REACTION OF PERFLUORO-2-METHYL-2-PENTENE AND PERFLUOROISOBUTYLENE WITH α-OXIDES IN THE PRESENCE OF CESIUM FLUORIDE

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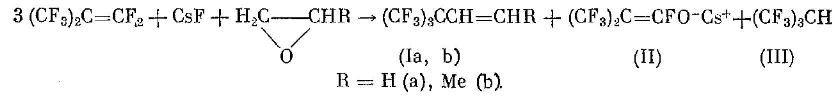
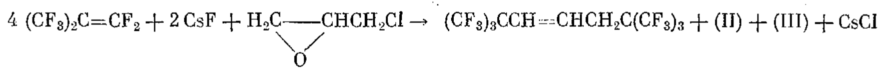
We have previously reported that the reaction of perfluoroisobutylene (PFIB) with ethylene oxide and propylene oxide in the presence of CsF results in the formation of trans olefins containing a perfluoro-tert-butyl group (Ia, Ib), cesium perfluoro-2-methylpropenolate (II), and 2-H-perfluoro-2-methylpropane (III) [1]:



$$3\,(CF_3)_2C{=}CF_2 + CsF + \underset{\diagdown O \diagup}{H_2C{-}CHR} \rightarrow \underset{(Ia,\ b)}{(CF_3)_3CCH{=}CHR} + \underset{(II)}{(CF_3)_2C{=}CFO^-Cs^+} + \underset{(III)}{(CF_3)_3CH}$$

$R = H$ (a), Me (b).

Epichlorohydrin reacts similarly with PFIB; however, in the olefin of type I obtained ($R = CH_2Cl$) the chlorine atom in the chloromethyl group is replaced by a second perfluoro-tert-butyl group [1]:



$$4\,(CF_3)_2C{=}CF_2 + 2\,CsF + \underset{\diagdown O \diagup}{H_2C{-}CHCH_2Cl} \rightarrow (CF_3)_3CCH{=}CHCH_2C(CF_3)_3 + (II) + (III) + CsCl$$

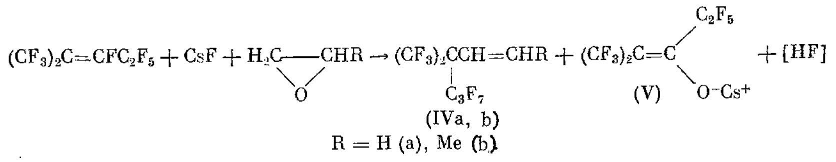
It was postulated that a necessary condition for the realization of these reactions is the formation of a stable perfluoro-tert-butyl anion [1].

More recently we showed that the hexafluoropropylene (HFP) dimer, i.e., perfluoro-2-methyl-2-pentene (PFMP), like PFIB, easily forms a stable tertiary carbanion, viz., the perfluoro(dimethylpropyl)methyl carbanion, as a result of the reversible addition of a fluoride ion:

$$(CF_3)_2C = CFC_2F_5 + CsF \rightleftarrows (CF_3)_2(C_2F_7)\bar{C}Cs^+$$

This carbanion reacts under fairly mild conditions (50-60°C) with practically quantitative yields with such highly electrophilic reagents as benzyl bromide and allyl bromide [2]. For this reason it seemed of interest to investigate the reaction of PFMP with various α-oxides.

As was expected, the reaction of PFMP with ethylene oxide and propylene oxide in the presence of CsF produces trans olefins containing the perfluoro-tert-alkyl group $(CF_3)_2C{-}C_3F_7$ (IVa and IVb) and cesium perfluoro-2-methyl-2-pentene-3-olate (V):



$$(CF_3)_2C{=}CFC_2F_5 + CsF + \underset{\diagdown O \diagup}{H_2C{-}CHR} \rightarrow \underset{(IVa,\ b)}{(CF_3)_2\underset{C_3F_7}{\underset{|}{C}}CH{=}CHR} + \underset{(V)}{(CF_3)_2C{=}C\begin{matrix}\diagup C_2F_5\\ \diagdown O^-Cs^+\end{matrix}} + [HF]$$

$R = H$ (a), Me (b).

Somewhat unexpected results were obtained when PFMP was reacted with epichlorohydrin. In this case, unlike the analogous reaction with PFIB, trans-1,1,1,7,7,8,8,9,9,9-decafluoro-2,6,6-tris(trifluoromethyl)-4-nonene (VI), 2-fluoro-2-pentafluoroethyl-3,3-bis(trifluoromethyl)-5-[α,α-dihydro-β,β-bis(trifluoromethyl)-perfluoroamyl]tetrahydrofuran (VII), and 2-H-perfluoro-2-methylpentane (VIII) are formed:

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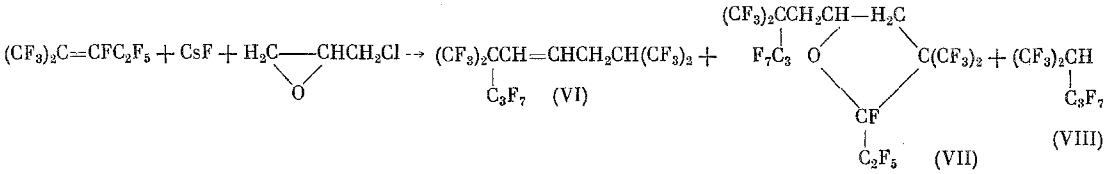
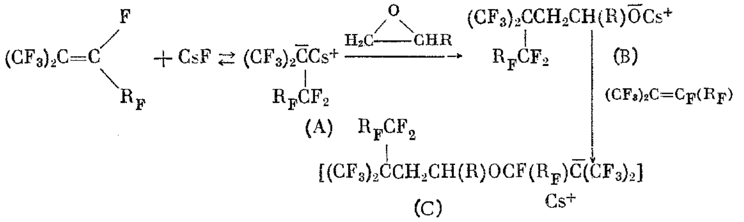
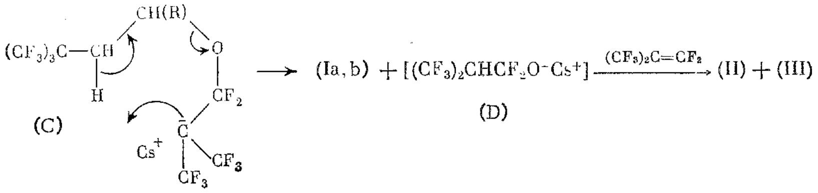


Despite some differences obtained when the α-oxides react with PFIB and PFMP, it is perfectly clear that the first steps in the reactions are identical in all cases:

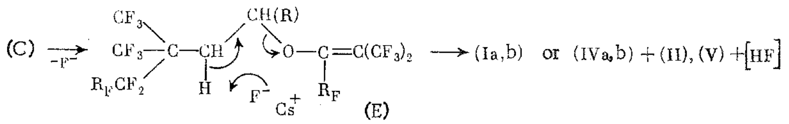


The perfluorinated tertiary carbanions (A) open the oxide ring to form the corresponding cesium alkoxides (B), and the latter react with a second olefin molecule to form intermediate carbanions (C). The further conversions of these carbanions determine the final products in each specific case.

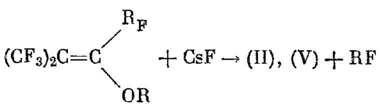
A mechanism for stabilization of carbanion C involving the intramolecular removal of a proton for the methylene group in the α position relative to the electron-acceptor perfluoro-tert-butyl group and cleavage of the C–O bond was previously proposed for the reaction of PFIB with α-oxides. This results in the formation of olefins Ia and Ib and an "adduct" of α-hydrohexafluoroisobutyryl fluoride with CsF (D). The action of a third molecule of PFIB, which acts as a dehydrofluorinating reagent, results in the formation of cesium perfluoro-2-methylpropenolate (II) and 2-H-perfluoro-2-methylpropane (III) [1]:



Another reaction scheme is possible. Carbanions of type C can eliminate F^- to form intermediate vinyl ethers (E). Under the action of a base (CsF in diglyme), the latter split off an acid, i.e., the enol $(CF_3)_2C = C(R_F)OH$, to form enolates II and V and olefins Ia and Ib or IVa and IVb:



This scheme is supported by the fact that alkylperfluoroalkenyl ethers (IX), which are derivatives of PFIB and PFMP, are capable of being split under the action of CsF to form the corresponding cesium perfluoroenolates (II and V) and alkyl fluorides [3]:



$$(CF_3)_2C{=}C(R_F)(OR) + CsF \rightarrow (II),\ (V) + RF$$

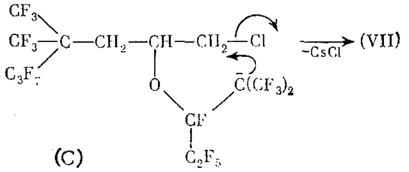
(IX)

It may be postulated that in certain cases the attack of F^- is directed at the β H atom of the alkyl group (splitting of ethers of type E) rather than at the α C atom of the same group (splitting of ethers of type IX), i.e., the perfluoroenolate anions are better leaving groups in the 1,2-elimination reactions.

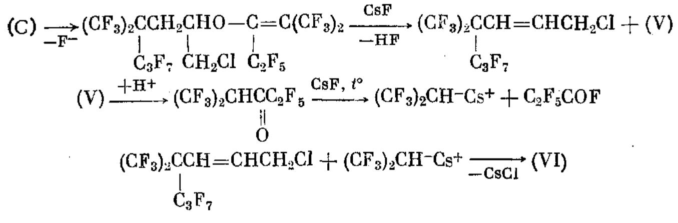
TABLE 1.

Compound	bp, °C (p, mm Hg)	IR (Raman) spectrum (ν, cm^{-1})	Yield, %	Found/Calculated, %		
				C	H	F
(IVa)	101–102	1650	82	27,3/27,7	0,73/0,87	71,7/71,4
(IVb)	118–120	1665	28	29,7/30,0	1,18/1,30	68,9/68,6
(Ia)	53–54	(1650)	77	[1]		
(Ib)	79–81	(1660)	77	[1]		
(VI)	105–106(70)	(1670)		28,0/28,2	0,80/0,98	70,8/70,8
(VII)	100(1)			26,6/26,6	0,89/0,74	69,9/70,3
(X)	105–106	1670		[6, 7]		

In the reaction of epichlorohydrin with PFMP carbanion C is stabilized differently, i.e., by the intramolecular replacement of Cl in the chloromethyl group to form the substituted tetrahydrofuran VII:



However, another path, which is analogous to one described above and produces olefin VI, is realized in parallel:

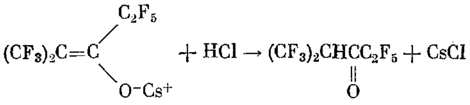


$$(C)\xrightarrow[-F^-]{}(CF_3)_2\underset{C_3F_7}{C}CH_2\underset{CH_2Cl}{C}HO-\underset{C_2F_5}{C}=C(CF_3)_2\xrightarrow[-HF]{CsF}(CF_3)_2\underset{C_3F_7}{C}CH=CHCH_2Cl+(V)$$

$$(V)\xrightarrow{+H^+}(CF_3)_2CH\underset{\overset{\|}{O}}{C}C_2F_5\xrightarrow{CsF,\ t^\circ}(CF_3)_2CH^-Cs^++C_2F_5COF$$

$$(CF_3)_2\underset{C_3F_7}{C}CH=CHCH_2Cl+(CF_3)_2CH^-Cs^+\xrightarrow[-CsCl]{}(VI)$$

The decomposition of 2-H-perfluoro-2-methyl-3-pentanone under the action of CsF was confirmed by a special experiment. In the reaction under consideration a ketone is formed when enolate V is reacted with HCl, whose source is the HF–CsCl system:



$$(CF_3)_2C=C\begin{matrix}C_2F_5\\O^-Cs^+\end{matrix}+HCl\rightarrow(CF_3)_2CH\underset{\overset{\|}{O}}{C}C_2F_5+CsCl$$

As we see, when PFIB and PFMP are reacted with ethylene oxide and propylene oxide, basically similar products, viz., olefins containing a perfluoro-tert-alkyl radical (Ia and Ib or IVa and IVb) and the corresponding cesium enolates (II and V), are formed. Some differences due to the nature of the original olefin are also characteristic of these reactions.

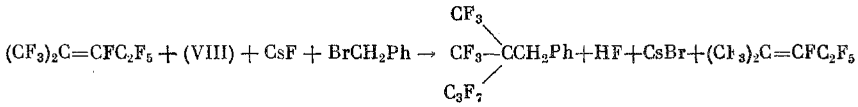
Apparently, because of the high electrophilicity of PFIB, the concentration of the perfluoro-tert-butyl anion in diglyme is significantly higher than that of the perfluoro-tert-hexyl anion $(CF_3)_2\bar{C}-C_3F_7$, as is confirmed by the ^{19}F NMR spectrum. Clearly for this reason, the α-oxides react with PFIB within several hours at 20–50°C, while their reactions with PFMP require heating to 130°C for 100 h or more.

When PFIB is reacted with α-oxides, III is formed along with olefins Ia and Ib and enolate II, while the corresponding product VIII was not detected in the products of the reaction of PFMP with ethylene oxide and propylene oxide. The reasons for this difference become clear when the specially devised experiments are considered.

1. When equimolar amounts of PFIB, III, CsF, and benzyl bromide are reacted, III remains unreacted:

$$(CF_3)_2C=CF_2 + (III) + CsF + BrCH_2Ph \rightarrow (CF_3)_3CCH_2Ph + CsBr + (III)$$

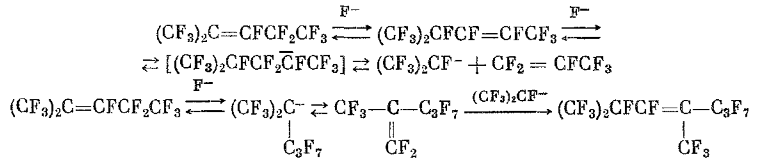
2. When equimolar amounts of PFMP, VIII, CsF, and benzyl bromide are reacted, PFMP remains unreacted:



$$(CF_3)_2C=CFC_2F_5 + (VIII) + CsF + BrCH_2Ph \rightarrow (CF_3)(C_3F_7)C(CF_3)CH_2Ph + HF + CsBr + (CF_3)_2C=CFC_2F_5$$

In each case a carbanion is generated in two equilibrium reactions, viz., the reversible addition of F^- to the perfluoroolefin (PFIB or PFMP) and the reversible deprotonation of the hydrofluoride of the perfluoroolefin (III or VIII). In the former case (the PFIB–III system), the preferable source of the carbanion is the perfluoroolefin (PFIB), and in the latter case (the PFMP–VIII system), it is the hydrofluoride (VIII). Clearly, for just this reason, hydrofluoride VIII was not detected in the reaction products.

The reaction of PFMP with ethylene oxide and propylene oxide in the presence of CsF is complicated by a secondary reaction, viz., the conversion of the dimer of HFP, i.e., PFMP, into the trimer of HFP, i.e., perfluoro-2,4-dimethyl-3-heptene (X), which is a mixture of the cis and trans isomers in a 3:1 ratio. The amount of the trimer X formed depends on the nature of the α-oxide. For example, in the case of ethylene oxide, its yield is 3%, and in the case of propylene oxide it is up to 23%. Trimer X is apparently formed according to the following scheme:



$$(CF_3)_2C{=}CFCF_2CF_3 \overset{F^-}{\rightleftarrows} (CF_3)_2CFCF{=}CFCF_3 \overset{F^-}{\rightleftarrows}$$
$$\rightleftarrows [(CF_3)_2CFCF_2\bar{C}FCF_3] \rightleftarrows (CF_3)_2CF^- + CF_2 = CFCF_3$$
$$(CF_3)_2C{=}CFCF_2CF_3 \overset{F^-}{\rightleftarrows} (CF_3)_2\underset{\displaystyle C_3F_7}{\underset{|}{C^-}} \rightleftarrows CF_3{-}\underset{\displaystyle CF_2}{\underset{\|}{C}}{-}C_3F_7 \xrightarrow{(CF_3)_2CF^-} (CF_3)_2CFCF{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}C_3F_7$$

which is similar to that proposed for the conversion of the isomeric trimers of HFP perfluoro-2-methyl-3-propyl-2-pentene and perfluoro-3-isopropyl-4-methyl-2-pentene into X under the action of F^- under severe conditions (100°C, 100 h) [4]. However, in our case, the source of the hexafluoroisopropyl anion is the molecule of the HFP dimer, i.e., PFMP. The oligomerization of HFP under severe conditions (130-200°C) produces trimer X exclusively [5]. Therefore, it may be postulated that trimer X is thermodynamically more stable than the other oligomers of HFP. Just this factor is apparently the driving forces for the conversion of the HFP dimer into the HFP trimer (X).

Under severe conditions PFMP is capable of being converted into the HFP trimer (X). Nevertheless, if the α-oxide is sufficiently active, the main reaction is the formation of olefins IVa and IVb and the cesium enolate V.

From the results presented it is seen that both terminal PFIB and internal PFMP react with different α-oxides in a basically similar manner. This reaction clearly has a general character for all fluorinated olefins capable of forming stable perfluorinated tertiary carbanions and can serve as a convenient method for synthesizing olefins with perfluoro-tert-alkyl groups.

EXPERIMENTAL

The ^{19}F NMR and ^1H NMR spectra (δ, ppm) were recorded on a Perkin–Elmer R-32 spectrometer (84.6 and 90 MHz) with TMS and CF_3COOH as external references. The GLC analysis of the reaction mixtures was carried out in a column (3 m × 3 mm) with 20% FS-1265 on Chromosorb W. The preparative separation was carried out in a column (4 m × 25 mm) with 20% QF-1.

3,3-Bis(trifluoromethyl)-4,4,5,5,6,6,6-heptafluoro-1-hexene (IVa). A suspension of 31 g (0.2 mole) of freshly calcined CsF in 70 ml of absolute diglyme was given an addition of 60 g (0.2 mole) of perfluoro-2-methyl-2-pentene (PFMP) and stirred for 0.5 h. Then the contents of the flask were transferred to a 200-ml autoclave, 8.8 g (0.2 mole) of ethylene oxide were added, and the mixture was heated for 100 h at 130°C. The low-boiling products (35 g) were collected in a trap (– 78°C) from the reaction mixture in a vacuum (15 torr) and distilled. This yielded 30 g of a fraction with bp 100-103°C containing 95% IVa and 5% perfluoro-2,4-

dimethyl-3-heptene (X) according to the GLC data. The mixture was separated with the aid of preparative GLC. Pure IVa was obtained (Tables 1 and 2). The residue of the reaction mixture was a solution of cesium perfluoro-2-methyl-2-penten-3-olate (V) in diglyme according to the ^{19}F NMR data. An oil precipitated when this solution was treated with 5% HCl. It was separated, washed with water, dried with $MgSO_4$, and distilled. This yielded 19.6 g (66%) of 2-H-perfluoro-2-methyl-3-pentanone with bp 60°C [8].

Trans-4,4-Bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-2-heptene (IVb). In a similar manner 31 g (0.2 mole) of CsF, 60 g (0.2 mole) of PFMP, 12 g (0.2 mole) of propylene oxide, and 70 ml of diglyme were heated in an autoclave for 130 h at 130°C. The low-boiling reaction products (59 g) were distilled off into a trap (−78°C) from the reaction mixture in a vacuum (15 torr). According to the ^{19}F NMR data, the residue was a solution of V in diglyme. The contents of the trap were distilled, and two fractions were collected.

Fraction 1 (43 g), bp 35-60°C. According to the GLC data, it is a mixture of unreacted PFMP (81.4%) and propylene oxide (18.6%). The extent of conversion of PFMP was 45%.

Fraction 2 (11.5 g), bp 105-120°C. According to the GLC data, it is a mixture of 45% IVb and 55% X. The mixture was separated by preparative GLC. This yielded 4.5 g (28%) of IVb and 5 g of X (see Tables 1 and 2).

Reaction of Perfluoro-2-methyl-2-pentene with Epichlorohydrin in the Presence of CsF. In a similar manner 120 g (0.4 mole) of PFMP, 20 g (0.2 mole) of epichlorohydrin, 62 g (0.4 mole) of CsF, and 100 ml of diglyme were heated in an autoclave for 80 h at 130°C. The reaction mixture was treated with water acidified with HCl, and the oil was separated, washed with water, dried with $MgSO_4$, and distilled. Three fractions were collected.

Fraction 1 (33 g), bp 55-82°C. According to the GLC data, it contains the original PFMP (51%), 2-H-perfluoro-2-methylpentane (VIII) (39%), and unidentified products (10%).

Fraction 2 (43 g), bp 95-135°C (70 mm Hg). According to the GLC data, it consists of trans-1,1,1,7,7,8,8,9,9,9-decafluoro-2,6,6-tris(trifluoromethyl)-4-nonene (VI) (65%), which was isolated with the aid of preparative GLC in a pure form (see Tables 1 and 2).

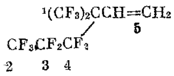
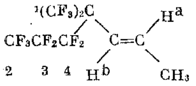
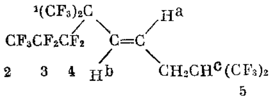
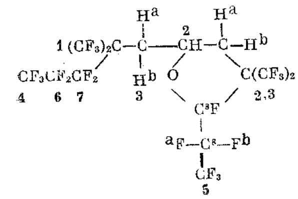
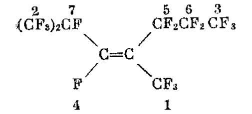
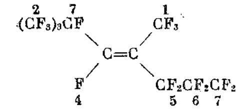
Fraction 3 (18 g), bp 102-113°C (10 mm Hg). According to the GLC data, it consists of 2-fluoro-2-pentafluoroethyl-3,3-bis(trifluoromethyl)-5-[α,α-dihydro-β,β-bis(trifluoromethyl)perfluoroamyl]tetrahydrofuran (VII) (90%), which was isolated with the aid of preparative GLC (see Tables 1 and 2).

Reaction of Perfluoroisobutylene, 2-H-Perfluoro-2-Methylpropane (III), and CsF with Benzyl Bromide. A mixture of 4 g (0.02 mole) of PFIB, 4.4 g (0.02 mole) of III, 3 g (0.02 mole) of CsF, and 3.5 g (0.02 mole) of benzyl bromide in 10 ml of diglyme was stirred at 20°C until the bromide disappeared (GLC monitoring). According to the ^{19}F NMR data, at the conclusion of the reaction, the reaction mass was a mixture of unreacted III and 1-phenyl-2,2-bis(trifluoromethyl)-3,3,3-trifluoropropane. From the reaction mixture 3.4 g of III were distilled off into a trap (−78°C). The residue was poured into water. An oil separated, and it was washed with water, dried with $MgSO_4$, and distilled. This yielded 7 g (88%) of 1-phenyl-2,2-bis (trifluoromethyl)-3,3,3-trifluoropropane with bp 158-160°C [9].

Reaction of Perfluoro-2-methylpentene, 2-H-Perfluoro-2-methylpentane (VIII), and CsF with Benzyl Bromide. A mixture of 6 g (0.02 mole) of PFMP, 6.4 g (0.02 mole) of VIII, 3 g (0.02 mole) of CsF, and 3.5 g (0.02 mole) of benzyl bromide in 20 ml of diglyme was stirred at ~20°C until the bromide disappeared (GLC monitoring). According to the ^{19}F NMR data, at the conclusion of the reaction, the reaction mixture consisted of unreacted PFMP and 1-phenyl-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane. The reaction mixture was poured into water, and the oil was separated, washed with water, dried with $MgSO_4$, and distilled. This yielded 5 h of the original PFMP with bp 49-52°C and 7.1 g (87%) of 1-phenyl-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane with bp 67-70°C (6 torr) [2].

Reaction of 2-H-Perfluoro-2-methyl-3-pentanone with CsF. A mixture of 6 g (0.02 mole) of 2-H-perfluoro-2-methyl-3-pentanone and 3 g (0.02 mole) of CsF in 10 ml of diglyme was stirred for 1 h at ~20°C. Partial dissolution of the CsF and warming of the reaction mixture, which consisted of the original ketone and cesium enolate V in a 1:1 ratio, according to the ^{19}F NMR data, were observed. The mixture was transferred to an ampul and heated for 6 h at 130°C. The ampul was opened, and the gas evolved was collected in a trap. According to the ^{19}F NMR data, the contents of the trap consisted of pure perfluoropropionyl fluoride (2.5 g, 75%). The residue was treated with water, and the oil was separated. According to GLC and ^{19}F NMR data, the oil is a complex mixture of unidentified products.

TABLE 2

Compound	^{19}F NMR spectrum (δ, ppm, J, Hz)	PMR spectrum (δ, ppm, J, Hz)
 (VIa)	δ_1 −13,3, δ_2 4,4, δ_3 46,2, δ_4 32,0; $J_{1-3} = 10,0$, $J_{2-4} = 14,0$, $J_{3-4} = 6,0$, $J_{1-4} = 12,0$	δ_5 5,4 br. s
 (IVb)	δ_1 −13,9, δ_2 4,6 δ_3 46,3, δ_4 31,9; $J_{1-3} = 10,0$, $J_{2-4} = 13,4$, $J_{1-4} = 12,0$	δ_{CH_3} 1,6, δ_{H^a} 6,3, δ_{H^b} 5,5; $J_{CH_3-H^a} = 6,8$, $J_{H^a-H^b} = 16,4$
 (VI)	δ_1 −13,4, δ_2 4,1, δ_3 49,3, δ_4 35,0, δ_5 −9,2; $J_{1-3} = 11,7$, $J_{1-4} = 8,8$, $J_{2-4} = 13,2$, $J_{5-H^c} = 7,5$	δ_{CH_2} 2,5, δ_{H^a} 6,3, δ_{H^b} 5,6, δ_{H^c} 2,7: $J_{CH_2-H^a} = 6,7$, $J_{H^a-H^b} = 16,7$, $J_{H^c-5} = 7,3$
 (VII)	δ_1 −14,4, δ_2 −13,3, δ_3 −12,0, δ_4 2,2, δ_5 2,2, δ_6 45,1, δ_7 29,3, δ_{8^a} 43,0, δ_{8^b} 46,7, δ_9 34,7, $J_{1-6} = 11,0$, $J_{1-7} = 13,0$, $J_{2-3} = 11,0$, $J_{4-7} = 14,0$, $J_{5-9} = 15,0$, $J_{8^a-8^b} = 290,0$, $J_{8^a-2} = 27,5$, $J_{8^b-2,3} = 17,0$	$\delta_{1^{a,b}}$ 2,1; 2,9, δ_2 4,9, $\delta_{3^{a,b}}$ 2,5; 2,8; $J_{1^a-1^b} = 14,7$, $J_{1^a-2} = 7,0$, $J_{1^b-2} = 8,5$, $J_{3^a-3^b} = 16,7$, $J_{3^a-2} = 4,0$, $J_{3^b-2} = 5,5$
 (X)	δ_1 − 19,0, δ_2 −1,9, δ_3 5,2, δ_4 8,8, δ_5 =25,0 δ_6 46,1, δ_7 105,0; $J_{1-4} = 29,5$, $J_{1-5} = 15,4$, $J_{1-6} = 9,2$, $J_{2-7} = 6,5$, $J_{2-5} = 3,1$, $J_{3-5} = 10,7$, $J_{3-7} = 3,6$, $J_{5-7} = 67,7$ $J_{6-7} = 32,5$	
 (X)	δ_1 −23,4, δ_2 −1,9, δ_3 5,2, δ_4 11,9, δ_5 30,3, δ_6 49,2, δ_7 105,7; $J_{1-7} = 43,9$, $J_{2-7} = 6,3$, $J_{2-1} = 3,1$, $J_{3-5} = 10,0$, $J_{5-1} = 17,0$, $J_{5-4} = 38,2$, $J_{6-1} = 8,2$, $J_{6-4} = 17,6$, $J_{7-4} = 6,3$	

CONCLUSIONS

1. Perfluoro-2-methyl-2-pentene reacts with α-oxides in the presence of CsF like perfluoroisobutylene. Olefins containing a perfluoro(dimethylpropyl)methyl group and cesium perfluoro-2-methyl-penten-3-olate are formed.

2. The reaction of perfluoro-2-methyl-2-pentene with epichlorohydrin in the presence of CsF results in the formation of trans-1,1,1,7,7,8,8,9,9,9-decafluoro-2,6,6-tris(trifluoromethyl)-4-nonene, 2-fluoro-2-pentafluoroethyl-3,3-bis(trifluoromethyl)-5-[α,α-dihydro-β,β-bis(trifluoromethyl)perfluoroamyl]tetrahydrofuran, and 2-H-perfluoro-2-methylpentane.

3. The hexafluoropropylene dimer perfluoro-2-methyl-2-pentene is partially converted under the action of CsF into the thermodynamically most stable hexafluoropropylene trimer perfluoro-2,4-dimethyl-3-heptene.

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TRANSFORMATIONS OF α,α-DIFLUOROCARBONYL COMPOUNDS

V. REACTION OF PERFLUORO-2-HEXANONE WITH PHENYLHYDRAZINE

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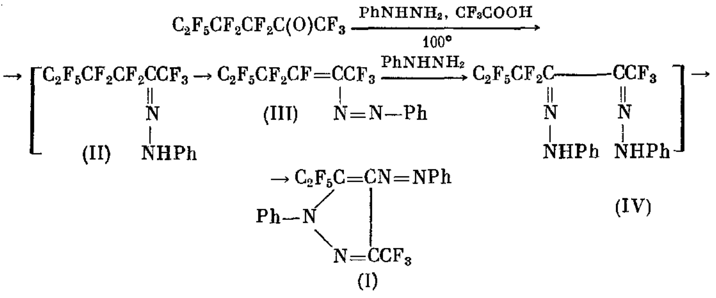
and I. L. Knunyants

UDC 542.91:547.284.6'
161:547.556.8

It has already been shown that ketones containing α-difluoromethylene groups form with excess of phenylhydrazine base or phenylhydrazine acetate, at an elevated temperature, bisphenylhydrazones of α-dicarbonyl compounds, or products of their dehydrofluorination, the corresponding pyrazoles. The α-difluoromethylene group of the ketones transforms into the phenylhydrazone group as the result of the initial reaction with the C=O group; in the monohydrazone formed, the F atoms of the neighboring CF_2 group become mobile due to the electron-donor phenylhydrazone grouping. Incompletely fluorinated ketones, such as pentafluoroacetone, methyl heptafluoropropyl ketone, phenyl heptafluoropropyl ketone, can also participate in this reaction [1].

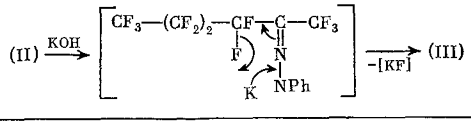
It was interesting to clarify whether this reaction can be extended to perfluoro ketones, i.e., whether the electron-donor ability of the phenylhydrazone group is sufficient to activate the α-difluoromethylene group in the perfluoro compounds, where this electron-donor ability should be distributed between two neighboring strongly electrophilic groupings. The present work describes the study of the reaction of perfluoro-2-hexanone with phenylhydrazine.

It was found that perfluoro-2-hexanone does not react with phenylhydrazine under the conditions previously used by us (in the presence of acetic or sulfuric acid, at 100°C). But when AcOH or H_2SO_4 are replaced by CF_3COOH, 1-phenyl-3-trifluoromethyl-4-phenylazo-5-pentafluoroethylpyrazole (I) is readily formed



Pyrazole (I) is formed as the result of successive transformations of perfluoro-2-hexanone into monohydrazone (II), azoolefin (III), and bisphenylhydrazone (IV), which is dehydrofluorinated to (I). To confirm the formation mechanism of pyrazole (I), we attempted to synthesize the above intermediate products.

The azoolefin (III) cannot be obtained under mild conditions described previously in [1]. Compound (III) is formed in good yield when product (II) is decomposed by solid KOH



A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1092-1095, May, 1981. Original article submitted July 15, 1980.

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