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PERFLUORINATED DIOXOLANES.

1. SYNTHESIS OF SOME DERIVATIVES OF PERFLUORO-4-OXO-1, 3-DIOXOLANE

V. S. Yuminov, S. V. Kartsov, V. L. Maksimov, and A. V. Fokin

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Derivatives of perfluorinated 4-oxo-1,3-dioxolanes are used as monomers for obtaining polymers with selective gas permeability [1, 2].

The most accessible of this series is perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane (I), synthesized in 65% yield by reaction of hexafluoropropylene oxide (HFPO) with benzophenone under rather stringent conditions (185°C) [2]. Dioxolane (I) is more conveniently obtained by reaction of HFPO with DMF at -20 to -10°C [3]. However, the yield of (I) is decreased to 34%, apparently because of its reaction with the by-product α , α -difluorotrimethylamine (DFTA) which is very reactive [4].

We showed that conversion of DFTA to a salt by treatment of the reaction mixture with anhydrous HCl increases the yield of (1) to 70%. Moreover, the fluoride catalyst is generated by the reaction and dioxolane (I) separates from the reaction mixture in the form of a fluoroorganic layer. Formation of (I) can be represented in scheme 1 involving participation of an intermediate fluorine- and hydrogen-containing dioxolane (FHD), the stability of which is determined by the substituent in position 2. Thus, the FHD CF3CFOCMe2OCF2 which contains weakly donating substituents in position 2 is stable [5]. In our case the presence of a strongly donating 2-substituent leads to the opening of the dioxolane ring with formation of trifluoropyruvyl fluoride and DFTA. It is known [6] that in the presence of fluorine ion, the source of which is in this case DFTA, trifluoropyruvyl fluoride dimerizes to (I):

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Ochtinsk Scientific-Industrial Unification "Plastpolimer," Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 392-395, February, 1988. Original article submitted May 27, 1986.



There are fragmentary reports on the properties of (I) [2, 6, 7]. We have studied the reactions of (I) with HFPO. Compound (I) with HFPO in diglyme (DG) in the presence of CsF at ~20°C forms a mixture of perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane (II) and perfluoro-2-oxo-2,5-dimethyl-2-(2'-oxa-3'-fluorocarbonylbutyl)-1,3-dioxolane (III) in a ratio of 1.4, and a small amount of HFPO dimer, the fluoroanhydride of perfluoro- α -propoxypropionic acid. Dimerization of HFPO under these conditions is a competing reaction and HFPO dimer is formed also with excess (I).

Addition of (I) to HFPO can be explained by the intermediate formation of alcoholate (IV), which then at the tertiary carbon of HFPO to give (III):



Actually, we have succeeded in obtaining (IV) by reaction of stoichiometric amounts of (I) and CsF in diglyme at 20°C. In the ¹⁹F NMR spectrum of (IV) at 20°C the signals of the CF₃=CFO groups are unresolved wide lines which upon cooling of the sample widen further at the beginning and at -50°C split into two groups of signals containing three (78.1, 80.0, and 82.2 ppm) and two (116.1 and 121.1 ppm) lines, respectively, which indicates the presence of conformational isomers. Compound (IV) is stable at 20°C and only upon heating to 100°C does it decompose, forming (V).

The structure of (III) was confirmed by IR and ¹⁹F NMR spectral data (Table 1). In the IR spectrum of (III) one wide carbonyl band is present at 1880 cm⁻¹ due to the C(0)0 and C(0)F groups.

Apparently dioxolane (III) is an intermediate in the formation of (II) from HFPO and (I) (scheme 2). This is confirmed by reaction of (III) with HFPO in the presence of fluorine ion, the only product being (II). In scheme 3 a proposed mechanism of this reaction is shown:



		¹⁹ F NMR spectrum			
Compound -	IR spec- trum, ∨, cm ⁻¹	nu- cleus	δ, ppm rela- tive to CFCl ₃	J, Hz	Relative intensity
$ \begin{array}{c} F_{3}^{2}C \\ COF^{i} \\ COF^{i} \\ F_{3}C \\ F_{3}C \\ F_{3}C \\ COF^{i} $	1875 1925 * ₩	1 † 2 3 †	+22,3, +22,4 -81,7 -121,1, -123,0		1 6 1
$\begin{array}{c c} 3.4 & 0 & 1 \\ F_{5}C & CF - CF_{3}^{2} \\ 6 & 5 & 0 \\ F_{5}C - CF & C = 0 \\ 0 & 0 \end{array} $ (II)	1840	1 † 2 3 4 5 † 6	$\begin{array}{c} -112,5, \ -116,2\\ -82,5\\ -81,0\\ -93,5\\ -125,3, \ -127,3\\ -81,1\end{array}$	J _{3,4} =150	0,8, 0,2 3 1 1 0,2, 0,8 3
$\begin{array}{c} \overset{8}{F_{s}C} & \overset{4,5}{CF_{s}} - O - CF - CF_{s} \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & &$	1880 1925 w	1+ 2+ 3+ 56+ 78	-26.326.5 -129.8, -130.4 -81.3, -81.5 -78.0 -85.0 -120.7, -121.0 -81.0 -78.5	J _{4.5} =160	0,6, 0,4 0,4, 0,6 0,4, 0,6 1 0,6, 0,4 3 3
$\begin{array}{c} 3^{1}\\ F_{3}C \\ C \\$	1840	1 2 3	-27 -119 -80		2 1 6
$\mathbf{F}_{3}^{2}\mathbf{C}-\mathbf{C}-\mathbf{C}\mathbf{F}_{2}^{1}-\mathbf{OCs} (\mathbf{V})$		12	-30.1 -82,2		2 3
$\begin{array}{c c} F_3^2 C & CF_3^1 \\ & C \\ & $	1870 s 1925 * •	√ 1,2 3 4	-80.5 -121.2 -81.7 -		6 1 3

TABLE 1. Spectral Characteristics of Compounds (I)-(VI)

*Band 1925 cm⁻¹ is characteristic of dioxolanes (I), (IV), and (VI) in a condensed phase or in nonpolar solvents. In polar solvents (dioxane-1,4, diglyme) it disappears, i.e., apparently caused by intermolecular interaction. +Two signals are caused by the presence of cis-trans isomers relative to the ring plane.

Compound (I) with hexafluoroacetone gives perfluoro-4-oxo-2,2,5-trimethyl-1,3-dioxolane (VI)* in quantitative yield.



^{*}In [8] the possibility of obtaining (VI) from hexafluoroacetone and trifluoropyruvyl fluoride was indicated; however, neither reaction conditions nor characteristics of the product (VI) are shown.

EXPERIMENTAL

GLC analysis of (I)-(III) and (VI) was carried out on a Tsvet-100 chromatograph with thermal conduction detector on a 6 m × 3 mm column packed with N-AW-HMDS chromaton with a deposited SKTFT-50 liquid phase (10%). The carrier gas (helium) flow was 30 ml/min. The analysis was carried out with linear programming in the range of 50-200°C. IR spectra were taken on an IKS-22 spectrometer with a NaCl prism. ¹⁹F NMR spectra were recorded on a Tesla-487B spectrometer (80 MHz) from CF₃COOH as external standard (see Table 1). CsF was dried by the method of [9]. The boiling points of compounds (I) and (II) agree with data of [6].

<u>Perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane (I)</u>. Into a three-neck 1liter flask with a stirrer and a tube for gas supply connected to a receiver cooled to -78° C, 75 g (1.03 moles) DMF were placed and at -30° C. 180 g (1.08 moles) HFPO were added. In the receiver there is an accumulation of 54 g of HFPO. The mixture was heated to 0°C and treated with 50 g (1.37 moles) HCl. The lower layer was separated and by distillation 77 g (70%) of (I) and 5 g (3%) of HFPO dimer (identical by GLC and ¹⁹F NMR with a sample obtained by the method of [10]) were obtained.

<u>Perfluoro-4-oxo-2,5-dimethyl-2-(2'-oxa-3'-fluorocarbonylbutyl)-1,3-dioxolane (III)</u>. Reaction of (I) with HFPO was carried out in a 2-liter stainless steel reactor supplied with a stirrer with built-in shielded motor and thermostatted jacket, thermocouple, one lower outlet valve and two upper valves. Into the reactor 550 g (1.91 moles) of (I), 30 g (0.2 mole) CsF, and 60 ml abs. diglyme were loaded. Over 2 h 380 g (2.29 moles) of HFPO were added by portions. The lower layer of the reaction mixture was separated and distilled. There was obtained 302 g (49%) of (III) with bp 121-122°C and 99% purity. Found, %: C 23.51; F 58.24. C₉F₁₄O₅. Calculated, %: C 23.79; F 58.59. In addition, 45 g of HFPO dimer, 310 g (44%) of (II) (bp 70°C), and 162 g (0.56 mole) unreacted (I) were obtained.

<u>Cesium Perfluoro-4-oxo-2,5-dimethyl-1,3-dioxolan-2-yl-methoxide (IV) (solutions in di-glyme)</u>. Into a 100 ml flask under an Ar flow 1.9 g (7 mmoles) of (I), 0.5 ml abs. diglyme, and 1.1 g (7 mmoles) CsF were placed, vigorously stirred for several min, and left for 4 h until complete homogenization of the liquid phase. Analysis of the mixture by ¹⁹F NMR showed complete transformation of (I) into (IV).

<u>Cesium Perfluoro-2-Oxopropoxide (V)</u>. The reaction mixture from the preceding example was heated in an Ar flow to 100°C for 1 h. According to ¹⁹F NMR compound (IV) was transformed quantitatively into (V) (95%).

<u>Perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane (II)</u>. Into a stainless steel ampul (80 ml) supplied with a manometer and valve, 50 g(0.11 mole) (III), 0.3 g (2 mmoles) CsF, and 5 ml abs. diglyme were placed. Then 25 g (0.15 mole) of HFPO were added and the reaction mixture was stirred for 1 h at 20°C. The lower layer was separated and distilled. There was obtained 57 g (93%) of (II), 5 g (0.01 mole) unreacted (III), and 6 g HFPO dimer.

<u>Perfluoro-4-oxo-2,2,5-trimethyl-1,3-dioxolane (VII)</u>. Into a stainless steel ampul (80 ml) supplied with a valve, manometer, and diaphragm, 44 g (0.15 mole) of (1), 5 ml abs. diglyme, 2 g (13 mmoles) CsF, and 50 g (0.30 mole) hexafluoroacetone were placed and stirred for 2 h at ~20°C. Unreacted hexafluoroacetone was removed and the lower (fluorinated) layer of the reaction mixture was separated and distilled. There was obtained 84 g (88%) of (VI) with bp 63-64°C. Found, %: C 23.07; F 61.01. $C_6F_{10}O_3$. Calculated, %: C 23.23; F 61.29.

CONCLUSIONS

1. Reaction of hexafluoropropylene oxide with DMF followed by treatment of the products with HCl gives perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane in high yield.

2. Perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane reacts with fluoride ion at 20°C with participation of only the fluorocarbonyl group forming cesium perfluoro-4oxo-2,5-dimethyl-1,3-dioxolan-2-yl-methoxide. At higher temperatures ionic fragmentation of the ring proceeds with cleavage of the ester bond.

3. Reaction of perfluoro-4-oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane with hexafluoropropylene oxide is a three-stage process with intermediate formation of the previously undescribed cesium perfluoro-4-oxo-2,5-dimethyl-1,3-dioxolan-3-yl-methoxide and perfluoro-4-oxo-2,5-dimethyl-2-(2'-oxa-3-fluorocarbonylbutyl)-1,3-dioxolane.

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PERFLUORINATED DIOXOLANES.

2. REACTION OF PERFLUORO-4-OXO-1,3-DIOXOLANES WITH FLUORINE ION

V. S. Yuminov, S. V. Kartsov, L. E. Vinogradov, UDC 542.91:547.729.7'161: and A. V. Fokin 546.16-128

Cleavage of an ester bond in perfluorinated cyclic compounds under the action of fluoride occurs only under fairly rigid conditions (>120°C) [1]. Information on the stability of perfluorinated 4-oxo-1,3-dioxolanes to the action of fluoride is unavailable.

In this work the action of fluoride on the substituted fluorodioxolanes perfluoro-4oxo-2,5-dimethyl-2-fluorocarbonyl-1,3-dioxolane (I), perfluoro-4-oxo-2,5-dimethyl-2-(2'-oxa-3'-fluorocarbonylbutyl)-1,3-dioxolane (III), and perfluoro-4-oxo-2,2,5-trimethyl-1,3,-dioxolane (VI) was studied. As the source of fluoride, catalytic amounts of CsF in anhydrous diglyme were used.

It was shown that resistance of the dioxolane ring toward fluoride primarily depends on the nature of the substituent in position 2. Thus, the dioxolane ring in (I) and (VI) from 0 to 80° C is resistant to the action of the CsF/diglyme system, and (III) under the same conditions is transformed in 10 min into (I) and perfluoro-2-oxo-3,6-dimethyl-1,4-dioxane (II). A mixture is formed with the following composition: (I) 24%, (II) 51%, and (III) 25% (75% conversion of (III)). The mixture composition does not change further (Fig. 1). A mixture of practically the same composition (corresponding to 24% conversion of the starting compounds) is formed by the action of fluoride on a mixture of (I) and (II) in a 1:2 molar ratio. As in the preceding case the composition of the reaction mixture becomes constant 10 min after the beginning of the reaction (Fig. 2). These results indicate the existance of equilibria involving opening of the ester bond in (I) and (II) under the action of fluoride [see scheme (1)].

Formation of (II) in high yield indicates it may have high thermodynamic stability compared with (III). This agrees with the fact that (II) in the absence of other reagents is cleaved by fluoride at the ester bond under significantly more rigid conditions (120-140°C [1]) than (III). This also agrees with the data on the high resistance to fluoride of sixmembered compared to five-membered perfluorolactones [2].

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR Moscow. Ochtinsk Scientific-Industrial Unification "Plastpolimer," Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 396-398, February, 1988. Original article submitted May 27, 1986.