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PRELIMINARY NOTE

Hexafluoropropene Trimer. Synthesis and Properties of Functional Derivatives

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Hexafluoropropene trimer (HFPT) is known [1,2,3] to be a mixture of ca. 65% perfluoro(2-methyl-3-isopropyl-2-pentene) (1), ca. 30% perfluoro(3-isopropyl-4-methyl-2-pentene) (II) and ca. 5% of an isomer with unknown structure. Thorough investigation of the HFPT reaction with nucleophilic agents showed, that O-nucleophilic (alcohols, phenols) easily reacted with HFPT in presence of triethylamine. In all cases the products are generated by substitution of one fluorine atom in the HFPT molecule, with $C_9F_{17}OR$ ethers being formed. They are always mixture of the isomeric vinylic (III) and allylic (1V) ethers. The ratio of ethers III and 1V depends on the nature of nucleophile. Thus, aliphatic alcohols mainly produce allylic ethers 1V*. For example, ethanol gives the ratio of iso-

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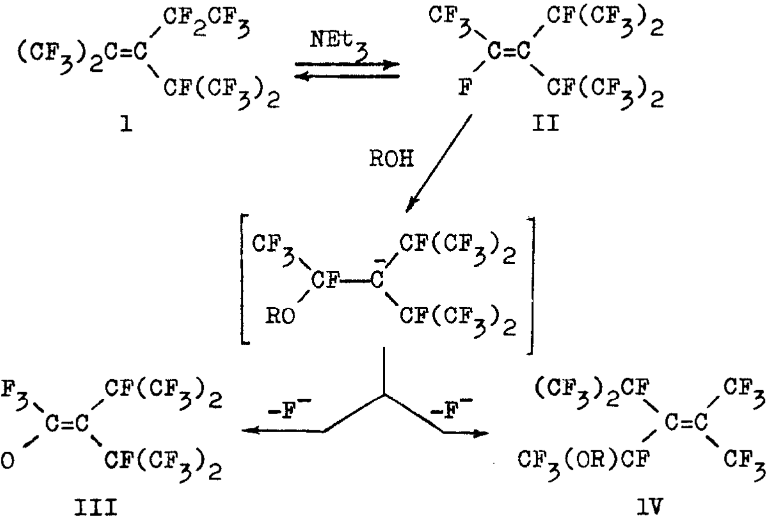
* It is evident from the ^{19}F NMR data that owing to hindered rotation around the sp^2-sp^3 carbon-carbon bond, the ethers always consist of two stable conformers.

meric ethers III:1V=1:13. Phenols, however, predominantly produce ethers III. For unsubstituted phenol the ratio of ethers III:1V=12:1.

It was demonstrated by special experiments that the reaction of O- nucleophiles with the individual perfluoropentene isomers (1 or II) in the presence of triethylamine yields the same mixture of ethers (III + 1V) as in above reaction of O-nucleophiles with HFPT (I + II mixture). Moreover, triethylamine was found to cause a reversible isomerization of each of the perfluoropentenes (1⇄II). An equilibrium mixture contains approximately 70% of pentene I and 30% of pentene II.

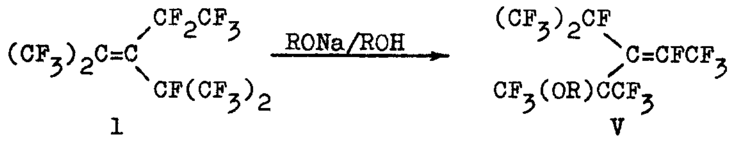
This suggests that of the two HFPT olefins, perfluoropentene II is the more active towards the O-nucleophiles. Its reaction rate with such nucleophiles is comparable to that of reversible isomerization of perfluoropentenes; as a result, ethers III and 1V are formed exclusively from isomeric pentene II by means of vinylic or allylic substitution, respectively.



R= C_6H_5, p-$CH_3C_6H_4$, p-BrC_6H_4, p-$C_2H_5OOCC_6H_4$, etc.

R= C_2H_5, $C_4F_9CH_2$, CHF_2-CF_2CH_2, CH_2ClCH_2, $CH_3OCH_2CH_2$, CH_2-CHCH$_2$ (O), CH_2=CHCH$_2$, etc.

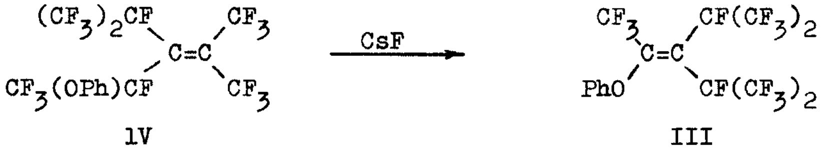
Alternative results were obtained for the reaction of HFPT with the alkaline metal alkoxides. In this case both perfluoro-(3-isopropyl-4-methyl-2-pentene) (II) and "less active" perfluoro(2-methyl-3-isopropyl-2-pentene) (1) enter the reaction. The reaction products contain, along with ethers 1V, the ethers (V) produced as a results of S_N2' substitution of fluorine in pentene 1:



R= C_2H_5, i-C_3H_7

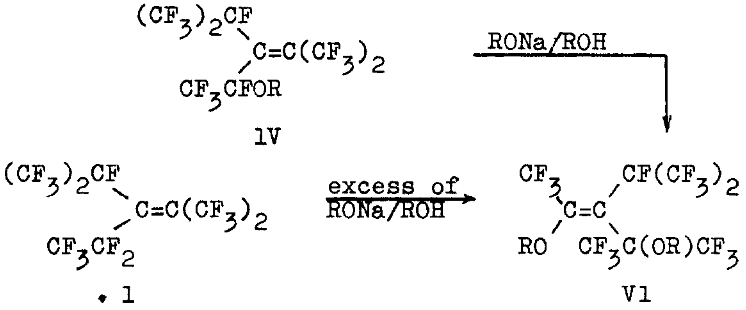
However, pentene 1 does not react with sodium phenoxide while pentene II gives with it a mixture of ethers III and 1V, the latter being predominant. This is a convenient preparative procedure for the isolation of olefin 1 from HFPT (1+II mixture). The reaction of HFPT with sodium phenoxide confirms greater activity of perfluoropentene II toward nucleophilic agents.

It is interesting to note that phenylperfluoro(2-methyl-3-isopropyl-2-penten-4-yl)ether (1V, R=Ph) isomerized into the respective ether III in the presence of cesium fluoride:

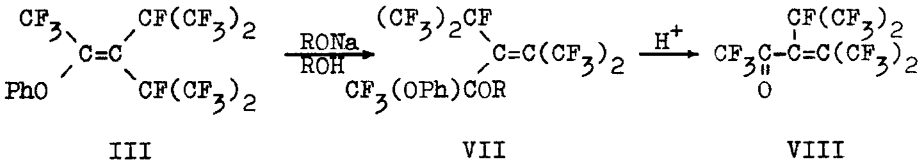


This reaction shows a principal possibility of isomerrization of type 1V allylic ethers into type III vinylic ethers.

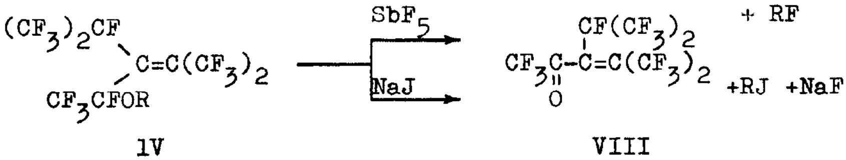
The ethers 1V and V are sufficiently electrophylic to react with the next sodium alkoxide molecule. Treatment of the allylic ethers 1V with one mole of alkoxide as well as the reaction of pure perfluoropentene 1 with two moles of alkoxide produces the same diether (V1):



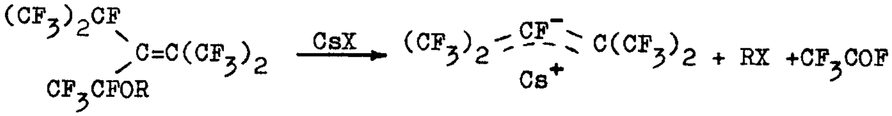
Phenylperfluoroisononenyl ether (III, R=Ph) reacts with sodium alkoxide to yield perfluoro(3-isopropyl-4-methyl-3-pentene-2-on) ketals (VII) converted to vinylketone (VIII) by acid hydrolysis:



Vinylketone VIII may be prepared also by reaction of the allylic ethers 1V with antimony pentafluoride as well as with sodium iodide:



The reaction with sodium iodide proceeds in a somewhat unexpected manner: here allylic ethers 1V act as alkylating agents. We found some other examples of alkylation by ethers 1V. Fluoride ion, perfluorotert.-butyl- and perfluoroisopropoxyanions easily react with ethers 1V. In these cases, however, the final reaction product is not vinylketon VIII but a cesium salt of mesomeric 1,1,3,3-tetrakis(trifluoromethyl)-2-fluoropropenyl carbanion (1X), prepared in our laboratory independently, from tetrakis(trifluoromethyl)allene and CsF [4]:



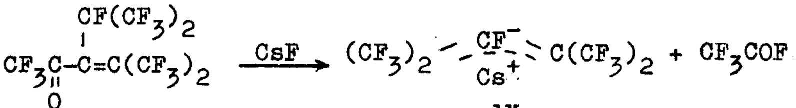
$$(CF_3)_2CF(CF_3CFOR)C{=}C(CF_3)_2 \xrightarrow{CsX} (CF_3)_2\overset{CF^-}{\underset{Cs^+}{\cdots}}C(CF_3)_2 + RX + CF_3COF$$

1V 1X

X= F, $(CF_3)_3C$, $(CF_3)_2CFO$

R= CH_3, C_2H_5, $CH_2CH{=}CH_2$, $CH_2\underset{O}{CH{-}CH_2}$

One could assume that vinylketone VIII is an intermediate product in the chain of transformations 1V → 1X. It was indeed shown by special experiments that vinylketone VIII is easily transformed into salt 1X in the presence of cesium fluoride:



$$CF_3\underset{\underset{O}{\|}}{C}{-}\overset{CF(CF_3)_2}{C}{=}C(CF_3)_2 \xrightarrow{CsF} (CF_3)_2\overset{CF^-}{\underset{Cs^+}{\cdots}}C(CF_3)_2 + CF_3COF$$

VIII 1X

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