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MIXED DIMERIZATION OF PERFLUOROISOBUTYLENE WITH FLUOROOLEFINS CATALYZED BY THE FLUORIDE ANION

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The transformations of fluoroolefins catalyzed by the F⁻ anion usually lead to their dimerization, mixed dimerization, or oligomerization and proceed by a vinyl substitution mechanism with stabilization of the intermediate carbanion through β -elimination of the F⁻ anion [1].

 $> C = CF_2 \stackrel{F}{\iff} > \overline{C} - CF_3 \xrightarrow{>C = CF_2} > \overline{C} - CF_2 - CF_3 \xrightarrow{|} > C = CF - CF_3 \xrightarrow{|} > C = CF - CF_3$

In contrast, the condensation of perfluoroisobutylene (PFIB) with olefins $CF_2=CFX$ (I) for X = F [2], OCF_3 , or OC_3H_7 [3] in the presence of CsF proceeds by combined nucleophilic addition, in which intermediate carbanion (A) reacts with a second PFIB molecule (pathway a), leading to (II). In this case, the corresponding codimers (III) are formed only as side-products (pathway b). It was of interest to the study the reaction of PFIB with CsF and olefins (I) for new examples since there was evidence that the ratio between pathways a and b depends on the nature of X in (I) [3] and extend this reaction to perfluorocycloolefins.

The reaction of PFIB with CsF and olefins (Ia)-(Ie) in monoglyme and diglyme proceeds under mild conditions (~20°C) and leads to codimers (IIIa)-(IIIe) in yields above 50%. The reaction rate increases in the series (Id) < (Ia) = (Ib) < (Ic) < (Ie), which corresponds to increasing activity of olefins (I) in nucleophilic reactions.

$$(CF_3)_2C = CF_2 \xrightarrow{\overline{F}} (CF_3)_3\overline{C} \xrightarrow{CP_z = CFX(I)} (CF_3)_3CCF_2\overline{C}FX$$

$$(CF_3)_3CCF_2CF_2CF_3CF = C(CF_3)_2 \xrightarrow{a, (CF_s)_2C = CF_s} | b \to (CF_3)_3CCF_2 = CF_3X$$

$$(II) \qquad (III_{a-e})$$

$$(A)$$

(II): X = F, OCF₃, OC₃F₇, CF₃ (c); (I), (III): X = CI (a), Br(b), CF₃(c), Ph(d), COOEt(e).

Only olefin (IIId) is the single product of the corresponding reaction and the condensation proceeds in a complex manner in the other cases. Thus, in addition to codimer (IIIa), which is formed in 50% yield, we find dienes $C_{10}F_{18}$ and $C_{14}F_{26}$ as well as chloroalkane $C_6F_{12}Cl_2$ (mass spectrometric data). The structures of these compounds were not unequivocally established but the chemical shifts and signal intensities in the ¹⁹F NMR spectra indicate the lack of $(CF_3)_3C$ and $(CF_3)_2C=CF$ groups in these products, which excludes the possibility that these products are formed through pathways a or b and suggests that they are products of the transformations of trifluorochloroethylene induced by the fluoride anion [4]. Analogously, dienes $C_{10}F_{18}$ and $C_{14}F_{26}$ are formed in the reaction of PFIB with $CF_2=CFBr$ (Ib) in addition to unsaturated bromide (IIIb).

The reaction of PFIB with $CF_2=CFCF_3$ (Ic) and the fluoride anion was studied by Young [1] and Sherer [5]. In the absence of solvent, $(CF_3)_2C=CFCF(CF_3)_2$ is formed in 95% yield at 170-180°C [1]. On the other hand, the reaction in DMF at 20°C leads to olefin (IIIc)

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without indication of the yield [5]. We found that the reaction of PFIB with CsF and (Ic) in diglyme at 0-20°C also leads to codimer (IIIc)* in 84% yield. In addition, ~2% combined addition product (IIc) is formed. The structure of (IIc) was supported by its oxidation to α -hydroxyketone (IV) [7] upon the action of KMnO₄.



We should note that olefin (IIc) cannot be obtained from olefin (IIIc), PFIB, and CsF. This indicates the formation of (IIc) by combined addition as a result of the direct reaction of the $(CF_3)_3\overline{C}$ anion with PFIB and hexafluoropropylene.

¹⁹F NMR spectroscopy shows that isomeric ester (V) and acrylate dimer (VI) are formed in the reaction of PFIB with ethyl trifluoroacrylate (Ie) in addition to ester (IIIe), whose structure was supported by its independent synthesis from $(CF_3)_3CCF=CFCOF$ [8]. These results show that the $CF_3\overline{C}FCO_2Et$ anion (VII) is generated in a system containing PFIB, acrylate (Ie), and CsF in addition to the $(CF_3)_3C\overline{C}$ anion. Anion (VII) competes successfully with the tertiary fluorocarbanion and reacts with both PFIB and (Ie).



It is interesting that the reaction of PFIB with CsF and perfluoromethacrylate esters, whose electrophilic activity is much greater than that of PFIB and ester (Ie), proceeds exclusively through the $(CF_3)_2\overline{CCO}_2R$ anion [6].

The reactions of perfluorocycloolefins with nucleophiles, as a rule, feature replacement of the vinyl (or allyl) fluorine atom rather than addition of the nucleophile at the double bond [9]. Accordingly, the condensation of PFIB with olefins (VIII) in the presence of CsF leads to substituted olefins (IX).⁺ The disubstitution product (Xa) was also isolated in low yield in the reaction of PFIB with fluorocyclobutene (n = 2) in addition to (IXa).



Thus, our results show that the substitution of the vinyl fluorine atom is a general process in the condensation of PFIB with (I) and (VIII) and may be used in the synthesis of higher fluoroolefins containing the $(CF_3)_3C$ group. Further evidence has been found to support our previous conclusions [3] that the reaction of intermediate carbanion (A) with PFIB (or other electrophiles [11]) is favored over β -elimination when substituent X in intermediate (A) destabilizes the carbanionic site due to the α -effect (X = F or OR_F) raising the reactivity of this site.

^{*}Olefin (IIIc) is formed in addition to $(CF_3)_3CBr$ also in the reaction of PFIB with CsF and 1,2-dibromohexafluoropropane [6].

⁺Chambers et al. [10] have discussed the reactions of perfluorocycloolefins with other fluorocarbanions.

EXPERIMENTAL

The ¹⁹F NMR spectra were taken on a Perkin-Elmer R-32 spectrometer at 84.6 MHz. The chemical shifts were given in ppm relative to CF_3CO_2H as the external standard. The IR spectra were taken on a UR-20 spectrometer.

<u>Reaction of Perfluoroisobutylene with Halotrifluoroethylenes</u>. A sample of 14.14 g (Ia) was passed with stirring and ice cooling into a mixture of 16 g freshly roasted CsF, 50 ml abs. monoglyme, and 32 g PFIB. Stirring was continued for 3 h. After 12 h, the mixture was poured into a solution of one part concentrated hydrochloric acid and five parts water. The organic layer was distilled at 3 mm over concentrated sulfuric acid to give 30 g of a mixture containing 70% olefin (IIIa), 12% $C_6F_{12}Cl_2$, 9% $C_{10}F_{18}$, and 7% $C_{14}F_{26}$ as indicated by gas-liquid chromatography. Subsequent fractionation gave 20 g (50%) olefin (IIIa), bp 85-86°C, n_D^{20} 1.3145. Found, %: C 22.90; F 66.32. C_6ClF_{11} . Calculated, %: C 22.75; F 66.03. IR spectrum: 1700 cm⁻¹ (C=C). ¹⁹F NMR spectrum: -13.3 d d (F¹), 24.7 d dec (F³), 72.0 d dec (F²), $J_{1-3} = 16.0$, $J_{1-2} = 12.2$, $J_{2-3} = 133$ Hz. Distillation of the residue gave 6 g of a fraction with bp 105-109°C containing $C_6F_{12}Cl_2$ and $C_{10}F_{18}$ and 2 g of a fraction containing $C_{14}H_{26}$, bp 55°C (3 mm).

Analogously, 9 g CsF, 11 g PFIB, and 8.5 g CF_2 =CFBr in 30 ml abs. monoglyme gave 10 g of a fraction with bp 90-105°C, containing 74% olefin (IIIb) [6] and 13.5% $C_{10}F_{18}$ as indicated by gas-liquid chromatography and 2.1 g of a fraction containing dienes $C_{14}F_{26}$, bp 48-53°C (3 mm).

Reaction of Perfluoroisobutylene with Hexafluoropropylene. A sample of 19 g (Ic) was introduced with stirring and cooling to 0°C to a mixture of 1 g CsF, 30 ml abs. diglyme, and 32 g PFIB. After 2 h, the reaction mass was poured into a solution prepared from one part concentrated hydrochloric acid and five parts water. The organic layer was distilled over concentrated sulfuric acid in vacuum. Fractional distillation gave 37 g [84% relative to (Ic)] olefin (IIIc), bp 72°C [5]. The residue gave 1.7 g (2.7%) perfluoro-2,4,6,6-tetra-methyl-2-heptane (IIc), bp 62-63°C.(21 mm), $n_D^{2^\circ}$ 1.3060. Found, %: C 23.85; F 76.02. $C_{11}F_{22}$. Calculated, %: C 24.0; F 76.0. IR spectrum: 1685 cm⁻¹ (C=C). ¹⁹F NMR spectrum: -22.0 m and -17.5 m (F⁶, F⁷), -15.4 m (F¹), -6.5 m (F³), 14.9 m (F⁵), 18.3 m (F²), 101.8 m (F⁴).

<u>1-Phenyl-perfluoro-3,3-dimethylbutene (IIId)</u>. A mixture of 6.2 g CsF, 8.2 g trifluorostyrene, and 12 g PFIB in 35 ml abs. monoglyme was maintained in a sealed ampul for seven days at 20°C, heated for 5 h at 70°C, and poured into a solution prepared from one part concentrated hydrochloric acid and five parts water The precipitated oil was extracted with ether. Unreacted (Id) was distilled off to give 13.1 g (71%) olefin (IIId), bp 88-90°C (25 mm), n_D^{20} 1.4050. Found, %: C 40.06; H 1.38; F 58.33. C₁₂H₅F₁₁. Calculated, %: C 40.22; H 1.40; F 58.38. ¹⁹F NMR spectrum: -14.3 d d (F¹), 57.5 d dec (F³), 81.3 d dec (F²), J₁₋₃ = 18.8, J₁₋₂ = 13.2, J₂₋₃ = 133 Hz.

Reaction of Perfluoroisobutylene with Ethyl Trifluoroacrylate in the Presence of CsF. A sample of 2.4 g ester (Ie) was added dropwise with stirring and ice cooling to a mixture of 1 g CsF, 20 ml abs. diglyme, and 3.5 g PFIB. The mixture was warmed to 20°C and the volatile compounds were removed in vacuum. The residue was poured into a solution prepared from one part concentrated hydrochloric acid and five parts water. The precipitated oil was extracted with ether, evaporated, and distilled over concentrated sulfuric acid at 3 mm. Subsequent distillation gave 1.8 g of a fraction with bp 77-80°C (45 mm) containing 70% ester (IIIe) and 30% ester (V) as indicated by gas-liquid chromatography. Found, %: C 30.42; H 1.44; F 59.06. $C_9H_5F_{11}O_2$. Calculated, %: C 30.50; H 1.41; F 59.02. The residue gave 1.1 g diester (VI), which was found identical to an authentic sample by gas-liquid chromatography and ¹⁹F NMR spectroscopy [12]. ¹⁹F NMR spectrum of (IIIe): -14.0 t (F¹), 66.7 m (F², F³), J₁₋₂ = J₁₋₃ = 15 Hz. ¹⁹F NMR spectrum of (V): -18.7 d d q (F¹), -17.1 d q (F²), 2.4 d d (F⁵), 12.2 m (F³), 88.0 m (F⁴), J₂₋₃ = 28.2, J₁₋₄ = 24.4, J₃₋₅ = 18.8, J₁₋₂ = J₁₋₃ = J₄₋₅ = 8.5 Hz.

Reaction of Perfluoroisobutylene with Perfluorocyclobutene. A sample of 12.8 g olefin (VIIIa) was introduced with stirring and cooling to 0°C into a mixture of 1.3 g CsF, 30 ml abs. monoglyme, and 16.2 g PFIB. After 1 h, the mixture was poured into water. The organic layer was distilled over concentrated sulfuric acid to give 27.5 g of a mixture containing 95% olefin (IXa) and 2.5% olefin (Xa) as indicated by gas-liquid chromatography. Subsequent fractionation gave 21.6 g (75%) olefin (IXa), bp 83-84°C, np^{20} <1.3. Found, %: C 26.81;

F 73.47. C_8F_{14} . Calculated, %: C 26.52; F 73.48. IR spectrum: 1745 cm⁻¹. ¹⁹F NMR spectrum: -11.1 m (CF₃), 23.0 m (CF), 37.6 m and 45.6 m (CF₂). Distillation of the residue gave olefin (Xa), bp 60°C (15 mm), np²⁰ 1.3220. Found, %: C 25.67; F 73.77. $C_{12}F_{22}$. Calculated, %: C 25.62; F 74.38. ¹⁹F NMR spectrum: -15.4 m (CF₃), 34.5 m (CF₂).

<u>Perfluoro-1-tert-butylcyclopentene (IXb)</u>. A sample of 12 g PFIB was introduced with stirring and cooling into a mixture of 1 g CsF, 30 ml abs. diglyme, and 16.5 olefin (VIIIb). After 0.5 h, the mixture was poured into water and the organic layer was distilled over concentrated sulfuric acid. Redistillation gave 28.1 g (89%) olefin (IXb), bp 107-108°C, n_D^{20} 1.3015. Found, %: C 26.20; F 73.54. C₉F₁₆. Calculated, %: C 26.21; F 73.79. IR spectrum: 1685 cm⁻¹. ¹⁹F NMR spectrum: -13'.0 d t (CF₃), 24.6 m (CF), 28.5 m, 46.0 m, and 56.5 m (CF₂), J_{CF₃-CF = 18.8, J_{CF₃-CF₂ = 8.9 Hz.}}

CONCLUSIONS

The reaction of perfluoroisobutylene with unsaturated compounds containing the trifluorovinyl group in the presence of cesium fluoride proceeds through vinyl substitution and leads to mixed dimers with the perfluoro-tert-butyl group. Perfluorocycloolefins react analogously.

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