The Synthesis of Trifluorovinyl Ethers

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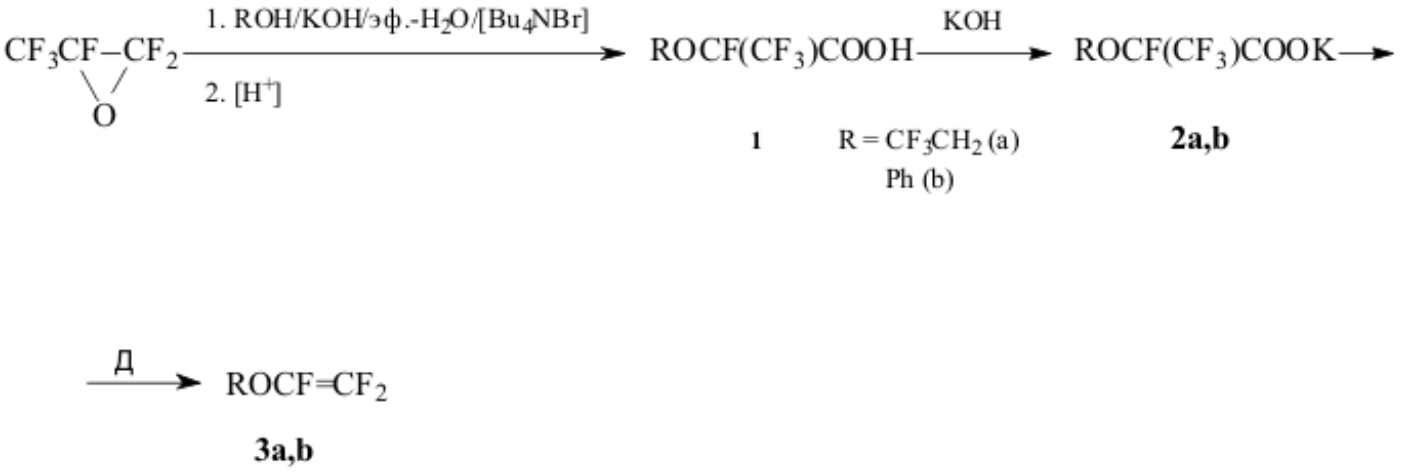
The thermolysis of alkali metals perfluoro-2-alkoxytetrafluoropropionates is a common method of preparing perfluoroalkylvinyl ethers, including such important industrial monomers as perfluoromethyl- and propylvinyl ethers, that are obtained in high yields (<90%)[1]. At the same time in the case of 2-alkoxytetrafluoropropionic acids **1** the thermal degradation of their salts **ROCF(CF_3)COOM** (**2**) (R = Me, Et, CF_3CH_2; 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.



1 R = CF_3CH_2 (a), Ph (b) **2a,b** **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 $MgSO_4$ 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 ^{19}F spectrum (δ, p.p.m.): -3.3 ($3F^1$); 4.0 ($3F^3$); 54,5 ($1F^2$).

$\overset{1}{CF_3}\overset{}{CH_2}O\overset{2}{CF}(\overset{3}{CF_3})COOH$

2-Phenoxytetrafluoropropionic acid 1b
was obtained similarly from HFPO and phenol in 40% yield, b.p. 93-98^{o}C/3 Torr; NMR ^{19}F 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^{o}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^{o}C). The volatile products were collected in a trap (-78^{o}C), the condensate was distilled to give 8.5g (67%) of ether **3a**, b.p. 41-44^{o}C (b.p. and NMR ^{19}F 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^{o}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^{o}C). The condensate was distilled to give 5.9g (63%) of ether **3b**, b.p. 132-134^{o}C (b.p. and NMR ^{19}F spectrum were identical to that described in [5,6]).

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References

1. P.R.Resnick, US Pat. 3692843 (1972)
2. M.Y.Pellerite, J.Fluor/Chem., 49 (1990), 43
3. D.Sianesi, A.Pasetti, F.Tarii, J.Org.Chem., 31 (1966), 2312
4. M.-H. Hang, S.Rozen, UA Pat. 5350497 (1994)
5. J.Plummer, L.A.Wall, Trans., 3 (1963), 220
6. A.E.Feiring, S.Rozen, E.R.Wonchoba, J.Fluor.Chem., 89 (1998), 31

Journal contents