Journal of Fluorine Chemistry, 17 (1981) 441–445
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands

Received August 19, 1980

Alkylating Properties of Fluorine-Containing Vinylic Ethers

V.F. SNEGIREV, K.N. MAKAROV and I.L. KNUNYANTS

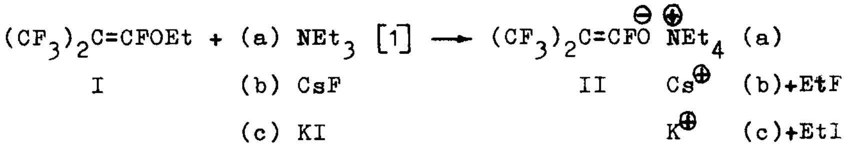
Institute of Organoelement Compounds, the U.S.S.R. Academy
of Sciences, Vavilova St., 28, Moscow 117312 (U.S.S.R.)

SUMMARY

Some fluorine-containing vinylic ethers show alkylating properties not only to organic (triethylamine), but also to inorganic nucleophylic agents (CsF, KJ) in polar aprotic solvents (diglyme, acetonitrile) yielding the corresponding enolates.

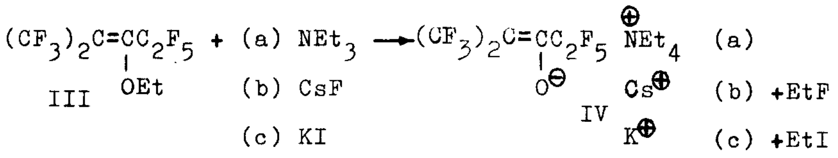
INTRODUCTION

Some fluorine-containing vinylic ethers, e.g. alkyl perfluoroisobutenyl ethers of type I, are known to be efficient alkylating agents. Interaction with tertiary amines involves the breakdown of O-alkyl bond and the formation of tetraalkyl ammonium perfluoro-2-methyl-1-propenol-1-ates (IIa) [1]. We found that vinylic ethers I are also subject to breakdown under the action of inorganic nucleophilic agents (CsF, KI) in polar aprotic solvents (diglyme, acetonitrile) with the formation of cesium and potassium perfluoro-2-methyl-1-propenol-1-ates (IIb,c) and corresponding halogen alkyls:



$$\begin{array}{lllll}
(CF_3)_2C{=}CFOEt\ + & (a)\ NEt_3\ [1] & \longrightarrow (CF_3)_2C{=}CF\overset{\ominus}{O} & \overset{\oplus}{N}Et_4 & (a) \\
\quad\mathrm{I} & (b)\ CsF & \qquad\qquad\mathrm{II} & Cs^{\oplus} & (b) + EtF \\
 & (c)\ KI & & K^{\oplus} & (c) + EtI
\end{array}$$

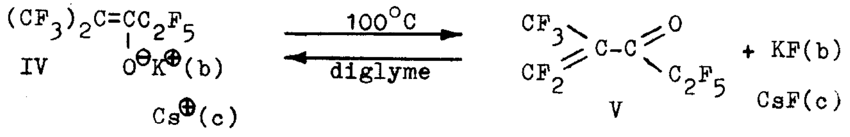
It was disclosed that vinylic ethers of type III also can take part in similar reactions. The ethers are derivatives of perfluoro-2-methyl-2-pentene (hexafluoropropene dimer) and are structurally analogous with ethers of type I.



$$\underset{III}{(CF_3)_2C{=}\underset{\displaystyle OEt}{C}C_2F_5} + \begin{matrix}(a)\ NEt_3\\(b)\ CsF\\(c)\ KI\end{matrix} \longrightarrow \underset{IV}{(CF_3)_2C{=}\underset{\displaystyle O^{\ominus}}{C}C_2F_5} \begin{matrix}\overset{\oplus}{N}Et_4 & (a)\\ Cs^{\oplus} & (b)\ +EtF\\ K^{\oplus} & (c)\ +EtI\end{matrix}$$

It was of interest to study the comparative alkylating ability of ethers of types I and III with respect to different nucleophilic agents. Breakdown of O-alkyl bond during interaction between equimolar amounts of ethers I and III and a nucleophilic agent (NEt_3, KI, CsF) was found to occur in all cases more easily in ethers I than in ethers III. These results demonstrate that in reactions of nucleophilic substitution, perfluoro-2-methyl-1-propenol-1-ate (II) is a better leaving group than perfluoro-2-methyl-2-pentenol-3-ate (IV).

The properties of obtained salts II and IV are strongly dependent on the nature of cation. Thus, tetraalkylammonium salt IVa* is a distillable liquid while potassium and cesium enolates (IIb,c and IVb,c) are crystalline substances easily soluble in polar solvents. Attempts to obtain analytical grade potassium and cesium enolates (IVb,c) failed. At a careful withdrawal of solvent in vacuum at 25°C, yellowish crystals are formed containing 2-3 solvent molecules per molecule of enolate IVb,c. At temperature growing to 60-70°C, enolates IV b,c start melting with decomposition giving rise to perfluoro-2-methyl-1-pentenone-3 (V) and potassium or cesium fluoride:



Decomposition of 'dry' enolates IVb,c is of reversible character. Interaction between α,β-unsaturated perfluoro ketone V and cesium and potassium fluorides in polar solvents readily furnishes starting enolates IVb,c.

---

*Recently [2] triethylammonium perfluoro-2-methyl-2-pentenol-3-ate (vacuum distillable liquid) has been synthesised in a reaction between perfluoro-2-methyl-2-pentene and water in the presence of triethylamine.

It has been shown recently [3] that cesium perfluoro-2-methyl-1-propenol-1-ate can be obtained in a similar manner, i.e. by treating bis-(trifluoromethyl)ketene with cesium fluoride in diglyme.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer at 84,6 MHz. CF_3COOH was used as external standard. IR spectra were obtained on a UR-20 spectrometer.

I. Interaction between ethers I and III and CsF

A flask with stirrer and reflux condenser joined to a trap (-78°C) was loaded with 15 ml of diglyme, 3.5 g (0.02 M) of freshly calcined CsF, and 4.5 g (0.02 M) of ether I. The mixture was continuously agitated and kept at 100°C for 8 hrs. The liquid collected in the trap was identical with ethyl fluoride according to ^{19}F and ^{1}H NMR data. The remaining portion of the reaction mixture was diglyme solution of cesium perfluoro-2-methyl-1-propenol-1-ate (IIb). IR spectrum: 1720 cm^{-1}. ^{19}F NMR spectrum: -29.0 (CF_3, d.q.); -27.7 (CF_3, d.q.); -79.0 (CF, q.q.). The ^{19}F spectrum coincides with that described earlier [3] .

Similarly, a diglyme solution of cesium perfluoro-2-methyl-2-pentenol-3-ate (IVb) was obtained from 6.5 g (0.02 M) of ether III [4] . IR spectrum: 1590 cm^{-1} (C=C). ^{19}F NMR spectrum: -26.0 (CF_3, q.t.); -21.2 (CF_3, q.); 5.6 (CF_3, s.); 41.2 (CF_2, q.).

II. Interaction between ethers I and III and KI

Mixture of 15 ml of diglyme, 3.5 g (0.02 M) of KI, and 4.5 g (0.02 M) of ether I was continuously agitated at 70°C for 4 hrs. Then the mixture was evacuated (25 mm Hg) at 20°C; condensate in the trap (-78°C) was, according to GLC and ^{1}H NMR data, identical with ethyl iodide. The remaining portion of the reaction mixture was, as ^{19}F NMR data showed, a diglyme solution of potassium perfluoro-2-methyl-1-propenol-1-ate (IIc).

Similarly, a diglym solution of potassium perfluoro-2-methyl-2-pentenol-3-ate (IVc) was obtained from 6.5 g (0.02 M) of ether III [4] .

^{19}F NMR spectra of diglyme solutions of potassium enolates (IIc, IVc) are completely identical with the spectra of solutions of cesium enolates (IIb, IVb).

III. Decomposition of potassium perfluoro-2-methyl-2-pentenol-3-ate (IVc). Synthesis of perfluoro-2-methyl-1-pentenone-3 (V)

The solvent was withdrawn from diglyme solution of potassium perfluoro-2-methyl-2-pentenol-3-ate (IVc) obtained from 6.5 g (0.02 M) of ether III in accordance with the technique described above (Section II), by evacuation (25 mm Hg) at 70°C. The residue obtained was heated in vacuum (10 mm Hg) at 150°C; decomposition products were collected in a trap (-78°C). There were obtained 3.4 g (61%) of perfluoro-2-methyl-1-pentenone-3 (V), b.p. 60-62°C. ^{19}F NMR spectra (36°C)*: -18.0 (CF_3, m.); -16.3 (CF_2, m.); 6.0 (CF_3, s.); 45.0 (CF_2, d.m.). Analisis: C, 26.31; F, 67.96%. $C_6F_{10}O$ requires C, 25.90; F, 68.75%.

IV. Synthesis of tetraethylammonium perfluoro-2-methyl-2-pentenolate (IVa)

Mixture of 6.5 g (0.02 M) of ether III [4] , 2 g (0.02 M) of triethylamine, and 15 ml of acetonitrile was refluxed for 8 hrs. After distilling off the solvent, obtained 7 g (82%) of tetraethylammonium perfluoro-2-methyl-2-pentenolate (IVa), b.p. 66°C/14 mm Hg. IR spectrum: 1580 cm^{-1} (C=C). ^{19}F NMR spectrum is absolutely identical with spectra of IVb,c. Analysis: C,39.08; H, 4.50; F, 49.13%. $C_{11}H_{20}F_{11}N$ requires C, 39.84; H, 4,68; F, 48.95%.

---

*The ^{19}F NMR spectrum is strongly temperature-dependent.

V. Combined reaction of ethers I and II with nucleophilic agents

a) With triethylamine

Mixture of 4.5 g (0.02 M) of ether I, 6.5 g (0,02 M) of ether III, and 2 g (0.02 M) of triethylamine was left for 20 hrs. The mixture consisted of two layers. Lower layer, according to ^{19}F NMR data, was a mixture of ethers I and III in a 1:3 ratio; upper layer was a mixture of corresponding tetraethylammonium enolates IIa and IVa in an inverse proportion.

b) With KI

Mixture of 4.5 g (0.02 M) of ether I, 6.5 g (0.02 M) of ether III, 2.4 g (0.02 M) of KI, and 15 ml of diglyme was continuously stirred at 70°C for 4 hrs. According to ^{19}F NMR data, the solution contained a mixture of starting ethers in 1:20 ratio and corresponding potassium enolates.

c) With CsF

Mixture of 4.5 g (0.02 M) of ether I, 6.5 g (0.02 M) of ether III, 3.0 g (0.02 M) of CsF, and 15 ml of diglyme was continuously stirred at 100°C for 2 hrs. ^{19}F NMR data showed that the solution contained the mixture of ether I with corresponding cesium enolate (IVb) in 4:1 ratio and unchanged ether III.

REFERENCES

1 I.L. Knunyants, E.M. Rokhlin and Yu.A. Cheburkov, **Zhn.** VKhO im. **Mendeleeva**, 15, (1), 15 (1970).

2 T.Martini and C. Schumann, J.Fluor.Chem., 8, 535 (1976).

3 L.L. Gervits, L.A. Rozov, N.S. Mirzabekyants, K.N. Makarov, Yu.V. Zeifman, Yu.A. Cheburkov and I.L. Knunyants, Izv. Akad. Nauk S.S.S.R., Ser.Khim., 1976,(7), 1676.

4 N. Ishikawa, A. Nagashima, Bull. Chem. Soc. Japan, 49, (2), 502 (1976).