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CYCLOADDITION OF PERFLUOROVINYL ETHERS TO DIENES

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It is known that a wide variety of fluoroalkenes dimerize at temperatures of 150°C and higher. In the presence of dienes, the fluoroalkenes react with them more readily than they dimerize [1] and preferentially form a four-membered ring.

Because of the absence in the literature of data for the reaction of dienes with perfluorovinyl ethers (PFVE) we have studied a series of PFVE (I)-(IV) with butadiene (V) and piperylene (VI).

 $\begin{array}{cccc} R_{F}OCF=CF_{2}+CH_{2}=CHCH=:CHR \rightarrow CF_{2}-CFOR_{F} \\ & & & \downarrow & \downarrow \\ (I)-(IV) & (V), (VI) & CH_{2}-CHCH=:CHR \\ & & (VII)-(XIII) \\ R_{F}=CF_{3}CF_{2}CF_{2} (I) \text{ and } R=H (VII), CH_{3} (VIII); R_{F}=(CF_{2}CF_{2}O)_{3}CF_{3} (II) \text{ and } R=H \\ (IX), CH_{3} (X); R_{F}=CF_{2}CF_{2}CF_{2}CF_{2}SO_{2}F (III) \text{ and } R=H (XI), CH_{3} (XII); R_{F}=\\ & & \downarrow \\ CF_{3} \\ = (CF_{2})_{5}CN (IV); R=H (XIII); R=H (V), CH_{3} (VI). \end{array}$

In the same way as fluoroalkenes, the PFVE more readily undergo a reaction with nonfluorinated dienes than cyclodimerize and form the corresponding cycloaddition products (VII) (XIII) in high yields. The reaction products of PFVE with butadiene and piperylene contain none of the PFVE cyclization dimers. These were specially synthesized by us using a high pressure (5-10 kbar) and temperature (>150°C).

$$\begin{array}{c} CF_2 = CFOR_F \rightarrow CF_2 - CFOR_F \\ & | \\ (II), (IV) \\ & CF_2 - CFOR_F \\ (XIV), (XV) \end{array}$$

 $R_{F} = (CF_{2}CF_{2}O)_{3}CF_{3}$ (11), (XIV), (CF₂)₅CN (IV), (XV).

Both the cycloaddition reactions of different fluoroalkenes with nonfluorinated dienes and the similar reactions of PFVE involve problems of orientation and stereochemistry. It has been shown that PFVE react with dienes to form four-membered cyclic products under these conditions and not by 1,4-cycloaddition to form the six-membered Diels-Alder products.

The cycloaddition of PFVE with a diene can occur by two routes (head-to-head or head-totail) to form compounds of type A or B.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2372-2377, October, 1988. Original article submitted June 12, 1987. $\begin{array}{ccc} CF_{2} - CFOR_{F} & CF_{2} - CFOR_{F} \\ CH_{2} - CHCH = CHR & RCH = CHCH - CH_{2} \\ (A) & (B) \end{array}$

Analysis of the ¹H and ¹⁹F NMR spectra of the cyclodimerization products of PFVE with butadiene indicates only one type of addition. On the basis of literature data for the cycloaddition of 1,3-butadiene to fluoroolefins [1] this should be of the head-to-head type. Compounds (VII), (IX), (XI), and (XIII) are formed as equal amounts of the cis and trans isomers relative to the ring.

The analysis of the reaction products of the vinyl ethers (I)-(III) with piperylene showed the presence of only compounds (VIII), (X), and (XII) and the absence of compounds of type (C) or (D) which might be formed by reaction of the perfluorovinyl group with the inner double bond of the piperylene.

 $\begin{array}{c} CF_2 \rightarrow CFOR_F & CF_2 \rightarrow CFOR_F \\ | & | \\ CH_3CH \rightarrow CHCH = CH_2 & CH_2 = CHCH \rightarrow CHCH_3 \\ (C) & (D) \end{array}$

The data obtained can be explained by the intercoordination of PFVE and diene and the nature of the products obtained, apparently, on the basis of kinetic factors.

Although many cycloaddition reactions are stereospecific [2, 3] the products of this reaction, as indicated above, are a mixture of cis and trans isomers (Fig. 1).

 19 F chemical shifts are strongly affected through space by the electric field of the dipole of neighboring bonds, e.g., in the so-called ortho effect for fluorobenzenes. The value of this effect depends upon the interatomic distances; the less the H to F distance the lower the field observed 19 F resonance [4]. On this basis the signal at 120 ppm can be assigned to the fluorine of the OCF in the cis and that at 140 ppm to the trans isomer.

In compounds (VIII), (X), and (XII) each of the cis and trans isomers (with respect to the ring) can also exist as cis or trans isomers of the exo-double bond. In fact, the ¹⁹F NMR spectra of these compounds show doubling of the F atom signals in the region 121-122 and 140-141 ppm with an intensity ratio for the four signals of 2:3:3:2. Assignment of these signals to specific C=C bond isomers needs additional investigations.

It is known the series of four-membered ring products obtained from fluoroalkenes and 1,3-dienes at 450-800°C undergoes rearrangement to six-membered ring adducts [5]. It turns out that heating compounds (VII) or (VIII) in an inert medium at 400-600°C in a flow system for several seconds leads to a complex mixture. From a spectroscopic analysis the presence of compounds with six-membered fluoroaromatic ring (XVI, XVII) can be inferred.



(XVI) (XVII)

R = H (VII), (XVI), CH_3 (VIII), (XVII).

Formation of (XVI), (XVII) is confirmed in the PMR spectrum of the reaction mixture which shows aromatic ring protons at 6.30-7.40 ppm and aromatic methyl protons at 2.10 ppm (XVII). The ¹⁹F NMR spectra show signals for the perfluoroalkoxy groups as well as multiplets



Fig. 1. Cis and trans isomers of fluorinated cyclobutanes (VII), (IX), (XI), and (XIII).

Com-	-Yield, %	Bp, °C (p, mm Hg)	Found, %		Empirical	Calculated, %			IR spectrum $C = C (u)$	
pound			С	н	F	formula	с	н	F	cm ⁻¹)
(VII) (VIII) (IX) (X) (XI) (XII) (XII) (XIII)	84 68 81 76 67 66 73	$\begin{array}{r} 123 *\\ 52-54 (20)\\ 66-67 (10)\\ 79-81 (10)\\ 77-79 (10)\\ 86-88 (10)\\ 71 (10)\end{array}$	33.29 35.87 27,39 28,98 24.67 28,09 33.77	2.04 2.41 1.11 1.43 1.29 1.59 1.61	58.92 56,43 59.97 59.29 53.84 52.06 57.01	$\begin{array}{c} C_9H_6F_{10}O\\ C_{10}H_8F_{10}O\\ C_{13}H_6F_{16}O,\\ C_{14}H_8F_{16}O,\\ C_{14}H_8F_{16}O,\\ C_{11}H_6F_{14}SO,\\ C_{12}H_8F_{14}SO,\\ C_{12}H_6F_{13}NO \end{array}$	33,75 35,93 27,46 28,86 24,40 28,01 33,72	1,88 2.39 1.06 1.37 1.20 1.56 1,40	59,37 56,89 60.21 58,76 53,20 51,75 57,84	1650 1650 1650 1650 1650 1650 2260 (C=N)

TABLE 1. Yield, Boiling Point, and Elemental Analytical Data for the Fluorinated Cyclobutanes (VII)-(XIII)

*At normal pressure.

at 108.4, 113.2, and 118.7 ppm (fluoroaromatic signals). In this case it seems that the reaction proceeds in the same way as in the synthesis of fluoro-substituted cyclohexenes [6].

EXPERIMENTAL

 $^{19}{\rm F}$ and $^{1}{\rm H}$ NMR spectra were measured on an RS-56M spectrometer (56.4 and 60 MHz respectively) and a Bruker WM-250 spectrometer (235.2 and 250 MHz). The $^{19}{\rm F}$ NMR chemical shifts were referenced to external CFCl₃ standard and the PMR shifts to internal TMS. IR spectra were recorded on a UR-10 spectrometer.

The perfluorovinyl ethers (PFVE) (I)-(III) were obtained by pyrolysis of the perfluoroacid fluorides over sodium carbonate or pyrolysis of the dry sodium salt of the corresponding acids. PFVE (IV) was prepared from dibromide (XVIII) $CF_2BrCFBrO(CF_2)_5CN$ by debromination using Zn powder and metallic iodine in diglyme similarly to [7]. The yield of (IV) was 86% with bp 109-110°C. Found: C 25.76; F 66.43; N 3.81%. $C_8F_{13}NO$. Calculated: C 25.74; F $\alpha' \beta' \gamma \beta \alpha$ 66.22; N 3.75%. IR spectrum (ν , cm⁻¹): 1835 ($CF_2=CFO$), 2260 (C=N). NCCF_2CF_2CF_2CF_2CF_2CF=CF_2. ¹⁹F NMR spectrum (δ , ppm): 84.6 m (2F, α -OCF₂), 105.2 m (2F, α' -CF₂CN), 114.8 m and 121.5 m (2F, C=CF₂), 121.0 m (2F, β^1 -CF₂), 122.3 m (2F, β -CF₂), 125.0 m (2F, γ -CF₂), 136.0 m (1F, OCF=C). Nitrile (XVIII) was prepared by bromination of CF_2 =CFO(CF₂)₅COF which was synthesized by method [8, 9] from the disodium salt of the product of addition of 1 mole of hexafluoropropylene oxide to perfluoroadipic acid difluoride. The acid fluoride group was converted $\delta \gamma \beta \alpha$ to the nitrile by [8]. $CF_2BrCFBrOCF_2CF_2CF_2CF_2CF_2CE=CM$ (XVIII), bp 40-41°C (1 mm). IR spectrum: 2260 cm⁻¹ (C=N). ¹⁹F NMR spectrum: 62.3 m (2F, CF_2Br), 70.1 m (1F, CFBr), AB-spectrum δ_A 80.4, δ_B 84.7, J_{AB} = 150 Hz (2F, OCF₂), 112.0 m (2F, α -CF₂CN), 127.5 m (2F, β -CF₂), 128.8 m and 132.0 m (4F, γ -, δ -CF₂CF₂).

<u>General Method for Preparing (VII)-(XIII)</u>. A steel autoclave of capacity 50 ml was charged with PFVE (I)-(IV) (0.05 mole) and diene (V), (VI) (0.05-0.06 mole). The autoclave was heated to 120°C and held for 6 h; the temperature was then raised to 140°C and held for a further 6 h. The liquid products were distilled in a nitrogen stream. The yields, boiling points, and spectral parameters are given in Table 1.

 $CF_{2} - CFOCF_{2}CF_{2}CF_{3} (VII).$

¹⁹F NMR spectrum (in (CD₃)₂CO,δ, ppm): two AB-spectra δ_A 79.3, δ_B 86.4, J_{AB} = 154 Hz, δ_A 80.5, δ_B 85.2, J_{AB} = 149 Hz (2F, α-CF₂ cis, trans isomers), two AB-spectra δ_A 108.3, δ_B 117.3, J_{AB} = 195 Hz, δ_A 108.1, δ_B 111.0, J_{AB} = 205 Hz (2F, 3-CF₂ cis, trans isomers), 81.8 m (3F, γ -CF₃), 129.8 m (2F, β-CF₂), 129.8 m and 139.5 m (1F, 2-OCF cis, trans isomers, relative intensities 1:1). PMR spectrum (δ, ppm): 5.80 m (1H, CH=), 5.30 m (2H, =CH₂), 3.30 (1H, 1-CH), 2.80 m and 2.45 m (2H, 4-CH₂).

In the PMR spectra of (IX), (XI), and (XIII) the chemical shifts (CS) of analogous groups agreed within experimental measurement accuracy with the CS of the indicated groups of compound (VII).

 $\begin{array}{c} \overset{3}{\text{CF}_2\text{CFOCF}_2\text{CF}_2\overset{\beta}{\text{CF}_2\text{CF}_2}\overset{\gamma}{\text{CF}_2\text{CF}_3} (\text{VIII}). \\ | & | \\ \text{CH}_2\text{CHCH} = \text{CHCH}_3 \end{array}$

¹⁹F NMR spectrum (in (CD₃)₂CO, δ , ppm): 80.3 and 86.5 m (2F, α -CF₂ cis, trans isomers), 82.3 m (3F, γ -CF₃), two AB-spectra δ_A 108.8, δ_B 111.5, J_{AB} = 195 Hz, δ_A 109.0, δ_B 118.3, J_{AB} = 190 Hz (2F, 3-CF₂ cis, trans isomers), 121.5 m, 122.3 m, 140.2 m, and 140.7 m (1F, 2-CF, relative intensities 2:3:3:2), 130.7 m (2F, β -CF₂). PMR spectrum: 5.50 complex m (2H, CH=CH), 1.80-3.70 complex m (3H, 1-CH, 4-CH₂), 1.70 m (3H, CH₃). In the PMR spectra of (X), (XII) the CS of analogous groups agreed with those of (VIII).

 $\begin{array}{c|c} & & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$

¹⁹F NMR spectrum (in (CD₃)₂CO, δ , ppm): 56.5 t (3F, δ -OCF₃), two AB-spectra δ_A 85.5, δ_B 91.7, $J_{AB} = 153$ Hz, δ_A 86.0, δ_B 91.0, $J_{AB} = 155$ Hz (1F, α -OCF₂ two isomers), 89.7 m (8F, β -CF₂OCF₂-CF₂OCF₂), 91.8 m (2F, γ -CF₂O), two AB-spectra δ_A 108.0, δ_B 111.5, $J_{AB} = 208$ Hz, δ_A 108.8, δ_B 118.5, $J_{AB} = 210$ Hz (2F, 3-CF₂ two isomers), 122.8 m and 140.4 m (1F, 2-CFO cis, trans isomers, relative intensities 1:1).

 $\overset{3}{\underset{C}{\text{CF}_{2}\text{CF}}} \overset{2}{\underset{C}{\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{2}\text{CF}_{3}} (X).$

¹⁹F NMR spectrum (in $(CD_3)_2CO$, δ , ppm): 121.4 m, 122.0 m, 140.4 m, 140.7 m (1F, 2-CFO, four isomers, relative intensities 2:3:3:2). The CS and intensities of the remaining groups agreed with those of (IX) within experimental accuracy.

 $\begin{array}{c} \overset{3}{} \overset{2}{} \overset{2}{} \overset{\alpha}{} \overset{\beta}{} \overset{\beta}{} \overset{\gamma}{} \overset{\delta}{} \overset{\beta}{} \overset{$

¹⁹F NMR spectrum (in (CD₃)₂CO, δ , ppm): -45.0 m (1F, SO₂F), 79.0 m, 80.0 m, and 85.0 m (7F, CF₃, α -, γ -CH₂), two AB-spectra δ_A 108.1, δ_B 110.8, J_{AB} = 208 Hz, δ_A 108.1, δ_B 117.8, J_{AB} = 212 Hz (2F, 3-CF₂), 112.5 m (2F, δ -CF₂), 121.5 m, 140.0 m (1F, 2-CFO two isomers), 145.5 m (1F, β -CF).

 CF_3 $CF_2CFOCF_2CFOCF_2CF_2SO_2F (XII).$ $| | CH_2CHCH=CHCH_3$ | 1

¹⁹F NMR spectrum (in (CD₃)₂CO, δ , ppm): 121.4 m, 122.2 m, 140.4 m, and 140.7 m (1F, 2CFO, four isomers, relative intensities 2:3:3:2). CS and intensities of the remaining groups agreed with those of (XI) within experimental accuracy.

 $\overset{3}{C}F_{2}\overset{2}{C}F_{0}\overset{\alpha}{C}F_{2}\overset{\beta}{C}F_{2}\overset{\gamma}{C}F_{2}\overset{\delta}{C}F_{2}\overset{\epsilon}{C}F_{2}\overset{\epsilon}{C}F_{2}CN \quad (XIII).$ $\overset{|}{L}\overset{|}{L} \overset{l}{C}HCH=CH_{2}$

¹⁹F NMR spectrum (in (CD₃)₂CO, δ , ppm): two AB-spectra δ_A 77.7, δ_{AB} = 152 Hz, δ_A 80.1; δ_B 84.9, J_{AB} = 148 Hz (2F, α -CF two isomers), two AB-spectra δ_A 107.5, δ_B 111.0, J_{AB} = 208 Hz, δ_A 108.2, δ_B 117.1, J_{AB} = 212 Hz (2F, 3-CF₂, two isomers), 105.3 m (2F, ϵ -CF₂), 121.4 m (2F, δ -CF₂), 122.2 m, 125.3 m (4F, β -, γ -CF₂), 121.0 m (cis), 138.9 m (trans) (1F, 2-CFO).

Synthesis of (XIV), (XV) was achieved by [10]. The inhibitor of radical polymerization used for (XIV) was the nitrile of perfluoroenanthic acid (up to 5%).

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Bp 107°C (8 mm). Found: C 21.06; F 66.81%, C₁₈F₃₆O₈. Calculated: C 21.01; F 66.54%. ¹⁹F NMR spectrum (δ , ppm): AB-spectra 86.5 dm, 88.4 dm (4F, α ⁻, α ¹-CF₂ cis isomer), JAB = 158 Hz, 85.5 dm, 88.6 dm, (4F, α -, α^1 -CF₂ trans isomer) J_{AB} = 158 Hz, 129 dm, 131.4 dm (4F, 3-, 4-CF₂ cis isomer), J_{AB} = 230 Hz, 127.5 dm, 131.8 dm (4F, 3-, 4-CF₂ trans isomer), J_{AB} = 230 Hz, 55.7 m (6F, δ -, δ '-CF₃), 79.7 m, 88.3 m, and 90.5 m (20F, β -, β '-, γ -, γ '-CF₂O), 136.5 m and 139.0 m (2F, 1-, 2-OCF cis-trans isomers, relative intensities 42:58).

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Bp 98-99°C (22 mm). Found: C 25.83; F 66.63; N 3.81%. C₁₆F₂₆N₂O₂. Calculated: C 25.74; F 66.22; N 3.75%. IR spectrum: 2260 cm⁻¹ (CEN). ¹⁹F NMR spectrum (δ, ppm): AB-spectrum δ_A 83.0, δ_B 85.0, J_{AB} = 142 Hz (4F, α -, α' -CF₂, cis isomer), AB-spectrum δ_A 81.5, δ_B 85.5, J_{AB} = 146 Hz (4F, α -, α '-CF₂, trans isomer), AB-spectrum δ_A 131.0, δ_B 135.5, J_{AB} = 226 Hz (4F, 3-, 4-CF₂ cis isomer), AB-spectrum δ_A 129.3, δ_B 135.8, J_{AB} = 230 Hz (4F, 3-, 4-CF₂ trans isomer), 106.9 m (4F, ϵ -, ϵ^1 -CF₂), 122.8 m (4F, δ -, δ^1 -CF₂), 124.0 m, 126.5 m, (8F, β -, β^1 -, γ-, γ'-CF₂), 138.7 m and 141.4 m (2F, cis-trans isomers, relative intensities 55:45).

Pyrolysis of Compounds (VII), (VIII). The vapor of compound (VII) in a N₂ stream was passed into a quartz tube filled with quartz packing and heated to 500°C. According to their ¹H and ¹⁹F NMR spectra the pyrolysates at the exit consisted of the starting cyclobutane (VII) and a mixture of isomeric perfluoropropoxybenzenes (XVI). Pyrolysis of (VIII) was carried out similarly. The yields of (XVI), (XVII) were to 15%).

CONCLUSIONS

Cycloaddition of perfluorovinyl ethers to butadiene or piperylene led to 1-vinyl- or 1-propenyl-2-perfluoroalkoxy-2,3,3-trifluorocyclobutanes as mixtures of cis and trans isomers.

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