Synthesis of Some Novel Trifluoromethanesulfonates and Their Reactions with Alcohols[1]

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Allyl triflate, propargyl triflate, pentyl triflate, 2-(2-fluoro-2,2-dinitroethoxy)ethyl triflate, 2-fluoro-2,2-dinitroethyl triflate, and 1,2,3-propanetritriflate were prepared from the alcohols using triflic anhydride and pyridine. 1,4-Butaneditriflate was formed from tetrahydrofuran and triflic anhydride. In the presence of potassium carbonate, pentyl triflate, allyl triflate, propargyl triflate, 1,4-butaneditriflate, and 2-(2-fluoro-2-2-dinitroethyoxy)ethyl triflate reacted in chlorinated hydrocarbon solvents at ambient temperature with 2-fluoro-2,2-dinitroethanol to give the corresponding ethers, without skeletal rearrangement. 1,2,3-Propanetritriflate underwent monosubstitution and elimination to yield 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate. Pentyl triflate and 2,2,2-trifluoroethanol gave pentyl 2,2,2-trifluoroethyl ether. When sodium sulfate was used instead of potassium carbonate to scavenge liberated triflic acid, pentyl triflate and 2,2-dinitropropanol gave a mixture of the 1-, 2-, and 3-pentyl ethers. Under these conditions, 2-fluoro-2,2-dinitroethanol, 2,2-dinitropropanol, and 2,2,2-trinitroethanol, as well as pentanol, reacted with isopropyl triflate to give the corresponding isopropyl ethers. Allyl triflate was allowed to react similarly with 2,2-dinitropropanol, 2,2,2-trinitroethanol, and 2,2-dinitro-1,3-propanediol to give the allyl ethers.

The high reactivity of the trifluoromethanesulfonate (triflate) group in solvolysis and displacement reactions has been the subject of a number of recent investigations. Thus, methyl and ethyl triflates were reported to undergo solvolysis more than 10^4 times as fast as the corresponding tosylates.[2,3] The use of the triflate leaving group in otherwise unreactive polycyclic systems has extended the range of solvolysis reactions,[4-6] and vinyl triflates have been used extensively in studies of vinyl cations.[7-10] No attempts have been reported, however, to prepare a triflate ester more reactive than the ethyl derivative. Such extremely reactive alkylating agents would be expected to extend the range of weakly nucleophilic reagents that can be alkylated.

The triflates prepared in this work are shown in Table I. Most of these compounds were synthesized from the corresponding alcohols by the commonly used[4] triflic anhydride–pyridine method. Methylene chloride and carbon tetrachloride were used as solvents. Methyl triflate, because of its low boiling point, was prepared conveniently, from dimethyl sulfate by a procedure previously used for the corresponding fluorosulfonate.[11] The reaction of tetrahydrofuran with triflic anhydride gave 1,4-butaneditriflate, a reaction similar to ring openings with mixed sulfonic–carboxylic anhydrides.[12] This ditriflate and 1,2,3-propanetriflate, prepared from glycerol, are the first reported polyfunctional examples.

Allyl triflate, propargyl triflate, and isopropyl triflate were not sufficiently stable for elemental analysis and were characterized by spectral data, described in the Experimental Section. Even pentyl triflate gave only partially acceptable analytical data, and these compounds were generally used as freshly prepared solutions for alkylations. Allyl triflate in carbon tetrachloride solution was completely decomposed in 3 days at ambient temperature. Electron-withdrawing substituents, such as nitro groups or additional triflate groups in the molecule, improved stability; neat 2-fluoro-2,2-dinitroethyl triflate was unchanged after several months at room temperature.

The reactivity of triflates with alcohols of low nucleophilicity was examined using 2,2,2-trinitroethanol, 2,2-dinitro-1,3-propanediol, 2,2-dinitropropanol, and 2-fluoro-2,2-dinitroethanol. With the exception of low yields of methyl ethers of 2,2-dinitropropanol and 2,2-dinitropropanediol prepared by heating the alcohols with dimethyl sulfate,[13] these alcohols have not been previously alkylated under neutral or acidic conditions. In the presence of base, nitronate salts are formed by loss of formaldehyde.[14] With aqueous base, 2-fluoro-2,2-dinitroethanol is the only one of the above alcohols with a sufficient equilibrium concentration of alkoxide ion to react with alkyl sulfates, allyl halides, or epoxides.[13]

Reactions of nitro alcohols with triflates were generally conducted in chlorinated hydrocarbon solvents. To avoid side reactions due to liberated triflic acid, anhydrous potassium carbonate or sodium sulfate was added as a heterogeneous acid scavenger. 2,2,2-Trinitroethanol, 2,2-dinitropropanol, and 2,2-dinitropropanediol could not be alkylated in the presence of potassium carbonate because deformylation took place.

In the presence of potassium carbonate, 2-fluoro-2,2-dinitroethanol reacted at ambient temperature with pentyl triflate, allyl triflate, propargyl triflate, 1,4-butaneditriflate, and 2-(2-fluoro-2,2-dinitroethoxy)-ethyl triflate to give the corresponding 2-fluoro-2,2-dinitroethyl ethers in yields of 43 to 75%.

$$ROSO_2CF_3 + FC(NO_2)_2CH_2OH \xrightarrow{K_2CO_3} ROCH_2CF(NO_2)_2$$

R = C_5H_{11}–, $CH_2{=}CHCH_2$–, $HC{\equiv}CCH_2$–, $-CH_2CH_2CH_2CH_2-$, $FC(NO_2)_2CH_2OCH_2CH_2-$

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TABLE I
PREPARATION OF TRIFLATES

Starting material	Registry no.	Product	Registry no.	Yield, %
n-$C_5H_{11}OH$	71-41-0	n-$C_5H_{11}OSO_2CF_3$	41029-43-0	85
$(CH_3)_2CHOH$	67-63-0	$(CH_3)_2CHOSO_2CF_3$	41029-44-1	82
$CH_2{=}CHCH_2OH$	107-18-6	$CH_2{=}CHCH_2OSO_2CF_3$	41029-45-2	75
$HC{\equiv}CCH_2OH$	107-19-7	$HC{\equiv}CCH_2OSO_2CF_3$	41029-46-3	80
$FC(NO_2)_2CH_2OH$	17003-75-7	$FC(NO_2)_2CH_2OSO_2CF_3$	41828-25-5	42
$FC(NO_2)_2CH_2OCH_2CH_2OH$	25172-17-2	$FC(NO_2)_2CH_2OCH_2CH_2OSO_2CF_3$	41029-48-5	87
$CH_2CH_2CH_2CH_2O$	109-99-9	$CF_3SO_2O(CH_2)_4OSO_2CF_3$	18934-34-4	73
$CH_2(OH)CH(OH)CH_2OH$	56-81-5	$CH_2(OSO_2CF_3)CH(OSO_2CF_3)CH_2OSO_2CF_3$	41029-50-9	98
$(CH_3)_2SO_4$	77-78-1	$CH_3OSO_2CF_3$	333-27-7	81

Application of the same reaction conditions to 2,2,2-trifluoroethanol and pentyl triflate gave an 86% yield of pentyl 2,2,2-trifluoroethyl ether.

$$CH_3(CH_2)_4OSO_2CF_3 + CF_3CH_2OH \xrightarrow{K_2CO_3} CH_3(CH_2)_4OCH_2CF_3$$

The reaction of 2-fluoro-2,2-dinitroethanol with 1,2,3-propanetritriflate in the presence of potassium carbonate gave 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate. No other products were observed when the reaction was not carried to completion. 1,2,3-Propanetritriflate did not react with potassium carbonate in the absence of 2-fluoro-2,2-dinitroethanol or with 2-fluoro-2,2-dinitroethanol in the presence of sodium sulfate. The product could be formed by displacement of a terminal triflate group followed by rapid elimination of triflic acid, or possibly *via* the initial elimination of triflic acid by the base, fluorodinitroethoxide ion.

$$CF_3SO_3CH_2CH(CF_3SO_3)CH_2(CF_3SO_3) \xrightarrow[K_2CO_3,\ CHCl_3]{FC(NO_2)_2CH_2OH}$$

$$[FC(NO_2)_2CH_2OCH_2CH(CF_3SO_3)CH_2(CF_3SO_3)] \xrightarrow{-CF_3SO_3H}$$

$$FC(NO_2)_2CH_2OCH_2{-}\underset{\displaystyle OSO_2CF_3}{\underset{|}{CH}}{=}CH_2$$

The reaction of 2-fluoro-2,2-dinitroethyl triflate with 2-fluoro-2,2-dinitroethanol in the presence of potassium carbonate was also attempted. No fluorodinitroethyl ether was formed and the triflate was decomposed. This reaction appears similar to that of 2-fluoro-2,2-dinitroethyl tosylate with alkoxides, which was reported to result in elimination of nitrous acid.[15]

Potassium carbonate functioned in the above reactions not only as a scavenger for triflic acid but also as a heterogeneous base catalyst. In order to study alkylations of neutral alcohols, rather than of the corresponding alkoxide ions, an essentially nonbasic scavenger is required. Sodium sulfate was used for this purpose because sulfuric acid is a weaker acid than triflic acid, and the equilibrium mixture should consist of sodium triflate and sodium bisulfate. Also, the moderately soluble triflic acid should be adsorbed physically.

The use of sodium sulfate instead of potassium carbonate, however, required the use of extended reactions periods or higher temperatures. Thus, under the same experimental conditions that produced a 75% yield of 2-fluoro-2,2-dinitroethyl pentyl ether from 2-fluoro-2,2-dinitroethanol and pentyl triflate, no reaction was observed when sodium sulfate was substituted for potassium carbonate. Sodium sulfate, however, allowed extension of the reaction to base-sensitive alcohols, such as 2,2-dinitropropanol and 2,2,2-trinitroethanol.

Pentyl triflate and 2,2-dinitropropanol reacted in refluxing 1,2-dichloroethane, with sodium sulfate as the acid scavenger, to give a 38% yield of 2,2-dinitropropyl pentyl ethers. This product consisted of 33.5% 1-pentyl ether, 58.8% 2-pentyl ether, and 7.6% 3-pentyl ether, and the products were shown to be stable to the reaction conditions. The potassium carbonate catalyzed reactions of 2-fluoro-2,2-dinitroethanol and pentyl triflate, on the other hand, gave no detectable secondary ethers. The reaction in the presence of sodium sulfate thus has the characteristics of a carbonium ion reaction, even with a relatively nonpolar solvent.

$$CH_3CH_2CH_2CH_2CH_2OSO_2CF_3$$

$$\downarrow -CF_3SO_3^-$$

$$[CH_3CH_2CH_2CH_2CH_2^+] \xrightarrow{CH_3C(NO_2)_2CH_2OH} CH_3CH_2CH_2CH_2CH_2OCH_2C(NO_2)_2CH_3$$

$$\downarrow$$

$$[CH_3CH_2CH_2\overset{+}{C}HCH_3] \longrightarrow CH_3CH_2CH_2\underset{\displaystyle OCH_2C(NO_2)_2CH_3}{\underset{|}{CH}}CH_3$$

$$\downarrow$$

$$[CH_3CH_2\overset{+}{C}HCH_2CH_3] \longrightarrow CH_3CH_2\underset{\displaystyle OCH_2C(NO_2)_2CH_3}{\underset{|}{CH}}CH_2CH_3$$

At ambient temperature isopropyl triflate in the presence of sodium sulfate reacted with 2-fluoro-2,2-dinitroethanol, 2,2-dinitropropanol, and 2,2,2-trinitroethanol to give the corresponding isopropyl ethers in yields of 75, 67, and 37%, respectively. Methylene chloride or chloroform was used as solvent, and the reactions were allowed to proceed for 12 hr.

$$(CH_3)_2CHOSO_2CF_3 + XC(NO_2)_2CH_2OH \longrightarrow (CH_3)_2CHOCH_2C(NO_2)_2X$$

$$X = F,\ CH_3,\ NO_2$$

Allyl triflate was reacted similarly with 2,2-dinitropropanol, 2,2,2-trinitroethanol, and 2,2-dinitro-1,3-propanediol to give allyl 2,2-dinitropropyl ether, allyl 2,2,2-trinitroethyl ether, and 2,2-dinitro-1,3-di(allyloxy)propane in yields of 53, 33, and 28%, respectively. In the latter case, no attempt was made to isolate the monoallyl ether which was undoubtedly also present.

$$CH_2{=}CHCH_2OSO_2CF_3 + CH_3C(NO_2)_2CH_2OH \longrightarrow CH_2{=}CHCH_2OCH_2C(NO_2)_2CH_3$$

$$CH_2{=}CHCH_2OSO_2CF_3 + (NO_2)_3CCH_2OH \longrightarrow CH_2{=}CHCH_2OCH_2C(NO_2)_3$$

$$CH_2{=}CHCH_2OSO_2CF_3 + (NO_2)_2C(CH_2OH)_2 \longrightarrow (CH_2{=}CHCH_2OCH_2)_2C(NO_2)_2$$

(15) H. G. Adolph, *J. Org. Chem.*, **36**, 806 (1971).

The fact that isopropyl triflate and allyl triflate react at ambient temperature with such a highly electronegatively substituted alcohol as 2,2,2-trinitroethanol is noteworthy. By contrast, 2,2,2-trinitroethanol and methyl triflate gave no methyl 2,2,2-trinitroethyl ether when the reagents were heated in refluxing 1,2-dichloroethane for 45 hr.

The above examples illustrate the use of these alkylating agents where less potent reagents do not react. These reagents should also be useful for alkylating normally reactive hydroxyl groups with other substituents that cannot tolerate acid or base, or that are thermally unstable. The reactivity of isopropyl triflate with normal alcohols was demonstrated using pentanol. A diluted methylene chloride solution of the reactants, stirred for 1 hr with sodium sulfate at ambient temperature, gave a 52% yield of isopropyl pentyl ether.

Thus, alkyl triflates that are too unstable for normal isolation and analysis can be prepared conveniently, diluted in unreactive solvents, and utilized as powerful alkylating agents under neutral conditions.

Experimental Section

General.—Explosive properties of polynitro ethers described below have not been investigated. Adequate safety shielding should be used in all operations. 2-Fluoro-2,2-dinitroethanol[16] is a severe skin irritant and contact should be avoided.

Proton and fluorine nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane and trichlorofluoromethane as the respective internal standards. Gas chromatographic separations were carried out on a Varian 920 instrument using a 12 ft × 3/8 in. aluminum column packed with 12% QF-1 on 60/80 mesh Chromosorb W. Infrared spectra were obtained with a Perkin-Elmer 700 instrument.

Trifluoromethanesulfonic Anhydride.—The published procedure[17] was used with the exception that the amount of phosphorus pentoxide was reduced by 50%. The yield was 73%, bp 82–84°.

Methyl Triflate.—Trifluoromethanesulfonic acid (50 g, 0.030 mol) was added with stirring to 45.5 g (0.36 mol) of dimethyl sulfate. Distillation through a short Vigreux column gave 42.2 g (81%) of methyl triflate, bp 98–99° (reported[18] bp 97°), nmr (CCl_4) δ 4.22 ppm (s).

1,4-Butanediditriflate.—A solution of 2.16 g (0.030 mol) of tetrahydrofuran in 100 ml of methylene chloride was added dropwise to a solution of 9.90 g (0.030 mol) of trifluoromethanesulfonic anhydride in 100 ml of methylene chloride at −78°. The reaction mixture was allowed to warm to room temperature and was washed with water and dried over sodium sulfate. Evaporation of solvent and recrystallization of the residue from methylene chloride gave 7.75 g (73%) of colorless crystals: mp 35–37°; proton nmr ($CDCl_3$) δ 4.63 (m, 4 H, CH_2O), and 2.03 ppm (m, 4 H, CH_2CH_2O); fluorine nmr ϕ 75.1 ppm (s); ir (CCl_4) 1403, 1200, 1138, and 920 cm^{-1} (OSO_2CF_3).

Anal. Calcd for $C_6H_8F_6O_6S_2$: C, 20.34; H, 2.27. Found: C, 20.30; H, 1.90.

Pentyl Triflate.—A solution of 1.76 g (0.020 mol) of pentanol and 1.58 g (0.020 mol) of pyridine in 5 ml of methylene chloride was added, dropwise with stirring, over a 45-min period, to a solution of 6.60 g (0.023 mol) of triflic anhydride in 20 ml of methylene chloride at 0°. After 15 min, the solution was washed with water, dried over sodium sulfate, and distilled to give 3.74 g (85%) of pentyl triflate: bp 53–54° (1 mm); proton nmr ($CDCl_3$) δ 4.55 (t, 2 H, CH_2O), 1.85 (m, 2 H, CH_2CH_2O), 1.45 (m, 4 H, CH_2), and 1.27 ppm (t, 3 H, CH_3): fluorine nmr ϕ 75.3 ppm (s, OSO_2CF_3); ir (CCl_4) 1425, 1200, 1140, and 930 cm^{-1} (OSO_2CF_3).

Anal. Calcd for $C_6H_{11}F_3O_3S$: C, 32.72; H, 5.03; F, 25.90. Found: C, 33.35; H, 4.88; F, 25.44.

Isopropyl Triflate.—A solution of 2.7 g (0.045 mol) of isopropyl alcohol and 3.6 g (0.045 mol) of pyridine in 15 ml of carbon tetrachloride was added dropwise with stirring at 0° to 12.7 g (0.045 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. Nmr analysis of the colorless solution indicated a 90 ± 5% yield of isopropyl triflate. In another experiment using methylene chloride as solvent, the organic layer was washed with water, dried, and concentrated. The residue could be vacuum transferred at ambient temperature (5 mm) to give a colorless liquid which darkened rapidly at room temperature. The compound decomposed suddenly on attempted vacuum distillation at 50°: proton nmr (CCl_4) δ 5.16 (septet, J = 7 Hz, 1 H, CH) and 1.50 ppm (d, 6 H, J = 7 Hz, CH_3); fluorine nmr ϕ 76.7 (s).

Allyl Triflate.—A solution of 1.31 g (0.0234 mol) of allyl alcohol and 1.84 g (0.0234 mol) of pyridine in 5 ml of carbon tetrachloride was added dropwise (15 min) with stirring at 0° to a solution of 7.75 g (0.0234 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. The insoluble pyridine salt was removed by filtration through sodium sulfate. The resulting colorless solution was analyzed by ir and nmr and used directly for alkylation reactions. Quantitative nmr analysis (chlorobenzene as internal standard) of aliquots indicated yields of 75 ± 5%. Impurities could not be detected by nmr or ir analysis: proton nmr (CCl_4) δ 6.03 (m, 1 H, —CH=), 5.43 (m, 2 H, $=CH_2$), and 4.92 ppm (m, 2 H, CH_2O): fluorine nmr ϕ 74.5 ppm (s); ir (CCl_4) 1625 (C=C), 1405, 1240, 1190, and 1140 cm^{-1} (OSO_2CF_3).

Propargyl Triflate.—A solution of 1.33 g (0.0241 mol) of propargyl alcohol and 1.88 g (0.024 mol) of pyridine in 5 ml of carbon tetrachloride was added dropwise at 0° with stirring to 7.87 g (0.028 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. The solution was filtered through sodium sulfate and used directly for alkylation reactions. The yield (nmr) was 80 ± 5%; proton nmr (CCl_4) δ 5.05 (d, 2 H, J = 2 Hz, $C{\equiv}CCH_2O$), and 2.77 ppm (t, 1 H, J = 2 Hz, $C{\equiv}CH$); fluorine nmr ϕ 74.0 ppm (s, OSO_2CF_3); ir (CCl_4) 3290, 2145 ($C{\equiv}CH$), 1410, 1210, 1140 cm^{-1} (OSO_2CF_3).

2-(2-Fluoro-2,2-dinitroethoxy)ethyl Triflate.—A solution of 20.6 g (0.104 mol) of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether[13] and 8.22 g (0.108 mol) of pyridine in 50 ml of methylene chloride was added dropwise over a period of 45 min with stirring to a solution of 29.3 g (0.104 mol) of trifluoromethanesulfonic anhydride in 100 ml of methylene chloride at 0°. After 15 min the mixture was washed with water and dried over sodium sulfate. Evaporation of solvent left a pale yellow oil, which was filtered through silica gel to give 29.1 g (87%) of the triflate: proton nmr ($CDCl_3$) δ 4.70 (d, 2 H, J_{HF} = 17 Hz, $FC{-}CH_2O$) 4.68 (m, 2 H, OCH_2CH_2OTr), and 4.05 ppm (m, 2 H, OCH_2CH_2OTr); fluorine nmr ϕ 110.9 (t, 1 F, J_{HF} = 17 Hz, $F{-}CCH_2{-}$) and 75.4 ppm (s, 3 F, CF_3SO_3O); ir (CCl_4) 1585 (NO_2), 1310, 1210, 1140 cm^{-1} (OSO_2CF_3).

Anal. Calcd for $C_5H_6F_4N_2O_8S$: C, 18.18; H, 1.83; N, 8.48. Found: C, 18.65; H, 1.82; N, 8.16.

1,2,3-Propanetritriflate.—A mixture of 6.14 g (0.067 mol) of glycerol and 16.9 g (0.214 mol) of pyridine was added to a solution of 60.0 g (0.213 mol) of trifluoromethanesulfonic anhydride in 150 ml of methylene chloride over a 30-min period at 0°. Filtration through silica gel and removal of solvent gave 32 g (98% yield) of analytically pure 1,2,3-propanetritriflate: mp 22–23° (from carbon tetrachloride); proton nmr ($CDCl_3$) δ 5.17 (m, 1 H, CH) and 4.67 ppm (d, J = 2.7 Hz, 4 H, CH_2O); fluorine nmr ϕ 74.67 (s, 6 F, $CH_2OSO_2CF_3$) and 74.87 ppm (s, 3 F, $CHOSO_2CF_3$).

Anal. Calcd for $C_6H_5S_3F_9O_9$: C, 14.76; H, 1.03; F, 35.04. Found: C, 14.60; H, 0.86; F, 35.10.

2-Fluoro-2,2-dinitroethyl Triflate.—By the above procedure 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 7.9 g (0.10 mol) of pyridine were treated with 28.2 g (0.10 mol) of trifluoromethanesulfonic anhydride. The crude product was filtered through silica gel and then was distilled to give 12.0 g (42%) of the triflate: bp 36–38° (0.5 mm); proton nmr (CCl_4) δ 5.38 ppm (d, J_{HF} = 14 Hz); fluorine nmr ϕ 81.0 (s, 3 F, OSO_2CF_3) and 111.0 ppm (t, 1 F, J_{HF} = 14 Hz, $F{-}CCH_2$); ir (CCl_4) 1590, 1425, 1300, 1220, 1135, and 1000 cm^{-1} (OSO_2CF_3).

Anal. Calcd for $C_3H_2F_4N_2O_7S$: C, 12.56; H, 0.71. Found: C, 12.43; H, 0.61.

1,2-Bis(2-fluoro-2,2-dinitroethoxy)ethane.—To a stirred solution of 16.5 g (0.050 mol) of 2(2-fluoro-2,2-dinitroethoxy)ethyl triflate and 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol in 100

(16) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(17) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(18) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

ml of methylene chloride was added 34.5 g (0.25 mol) of anhydrous potassium carbonate. Stirring was continued for 16 hr and then the reaction mixture was added to ice–water and the organic phase was washed with 5% aqueous sodium hydroxide solution and dried over sodium sulfate. Removal of solvent gave 13.03 g (78%) of 1,2-bis(2-fluoro-2,2-dinitroethoxy)ethane, bp 117–119° (0.01 mm), which solidified on standing at 0°: mp 28–29°; d^{25} 1.539; nmr ($CDCl_3$) δ 4.57 (d, 4 H, J_{HF} = 16 Hz, FC–CH_2O) and 3.80 ppm (s, 4 H, OCH_2CH_2O); ir ($CDCl_3$) 1590, 1310, and 1120 cm^{-1} (C–O–C).

Anal. Calcd for $C_6H_8F_2N_4O_{10}$: C, 21.56; H, 2.41; N, 16.76. Found: C, 21.19; H, 2.20; N, 16.46.

2-Fluoro-2,2-dinitroethyl Pentyl Ether.—The reaction of 2.20 g (0.010 mol) of pentyl triflate and 1.54 g (0.010 mol) of 2-fluoro-2,2-dinitroethanol by the above procedure gave 1.64 g (73%) 2-fluoro-2,2-dinitroethyl pentyl ether: bp 46–48° (0.04 mm); nmr (CCl_4) δ 4.43 (d, 2 H, J_{HF} = 17 Hz, FC–CH_2O), 3.90 (t, 2 H, J = 6 Hz, OCH_2), 1.27 (broad m, 6 H, CH_2), and 0.87 ppm (m, 3 H, CH_3); ir (CCl_4) 1590, 1305 (NO_2), and 1120 cm^{-1} (C–O–C).

Anal. Calcd for $C_7H_{13}FN_2O_5$: C, 37.49; H, 5.84. Found: C, 37.78; H, 5.46.

Allyl 2-Fluoro-2,2-dinitroethyl Ether.—By the same procedure a solution of 0.03 mol of allyl triflate in carbon tetrachloride (described above) was reacted with 5.39 g (0.035 mol) of 2-fluoro-2,2-dinitroethanol and 13.8 g (0.10 mol) of potassium carbonate in 50 ml of methylene chloride for 3 hr to give 2.75 g (47%) of allyl 2-fluoro-2,2-dinitroethyl ether, bp 34–35° (0.2 mm), which had ir and nmr spectra identical with those of an authentic sample.[13]

2-Fluoro-2,2-dinitroethyl Propargyl Ether.—By the above procedure, 0.0238 mol of propargyl triflate solution, 4.59 g (0.0298 mol) of 2-fluoro-2,2-dinitroethanol and 10 g (0.07 mol) of potassium carbonate in 30 ml of methylene chloride (12 hr) gave 1.93 g (43%) of 2-fluoro-2,2-dinitroethyl propargyl ether, bp 32–34° (0.1 mm), which had ir and nmr spectra identical with those of an authentic sample.[19]

1,4-Bis(2-fluoro-2,2-dinitroethoxy)butane.—A mixture of 3.54 g (0.10 mol) 1,4-butaneditriflate, 6.16 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol, and 23 g (0.167 mol) of potassium carbonate was stirred 18 hr at ambient temperature. The mixture was diluted with water, and the product was extracted with methylene chloride, dried over sodium sulfate, stripped of solvent, and purified by column chromatography on silica gel to give 2.71 g (75%) of 1,4-bis(2-fluoro-2,2-dinitroethoxy)butane, a colorless oil: proton nmr ($CDCl_3$) δ 4.52 (d, 4 H, J_{HF} = 18 Hz, FC–CH_2O), 3.63 (m, 4 H, OCH_2C), and 1.63 ppm (m, 4 H, CH_2CO); fluorine nmr ϕ 112.6 (t, J_{HF} = 18 Hz); ir (CCl_4) 1590, 1315 (NO_2).

Anal. Calcd for $C_8H_{12}F_2N_4O_{10}$: C, 26.52; H, 3.34; N, 15.46. Found: C, 26.82; H, 3.24; N, 14.93.

Reaction of 2-Fluoro-2,2-dinitroethanol and 1,2,3-Propanetritriflate.—To a stirred solution of 5.0 g (0.0124 mol) of 1,2,3-propanetritriflate and 5.3 g (0.0344 mol) of 2-fluoro-2,2-dinitroethanol in 15 ml of chloroform was added to 5.5 g (0.040 mol) of potassium carbonate, and the mixture was stirred for 16 hr. The mixture was added to 100 ml of ice–water and the product was extracted with 50 ml of methylene chloride and dried over sodium sulfate. Distillation gave 2.6 g (61%) of 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate, bp 83° (0.2 mm); proton nmr ($CDCl_3$) δ 5.31 (AB quartet, 2 H, CH_2=), 4.77 (d, 2 H, J_{HF} = 18 Hz, FC–CH_2), and 4.25 ppm (s, 2 H, CH_2O); fluorine nmr ϕ 111.2 (t, 1 F, FC) and 74.8 ppm (s, 3 F, OSO_2CF_3).

Anal. Calcd for $C_6H_6F_4N_2SO_8$: C, 21.06; H, 1.76. Found: C, 21.35; H, 1.88.

Pentyl 2,2,2-Trifluoroethyl Ether.—A mixture of 2.20 g (0.010 mol) of pentyl triflate, 1.10 g (0.010 mol) of 2,2,2-trifluoroethanol, 4.14 g (0.030 mol) of potassium carbonate, and 15 ml of methylene chloride was stirred for 48 hr. The mixture was washed with water, dried over sodium sulfate, and stripped of solvent. Vacuum transfer of the residue gave 1.46 g (86%) of pentyl 2,2,2-trifluoroethyl ether. An analytical sample was isolated by glpc: nmr (CCl_4) δ 3.73 (q, 2 H, J_{HF} = 8 Hz, OCH_2CF_3), 3.57 (t, 3 H, J = 6 Hz, O–CH_2CH_2), 1.92–1.08 (m, 6 H, CH_2), and 0.95 ppm (m, 3 H, CH_3).

Anal. Calcd for $C_7H_{13}F_3O$: C, 49.40; H, 7.70. Found: C, 49.42; H, 7.73.

(19) V. Grakauskas, *J. Org. Chem.*, in press.

Allyl 2,2,2-Trinitroethyl Ether.—A solution of (0.030 mol) of allyl triflate in carbon tetrachloride was added to 5.5 g (0.030 mol) of 2,2,2-trinitroethanol, 100 ml of methylene chloride, and 5 g of sodium sulfate, and the mixture was stirred for 48 hr. The mixture was washed with water and dried over sodium sulfate and the solvent was removed under vacuum. Column chromatography of the dark residue on silica gel gave 1.72 g (33%) of allyl 2,2,2-trinitroethyl ether, a pale yellow oil: nmr ($CDCl_3$) δ 5.83 (m, 1 H, —CH=C<), 5.30 (m, 2 H, =CH_2), 4.67 (s, 2 H, $CH_2C(NO_2)_3$), and 4.20 ppm (m, 2 H, OCH_2C=C); ir (CCl_4) 1630 (C=C); 1590, 1300 (NO_2), and 1120 cm^{-1} (–O–).

Anal. Calcd for $C_5H_7N_3O_7$: C, 27.15; H, 3.19; N, 19.00. Found: C, 27.26; H, 3.25; N, 18.88.

Allyl 2,2-Dinitropropyl Ether.—Substitution of 2,2-dinitropropanol for 2,2,2-trinitroethanol in the preceding experiment gave after chromatography, 2.36 g (53%) of allyl 2,2-dinitropropyl ether, a colorless oil: nmr (CCl_4) δ 5.63 (m, 1 H, CH=C), 5.23 (m, 2 H, =CH_2), 4.20 ppm (s, 2 H, $(NO_2)_2CCH_2O$), 4.03 (m, 2 H, OCH_2C=), and 2.17 ppm (s, 3 H, $CH_3C(NO_2)_2$); ir (CCl_4) 1630 (C=C), 1580, 1320 (NO_2), and 1100 cm^{-1} (–O–C).

Anal. Calcd for $C_6H_{10}N_2O_5$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.58; H, 5.27; N, 14.98.

2,2-Dinitro-1,3-di(allyloxy)propane.—By the above procedure, 1.83 g (0.011 mol) of 2,2-dinitro-1,3-propanediol was treated with (0.022 mol) of allyl triflate for 48 hr. The crude solution was washed with 5% sodium hydroxide to remove starting material and monoalkylation product. Chromatography on silica gel gave 0.755 g (28%) of the diallyl ether: nmr (CCl_4) δ 5.77 (m, 2 H, CH=C), 5.43 (m, 4 H, =CH_2), 4.27 (s, 4 H, $OCH_2C(NO_2)_2$), and 4.03 ppm (m, 4 H, OCH_2C); ir (CCl_4) 1625 (C≡C), 1582, 1320 (NO_2), and 1095 cm^{-1} (C–O–C).

Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.89; H, 5.73; N, 11.38. Found: C, 43.34; H, 5.69; N, 11.29.

Reaction of 2,2-Dinitropropanol with Pentyl Triflate.—A mixture of 4.0 g (0.0182 mol) of pentyl triflate and 4.1 g (0.0273 mol) of 2,2-dinitropropanol, 5 g of sodium sulfate, and 50 ml of 1,2-dichloroethane was refluxed for 6 hr. The mixture was washed with water and with 5% sodium hydroxide, dried over sodium sulfate, stripped of solvent, and chromatographed on silica gel to give 1.52 g (38%) of a mixture of three 2,2-dinitropropyl pentyl ethers (glpc area ratio 0.13:1:0.57 in the order of retention times).

The major component was 2,2-dinitropropyl 2-pentyl ether: nmr (CCl_4) δ 5.87 (s, 2 H, $C(NO_2)_2CH_2O$), 3.50 (m, 1 H, O–CH–), 2.17 (s, 3 H), $CH_3C(NO_2)_2$), 1.40 (broad m, 4 H, CH_2), 1.15 (d, 3 H, J = 6 Hz, CH_3CHO), and 0.90 ppm (m, 3 H, CH_3); ir (CCl_4) 1560 and 1320 cm^{-1} (NO_2).

Anal. Calcd for $C_8H_{16}N_2O_5$: C, 43.62; H, 7.32. Found: C, 43.21; H, 7.20.

The third component was identified as 2,2-dinitropropyl 1-pentyl ether: nmr (CCl_4) δ 4.17 (s, 2 H, $C(NO_2)_2CH_2$), 3.50 (t, 2 H, J = 6 Hz, OCH_2), 2.15 (s, 3 H, $CH_3C(NO_2)_2$), 1.37 (broad m, 6 H, CH_2), and 0.90 (m, 3 H, CH_3); ir (CCl_4) 1560, 1320, and 1110 cm^{-1} (C–O–C).

Anal. Calcd for $C_8H_{16}N_2O_5$: C, 43.62; H, 7.32; N, 12.72. Found: C, 43.53; H, 7.04; N, 13.02.

The least abundant component was not isolated in sufficient quantity for elemental analysis, but the nmr spectrum indicated that the compound was 2,2-dinitropropyl 3-pentyl ether: nmr (CCl_4) δ 4.20 (s, 2 H, $CH_2C(NO_2)_2$), 3.47 (m, 1 H, CH_2CHCH_2), 2.17 (s, 3 H, $C(NO_2)_2CH_3$), and 1.7–0.7 (broad m, 10 H).

2-Fluoro-2,2-dinitroethyl Isopropyl Ether.—A mixture of 1.54 g (0.010 mol) of 2-fluoro-2,2-dinitroethanol, 1.92 g (0.010 mol) of isopropyl triflate, 3 g of sodium sulfate, and 3 ml of chloroform was stirred for 12 hr at ambient temperature. The solution was washed with water and with 5% sodium hydroxide, dried, and distilled to give 1.45 g (74%) of 2-fluoro-2,2-dinitroethyl isopropyl ether: bp 52° (0.4 mm); proton nmr (CCl_4) δ 4.38 (d, 2 H, J_{HF} = 18 Hz, CH_2), 3.37 (septet, 1 H, J = 7 Hz, CH_3), and 1.11 (d, 6 H, J = 7 Hz, CH_3); fluorine nmr ϕ 111.5 ppm (t, J_{HF} = 18 Hz).

Anal. Calcd for $C_5H_9FN_2O_5$: C, 30.61; H, 4.62. Found: C, 30.86; H, 4.65.

2,2-Dinitropropyl Isopropyl Ether.—By the above procedure, using methylene chloride as solvent, 7.70 g (0.05 mol) of 2,2-dinitropropanol and (0.040 mol) of isopropyl triflate (12 hr) gave 5.14 g (67%) of 2,2-dinitropropyl isopropyl ether: bp 45–47° (0.07 mm); nmr (CCl_4) δ 4.13 (s, 2 H, $C(NO_2)_2CH_2O$), 3.62 (septet, 1 H, J = 6 Hz), 2.13 (s, 3 H, $CH_3C(NO_2)_2$), and 1.15

ppm (d, 6 H, J = 6 Hz, $(CH_3)_2C$); ir (CCl_4) 1560, 1320 (NO_2), and 1110 cm^{-1} (C–O–C).

Anal. Calcd for $C_6H_{12}N_2O_5$: C, 37.49; H, 6.30. Found: C, 37.62; H, 6.36.

Isopropyl 2,2,2-Trinitroethyl Ether.—Isopropyl triflate (0.040 mol) and 2,2,2-trinitroethanol (9.05 g, 0.050 mol) were allowed to react using the above procedure, except that washing with sodium hydroxide solution was omitted and the crude product was passed through a short column of silica gel to give isopropyl 2,2,2-trinitroethyl ether in 38% yield. The analytical sample was distilled in a molecular still at 0.1 mm, bath temperature 50°: nmr (CCl_4) δ 4.60 (s, 2 H, CH_2), 3.80 (septet, 1 H, J = 7 Hz, CH), and 1.25 ppm (d, 6 H, J = 6 Hz, CH_3); ir (CCl_4) 1565, 1315 (NO_2), and 1120 cm^{-1} (C–O–C).

Anal. Calcd for $C_5H_9N_3O_7$: C, 26.91; H, 4.06. Found: C, 27.30; H, 4.29.

Reaction of Isopropyl Triflate with Pentanol.—A mixture of 0.44 g (0.0050 mol) of pentanol, 0.95 g (0.0050 mol) of isopropyl triflate, 1.0 g of sodium sulfate, and 10 ml of methylene chloride was stirred for 1 hr. The mixture was washed with 30 ml of water, dried, and stripped of solvent. Vacuum transfer of the residue gave 0.57 g of a mixture containing 60% isopropyl pentyl ether (52% conversion) and 40% 1-pentanol, separated by glpc and compared with authentic samples. A reference sample of isopropyl pentyl ether was prepared by the reported method:[20] bp 131–132°; nmr (CCl_4) δ 3.40 (septet, 1 H, J = 6 Hz, CHO), 3.27 (t, 2 H, J = 6 Hz, CH_2O), 1.37 (m, 6 H, CH_2), 1.08 (d, 6 H, J = 6 Hz, $(CH_3)_2C$), and 0.90 ppm (m, 3 H, CH_3).

Registry No.—Trifluoromethanesulfonic anhydride, 358-23-6; 1,2-bis(2-fluoro-2,2-dinitroethoxy)ethane, 41029-52-1; 2-fluoro-2,2-dinitroethyl pentyl ether, 41029-53-2; allyl 2-fluoro-2,2-dinitroethyl ether, 25171-99-7; 2-fluoro-2,2-dinitroethyl propargyl ether, 40696-43-3; 1,4-bis(2-fluoro-2,2-dinitroethoxy)butane, 41029-56-5; 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate, 41029-57-6; pentyl 2,2,2-trifluoroethyl ether, 41029-58-7; allyl 2,2,2-trinitroethyl ether, 41029-59-8; allyl 2,2-dinitropropyl ether, 41029-60-1; 2,2-dinitro-1,3-di(allyloxy)propane, 41029-61-2; 2,2-dinitropropyl 2-pentyl ether, 41029-62-3; 2,2-dinitropropyl 1-pentyl ether, 41029-63-4; 2,2-dinitropropyl 3-pentyl ether, 41029-64-5; 2-fluoro-2,2-dinitroethyl isopropyl ether, 41029-65-6; 2,2-dinitropropyl isopropyl ether, 41029-66-7; isopropyl 2,2,2-trinitroethyl ether, 41029-67-8; 2,2,2-trifluoroethanol, 75-89-8; 2,2,2-trinitroethanol, 918-54-7; 2,2-dinitropropanol, 918-52-5; 2,2-dinitro-1,3-propanediol, 2736-80-3; isopropyl pentyl ether, 5756-37-6; trifluoromethanesulfonic acid, 1493-13-6; tetrahydrofuran, 109-99-9.

(20) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5747 (1965).

Stereochemistry in the Solvolytic Ring Contraction of 2,2,4aα-Trimethyl-1-decalyl Methanesulfonate. A Model Reaction Pertaining to Triterpene Biogenesis[1a]

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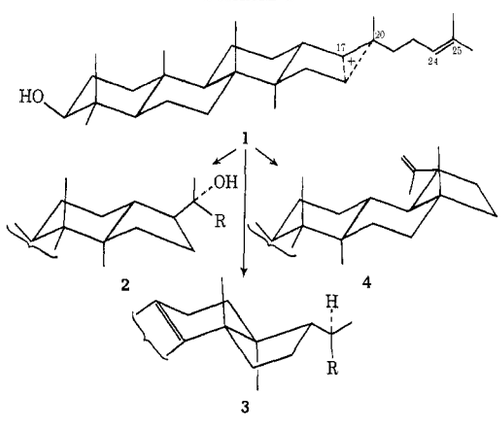
2,2,4aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-ol (**5**-OH) and its 2β-trideuteriomethyl analog (**5**-d_3-OH) were synthesized by reduction-methylation of 4aβ-methyl-2-*n*-butylthiomethylene-3,4,4aβ,-5,6,7,8,8a(α and β)-octahydronaphthalen-1(2*H*)-ones (**8b**) and, after separation of the trans isomer from the mixture of trimethyldecalones (**9** and **10**), lithium–ammonia reduction. Solvolysis of the corresponding methanesulfonates (**5**-OMs and **5**-d_3-OMs) effects efficient ring contraction to 3aα,4,5,6,7,7aβ-hexahydro-3aα-methyl-1β-indanyldimethylcarbinol derivatives (**6**-OR and **6**-d_3-OR). Since the trideuteriomethyl group in the labeled product (**6**-d_3-OR) was equally distributed between the two diastereotopic positions, a bridged species (**21**), akin to a bridged ion (**1**) postulated in triterpene biogenesis, cannot be the sole intermediate in the rearrangement. Intervention of the classical tertiary carbocation (**22**) is presumed to cause the label distribution. Attempts to intercept the intermediate by azide trapping and the use of leaving groups bearing a second nucleophilic site (*o*-carboxysulfonate and *o*-thiocarboxysulfonate) were unsuccessful.

The hypothetical bridged ion **1** (Scheme I)[1c] represents a key branching point in the traditional schemes for the biogenesis of many tetracyclic and pentacyclic triterpenes.[2–4] Three different reaction modes are proposed for this intermediate: (a) direct capture by a water molecule to give dammarenediol I (**2**); (b) 17 → 20 hydride shift followed by a backbone rearrangement to tirucallol (**3**); (c) cyclization into the side chain double

SCHEME I



(1) (a) Taken in part from the Ph.D. Thesis of S. K. C., University of Illinois, 1972. (b) A. P. Sloan Foundation Fellow, 1971–1973. (c) The carbonium ion intermediates in such biogenetic schemes are represented by the bridged type formulation (*e.g.*, **1**) chiefly as a convenient method to correlate and predict the stereochemistry of the individual transformations. The importance of internal stabilization due to delocalization *via* bridging in the course of the biosynthetic transformation remains a matter of speculation.

(2) (a) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); (b) G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, **77**, 5069 (1955); (c) L. Rúzicka, *Proc. Chem. Soc.*, 341 (1959).

(3) For reviews and discussion see (a) G. Ourisson, P. Crabbé, and O. R. Rodig, "Tetracyclic Triterpenes," Holden-Day, San Francisco, Calif., 1964; (b) T. A. Geissman and D. H. G. Crout, "Organic Chemistry of Secondary Plant Metabolism," W. H. Freeman, San Francisco, Calif., 1969; (c) J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins," W. A. Benjamin, New York, N. Y., 1964; (d) K. B. Sharpless, Ph.D. Thesis, Stanford University, 1968.

(4) (a) A biogenetic scheme involving temporary nucleophilic interception of the carbonium ion at certain stages (X group) has recently been suggested. Although different in some stereochemical details, this scheme postulates similar stereoelectronically controlled mechanisms: J. W. Cornforth, *Angew. Chem., Int. Ed. Engl.*, **7**, 903 (1968). (b) A similar bridged ion in the E ring of β-amyrin has been proposed.[2a,c] Recent biosynthetic experiments have verified that the identity of the geminal E ring methyl groups is maintained in the predicted manner in the formation of the E ring of β-amyrin: T. Suga, T. Shishibori, and S. Komoto, *Chem. Lett.*, 313 (1972).

That the distinction between these two methyl groups is also preserved in the biosynthesis of lupeol and the related triterpenes, betulin and betulinic acid, has been verified by D. Arigoni and coworkers at the ETH, Zurich: L. Botta, Dissertation No. 4098 (1968); L. Guglielmetti, Dissertation No. 3299 (1962).