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THE NEW REACTION OF OCTAFLUOROISOBUTENE WITH α-OXIDES. SYNTHESIS OF OLEFINS WITH PERFLUOROTERTIARY BUTYL SUBSTITUENT.

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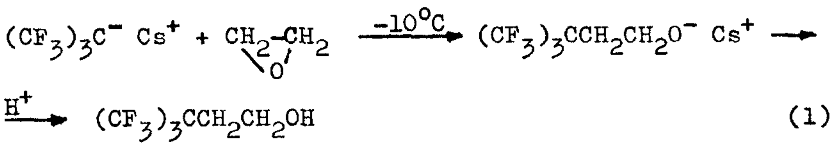
SUMMARY

α -Oxides, in particular, ethylene and propene oxides and epichlorohydrine react with octafluoroisobutene (OFIB) in the presence of cesium fluoride to give perfluorotert.butylethylene, trans-1-(perfluorotert.butyl)-1-propene and trans-1,3-bis-(perfluorotert.butyl)-1-propene respectively. 2-H-nonafluoroisobutane and cesium heptafluoroiso-1-buten-1-olate are general products for the all above reactions. The same cesium salt is formed when molar quantities of bis(trifluoromethyl)-ketene and cesium fluoride are heated in diglime.

INTRODUCTION

Synthesis of 2-(perfluorotert.butyl)ethanol from perfluorotert.butyl anion and ethylene oxide has been described [1].

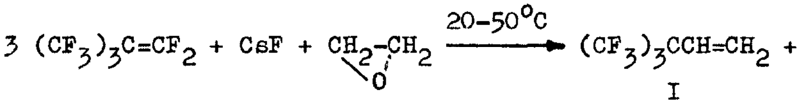


$$(CF_3)_3C^- \; Cs^+ + \underset{\diagdown O \diagup}{CH_2-CH_2} \xrightarrow{-10^oC} (CF_3)_3CCH_2CH_2O^- \; Cs^+ \longrightarrow \xrightarrow{H^+} (CF_3)_3CCH_2CH_2OH \tag{1}$$

We now reinvestigated the process and found that slightly increase in the temperature leads to some other results. Under these conditions perfluorotert.butyl olefins are main reaction products.

RESULTS AND DISCUSSION

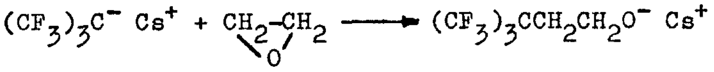
Octafluoroisobutene, CsF and ethylene oxide react smoothly to give perfluorotert.butylethylene (I), nonafluoroisobutane (II) and cesium salt of mesomeric anion (III).



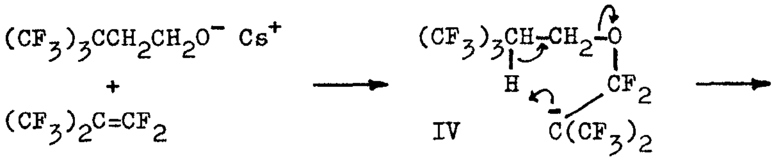
$$3\ (CF_3)_3C{=}CF_2 + CsF + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \xrightarrow{20-50^{o}C} \underset{I}{(CF_3)_3CCH{=}CH_2} + \underset{II}{(CF_3)_3CH} + \underset{III}{(CF_3)_2C\overset{\dots}{=}CF\overset{\dots}{=}O^-\ Cs^+} \qquad (2)$$

The maximum (practically quantitative) yield of perfluorotert.butylethylene was attained at the ratio of OFIB:CsF:ethylene oxide = 3:1:1. Other ratios decrease the yield of perfluoro-tert.butylethylene and leave unreacted starting agents. The following reaction intermediate steps may be considered to explaine the results.

$$(CF_3)_2C{=}CF_2 + CsF \longrightarrow (CF_3)_3C^-\ Cs^+ \qquad (3)$$



$$(CF_3)_3C^-\ Cs^+ + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow (CF_3)_3CCH_2CH_2O^-\ Cs^+ \qquad (4)$$



$$(CF_3)_3CCH_2CH_2O^-\ Cs^+ + (CF_3)_2C{=}CF_2 \longrightarrow \text{IV} \longrightarrow$$

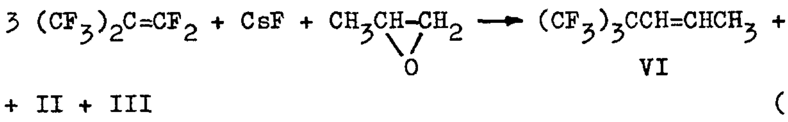
$$(CF_3)_3CCH{=}CH_2 + \underset{V}{(CF_3)_2CHCF_2O^-\ Cs^+} \qquad (5)$$

$$(CF_3)_2CHCF_2O^-\ Cs^+ + (CF_3)_2C{=}CF_2 \longrightarrow \underset{III}{(CF_3)_2CCFO^-\ Cs^+} + (CF_3)_3CH \qquad (6)$$

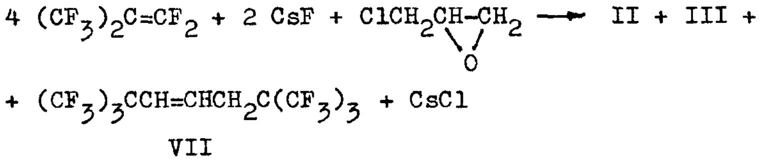
The first and second steps of this process are obvious: perfluorotert.butyl anion generated from OFIB and CsF opens an oxide ring to give cesium 2-(perfluorotert.butyl)ethylate.

It reacts with the second OFIB molecule yielding the carbanion intermediate (IV) (eq. 5). Perfluorotert.butyl group being sufficiently strong electronegative substituent (Taft σ^* constant of $(CF_3)_3C$ group 1.48 [2]) causes some proton liability of α-hydrogen. Thus carbanion (IV) is stabilized with simultaneous intramolecular proton abstraction from methylene in the α-position to $(CF_3)_3C$ group and the C-O bond cleavage giving rise to perfluorotert.butylethylene and cesium fluoride - - α-H-hexafluoroisobutyryl fluoride "adduct" (V). The third OFIB molecule (eq. 6) may cause dehydrofluorination of the "adduct" with the formation of nonafluoroisobutane and mesomeric anion cesium salt (III). The latter was registered in solution by means of the NMR ${}^{19}F$ method and by isolation its products of subsequent transformations (see below). Similar triethylammonium and tetraethylammonium salts have been described [3,4].

This reaction was extended to other α-oxides, in particular, to propene oxide and epichlorohydrine. Under the mild conditions the reaction leads directly to the respective olefins with the high yields.



$$3\ (CF_3)_2C{=}CF_2 + CsF + \underset{\diagdown\ \diagup \atop O}{CH_3CH{-}CH_2} \longrightarrow \underset{VI}{(CF_3)_3CCH{=}CHCH_3} + II + III \qquad (7)$$



$$4\ (CF_3)_2C{=}CF_2 + 2\ CsF + \underset{\diagdown\ \diagup \atop O}{ClCH_2CH{-}CH_2} \longrightarrow II + III + \underset{VII}{(CF_3)_3CCH{=}CHCH_2C(CF_3)_3} + CsCl \qquad (8)$$

Thus the reaction is of general character and may be discussed as a new preparatively convenient procedure for the synthesis of different olefins with $(CF_3)_3C$ substituent.

The cesium salt (III) formation in all these reactions is interesting as itself. As it was mentioned above it might be generated by the action of OFIB on cesium fluoride - hexafluoroisobutyryl fluoride "adduct" (eq. 6). Actually the reaction of hexafluoroisobutyryl fluoride with excess of cesium fluoride showed no cesium salt (III) formation. Only the addition of molar quantity of OFIB rapidly yielded the salt (III) and nonafluoroisobutane. In this case OFIB acts as an effective dehydrofluorinating agent.

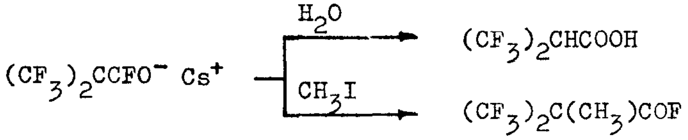
$$(CF_3)_2CHCOF + CsF + (CF_3)_2C{=}CF_2 \longrightarrow (CF_3)_2CCFO^- \, Cs^+ + (CF_3)_3CH \qquad (9)$$

On the other hand the cesium salt (III) may be easily prepared from bis(trifluoromethyl)ketene and cesium fluoride in diglime.

$$(CF_3)_2C{=}C{=}O + CsF \longrightarrow (CF_3)_2CCFO^- \, Cs^+ \qquad (10)$$

This result was somewhat unexpected since it has been shown previously that bis(trifluoromethyl)ketene isomerizes into perfluoromethacryloyl fluoride in the presence of a catalytic quantity of fluoride ion at high temperature (300°C) [3]. In diglime at room temperature depending on the catalyst amount the formation of β-lactone-dimer of bis(trifluoromethyl)ketene or tetrakis(trifluoromethyl)allene and δ-lactone-dimer [5] has been observed.

Salt (III) hydrolysis leads to α-H-hexafluoroisobutyric acid, its treatment with methyl iodide afforded α-methylhexafluoroisobutyryl fluoride.



$$(CF_3)_2CCFO^- \, Cs^+ \begin{cases} \xrightarrow{H_2O} (CF_3)_2CHCOOH \\ \xrightarrow{CH_3I} (CF_3)_2C(CH_3)COF \end{cases} \qquad (11)$$

EXPERIMENTAL

The PMR spectra (δ in ppm) were registered on "Perkin Elmer R-10" spectrometer with TMS (external) as a reference. The ^{19}F NMR spectra were recorded on "Hitachi H-6013" spectrometer at 56.46 MHz with CF_3COOH (external).

Preparation of perfluorotert.butylethylene (I)

Absolute diglime (50 ml) and freshly calcinated cesium fluoride (9 g) were placed in a three-necked flask equipped with a stirrer, bubbler and reflux condenser cooled with dry ice. OFIB (30 g) was passed into the reaction mixture. The bubbler was then replaced by a dropping funnel and the solution of 2.2 g of ethylene oxide in 10 ml of diglime was added at stirring for 30 min, dropwise. The mixture was allowed to stay overnight and was heated for 3 hr at 40-50°C at stirring. The low-boiling fraction (22.8 g) was removed into a trap (-78°C) under vacuo. Rectification of this fraction gave 9.7 g of nonafluoroisobutane (II), b.p. 14-22°C and 9.5 g (77%) of perfluorotert.butylethylene, b.p. 53-54°C (cited [6]: 55-56°C).

The residue is the diglime solution of cesium salt (III): its IR spectrum had the adsorption band at 1720 cm^{-1}. After pouring into acidified (HCl) water the lower layer was separated and distilled from the mixture with equal amount of concentrated sulfuric acid to give 7 g of α-H-hexafluoroisobutyric acid, b.p. 126-132°C (cited [7]: 124-126°/750 mm Hg).

Trans-1-(perfluorotert.butyl)-1-propene and trans-1,3-bis(perfluorotert.butyl)-1-propene were obtained similarly. Some properties of the olefins are given in table 1. NMR data for these olefins and salt (III) are summarized in table 2.

Preparation of cesium heptafluoroiso-1-buten-1-olate (III)

(a) From α-H-hexafluoroisobutyryl fluoride

Absolute diglime (20 ml) and freshly calcinated cesium fluoride (6.0 g) were placed into a three-necked flask with stirrer, dropping funnel and reflux condenser cooled with dry ice. α-H-Hexafluoroisobutyryl fluoride (5 g) was added dropwise. The reaction mixture was heated at 60-70° at stirring for 1 hr. The ^{19}F NMR showed no salt (III) formation. OFIB (5 g) was bubbled through the mixture and the solution was allowed to stay overnight. The light fraction (3 g) of

TABLE 1

Properties of the olefins with perfluorotert.butyl substituent

Compound $R=(CF_3)_3C$	B.p. ^oC	Yield %	Raman spectral data $(C=C)/cm^{-1}$	Analysis: Found (Calcd) C	H	F
$R-CH=CH_2$	53-54	77	1650			
$RCH=CHCH_3$	79-81	77	1660	32.1 (32.3)	1.8 (1.9)	65.8 (65.8)
$RCH=CHCH_2R$	140-144	87	1660	27.5 (27.6)	0.9 (0.8)	71.7 (71.6)

nonafluoroisobutane was removed under vacuo of water-jet pump into a trap. The residue was a solution of cesium salt (III).

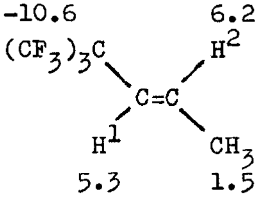
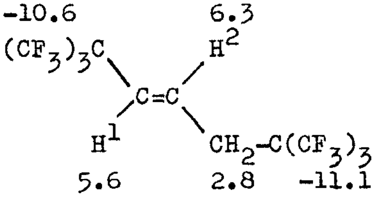
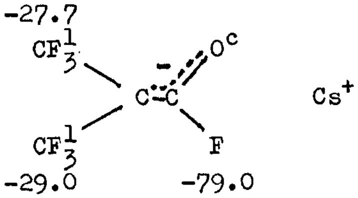
Methyl iodide (3.5 g) was added to the solution and the mixture was heated for 1 hr at 60°C. Rectification of the mixture gave 4.5 g (85%) of α-methylhexafluoroisobutyryl fluoride, b.p. 46-47°C (cited [8]: 47-47.5°C).

(b) From bis(trifluoromethyl)ketene

Absolute diglim (10 ml) and freshly calcinated cesium fluoride (6 g) were placed in a three-necked flask with a mechanical stirrer, reflux condenser cooled with dry ice and the bubbler. Bis(trifluoromethyl)ketene (7 g) was bubbled into the mixture under vigorous stirring. Heating of the mixture was observed. After 2 hr of stirring the mixture practically homogenized and it was the solution of cesium salt (III) (by NMR ^{19}F).

TABLE 2

NMR spectral data

Chemical shifts[a]	Coupling constants in Hz
-10.9 5.6[b] $(CF_3)_3C\text{-}CH{=}CH_2$	
	H^1- H^2 17.3 H^1- CH_3 6.8 H^2- CH_3 1.5
	H^1- H^2 16.0 H^1- CH_2 6.7
	CF_3^1- CF_3^2 10.7 CF_3^1- F 19.4 CF_3^2- F 12.1

[a] ^1H δ ppm from TMS, ^{19}F ppm from CF_3COOH

[b] Broad signal

[c] Diglim solution

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