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Previously we had reported the synthesis and properties of some polyfluoro-containing keto and enol forms of the cyclobutane and cyclohexane series [1-3]. The present paper is devoted to the synthesis and study of the properties of 1-hydroxyheptafluoro-1-cyclopentene (II). The latter was obtained by heating 1-benzyloxyheptafluoro-1-cyclopentene (I) in the presence of conc. H_2SO_4 , with the simultaneous removal of the volatile products by distillation.



Enol (II) is a colorless liquid with bp101°C. It is stable when stored, is resistant to acids (CF₃SO₃H, H_2SO_4), and easily reacts with CH_2N_2 to give 1-methoxyheptafluoro-1-cyclopentene (III). Enol(II) is dehydro-fluorinated in the presence of water or ethanol, and the thus formed hexafluoro-2-cyclopenten-1-one enters into the vinyl substitution reaction. The fluoro-containing β -substituted cyclopentenones (IVa, b) are the sole products of these reactions.



 $R = H (a), C_2H_5 (b)$

Hexafluoro-2-cyclopenten-1-one is also the intermediate product in the reaction of enol (II) with aqueous KOH solution, which then undergoes haloform decomposition to give the unsaturated acid (V).

$$(II) \xrightarrow{KOH} \begin{bmatrix} F_2 & O \\ F_2 & F \end{bmatrix} \xrightarrow{O} CCF_2CF_2CF = CFH \xrightarrow{HCI} HOOCCF_2CF_2CF = CFH (V)$$

An attempt to obtain the keto form (2-hydroheptafluorocyclopentanone) corresponding to enol (II) by the hydrolysis of 2-hydroheptafluorocyclopentanone oxime (VI) proved unsuccessful. The latter does not react with conc. HCl and decomposes when heated with 80% H₂SO₄ solution. It should be mentioned that we previously obtained 2-hydropentafluorocyclobutanone [3] and 2-hydrononafluorocyclohexanone [2] under similar conditions. Oxime (VI) was synthesized as described in [4] from perfluorocyclopentene and the free hydroxylamine.



The decarboxylation of the dry K salt of acid (V) gives a very peculiar result. 1-Hydro-1,1,4,4,4pentafluoro-2-butyne (VII) was obtained as the result of heating this compound at atmospheric pressure:

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Apparently, the intermediately formed 1-hydropentafluoro-1,3-butadiene is isomerized to acetylene (VII) under the influence of KF. A similar isomerization is described in the literature for perfluorobutadiene in the presence of CsF [5]. At the same time, it is known that the decarboxylation of the Na salt of 2, 2, 3, 3, 4, 5,5-heptafluoro-4-penten-1-oic acid under conditions that differ somewhat from those used by us leads to perfluorobutadiene [6].

EXPERIMENTAL

The PMR spectra were taken on a Perkin-Elmer R-12 spectrometer (60 MHz) using HMDS as the internal standard, while the ¹⁹F NMR spectra were taken on a Hitachi spectrometer (56.46 MHz) using CF₃COOH as the external standard. The chemical shifts are given in ppm from HMDS and CF₃COOH, respectively. The IR spectra were taken on a UR-20 spectrometer (as a thin layer). The Raman spectrum was recorded on a Ramanor HG-2S instrument using the 5145 Å line of a CR-8 ionic argon laser with a power of 100 MW for excitation. The mass spectrum was obtained on a AEI MS-30/DS-50 instrument at an ionizing voltage of 70 eV.

<u>1-Benzyloxyheptafluoro-1-cyclopentene (I)</u>. To a stirred mixture of 7.5 g of benzyl alcohol and 15.2 g of perfluorocyclopentene was added 3.9 g of KOH in 10 ml of water at ~0°C. The mixture was then stirred for 30 min at 0°, after which the temperature was brought up to ~20°, the mixture was poured into water, and I the lower layer was separated, dried over MgSO₄, and distilled to give 12.8 g (61.6%) of (I), bp 62-64° (0.5 mm). Found: C 48.21; H 2.36; F 44.41%. $C_{12}H_7F_7O$. Calculated: C 48.00; H 2.35; F 44.31%. PMR spectrum: 6.9 s (C_6H_5), 4.66 d (CH_2), $J_{CH_2/C}F=2.6$ Hz. ¹⁹F NMR spectrum: 35.5 m (CF_2 '), 37.6 m (CF_2 "), 50.7 m (CF_2 "), 83.0 m (CF). The ratio of the intensities was 2:2:2:1. Infrared spectrum (ν , cm⁻¹): 1725 (C = C).

<u>1-Hydroxyheptafluoro-1-cyclopentene (II)</u>. To. 2.8 g of ether (I) was added 3-4 drops of conc. H_2SO_4 and the reaction mixture was heated, with the simultaneous removal of the volatile products by distillation. We obtained 1.7 g (83.5%) of (II), bp 100-103°. Found: C 28.58; H 0.6; F 64.00%. C₅HF₇O. Calculated: C 28.59; H 0.48; F 63.31%. PMR spectrum: 5.7 s (OH). ¹⁹F NMR spectrum: 36.7 m (CF₂'), 38.5 m (CF₂"), 51.2 m (CF₂"), 84.6 m (CF).

<u>1-Methoxyheptafluoro-1-cyclopentene (III)</u>. To an ether solution of CH_2N_2 (2.1 g of CH_2N_2 in 75 ml of ether) at -10° was added in drops a solution of 2.3 g of (II) in 4 ml of abs. ether, after which the temperature was brought up to ~20° and the mixture was distilled. We obtained 1.0 g (40.8%) of (III), bp 101-104°; cf. [7]. PMR spectrum: 3.9 d (CH₃), $J_{CH_3/CF} = 3.3$ Hz. ¹⁹F NMR spectrum: 52.0 m (CF₂''), 37.2 m (CF₂''), 36.0 m (CF₂'''), 87.8 m (CF). The IR spectrum coincided with the published spectrum [7].

<u>1-Hydroxypentafluoro-1-cyclopenten-3-one (IVa).</u>* With stirring, 3.2 g of (II) was added to 4 ml of water. At the end of exothermic reaction the mixture was cooled to ~20°, extracted with ether, and dried over MgSO₄. The ether was evaporated, and the residue was sublimed at 0.5 mm of Hg to give 1.0 g (35.5%) of (IVa), mp 89-93°. Found: C 31.97, H 0.9; F51.02%. C₃HF₅O₂. Calculated: C 31.95; H 0.53; F 50.53%. PMR spectrum (in CH₃CN): 8.9 s (OH). ¹⁹FNMR spectrum (in CH₃CN): 44.5 d (C F₂', CF₂"), 76.2 quint. (CF), J_{CF₂}'/_C F⁼ J CH₂"/_CF = 8.0 Hz. Infrared spectrum (ν , cm⁻¹): 1675 (C = C), 1765 (C = O).

<u>1-Ethoxypentafluoro-1-cyclopenten-3-one (IVb)</u>. To 3 ml of ethanol was added 2.33 g of (II). At the end of exothermic reaction the mixture was poured into water, and the lower layer was separated, dried over MgSO₄, and distilled to give 0.7 g (27.5%) of (IVb), bp 74-75° (12 mm). Found: C 37.83; H 2.25; F 43.86%. $C_7H_5F_5O_2$. Calculated: C 38.90; H 2.33; F 43.95%. PMR spectrum: 1.11 t (CH₃), 4.34 m (CH₂), $J_{CH_2CH_3} = 6.7$, $J_{CH_2/CF} = 2.0$ Hz. ¹⁹FNMR spectrum: 41.5 m (CF₂'), 46.8 m (CF₂''), 77.4 m (C F). Infrared spectrum (ν , cm⁻¹): 1665 (C = C), 1770 (C = O).

2,2,3,3,4,5-Hexafluoro-4-penten-1-oic acid (V). To a stirred solution of 4.4 g of KOH in 10 ml of water, cooled to 0°, was added 4.1 g of (II), maintaining the temperature at 30-35°. At the end of exothermic reaction the mixture was diluted with 20 ml of water, acidified with conc. HCl, and extracted with ether. The ether extract was dried over MgSO₄ and then distilled to give 2.1 g (51.0% of (V), bp 95-98° (40 mm). The analytical sample was redistilled over a mixture of P₂O₅ and conc. H₂SO₄. Found: C 28.75; H1.13; F 54.13%. C₅H₂F₆O₂. Calculated: C 28.86; H 0.99; F 54.78%. PMR spectrum: 11.6 s (OH), 6.8 dd (CFH), JF/H(gem) = 70.6, JCH/F(vic) = 13.3 Hz. ¹⁹FNMR spectrum: 41.0 m (CF₂', CF₂"), 75.1 d.m (CFH), 78.0 (CF), JF/H(gem) = 72.5,

*The K salt of compound (IVa) was obtained in [8].

JCFH/C F=6.5 Hz. The ratio of the intensities was 4:1:1. Infrared spectrum (ν , cm⁻¹): 1730 (C=C), 1765 (C=O), 3100 (OH).

2-Hydroheptafluorocyclopentanone Oxime (VI). With stirring, 20.1 g of perfluorocyclopentene was added in drops to a solution of 6.3 g of hydroxylamine in 100 ml of abs. ether, maintaining the temperature below 30°. At the end of exothermic reaction the mixture was filtered, and the filtrate was distilled to give 12.3 g of a fraction with bp 42-44° (11 mm). Redistillation over a mixture of conc. H_2SO_4 and P_2O_5 gave 5.0 g of (VI), bp 33° (8 mm). Found; C 26.64; H 0.91; F 59.06%. $C_5H_2F_7ON$. Calculated: C 26.68; H 0.89; F 59.09%. PMR spectrum: 5.4 d.m (CFH), 9.7 br.s (OH), $J_F/H(gem) = 50.6$ Hz.

CONCLUSIONS

1. A method was developed for the synthesis of 1-hydroxyheptafluoro-1-cyclopentene and its properties were studied.

2. 1-Hydro-1, 1, 4, 4, 4-pentafluoro-2-butyne was obtained for the first time by the decarboxylation of the potassium salt of 2, 2, 3, 3, 4, 5-hexafluoro-4-penten-1-oic acid.

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