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NUCLEOPHILIC CONDENSATION OF OCTAFLUOROISOBUTYLENE WITH TETRAFLUOROETHYLENE*

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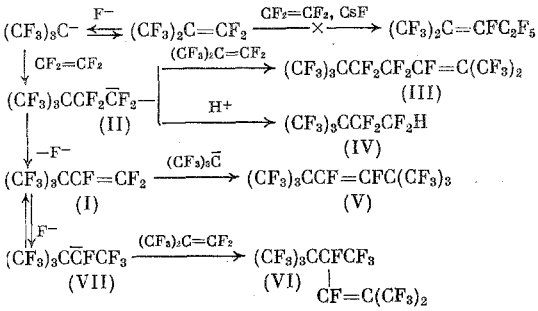
Perfluoroalkyl carbanions add to the electrophilic multiple bonds of fluoroolefins [2, 3], as shown in numerous dimerization, oligomerization, and codimerization reactions of fluoroolefins under the catalytic action of fluoride ion. In the last case, the character of the products is determined by the reactivity of the fluoroolefins and the corresponding carbanions, and also by the conditions of the reaction, which in general is reversible and kinetically or thermodynamically controlled [4, 5]. Irrespective of this, the process proceeds according to a substitution scheme (vinylic or allylic) with attack of the fluorocarbanion at the multiple bond of the fluoroolefin, and stabilization of the intermediately formed new fluorocarbanion by elimination of F^- ion. A characteristic example of these reactions is the codimerization of octafluoroisobutylene (OFIB) with hexafluoropropylene, leading under kinetic control conditions to olefin $(CF_3)_3CCF{=}CFCF_3$, via the anionic intermediate $(CF_3)_3CCF_2\bar{C}FCF_3$ [6]. According to the above, it could be expected that during the codimerization of OFIB with tetrafluoroethylene (TFE), perfluoro(tert-butylethylene) (I) is formed.

However, in the present work it was shown that the reaction between OFIB and TFE in the presence of CsF gives olefin $C_{10}F_{20}$ (III) as the main product, and also the monohydride (IV) and isomers of (III), the fluoroolefins (V) and (VII).† The reaction is carried out in MeCN or diglyme under mild conditions (~20°C), the amount of isomers (V) and (VI) formed in diglyme being somewhat larger than in MeCN. With increase in temperature to 60-70°C, the rate of the reaction increases, but the ratio between the products practically does not change.



The results show, first, that perfluoro-tert-butyl anion is the anion with which the codimerization takes place. Under the conditions studied, perfluoroethyl anion is apparently not generated, as indicated, for example, by the absence of the olefin $(CF_3)_2C = CFC_2H_5$ in the reaction mixture. It is especially interesting that the intermediate carbanion (II), formed during the addition of $(CF_3)_3C^-$ to the multiple bond of TFE, can be induced into a reaction with a second molecule of OFIB, in preference over the usual paths of stabilization, i.e., β-elimination of F^- leading to olefin (I) or proton capture from the medium with formation of hydride (IV). This unusual result of codimerization, which is markedly different than known ones, is apparently due to the increased nucleophilicity of carbanion (II) and high electrophilicity of the C=C bond in OFIB. It should be noted

* Preliminary communication, see [1].

†It was noted in review [2] that the condensation of OFIB with TFE catalyzed by F^- gives a mixture of products, but no information on their nature was given.

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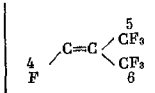
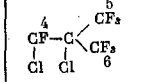
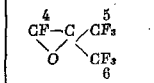
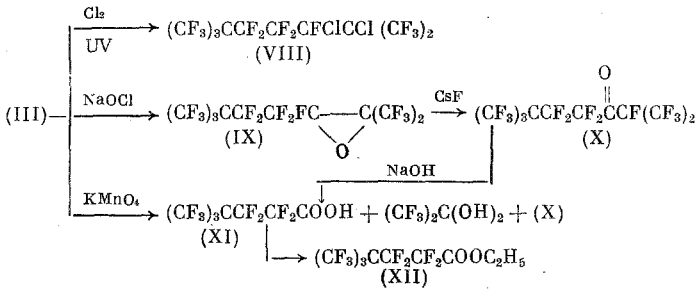
TABLE 1. Physicochemical Properties and IR and ^{19}F NMR Spectra of Compounds $(CF_3)_3CCF_2CF_2R$

Compound	R	bp, °C (p, mm Hg)	n_D^{20}	Empirical formula	Found, % / Calculated, % C	H	F	IR spectrum (ν, cm^{-1})	^{19}F NMR spectra: chemical shifts, ppm F^1 *	F^2	F^3	F^4	F^5	F^6	J, Hz
(III)		138–140	1,3020	$C_{10}F_{20}$	24,0 / 24,0		75,60 / 76,0	1690	−15,1	+25,4 m	+32,4 m	+16,6 m	−19,7 m	−16,9 d.q	$J_{F^4-F^6}=32,0$, $J_{F^5-F^6}=9,4$
(IV)	H	69–70	<1,3	C_6HF_{13}	22,41 / 22,50	0,35 / 0,31	76,50 / 77,19		−14,0	+39,9 d.dec	+58,1 d.dec				$J_{F^3-H}=53$, $J_{F^2-H}=5,65$
(VIII)		67–70(7)	1,3310	$C_{10}F_{20}Cl_2$	20,99 / 21,02		66,19 / 66,55		−15,8	+21,1 m	+28,5 m	+45,3 m	−12,7 m	−11,6 m	
(IX)		140–142	1,2950	$C_{10}F_{20}O$	23,20 / 23,26		73,67 / 73,64	1460	−15,2	+25,4 m	+36,4 m	+68,4 t.q	−10,0 m	−9,2 d.q	$J_{F^3-F^4}=22,7$, $J_{F^4-F^6}=22,7$, $J_{F^5-F^6}=9,4$
(X)	$COCF(CF_3)_2$	139–140	1,2980	$C_{10}F_{20}O$	23,09 / 23,26		73,85 / 73,64	1785	−15,0	+25,0 m	+35,1 m	+112,1 m	−2,9 d.t.t		
(XI)	COOH	60–61; 5 (1)	1,3210	$C_7HF_{13}O_2$	23,43 / 23,08	0,28 / 0,27		1780	−15,5	+26,0 dec	+37,0 dec				$J_{F^2-F^5}=J_{F^3-F^5}=3,5$, $J_{F^4-F^5}=7,0$
(XII)	COOEt	68–70(24)	1,3195	$C_9H_5F_{13}O_2$	27,39 / 27,55	1,30 / 1,28		1790	−15,1	+27,1 t.dec	+37,5 t.dec				$J_{F^2-F^3}=2,5$

* In all cases, triplet of triplets; $J_{F^1-F^2}=10.5$–11.5, $J_{F^1-F^3}=13.5$–14.1 Hz, apart from (IV), for which $J_{F^1-F^3}=6.6$ Hz.

that the C- or O-anions generated by the addition of $(CF_3)_3C^-$ to acrylonitrile [7] or aromatic aldehydes [8] can also enter into further vinyl substitution reactions with OFIB. Also, the presence of olefins (V) and (VI) in the reaction mixture indicates that anion (II) is stabilized to a certain extent in the normal way, giving olefin (I). Under the reaction conditions, the latter enters into a further reaction with OFIB and CsF, and gives disubstitution product, olefin (V), and also generates anion (VII), which reacts with OFIB similarly to anion (II). This scheme is confirmed experimentally (see below). The structure of olefin (III) was confirmed by spectral methods and by chemical transformations. Olefin (III) is readily chlorinated during UV irradiation, and by oxidation with NaOCl according to [9], gives α-oxide (IX) in a good yield. Under the catalytic action of CsF, the latter isomerizes into fluoro ketone (X). The reaction of olefin (III) with $KMnO_4$ also gives in normal way the acid (XI) and hexafluoroacetone hydrate. Ketone (X) was unexpectedly observed among the products of this reaction; its formation can be explained by the epoxidation of (III) by the action of $KMnO_4$, followed by isomerization of the α-oxide (IX) thus formed into ketone (X) under the reaction conditions



The pyrolysis of the Na salt of acid (XI) gives olefin (I) in a high yield

$$(CF_3)_3CCF_2CF_2COONa \xrightarrow[-CO_2,\ -NaF]{t^\circ} (CF_3)_3CCF{=}CF_2 \quad (I)$$

As expected, under mild conditions (diglyme, ~20°C), olefin (I) reacts with OFIB in the presence of CsF, giving the isomeric olefins (V) and (VI).

Thus, codimerization of OFIB with TFE in the presence of CsF is characterized by the fact that two molecules of OFIB enter the reaction per molecule of TFE. This reaction is an original example of a combined electrophilic addition to fluoroolefin (TFE) with participation of a fluoro carbanion as a nucleophile and OFIB as an electrophile.

$$R_F^- + CF_2{=}CF_2 + A{-}X \xrightarrow[-X^-]{} R_F{-}CF_2CF_2{-}A$$

It is clear that during electrophilic catalysis (SbF_5), the reaction of OFIB with TFE leads to an entirely different result: olefins $CF_3CR{=}CFC_2H_5$ ($R = CF_3$ or C_3F_7) are formed via the intermediate perfluorinated allyl cations [10].

EXPERIMENTAL

The NMR spectra were run on a Perkin–Elmer R-32 spectrometer (^1H, 90 MHz and ^{19}F 84.6 MHz) with reference to TMS and CF_3COOH as external standards; the IR spectra were measured on a UR-20 apparatus, the Raman spectra on a Ramanor-HG-2S spectrometer with excitation by argon laser (5145 Å), and the mass spectra on a Varian MAT CH-8 apparatus, with electron energy of 70 eV, temperature of ionic source ~150°C (m/z, the suggested assignment, and relative intensity,% are given). For analytical and preparative GLC, Krytox and FS-1265 on Chromosorb W were used. The physicochemical and spectral characteristics of compounds $(CF_3)_3CCF_2CF_2R$ are listed in Table 1.

Reaction of Octafluoroisobutylene with Tetrafluoroethylene in the Presence of CsF. A mixture of 19.5 g of OFIB, 7.5 g of TFE, 1.5 g of CsF, and 40 ml of absolute MeCN was shaken for 24 h in a 100 ml autoclave (total holding time 6 days). After removal of gaseous products, the residue was poured into HCl (1 : 5). From the organic layer, after drying over $CaCl_2$, 24 g of a mixture was obtained, which contained (GLC) 66% of olefin (III), 14.5% of hydride (IV), and < 1% of olefin (V). By distillation, 7 g of a fraction consisting of hydride (IV), bp 25-45°C (70 mm) was obtained. Distillation of residue gave 14.7 g (60%) of perfluoro-2,6,6-trimethyl-2-heptene (III). Mass spectrum: 500 (M^+), 0.02; 481 ($M^+ - F$), 11.1; 281 ($M^+ - C_4F_9$), 10.2; 269 ($C_5F_{11}^+$) 4.9; 231 ($C_5F_9^+$), 26.1; 212 ($C_5F_8^+$), 3.6; 193 ($C_5H_7^+$) 1.0; 181 ($C_4F_7^+$), 58.7; 143 ($C_4F_5^+$), 3.7; 131 ($C_3F_5^+$); 1.0; 124 ($C_4F_4^+$), 1.0; 112 ($C_3F_4^+$), 1.4; 100 ($C_2F_4^+$), 1.8; 93 ($C_3F_3^+$), 7.0; 69 (CF_3^+), 100; 31 (CF^+), 1.8. Metastable ions: $C_{10}F_{19} - CF_4 \rightarrow C_9F_{15}^+$ (* 321.1); $C_{10}F_{19}^+ - C_4F_8 \rightarrow C_6F_{11}^+$ (* 164.2); $C_6F_{11}^+ - C_2F_4 \rightarrow C_4F_7^+$ (* 116.6); $C_5F_{11}^+ - CF_4 \rightarrow C_4F_7^+$ (* 121.8);

$C_5F_9^+ - CF_2 \rightarrow C_4F_7^+$ (* 141.8); $C_5F_8^+ - CF_3 \rightarrow C_4F_5^+$ (* 96.46); $C_5F_8^+ - CF_2 \rightarrow C_4F_6^+$ (* 123.8); $C_4F_7^+ - C_3F_4 \rightarrow CF_3^+$ (* 26.3); $C_4F_6^+ - CF_3 \rightarrow C_3F_3^+$ (* 53.4), $C_4H_5^+ - CF_2 \rightarrow C_3F_3^+$ (* 60.48). Hydride (IV) was purified by preparative GLC. PMR spectrum: 5.85 t.t (CH); $J_{gem-F-H} = 53$, $J_{vic-F-H} = 6$ Hz.

Under similar conditions, the reaction between OFIB and TFE in diglyme gives a mixture containing 67% of (III), 4% of (IV), 5% of (V), and 2% of (VI).

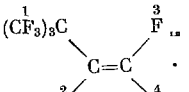
2,3-Dichloroperfluoro-2,6,6-trimethylheptane (VIII). A solution of 2 g of olefin (III) in 5 ml of Freon-113 was saturated with chlorine under UV irradiation. At the end of the reaction (GLC control), 0.8 g (35%) of chloride (VIII) was isolated by distillation.

Perfluoro-2,6,6-trimethyl-2-heptene Oxide (IX). A solution of NaOCl (prepared from 15.3 g of NaOH, 45 ml of water, and 9 g of Cl_2), 15.2 g of olefin (III), and 8 ml of diglyme was stirred for 1.5 h at ~20°C. The lower layer was separated and dried over $CaCl_2$. By distillation, 11.7 g (75%) of oxide (IX) was obtained.

Perfluoro-2,6,6-trimethylheptan-3-one (X). A mixture of 2.5 g of oxide (IX), 0.1 g of CsF, and 4 ml of absolute diglyme was stirred for 8 h at ~20°C. A 10-ml portion of concentrated H_2SO_4 was added, and by distillation in vacuo, 2.1 g (86%) of ketone (X), bp 49-51°C (23 mm), were obtained.

Perfluoro-γ,γ-dimethylvaleric Acid (XI). Potassium permanganate was added in portions, with stirring and cooling, to a mixture of 15 g of olefin (III), 30 ml of acetone and 3 ml of water until a stable violet color appeared. The mixture was then boiled for 30 min, the precipitate was filtered, and the filtrate was diluted with water, and acidified with HCl (1 : 5). The organic layer was extracted by Freon-113. According to ^{19}F NMR data, a mixture of 56% acid (XI), 35% of ketone (X), and 15% of hexafluoroacetone hydrate was obtained. To decompose ketone (X), the mixture was shaken with 10% aqueous KOH, and then acidified, and from the organic layer, after drying and removal of the solvent by distillation over concentrated H_2SO_4, 7.4 g (68%) of acid (XI) were isolated. PMR spectrum: 11.4 s (HO).

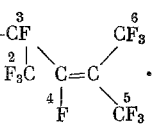
A mixture of 3.4 g of acid (XI) and 5 ml of concentrated H_2SO_4 was boiled for 40 min, and then poured into water. From the lower layer, by distillation, 3 g (82%) of ester (XII) were isolated. PMR spectrum: 1.1 t (Me), 4.2 q (CH_2); J = 7 Hz.

Perfluoro-3,3-dimethyl-1-butene (I). A 6.5-g portion of dry Na salt of acid (XI) was heated in a distillation flask over a gas burner flame. From the distillate, after repeated distillation, 3.9 g (78%) of olefin (I), bp 56-57°C, n_D^{20} <1.3, were obtained. Found: C 25.53; F 75.96%. C_6F_{12}. Calculated: C 24.0; F 76.0%. Raman spectrum (ν, cm^{-1}): 1774.  . ^{19}F NMR spectrum: −12.5 d.d (F^1), +13.8 d.d. (F^4), +25.6 d.d.dec. (F^3), +104.9 d.d.dec. (F^2); $J_{F^2-F^3}$ =113, $J_{F^3-F^4}$=52.6, $J_{F^2-F^4}$ =45.1, $J_{F^1-F^3}$=15, $J_{F^1-F^2}$ =11.3 Hz. Mass spectrum: 300 (M^+), 15.1; 281 ($M^+ - F$), 11.8; 231 ($M^+ - CF_3$), 15.7; 212 ($C_5F_8^+$), 4.1; 193 ($M^+ - F - CF_4$), 15.9; 181 ($C_4F_7^+$), 30.1; 143 ($C_4F_5^+$), 5.8; 124 ($C_4F_4^+$), 1.14; 112 ($C_3F_4^+$), 1.3; 100 ($C_2F_4^+$), 2.4; 93 ($C_3F_3^+$), 11.8; 74 ($C_3F_2^+$), 1.9; 69 (CF_3^+), 100; 50 (CF_2), 1.2; 31 (CF^+) 5.8. Metastable ions: $M^+ - CF_3 \rightarrow C_5F_9^+$ (* 177.9); $C_6F_{11}^+ - CF_2 \rightarrow C_5F_9^+$ (* 189.9); $C_6F_{11}^+ - C_2F_4 \rightarrow C_4F_7^+$ (* 116.6); $C_5F_9^+ - CF_2 \rightarrow C_4F_7^+$ (* 141.8); $C_5F_8^+ - CF_3 \rightarrow C_4F_5^+$ (* 96.46); $C_5F_7^+ - CF_2 \rightarrow C_4F_5^+$ (* 105.95); $C_4F_7^+ - C_3F_4 \rightarrow CF_3^+$ (* 26.3); $C_4F_6^+ - CF_3 \rightarrow C_3F_3^+$ (* 53.4); $C_4F_5^+ - CF_2 \rightarrow C_3F_3^+$ (* 60.48).

Reaction between Perfluoro-3,3-dimethyl-1-butene and Perfluoroisobutylene in the Presence of CsF. A mixture of 1.4 g of CsF, 5.3 g of olefin (I), 3.6 g of OFIB, and 20 ml of absolute diglyme was held for 3 days in a sealed ampul. The mixture was poured into dilute HCl, and the organic layer was dried over $MgSO_4$. By distillation, 7.7 g of a fraction with bp 75-137°C were isolated, containing (GLC) 38% of olefin (V) and 48% of olefin (VI), which were separated by preparative GLC.

Pure (V): mp 40-42°C. Found: C 24.40; F 76.14%. $C_{10}F_{20}$. Calculated: C 24.0; F 76.0%. Raman spectrum (ν, cm^{-1}) (in CCl_3F): 1700. ^{19}F NMR spectrum (in CCl_3F): −14.9 t (CF_3), +64.0 m (CF); J_{CF_3-F}=16.9 Hz. Mass spectrum: 500 (M^+), 4.6; 481 ($M^+ - F$), 5.0; 412 ($M^+ - CF_4$), 2.75; 393 ($M^+ - F - CF_4$), 15.1; 343 ($M^+ - CF_4 - CF_3$), 5.9; 255 ($C_7F_9^+$), 2.9; 231 ($C_5F_9^+$), 2.0; 205 ($C_6F_7^+$), 1.2; 181 ($C_4F_7^+$), 3.7; 93 ($C_3F_3^+$), 2.2; 69 (CF_3^+) 100. Metastable ions: $C_{10}F_{19}^+ - CF_4 \rightarrow C_9F_{15}^+$ (* 321.1); $C_9F_{16}^+ - CF_3 \rightarrow C_8F_{13}^+$ (* 285.6); $C_9F_{15}^+ - CF_4 \rightarrow C_8F_{11}^+$ (* 236.7); $C_6F_{11}^+ - CF_2 \rightarrow C_5F_9^+$ (* 190); $C_5F_9^+ - CF_2 \rightarrow C_4F_7^+$ (* 141.8).

Pure (VI): bp 130°C, n_D^{20} 1.3040. Found: C 23.98; F 76.34%. $C_{10}F_{20}$. Calculated: C 24.0; F 76.0%.

Raman spectrum (ν, cm^{-1}): 1675. ^{19}F NMR spectrum: −22.6 d.m.  .(F^6), −18.0 d.q (F^5), −16.9 d.d.q.q. (F^1), −7.2 m (F^2), +12.7 m (F^4), +95.75 m (F^3); $J_{F^3-F^6}$ = 55.5; $J_{F^4-F^5}$ = 38.5; $J_{F^1-F^2} = J_{F^1-F^3} = J_{F^1-F^4} = J_{F^5-F^6}$ = 11.3; $J_{F^1-F^6}$ = 1.9 Hz. Mass spectrum: 500 (M^+) 0.2; 481 ($M^+ - F$) 4.7; 412 ($C_9F_{16}^+$), 3.4; 393 ($C_9F_{15}^+$), 1.0; 343 ($C_8F_{13}^+$), 2.6; 281 ($M^+ - C_4F_9$), 9.8; 255 ($C_7F_9^+$), 1.4; 231 ($C_5F_9^+$), 1.8; 212 ($C_5F_8^+$), 1.1; 181 ($C_4F_7^+$), 20.0; 143 ($C_4F_5^+$), 1.6; 93 ($C_3F_3^+$), 3.4; 69 (CF_3^+), 100; 31 (CF^+), 1.0. Metastable ions: $C_{10}F_{19}^+ - C_4F_8 \rightarrow C_6F_{11}^+$ (*164.2); $C_9F_{16}^+ - CF_3 \rightarrow C_8F_{13}^+$ (*285.6); $C_6F_{11}^+ - C_2F_4 \rightarrow C_4F_7^+$ (*116.6); $C_6F_9^+ - CF_2 \rightarrow C_4F_7^+$ (*141.8).

CONCLUSIONS

A CsF-catalyzed condensation of octafluoroisobutylene with tetrafluoroethylene leads to perfluoro-2,6,6-trimethyl-2-heptene as a result of a combined addition of perfluoro-tert-butyl anion and octafluoroisobutylene to the multiple bond of tetrafluoroethylene.

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