The Synthesis of Trifluorovinyl Ethers

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The thermolysis of alkali metals perfluoro-2-alkoxytetrafluoropropionates is a common method of preparing perfluoroalkylvinyl ethers, including such important industrial monomers as perfluoromethyl- and propylvinyl ethers, that are obtained in high yields (<90%)[1]. At the same time in the case of 2-alkoxytetrafluoropropionic acids **1** the thermal degradation of their salts **ROCF(CF₃)COOM** (**2**) (R = Me, Et, CF₃CH₂; M = alkali metal cation) leads to the formation of complex mixture of products, containing minute quantities of trifluorovinyl ethers. Thus the thermolysis of **1** (R = CF3CH2; M = Na) afforded ether **3a** in 4% yield [2].

We have shown that ether **3a** can be obtained by thermolysis of salt **2** ($R = CF_3CH_2$; M = K) (**2a**) in 67% yield. Similarly ether **3b** was prepared from **2** (R = Ph; M = K) (**2b**) in 63% yield. The starting acids ROCF(CF_3)COOH (**1**) [$R = CF_3CH_2$ (**1a**); Ph (**1b**)] were obtained by the reaction of the corresponding alcohols with hexafluoropropene oxide (HFPO) and alkali in a system H_2O -ether in the presence of phase-transfer catalyst Bu_4NBr and subsequent acidification of the reaction mixture, that simplified the method of synthesis **1** described earlier [3].

The results obtained confirm the conclusion [2] that chemical behavior of salts 2 under the conditions of thermolysis depends to a considerable extent on the nature of both cation and alkoxy substituent.

 $\begin{array}{c} CF_{3}CF-CF_{2} & \xrightarrow{1. \text{ ROH/KOH/}{3}\varphi.-H_{2}O/[Bu_{4}NBr]} \\ & \searrow \\ O \end{array} \xrightarrow{} ROCF(CF_{3})COOH \xrightarrow{} ROCF(CF_{3})COOH \xrightarrow{} ROCF(CF_{3})COOK \xrightarrow{} \\ & 1 \qquad R = CF_{3}CH_{2}(a) \qquad 2a,b \\ & Ph (b) \end{array}$

 $\square \rightarrow \text{ROCF}=\text{CF}_2$

3a,b

2-(2,2,2-Trifluoroethoxy)tetrafluoropropionic acid 1a

Hexafluoropropene oxide (16,6 g, 0,1 mol) was gradually introduced into the mixture of 19,3g (0,19 mol) trifluoroethanol, 19g (0,34 mol) KOH, 40 ml of H_2O , 50 ml of ether and 1,5g of Bu_4NBr at <30°C, then the mixture was stirred 1h at room temperature, acidified

with 30% hydrochloric acid, ethereal layer was separated, dried with MgSO₄ and distilled to give a fraction with b.p. 82-92°C/35 Torr. The following rectification afforded 16g (68% based on HFPO taken into reaction) of **1a**, b.p. 61-63°C/10 Torr. (lit. data: b.p. 125-127°C [2]). NMR ¹⁹F spectrum (δ , p.p.m.): -3.3 (3F¹); 4.0 (3F³); 54,5 (1F²).

1 2 3 CF₃CH₂OCF(CF₃)COOH

2-Phenoxytetrafluoropropionic acid 1b

was obtained similarly from HFPO and phenol in 40% yield, b.p. 93-98°C/3 Torr; NMR ¹⁹F spectrum (δ ,p.p.m.): 5,2 (3F); 42,5 (1F). The acid was transformed into its K-salt**2b** without further purification.

2,2,2-Trifluoroethyltrifluorovinyl ether 3a.

A solution of 16g (0,065 mol) **1a** in MeOH was neutralized with solution of KOH in MeOH (phenolphthalein as indicator), evaporated under reduced pressure, the residue was dried over P_2O_5 at 110°C/2-3 Torr., then pulverized, mixed with 20g of dry sand and subjected to thermolysis at 10-15 Torr by heating in the flame of Bunsen burner (or in Wood alloy bath at 225-280°C). The volatile products were collected in a trap (-78°C), the condensate was distilled to give 8.5g (67%) of ether **3a**, b.p. 41-44°C (b.p. and NMR ¹⁹F spectrum were identical to that described in [2,4]).

Phenyltrifluorovinyl ether 3b.

A mixture of 10.4g (0.037 mol) salt **2b** (dried over P_2O_5 at 110-115°C/3 Torr.) and 13g of dry sand was subjected to thermolysis under vacuum of oil pump, collecting the volatile products in a trap (-78°C). The condensate was distilled to give 5.9g (63%) of ether **3b**, b.p. 132-134°C (b.p. and NMR ¹⁹F spectrum were identical to that described in [5,6]).

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