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SULPHUR-OXYGEN *VERSUS* CARBON-OXYGEN SCISSION IN TRIFLUOROMETHANESULPHONATES*

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SUMMARY

Previously, only C–O scission has been reported in the reactions of trifluoromethanesulphonates (triflates) with nucleophiles. However, 1*H*,1*H*-perfluoroalkyl triflates undergo predominently S–O scission in their reactions with 1*H*,1*H*-perfluoroalkoxides and with ethoxide. In this respect, they resemble the reported behaviour of certain tosylates in the dependence of C–O *versus* S–O scission on the nature of the nucleophile.

INTRODUCTION

1*H*,1*H*-Perfluoroalkyl trifluoromethanesulphonates (triflates) are sufficiently reactive [triflate (I), ($R_F = CF_3$) undergoes reaction with iodide about 10^5 times faster than does 1-bromo-2,2,2-trifluoroethane[1]] to permit triflate displacement (C–O scission) by a variety of nucleophiles[1–4]. Hansen[1] reported that triflate (I) ($R_F = CF_3$), in contrast to the highly unreactive tosylate[5], readily underwent reaction with diethylamine in refluxing benzene to give tertiary amine (II) ($R_F = CF_3$; $X = NEt_2$) (84%).

$$\underset{\text{(I)}}{R_FCH_2OSO_2CF_3} + X^- \rightarrow \underset{\text{(II)}}{R_FCH_2X} + CF_3SO_3^-$$

Tosylate (II) ($R_F = C_3F_7$; X = OTs) (70%) was also produced from triflate (I) ($R_F = C_3F_7$) and lithium tosylate in dimethylformamide at 120 °C. C–O scission in triflates by mercaptides, aroxides, thiocyanate ion and diethyl phosphite is reported in patents[2,3]. Burdon and McLoughlin[4] obtained the fluoro-ether (IV) (R_F, $R_F' = CF_3$) (65%) from triflate (I) ($R_F = CF_3$) and fluoroalkoxide (III)

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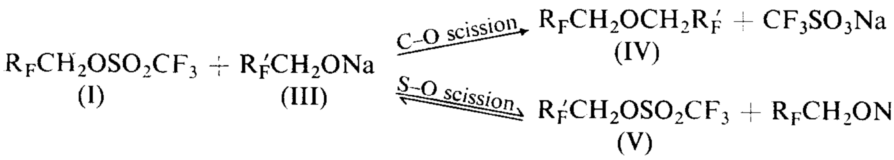
($R_F' = CF_3$) in refluxing 2,2,2-trifluoroethanol, and considered that the reaction would be generally applicable for the synthesis of polyfluoro-ethers (IV) (R_F, R_F' = fluoroalkyl). Our interest in routes to polyfluoro-ethers has led us to test this prediction.

RESULTS AND DISCUSSION

Our investigations have demonstrated that 1*H*,1*H*-perfluoroalkoxides effect S–O scission more readily than C–O scission in 1*H*,1*H*-perfluoroalkyl triflates, and have provided the first examples of this mode of scission in triflates. This inevitably limits the usefulness of the reaction.

Reactions of triflate (I) ($R_F = C_3F_7$) with fluoroalkoxide (III) ($R_F' = CF_3$) in 2,2,2-trifluoroethanol, tetramethylene sulphone (TMS) and hexamethylphosphoramide (HMPA), and of triflates (I) ($R_F = CF_3$) and (I) ($R_F = C_3F_7$) with fluoroalkoxide (III) ($R_F' = C_3F_7$) in 1*H*,1*H*-heptafluorobutanol were investigated. Reaction mixtures were quantitatively examined by GLC using an internal standard. The fluoro-ethers (IV) ($R_F = CF_3$, $R_F' = C_3F_7$) and (IV) (R_F, $R_F' = C_3F_7$) could not be isolated in a pure state, and their identification is based upon consistent mass-spectral data. Results are summarised in Table 1.



$$\text{(V)} + R_F'CH_2ONa \xrightarrow{\text{C–O scission}} \underset{\text{(VI)}}{(R_F'CH_2)_2O} + CF_3SO_3Na$$

Triflate (I) ($R_F = C_3F_7$) and fluoroalkoxide (III) ($R_F' = CF_3$) (4 equiv.) in 2,2,2-trifluoroethanol at 80 °C gave the symmetrical ether (VI) ($R_F' = CF_3$) (*ca.* 70%) as a consequence of initial S–O scission, and less than 4% of the direct C–O scission product (IV) ($R_F = C_3F_7$, $R_F' = CF_3$). The stability of the fluoro-ethers under these conditions was separately demonstrated: fluoro-ether (IV) (R_F, $R_F' = CF_3$) was stable to sodium ethoxide in ethanol at 80 °C.

Triflate (I) ($R_F = CF_3$) and fluoroalkoxide (III) ($R_F' = C_3F_7$) (4 equiv.) in 1*H*,1*H*-heptafluorobutanol at 80 °C gave triflate (V) ($R_F' = C_3F_7$) (*ca.* 35%) as the main product, and fluoro-ethers (IV) ($R_F = CF_3$, $R_F' = C_3F_7$) (< 10%) and (VI) ($R_F' = C_3F_7$) (*ca.* 5%).

TABLE 1

REACTIONS OF TRIFLATES (I) WITH SODIUM POLYFLUOROALKOXIDES[a]

No.	Reactants $R_FCH_2OSO_2CF_3$ (I)	 $R_F'CH_2ONa$ (III)	Solvent	Reaction temp. (°C)/time (h)	Products (mol %) $R_FCH_2OSO_2CF_3$ (I)	 $R_FCH_2OCH_2R_F'$ (IV)	 $R_F'CH_2OSO_2CF_3$ (V)	 $(R_F'CH_2)_2O$ (VI)
1[c]	$R_F = C_3F_7$	$R_F' = CF_3$	CF_3CH_2OH	80/8.5 (80/15.5)	0	4(4)[b]	34(31)[b]	70(75)
2[d,e]	$R_F = C_3F_7$	$R_F' = CF_3$	TMS	55/4 (30/21)	0	22(15)[b]	180(126)[b]	39(32)
3[f,e]	$R_F = C_3F_7$	$R_F' = CF_3$	HMPA	55/1 (30/16.5)	0	7(5)[b]	56(38)[b]	15(17)
4[g]	$R_F = CF_3$	$R_F' = C_3F_7$	$C_3F_7CH_2OH$	80/18 (80/15)	—	13(8)[b]	38(35)	8(5)
5[h]	$R_F = C_3F_7$	$R_F' = C_3F_7$	$C_3F_7CH_2OH$	80/23 (80/23) 100/16 (100/16)	25(22)	34(34)	—	—

[a] See Experimental section for general procedure: repeated similar experiments in parentheses.

[b] $CF_3CH_2OCH_2C_3F_7$ and $CF_3CH_2OSO_2CF_3$ were not adequately resolved by GLC and limiting yields are given.

[c] Programmed GLC (80–180 °C) showed only traces of high retention time products.

[d] Triflate (I) ($R_F = C_3F_7$) insoluble in TMS. Exothermic reaction controlled by mixing reactants at *ca.* 5 °C. Programmed GLC (80–180 °C) showed a complex pattern of low intensity unidentified high retention time peaks.

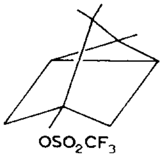
[e] Solvent caused peak broadening. In the second experiment, water (5 cm^3) and a solution of the internal standard in bromobenzene (1.0 g) was added and, after shaking and centrifuging, the organic layer analysed by GLC.

[f] Reactants mixed at *ca.* 5 °C. Programmed GLC (80–180 °C) showed that the formation of high retention time products was most significant in this solvent but, by superimposition GLC, only a few components were common to experiments 3 and 2.

[g] Sodium salt prepared *in situ* using NaH. Products distilled *in vacuo* and characterised by GLC–MS.

[h] Sodium salt prepared *in situ* using NaH. Programmed GLC (72–180 °C) showed a large number of low intensity high retention time peaks.

The behaviour of these triflates is in marked contrast to that of compound (VII),



(VII)

a triflate of low reactivity which was shown to undergo exclusively C–O scission on solvolysis in ^{18}O-enriched aqueous ethanol in the presence of triethylamine[6]. On the other hand, the dependence of C–O *versus* S–O scission in triflates (I) on the nature of the nucleophile is similar to the reported behaviour of neopentyl[7] and 2,4-dinitrophenyl[8] tosylates. Nucleophiles such as thiophenoxide, morpholine, piperidine and iodide effected mainly C–O scission, whereas methoxide and phenoxide effected mainly S–O scission. The mode of scission was not related to nucleophilic reactivity constants (Swain and Scott's treatment) but rather to reagent polarisability[8]. We thus concluded that the methanolysis rates of triflates (I) ($R_F = CF_3$), ($R_F = H(CF_2)_2$), ($R_F = C_2F_5$) and ($R_F = C_3F_7$) reported by Hansen[1] most probably do not exclusively reflect C–O scission rates. S–O scission is, in fact, dominant. Treatment of triflates (I) ($R_F = CF_3$) and (I) ($R_F = C_3F_7$) with sodium ethoxide (2 equiv.) in ethanol at 0–20 °C gave diethyl ether in 37% and 43% yields, respectively, as a result of initial S–O scission, together with the corresponding fluoro-ethers, 1,1,1-trifluoro-3-oxapentane and 5,5,6,6,7,7,7-heptafluoro-3-oxaheptane in 23% and 17% yields, respectively, formed by direct C–O scission. These fluoro-ethers were readily prepared in high yields by treatment of bromoethane with the appropriate sodium fluoroalkoxide in HMPA.

The use of triflates, even for the synthesis of symmetrical fluoro-ethers, is limited because of the low reactivity and inadequate stability[9] of the higher fluoroalkoxides. Reaction of triflate (I) ($R_F = C_3F_7$) with fluoroalkoxide (III) ($R_F' = C_3F_7$) (4 equiv.) in 1*H*,1*H*-heptafluorobutanol at 80–100 °C went to *ca.* 75% completion to give a moderate yield (*ca.* 35%) of fluoro-ether (IV) (R_F, $R_F' = C_3F_7$) and a complex mixture of unidentified products. Highly polar, aprotic solvents are not good media for these reactions (see Table 1): in TMS and especially in HMPA, triflate (I) ($R_F = C_3F_7$) and fluoroalkoxide (III) ($R_F' = CF_3$) afforded very complex product mixtures. Thus, even the triflate group is insufficiently reactive to compete effectively with the enhanced instability of the fluoroalkoxides in these solvents.

EXPERIMENTAL

GLC was carried out (on-column injection) using a Pye series 104 chromatograph (1.5 m × 6 mm column; 10% polydiethyleneglycol succinate on 60–80 AW Chromosorb P), which was coupled to a Kent Chromalog 2 integrator for quantitative analysis. A gas chromatograph–mass spectrometer combination (Perkin–Elmer Model 881, Hitachi Perkin–Elmer RMU-7 mass spectrometer: 2 m × 3.2 mm column with the above packing) (GLC–MS) was used to characterise components in mixtures. NMR spectra were measured with a Perkin–Elmer R10 spectrometer operating at 60 MHz for ^1H (tetramethylsilane as internal standard) and 56.4 MHz for ^{19}F (trifluoroacetic acid as external standard).

Materials

Fifty per cent sodium hydride oil dispersion was used as such or washed with petroleum ether, b.p. 40–60 °C, and dried *in vacuo*. TMS and HMPA were distilled under reduced pressure and tetrahydrofuran (THF) distilled over potassium. GLC-pure 2,2,2-trifluoroethanol and 1*H*,1*H*-heptafluorobutanol were obtained by fractionation. Sodium 2,2,2-trifluoroethoxide and sodium 1*H*,1*H*-heptafluorobutoxide were prepared by treatment of the alkanols with sodium hydride in ether: after removal of ether-insoluble solids (centrifuge), solvent (rotary evaporator) and drying ($MgSO_4$) at room temperature *in vacuo*, they were obtained as a white powder and a brownish yellow wax[9], respectively. GLC-pure 2,2,2-trifluoroethyl triflate [(I) ($R_F = CF_3$)], b.p. 91.5–92 °C (lit.[1], 89–91 °C) and 1*H*,1*H*-heptafluorobutyl triflate [(I) ($R_F = C_3F_7$)], b.p. 118–119 °C (lit.[1], 118–120 °C) were prepared as described by Hansen[1] except that trifluoromethanesulphonyl chloride, obtained as described by Haszeldine[10], was used.

1,1,1-Trifluoro-3-oxapentane and 5,5,6,6,7,7,7-heptafluoro-3-oxaheptane

Fifty per cent sodium hydride oil dispersion (6.0 g) was added to a stirred solution of 2,2,2-trifluoroethanol (13.0 g, 130 mmol) in HMPA (65 cm^3) at 5–10 °C under nitrogen. Bromoethane (10.0 g, 92 mmol) was carefully added to the heterogeneous mixture in order to prevent excessive frothing. After 2 h at room temperature, distillation *in vacuo* (oil bath < 50 °C) afforded condensate (collected at -196 °C), which was distilled to give GLC-pure 1,1,1-trifluoro-3-oxapentane (9.0 g, 76%), b.p. 50–51 °C, n_D^{20} 1.3060 (lit.[11], b.p. 49.9 °C, n_D^{20} 1.3042); *m/e* 128 (low intensity, M^+) and prominent peaks at 127 ($M^+ - H$), 113 ($M^+ - CH_3$), 83 ($CF_3CH_2^+$), 81, 69 (CF_3^+), 64, 63, 61, 59 ($M^+ - CF_3$), 47, 45 ($C_2H_5O^+$), 43, 33, 31 (CH_3O^+), 29 (base, $C_2H_5^+$), 27 and 15 (CH_3^+); ^1H NMR: 8.80 τ (triplet, $^3J(HH) = 7.2$ Hz, CH_3), 6.36 τ (quartet, $^3J(HH) = 7.2$ Hz, 4-CH_2), 6.23 τ (quartet, $^3J(HF) = 9.1$ Hz, 2-CH_2); ^{19}F NMR: $\delta_F = -1.8$ ppm (triplet, $^3J(FH) = 9.1$ Hz, CF_3).

5,5,6,6,7,7,7-Heptafluoro-3-oxaheptane (nc) (84%, 98% pure) was prepared similarly except that the reaction was carried out in HMPA containing THF (40%). Fractionation gave GLC-pure ether (66%), b.p. 84.5–86.5 °C, n_D^{20} 1.3010 (Found: C, 31.9; H, 3.1; F, 58.4%. $C_6H_7F_7O$ requires C, 31.6; H, 3.1; F, 58.3%); *m/e* 228 (low intensity, M^+) and prominent peaks at 227 ($M^+ - H$), 213 ($M^+ - CH_3$), 181, 161, 119, 113, 100, 95, 83, 81, 69, 64, 61, 59 ($M^+ - CF_3$), 51, 45, 43, 41, 33, 31, 29 (base), 27 and 15; ^{1}H NMR: 8.78 τ (triplet, ^3J(HH) = 7.1 Hz, CH_3), 6.34 τ (quartet, ^3J(HH) = 7.1 Hz, 2-CH_2), 6.10 τ (triplet, ^3J(HF) = 14.0 Hz, ^4J(HF) = 1.6 Hz, 5-CH_2); ^{19}F NMR: δ_F = 4.7 ppm (triplet, ^4J(FF) = 9.3 Hz, CF_3), 51.7 ppm (multiplet, 6-CF_2) and 44.2 ppm (multiplet, ^4J(FF) = 9.3 Hz, 5-CF_2).

*Reaction of 1*H,*1*H*-heptafluorobutyl triflate*[(I) ($R_F = C_3F_7$)] *with sodium 2,2,2-trifluoroethoxide* [(III) ($R_F' = CF_3$)] *in 2,2,2-trifluoroethanol*

1*H*,1*H*-Heptafluorobutyl triflate [(I) ($R_F = C_3F_7$)] (15.0 g, 45.2 mmol) was added to the stirred white paste obtained by treatment of 2,2,2-trifluoroethanol (32 g) with 50% sodium hydride oil dispersion (2.6 g) under nitrogen. The mixture, which soon became mobile, was heated under reflux for 2.5 h and then distilled *in vacuo* at room temperature (4 h) to give condensate (31.2 g) which was collected at −196 °C. Fractionation (45 cm × 7 mm spinning-band column) gave bis-(2,2,2-trifluoroethyl)ether (VI) ($R_F' = CF_3$) (4.3 g), b.p. 60–61 °C, which contained 2,2,2-trifluoroethanol (15%) (GLC at 72 °C). Treatment with sodium hydride and distillation *in vacuo* at room temperature afforded the pure ether (3.5 g, 43%), n_D^{20} 1.280 (lit.[4], 1.301); *m/e* 182 (low intensity, M^+) and prominent peaks at 163 ($M^+ - F$), 113 (base, $M^+ - CF_3$), 83 ($CF_3CH_2^+$), 69, 64, 63, 61, 33 and 31; ^{1}H NMR: 6.02 τ (quartet, J(HF) = 8.4 Hz, CH_2); ^{19}F NMR: δ_F = −11.2 ppm (triplet, J(FH) = 8.4 Hz, CF_3). Continued fractionation (GLC-monitored) afforded fractions (i) 0.7 g, b.p. 61–70.5 °C, (ii) 1.7 g, b.p. 70.5–71.8 °C, (iii) 1.0 g, b.p. 71.8–72.3 °C, (iv) 1.0 g, b.p. 72.3–72.5 °C, (v) 1.6 g, b.p. 72.5–72.7 °C and (vi) 12.5 g, b.p. 72.7–73.5 °C. GLC at various temperatures (45–100 °C) showed that the suspected fluoro-ether (IV) ($R_F = C_3F_7$; $R_F' = CF_3$) and triflate (V) ($R_F' = CF_3$), which were poorly resolved, co-distilled with the well-resolved 2,2,2-trifluoroethanol. The proportion of the suspected fluoro-ether to the triflate decreased and the concentration of the fluoro-alcohol increased as the fractionation proceeded. Examination of fraction (iii) by GLC–MS confirmed these structural assignments. The first component (15 wt.%) gave a fragmentation pattern fully consistent with fluoro-ether (IV) ($R_F = C_3F_7$; $R_F' = CF_3$) (nc) [prominent peaks at *m/e* 263 ($M^+ - F$), 213 ($M^+ - CF_3$), 133, 131, 119, 113 (base, $M^+ - C_3F_7$), 100, 95, 83, 81, 69, 65, 64, 61, 51, 33, 31 and 29], and the second component (25 wt.%) had a spectrum identical with that of an authentic sample of triflate (V) ($R_F' = CF_3$). The pot residue (6.1 g) was (GLC) a mixture of 1*H*,1*H*-heptafluorobutanol (90%) and 2,2,2-trifluoroethanol (10%). Treatment with ice-cold water (3 × 5 cm^3) afforded the pure fluorobutanol (3.6 g) which had an IR spectrum indistinguishable from that of an authentic sample.

*Reaction of 1*H,*1*H*-heptafluorobutyl triflate* [(I) ($R_F = C_3F_7$)] *with sodium 1*H,*1*H*-heptafluorobutoxide* [(III) ($R_F' = C_3F_7$)] *in 1*H,*1*H*-heptafluorobutanol*

1*H*,1*H*-Heptafluorobutyl triflate [(I) ($R_F = C_3F_7$)] (1.66 g, 5.0 mmol) was added to the stirred white paste prepared by adding sodium hydride (136 mg, 5.6 mmol) to 1*H*,1*H*-heptafluorobutanol (5.0 g) under nitrogen, and the mixture heated at 80 °C for 16 h, and then under reflux for 24 h. GLC at 90 °C showed that the ratio (r) of the approximate relative peak areas of suspected fluoro-ether (IV) (R_F, $R_F' = C_3F_7$) to unconsumed triflate (I) ($R_F = C_3F_7$) after these heating periods were 1:3 and 3:2, respectively. Distillation at room temperature *in vacuo* afforded condensate (3.5 g) which was collected at −196 °C and had $r = 3:2$. This was heated under reflux for 20 h with freshly prepared sodium 1*H*,1*H*-heptafluorobutoxide [(III) ($R_F' = C_3F_7$)] (1.1 g, 5.0 mmol) after which time $r = 5:1$. Re-distillation gave product (3.4 g) which contained (GLC at 85 °C) four components of relative peak areas: 1, [(I) ($R_F = C_3F_7$)]; 0.6, (unknown); 4.5, [suspected (IV) (R_F, $R_F' = C_3F_7$)]; and 20, (1*H*,1*H*-heptafluorobutanol). Resolution by preparative-scale GLC (Autoprep, 6 m × 9.5 mm column) employing poly(diethyleneglycol succinate) (best stationary phase), silicone, Apiezon, or poly(oxy-*m*-phenylene) was inadequate to permit isolation of the pure fluoro-ether. However, GLC–MS showed that the first component had a spectrum identical with that of authentic (I) ($R_F = C_3F_7$) and that the third component had a fragmentation pattern quite consistent with structure (IV) (R_F, $R_F' = C_3F_7$) (nc) [*m*/*e* 363 (low intensity, $M^+ - F$) and prominent peaks at 213 ($M^+ - C_3F_7$), 161, 119, 113, 95, 69, 57, 56, 51, 41, 33, 31 (base) and 29].

Reactions of triflates (I) with polyfluoroalkoxides (III). General procedure for quantitative reactions

The triflate (*ca.* 0.32 mmol), sodium polyfluoroalkoxide (*ca.* 1.35 mmol) and solvent (1.0 g) were weighed into a B10 tube (*ca.* 7 cm^3 capacity) equipped with water condenser. When the sodium salt was prepared *in situ* using sodium hydride, a nitrogen atmosphere was employed. The reaction mixture was allowed about 10 min to reach the appropriate temperature (±1 °C), and the system stoppered. Reaction mixtures were quantitatively examined by GLC at 72 °C employing benzene (0.10–0.20 mmol added after the period of heating) as an internal standard. The relative sensitivities of the detector for pure compounds with respect to benzene were pre-determined. The pure fluoro-ethers (IV) ($R_F = CF_3$, $R_F' = C_3F_7$) and (IV) (R_F, $R_F' = C_3F_7$) were not available and were assumed to show the same response per g as (IV) (R_F, $R_F' = CF_3$). The results are given in Table 1.

Reactions of triflates (I) with sodium ethoxide

(i) 2,2,2-Trifluoroethyl triflate [(I) ($R_F = CF_3$)]

The triflate (I) ($R_F = CF_3$) (228 mg, 1.0 mmol) was added to sodium ethoxide (137 mg, 2.0 mmol) in absolute ethanol (1.0 g) at *ca.* 5 °C, at which temperature reaction occurred. After 10 min, the mixture was allowed to reach room temperature and examined by GLC (at 50 °C) after 1 h and 18 h. There was no change in the yields of the two products, diethyl ether and suspected 1,1,1-trifluoro-3-oxapentane [(IV) ($R_F = CF_3$, $R_F' = CH_3$)] (incompletely resolved peaks, area ratio *ca.* 2:1), during this time. GLC–MS examination of the condensate obtained by distillation *in vacuo*, and comparison with the spectra of the authentic compounds, confirmed these assignments.

A quantitative experiment (GLC at 50 °C), in which cyclohexene added at the completion of the reaction was used as an internal standard, afforded diethyl ether (38%) and 1,1,1-trifluoro-3-oxapentane (22%). In a duplicate experiment, these yields were 37% and 24%, respectively.

*(ii) 1*H,*1*H-*Heptafluorobutyl triflate [(I) ($R_F = C_3F_7$)]*

The triflate (I) ($R_F = C_3F_7$) (160 mg, 0.48 mmol) was added to sodium ethoxide (69 mg, 1.01 mmol) in absolute ethanol (0.50 g) at *ca.* 5 °C. After 10 min, the mixture was allowed to warm to room temperature and examined by GLC (at 50 °C) after 1 h and 21 h. There was no change in the yields of the two products, diethyl ether and suspected 5,5,6,6,7,7,7-heptafluoro-3-oxaheptane [(IV) ($R_F = C_3F_7$, $R_F' = CH_3$)] (well-resolved peaks, area ratio *ca.* 2:1), during this time. GLC–MS examination of the condensate obtained by distillation *in vacuo*, and comparison with the spectra of the authentic compounds, confirmed these assignments.

A quantitative experiment (GLC at 50 °C), in which cyclohexene added at the completion of the reaction was used as an internal standard, afforded diethyl ether (43%) and 5,5,6,6,7,7,7-heptafluoro-3-oxaheptane (18%). In a duplicate experiment, the yields were 43% and 16%, respectively.

Stability of bis(2,2,2-trifluoroethyl)ether [(IV) (R_F, $R_F' = CF_3$)] to ethanolic sodium ethoxide

A solution of the fluoro-ether (IV) (R_F, $R_F' = CF_3$) (88.7 mg, 0.49 mmol) and sodium ethoxide (0.14 g, 2.1 mmol) in absolute ethanol was heated in a sealed tube in the absence of air at 81 °C for 16 h. Programmed GLC (82–180 °C) showed only peaks corresponding to the fluoro-ether and solvent. Quantitative GLC at 82 °C with toluene (52.2 mg) as internal standard showed that the fluoro-ether (87.0 mg, 97%) was present.

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