^{19}F NMR spectrum: 2.1 (CF_3, $J_{CF_3-F_A^2}$ = 11.3, $J_{CF_3-F_B^2}$ = 6.2 Hz), 32.7 ($\underline{CF_2}CF_3$, $J_{CF_2-F_A^2}$ = 29.2), 34.1 and 43.7 ($2CF_2^2$, AB system, J_{A-B} = 291 Hz), 39.5 and 60.7 ($2CF_2^3$, AB system, J_{A-B} = 282), 46.6 and 64.8 (CF_2^4, AB system, J_{A-B} = 296 Hz). Found: C 23.21; F 68.56; Cl 8.56%. $C_8F_{15}Cl$. Calculated: C 23.05; F 68.43; Cl 8.42%.

CONCLUSIONS

Perfluoro-1-alkylcyclocarbanions were synthesized from perfluoro-1-ethylcyclobutene, perfluoro-1-methylcyclopentene, perfluoro-1-ethylcyclohexene and CsF in DMF and were identified by ^{19}F and ^{13}C NMR spectra.

Perfluoro-1-alkylcyclocarbanions add chlorine to form 1-chloro-1-perfluoroalkylcycloalkanes.

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REACTIONS OF PERFLUORO-1-ALKYLCYCLOALKENES WITH ALCOHOLS AND PROPERTIES OF VINYL ETHERS FORMED

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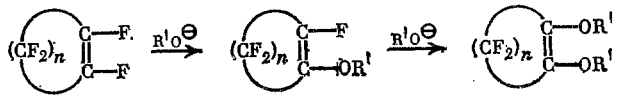
UDC 542.91:547.361.2'26'161

Perfluorocycloalkenes react smoothly with alcoholates by substitution of vinyl F atoms by the R'O group. Perfluorocyclobutene [1-3] and perfluorocyclopentene [1, 2] form successively mono- and disubstituted derivatives:



where n = 2, 3, R' = Me, Et, CH_2CF_3.

Perfluorocyclohexene [3-5] reacts in a somewhat more complex way: the carbanion (A), formed intermediately during attack by a nucleophile, becomes stabilized, due not only to elimination of the "vinyl" fluorine atom (F_a) but also of the "allyl" fluorine (F_b). Di- and trialkoxy derivatives were found in the high-boiling fraction (~10%). Addition products of alcohols to the multiple bond were practically not detected, and they were obtained by another method [6]. In the present work, we studied the reactions of alcohols with perfluorocycloalkenes (Iα, β, γ) containing a perfluoroalkyl substituent at the 1 position. It

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1331-1340, June, 1986. Original article submitted February 19, 1985.

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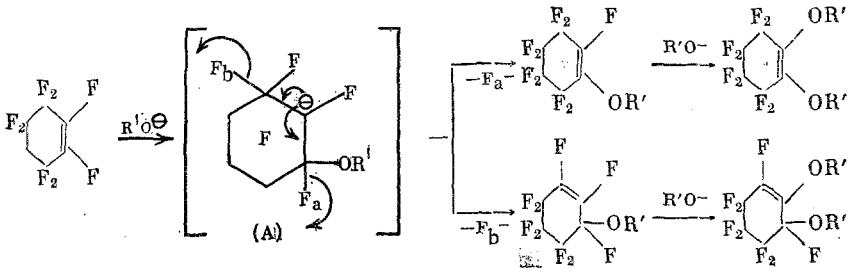
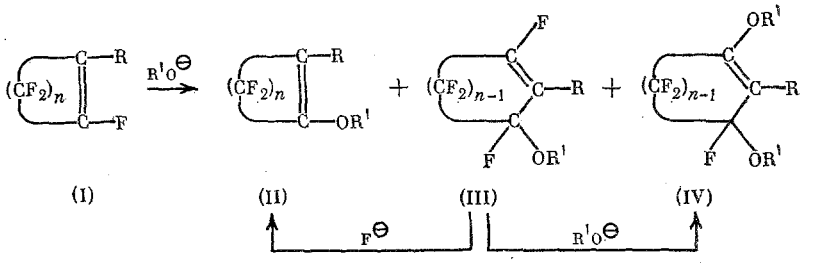
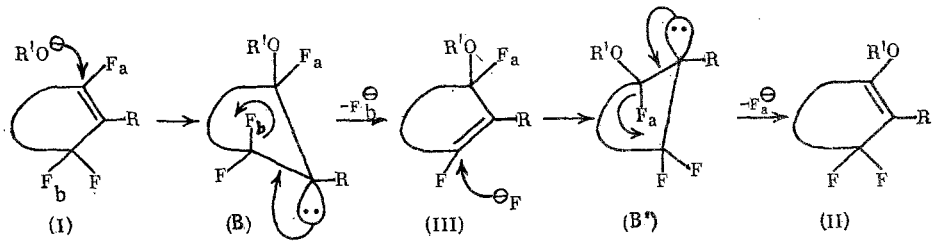


was shown that cycloolefins (Iα, β, γ) readily react with alcohols only in the presence of catalytic amounts of Et_3N to form products of the substitution of one or two F atoms by alkoxy group. The yield of the substituted derivatives (IV) increases with increase in the amount of alcohol and Et_3N taken. The initially formed "allyl" substitution product (III) readily isomerizes in the presence of a fluoride ion into the thermodynamically more stable vinyl ether (II)



where R = C_2F_5, n = 2 (α); R = CF_3, n = 3 (β); R = C_2F_5, n = 4 (γ); R′ = = Me (a); Et (b); $Cl(CH_2)_2$ (c); $CH_2=CHCH_2$ (d).

In the reaction of perfluoro-1-ethylcyclohexene (Iγ) with alcohols, the main product is the ether (IIIγ). The preferential formation of the "allyl" substitution product is explained by the fact that the strong electron-accepting perfluoroalkyl substituent R stabilizes the carbanion (B) to a greater extent than the fluorine atom [compare with carbanion (A)]. However, the bulky perfluoroalkyl substituent, by occupying the sterically more favorable equatorial position, determines the axial orientation of the unshared electron pair (UEP). This should favor the elimination of the "allylic" fluorine atom F_b, the only one present in the trans position with respect to the UEP of the carbanion (B) (cf. [4, 6]):



As already shown, the isomerization of (IIIγ) into (IIγ) proceeds by the action of fluoride ion. Carbanion (B′) is thus generated, in which the F_a atom is already transoid.

In contrast, in the case of four- and five-membered rings (Iα, β), vinyl ethers (II) predominate in the reaction products. This is possibly due to the fact that in this case the (B) ⇄ (B′) transformation proceeds due to rapid inversion of the UEP of the carbanion, caused by the noticeably smaller, than in the case of the six-membered ring, electronic and steric interactions of both the bulky perfluoroalkyl substituent (R) and the UEP with other ring substituents (the F atoms, the OR′ group) in a planar transition state (B″)

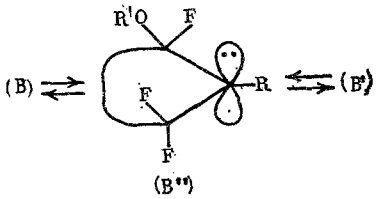
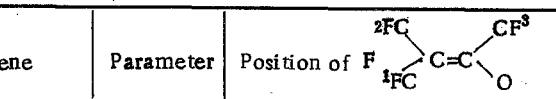
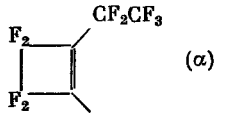
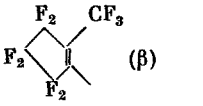
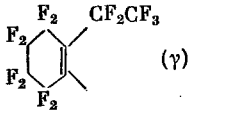
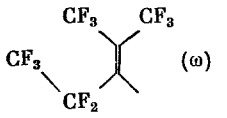
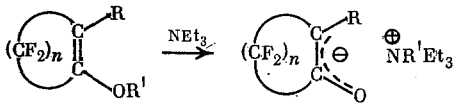


TABLE 1. Changes in ^{19}F NMR Chemical Shifts in Enolates (VI) and Salts (VII) Compared with Initial Ethers (II) [$\Delta\delta_1$ = δ(VI) − δ(II); $\Delta\delta_2$ = δ(VII) − δ(II)]

Structure of perfluoroalkene	Parameter	Position of F 		
		1	2	3
 (α)	$\Delta\delta_1$ $\Delta\delta_2$	−6,6 −0,1	−10,2 −2,1	4,4 1,4
 (β)	$\Delta\delta_1$ $\Delta\delta_2$	−5,0 −0,5	−12,5 −1,4	9,5 3,4
 (γ)	$\Delta\delta_1$ $\Delta\delta_2$	−4,5 1,0	−16,3 −2,1	5,4 3,3
 (ω)	$\Delta\delta_1$	−5,3	−7,6	1,8

*The sign − corresponds to a shift to the weak field.

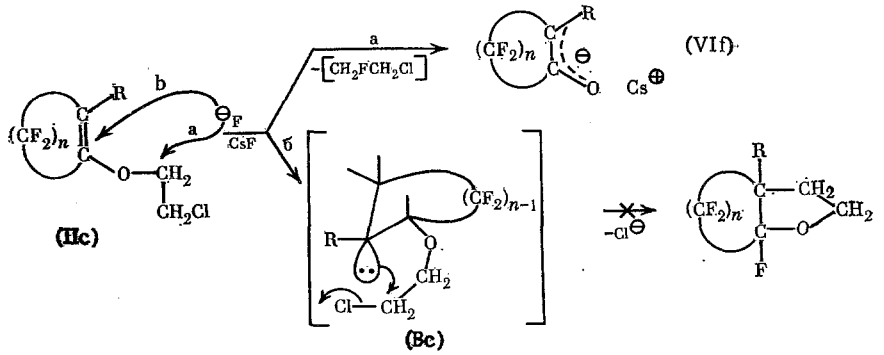
We studied certain chemical properties of the cycloalkenyl ethers formed. It is known [7, 8] that alkyl perfluoroalkenyl ethers are able to alkylate nucleophiles such as Et_3N and anion F^-. Similar reactions are characteristic of ethers (II):



(II) (VI)

The rate of alkylation of triethylamine by alkyl perfluorocycloalkenyl ethers increases with increase in the size of the ring, and for the cyclohexenyl ether (IIγ) it is only inappreciably lower than the rate of alkylation by the acyclic analog $(CF_3)_2C{=}C(OEt)C_2F_5$ (Vb). For the ethyl ethers (IIαb-γb) the following series of increase in the relative rate of alkylation of triethylamine was found: (IIα):(IIβ):(IIγ):(V) = 1:2:5:6.

β-Chloroethyl ethers (IIc) alkylate anion F^- to form enolates (VIf):

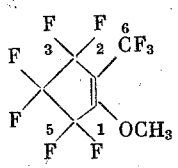
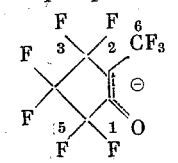


(IIc) (Bc) (VIf)

In this case there is no cyclization typical of acyclic β-chloroethyl perfluoroalkenyl ethers [9].

Compared with the initial ethers (II), for enolates (VI) downfield shifts of the signals

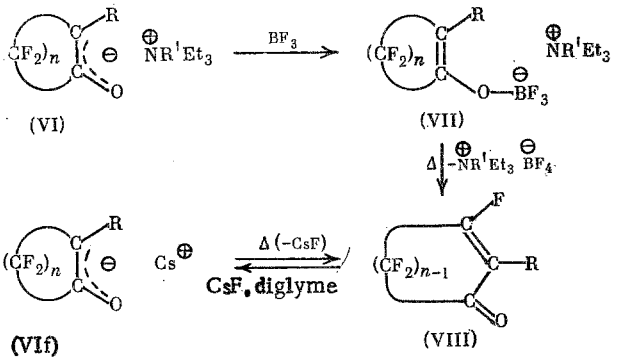
TABLE 2. Data of ^{13}C NMR Spectra of Ether (IIβa) (δ_{et}) and Enolate (VIβ) (δ_{en})

Compound	δ, ppm					
	C¹	C²	C³	C⁴	C⁵	C⁶
 (IIβa)	156,7	118,2	112,4	109,8	114,2	119,6
 (VIβ)	168.6	88,2	122,7	114,0	113,8	127,2
$\Delta\delta^* = \delta_{et} - \delta_{en}$	−11,9	30,0	−10,3	−4,2	0,4	−7,6

*The sign − corresponds to a shift to the weak field.

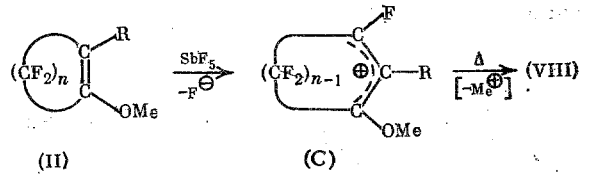
of the fluorine nuclei at positions 1 and 2 are characteristic (Table 1), which indicates the mesomeric nature of these enolates. Analysis of the ^{13}C NMR spectra on the example of cyclopentenyl derivatives, the methyl ether (IIβa) and the corresponding enolate (IV β) (Table 2) showed that in enolates of type (VI), the double bond actively participates in the delocalization of the negative charge. A 30-ppm shift of the C^2 signal to the strong field, compared with the case of the initial ether, indicates an actual increase in the electron density on this C atom.

When treated by BF_3 etherate, enolates (VI) give stable (20°C) salts (VII). The negative charge is probably localized on the B atom. In fact, with respect to the ^{19}F NMR spectra, compounds (VII) do not appreciably differ from ethers (II) (see Table 1), i.e., the C=C double bond in salts (VII) probably does not participate in the delocalization of the negative charge

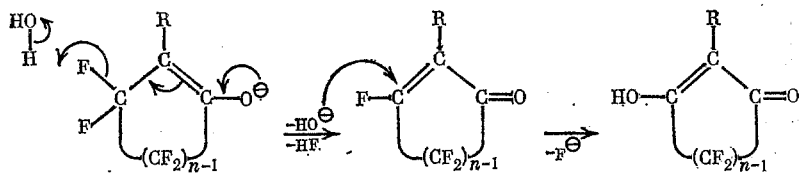


When salts (VII) are heated to 100°C, $\overset{\oplus}{N}R'Et_3\overset{\ominus}{B}F_4$ splits off, and cyclic vinyl ketones (VIII) are formed. The pyrolysis of cesium enolates (VIf) (after removal of the solvent) also gives vinyl ketones (VIII).

A convenient method for preparing ketones (VIII) is the reaction of vinyl ethers (II) with SbF_5. We have already found [10] that stable intermediates in these reactions are the mesomeric cycloalkenyl cations (C). During their thermal decomposition, ketones (VIII) are liberated:



Enolates (VI) are readily hydrolyzed and convert to β-hydroxyvinyl ketones (IX). The allylic fluorine atoms in the ring are probably fairly mobile. One of them readily splits off as an anion, and the other, in the vinyl ketone (VIII) that is formed, is replaced by a hydroxyl:

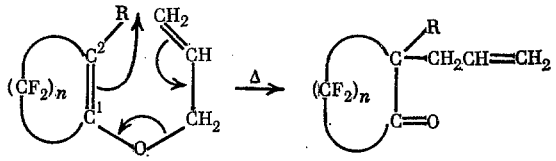


(VI) (VIII) (IX)

It should be noted that β-hydroxyvinyl ketones (IX) smoothly form from their vinyl ethers (II) if the alkylation of triethylamine is carried out in the presence of water, and in the reaction of olefins (I) with water, in the presence of Et_3N or KOH (cf. [8, 11-13]).

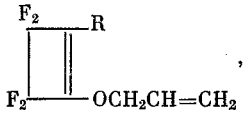
As known [14], allyl vinyl ethers with fluorine-containing substituents in the vinyl part of the molecule so readily enter into a Claisen rearrangement that many of them cannot be obtained in the pure state; the corresponding ketones are liberated immediately in the course of the reaction.

However, allyl perfluorocycloalkenyl ethers (IIαd-γd) (R' = $CH_2CH{=}CH_2$) were found to be stable and distill at 40-60°C without isomerization:



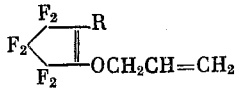
(IIα-γd) (Xα-γ)

Allyl ethers that are stable at 50-60°C have already been obtained in [14, 15]



where R = F, Cl, MeO. Their stability is probably related to steric hindrances for a coordinated rearrangement because of a relatively large C=O—O angle. The isomerization of 1-allyloxy-2-chloroperfluorocyclobutene (R = Cl) into 2-allyl-2-chloroperfluorocyclobutanone requires heating (8 h at 120-130°C [14]. The allyl ether (IIαd) (R = C_2F_5) is 50% converted into the corresponding ketone (Xα) after 2 days at 100°C.

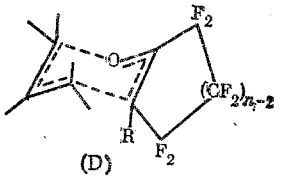
With increase in the size of the ring, the stability of the allyl ethers decreases and depends on the nature of the substituent at C^2. In five-membered rings, with R = F [14], the ether is unstable (2-allylperfluorocyclopentanone separates at once from the reaction



mixture), but in contrast, when R = Cl [16], first an allyl ether is obtained, which converts into a ketone only on a prolonged boiling to the extent of 85%, i.e., the half-conversion time is $t_{1/2} \approx 3.5$ h. The allyl ether (IIβd) (R = CF_3) is 50% rearranged in the course of 1 h at 100°C. Strong electron-accepting substituents (F and R_F) polarize the double bond and thus increase the nucleophilicity of the C^2 atom. The Cl atom is less electronegative than F and more bulky, and therefore the allyl ether with R = Cl is more stable than its analog with R = F. Increase in the stability of the allyl ether (IIβd) (R = CF_3) is probably due to a purely steric factor.

It is known [17] that the Claisen rearrangement, as a 3,3-sigmatropic rearrangement, proceeds through a six-π-electronic six-centered cyclic transition state, with an energetically

more favorable chair conformation [see (D)]. The rate of the reaction should thus be influenced to a considerable degree by the volume of substituent R which because of the cyclic structure of the "vinyl" part of the molecule of the ether, will always be present in a pseudoaxial position. The larger this volume, the stronger will be the 1,3-pseudoaxial interaction. Hence, increase in the volume of substituent R leads to slowing down of the rearrangement.



(D)

It is clear that the higher stabilization of the allyl ether (IIγd) compared with (IIβd) is due to a steric factor: increase in the ring size would probably lead to the acceleration of the rearrangement, since the isomerization of the acyclic analog $(CF_3)_2C{=}C(OCH_2CH{=}CH_2)C_2F_5$ (Vd) proceeds fairly rapidly ($t_{1/2} \approx 1$ h at 36°C). However, with increase in the volume of the substituent R from CF_3 (IIβd) to C_2F_5 (IIγd), the isomerization slows down ($t_{1/2}$ = 1.5 h at 100°C).

It should be noted that the presence of a fluorine ion does not influence the rate of isomerization of the allyl ethers (IIαd-γd).

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra (δ, ppm, J, Hz) were obtained on a Perkin-Elmer R-32 spectrometer (84.6 and 90 MHz, respectively) with reference to CF_3CO_2H and TMS as external standards. The IR spectra (ν, cm^{-1}) were run on a UR-20 spectrophotometer.

1-Methoxyperfluoro-2-ethylcyclobutene (IIαa). A mixture of 3.2 g (0.1 mole) of methanol and 0.1 g (1 mmole) of Et_3N was added dropwise, with stirring (0°C), to 13.1 g (0.05 mole) of perfluoro-1-ethylcyclobutene (Iα). After 1 h, the mixture was treated with water, and the organic layer was dried over $CaCl_2$. Yield, 10.7 g (78%) of a mixture of (IIαa) and 3-methoxyperfluoro-2-ethylcyclobutene (IIIαa) (4:1), bp 106-110°C. For (IIIαa): ^{19}F NMR spectrum: 9.3 m (CF_3), 40.9 m (CF_2), 49.8 m and 56.4 (CF_2, AB system, J = 216), 52.0 m (CF=), 66.4 m (CF). PMR spectrum: 3.3 s (CH_3). A 10-g portion of a mixture of (IIαa) and (IIIαa) was added to a suspension of 0.5 g of CsF in 10 ml of absolute diglyme, and the mixture was stirred for 2 h (20°C). After treatment with water, the organic layer was dried over $CaCl_2$. Yield, 9.1 g of (IIαa), bp 109°C. IR spectrum: 1692, 1710 (C=C), ^{19}F NMR spectrum: 8.8 s (CF_3), 35.0 m (CF_2), 36.0 s (CF_2), 40.2 m (CF_2). PMR spectrum: 3.8 s (CH_3). Found: C 30.98; H 1.01; F 62.63%. $C_7H_3F_9O$. Calculated: C 30.66; H 1.09; F 62.41%.

1-Ethoxyperfluoro-2-ethylcyclobutene (IIαb). In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-ethylcyclobutene (Iα), 4.6 g (0.01 mole) of ethanol, and 0.5 g (5 mmoles) of Et_3N, 10.4 g (71%) of (IIαb) were obtained, bp 127°C. IR spectrum: 1690, 1708 (C=C), ^{19}F NMR spectrum: 8.7 s (CF_3), 34.8 m (CF_2), 36.2 s (CF_2), 40.1 m (CF_2). Found: C 33.41; H 1.62; F 60.08%. $C_8H_5F_9O$. Calculated: C 33.33; H 1.74; F 59.37%.

1-Allyloxyperfluoro-2-ethylcyclobutene (IIαe). In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-ethylcyclobutene (Iα), 5.8 g (0.1 mole) of allyl alcohol and 0.1 g (1 mmole) of Et_3N, 11.4 g (76%) of a 4:1 mixture of (IIαe) and 3-allyloxyperfluoro-2-ethylcyclobutene (III αe) were obtained, bp 50-54°C (32 mm). For (IIIαe): ^{19}F NMR spectrum: 9.1 m (CF_3), 40.8 m (CF_2), 49.4 and 55.0 (CF_2, AB system, J = 214), 52.2 m (CF=), 62.9 m (CF). PMR spectrum: 3.9 m (CH_2O), 4.7-5.8 a set of m ($CH{=}CH_2$). A 11 g portion of a mixture of (IIαe) and (IIIαe) was added to a suspension of 0.5 g of CsF in 10 ml of absolute diglyme, and the mixture was stirred for 2 h (20°C). After treatment with water, the organic layer was separated and dried over $CaCl_2$. Yield 9.7 g of (IIαe), bp 47°C (30 mm). IR spectrum: 1665 ($C{=}CH_2$), 1697 and 1712 (C=C). ^{19}F NMR spectrum: 8.7 s (CF_3), 34.4 m (CF_2), 36.4 m (CF_2), 38.4 m (CF_2). PMR spectrum: 4.3 m (CH_2O), 4.7-5.8 a set of m ($CH{=}CH_2$). Found: C 35.88; H 1.43; F 57.21%. $C_9H_5F_9O$. Calculated: C 36.00; H 1.67; F 57.00%.

1-Methoxyperfluoro-2-methylcyclopentene (IIβa). In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-methylcyclopentene (Iβ), 3.2 g (0.1 mole) of methanol, and 0.1 g (1 mmole) of Et_3N, 11.1 g (81%) of (IIβa), bp 112°C, were obtained. IR spectrum: 1682 (C=C). ^{19}F NMR spectrum: −17.9 m (CF_3), 29.8 m (CF_2), 37.2 m (CF_2), 53.5 m (CF_2). PMR spectrum:

3.9 s (CH_3). Found: C 30.52; H 0.99; F 62.84%. $C_7H_3F_9O$. Calculated: C 30.66; H 1.09; F 62.41%.

1-Ethoxyperfluoro-2-methylcyclopentene (IIβb). In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-methylcyclopentene (Iβ), 4.6 g (0.1 mole) of ethanol, and 0.1 g (1 mmole) of Et_3N, 11.1 g (77%) of (IIβb), bp 66°C (72 mm), were obtained. IR spectrum: 1683 (C=C), ^{19}F NMR spectrum: −17.3 m (CF_3), 30.1 m (CF_2), 37.2 m (CF_2), 54.2 m (CF_2). PMR spectrum: 4.3 q (CH_2), 1.4 t (CH_3). Found: C 33.35; H 1.81; F 59.25%. $C_8H_5F_9O$. Calculated: C 33.33; H 1.74; F 59.37%.

In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-methylcyclopentene (Iβ), 2.3 g (0.5 mole) of ethanol, and 5 g (0.05 mole) of Et_3N, 7.5 g (52%) of (IIββ) and 4.7 g of 1,3-diethoxyperfluoro-2-methylcyclopentene (IVβb), bp 84°C (12 mm), were obtained. IR spectrum: 1672(C=C). ^{19}F NMR spectrum: −19.1 d.m. (CF_3), 44.9 d.m. (CF_2), 42.8 q.t.m (CF), 50.3 m (CF_2), J_{CF_3-CF} = 15, J_{CF_2-CF} = 14 Hz. Found: C 37.84; H 3.25; F 48.62%. $C_{10}H_{10}F_8O_2$. Calculated: C 38.22; H 3.18; F 48.41%.

1-β-Chloroethoxyperfluoro-2-methylcyclopentene (IIβc). In a similar way, from 13.1 g (0.05 mole) of perfluoro-1-methylcyclopentene (Iβ), 8.1 g (0.1 mole) of β-chloroethanol, and 0.2 g (2 mmoles) of Et_3N, 11.3 g (70%) of (IIβc), bp 61°C (28 mm) were obtained. IR spectrum: 1683 (C=C). ^{19}F NMR spectrum: −17.9 m (CF_3), 29.8 m (CF_2), 36.6 m (CF_2), 53.2 m (CF_2). PMR spectrum: 3.6 m (CH_2Cl), 4.3 m (CH_2O). Found: C 28.01; H 1.27; F 53.14%. $C_8H_4F_9ClO$. Calculated: C 29.77; H 1.24; F 53.02%.

1-Allyloxyperfluoro-2-methylcyclopentene (IIβe). In a similar way, from 13.1 g (0.5 mole) of perfluoro-1-methylcyclopentene (Iβ), 5.8 g (0.1 mole) of allyl alcohol, and 0.1 g (1 mmole) of Et_3N, 11.6 g (77%) of (IIβe), bp 51°C (42 mm), were obtained. IR spectrum: 1650 (C=CH_2), 1680 (C=C). ^{19}F NMR spectrum: −17.5 m (CF_3), 29.9 m (CF_2), 36.8 m (CF_2), 53.7 m (CF_2). PMR spectrum: 4.5 m (CH_2), 4.8-5.8 a set of m (CH=CH_2). Found: C 36.13; H 1.58; F 57.15%. $C_9H_5F_9O$. Calculated: C 36.00; H 1.67; F 57.00%.

1-Methoxyperfluoro-2-ethylcyclohexene (IIγa). In a similar way, from 18.1 g (0.05 mole) of perfluoro-1-ethylcyclohexene (Iγ), 3.2 g (0.1 mole) of methanol, and 0.2 g (2 mmoles) of Et_3N, 14.2 g (76%) of 3-methoxyperfluoro-2-ethylcyclohexene (IIIγa), bp 128°C, were obtained. IR spectrum: 1703 (C=C). ^{19}F NMR spectrum: 7.4 d.m. (CF_3, J = 13.3), 36.0 m (CF=), 48.2 m (CF), 32.9 and 36.7 (CF_2, AB system, J = 282), 42.5 and 48.7 (CF_2, AB system, J = 296), 52.3 m (CF_2), 55.2 and 61.2 (CF_2, AB system, J = 278). PMR spectrum: 3.4 s (CH_3). A 14-g portion of (IIIγa) was added to a suspension of 0.5 g of CsF in 10 ml of absolute diglyme, and the mixture was stirred for 2 h (20°C). After treatment with water, the organic layer was separated and dried over $CaCl_2$. Yield, 13.2 g of (IIγa), bp 135°C. IR spectrum: 1647 (C=C). ^{19}F NMR spectrum: 7.2 m (CF_3), 29.4 m (CF_2), 33.3 t. m. (CF_2, J = 14), 37.4 m (CF_2), 58.0 m [$(CF_2)_2$]. PMR spectrum: 3.8 s (CH_3). Found: C 28.86; H 0.88; F 65.96%. $C_9H_3F_{13}O$. Calculated: C 28.88; H 0.80; F 66.04%.

1-Ethoxyperfluoro-2-ethylcyclohexene (IIγb). In a similar way, from 18.1 g (0.05 mole) of perfluoro-1-ethylcyclohexene (Iγ), 4.6 g (0.1 mole) of ethanol, and 0.2 g (2 mmoles) of Et_3N, 13.6 g (70%) of 3-ethoxyperfluoro-2-ethylcyclohexene (IIIγb), bp 72°C (30 mm), were obtained. IR spectrum: 1705 (C=C). ^{19}F NMR spectrum: 6.7 d.m. (CF_3, J = 14.3), 35.0 m (CF=), 46.2 m (CF), 32.1 and 36.2 (CF_2, AB system, J = 283), 42.0 and 48.1 (CF_2, AB system, J = 299), 51.0 m (CF_2), 54.3 and 59.5 (CF_2, AB system, J = 278). A 13-g portion of (IIIγb[2]) was added to a suspension of 0.5 g of CsF in 10 ml of absolute diglyme, and the mixture was stirred for 2 h (20°C). After treatment with water, the organic layer was separated and dried over $CaCl_2$. Yield, 12 g of (IIγb), bp 74°C (28 mm). IR spectrum: 1648 (C=C). ^{19}F NMR spectrum: 6.3 m (CF_3), 28.7 m (CF_2), 34.1 t.m. (CF_2, J = 14), 37.6 m (CF_2), 58.4 m [$(CF_2)_2$]. PMR spectrum: 4.2 q (CH_2), 1.3 (CH_3). Found: C 30.78; H 1.33; F 63.55%. $C_{10}H_5F_{13}O$. Calculated: C 30.93; H 1.29; F 63.66%. In a similar way, from 18.1 g (0.05 mole) of (Iγ), 4.6 g (0.1 mole) of ethanol, and 0.5 g (5 mmoles) of Et_3N, 13 g (67%) of (IIγb) were obtained.

1-β-Chloroethoxyperfluoro-2-ethylcyclohexene (IIγc). In a similar way, from 18.1 g (0.05 mole) of perfluoro-1-ethylcyclohexene (Iγ), 8.1 g (0.1 mole) of β-chloroethanol, and 0.5 g (5 mmoles) of Et_3N, 14.4 g (68.8%) of (IIγc), bp 88°C (20 mm), were obtained. IR spectrum: 1648 (C=C). ^{19}F NMR spectrum: 5.7 m (CF_3), 28.7 (CF_2), 33.0 t.m. (CF_2, J = 14), 35.9 m (CF_2), 57.2 m [$(CF_2)_2$]. PMR spectrum: 3.6 m (CH_2Cl), 4.3 (CH_2O). Found: C 28.52; H 1.08; F 58.13%. $C_{10}H_4F_{13}ClO$. Calculated: C 28.40; H 0.95; F 58.46%.

1-Allyloxyperfluoro-2-ethylcyclohexene (IIγe). In a similar way, from 18.1 g (0.05 mole) of perfluoro-1-ethylcyclohexene (Iγ), 5.8 g (0.1 mole) of allyl alcohol, and 0.5 g (5 mmoles) of Et_3N, 14.4 g (71%) of (IIγe), bp 57° (22 mm), were obtained. IR spectrum: 1650 (C=C), IR spectrum: 1650 (C=C). ^{19}F NMR spectrum: 6.1 m (CF_3), 28.9 (CF_2), 32.6 t.m. (CF_2, J = 14.3), 36.3 m (CF_2), 57.5 m ((CF_2)$_2$). PMR spectrum: 4.6 m (CH_2), 4.8-5.8 a set of m (CH=CH_2). Found: C 33.09; H 1.43; F 61.68%. $C_{11}H_5F_{13}O$. Calculated: C 33.00; H 1.25; F 61.75%.

Tetraethylammonium Perfluoro-2-methylcyclopentenol-1-ate (VIβb). A mixture of 8.6 g (0.03 mole) of 1-ethoxyperfluoro-2-methylcyclopentene (IIβb) and 3 g (0.03 mole) of Et_3N was allowed to stand for 48 h at 20°C, and the volatile products were removed (30 min, 10 mm). From the residue, 10.6 g (91%) of (VIβb) were obtained. IR spectrum: 1650 (C=C). ^{19}F NMR spectrum (in CH_3CN): −22.8 m (CF_3), 17.4 m (CF_2), 46.7 m (CF_2), 52.7 m (CF_2). Found: C 43.39; H 5.29; F 44.08%. $C_{14}H_{20}F_9ON$. Calculated: C 43.19; H 5.14; F 43.96%.

Tetraethylammonium Perfluoro-2-ethylcyclobutenol-1-ate (VIαb). In a similar way, from 8.6 g (0.03 mole) of 1-ethoxyperfluoro-2-ethylcyclobutene (IIαb) and 3 g (0.03 mole) of Et_3N, 10.2 g (88%) of (VIβb) were obtained. IR spectrum: 1695, 1710 (C=C). ^{19}F NMR spectrum (in CH_3CN): 7.8 m (CF_3), 24.8 m (CF_2), 29.4 m (CF_2), 44.6 m (CF_2). Found: C 43.51; H 5.17; F 43.87%. $C_{14}H_2OF_9ON$. Calculated: C 43.19; H 5.14; F 43.96%.

Tetraethylammonium Perfluoro-2-ethylcyclohexenol-1-ate (VIγb). In a similar way, from 11.6 g (0.03 mole) of 1-ethoxyperfluoro-2-ethylcyclohexene (IIγb) and 3 g (0.03 mole) of Et_3N, 13.2 g (90%) of (VIγb) were obtained. IR spectrum: 1610 (C=C). ^{19}F NMR spectrum: 5.6 m (CF_3), 13.1 m (CF_2), 28.8 t. m (CF_2, J = 13.8), 42.8 m (CF_2), 54.9 m [(CF_2)$_2$]. Found: C 39.06; H 4.21; F 50.62%. $C_{16}H_{20}F_{13}ON$. Calculated: C 39.26; H 4.09; F 50.51%.

Competing Reactions of Ethyl Ethers (IIαb), (IIβb), (IIγb), and (V) with Triethylamine. From a homogeneous tricomponent mixture of equimolar amounts (∼0.01 mole) of 1-ethoxyperfluoro-2-methylcyclopentene (IIβb), Et_3N, and (IIαb), (IIγb), or (V), two layers gradually formed. After the mixture was left to stand for 48 h at 20°C, in the lower layer, mixtures of the initial ethers were found in a ratio of (IIαb)/(IIβb) = 2:1, (IIγb)/(IIβb) = 2:5, (V)/(IIβb) = 1:3, while in the upper layer there were mixtures of the corresponding enolates in a reversed ratio (according to the ^{19}NMR data).

Reaction of β-Chloroethyl Ethers (IIβc) and (IIγc) with CsF. A 6.5-g portion (0.02 mole) of 1-β-chloroethoxyperfluoro-2-methylcyclopentene (IIβc) was added to a suspension of 3.5 g (0.023 mole) of a freshly calcined CsF in 30 ml of absolute diglyme, and the mixture was stirred for 6 h at 120°C. According to ^{19}F NMR data, the reaction mixture is a solution of cesium perfluoro-2-methylcyclopentenol-1-ate (VIβf) in diglyme. In a similar way, from 8.5 g (0.02 mole) of 1-β-chloroethoxyperfluoro-2-ethylcyclohexene (IIγc) and 3.5 g (0.02 mole) of CsF in 30 ml of absolute diglyme, a solution of cesium perfluoro-2-ethylcyclohexenol-1-ate (VIγf) in diglyme was obtained.

The IR and ^{19}F NMR spectra of the solutions of cesium enolates (VIβf) and (VIγf) obtained were practically identical to the spectra of solutions of tetraethylammonium enolates (VIβb) and (VIγb), respectively.

Diglyme was removed from the solutions by distillation in vacuo (70°C at 25 mm). The residues were heated in vacuo (150°C at 10 mm) and in the traps (−78°C), 2.5 g (53%) of perfluoro-2-methylcyclopenten-3-one (VIIIβ) and 3.9 g (57%) of perfluoro-2-ethylcyclohexen-3-one (VIIIγ), respectively, were collected.

Perfluoro-2-ethylcyclobuten-3-one (VIIIα). A 2.9-g portion (0.02 mole) of $Et_2O{\cdot}BF_3$ was added dropwise, with stirring (0°C), to a solution of 7.8 g (0.02 mole) of tetraethylammonium perfluoro-2-ethylcyclobutenol-1-ate (VIαb) in 10 ml of absolute diglyme. Ether was removed (30 min at 100 mm). According to ^{19}F NMR data, the reaction mixture is a solution of salt (VIIαb) in diglyme. IR spectrum: 1700, 1710 (C=C). ^{19}F NMR spectrum: 7.6 m (CF_3), 31.8 m (CF_2), 34.9 m (CF_2), 38.3 m (CF_2), 76.1 m ($O\overset{\ominus}{B}F_3$). By distillation, 2.9 g (61%) of (VIIIα), bp 35°C, were obtained. IR spectrum: 1645, 1675 (C=C), 1810 (C=O). ^{19}F NMR spectrum: 7.8 m (CF_3), 33.5 m (CF), 37.5 m (CF_2), 37.7 m (CF_2). Found: C 30.28; F 63.17%. C_6F_8O. Calculated: C 30.00; F 63.33%.

Perfluoro-2-methylcyclopenten-3-one (VIIIβ). In a similar way, from 7.8 g (0.02 mole) of tetraethylammonium perfluoro-2-methylcyclopentenol-1-ate (VIβb) in 10 ml of absolute diglyme and 2.9 g (0.02 mole) of $Et_2O{\cdot}BF_3$, a solution of salt (VIIβb) in diglyme was obtained. IR spectrum: 1658 (C=C). ^{19}F NMR spectrum: −18.3 m (CF_3), 28.5 m (CF_2), 40.6 (CF_2), 54.3

m (CF_2), 76.1 m ($\overset{\ominus}{O}BF_3$). By distillation, 3.2 g (67%) of (VIIIβ), bp 54°C, were obtained. IR spectrum: 1695, 1705 (C=C), 1785 (C=O). ^{19}F NMR spectrum: −13.9 d (CF_3), 20.4 q.t.t. (CF), 49.1 d (CF_2^1), 51.2 m (CF_2^2), J_{CF_2-CF} = 14.7, $J_{CF_3-CF_2^1}$ = 1.9, $J_{CF_2^1-CF}$ = 15.0, $J_{CF_2^2-CF}$ = 3.8. Found: C 29.87; F 63.47%. C_6F_8O. Calculated: C 30.00. F 63.33%.

Perfluoro-2-ethylcyclohexen-3-one (VIIIγ). In a similar way, from 9.8 g (0.02 mole) of tetraethylammonium perfluoro-2-ethylcyclohexenol-1-ate (VIγb) in 10 ml of absolute diglyme and 2.9 g (0.02 mole) of $Et_2O \cdot BF_3$, a solution of salt (VIIγb) in diglyme was obtained. IR spectrum: 1640 (C=C). ^{19}F NMR spectrum: 6.7 m (CF_3), 27.3 m (CF_2), 34.3 t.m. (CF_2, J = 14), 40.7 m (CF_2), 57.8 [$(CF_2)_2$], 76.4 m ($\overset{\ominus}{O}BF_3$). By distillation, 4.8 g (71%) of (VIIIγ), bp 87°C, were obtained. IR spectrum: 1670 (C=C), 1755 (C=O). ^{19}F NMR spectrum: 8.2 d.m. (CF_3), 18.1 m (CF), 36.7 d.m. (CF_2^1), 44.8 m (CF_2), 50.4 m (CF_2), 59.1 (CF_2), $J_{CF_2^1-CF}$ = 29.1, J_{CF_3-CF} = 7.1. Found: C 28.57; F 68.61%. $C_8F_{12}O$. Calculated: C 28.24; F 67.06%.

Perfluoro-2-methylcyclopenten-3-one (VIIIβ). A ∿1-g portion (∿5 mmoles) of SbF_5 was added dropwise to 11 g (0.04 mole) of 1-methoxyperfluoro-2-methylcyclopentene (IIβa), and the product, boiling at 50-60°C was distilled slowly. Yield, 4.7 g (49%) of (VIIIβ).

Perfluoro-2-ethylcyclohexen-3-one (VIIIγ). In a similar way, from 11.2 g (0.03 mole) of 1-methoxyperfluoro-2-ethylcyclohexene (IIγa) and ∿1 g (∿5 mmoles) of SbF_5, 5.4 g (53%) of (VIIIγ) were obtained (a fraction boiling at 85-90°C).

1-Hydroxyperfluoro-2-ethylcyclobuten-3-one (IXα). A 2-ml portion of water was added dropwise to 3.9 g (0.01 mole) of tetraethylammonium perfluoro-2-ethylcyclobutenol-1-ate (VIαb), and, then with stirring, 15 ml of ether were added. The ether layer was decanted and dried over $CaCl_2$. Ether was evaporated and the residue distilled. Yield, 1.0 g (42%) of (IXα), bp 89°C (1 mm) (cf. [18]).

1-Hydroxyperfluoro-2-ethylcyclohexen-3-one (IXγ). In a similar way, from 4.9 g (0.01 mole) of tetraethylammonium perfluoro-2-ethylcyclohexenol-1-ate (VIγb), after the evaporation of ether and sublimation of the residue at 0.5 mm, 1.2 g (36%) of (IXγ), mp 77°C, was obtained. IR spectrum: 1625, 1715 (C=C–C=O). ^{19}F NMR spectrum: 7.5 m (CF_3), 33.3 m (CF_2), 45.8 m [$(CF_2)_2$], 58.7 m (CF_2). Found: C 30.10; H 0.49; F 64.70%. $C_8HO_2F_{11}$. Calculated: C 29.81; H 0.31; F 64.91%.

1-Hydroxyperfluoro-2-methylcyclopenten-3-one (IXβ). a) In a similar way, from 3.9 g (0.01 mole) of tetraethylammonium perfluoro-2-methylcyclopentenol-1-ate (VIβb), by sublimation of the residue at 0.5 mm, 1 g (41%) of (IXβ), mp 69°C, was obtained. IR spectrum: 1655, 1760 (C=C–C=O). ^{19}F NMR spectrum (in ether): −17.8 s (CF_3), 50.3 s [$(CF_2)_2$]. Found: C 30.16; H 0.71; F 55.64%. $C_6HF_7O_2$. Calculated: C 30.25; H 0.42; F 55.80%.

b) A solution of 1 ml Et_3N and 1 ml of water in 10 ml of acetone was added dropwise, with stirring, to 2.7 g of 1-methoxyperfluoro-2-methylcyclopentene (IIβa). After 2 h, acetone was evaporated, and 10 ml of ether were added to the residue. According to ^{19}F NMR data, the ether layer is a solution of (IXβ).

c) A solution of 0.1 g of Et_3N and 1 ml of water in 10 ml of acetone was added dropwise, with stirring (0°C), to 2.6 g (0.01 mole) of perfluoro-2-methylcyclopentene (Iβ). Acetone was evaporated in vacuo (25 mm), and 10 ml of ether were added to the residue. According to ^{19}F NMR data, the ether solution is a solution of (IXβ):

2-Allylperfluoro-2-ethylcyclobutanone (Xα). A 5-g portion of 1-allyloxyperfluoro-2-ethylcyclobutene (IIαd) was held in a sealed ampule for 8 h at 130°C. Yield, 4.7 g (94%) of (Xα), bp 119°C. IR spectrum: 1645 (C=C), 1835 (C=O). ^{19}F NMR spectrum: 3.3 d.d. (CF_3, J = 5.6, J = 7.5), 33.6 m (CF_2), 45.8 m (CF_2), 45.0 and 49.0 (CF_2, AB system, J = 268). PMR spectrum: 2.4 m (CH_2), 4.6-5.8 a set of (CH=CH_2). Found: C 35.76; H 1.72; F 57.12%. $C_9H_5F_9O$. Calculated: C 36.00; H 1.67; F 57.00%.

2-Allylperfluoro-2-methylcyclopentanone (Xβ). A 5-g portion of 1-allyloxyperfluoro-2-methylcyclopentene (IIβd) was held in a sealed ampule for 8 h at 100°C. Yield, 4.7 g (94%) of (Xβ), bp 123°C. IR spectrum: 1650 (C=C), 1800 (C=O), ^{19}F NMR spectrum: −12.5 ppm (CF_3, J = 16.9), 39.8 and 47.8 (CF_2, AB system, J = 268), 46.5 and 56.3 (CF_2, AB system, J = 301), 52.0 and 66.2 (CF_2, AB system, J = 263). PMR spectrum: 2.6 m (CH_2), 4.8-5.8 a set of m (CH=CH_2). Found: C 36.24; H 1.61; F 57.22%. $C_9H_5F_9O$. Calculated: C 36.00; H 1.67; F 57.00%.

2-Allylperfluoro-2-ethylcyclohexanone (Xγ). In a similar way, from 5 g of 1-allyloxyperfluoro-2-methylcyclohexene (IIγd), 4.5 g (90%) of (Xγ), bp 148°C, were obtained. IR spectrum: 1650 (C=C), 1770 (C=O). ^{19}F NMR spectrum: −0.7 d.m. (CF_3, J = 21.6), 27.3 and 29.9 (CF_2, AB system J = 297), 35.5 and 43.7 (CF_2, AB system, J = 293), 44.3 and 54.3 (CF_2, AB system, J = 301), 44.3 and 60.3 (CF_2, AB system, J = 288), 50.2 and 65.0 (CF_2, AB system, J = 290). PMR spectrum: 2.9 m (CH_2), 4.6-5.8 a set of m ($CH=CH_2$). Found: C 32.91; H 1.39; F 61.73%. $C_{11}H_5F_{13}O$. Calculated: C 33.00; H 1.25; F 61.75%.

CONCLUSIONS

1. Perfluoro-1-alkylcycloalkenes react with alcohols to form products of "vinyl" and "allyl" substitution.

2. Alkyl perfluorocycloalkenyl ethers readily alkylate the fluoride ion and triethylamine, and by the action of SbF_5 convert into α, β-unsaturated perfluoro ketones.

3. When allyl perfluorocycloalkenyl ethers are heated, they isomerize into the corresponding α-allylperfluorocycloalkanones.

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