ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 8, pp. 1640–1642. © Pleiades Publishing, Ltd., 2011. Original Russian Text © A.I. Rakhimov, A.V. Miroshnichenko, Do Duong Phuong Thao, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 8, pp. 1295–1297.

Features of the Reaction of Polyfluoroalkyl Chlorolsulfites with Allyl Alcohol

A. I. Rakhimov, A. V. Miroshnichenko, and Do Duong Phuong Thao

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia e-mail: rakhimov@sprint-v.com.ru

Received July 13, 2010

Abstract—Unlike the saturated aliphatic and aromatic alcohols, allyl alcohol under the same conditions reacts with polyfluoroalkyl chlorosulfites to form not ethers, but polyfluorinated alcohols. The exception is polyfluoroalkyl chlorosulfites with the chain length of more than five carbon atoms. Allyl ethers of polyfluorinated alcohols of general formula $CH_2=CHCH_2OCH_2(CF_2CF_2)_nH$ (n = 1-3) were obtained, when the reaction proceeded in the presence of potassium carbonate, owing to its participation in a specific orientation of the reaction centers in the resulting intermediate structure, which is easily transformed into allyl ethers of polyfluorinated alcohols.

DOI: 10.1134/S107036321108010X

The monohydric saturated and aromatic alcohols react with polyfluoroalkyl chlorosulfites to afford ethers [1-5]. But the attempt to synthesize in these conditions (catalysis with *N*,*N*-dimethylformamide) the

allyl ethers of polyflurinated alcohols failed. The reaction of allyl alcohol with polyfluoroalkyl chlorosulfite gives rise to polyfluorinated alcohol. Perhaps, the hydrolysis of chlorosulfite proceeds as follows:

 $H(CF_2CF_2)_nCH_2OSOC1 + CH_2=CHCH_2OH$



The chlorine atom of chlorosulfite group attacks the methylene carbon atom of allyl fragment with simultaneous nucleophilic substitution of chlorosulfite groups with hydroxy one via the transition state **I**. The substitution is accompanied by the simultaneous release of sulfur dioxide. Allyl ether of the polyfluorinated alcohol is formed as a by-product. In the case of low-molecular chlorosulfite (n = 1) only traces of allyl ether were observed. When the chlorsulfite with n = 3 was used, the ether content increased to 30%. This is probably due to the increasing influence of the steric factor: as the bulk of thrpolyfluoroalkyl

substituent increases, it prevents the complex I formation, leading to the polyfluorinated alcohol.

We studied a possibility to change the reaction direction using potassium carbonate. As expected, its molecule can interact with the polar group of both reagents and orient the reaction centers appropriately to form the structure **II**. The latter transforms readily into the reaction products, the allyl ethers **IIIa–IIIc**.

As a result of the reaction of allyl alcohol with polyfluoroalkyl chlorosulfites in the presence of

$H(CF_2CF_2)_nCH_2OSOCI + CH_2=CHCH_2OH$



n = 1 (IIIa), 2 (IIIb), 3 (IIIc).

potassium carbonate the yield of allyl ethers **IIIa–IIIc** was increased to 40.4–66.2%.

Since the reaction of polyfluoroalkylchlorosulfites with monohydric alcohols (catalysis with DMF) proceeds via two stages (in the first stage at -10 to -5° C a complex is formed, and in the second at 30°C it decomposes to alkylpolyfluoroalkyl ether) [4], the reaction with allyl alcohol was also performed in two stages. Initially the reagents (allyl alcohol, potassium carbonate, and polyfluoroalkyl chlorosulfite) were mixed in chloroform at from -10 to -5° C, and then the reaction mixture was heated to 30°C and kept for 3-5 h. The potassium chloride and potassium hydrogen carbonate precipitates were filtered off. The solvent was removed and the residue was distilled in a vacuum. The resulting allyl ethers were colorless heavy liquids. The synthesized allyl ethers were identified by the IR and ¹H NMR spectroscopy. A characteristic feature of the IR spectra of the ethers is a strong absorption band originating from the stretching vibrations of CH2-O-CH2 bonds [6]. Moreover, the introduction of allyl group has no significant effect on a narrow absorption range (1000–1150 cm⁻¹). In the IR spectra of ethers **IIIa** and **IIIc** the stretching vibrations of C–O–C bond are observed at 1154 and 1163 cm⁻¹, respectively, as strong absorption bands. The absorption band of an isolated double bond usually occurs in the range of 1680–1620 cm^{-1} [6]. For the synthesized ethers IIIa-IIIc the respective absorption band of medium intensity is observed at 1686 cm⁻¹, which is caused by the inductive effect of the electronwithdrawing perfluorinated carbon chain. In the IR spectra of the ether IIIa there is an absorption band at 3023 cm^{-1} , which is shifted to the region of 3040 cm^{-1} (IIIb, IIIc) as the perfluorocarbon chain increases. It belongs to the stretching vibrations of C-H bond in CHF₂-group.

In the ¹H NMR spectra of the obtained allyl ethers **IIIa–IIIc** there are triplet of triplet signals of the protons of HCF₂CF₂ group at 5.8 (**IIIa**, **IIIb**) and 1.6 ppm (**IIIc**) with the spin-spin coupling constants J_{HF} 4.2–5.5 and 51.9–52.5 Hz, which corresponds to the published data [7]. α -Methylene group in H(CF₂CF₂)_nCH₂-fragment appears as a triplet with the spin–spin coupling constant J_{HF} 13.2–14.1 Hz. The spectral analysis of the allyl group in the synthesized ethers **IIIa–IIIc** allows us to identify the corresponding protons.



 δ_A 5.81 ppm (multiplet), δ_{B2} 5.23 ppm (multiplet), δ_{C2} 4.39 ppm (doublet).

The known approach to allyl ethers of polyfluorinated alcohols via the reaction of allyl bromide and iodide with potassium alcoholates [8] is less effective. The disadvantages of this method are low accessibility of allyl iodide (bromide) and the longer reaction time as compared with the synthesis of the ethers by the new method, the reaction of polyalkyl chlorosulfites with allyl alcohol in the presence of potassium carbonate.

EXPERIMENTAL

The ¹H NMR spectra (300 MHz) were taken on a Varian Mercury-300 instrument in CCl₄, internal reference tetramethylsilane. The IR spectra were obtained on a Specord-M82 from a thin layer (liquid film). The fluorine content was determined by the direct potentiometry with a fluoride-selective electrode.

3-(2,2,3,3-Tetrafluoro)propoxy-1-propene (IIIa). In a three-neck reactor equipped with a thermometer, reflux condenser, and a stirrer, was placed a solution of 1.49 g (0.0256 mol) of allyl alcohol in 30 ml of chloroform and 3.54 g (0.0256 mol) of K₂CO₃. To the mixture cooled to -15° C was added a solution of 5.5 g (0.02564 mol) of 1,1,3-trihydroperfluoropropyl chlorosulfite in 10 ml of chloroform. Then the reaction mixture was heated to 30°C and kept under stirring for 3 h. After the removal of the precipitate, solvent and unreacted alcohol, the target product was distilled in a vacuum. Yield 2.92 g (66.2%), bp 95-98°C (15 mm Hg), $n_{\rm D}^{20}$ 1.3660, d_4^{20} 1.4286. IR spectrum, v, cm⁻¹: 520 m. narrow, 666 m, 760 br.m, 749 br.s, 880 s. narrow, 940 s. narrow, 980 s. narrow, 1043 m, 1077 w, 1111 w, 1154 br.s (C–O–C), 1197 br.s (CF₂), 1231 br.s, 1317 m, 1386 w, 1446 s, 1480 m, 1574 br.w, 1686 br.m (C=C), 2886 v.w (CH₂-O), 2920 v.w, 2997 m (CH₂, CH), 3023 br.w (CHF₂), 3134 w.

3-(2,2,3,3,4,4,5,5-Octafluoro)pentoxy-1-propene (IIIb) was obtained similarly to IIIa. Yield 40.4%, bp 98–100°C (15 mm Hg), n_D^{20} 1.3635, d_4^{20} 1.4418. IR spectrum, v, cm⁻¹: 520 m. narrow, 666 m, 760 br.m, 803 br.s, 887 s. narrow, 940 s. narrow, 991 s. narrow, 1043 m, 1069 w, 1112 w, 1163 br.s (C–O–C), 1197 br.s (CF₂), 1249 br.s, 1317 m, 1386 w, 1437 s, 1489 m, 1566 br.w, 1686 br.m (C=C), 2886 v.w (CH₂–O), 2920 v.w, 2989 m (CH₂, CH), 3040 br.w (CHF₂), 3126 w. ¹H NMR spectrum, δ , ppm (*J*, Hz): 5.803 t. t (HCF₂, *J* 51.6, 5.4), 4.285 t (CF₂CH₂, *J* 14.1), 4.46 d (CH₂C=, *J* 26.7), 5.894 m (CH=), 5.296 m (=CH₂). Found F, %: 54.29. C₈H₇F₈O. Calculated F, %: 55.88.

3-(2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoro)heptoxy-1-propene (IIIc) was obtained similarly to **IIIa**. Yield 51.6%, bp 90°C (6 mm Hg), n_D^{20} 1.3560, d_4^{20} 1.4816. IR spectrum, v, cm⁻¹: 520 m. narrow, 614 w, 640 v.w, 700 br.s, 743 br.s, 769 br.s, 811 w, 837 w, 889 s. narrow, 931 s. narrow, 991 s. narrow, 1077 s. narrow, 1086 s. narrow, 1129 w, 1189 br.s (C–O–C), 1240 br.s (CF₂), 1334 w, 1420 w, 1437 m, 1497 m, 1574 br.w, 1644 br.m (C=C), 2886 v.w (CH₂–O), 2929 v.w, 3006 m (CH₂, CH), 3049 br.w (CHF₂), 3143 w. ¹H NMR spectrum, δ , ppm (*J*, Hz): 6.017 t.t (HCF₂, *J* 51.6, 5.1), 3.931 t (CF₂CH₂, *J* 14.1), 4.39 d (CH₂C=, *J* 22.5), 5.814 m (CH=), 5.259 m (=CH₂). Found F, %: 60.77. C₁₀H₇F₁₂O. Calculated F, %: 61.29.

REFERENCES

- 1. Rakhimov, A.I. and Fisechko, R.V., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 10, p. 1750.
- 2. Rakhimov, A.I. and Fisechko, R.V., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 2, p. 338.
- Rakhimov, A.I., Nalesnaya, A.V., and Fisechko, R.V., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 3, p. 523.
- 4. Rakhimov, A.I., Nalesnaya, A.V., and Fisechko, R.V., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 11, p. 1842.
- Rakhimov, A.I., Nalesnaya, A.V., Zauer, E.A., and Fisechko, R.V., *Izv. VolGTU, Ser. Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimernykh materialov*, 2009, iss. 6, no. 2, p. 36.
- Bellami, L., *Infrakrasnye spektry slozhnykh molekul* (IR Spectra of Complex Molecules), Moscow: Inostrannaya Literatura, 1963, 590 p.
- Ionin, B.I. and Ershov, B.A., YaMR-Spektroskopiya v organicheskoi khimii (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1967.
- Rakhimov, A.I., Shurubtsova, E.V., and Storozhakova, N.A., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 2, p. 345.