a), -9.8 (b), -8.1 (c), 3.3 (d), -0.7(e), 23.1 (f), 96.1 (g)	12.0(a-b), 6.0 (b-c), 12.0(b-e), 8.o(d-e), 8.0(d-g), 8.0(e-g), 18.0(e-f), 22.4(d-f)
IVa'' R = Et	-18.5(a), -9.8(b), -8.1(c), -3.3(d), -0.7(e), 23.1(f), 95.0(g)	15.0(a-b), 8.0(d-e), 6.0(e-g), 6.0(d-g) 22.0(e-f), 23.5(d-f)
IVb' R = n-Pr	-19.3(a), -10.3(b), -7.9(c), -3.1 (d), -0.8(e), 23.0(f), 96.6 (g)	12.0(a-b), 2.4(a-c), 6.4(b-c), 6.4(b-f), 11.5(b-e), 8.5(d-e), 8.5(e-g), 8.5(d-g), 18.5(e-f), 22.0(d-f)
IVb'' R = n-Pr	-17.9(a), -10.0(b) -7.2(c), -3.1(d), -2.2(e), 22.0(f), 95.0(g)	15.0(a-b), 2.4(a-c), 7.0(b-f), 8.5(d-f), 5.8(e-g), 5.8(d-g), 21.5 (e-f), 23.0(d-f)

(Continued)

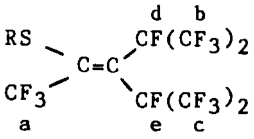
guration in both cases. Interaction between F^b and F^c is observed in the E,E-isomer, the absence of such interaction in Z,E-isomer seems to follow from changes in the F^b and RS positions.

Previously isolated isomers (IVb') and (IVb'') were shown to equilibrate to 3:2 mixture on heating and on UV-irradiation.

The ^{19}F NMR spectra of dienes (IVa), (IVc-e) consist of two series of signals, corresponding to E,E- and Z,E-isomers, analogous with the spectra of products (IVb') and (IVb'') (Table 3).

TABLE 3

^{19}F NMR spectra data of compounds obtained

Compound	Chemical shift [ppm]*	Coupling constant J_{F-F} [Hz]
		
IIIa R = Et	-22.2 (a), -8.7(b), -5.4 (c), 80.9 (d), 84.5 (e)	63.3(a-e), 37.3(c-d), 11.0 (d-e)
IIIb R = n-Bu	-22.2 (a), -9.1 (b), -5.4(c), 81.2 (d), 84.7 (e)	63.0 (a-e), 37.5(c-d), 11.6 (d-e)
IIIc R = t-Bu	-21.4(a),-9.3 (b), -5.8 (c) 82.2 (d) 83.5 (d)	63.0(a-e), 38.5(c-d), 12.3 (d-e)
IIId R = Ph	-25.7 (a), -8.7 (b), -5.2 (c), 81.9 (d) 86.6 (e)	63.3 (a-e), 38.5 (c-d), 11.5 (d-e)

(Continued overleaf)

TABLE 3 (Cont.)

Compound	Chemical shift [ppm]*	Coupling constant J_{F-F} [Hz]
IVc' R = n-Bu	-18.4 (a), -10.0(b), 7.0(c), -3.1 (d), -0.8 (e), 23.1 (f), 86.2 (g)	
IVc'' R = n-Bu	-17.7 (a), -10.0(b), -7.3 (c), -3.1 (d), 2.2 (e), 21.8 (f), 95.2 (g)	
IVd' R = t-Bu	-20.1 (a), -16.0(b), -10.1 (c), -4.0 (d), 0.4 (e), 23.1 (f), 94.1 (g)	
IVd'' R = t-Bu	-17.7 (a), -16.6 (b), -10.3 (c), -5.1 (d), -0.3 (e), 21.9 (f) 95.9 (g)	
IVe' R = Ph	-18.9 (a), -13.9 (b), -7.6 (c), -3.1 (d), - -0.7 (e), 22.6 (f), 96.4 (g)	10.0(a-b), 6.4(b-c), 12.0(b-e), 8.5(d-e), 8.5 (e-g), 8.5(d-g), 18.3(e-f), 22.0(d-f)
IVe'' R = Ph	-17.9 (a), -13.7(b), -7.7(c), -3.4 (d), -2.4 (e), 21.0 (f), 95.1 (g)	15.0(a-b), 8.5(d-e), 5.8 (e-g), 5.8(d-g), 22.5(e-f), 21.5(d-f)

* Chemical shifts are reported relative to external CF_3COOH (negative shifts are downfield).

** There are two groups of signals in ^{19}F NMR spectra of product (V), which point to the presence of two stable conformers (Vx, Vy) arising from hindered rotation of the isopropyl group.

EXPERIMENTAL

^{1}H, ^{19}F and ^{13}C - NMR spectra were recorded on a Bruker WP-200 SY (200, 188.3 and 50.1 MHz) spectrometer. Mass-spectra (70 eV) were recorded on a VG-7070-E mass spectrometer. Infrared spectra were recorded on a UR-20 spectrometer. Analytical GLC was performed on columns (5 m x3 mm) packed with 20% QF-1 on Chromosorb N. Preparative GLC separations were made on a Perkin-Elmer F-1 chromatograph with a column (4 m x20 mm) packed with 20% Krytox or 20% QF-1 on Chromosorb N. Compounds (I) and (II) were isolated from the commercially available mixture of HFP trimers by preparative GLC and distillation.

Interaction between perfluoro-3-isopropyl-4-methyl-2-pentene (I) and thiols (general procedure)

Into a mixture of trimer (I) (4.5 g, 0.01 mol) and ether (10 ml) a solution of corresponding thiol (0.01 mol) and triethylamine (1.0 g, 0.01 mol) in ether (10-15 ml) was added dropwise under stirring at -20°C for 20 min. After 1 h of stirring at -20°C to -15°C the reaction mixture was allowed to warm to room temperature, then washed with 5% HCl. The organic layer was dried over $MgSO_4$. After removing the ether the residue was distilled at a reduced pressure, giving product (III).

Reaction of perfluoro-2-methyl-3-isopropyl-2-pentene (II) with thiols (general procedure)

A solution of trimer (II) (4.5 g, 0.01 mol) in ether was added dropwise to an ether solution of the corresponding thiol (0.03 mol) and triethylamine (3.0g, 0.03 mol) cooled to -20°C (under stirring). After 2 h of stirring the ether was distilled at reduced pressure over H_2SO_4. The compounds (IV) were obtained. Disulfides in the reaction mixture were determined with GLC or were isolated by distillation from special experiments.

Interaction between HFP trimers with tert.-butanethiol

A solution of the trimer (I),(II) or mixture of them (22.5 g, 0.05 mol), tert.-butanethiol (13.5 g, 0.15 mol) and Et_3N (15.0 g, 0.15 mol) in ether (60 ml) was refluxed for 30 h (b.p. 40-45°C). The reaction mixture was treated as described above. After removing the ether the residue was distilled under reduced pressure. A mixture of products (IIIc), (V), (IVd) (15.8 g) was thus obtained. The components were separated from each other by preparative GLC. A mixture of unreacted trimers (I), (II) and thiete (VI) was collected in a trap at -60°C.

Perfluoro-2,4,4-trimethyl-3-isopropyl-3-thiete (VI)

Product (IIIc) (1.2 g) was heated under 200°C in a sealed glass tube for 30 min and the material was distilled. The product (VI) (0.8 g, 76%) had b.p. 120-121°C.

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