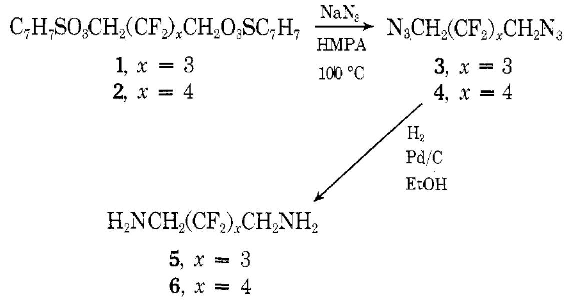
crude diazide was reduced directly to the diamine **5** in 82–90% yield by catalytic hydrogenation in ethanol at 3 atm using 10% Pd/C catalyst.[4] A similar sequence of reactions led to 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine (**6**).



Experimental Section[5]

2,2,3,3,4,4-Hexafluoropentane-1,5-diazide (3). A mixture of 20.0 g (0.038 mol) of ditosylate **1**,[1] 10.0 g (0.15 mol) of sodium azide, and 70 ml of HMPA was stirred and heated in an oil bath[6] at 100–110 °C for 19 h. The mixture was cooled and ca. 300 ml of water was added. The aqueous mixture was extracted three times with ether, washed twice with water, dried over $MgSO_4$, and evaporated in vacuo to leave 10.2 g (99%) of product as a pale yellow oil: ν_{max} (neat) 2100 (s), 2150 (sh), 2210 cm^{-1} (sh); NMR ($CDCl_3$) δ 2.4–4.0 (m). The purity of **3** was estimated by integrating the CH_2 multiplet against a small amount of aromatic resonance still present from unreacted tosylate, and was of the order of 90 ± 3%.

2,2,3,3,4,4,5,5-Octafluorohexane 1,6-Di-*p*-toluenesulfonate (2). To a solution of 100 g (0.38 mol) of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol[7] in 500 ml of dry pyridine cooled in an ice bath was added 195.0 g (1.0 mol) of *p*-toluenesulfonyl chloride in several portions with strong stirring. The temperature of the reaction was maintained at 30 °C or less until the end of the addition. After the reaction mixture was kept chilled for a further 2 h, it was allowed to equilibrate to room temperature and left overnight. The mixture was poured into 2 l. of cold 1 N HCl and the precipitate collected. Trituration of the moist solid with methanol gave 188.2 g (87%) of white solid, mp 134–136 °C.

Anal. Calcd for $C_{20}H_{18}F_8O_6S_2$: C, 42.08; H, 3.18; F, 26.67. Found: C, 41.65; H, 2.87; F, 26.48.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diazide (4). This was prepared *in a like manner as* **3** *from the ditosylate* **2** *in* 92 ± 3% crude yield.

2,2,3,3,4,4-Hexafluoropentane-1,5-diamine (5). To a solution of 10.7 g of diazide **3** in 60 ml of absolute ethanol was added 1–2 g of 10% palladium on carbon. The mixture was hydrogenated at 48 psi for 5 h and filtered, and the solvent evaporated under reduced pressure. Distillation of the residual oil gave 8.1 g (90%) of colorless oil, bp 65–67 °C (0.7 mm),[8] $n^{25}{}_{D}$ 1.373, which darkened slightly on standing. A sample in ethanol was treated with ethereal HCl and the precipitate recrystallized from ethanol–ether, mp 305–310 °C dec.

Anal. Calcd for $C_5H_8F_6N_2\cdot 2HCl$: C, 21.22; H, 2.81; N, 9.90. Found: C, 21.37; H, 3.46; N, 9.91.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diamine (6). This compound was prepared similarly as described for **5** in 87% yield, bp 95–98 °C (0.6 mm), mp 44–45 °C (reported[2] 44–45 °C).

Registry No.—**1**, 632-01-9; **2**, 58191-47-2; **3**, 58191-48-3; **4**, 58191-49-4; **5**, 336-33-4; **5** 2HCl, 58191-50-7; 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, 355-74-8.

References and Notes

(1) B. S. Marks and G. C. Schweiker, *J. Am. Chem. Soc.*, **80**, 5789 (1958).
(2) E. T. McBee, P. A. Wiseman, and G. B. Backman, *Ind. Eng. Chem.*, **39**, 415 (1947).
(3) H. A. Brown and G. V. D. Tiers, *J. Org. Chem.*, **22**, 454 (1957).
(4) For examples of this procedure see J. H. Bayer and F. C. Canter, *Chem. Rev.*, **54**, 38 (1954).
(5) Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer. NMR spectra were measured on a Varian Associates T-60 spectrophotometer using Me_4Si as an internal standard. Combustion analyses were done by Galbraith Laboratories, Knoxville, Tenn.
(6) The use of a heating mantle is not advisable. In one experiment employing a mantle, superheating occurred which led to a vigorous reaction with concomitant decomposition to dark tarry materials.
(7) E. T. McBee, W. F. Marzluff, and O. R. Pierce, *J. Am. Chem. Soc.*, **74**, 444 (1952).
(8) R. Gosnell and J. Hollander, *J. Macromol. Sci., Phys.*, **1**, 831 (1967), report this compound, apparently erroneously, as having mp 52–53 °C, bp 40–45 °C (1.0 mm).

Synthesis and Reactions of Perfluorodialdehydes

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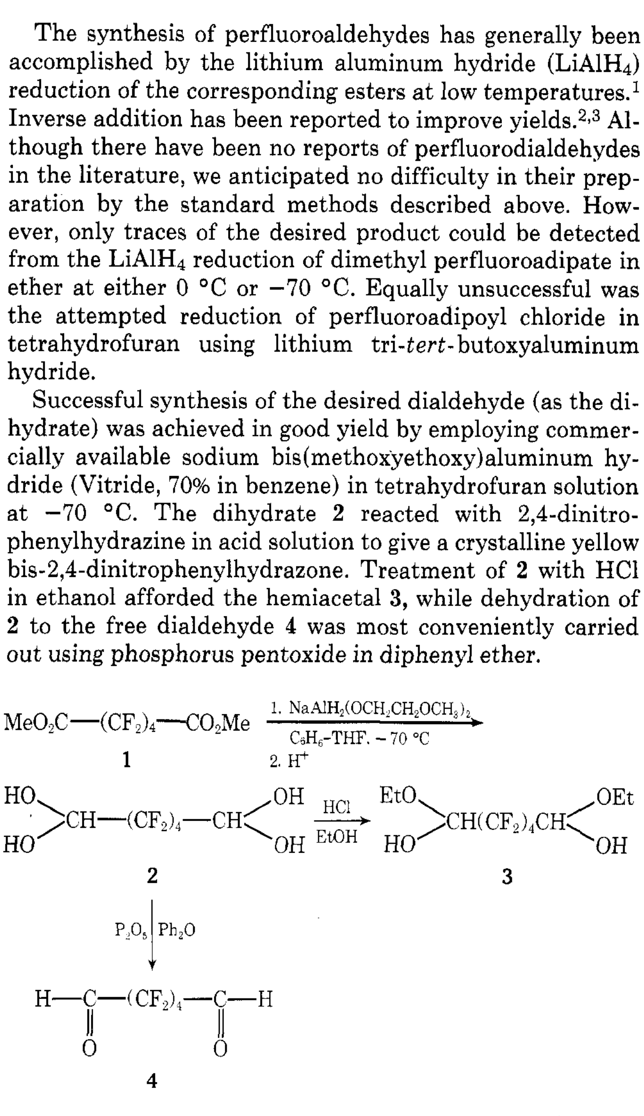
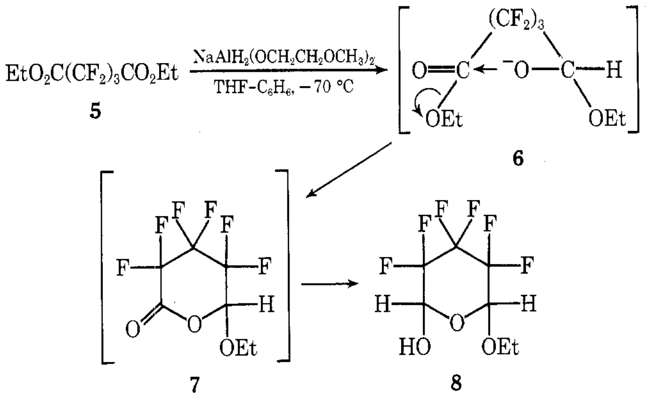
The synthesis of perfluoroaldehydes has generally been accomplished by the lithium aluminum hydride ($LiAlH_4$) reduction of the corresponding esters at low temperatures.[1] Inverse addition has been reported to improve yields.[2,3] Although there have been no reports of perfluorodialdehydes in the literature, we anticipated no difficulty in their preparation by the standard methods described above. However, only traces of the desired product could be detected from the $LiAlH_4$ reduction of dimethyl perfluoroadipate in ether at either 0 °C or −70 °C. Equally unsuccessful was the attempted reduction of perfluoroadipoyl chloride in tetrahydrofuran using lithium tri-*tert*-butoxyaluminum hydride.

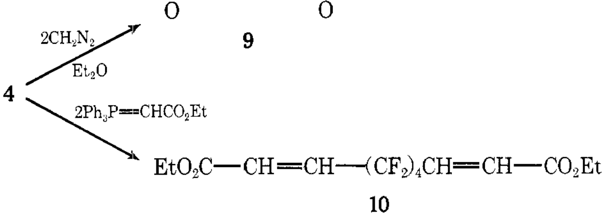
Successful synthesis of the desired dialdehyde (as the dihydrate) was achieved in good yield by employing commercially available sodium bis(methoxyethoxy)aluminum hydride (Vitride, 70% in benzene) in tetrahydrofuran solution at −70 °C. The dihydrate **2** reacted with 2,4-dinitrophenylhydrazine in acid solution to give a crystalline yellow bis-2,4-dinitrophenylhydrazone. Treatment of **2** with HCl in ethanol afforded the hemiacetal **3**, while dehydration of **2** to the free dialdehyde **4** was most conveniently carried out using phosphorus pentoxide in diphenyl ether.



When the Vitride reduction of diethyl perfluoroglutarate was effected under similar conditions, the dialdehyde was obtained in the form of the cyclic hemiacetal **8**, formation of which seems best explained by intramolecular cyclization of the initial reduction product **6** to **7** followed by further reduction to **8**. Reaction of perfluoro diesters with Vitride at room temperature afforded consistent yields of greater than 90% of perfluoro diols. Although $LiAlH_4$ reductions were also satisfactory in providing diols,[4] the convenience and greater safety margin of Vitride makes it the reagent of choice—especially in those cases where large quantities of material are required.



The dialdehyde **4** underwent reaction with diazomethane to give the diepoxide **9** and afforded the diolefin **10** via a Wittig reaction using carbethoxymethylenetriphenylphosphorane.



The importance of difunctional perfluorinated compounds has been extensively reviewed.[5] Consequently, the ready accessibility of the synthetically versatile perfluorinated dialdehydes should provide a valuable addition to the chemistry of highly fluorinated compounds.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were obtained with a Varian Associates T-60 instrument. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Vitride reagent was obtained from Eastman Organic Chemicals Co.; dimethyl perfluoroadipate was obtained from PoChemco Chemical Co.; and diethyl perfluoroglutarate was purchased from PCR Inc.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-dialdehyde (4). In a 3-l. three-neck round-bottom flask fitted with a mechanical stirrer, dropping funnel equipped with a drying tube, and low-temperature thermometer was placed a solution of 50.0 g (0.158 mol) of dimethyl perfluoroadipate in 450 ml of dry tetrahydrofuran. The reaction mixture was cooled to −70 °C (dry ice-acetone) and 67.5 ml (0.238 mol) of Vitride (70% in benzene) diluted with 50 ml of THF was added dropwise over 30 min with vigorous stirring. The temperature of the reaction was maintained at ≤ -70 °C during the addition and at −70 °C for 2.5 h after addition was complete. To the viscous mixture 500 ml of 20% sulfuric acid previously chilled to 5 °C was added dropwise. The temperature of the reaction was allowed to rise to −50 °C and maintained until the excess Vitride had been decomposed. The mixture was then allowed to warm spontaneously to room temperature. Ether (400–600 ml) was added with vigorous stirring until a homogeneous two-phase system was obtained. The layers were separated and the aqueous phase extracted with an additional 200–300 ml of ether. The combined ether extracts were washed to neutrality with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The dialdehyde dihydrate **2** was left as a thick syrup, 45.2 g (96%), ν_{max} (neat) 3600–2000 cm^{-1} (br).

Crude **2** from above was stirred with 3 equiv of phosphorus pentoxide in 60 ml of diphenyl ether[6] for 10 min and then the mixture was distilled through a 60-mm Vigreux column taking care to exclude moisture. The material so collected (28.1 g) was redistilled to give 26.5 g (65%) of **4** as a colorless liquid: bp 122–123 °C; $n^{26}{}_D$ 1.3170; ν_{max} (neat) 2900, 2850 (sh), 1765 cm^{-1}; NMR ($CDCl_3$) δ 9.47 (m).

Because of the ease with which **4** underwent hydration, a sample was converted to the bis-2,4-dinitrophenylhydrazone for analysis, mp 228–230 °C (EtOH).

Anal. Calcd for $C_{18}H_{10}F_8N_8O_8$: C, 35.00; H, 1.62; N, 18.13. Found: C, 34.98; H, 1.62; N, 17.78.

2,2,3,3,4,4,5,5-Octafluoro-1,6-diethoxy-1,6-hexanediol (3). A solution of 5.0 g (0.017 mol) of crude **2** in 25 ml of absolute ethanol was saturated with HCl and allowed to remain overnight at room temperature. The precipitate was collected and washed with benzene to give 5.6 g (84%) of pure **3**: mp 110–111 °C; NMR (Me_2SO-d_6) δ 1.10 (t, 3 H, J = 6.5 Hz), 3.24–3.90 (m, 2 H), 4.94 (t, 1 H, J = 11 Hz), 7.34 (br s, 1 H, exchanges).

Anal. Calcd for $C_{10}H_{14}F_8O_4$: C, 34.30; H, 4.02. Found: C, 34.33; H, 4.04.

2-Ethoxy-6-hydroxy-3,3,4,4,5,5-hexafluoropyran (8). A solution of 30.3 g (0.105 mol) of Vitride (70% in benzene) in 30 ml of dry THF was added dropwise over 45 min to a stirred solution of 25.0 g (0.084 mol) of diethyl perfluoroglutarate in 200 ml of THF at −70 °C. The mixture was stirred for an additional 2 h at −70 °C followed by work-up as described for **4** to give 16.8 g (87%) of **8** as a pale yellow liquid. Distillation afforded a colorless oil [bp 65–70 °C (1.7 mm); $n^{26}{}_D$ 1.3671; ν_{max} (neat) 3350 cm^{-1} (broad); NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 6.5 Hz), 3.46–4.10 (m, 2 H, J = 4 Hz), 5.07–5.26 (m, 2 H), 8.33 (br s, 1 H, exchanges)] which on prolonged storage (1 month) solidified to a white, crystalline product, mp 84–86 °C (C_6H_6).

Anal. Calcd for $C_7H_8F_6O_3$: C, 33.05; H, 3.17; F, 44.90. Found: C, 32.76; H, 3.01; F, 44.46.

A sample of **8** when treated with 2,4-dinitrophenylhydrazine gave a crystalline yellow bishydrazone, mp 214–216 °C (EtOH).

Anal. Calcd for $C_{17}H_{10}F_6N_8O_8$: C, 35.95; H, 1.76; N, 19.73, F, 20.10. Found: C, 36.12; H, 1.42; N, 19.46; F, 20.60.

1,2,7,8-Diepoxy-3,3,4,4,5,5,6,6-octafluorooctane (9). To a solution of diazomethane (ca. 120 mmol) in 200 ml of ether cooled to 5 °C in an ice bath was added 10.0 g (39.0 mmol) of **4** dropwise over 15 min. The solution was stirred for 30 min and then allowed to stand unstoppered at room temperature for 16 h at which time the yellow color indicative of diazomethane had been discharged. The solution was purged with nitrogen followed by evaporation in vacuo at ambient temperature to leave 11.0 g of viscous, pale yellow oil. Distillation afforded 5.5 g (49%) of colorless liquid: bp 70–75 °C (0.025 mm); $n^{26}{}_D$ 1.3622; NMR ($CDCl_3$) δ 3.04 (m, 2 H), 3.53 (m, 1 H); ν_{max} (neat) 910 cm^{-1}.

Anal. Calcd for $C_8H_6F_8O_2$: C, 33.59; H, 2.11. Found: C, 34.01; H, 2.29.

Diethyl 4,4,5,5,6,6,7,7-Octafluorodecane-2,8-dienedioate (10). A mixture of 8.1 g (2.3 mmol) of carbethoxymethylenetriphenylphosphorane and 3.0 g (1.2 mmol) of **4** in 40 ml of toluene was heated at reflux for 18 h under an atmosphere of nitrogen. The solution was chilled in ice, and the precipitated triphenylphosphine oxide was collected. The filtrate was diluted with 200 ml of petroleum ether and a second crop of phosphine oxide removed. Evaporation of solvent under reduced pressure left an oil from which the residual phosphine oxide was removed by trituration with petroleum ether. Distillation of the evaporated petroleum ether supernatant gave 3.4 g (74%) of **10** as a colorless liquid, bp 148–153 °C (7.0 mm), $n^{25}{}_D$ 1.450.

Anal. Calcd for $C_{14}H_{14}F_8O_4$: C, 42.25; H, 3.52; F, 38.19. Found: C, 42.66; H, 3.28; F, 37.91.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol. A solution of 100.7 g (0.316 mol) of dimethyl perflouroadipate in 100 ml of dry THF was added dropwise over 1 h to a mechanically stirred solution of 210 ml (0.750 mol) of Vitride (70% in benzene) dissolved in 300 ml of THF. A slow reflux was maintained throughout the addition. Following completion of the addition stirring was continued for 1 h at room temperature. The mixture was cooled in an ice bath and 500 ml of chilled 20% H_2SO_4 (v/v) was added dropwise, followed by 450 ml of ether. The mixture was allowed to warm to room temperature. The ether phase was decanted and 500 ml of water was added to the reaction vessel. Rapid stirring was continued until all of the pasty white solid had been dissolved. After the ether extraction was repeated, the combined ethereal extracts were washed to neutrality with cold water and dried over $MgSO_4$. Removal of solvent in vacuo gave an amber syrup which solidified readily upon cooling to give 78.5 g (95%) of diol as a tan solid, mp 63–66 °C (lit.[4] mp 68 °C). This material was found to be sufficiently pure for further conversions. When desirable, purification appears best effected by distillation: bp 100–110 °C (1.5 mm); mp 67–68 °C.

Registry No.—**1**, 3107-98-0; **2**, 58191-51-8; **3**, 58191-52-9; **4**, 58191-53-0; **4** bis-2,4-DNPH, 58191-54-1; **5**, 424-40-8; **8**, 58191-55-2; **8** bis-2,4-DNPH, 58191-56-3; **9**, 58191-57-4; **10**, 58191-58-5; 2,4-dinitrophenylhydrazine, 119-26-6; diazomethane, 334-88-3; (carbethoxymethylene)triphenylphosphorane, 1099-45-2; 2,2,3,3,4,-4,5,5-octafluorohexane-1,6-diol, 355-74-8.

References and Notes

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(4) E. T. McBee, W. F. Marzluff, and O. R. Pierce, *J. Am. Chem. Soc.*, **74,** 444 (1952).
(5) I. L. Knunyants, L. Chih-Yuan, and V. V. Shokina, *Russ. Chem. Rev.*, **32,** 461 (1963).
(6) Previously dried by heating over phosphorus pentoxide so that no materials of bp <160 °C remained. Decantation of the clear supernatant from the dark residue was found to be satisfactory.

Solvolysis in Strong Acids. III. The Question of Alkyl–Oxygen Cleavage in Alkyl Tosylate Solvolysis[1]

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Simple primary alkyl *p*-toluenesulfonates solvolyze at markedly different rates in concentrated sulfuric acid. Mechanistic interpretations supported by investigations of first-formed products and kinetic isotope effects have been reported.[2] Recently, Harris has reviewed these and closely related studies within the general context of solvolytic substitution.[3,4] Our studies in this area have continued along several lines. One topic of interest has been the solvolytic behavior of some simple alkyl tosylates containing the trifluoromethyl group.[5]

Systems such as 2,2,2-trifluoroethyl tosylate and 1,1,1-trifluoro-2-propyl tosylate react most sluggishly under S_N2-like conditions.[6] The remarkable stability of the 2,2,2-trifluoroethyldiazonium ion indicates that S_N1-like reactions of these systems should also proceed with great reluctance.[7] Consequently, we were surprised to find that 2,2,2-trifluoroethyl tosylate and 1,1,1-trifluoro-2-propyl tosylate solvolyzed in the 85–100% sulfuric acid region at rates comparable to those of ethyl tosylate, but 3,3,3-trifluoro-1-propyl tosylate solvolyzed in sulfuric acid at rates significantly slower than those observed for methyl tosylate. Some of the relevant kinetic data are shown in Figure 1.[8] The fluorinated tosylates underwent solvolysis without rearrangement.

A consistent mechanistic representation that presumed alkyl–oxygen cleavage for the entire set of alkyl tosylates (Figure 1) was difficult to formulate. Further study of the seemingly aberrant fluorinated alkyl tosylates appeared necessary. We report here a correlated stereochemical and ^{18}O-labeling study which shows that solvolysis of 1,1,1-trifluoro-2-propyl tosylate in 98% sulfuric acid occurs with complete retention of configuration because solvolysis *does not* involve cleavage of the alkyl–oxygen bond.

An earlier survey study of asymmetric reductions with the lithium aluminum hydride–quinine complex indicated that a useful enantiomeric excess of (+)-1,1,1-trifluoro-2-propanol [(+)-**1**] could be produced by this reducing system.[9] After optimizing conditions, (+)-**1** could be conveniently prepared in 30% enantiomeric excess by reduction of 1,1,1-trifluoroacetone at 25 °C with an ethereal slurry of the 1:1 complex. 1,1,1-Trifluoro-2-propanol-^{18}O (**1**-^{18}O) was prepared by hydration of anhydrous trifluoroacetone with 50 atom % $H_2{}^{18}O$ followed by acid-catalyzed dehydration and subsequent reduction with lithium aluminum hydride in diglyme.

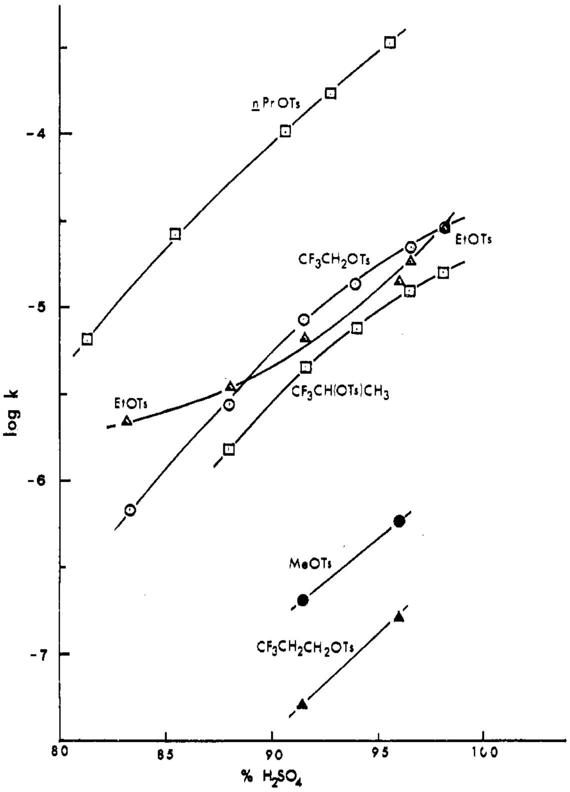
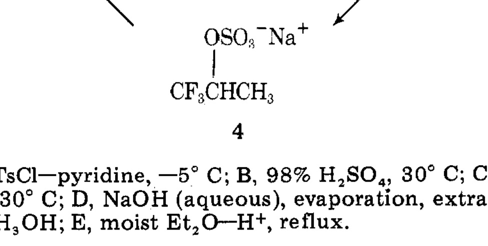


Figure 1. First-order rates (s^{-1}) of solvolysis of some simple alkyl tosylates in concentrated sulfuric acid solutions at 30 °C. A plot of log *k* vs. % H_2SO_4.

Samples of chiral and isotopically labeled **1** were carried through the reaction cycles depicted in Scheme I as steps A, B, D, E and steps C, D, E. The rotation of (+)-**1** before and after passing through the reaction cycles was found to be identical within experimental error (Table I). The rotations of intermediates **3** and **4** were found to be path independent (Table II). Finally, the oxygen-18 content of **1**-^{18}O was found to be unchanged after passage through the reaction cycles (Table III).

Scheme I[a]



[a] A, TsCl—pyridine, −5° C; B, 98% H_2SO_4, 30° C; C, 98% H_2SO_4, 30° C; D, NaOH (aqueous), evaporation, extraction with CH_3OH; E, moist Et_2O—H^+, reflux.

The conclusions are clear. No step in the cycles involves measurable cleavage of the alkyl–oxygen bond. Complete retention of configuration is a trivial consequence of this fact.