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PRELIMINARY NOTE

Perfluoro-3,3-dimethyl-2(E)-pentene by Fluoride Ion Catalyzed Addition of Octafluoroisobutene to Hexafluoropropene

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The fluoride ion catalyzed [1] oligomerization of perfluoroolefins has been employed extensively to prepare higher homologs [2,3,5-10]. When unlike partners react, the reaction might take either of two courses, depending on which olefin accepts fluoride ion to become the nucleophile. In all reported cases where the structure of the product allows the mechanism to be inferred, the less substituted (by carbon) olefin becomes the nucleophile, albeit at the more substituted center.
e.g.

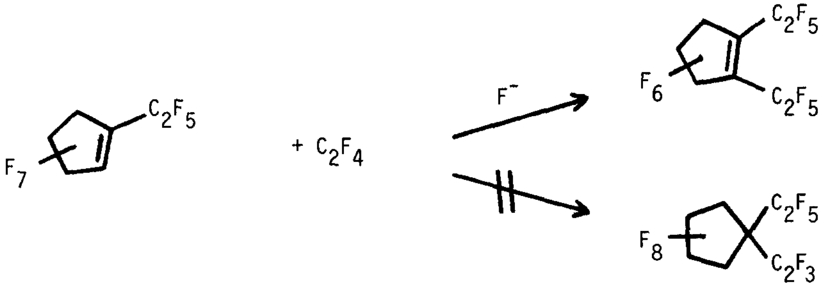
[2,3]

$$CF_2{=}CFCF_3 + (CF_3)_2C{=}CFC_2F_5 \xrightarrow{F^-} (CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2$$

$$CF_2{=}CFCF_3 + (CF_3)_2C{=}CFC_2F_5 \nrightarrow CF_3CF{=}CFC(CF_3)_2CF_2C_2F_5$$

and

[9]



The unobserved reactions might have been expected because the tertiary anions should be the more abundant intermediates owing to their greater stability, but considerations of steric hinderance or product stability evidently rule instead. We wish to report a counter-example.

When a mixture of hexafluoropropene (HFP) and octafluoroisobutene (OFIB) [toxic] obtained by pyrolysis of octafluorocyclobutane [11] was passed into a flask equipped with a dry ice-cooled cold finger and containing a stirred suspension of ball-milled, anhydrous potassium fluoride in dimethylformamide, a clear lower layer accumulated. Upon water washing and distillation, the major component of this layer boiled at 71-72°, lacked ir absorption in the double bond region, and had a mass spectrum consistent only with composition C_7F_{14} [12]. These data plus the ^{19}F spectrum establish the structure of the product as **1**, rather than **2** which Young and Bennett report for the adduct of the same two olefins over CsF at 200° [5,10].

$E\text{-}(CF_3)_3CCF{=}CFCF_3$

1

$(CF_3)_2CFCF{=}C(CF_3)_2$

2

The ^{19}F spectrum of **1** consists of a doublet of doublets ($J = 14.2$ and 16.2 Hz) at -63.3 ppm (upfield) from internal $CFCl_3$, a broadened doublet ($J = 16$ Hz) at -68.6 ppm, and a multiplet at -150 ppm, in the ratio 9:3:2 [13]. The four and five bond couplings are somewhat larger than those reported by Schumann and Cavagna for $E\text{-}(CF_3)_2CFCF{=}CFCF_3$ [14], presumably owing to greater interaction between non-bonding orbitals in the more crowded tert-butyl compound.

We have found **1** to be a ubiquitous by-product in the F^- promoted chemistry of HFP-contaminated OFIB; the addition of OFIB to other fluoroolefins is under study.

We would like to thank Dr. K. L. Servis for measuring the 94 MHz spectrum of 1 and Mr. R. Haack for the mass spectrum. This paper presents the results of one phase of research conducted at the Jet Propulsion Laboratory, California Institute of Technology, for the National Institutes of Health, by agreement with the National Aeronautics and Space Administration.

1 Amines are also used as catalysts [2,3], but in such cases the effective catalyst is probably a quaternary ammonium fluoride formed in a preliminary reaction between the amine and olefin [4].

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12 m/e, %: 350(m+), 1.80; 331, 1.56; 262, 1.48; 243, 6.54; 212, 2.47; 193, 1.53; 181, 4.49; 150, 1.71; 143, 2.72; 131, 6.26; 124, 2.32; 112, 1.32; 100, 1.50; 74, 1.20; 70, 1.02; 69, 100. Measured on a Finnegan Model 3200 quadrupole instrument.

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