2. The formation of $HRe(CO)_5$ in the photochemical reaction of $Re_2(CO)_{10}$ with $HSiEt_3$ has been shown by UV spectroscopy.

3. The system $Mn_2(CO)_{10}$ + $HSiEt_3$ has been shown for the first time to be capable or reducing 1,1-dichloroalkanes.

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PARTIAL OXIDATION OF INTERNAL FLUOROOLEFINS BY POTASSIUM PERMANGANATE

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UDC 542.943:547.413.5:546.717'32

Oxidation of fluoroolefins is widely used in the synthesis of oxygen-containing fluoroorganic compounds [1]. In recent years extensive research has been devoted to methods for obtaining fluorinated α-oxides based on ionic and radical epoxidation of fluoroolefins by means of hydroperoxides, hypochlorites, molecular oxygen, and potassium permanganate in hydrogen fluoride [2]. A significant feature of these processes is the preservation of the carbon skeleton of the original fluoroolefin molecule. At the same time, the oxidation of terminal as well as internal fluoroolefins by permanganate in an aqueous or acetone medium usually occurs with cleavage of the C=C bond. The reaction has a common mechanism in a variety of fluoroolefins and is often used for preparative synthesis of fluorinated ketones as well as mono- and dicarbonic acids [3, 4]. The accepted reaction mechanism includes hydroxylation of the double bond by permanganate, accompanied by dehydrofluorination of the geminal fluorocarbinol and formation of an intermediate fluorocarbonyl compound; oxidative rupture of the C–C bond in the latter leads to the final products [5]. In accordance with this scheme, the oxidation of disubstituted internal fluoroolefins should lead to the initial formation of α-diketones:

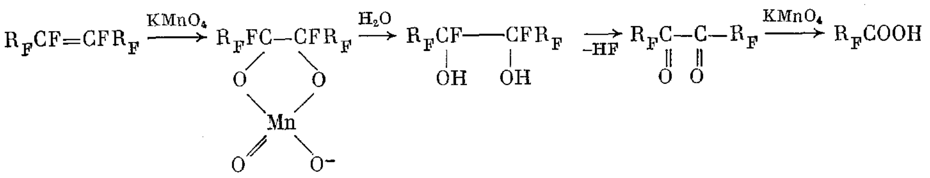

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TABLE 1. Conditions for the Oxidation of Fluoroolefins by $KMnO_4$ and Characteristics of the Compounds Obtained

Compound	Olefin: $KMnO_4$ ratio (molar)	Olefin conversion, %	Isolation method	Yield per reacted olefin, %	bp, °C (p, mm Hg)	Found, %		
						C	H	F
(IIb) [9]	0,4	60	B	39,5	57–58			
(IIc) [9]	0,4	56	A	53	54–56			
(IId)	0,7	100	A	79	71–72	24,43		65,63
(III)	0,35	54	C	40	50–51 (21)	28,88	1,0	
(Va)	0,36	62,5	A	53	80–82	22,80	0,33	66,46
(Vb)	0,75	100	A	42	46 (5)	23,48	0,30	70,37
(Vc)	1	100	A	83	50–51 (1)	22,76	0,20	
(Vd) [10]	0,7	85	C	15	*			
(VI)	0,35	52	B	9,7	70	28,12		59,38
(VII)	0,5	100	B	27,6	94–96	25,90	0,41	61,61
(IXa) [11]	0,7	100	B	68	61–62 (68)			
(IXb)	0,7	100	B	65	64–65 (22)	21,91	0,50	

TABLE 1 (continued)

Compound	Empirical formula	Calculated, %			IR spectrum ν, cm⁻¹ (C=O)
		C	H	F	
(IIb) [9]					
(IIc) [9]					
(IId)	$C_7F_{12}O_2$	24,42		66,28	1755, 1790
(III)	$C_7H_3F_7O_4$	29,47	1,05		
(Va)	$C_6HF_{11}O_2$	22,93	0,32	66,56	1770
(Vb)	$C_{10}HF_{19}O_2$	23,35	0,19	70,24	1780
(Vc)	$C_{11}HF_{21}O_3$	22,76	0,17		1785
(Vd) [10]					
(VI)	$C_6F_8O_2$	27,76		59,21	1780
(VII)	$C_6HF_9O_2$	26,09	0,36	61,96	1810
(IXa) [11]					
(IXb)	$C_8H_2F_{16}O_2$	22,12	0,46		

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*mp = 42-44°C (from hexane).

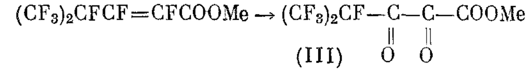
Similarly, the oxidation of trisubstituted fluoroolefins should afford α-hydroxyketones. However, until now partial oxidation of fluorinated unsaturated compounds by permanganate has been carried out successfully only in alkyl perfluoroalkenyl ethers [6] and tetrasubstituted perfluorinated ethylenes [7, 8].

In the present work we have shown that the oxidation of internal fluoroolefins by permanganate under strictly controlled conditions can be carried out with preservation of the C–C bond. In the process we obtained aliphatic and alicyclic fluorine-containing α-hydroxycarbonyl compounds.

$$CF_3CF{=}CFR \rightarrow CF_3COCOR$$

(I) (II)

$R = CF_3$ (a), n-C_3F_7 (b), i-C_3F_7 (c), $(CF_3)_3C$ (d).



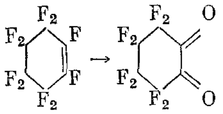
$$(CF_3)_2CFCF{=}CFCOOMe \rightarrow (CF_3)_2CF{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}COOMe$$

(III)

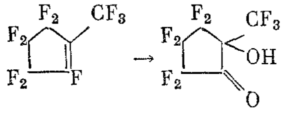
$$(CF_3)_2C{=}CFR \rightarrow (CF_3)_2C(OH)COR$$

(IV) (V)

$R{=}C_2F_5$ (a), $(CF_3)_3CCF_2CF_2$ (b), $(CF_3)_3CCF_2CF(OCF_3)$ (c), Ph (d).



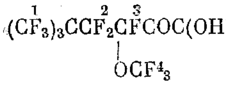
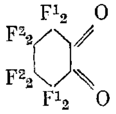
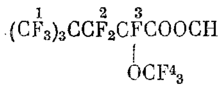
(VI)



(VII)

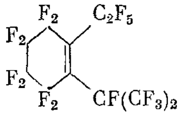
We also synthesized α-glycols (IX) from tetraperfluoroalkyl-substituted olefins (VIII). However, oxidation of cycloolefin (X) yielded only the ring-scission product, perfluorinated diketone (XI).

TABLE 2. ^{19}F NMR Spectral Parameters

Compound	δ, ppm, J, Hz
$\overset{1}{C}F_3COCOC(\overset{2}{C}F_3)_3$ (IId)	−14,6 s (F^2), −1,9 s (F^1)
$(\overset{1}{C}F_3)_2\overset{2}{C}FCOCOCOOCH_3$ (III)	3,1 d (F^1), 111,4 hepta (F^2), $J_{1\text{-}2} = 7,5$
$\overset{1}{C}F_3\overset{2}{C}F_2COC(OH)(\overset{3}{C}F_3)_2$ (Va)	−2,9 t (F^3), 5,5 s. (F^1), 42,3 hepta (F^2), $J_{2\text{-}3} = 7$
$(\overset{1}{C}F_3)_3C\overset{2}{C}F_2\overset{3}{C}F_2COC(OH)(\overset{4}{C}F_3)_2$ (Vb)	−14,2 t (F^1), −2,5 ttt (F^4), 25,3 m (F^2), 33,3 m(F^3), $J_{1\text{-}3} = 14,1$, $J_{1\text{-}2} = 11,2$, $J_{3\text{-}4} = 7$, $J_{2\text{-}4} = 3,5$
 $(\overset{1}{C}F_3)_3C\overset{2}{C}F_2\overset{3}{C}F(OCF^4_3)COC(OH)(\overset{5}{C}F_3)_2$ (Vc)	−24, 4 m (F^4), −15,6 tt (F^1), −2,6 and −2,1 m (F^5), 17,5 m (F^2), 51,5 m (F^3), $J_{1\text{-}3} = 15$, $J_{1\text{-}2} = 12,2$
 (VI)	47,8 s (F^1), 57,0 s (F^2)
$(\overset{1}{C}F_3)_2C(OH)C(OH)(\overset{2}{C}F_2\overset{3}{C}F_3)_2$ (IXb)	−8,7 m (F^1), 0,6 m (F^3), 34,0 m (F^2)
$\overset{1}{C}F_3\overset{2}{C}F_2COOCH(\overset{3}{C}F_3)_2$ (XIIIa)	−2,4 d (F^3), 7,4 s (F^1), 45,3 s (F^2), $J_{3\text{-}H} = 5,5$
 $(\overset{1}{C}F_3)_3C\overset{2}{C}F_2\overset{3}{C}F(OCF^4_3)COOCH(\overset{5}{C}F_3)_2$ (XIIIc)	−20,7 d (F^4), −15,3 tt (F^1), −2,7 m (F^5), 24,0 m (F^2), 50,0 m (F^3), $J_{1\text{-}3} = 14,1$, $J_{1\text{-}2} = 11,3$
$(\overset{1}{C}F_3)_3C\overset{2,3}{C}F_2\overset{4}{C}FHO\overset{5}{C}F_3$ (XIV)	−15,5 m (F^5), −14,1 ddd (F^1), 34,8 and 40,0 m (F^2, F^3, AB-system), $J_{2\text{-}3} = 298$, $J_{4\text{-}H} = 54$, $J_{2\text{-}H} = 10$, $J_{1\text{-}2} = J_{1\text{-}3} = J_{1\text{-}4} = 9,8$, $J_{3\text{-}H} = 3$

$$\underset{(VIII)}{(CF_3)_2C{=}CR_2} \rightarrow \underset{(IX)}{(CF_3)_2C(OH)CR_2OH}$$

$R{=}CF_3$ (a), C_2F_5 (b)



$\rightarrow C_2F_5CO(CF_2)_4COCF(CF_3)_2$

(X) (XI)

The maximal product yield was attained at a molar olefin:permanganate ratio of 1:0.3-0.7 and a temperature of < 0°C. However, even under optimal conditions – at 50% fluoroolefin conversion – it was not possible to avoid fluoroolefin oxidation with complete cleavage of the C=C bond. Thus in the case of perfluorobutene-2 or perfluorocyclohexene, the primary products were the corresponding acids, and the yield of α-diketones did not exceed 10%. At the same time, elongation of the fluorocarbon chain, and especially α-branching, increased the α-diketone yield to such an extent that the reaction may be of preparative value for the synthesis of di- and polycarbonyl compounds (Table 1; cf. [9]). It should be noted that olefin (IVa) is much more active than (Ic) in the reaction with $KMnO_4$: when an equimolar mixture of (Ic) and (IVa) was oxidized with an insufficient amount of $KMnO_4$, α-hydroxyketone (Va) was formed exclusively. Since olefin (IVa) is more electrophilic than (Ic), this confirms the nucleophilic nature of the reaction of fluoroolefins with $KMnO_4$ [5].

Resistance to oxidative cleavage with α-branching also increases in many trisubstituted fluoroolefins. For example, the oxidation of olefin (IVb) in aqueous acetone at −30°C affords a mixture of 70% α-hydroxyketone (Vb)* and 30% $(CF_3)_3CCF_2CF_2COOH$ (XII). At the same time

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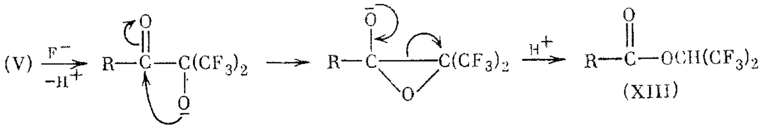
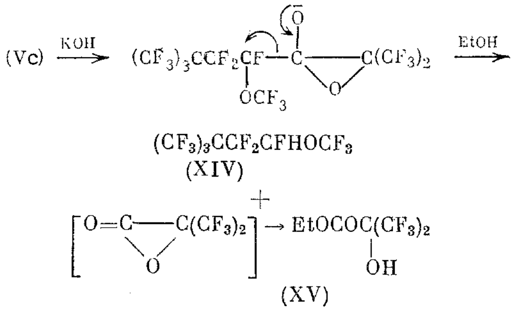
*Compound (Vb) was obtained earlier as an admixture of acid (XII), but was mistakenly described as a perfluoroketone [12].

α-hydroxyketone (Vc) is formed in high yield at 20°C even in the presence of excess $KMnO_4$. It is interesting to note that under more drastic conditions compound (Vc) is isomerized to ester (XIIIc). This type of conversion is also characteristic for other α-hydroxyketones (V), and is readily effected by the fluorine anion. This reaction, representing a 1,2-migration of the acyl group from atom C to O, probably occurs via the following mechanism (see [13]):



R = C_2F_5 (a), Ph (b), $(CF_3)_3CCF_2CFOCF_3$ (c).

Apparently, isomerization to ester (XIII) is accompanied by alkaline hydrolysis of α-hydroxyketones (Vb) and (Vd), leading to acids (XII) and PhCOOH, respectively. At the same time, α-hydroxyketone (Vc), when exposed to alkali in alcohol, undergoes haloform decomposition to form monohydroether* (XIV) along with α-hydroxyacid ester (XV).



The results obtained by us confirm the previously adopted mechanism of stepwise cleavage of the C=C bond in fluoroolefins, a mechanism that provides for the intermediate formation of fluorocarbonyl compounds. Under ordinary conditions these compounds decompose more rapidly than they are formed. Therefore, internal fluoroolefins can be oxidized with preservation of the C–C bond only if they contain substituents that decrease the reactivity of the carbonyl group by means of steric (or electronic, as in alkyl perfluoroalkenyl ethers [6]) effects. For the same reasons, partial oxidation of terminal fluoroolefins cannot be carried out with a satisfactory yield [14]. It should be noted that in many nonfluorinated internal olefins complete rupture of the C=C bond by $KMnO_4$ usually does not occur. This, apparently, is due to the lower tendency of the carbonyl compounds formed during oxidation to undergo nucleophilic attack by the permanganate anion [15].

Thus the data obtained by us show that the depiction of $KMnO_4$ as a reagent causing only complete cleavage of the C=C bond in fluoroolefins [1, 5], is not realistic.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Perkin-Elmer R-32 instrument (84.6 MHz), with CF_3COOH as internal standard. IR spectra were recorded on a UR-20 instrument.

Oxidation of Fluoroolefins by $KMnO_4$ (Standard Procedure). Aliquots of $KMnO_4$ were added, with mixing, at −30 to −20°C (20°C for compound IVc) to 65 mmoles of fluoroolefin in 120 ml acetone and 5 ml water. After 30 min SO_2 was bubbled through the mixture (at the same temperature) till decolorization. The reaction mixture was then diluted with water, and the unreacted olefin and part of the acetone were removed at 20°C in a trap (−78°C) in a vacuum (10 mm Hg). The organic layer of the residue was separated and distilled over conc. H_2SO_4 (method A). In method B the residue, after separation of unreacted olefin, was extracted with ether, concentrated, and distilled over conc. H_2SO_4. In method C the reaction mixture, after dilution with water, was extracted with ether, and the products were isolated by distillation. In the case of ester (III), the unreacted olefin was removed at <30°C in a vacuum (3 mm Hg), and the residue was distilled over conc. H_2SO_4. α-Hydroxyketone (Vb) was freed from acid (XII) by washing with bicarbonate solution.

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*Compound (XIV) was also obtained in the reaction of (Vc) with $KMnO_4$.

Oxidation of Perfluorobutene-2 (Ia). After isolation according to method B, 18 g of (Ia) and 4.2 g of $KMnO_4$ yielded 10.8 g of the original (Ia) and 2.2 g of a fraction with bp of 25-65°C (33 mm), consisting of a mixture of 60% CF_3COOH and 40% α-diketone (IIa) dihydrate. The product was identified by its ^{19}F NMR spectrum (signal at 3.8 ppm) and by conversion to 2,3-bis(trifluoromethyl)quinoxaline (mp 117-119°C; cf. [9]).

Perfluoro-(1-ethyl-6-isopropyl)cyclohexene (X). A weak stream of perfluoropropylene was bubbled for 8 h, with vigorous mixing, through a mixture containing 10 g CsF, 20 g perfluoroethylcyclohexene, and 50 ml abs. MeCN. The reaction mixture was decanted into water; the organic layer was separated, dried over $MgSO_4$, and distilled. The product contained 9.2 g of the initial fluoroolefin (bp 89-91°C) and 12.4 (81%) of compound (X) (bp 141-142°C). Found (%): C 25.51, F 74.98 ($C_{11}F_{20}$); calculated (%): C 25.78, F 74.2. ^{19}F NMR spectrum: −6.0 and −4.0 m (CF_3); 21.0, 31.3, 59.2 m (CF_2); 86.5 m (CF).

Perfluoro-2-methyldecanedione-3,8 (XI). A 4.8-g portion of $KMnO_4$ was added gradually to 7.5 g of olefin (X) in 70 ml of acetone and 10 ml water. At the end of the exothermal reaction the mixture was mixed for 5 h at 20°C and diluted with water. The residue was filtered; the filtrate was extracted with ether, washed with bisulfite solution, and dried over $MgSO_4$. The residue, after evaporation of the ether, was distilled over conc. H_2SO_4. A 5.1-g yield (64%) of compound (XI) was obtained; bp 62-64°C (22 mm). Found (%): C 24.36, F 69.44 ($C_{11}F_{20}O_2$); calculated (%): C 24.26, F 69.85. IR spectrum: 1790 cm^{-1} (C=O). ^{19}F NMR spectrum: −2.4 and 6.2 m $(CF)_3$; 40.0, 41.0, 43.4, 44.1 m (CF_2); 113.8 m (CF).

Isomerization of α-Hydroxyketones (V) by CsF. A mixture containing 19.6 g of α-hydroxyketone (Vc), 1.7 g CsF, and 20 ml abs. monoglyme was heated for 0.5 h at 60-65°C. The mixture was then decanted over HCl (1:5), and the organic layer was distilled over conc. H_2SO_4. A 12.4-g yield (63.5%) of ester (XIIIc) was obtained; bp 72-73°C (20 mm). Found (%): C 22.58, H 0.14, F 68.83 ($C_{11}HF_{21}O_3$); calculated (%): C 22.76, H 0.17, F 68.79. The ^{19}F NMR spectra are given in Table 2.

A mixture consisting of 6.5 g α-hydroxyketone (Va), 1.7 g CsF, and 15 ml diglyme was heated for 6 h at 70°C and evaporated in a vacuum (10 mm Hg). The product, 2.5 g (38%) of ester (XIIIa) with a bp of 61-63°C, was identical (GLC, NMR) to that in the reaction of C_2F_5COCl with $(CF_3)_2CHOH$ in the presence of Et_3N.

In a similar manner, the reaction of compound (Vc) with CsF in monoglyme (80°C, 10 h) afforded ester (XIIIb), mp 51-54°C (from pentane), without depression of a mixed probe with a known sample [16].

Perfluoro-[1-hydro-3,3-(dimethyl)butyl]methyl Ether (XIV). A mixture consisting of 4.3 g α-hydroxyketone (Vc), 0.8 g $KMnO_4$, 25 ml acetone, and 3 ml water was mixed for 30 h at 20°C. Treatment according to method A afforded 2 g of a mixture containing 60% of compound (XIV) and 40% of compound (Vc). Distillation of the mixture yielded pure (XIV) with a bp of 91-92°C. Found (%): C 21.67, H 0.17, F 73.72 ($C_7HF_{15}O$); calculated (%): C 21.76, H 0.26, F 73.83.

A 5-g portion of α-hydroxyketone (Vc) was dissolved in 5% alcoholic KOH. After 1 h at 20°C, ether (XIV) was obtained in the bottom layer. The residue was diluted with water and acidified. The organic layer contained a mixture of compounds (XIV) and (XV) (GLC).

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CONCLUSIONS

1. Under strictly controlled conditions, internal fluoroolefins are oxidized by potassium permanganate with preservation of the carbon—carbon bond and form aliphatic and alicyclic fluorine-containing α-dicarbonyl and α-hydroxycarbonyl compounds.

2. Fluorine-containing α-hydroxyketones undergo nucleophilic isomerization involving 1,2-migration of the perfluoroacyl group from atom C to O.

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SYNTHESIS AND PROPERTIES OF ESTERS OF 2-CYANO-3,3,3-TRIFLUOROPROPIONIC ACID*

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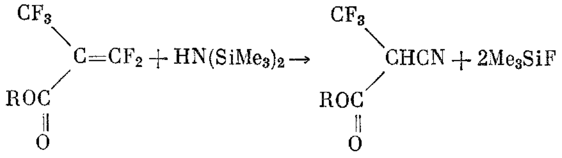
and A. V. Fokin

UDC 542.91:547.464.5'161

Esters of 2-cyano-3,3,3-trifluoropropionic acid (Ia-c) can be regarded as analogs of 2-H-hexafluoroisobutyronitrile (II), which is a strong CH-acid [2] able to react with electrophilic reagents [3-7].

We showed that esters (Ia-c) are obtained readily and in high yields from available esters of perfluoromethacrylic acid by reaction with hexamethyldisilazane (HMDS).

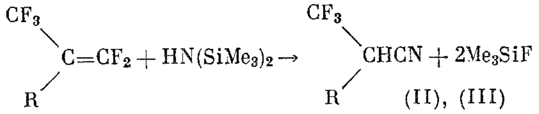


(Ia–c)

R = Me (a), Et (b), *i*-Pr (c).

The reaction is carried out with moderate cooling and is completed at 20°C.

This reaction could also be extended to other highly electrophilic terminal polyfluoroalkenes. Thus, nitrile (II) was obtained in a >50% yield by the reaction of HMDS with a large excess of octafluoroisobutylene. 2-Fluorosulfonylpentafluoropropylene reacts extremely vigorously with HMDS to form 2-fluorosulfonyl-3,3,3-trifluoropropionitrile (III) in a yield of up to 40%



R = CF_3 (II), FSO_2 (III).

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*For preliminary communication, see [1].

The A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2262-2266, October, 1987. Original article submitted March 4, 1986.

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