Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Short Communication

Formation of α,α,α′,α′-tetrafluorodiethylethers in the reaction of sulphur tetrafluoride with monocarboxylic acids

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(Received April 24, 1972)

The reactions of sulphur tetrafluoride with different types of carboxylic acids lead to the transformation of carboxyl groups into trifluoromethyl groups[1]. With dicarboxylic acids the formation of cyclic α,α,α′,α′-tetrafluoroethers in addition to mono- and bis-trifluoromethyl derivatives has been reported[1,2].

We have now found that formation of linear α,α,α′α′-tetrafluoroethers (IV) as the side-products in the reactions of aliphatic monocarboxylic acids with sulphur tetrafluoride is rather common. This communication describes investigations of the conditions of the reactions in which tetrafluoroethers (IV) were formed from acetic and chloroacetic acids.

$$\underset{\text{(I)}}{\mathrm{RCOOH}} \xrightarrow{\mathrm{SF_4}} \underset{\text{(II)}}{\mathrm{RCOF}} \xrightarrow{\mathrm{SF_4}} \underset{\text{(III)}}{\mathrm{RCF_3}} + \underset{\text{(IV)}}{\mathrm{RCF_2OCF_2R}}$$

Results are summarized in Table 1.

TABLE 1

REACTION CONDITIONS FOR THE FORMATION OF TETRAFLUOROETHERS

Acid RCOOH	Reaction conditions[a]		Yield of products[b] (%)	
R	Temperature[c] (°C)	Time (h)	RCF_3	RCF_2OCF_2R
CH_3	60	3	85	—
	—10	48	28	16
CH_2Cl	65	3	51	24
$CHCl_2$	60	3	58	14
CCl_3	60	3	d	
	110	6	d	

[a] 2.4 Mole SF_4/mole of the acid were used. Experiments were done in 0.3–1.0 mole scale.
[b] GLC yield based on the starting acid.
[c] Temperature ±5°.
[d] Trichloroacetyl fluoride was obtained in quantitative yield. No other products were detected.

The following reaction conditions were chosen as the standard for comparing the reactivities of the acids: temperature 60°, time 3 h and reactant ratio

2.4 mole SF_4/mole of the acid. Under these conditions appreciable yields of tetrafluoroethers (IV) were obtained from mono-and di-chloroacetic acids.

Reaction temperatures and times were varied in order to obtain suitable yields of (IV) from other acids. Acyl fluorides (II) are formed readily at or below room temperature[1] and their formation was quantitative with each of the acids investigated. Consequently, under the reaction conditions used, the reactivities of the acids (or more strictly, of the acyl fluorides) manifest themselves during the later stages of the reaction. Acetyl fluoride was the most reactive, its conversion under standard conditions being the greatest, a conversion of *ca.* 80% being attained even at room temperature. Trichloracetyl fluoride was the least reactive and failed to react even under conditions much more drastic than those of the standard*. The reactivities of mono- and di-chloroacetyl fluorides were intermediate and fairly high, as evaluated from their conversions.

The yields of 1,1,1-trifluoroethanes (III) depend on the reaction conditions and on the amounts of tetrafluoroethers formed simultaneously. Under standard conditions, the yield of 1,1,1-trifluoroethane from acetic acid was very high and the yields of chlorotrifluoroethanes (III) from chloroacetic acids not so high on account of the considerable amounts of ethers (IV) formed. Trifluoroethanes (III) were identified from their physical constants (boiling point, refractive index and density) as compared with literature data[3,4] and by their IR, NMR, and mass spectra.

The yields of tetrafluoroethers (IV) depend on their stabilities under the reaction conditions. The β-chlorinated ethers are stable in the reaction mixture and yields up to 25% were obtained even at elevated temperatures. The unsubstituted tetrafluoroether $(CH_3CF_2)_2O$ (V) is less stable in the reaction medium. It could be obtained in appreciable yield only when the reaction was continued for a long period of time below room temperature. Above room temperature, (V) is dissociated in the reaction mixture into fragments which are further fluorinated to 1,1,1-trifluoroethane, as only this compound and acetyl fluoride were found in the reaction product obtained from acetic acid under standard conditions. Pure ethers (IV) are colourless liquids, stable at temperatures up to 300°.

The structures of $\alpha,\alpha,\alpha',\alpha'$-tetrafluoroethers were determined by elemental analysis, molecular weight determination and spectroscopic investigation. IR spectra exhibited neither OH nor C=O absorption bands. A group of strong bands between 1080–1350 cm^{-1} was ascribed to C–F and C–O–C vibrations. NMR spectra were comprised of complex symmetrical signals: one corresponding to protons and the other to fluorine nuclei. These conformed to the expected spectra provided that rapid rotation occurs around all the bonds and that chemical equivalence and magnetic non-equivalence of nuclei exists within each group of

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* The lack of reactivity is due to electronic rather than steric effects, since the same behaviour was observed with the less crowded trifluoroacetic acid.

nuclei. Mass spectra showed no molecular peaks or molecular peaks of very low intensity. The most abundant peaks observed corresponded to [$M^+ - R$] and [RCF_2^+].

Studies on the scope and mechanism of formation of tetrafluoroethers (IV) are in progress and will be reported in a forthcoming communication.

Experimental

A typical preparative reaction procedure is described below. Specific conditions and results of individual experiments are given in Table 1.

In general, a 0.25 or 0.5 l stainless-steel autoclave was charged with a suitable acid, checked for tightness with compressed nitrogen, cooled in a dry ice–acetone mixture, evacuated to 1–2 mmHg and charged with SF_4 by weight from a storage cylinder. An exothermic reaction—the formation of an acyl fluoride—occured, but the charging was continued until the required quantity of SF_4 was condensed in the autoclave. Upon completion of the reaction, the autoclave was allowed to cool and the SOF_2, HF, the excess of SF_4 and unreacted acyl fluoride vented into a caustic trap. The gaseous trifluoroethanes were condensed in a dry ice-cooled condenser which followed the caustic trap. The liquid reaction mixture was poured on to ice, separated and washed subsequently with water, aqueous $NaHCO_3$ and water, and then dried over $MgSO_4$. The products were separated by distillation through a short fractionating column.

Bis(1,1-difluoroethyl)ether (V) (nc), prepared as above, exhibited a boiling point of 49.5°/754 mmHg and $d_4^{20} = 1.1948$. (Found: C, 33.0; H, 4.1; F, 52.1%. $C_4H_6F_4O$ requires: C, 32.9; H, 4.15; F, 52.0%.) The ^1H NMR spectrum (CCl_4/TMS) showed an absorption at δ 1.83 (m) and the ^{19}F NMR spectrum (CCl_4/CCl_3F) an absorption at ϕ −63.7 ppm (m), (Jeol 100 and 94.07 MHz, respectively; ^{19}F upfield shifts reported as negative). The mass spectrum had no molecular peak, but had peaks at *m/e* 131 [$M^+ - CH_3$], 116 [$M^+ - 2CH_3$] and 65 [$CH_3CF_2^+$].

Bis(2-chloro-1,1-difluoroethyl)ether (VI) (nc) exhibited the following characteristics: b.p. 135.0°/754 mmHg, m.p. −43°, n_D^{20} 1.3730, d_4^{20} 1.5214. (Found: C, 22.4; H, 2.2; Cl, 32.6; F, 35.4%; mol. wt., 214. $C_4H_4Cl_2F_4O$ requires: C, 22.3; H, 1.9; Cl, 33.0; F, 35.4%; mol. wt., 214.) The infrared spectrum of the neat sample exhibited the following values of $\nu_{max.}$ (cm^{-1}): 3050 (w), 2980 (w), 1440 (m) (CH_2), 1345 (s), 1330 (s), 1285 (s), 1235 (vs), (br), 1130 (s), 1080 (vs), (br) (C–F) and (C–O–C) and 765 (m) (C–Cl). The ^1H NMR spectrum (CCl_4) showed an absorption at δ 3.85 (m) and the ^{19}F NMR spectrum (CCl_4) a complex multiplet based on a quintet at ϕ −75.1 ppm. The mass spectrum had peaks at *m/e* 214 [M^+], 165, 167 [$M^+ - CH_2Cl$], 99, 101 [$CH_2ClCF_2^+$] and 49, 51 [CH_2Cl^+] of relative intensities 3:1.

Bis(2,2-dichloro-1,1-difluoroethyl)ether (VII) (nc) exhibited a boiling point of 64.5°/16 mmHg, n_D^{20} 1.4043 and d_4^{20} 1.6497. (Found: C, 17.15; H, 1.0; Cl, 49.95; F, 26.7%; mol. wt., 282. $C_4H_2Cl_4F_4O$ requires: C, 16.9; H, 0.7; Cl, 50.0; F, 26.8%; mol. wt., 282.) The ^1H NMR spectrum (CCl_4) displayed a quintet at δ 5.88 and the ^{19}F NMR spectrum (CCl_4) a triplet at ϕ −80.76 ppm. The mass spectrum had peaks at *m/e* 282, 284, 286, 288 [M^+] (relative intensities 9:9:6:1), 199, 201, 203 [$M^+ - CHCl_2$], 133, 135, 137 [$CHCl_2CF_2^+$] and 83, 85, 87 [$CHCl_2^+$] (relative intensities 9:6:1).

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