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RESEARCH IN ENERGETIC COMPOUNDS

by

K. Baum, P.T. Berkowitz, S.E. Bottomley and W.A. Vinson

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RESEARCH IN ENERGETIC COMPOUNDS

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3-Nitrooxetane
3-Azidooxetane
1-Fluoro-1-nitroethylene
2-Fluoro-2,2-dinitroethyl glycidyl ether
Polymerization

Nuclear magnetic resonance spectra
Infrared spectra
Chromatography

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

3-Chloro-2-hydroxy-1-propyl acetate, obtained from acetic acid and epichlorohydrin, was converted to its tetrahydropyranyl ether which was cyclized with base. Hydrolysis gave 3-hydroxyoxetane in 37% overall yield. This compound was converted to the tosylate, the bromide and the iodide, none of which underwent displacement by nitrite ion. The reaction of 3-oxetyl tosylate with potassium azide gave 3-azidooxetane which on hydrogenation gave 3-aminooxetane, also obtained from the tosylate and ammonia. Oxidation of the amine with m-

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20. ABSTRACT (cont'd.)

chloroperbenzoic acid gave 3-nitrooxetane.

Fluoronitromalonate esters were hydrolyzed to fluoronitroacetates, which, with formaldehyde gave the 2-fluoro-3-hydroxy-2-nitropropionates. The hydroxyls were protected as the tetrahydropyranyl ethers. Base hydrolysis of the ester groups followed by acid hydrolysis of the tetrahydropyranyl groups gave 2-fluoro-2-nitroethanol. Subsequently a one step synthesis of this compound from diethyl fluoronitromalonate, potassium carbonate and formaldehyde was developed. 1-Fluoro-1-nitroethylene was prepared by reactions of 2-fluoro-2-nitroethanol with acetic anhydride and potassium acetate, with phthalic anhydride and also with dicyclohexyl carbodiimide.

2-Fluoro-2,2-dinitroethyl glycidyl ether was polymerized with triflic acid, triflic acid hydrates and triflic anhydride to give polymers with molecular weights up to 1800. NMR evidence indicated that triflate esters were intermediates.

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I.   Introduction

This report summarizes the research under Contract N00014-78-C-0147 during the period 1 March 1979 through 29 February 1980. Work was continued in the area of nitrooxetane chemistry, leading to the first synthesis of 3-nitrooxetane. A convenient route to functional oxetane intermediates was developed. Work was initiated on the chemistry of 1-fluoro-1-nitroethylene, and new routes to this olefin were found. Additional studies of the polymerization of 2-fluoro-2,2-dinitroethyl glycidyl ether with acidic catalysts provided evidence for a novel polymerization pathway.

II. Oxetane Synthesis

A. Discussion

Previously on this program[1] 3-fluoro-3-nitrooxetane was synthesized and polymerized, and efforts were initiated to synthesize 3,3-dinitrooxetane. The method used for 3-fluoro-3-nitrooxetane, the base-catalyzed ring closure of the monotriflate of 2-fluoro-2-nitro-1,3-propanediol could not be applied to nonfluorinated analogs. Fluorine inhibits deformylation of adjacent methylol groups, an effect that is apparently critical for the ring closure. Triflates of 2,2-dinitropropanediol and of trihydroxymethylnitromethane gave only decomposition products.

$$HOCH_2\underset{NO_2}{\overset{F}{C}}CH_2OSO_2CF_3 \xrightarrow{OH^-} {}^-OCH_2\underset{NO_2}{\overset{F}{C}}CH_2OSO_2CF_3 \longrightarrow \text{[oxetane ring with } NO_2, F\text{]}$$

$$HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OSO_2CF_3 \xrightarrow{OH^-} \overset{NO_2}{\underset{NO_2}{\ominus C}}-CH_2OSO_2CF_3 \longrightarrow \left[\underset{NO_2}{\overset{NO_2}{C}=CH_2}\right] \longrightarrow \text{decomp}$$

$$(HOCH_2)_2\underset{NO_2}{C}CH_2OSO_2CF_3 \longrightarrow \left[HOCH_2\underset{NO_2}{C}=CH_2\right] \longrightarrow \text{decomp}$$
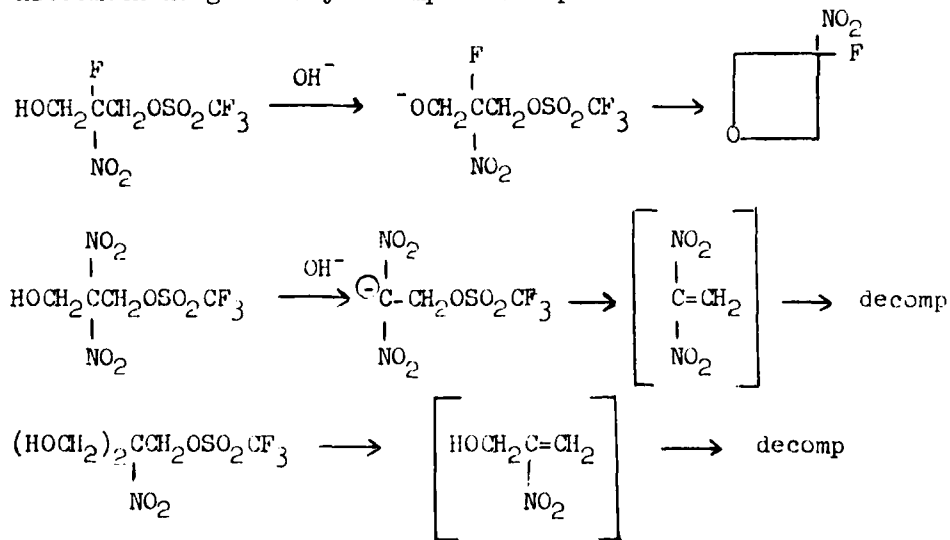
Consequently efforts to synthesize a nonfluorinated nitrooxetane were based on conversions of other functional groups on the oxetane ring to nitro groups. Known 3-functional oxetanes suitable for displacement reactions include the bromide, the iodide and the tosylate. The bromide and the iodide have been prepared from the tosylate which, in turn, was obtained from the

alcohol.[2]   The alcohol was prepared as follows:

$$CH_2=CH-CH_2OH \xrightarrow{Cl_2} ClCH_2-CH-CH_2OH \text{ (O-CH}_2\text{-CH=CH}_2\text{)} + CH_2-CH-CH_2OH \text{ (Cl / OCH}_2\text{-CH=CH}_2\text{)}$$

$$\xrightarrow[H_2O]{NaOH} \quad \xrightarrow[KOt\text{-}Bu]{DMSO} \quad \xrightarrow[H^+]{MeOH\text{-}H_2O}$$
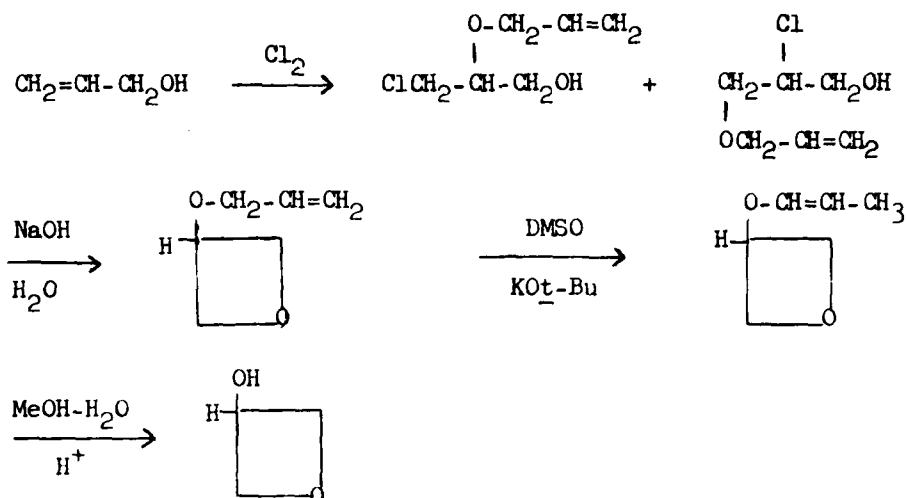
Chlorination of allyl alcohol, at only 20% conversion, was re-
ported to give a 65:35 mixture of 2-allyloxy-3-chloropropanol and 3-allyloxy-
2-chloropropanol, as well as a variety of other products. Treatment with
refluxing aqueous sodium hydroxide gave an 8% yield of 3-allyloxyoxetane.[3]
Treatment of allyl alcohol with 0.25 equivalent of t-butyl hypochlorite
and a catalytic amount of p-toluenesulfonic acid was reported to give a
similar mixture of the above alkoxychloropropanols.[4] We repeated the latter
reaction and converted the mixture to 3-allyloxyoxetane in 11% yield, based
on t-butyl hypochlorite.

Treatment of 3-allyloxyoxetane in dimethyl sulfoxide with potassium
tert-butoxide afforded 3-propenoxyoxetane in 85% yield.[2] 3-Hydroxyoxetane was
obtained in 84% yield after treatment of 3-propenoxyoxetane with a catalytic
amount of sulfuric acid in aqueous methanol for 5 days at room temperature.[2]

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A more satisfactory synthesis of 3-hydroxyoxetane was developed based on the acetic acid adduct of epichlorohydrin. The hydroxyl group was protected as the base-stable but acid-labile tetrahydropyranyl ether, and base treatment simultaneously hydrolyzed the ester and effected ring closure. This blocking prevented epoxide formation.
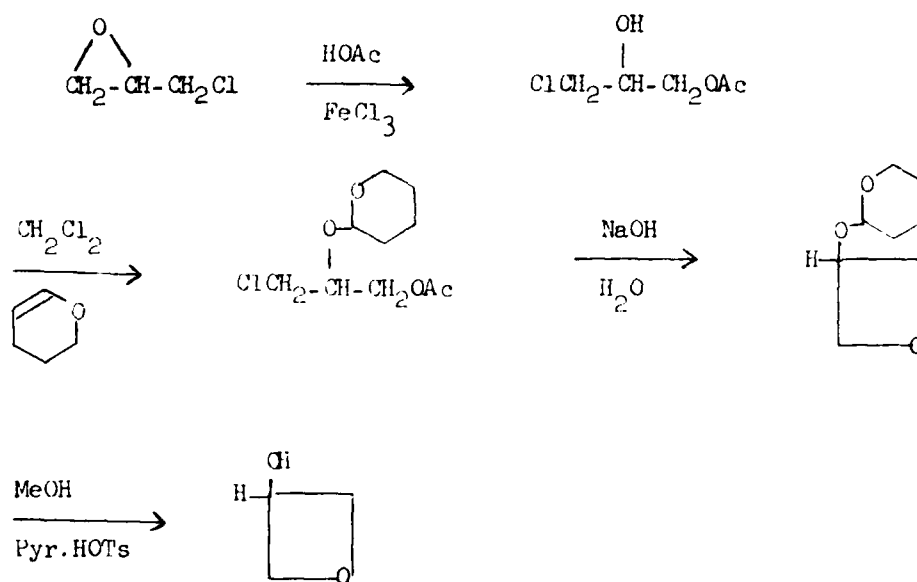
Reaction of epichlorohydrin in glacial acetic acid with a catalytic amount of anhydrous ferric chloride gave a 93% yield of 3-chloro-2-hydroxy-1-propyl acetate.[5] Treatment of 3-chloro-2-hydroxy-1-propyl acetate with dihydropyran in methylene chloride with a catalytic amount of pyridinium p-toluenesulfonate[6] afforded 3-chloro-2-tetrahydropyranyloxy-1-propyl acetate. Refluxing 3-chloro-2-tetrahydropyranyloxy-1-propyl acetate in aqueous sodium hydroxide for 17 hours gave 3-tetrahydropyranyloxyoxetane. Hydrolysis of the tetrahydropyranyl ether was effected by heating in methanol solution

with a catalytic amount of pyridinium p-toluenesulfonate. The overall yield of 3-hydroxyoxetane, based on epichlorohydrin, was 37%, and it was not necessary to purify the intermediate products.

Reported procedures[2] were used to prepare the halide and tosylate derivatives of 3-hydroxyoxetane. Attempts to convert the bromide to the nitro compound by displacements with nitrite ion were unsuccessful. 3-Bromooxetane did not react with silver nitrite in carbon tetrachloride over a 24 h period at room temperature. Neither did 3-bromooxetane react with sodium nitrite in N,N-dimethylformamide in 6 days at room temperature. Heating this mixture at 100°C for 24 h however, resulted in consumption of 3-bromooxetane, but 3-nitrooxetane was not detected.

3-Iodooxetane did not react with silver nitrite in carbon tetrachloride, acetonitrile, or ether in 3 days at room temperature. Reaction of 3-iodooxetane with sodium nitrite in N,N-dimethylformamide also failed to give 3-nitrooxetane. After 17 h at room temperature, no reaction had taken place, and, after 12 h at 100°C, 3-iodooxetane was decomposed.
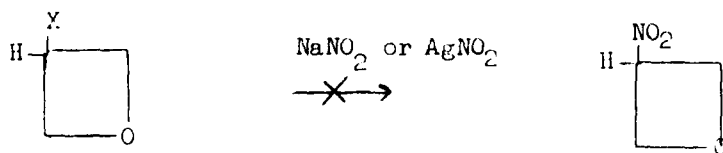
X = Br, I

The unreactivity of the above 3-halooxetanes is not altogether surprising. The displacement of 3-oxetyl tosylate with alkali metal halides in triethylene glycol required a temperature of about 170°C, and 3-iodooxetane did not react appreciably with diethylamine below 200°C.[2] Similarly,

reaction of 3,3-bis(iodomethyl) oxetane with silver nitrite in refluxing ether afforded only a 3% yield of 3,3-bis(nitromethyl) oxetane.[7]

As it has recently been shown that cyclohexylamine could be oxidized to nitrocyclohexane in 75% yield by the use of m-chloroperbenzoic acid,[8] consideration was next given to the oxidation of 3-aminooxetane to 3-nitrooxetane. 3-Aminooxetane has been prepared by the reduction at high pressure (1000 psi) of 3-oximinooxetane,[9] but the preparation of this starting material involved a multistep sequence.

More straightforward procedures were developed based on the available tosylate. Reaction of 3-oxetyl tosylate with potassium azide in hexamethylphosphoramide at $87^{\circ}C$ afforded 3-azidooxetane in a 50% isolated yield. Ring-opening of the oxetane by azide was a significant side reaction. Reaction of 3-oxetyl tosylate with potassium azide and 18-crown-6 in refluxing acetonitrile afforded only a 28% yield of 3-azidooxetane.

Hydrogenation of 3-azidooxetane at atmospheric pressure in methanol with 10% Pd-C afforded 3-aminooxetane in 57% isolated yield. It was also found that reaction of 3-oxetyl tosylate with ammonia at $110^{\circ}C$ for 16 h gave a 16% yield of 3-aminooxetane. It is possible that the ammonium p-toluenesulfonate formed in the above reaction is capable of effecting ring-opening of 3-aminooxetane.

Oxidation of 3-aminooxetane with four equivalents of m-chloroperbenzoic acid in refluxing 1,2-dichloroethane gave 3-nitrooxetane in 75% yield. The oxidative nitration of this product to yield dinitrooxetane will be investigated.

OTs → (KN₃ / HMPA) → N₃ → (MeOH / H₂) → NH₂ → ({O} / ClCH₂CH₂Cl) → NO₂

$$\text{OTs} \xrightarrow[\text{HMPA}]{\text{KN}_3} \text{N}_3 \xrightarrow[\text{H}_2]{\text{MeOH}} \text{NH}_2 \xrightarrow[\text{ClCH}_2\text{CH}_2\text{Cl}]{\{O\}} \text{NO}_2$$

NH₃, 100°C
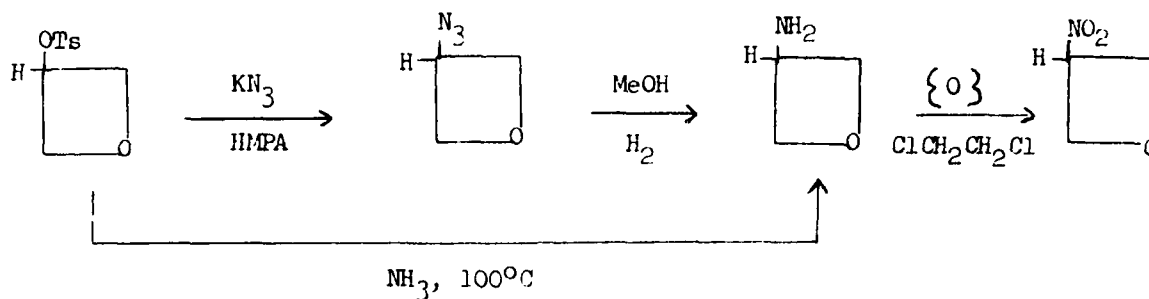
B. Experimental

3-Chloro-2-tetrahydropyranyloxy-1-propyl acetate. A solution of 271.9 g (1.78 moles) of 3-chloro-2-hydroxy-1-propyl acetate, 244 ml (2.67 moles) of freshly distilled dihydropyran, and 44.7 g (0.178 moles) of pyridinium p-toluenesulfonate in 1800 ml of methylene chloride was stirred at room temperature. After 30 min the reaction became exothermic enough to cause the methylene chloride to reflux. The reaction mixture was then cooled in an ice-bath and stirred overnight. After 2c h the reaction mixture was washed with 500 ml of water and 250 ml of half-saturated sodium chloride solution. The methylene chloride solution was then dried over sodium sulfate and solvent was removed in vacuo. After the residue was dried at 0.03 mm vacuum for 1.5 h, there remained 473.3 g of crude 3-chloro-2-tetrahydropyranyloxy-1-propyl acetate:
^{1}H NMR (CDCl₃) δ 1.63 (br. s, 6 H, (CH₂)₃); 2.09 (s, 3 H, CH₃CO); 3.5-4.3 (7 H, CH₂CHCH₂); 4.73 (br. s, 1 H, -O-CH); IR (neat, NaCl) 3000, 2910 (C-H); 1740 cm^{-1} (-O-CO-CH₃). The above THP ether is thermally unstable. Efforts to purify 3-chloro-2-tetrahydropyranyloxy-1-propyl acetate by gc or distillation resulted in removal of the THP group.

3-Tetrahydropyranyloxyoxetane. To 476 g of crude 3-chloro-2-tetrahydropyranyloxy-1-propyl acetate was added 216 g (5.4 moles) of sodium hydroxide in 500 ml of water. The reaction mixture was heated at reflux for 17 h. The upper

organic layer was separated and taken up in 350 ml of methylene chloride. The methylene chloride solution was dried over sodium sulfate and solvent was removed in vacuo to leave 320.9 g of 3-tetrahydropyranyloxyoxetane: ^{1}H NMR ($CDCl_3$) δ 1.63 (br. s, 6 H, (CH_2); 3.2-4.4 (m, 2 H, -OCH_2); 4.47 (br. s, 1 H, CH); 4.67 (br. s, 4 H, O(CH_2)); 5.17 (br. s, 1 H, O-CH); IR (CH_2Cl_2) 2970, 2910 (C-H); 980 cm^{-1} (oxetane).

Extraction of the aqueous layer with ether (2x250 ml), drying over sodium sulfate and removal of solvent in vacuo, gave an additional 10.3 g for an overall crude yield of 331.2 g. While 3-tetrahydropyranyloxyoxetane could be distilled (48-65^C/0.2 mm) extensive loss of the THP group occurred.

3-Hydroxyoxetane. A solution of 205 g of crude 3-tetrahydropyranyl-oxetane and 11.3 g (0.045 moles) of pyridinium p-toluenesulfonate in 3 l of methanol(0.015 M in PPTS) was refluxed for 14 h. The methanol was removed in vacuo and the residue was extracted with ether (300 ml and 2 x 50 ml). The ether was decanted and filtered through sodium sulfate. After the ether was removed in vacuo, the residue was vacuum distilled to give 50.6 g of 3-hydroxyoxetane: bp. 69-75° /12 mm (lit. 72-73/9 mm).[2] The overall yield of 3-hydroxyoxetane from 3-chloro-2-hydroxy-1-propyl acetate was 40.0%, and from epichlorohydrin the overall yield is 37.1%.

3-Azidooxetane. A. A solution of 7.31 g (0.032 mole) of 3-oxetyl tosy-late and 2.80 g (0.034 mole) of potassium azide in 80 ml of hexamethylphosphor-amide was stirred at 87°C for 6 h and then overnight at room temperature. The precipitate of potassium tosylate was filtered, and the filtrate was vacuum distilled to afford 1.86 g of 3-azidooxetane, bp 86-95°C (49 mm) that was 92% pure as per ^{1}H NMR (50% yield). Preparative gc (9% QF-1 on Chromasorb W; 100°)

afforded an analytical sample of 3-azidooxetane: ^{1}H NMR (CDCl$_3$) δ 4.60 (m, 4 H, CH$_2$OCH$_2$); 4.76 (m, 1 H, CH-N$_3$); IR (CH$_2$Cl$_2$) 3000, 2930 (C-H); 2150 (-N$_3$); 980 cm^{-1} (oxetane).

Anal. Calcd for C$_3$H$_5$N$_3$O; C, 36.36; H, 5.09, N, 42.41. Found: C, 36.2?; H, 4.82; N, 43.06.

B. To a solution of 2.28 g (0.01 mole) of 3-oxetyl tosylate in 35 ml of dry acetonitrile was added 0.41 g (0.001 mole) of 18-Crown-6 (75%) and 1.00 g (0.012 mole) of potassium azide. The solution was heated at reflux for 47 h and an additional 0.60 g (0.0025 mole total) of 18-Crown-6 was added. Heating was continued for an additional 43 h. After the reaction mixture was cooled to room temperature and filtered, the acetonitrile was distilled and the residue vacuum distilled (65°/40 mm) to afford 0.274 g (28%) of 3-azidooxetane, which was pure by ^{1}H NMR.

3-Aminooxetane. A. To a solution of 1.50 g (0.013 mole) of 3-azidooxetane (92%) in 30 ml of methanol was added 0.750 g of 10% palladium on carbon. The resulting suspension was stirred vigorously while hydrogen gas was introduced over 15 minutes. The hydrogen was generated by the addition of 23 ml of 2N hydrochloric acid to 1.50 g (0.039 mole) of sodium borohydride in 30 ml of water. The reaction mixture was stirred one hour longer and was then filtered through celite. The methanol was distilled and the resulting residue was vacuum distilled to afford 0.543 g (57.2%) of 3-aminooxetane, bp 70-73° (89 mm) (lit. 80-82°/100 mm);[2] IR(CCl$_4$) 3450 (-NH$_2$); 3000, 2910 (C-H); 1615 (-NH$_2$); 980 cm^{-1} (oxetane).

B. To 2.28 g (0.01 mole) of 3-oxetyl tosylate in a 100 ml stainless steel bomb was added 30 ml of liquid ammonia. The bomb was sealed and heated at 102-112°C for 16 h. The bomb was cooled in a dry ice-acetone bath, and 5 ml of a 1.3%

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sodium hydroxide solution was then carefully added. The brown aqueous solution was extracted with methylene chloride (3 x 20 ml) and ether (25 ml). The extracts were then combined and dried over sodium sulfate. Solvent was distilled and the residue was vacuum distilled to afford 0.114 (16%) of 3-amino-oxetane, bp 70°C (80 mm).

3-Nitrooxetane. To a solution of 1.28 g (6.3 mmol) of m-chloroperbenzoic acid (85%) in 9.4 ml of refluxing 1,2-dichloroethane was added over 3 min 0.114 g (1.56 mmol) of 3-aminooxetane in 1.6 ml of 1,2-dichloroethane. The reaction mixture was refluxed for 3 h and was then cooled to -20°C. The precipitate of m-chlorobenzoic acid was filtered, and the filtrate was evaporated to dryness in vacuo. The resulting solid residue was extracted with 25 ml of water, and the water was extracted with methylene chloride (2 x 25 ml). Removal of the methylene chloride in vacuo left 0.143 g of a solid residue, which was extracted with a small volume of methylene chloride. Preparative gc (9% QF-1 on Chromasorb W; 120°) afforded 0.060 g (75% yield, based on 50% gc recovery) of 3-nitrooxetane; ^{1}H NMR ($CDCl_3$) δ 4.83 and 4.93 (s, 4 H, CH_2-O-CH_2); 5.23 (m, 1 H, $CHNO_2$); IR (CH_2Cl_2) 2990, 2940 (C-H); 1550, 1370 (NO_2); 985 cm^{-1} (oxetane).

Anal. Calcd for $C_3H_5NO_3$: C, 34.96; H, 4.89. Found: C, 34.77; H, 4.87.

III. Chemistry of 1-Fluoro-1-nitroethylene

A. Discussion

In previous work on this program involving base-catalyzed reactions of 2-fluoro-3-hydroxy-2-nitropropyl-p-toluenesulfonate, 1-fluoro-1-nitroethylene was implicated as an intermediate.[1] The only publication dealing with this olefin is a communication by Eremenko[10] describing its preparation by thermolysis

of 2-fluoro-2-nitroethyl acetate; no chemical properties were given. The starting material, 2-fluoro-2-nitroethanol was obtained by the high dilution fluorination of 2-nitroethanol. Our synthesis work in the area of 2-fluoro-2-nitro-1,3-propanediol chemistry provided what appeared to be more practical routes to 1-fluoro-1-nitroethylene, and therefore an investigation of this potentially useful olefin was initiated.

The first approach that was taken was to hydrolyze fluoronitro-malonate esters by a published procedure[11] to give fluoronitroacetates. Addition of formaldehyde[12] gave the alkyl 2-fluoro-3-hydroxy-2-nitropropionates in 73 to 89% overall yield.

$$
(ROC)_2CFNO_2 \xrightarrow[\substack{EtOH \\ 0^o}]{KOH} ROCCHFNO_2 \xrightarrow[KOH]{CH_2O} ROCCFNO_2CH_2OH
$$

$$R = CH_3, C_2H_5$$
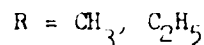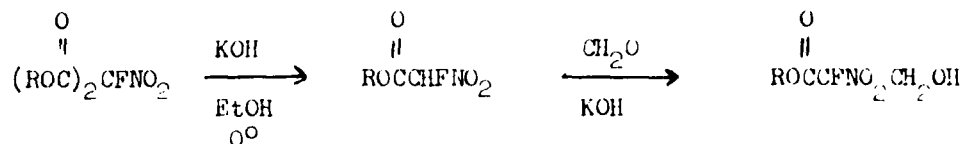
Attempts to hydrolyze and decarboxylate the hydroxyesters directly to fluoro-nitroethanol gave complex mixtures. Consequently the hydroxyl group was protected by a reaction with dihydropyran in the presence of pyridinium p-toluene-sulfonate. The ester group of the blocked compound was hydrolyzed with base to give the tetrahydropyranyl ether of fluoronitroethanol. This protecting group can be removed cleanly with pyridinium p-toluenesulfonate.[13] An overall yield of 60% of 2-fluoro-2-nitroethanol from the hydroxyester was thus obtained.

$$\text{ROCCFNO}_2\text{CH}_2\text{OH} \quad \xrightarrow[\text{Pyr OTs}]{} \quad \text{ROCCFNO}_2\text{CH}_2\text{O}$$

$$\xrightarrow{\text{NaOH}} \quad \text{HCFNO}_2\text{CH}_2\text{-O} \quad \xrightarrow[\text{Pyr OTs}]{\text{CH}_3\text{OH}} \quad \text{HCFNO}_2\text{CH}_2\text{OH}$$
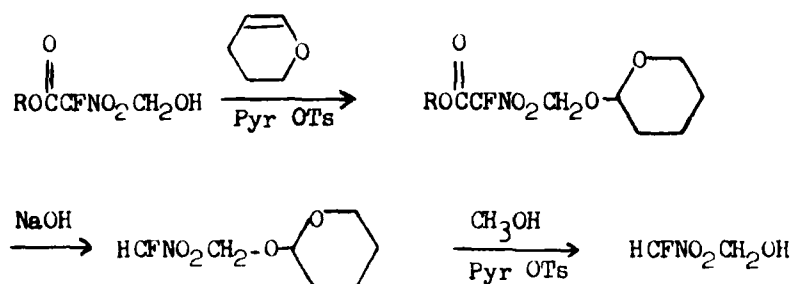
Subsequently, investigation of reaction conditions for the malonate hydrolysis led to a simple one step preparation of fluoronitroethanol. It was found that the hydrolysis of diethyl fluoronitromalonate with potassium carbonate in the presence of one equivalent of formaldehyde, followed by acidification gave fluoronitroethanol in distilled yields of 62-70%.

$$(\text{EtOC})_2\text{CFNO}_2 \quad \xrightarrow[\text{2) } H_3O^+]{\text{1) } K_2CO_3, CH_2O \;\; -15^\circ C} \quad \text{HCFNO}_2\text{CH}_2\text{OH}$$
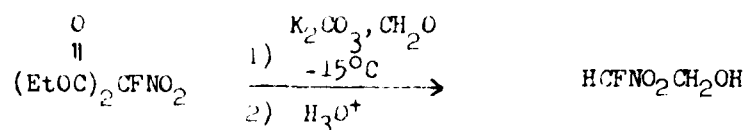
The reported[10] method for preparing 1-fluoro-1-nitroethylene consists of heating 2-fluoro-2-nitroethyl acetate with potassium acetate at 130-140°C. The preparation of the acetate from the alcohol was straightforward. Repeating the reported elimination, however, gave us less than a 10% yield of the olefin, and the product was contaminated with acetic acid.

$$\text{HCFNO}_2\text{CH}_2\text{OH} \quad \xrightarrow{\text{Ac}_2\text{O}} \quad \text{HCFNO}_2\text{CH}_2\text{OAc} \quad \xrightarrow[\Delta]{\text{KOAc}} \quad \text{CH}_2=\text{CFNO}_2$$
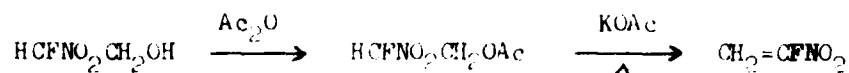
The spectral properties of the olefin were consistent with the assigned structure. The F[19] NMR spectrum showed a broad doublet (J= 33 Hz) at 107.4 ppm, and the proton NMR spectrum showed a doublet of doublets (J= 33.5 Hz) at 56.07 (1 H) and a multiplet (1 H) at 5.63. The IR spectrum showed a nitro band at 1560 cm^{-1}.

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Dehydration of fluoronitroethanol was also attempted using the phthalic anhydride method that has been used for simple nitroolefins.[14] A 10% yield of fluoronitroethylene was obtained. The use of free-radical inhibitors and the silylation of the glassware did not increase the yield. The use of dicyclohexyl carbodiimide as a dehydrating agent was also examined. Yields of fluoronitroethylene were 10-15%, and the product was contaminated with cyclohexene.

Preliminary attempts were made to polymerize fluoronitroethylene. Aqueous base reactions gave hydration to fluoronitroethanol or decomposition with loss of fluoride ion. Triethylamine reacted explosively with fluoronitroethylene at room temperature. Fluoronitroethylene was not affected by azobisisobutyronitrile in refluxing benzene. Further polymerization studies are in progress.

B. Experimental

Ethyl fluoronitroacetate. A solution of 5.6 g (0.100 mol) of potassium hydroxide in 50 ml of ethanol was added over a 1 h period to diethyl fluoro nitromalonate (22.3 g, 0.100 mol) in 100 ml of ethanol at $0°$. The resulting yellow slurry was stirred for 30 min at $0°C$, and was then poured into 125 ml of ice-cold 1 $\underline{N}$ hydrochloric acid. The product was extracted with methylene chloride (3 x 100 ml), and the combined organic portions were dried over magnesium sulfate and concentrated under vacuum to give 14.0 g of pale yellow oil. NMR analysis indicated a 96:4 ratio of ethyl fluoronitroacetate to diethyl fluoronitromalonate and an 82% yield of ethyl fluoronitroacetate. The crude product was used in subsequent steps without further purification: ^{1}H NMR (CDCl$_3$) δ 6.17 (d, J= 47 Hz, CHF, 1 H), 4.30 (q, J= 7 Hz, CH$_2$, 2 H), and 1.38 (t, J= 7 Hz, CH$_3$, 3 H); ^{19}F NMR (CDCl$_3$) ϕ 150 (d, J= 47 Hz).

Methyl 2-fluoro-3-hydroxy-2-nitropropanoate. To a solution of 6.000 g (43.8 mmol) of methyl fluoroacetate in 20 ml of formalin was added, with stirring at 0°C, 4 drops of 40% potassium hydroxide. The reaction mixture was stirred 0.5 h at 0°C and 0.5 h at room temperature. The solution was acidified to pH-1 with hydrochloric acid, added to 50 ml of 50% saturated sodium chloride solution and extracted with methylene chloride. The organic solution was dried over magnesium sulfate and concentrated under vacuum. Short-path distillation of the residue ($85-95^\circ$C, 0.4 mm) provided 6.53 g (89% yield) of pale yellow oil which was homogeneous by TLC and NMR analysis; TLC (1:1 EtOAc/Pet ether; Rf= 0.37); IR (film) 3500 (s, OH), 1760 (s, C=O), 1580 and 1460 cm^{-1} (s, NO$_2$); ^{1}H-NMR (CDCl$_3$) δ 3.33-4.90 (bm, 3 H), 3.90 (s, CO$_2$Me); ^{19}F-NMR (CDCl$_3$) ϕ 136.1 (t, J=20.5 Hz).

Methyl 2-fluoro-3-hydroxy-2-nitropropanoate Tetrahydropyran derivative. A solution of 4.80 g (28.74 mmol) of methyl 2-fluoro-3-hydroxy-2-nitropropanoate, 0.77 g (3.07 mmol) of pyridinium p-toluenesulfonate and 4.1 ml (45 mmol) of dihyropyran in 35 ml of methylene chloride was stirred at room temp. for 4 h. The reaction mixture was then poured into 50 ml of water and the organic layer was separated and the aqueous layer was extracted twice with methylene chloride. The combined organic solutions were dried over magnesium sulfate and stripped of solvent under vacuum to give 7.26 g of residue. Attempted purification by either distillation or GLC resulted in decomposition. Infrared analysis of the crude product indicated absence of hydroxyl groups; ^{1}H-NMR (CDCl$_3$) δ 3.20-5.00 (m, 5 H), 3.87 (s, 3 H) and 1.63 (m, 6 H); ^{19}F-NMR (CDCl$_3$) ϕ 134.3 (t, J$\cong$ 16 Hz).

Ethyl 2-fluoro-3-hydroxy-2-nitropropanoate. To a solution of crude

ethyl fluoronitroacetate, obtained from 0.1 mol of diethyl fluoronitro

malonate, and 40 ml of formalin in 100 ml of methanol, was added 5 drops of

40% potassium hydroxide. In 1 h the mixture was acidified with 10 ml of

5 $\underline{N}$ hydrochloric acid, poured into 50 ml of brine, and extracted with methyl-

ene chloride. The methylene chloride solution was dried over magnesium sul-

fate and solvent was removed. Short-path distillation (83-88°C, 0.4 mm)

yielded 13.2 g of ethyl 2-fluoro-3-hydroxy-2-nitropropanoate (73% overall yield

from diethyl fluoronitromalonate); IR (film) 3350 (s, OH), 1770 (vs, C=O), and

1590 cm^{-1} (vs, NO_2); ^{1}H-NMR ($CDCl_3$)δ 4.10-4.70 (m, 2 H, CH_2OH), 4.37 (q, J=

7 Hz, 2 H), 3.53 (s, 1 H, OH), and 1.37 (t, J=7 Hz, 3 H); ^{19}F-NMR ($CDCl_3$) ϕ

136.2 (t, J=18 Hz).

Ethyl 2-fluoro-3-hydroxy-2-nitropropanoate Tetrahydropyran derivative.

The title compound was obtained in essentially quantitative yield using the

procedure described above for the methyl ester. This THP ether was similarly

unstable to purification by either distillation or GLC; IR(film) No hydroxyl

present; 1770 (vs, C=O), 1590 and 1460 cm^{-1} (NO_2); ^{1}H-NMR($CDCl_3$) δ ~ 3.30-4.80

m, 5 H), 4.33 (q, J=7 Hz, 2 H, OCH_2CH_3), ~1.00-2.00 (m, 6 H) and 1.33 (t, J=

7 Hz, 3 H); ^{19}F-NMR ($CDCl_3$) ϕ 134.2 (m).

2-Fluoro-2-nitroethanol Tetrahydropyran derivative. The crude product

from 26.7 mmol of methyl 2-fluoro-3-hydroxy-2-nitropropanoate and dihydro-

pyran was dissolved in 50 ml of 1:1 methanol/water and 2.3 g (57 mmol) of so-

dium hydroxide in 10 ml of water was added over a 15 min period at 0°C. The

mixture was allowed to stand 3 h at 0° and 16 h at room temp. The resulting

yellow suspension was slowly acidified at 0° (4 $\underline{N}$ HCl) to pH 1, and the product extracted three times with methylene chloride. The organic solution was dried over magnesium sulfate and solvent was removed to give 4.17 g of orange oil. The crude product was not stable to distillation. Infrared analysis showed a lack of carbonyl absorption; ^{1}H-NMR $(CDCl_3)$ δ 5.97 (dt, J= 48 and ~3 Hz, 1 H), 3.20-4.80 (complex m, 5 H), and 1.60 (m, 6 H); ^{19}F-NMR $(CDCl_3)$ ϕ 154.6 (complex pattern). The same product was obtained in 98% overall yield from ethyl 2-fluoro-3-hydroxy-2-nitropropanoate.

2-Fluoro-2-nitroethanol. A) A solution of 1.92 g (10 mmol) of 2-fluoro-2-nitroethanol tetrahydropyran derivative and 0.30 g (1.2 mmol) of pyridinium p-toluenesulfonate in 20 ml of methanol was heated at 55-65° for 2 h. The methanol was removed under vacuum and the resulting oil was triturated with ether (4 x 10 ml). The combined triturants were concentrated to afford 1.10 g of orange oil. NMR analysis indicated the presence of desired alcohol and the THP ether of methanol; IR (film) 3500 (vs, OH), and 1590 cm^{-1} (vs, NO_2); ^{1}H-NMR $(D_6$-acetone) δ 6.13 (dt, J= 48 and ~2 Hz, 1 H), 4.77 (bs, 1 H, OH), and 4.00-4.60 (m, 2 H); ^{19}F-NMR $(D_6$-acetone) ϕ 157.2 (dt, J= 48 and 20 Hz). B) To a solution of 77.8 g (0.349 mol) of diethyl fluoronitromalonate and 28 ml of formalin (0.35 mol of formaldehyde) in 400 ml of methanol at -10°C was added 51 g (370 mmol) of potassium carbonate dissolved in 400 ml of water over a 0.5 h period. The cooling bath was then removed and the yellow-orange slurry was slowly warmed to room temperature. After 0.5 h the mixture was cooled to 0° and 175 ml of 5 $\underline{N}$ hydrochloric acid was added. The resulting solution was extracted with 400 ml of ethyl acetate and 4 x 200 ml of ether.

The combined organic solutions were dried over magnesium sulfate, concentrated and distilled to give 28 g of colorless liquid, bp 75-85°C (0.2-0.5 mm). ^{19}F-NMR analysis indicated that the product was contaminated by 7% of an unknown impurity (multiplet at 148.3 ppm) and 9% of ethyl 2-fluoro-3-hydroxy-2-nitropropanoate. The yield of fluoronitroethanol was 62%. Increasing the reaction time at room temperature from 0.5 h to 1 h provided a 69% distilled yield of fluoronitroethanol 95% pure by ^{19}F-NMR analysis. Slow distillation using a 10 cm Vigreaux column yields a highly pure product (57-58°, 0.2 mm) which is identical to the fluoronitroethanol prepared by the multi-step route described above.

2-Fluoro-2-nitroethyl acetate. Fluoronitroethanol (5.0 g, 46 mmol) was added with stirring to 5 ml of acetic anhydride, and the solution was heated at 50°C for 0.5 h. Solvent was removed under vacuum. Kugelrohr distillation gave 5.2 g (75%) of colorless oil, at 65-75°C (0.1 mm). IR (film) no hydroxyl present; 1760 (vs), and 1590 cm^{-1} (vs); ^{1}H-NMR (CDCl$_3$) ƒ 6.03 (dt, J=48 and 3 Hz, 1 H), 4.40-4.87 (m, 2 H) and 2.10 (s, 3 H); ^{19}F-NMR (CDCl$_3$) φ 155.6 (dt, J=48 and 18 Hz).

1-Fluoro-1-nitroethylene. A) from fluoronitroethanol. A mixture of 1.10 g (10 mmol) of fluoronitroethanol and 1.5 g (10 mmol) of phthalic anhydride was heated at 165-195°C (60 mm). A 10 cm Vigreaux column attached to the reaction flask prevented the fluoronitroethanol from distilling over. During a 2 h period of heating a small quantity (200 mg) of fluoronitroethylene and water was collected in a -80°C receiver. The product was dried over calcium chloride and redistilled at 25°C (60 mm), to give a pale yellow oil,

a potent lachrymator: IR $(CDCl_3)$ 1560 and 1300 cm^{-1} (vs); ^{1}H-NMR $(D_6$-acetone) δ 6.07 (dd, J=33 and 5 Hz, 1 H) and ~5.63 (bm, 1 H); ^{19}F-NMR $(D_6$-acetone) ϕ 107.4 (bd, J=33 Hz).

B) from 2-fluoro-2-nitroethyl acetate. A mixture of 1 g of 2-fluoro-2-nitro-ethyl acetate and .05 g of potassium acetate were heated at 130-170°C at at-mospheric pressure. A short-path distillation apparatus with dry-ice/acetone cooled receiver was attached to the heated reaction flask. Only ~ 100 mg of a mixture of desired product and acetic acid were collected. The fluoroni-troethylene formed was identical to the product obtained by phthalic anhy-dride dehydration of fluoronitroethanol.

IV.   Polymerization of 2-Fluoro-2,2-dinitroethyl glycidyl Ether

A.   Discussion

Earlier on this program, success in using phosphorous pentafluoride to polymerize 3-fluoro-3-nitrooxetane to a difunctional hydroxyl-terminated polymer led to a study of the use of this catalyst to polymerize the energetic epoxide, 2-fluoro-2,2-dinitroethyl glycidyl ether.[1] A cyclic dimer, a mono-functional hydroxy polymer and a diol of molecular weight 1800 were obtained by conducting the polymerization at -78°C. The three materials were readily separated by column chromatography, but the yield of the desired diol was rela-tively low.

The polymerization of epoxides with simple Lewis acids such as PF_5 is generally ascribed[15] to proton initiation. That is, trace amounts of water complex with the catalyst, and this complex provides reactive hydrogen ions that initiate polymerization. A strong proton acid might therefore be ex-

pected to give similar results. The strongest of the common acids, triflic acid, has received relatively little attention as a catalyst in epoxide polymerization.[16] Because of the profound effect of water in initiation and chain transfer, we examined the polymerization of fluorodinitroethyl glycidyl ether with triflic acid, its anhydride and its hydrates.

Preliminary experiments showed a large difference in reaction rates between the phosphorous pentafluoride and triflic acid systems. Thus, while solution polymerizations with PF_5 were complete within minutes at $-78^{\circ}C$, the triflic acid catalysts required on the order of a week at room temperature. In order to provide reasonable reaction rates higher temperatures were used and polymerizations were conducted without solvents. A series of exploratory experiments conducted with neat epoxide at $80^{\circ}C$ with hydrated triflic acid as catalyst is described in Table I. These experiments were carried out on a 1-2 millimole scale, and yields were determined by preparative thin layer chromatography. Unreacted monomer, cyclic dimer and polymer were readily separated. No monofunctional material similar to that obtained with PF_5 catalysis was formed.

An unexpected result of these experiments is the increase in polymer molecular weight that is observed with time when one compares runs with the same type and amount of catalyst. This result is contrary to those of published studies of cationic polymerizations in which oxonium ions are the propagating species; as monomer becomes depleted, chain termination should become statistically more predominant. Further information was obtained by following the course of the reaction by fluorine NMR spectroscopy. The chemical shift of triflate esters is different from that of triflic acid and its complexes.

Table I

Polymerization of Fluorodinitroethyl Glycidyl
Ether with Triflic Acid Hydrates[a]

No.	Catalyst	Mole % Cat.	Time (hrs)	% Rx	MW	Polymer Yield[b] (%)	Color	Dimer Yield[b] (%)
1.	CF_3SO_3H-0.2 H_2O	5.0	17.5	100	1777	34	d. brown	29
2.	CF_3SO_3H-0.2 H_2O	5.0	4.5	95	1252	40	colorless	23
3.	CF_3SO_3H-0.2 H_2O	5.0	1.6	70	835	45	colorless	17
4.	CF_3SO_3H-1.0 H_2O	5.0	17.5	100	1532	46	d. brown	18
5.	CF_3SO_3H-1.0 H_2O	5.0	4.25	100	1345	58	brown	16
6.	CF_3SO_3H-1.0 H_2O	5.0	1.5	95	904	60	colorless	11
7.	CF_3SO_3H-1.0 H_2O	1.5	28.5	100	1248	39	colorless	27
8.	CF_3SO_3H-1.0 H_2O	3.0	9	100	1582	33	brown	23
9.	CF_3SO_3H-1.0 H_2O	7.5	1.2	100	1187	64	brown	9
10.	CF_3SO_3H-2.0 H_2O	2.6	21.2	100	1529	43	d. brown	24

a. No solvent, 80°C.
b. Based on fluorodinitroethyl glycidyl ether consumed.

Up to the 100% monomer conversion point, triflate esters were observed to predominate, even when the dihydrate catalyst was used. When heating was continued long after the 100% conversion point, unbound triflic acid was the predominant species in the NMR.

The NMR data, the molecular weight results and the low-reaction rates compared to those for PF_5 catalysis are all consistent with a mechanism involving triflic acid addition to epoxide. Insertion of triflate esters into the epoxide group provides propagation, whereas alkylation of hydroxyls as well as hydrolysis provide termination. Alkylations of alcohols by triflates have been reported with simple substrates.[17]

$$CF_3SO_3H \; + \; \underset{O}{CH_2-CH_2-R} \; \longrightarrow \; CF_3SO_2CH_2CH_2R \atop OH$$

$$\underset{O}{CH_2-CH_2-R} \longrightarrow \; CF_3SO_3-\left[CH_2CH-O-\right]_2 \overset{R}{|} -H \; \longrightarrow \; CF_3SO_3-\left[CH_2CH-O-\right]_n \overset{R}{|} -H$$

$$2CF_3SO_3-\left[CH_2CH-O-\right]_n \overset{R}{|} -H \; \longrightarrow \; HO\left[CH_2CH-O-\right]_{2n} \overset{R}{|} -H \; + \; CF_3SO_3H$$

$$CF_3SO_3-\left[CH_2CH-O-\right]_n \overset{R}{|} -H \; + \; H_2O \; \longrightarrow \; HO\left[CH_2CH-O-\right]_n \overset{R}{|} -H \; + \; CF_3SO_3H$$
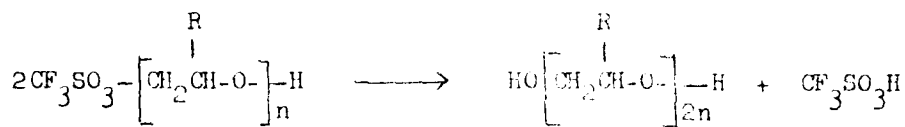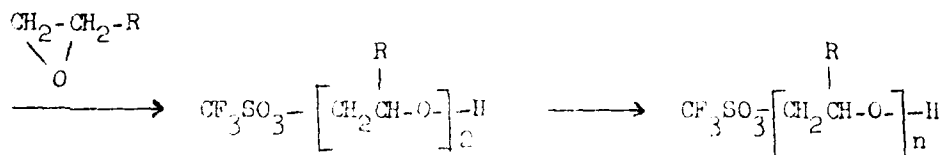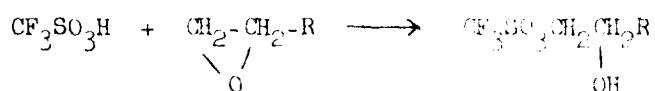
Larger scale experiments using 10 millimoles of fluorodinitroethyl glycidyl ether were carried out to compare catalysis by triflic anhydride, triflic acid and triflic acid monohydrate. The reactions were carried out at $80^\circ C$ without solvent with 5 mole % of the catalyst. Loss of starting material was

followed by TLC and NMR, and the reactions were discontinued when the epoxide was gone. The triflic anhydride reaction was complete in 4.75 hours. A 26% yield of the normal polymeric fraction with a molecular weight of 923 was obtained. The cyclic dimer fraction was resolved into two compounds, obtained in yields of 16 and 21% respectively. Work to identify these materials is in progress. The triflic acid reaction was complete in 4.25 hours, and gave a 37% yield of polymer with an osmometric molecular weight of 1451 and a functionality of 1.72. The same nonfunctional dimeric materials were obtained in yields of 21 and 25% respectively. The triflic acid monohydrate reaction was completed in 2 hours, and gave a 45% yield of polymer with a molecular weight of 1207. The functionality of this material, determined by silylation and NMR was found to be 1.86. The dimeric products were obtained in yields of 18% and 17%. The structures of the dimers as well as that of another material that is held tightly by silica gel remain to be determined.

Preliminary attempts were made to extend polymer molecular weight by adding additional monomer after the initial reaction period, and also to add mild bases to promote chain coupling. Heating the epoxide with 5 mole % triflic acid hydrate for 1.5 hours, adding an additional mole of epoxide and heating for 3 hours, and stirring with potassium carbonate for 22 hours gave a 41% yield of polymer with a molecular weight of 1629.

A sample of the monomeric ditriflate, $FC(NO_2)_2CH_2OCH_2CHCH_2OSO_2CF_3$,
$$OSO_2CF_3$$
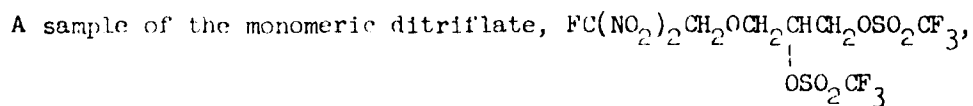
was synthesized for investigations of the insertion reaction.

B. Experimental

Polymerization of 2-Fluoro-2,2-dinitroethyl Glycidyl Ether with

Triflic Acid Monohydrate. Trifluoromethanesulfonic acid monohydrate (0.055 ml,

0.55 mmol was added slowly with stirring to 2.33 g (1.60 ml, 0.0111 mol) of

2-fluoro-2,2-dinitroethyl glycidyl ether. The reaction mixture was heated at

$80 \pm 2^{\circ}C$ with stirring until consumption of the monomer, followed periodically

by TLC was complete (2 h). The mixture was dissolved in 10 ml of methylene

chloride, stirred for 5 min with sodium sulfate and filtered. Removal of the

solvent under vacuum gave 1.925 g of a pale yellow viscous oil. A 0.377 g

portion was fractionated by preparative TLC (silica gel 60, 2 mm thick, 4:1

methylene chloride-ethyl acetate, UV detection). Components were isolated by

extraction with ethyl acetate. Dimers identical to those described for the

triflic anhydride reaction were obtained: R_f 0.41-0.54 (0.068 g) and R_f 0.61-

0.71 (0.064 g). The polymer fraction, R_f 0.09-0.31, 0.168 g, had a molecular

weight of 1207 (VPO): proton NMR $(CDCl_3)$ δ 3.2-3.9 (m, $-OCHCH_2O-$) and 4.55 ppm

(d, J= 17 Hz, OCH_2CF), relative areas 53:21; fluorine NMR ϕ 110 ppm (t, J= 17 Hz,

CF). This material was dissolved in 5 ml of 1,2-dichloroethane and 2 ml of

hexamethyldisilazane and 0.5 ml of trimethylsilyl chloride were added. The

mixture was refluxed for 1.5 h and volatiles were removed under vacuum. The

mixture was dissolved in 5 ml of methylene chloride and filtered, and the solu-

tion was stripped of solvent under vacuum. NMR integration of the silyl pro-

tons showed an equivalent weight of 450, or hydroxyl functionality of 1.86.

Polymerization of 2-Fluoro-2,2-dinitroethyl Glycidyl Ether with

Triflic Acid. The above procedure using 0.049 ml (0.55 mmol) of trifluoromethane-

sulfonic acid as catalyst resulted in disappearence of monomer in 4.25 h to give 1.886 g of tan viscous oil. A 0.376 g aliquot gave, by preparative TLC, 0.080 g with R_f 0.45-0.57 0.092 g with R_f 0.62-0.75, and 0.139 g of polymer fraction with a molecular weight of 1451. Silylation showed an equivalent weight of 843 or 1.72 functionality.

Polymerization of 2-Fluoro-2,2-dinitroethyl Glycidyl Ether with Triflic Anhydride. The above procedure using 0.093 ml (0.55 mmol) of triflic anhydride as catalyst resulted in consumption of monomer in 4.75 h to give after work-up 2.11 g of brown viscous oil. Preparative TLC of a 0.374 g aliquot gave 0.062 g of the material with R_f 0.49-0.56 (molecular weight 509), 0.078 g with R_f 0.58-0.70 (molecular weight 496), and 0.097 g of polymer, (molecular weight 923).

2-Fluoro-2,2-dinitroethoxy-1,2-propaneditriflate. A solution of 0.23 g (1.0 mmol) of 2-fluoro-2,2-dinitroethoxy-1,2-propanediol and 0.20 ml (2.5 mmol) of pyridine in 1.5 ml of methylene chloride was added, dropwise with stirring, to 0.36 ml (2.14 mmol) of triflic anhydride at 0°. After 20 min, the solution was washed with water (3 x 3 ml) and with saturated sodium chloride solution (3 ml) and was dried over sodium sulfate. Removal of solvent gave 0.38 g (77%) of colorless oil: proton NMR $(CDCl_3)$ δ 4.0 (d, J= 5 Hz, $CHCH_2$-O), 4.6 (d, J= 4 Hz, $CF_3SO_2OCH_2$), 4.6 (d, J= 16 Hz, CH_2CF) and 5.1 ppm (quint, J= 4 Hz, CH_2CHCH_2); fluorine NMR $(CDCl_3)$ ϕ 73.0 (s, $CF_3SO_2OCH_2$), 73.4 (s, CF_3SO_2OCH) and 108.8 ppm (t, J= 16 Hz, $CFNO_2$).

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