Journal of Fluorine Chemistry, *29* (1985) 349–354

Received: December 31, 1984; accepted: February 12, 1985

REACTION OF ALKYL 2-CHLORO-1,1,2-TRIFLUOROETHYL ETHERS WITH LEWIS ACIDS

MILOS HUDLICKY

Department of Chemistry, Virginia Polytechnic Institute and State
University, Blacksburg, Virginia 24061 (U.S.A.)

SUMMARY

Ethyl 2-chloro-1,1,2-trifluoroethyl ether heated with boron trifluoride etherate gave ethyl fluoride and chlorofluoroacetyl fluoride. When heated with aluminum chloride, it afforded a mixture of ethyl fluoride, ethyl chloride, chlorofluoroacetyl fluoride, and chlorofluoroacetyl chloride. Treatment of the acyl halides with ethanol yielded ethyl chlorofluoroacetate. Butyl and octyl 2-chloro-1,1,2-trifluoroethyl ethers gave directly butyl and octyl chlorofluoroacetates, respectively, under similar conditions.

INTRODUCTION

Treatment of perfluoroalkyl ethers with aluminum chloride at 175°-220° results in a cleavage of the ether bond with simultaneous partial replacement of fluorine by chlorine. Perfluorotetrahydropyran was thus converted to 5,5,5-trichlorohexafluoropentanoyl chloride, and perfluorodibutyl ether to a mixture of 1,1,1-trichloroheptafluorobutane and heptafluorobutyryl chloride [1].

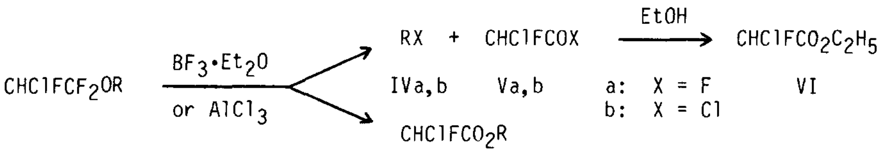
In 1970, this author attempted to apply the above cleavage to alkyl 2-chloro-1,1,2-trifluoroethyl ether, expecting that such a reaction could give an alkyl halide and an acyl halide which could be converted easily to esters of chlorofluoroacetic acid. Such a reaction, using only catalytic amounts of a Lewis acid, might be an alternative to the conversion of alkyl chlorotrifluoroethyl ethers to alkyl chlorofluoroacetates by means of a large excess of sulfuric acid [2,3]. The expected cleavage did occur, but the yields of the esters were lower than those obtained previously with sulfuric acid [2,3].

0022-1139/85/$3.30

Recently, D. C. England described cleavage of fluoroalkyl methyl and ethyl ethers to alkyl fluorides and fluorinated carbonyl compounds [4]. His paper prompted the publication of this author's results, some of which were independently obtained in England's laboratory [5].

RESULTS

Ethyl, butyl, octyl, and phenyl 2-chloro-1,1,2-trifluoroethyl ethers were heated at 100° with 0.25-0.5 mol of boron trifluoride etherate or with 0.09-0.35 mol of anhydrous aluminum chloride. While the phenyl ether did not react and was recovered unchanged, the three aliphatic ethers reacted according to the following scheme:



I R = C_2H_5

II R = C_4H_9

III R = C_8H_{17}

VII R = C_4H_9

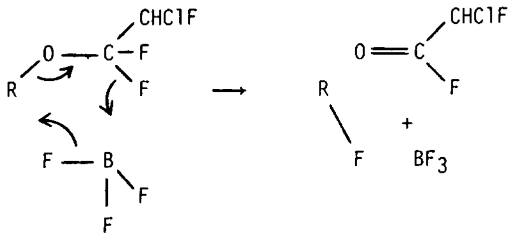
VIII R = C_8H_{17}

Ethyl 2-chloro-1,1,2-trifluoroethyl ether (I) and boron trifluoride etherate gave ethyl fluoride (IVa; R = Et) and chlorofluoroacetyl fluoride (Va) which on mixing with ethanol gave ethyl chlorofluoroacetate (VI). With aluminum chloride, the reaction yielded a mixture containing (IVa,b; R = Et), (Va) and (Vb). The two latter compounds were converted to (VI) by ethanol.

When butyl 2-chloro-1,1,2-trifluoroethyl ether (II) was treated with aluminum chloride under similar conditions, the cleavage to alkyl and acyl halides occurred only partially, resulting in the formation of butyl chlorofluoroacetate (VII) as the main product. Analogously, the octyl ether (III) afforded octyl chlorofluoroacetate (VIII). The oxygen necessary for such a conversion evidently came from the glass equipment, as a considerable loss of glass from the reaction flasks was noticed.

The mechanism of the conversion of alkyl fluoroalkyl ethers to alkyl fluorides and acyl fluorides has been discussed in England's paper [4].

The formation of alkyl halides may result from an ionic cleavage via an alkyl carbonium ion, or from a concerted process via a six-membered transition state:



The cleavage of butyl 2-chloro-1,1,2-trifluoroethyl ether (II) gave, in addition to butyl chlorofluoroacetate and chlorofluoroacetyl chloride and fluoride, a complex mixture containing 6.4% of 1-butene, 47.0% of trans-2-butene, 10.7% of 1-fluorobutane, 3.4% of 2-fluorobutane, 2.6% of 1-chlorobutane, 25.6% of 2-chlorobutane, and 1.1% of chlorofluoroacetyl chloride. Concerted cleavage would give normal butyl fluoride and chloride, whereas the ionic cleavage would yield, in addition to normal alkyl halides, products of a reaction of a carbonium intermediate: rearranged alkyl halides (sec-butyl halides) and/ or alkenes. The presence of large quantities of 2-chlorobutane, and of 2-butene which could be formed only from a secondary (rearranged) carbonium ion, indicates that the ionic mechanism is more likely. (Conversion of primary halides to secondary halides under the conditions used is relatively slow, as proved by a parallel experiment with 1-chlorobutane and aluminum chloride.)

EXPERIMENTAL

Refractive indices were measured on a Bausch and Lomb Abbe refractometer. Gas-liquid chromatography was carried out on a Gow Mac chromatograph series 150 with a thermal conductivity detector, columns of Carbowax 20M and DC 200, and helium as a carrier gas at a flow rate of approximately 100 mL/min. ^1H and ^{19}F NMR spectra were taken on a Varian EM 390 Spectrometer at 90 MHz and 84.6 MHz, respectively, using TMS, fluorotrichloromethane (F11) and hexafluorobenzene (HBF) as internal standards in carbon tetrachloride solutions. Fluorine chemical shifts are given in ppm from F11, negative upfield. ^1H NMR was also taken on a Bruker WP 270 SY Spectrometer at 270 MHz.

Chemicals

Reagent grade chemicals were used in the reactions and in the syntheses of the starting materials. Alkyl 2-chloro-1,1,2-trifluoroethyl ethers were prepared according to the literature [2,3,6].

Ethyl 2-Chloro-1,1,2-trifluoroethyl Ether (I)

^{1}H NMR: CH_3, 1.40 (t); CH_2, 4.05 (q); CHClF, 6.00 (dt). J_{HFgem} = 49 Hz; J_{HFvic} = 4 Hz.

Butyl 2-Chloro-1,1,2-trifluoroethyl Ether (II)

B.p. 128-129°; n_D^{25} 1.3670. Lit: b.p. 124.5°/630 mm; n_D^{20} 1.36796 [6]. ^{1}H NMR: CH_3, 0.98 (t); CH_2CH_2, 1.12-1.82 (m); CH_2O, 3.96 (t); CHClF, 5.97 (dt); J_{HFgem} = 48 Hz; J_{HFvic} = 4 Hz. ^{19}F NMR: CF_2, -88.0 (m); CHClF, -153.4 (dt), J_{HFgem} = 48 Hz, J_{HFvic} = 4 Hz.

Octyl 2-Chloro-1,1,2-trifluoroethyl Ether (III)(nc)

B.p. 198-200°, 109-111°/23 mm. Purity up to 95% according to gas-liquid chromatography; the product could not be separated entirely from octanol, b.p. 196°. ^{1}H NMR: CH_3, 0.90 (t); $(CH_2)_6$, 1.33 (broad m); CH_2O, 3.98 (t); CHClF 6.03 (dt); J_{HFgem} = 49 Hz; J_{HFvic} = 4 Hz. ^{19}F NMR: CF_2, -88.8 (m); CHClF, -153.6 (dt); J_{HFgem} = 49 Hz; J_{HFvic} = 4 Hz.

Reaction of Ethyl 2-Chloro-1,1,2-trifluoroethyl Ether with Boron Trifluoride Etherate

In a 50 mL flask surmounted by a reflux condenser connected to a dry ice trap, 16.2 g (0.1 mol) of ethyl 2-chloro-1,1,2-trifluoroethyl ether (I) was heated on a steam bath with 7.0 g (0.05 mol) of boron trifluoride etherate for 16 h and 45 min. The contents of the dry ice trap (6.6 g of a fuming liquid) was distilled trap-to-trap at room temperature through a solution of 3N sodium hydroxide (20 mL) giving 2.1 g (0.044 mol, 43.8%) of ethyl fluoride (IVa, R = Et), and 3.4 g of a residue. NMR spectrum of ethyl fluoride in carbon tetrachloride: ^{1}H: CH_3, 1.35 (dt); J_{HFvic} = 25 Hz; J_{HH} = 7 Hz; CH_2, 4.45 (dq); J_{HFgem} = 47 Hz; J_{HH} = 7 Hz. ^{19}F NMR: -211.9 (m). Lit. -213 [7].

Distillation of the contents of the reaction flask (14.2 g) afforded 3.3 g of chlorofluoroacetyl fluoride (Va) distilling at 34-44°, 1.2 g of an intermediate fraction, and 7.4 g of crude boron trifluoride etherate which on redistillation gave 5.5 g (78.5%) of pure recovered boron trifluoride etherate, b.p. 118-123°.

Distillation of the dry ice trap residue (3.4 g) and the intermediate fraction (1.2 g) yielded 1.9 g of additional chlorofluoroacetyl fluoride (total yield, 5.2 g, 45.4%), b.p. 34-44° (lit. b.p. 49-50° [8]). Treatment of chlorofluoroacetyl fluoride with 6 mL of ethanol gave 5.1 g (80%) of crude and 3.0 g (47%, 21.4% overall) of distilled ethyl chlorofluoroacetate (VI). b.p. 123-128°, $n_D^{22.5}$ 1.3924. Lit. b.p. 128°, n_D^{25} 1.3927 [3]. ^{1}H NMR: CH_3, 1.37 (t); CH_2, 4.38 (q); CHClF, 6.28 (d); J_{HFgem} = 51 Hz. ^{19}F NMR: -147.2 (d); J_{HFgem} = 51 Hz.

Reaction of Ethyl 2-Chloro-1,2,2-trifluoroethyl Ether with Aluminum Chloride

Heating of 27.5 g (0.17 mol) of ethyl 2-chloro-1,1,2-trifluoroethyl ether (I) with 2 g (0.015 mol) of anhydrous aluminum chloride on a steam bath for 1 h and 35 min and work up similar to that of the previous experiment gave a mixture of 4.3 g of ethyl fluoride and chloride (IVa,b; R = Et), 11.2 g (57.5%) of crude chlorofluoroacetyl fluoride (Va), distilling at 39-69°, and 3.8 g (17%) of crude chlorofluoroacetyl chloride (Vb), distilling at 69-86° (lit. b.p. 69.5° [2]). Treatment of both acyl halides with ethanol afforded 11.6 g (48.5%) of crude ethyl chlorofluoroacetate.

Reaction of Butyl 2-chloro-1,1,2-trifluoroethyl Ether with Aluminum Chloride

To 19.06 g (0.1 mol) of butyl 2-chloro-1,1,2-trifluoroethyl ether (II) was added 4.0 g (0.03 mol) of anhydrous aluminum chloride. The mixture was stirred magnetically and heated at 100° under a reflux condenser connected to a dry ice trap. After 1 h, 14.5% of the ether reacted; after 3.75 h, 48%; after 8.25 h, all of the ether reacted.

The condensate in the dry ice trap (3.45 g) consisted, according to ^{1}H and ^{19}F NMR, of the following compounds (in mol %): 1-butene (3.9%); ^{1}H NMR: CH_3, 1.03 (t); CH_2CH_2, 1.73 (m); $=CHC\underline{H}_2$, 2.05 (m); $=C\underline{H}CH_2$, 5.83 (m); $=CH_2$, cis 4.90 (d), J = 11.5 Hz; $=CH_2$, trans 4.95 (d); J = 18 Hz; trans-2-butene (28.9%); ^{1}H NMR: CH_3, 1.60 (m); =CH, 5.40 (m); 1-fluorobutane (4.9%); ^{1}H NMR: CH_3, 0.96 (t); CH_2CH_2, 1.73 (m); CH_2F, 4.43 (dt); J_{HFgem} = 49 Hz; J_{HH} = 6.5 Hz; ^{19}F NMR: -219 (heptet) (lit. -218.6 [9]); 2-fluorobutane (1.6%); ^{19}F NMR: -174.7 (m) (lit. -173.2 [9]); 1-chlorobutane (1%); ^{1}H NMR: CH_2Cl, 3.51 (t); 2-chlorobutane (9.6%); ^{1}H NMR: CH_3CH_2, 1.03 (t); CH_2, 1.50 (d); CH_3CHCl hidden in a multiplet at 1.73; CHCl, 3.94 (sextet); and chlorofluoroacetyl chloride (1.1%); ^{1}H NMR: 6.30 (d), J_{HFgem} = 50 Hz; ^{19}F NMR: -147.8; J_{HFgem} = 50. ^{1}H NMR of authentic 2-chlorobutane: 0.98 (t), 1.48 (d), 1.72 (q), and 3.80 (sextet).

A semi-solid, dark brown-violet residue consisted, according to the NMR spectrum, of approximately equal parts of chlorofluoroacetyl chloride and butyl chlorofluoroacetate. Treatment of the residue with water, followed by extraction with ether, afforded 6.89 g of the crude ester which on distillation yielded 5.14 g (30.5%) of pure VII, distilling at 158-163° at 740 mm; n_D^{25} 1.4077. Lit. b.p. 165-166°; n_D^{25} 1.4067 [2]. ^{1}H NMR: CH_3, 0.99 (t); CH_2CH_2, 1.22-1.90 (m), CH_2O, 4.31 (t); CHClF, 6.30 (d); J_{HFgem} = 51 Hz. ^{19}F NMR: -147.0 (d); $J_{HF\ gem}$ = 51 Hz. NMR of authentic VII prepared by hydrolysis of (II) with sulfuric acid: ^{1}H NMR: CH_3, 0.99 (t); CH_2CH_2, 1.14-1.97 (m), CH_2O, 4.31 (t); CHClF, 6.31 (d); J_{HFgem} = 51 Hz. ^{19}F NMR: -147.1 (d).

Loss of 1.01 g of glass from the reaction flask may account for the surprising formation of the ester (VII). The reaction of hydrogen fluoride with glass evidently provided enough water necessary for the conversion of the CF_2O to the CO_2 group.

Reaction of Octyl 2-chloro-1,2,2-trifluoroethyl Ether with Boron Fluoride Etherate

Heating of 2.5 g of 82% pure octyl 2-chloro-1,1,2-trifluoroethyl ether (0.0083 mol) with 0.50 g (0.0035 mol) of boron trifluoride etherate at 100° for 3 h, steam distillation, extraction of the steam distillate, and distillation of the ether extract gave 0.72 g of octyl chlorofluoroacetate, containing, according to gas-liquid chromatography, 0.66 g of the pure compound. Yield 35.5%, based on pure octyl chlorotrifluoroethyl ether. ^{1}H NMR: CH_3, 0.90 (t), $(CH_2)_6$, 1.33 (m), CH_2O, 4.28 (t); J = 6 Hz; CHClF, 6.24 (d); J = 52 Hz. ^{19}F NMR: CHClF, -146.8 (d).

REFERENCES

1 G. V. D. Tiers, J. Am. Chem. Soc., 77, (1955) 4837, 6703, 6704.

2 J. A. Young and P. Tarrant, J. Am. Chem. Soc., 71, (1949) 2432.

3 B. Englund, Org. Syn., 34, (1954) 49; Coll. Vol. 4 (1963) 184, 423.

4 D. C. England, J. Org. Chem., 49 (1984) 4007.

5 D. C. England, private communication.

6 J. D. Park, D. K. Vail, K. R. Lea, J. R. Lacher, J. Am. Chem. Soc., 70, (1948) 1550.

7 D. D. Elleman, L. C. Brown, D. Williams, J. Mol. Spect., 7 (1961) 307.

8 H. Kitano and K. Fukui, J. Chem. Soc. Jpn., 58, (1955) 453.

9 F. J. Weigert, J. Org. Chem., 45 (1980) 3476.