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JAN 81 K BAUM, P T BERKOWITZ, W A VINSON N00014-78-C-0147
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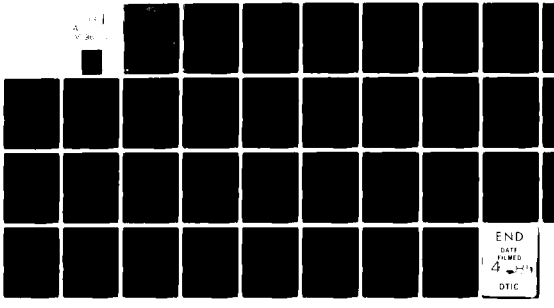

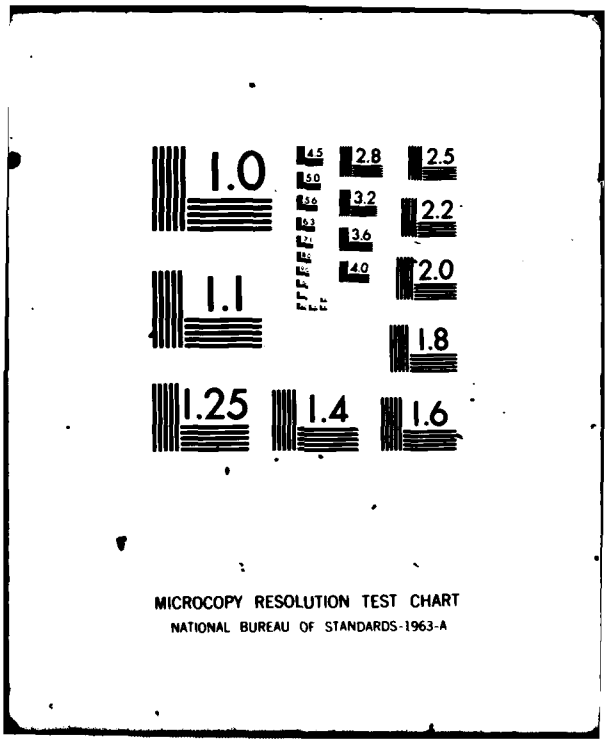
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REPORT No. ONR-2-3 (Interim)

PERIOD COVERED: 1 March 1980 THROUGH 31 DECEMBER 1980

RESEARCH IN ENERGETIC COMPOUNDS

A Report on Work Sponsored by

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Contract N00014-78-C-0147
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January 1981

Fluorochem, Inc.
680 South Ayon Ave.
Azusa, California 91702

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RESEARCH IN ENERGETIC COMPOUNDS

by

K. Baum, P.T. Berkowitz and W.A. Vinson

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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)

3,3-Dinitrooxetane was synthesized by the oxidative nitration of 3-nitrooxetane. 3,3-Dinitrooxetane underwent addition of triflic acid under mild conditions. The polymerization of 3-azidooxetane with BF_3 gave a diol with a molecular weight of 2100. Process studies were initiated to enable the preparation of larger quantities of this polymer. The reaction sequence consisted of the addition of acetic acid to epichlorohydrin, blocking the resulting hydroxyl with dihydropyran, cyclization with sodium hydroxide, and deblocking to give 3-hydroxyoxetane. The latter was converted to the tosylate, which underwent

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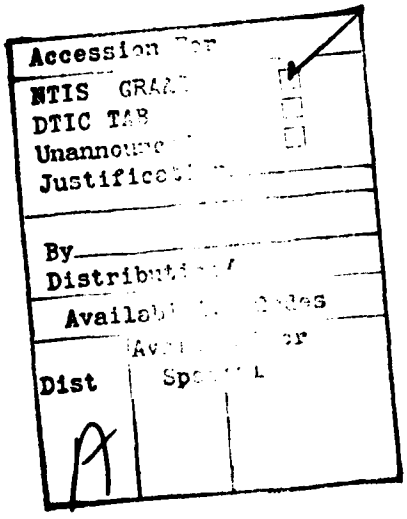
20. ABSTRACT (cont'd.)

displacement with sodium azide. The relatively expensive blocking agent, dihydropyran, was replaced with ethyl vinyl ether, with similar results. The yield in the tosylate preparation step was improved with 4-dimethylaminopyridine catalysis. The azide displacement step was carried out with the inexpensive and nontoxic solvent, triethylene glycol, in place of hexamethyl phosphoramide. An alternative route, consisting of the addition of IN_3 to allyl alcohol followed by reaction with base, failed to give 3-azidooxetane. The synthesis of 1-fluoro-1-nitroethylene was improved by using alumina for the dehydration of 2-fluoro-2-nitroethanol. Polymers with molecular weight as high as 30,000 were obtained from fluorodinitroethyl glycidyl ether and the triethylaluminum-water catalyst, but reproducibility and functionality were poor. Earlier work on the chemistry of triflates and tosylates derived from 2-fluoro-2-nitropropanediol is summarized as journal articles.



CONTENTS

C O N T E N T S (Cont'd)

I. Introduction

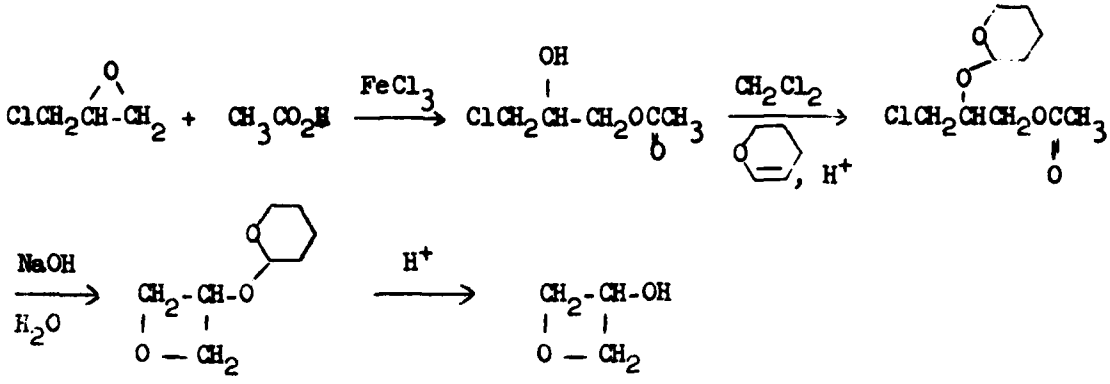
This report summarizes the research under Contract N00014-78-C-0147 during the period 1 March 1980 through 31 December 1980. Emphasis was continued on the area of nitrooxetane chemistry, leading to the first synthesis of 3,3-dinitrooxetane. An intermediate in this synthesis, 3-azidooxetane, provided potentially useful polymers, and process studies were initiated to provide larger quantities of this monomer. Additional exploratory studies were carried out on the chemistry of 1-fluoro-1-nitroethylene and the polymerization of fluorodinitroethyl glycidyl ether. A published article on the chemistry of 3-fluoro-3-nitrooxetane is presented as Appendix A, and related work dealing with fluoronitrotosylates is summarized in Appendix B.

II. Oxetane Chemistry

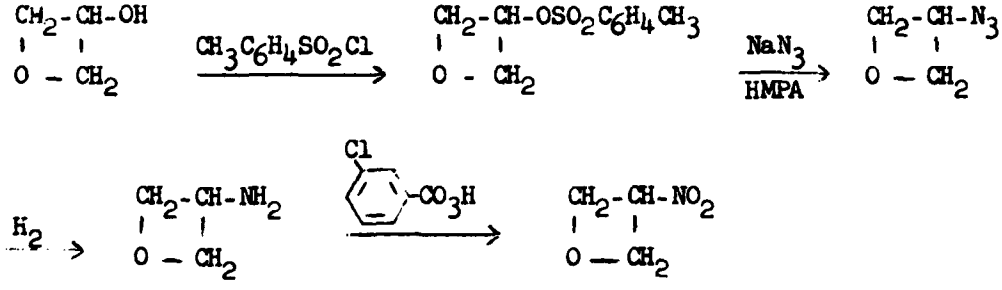
A. Discussion

For the past several years, studies of the synthesis and polymerization of nitrooxetanes have been emphasized on this program. Initially,[1] the work was concerned with 3-fluoro-3-nitrooxetane, and the compound was obtained by the base catalyzed cyclization of the monotriflate, $HOCH_2CF(NO_2)$-$CH_2OSO_2CF_3$. Attempts to prepare 3,3-dinitrooxetane similarly from $HOCH_2C$-$(NO_2)_2CH_2OSO_2CF_3$ were unsuccessful,however, because of the tendency of this alcohol to deformylate. The approach was then taken to prepare a functional oxetane first and then to introduce nitro groups selectively.[2] A practical route to 3-hydroxyoxetane from epichlorohydrin was developed[3] in which acetic acid was added initially to the epoxide. The resulting secondary hydroxyl

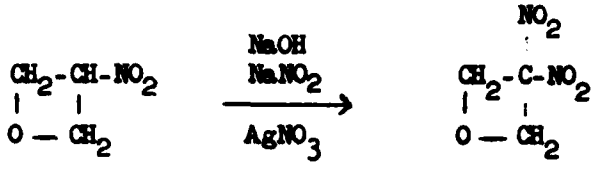
group was protected as the base-resistant dihydropyranyl ether, and ester hydrolysis and cyclization was accomplished with base.



This alcohol was converted to the corresponding tosylate with p-toluenesulfonyl chloride, and displacement of the tosylate group with azide ion gave 3-azidooxetane. Hydrogenation of the azide gave the amine, which, in turn, was oxidized with m-chloroperbenzoic acid to give 3-nitrooxetane.[3]



This reaction sequence aimed at the synthesis of 3,3-dinitrooxetane has now been completed. The desired compound was obtained in 32% yield by oxidative nitration of the mononitro compound. The material is a solid with a melting point of 70-71°C and a density of 1.65. Treatment of 3,3-dinitro-



oxetane with phosphorus pentafluoride in methylene chloride resulted in no reaction, although 3-fluoro-3-nitrooxetane was polymerized readily under the same conditions. This result is consistent with calculations of Dr. Joyce Kaufman indicating extremely low basicity for the ether oxygen of 3,3-dinitrooxetane. Nevertheless, it was found that this oxetane reacted with only a slight excess of triflic acid in chloroform to give 2,2-dinitro-3-hydroxy-1-propyl triflate. The ring is thus amenable to electrophilic opening. Efforts to polymerize 3,3-dinitrooxetane will be continued.

An intermediate in the preparation of dinitrooxetane, 3-azidooxetane, was also of interest in its own right as a monomer. Results of a preliminary screening of the effects of common catalysts on the polymerization of 3-azidooxetane are shown in Table I. Functionality was determined by the silylation method.[2] An arbitrary catalyst level of 10 mole % was used, with

Table I

Catalyst (10 mole %)	Molecular Weight (Vapor Osmometer)	Functionality
$BF_3 \cdot Et_2O$	2100	2.0
$BF_3 \cdot H_2O$	1000	1.6
BF_3 (gas)	1400	1.7
PF_5 (gas)	1600	1.3
$(CF_3SO_2)_2O$	440	-

methylene chloride as the solvent. These results are not optimized with respect to catalyst level, reaction time and temperature. Not much quantitative significance can therefore be attached to the differences in the first three examples. Nevertheless, it is seen that the preparation of polymers with useful molecular weights and functionalities is feasible.

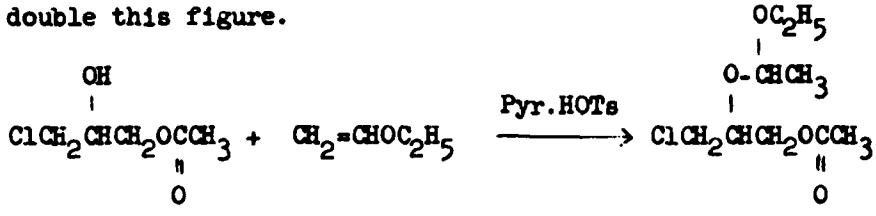
A qualitative determination of the thermal stability of the polymer was made by heating samples and observing the decrease of azide absorption in the IR spectrum. No change was observed after 15 min at 100°C, but a 17% azide loss occurred in 15 min at 125°C and a 27% loss in 15 min at 145°C. The monomer was unchanged after 1 h at 150°C.

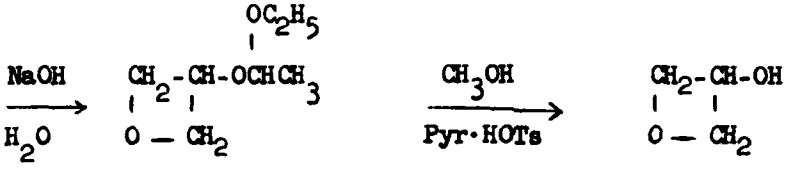
Symmetrically substituted oxetane polymers are generally high melting solids. In contrast, the 3-azidooxetane polymer is a viscous oil, with the potential of providing cured rubbers with low glass transition temperatures.

This favorable combination of polymer properties led to efforts to refine the synthesis procedures to enable the preparation of sufficient material for evaluation. The overall yield of 3-hydroxyoxetane from epichlorohydrin obtained previously[3] was 37%. Minor changes in work-up procedures improved this yield to 47%.

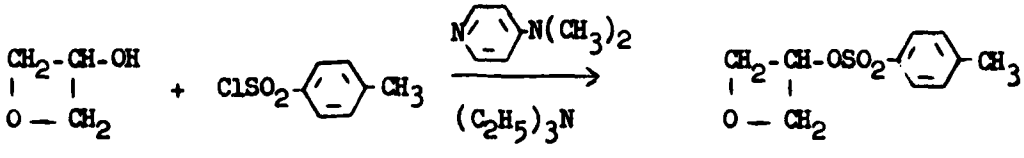
The most costly reagent in the process is the hydroxyl blocking agent, dihydropyran ($25/lb). The sequence was therefore repeated using ethyl vinyl ether ($1.40/lb), which has also been used as a blocking agent.[4] The reaction of 3-chloro-2-hydroxy-1-propyl acetate with ethyl vinyl ether catalyzed by pyridinium p-toluenesulfonate[5] gave an almost quantitative

crude yield of 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate. Hydrolysis and ring closure of this blocked acetate took place when the material was heated with aqueous sodium hydroxide. The blocking group was then removed with methanol and pyridinium p-toluenesulfonate. A 39% yield, based on epichlorohydrin of distilled 3-hydroxyoxetane, was obtained. Hydroxyoxetane polymerizes easily, and NMR based yields prior to distillation were approximately double this figure.



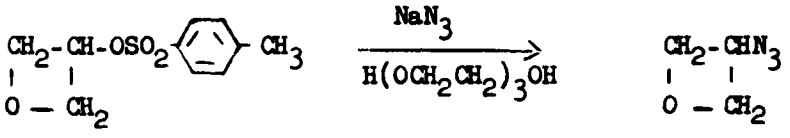


The yield in the conversion of 3-hydroxyoxetane to the tosylate was also improved. 4-Dimethylaminopyridine has been reported to catalyze acylation reactions.[6] In the presence of this compound and triethylamine, 3-hydroxyoxetane reacted with p-toluenesulfonyl chloride to give the tosylate in yields of 82-88%.

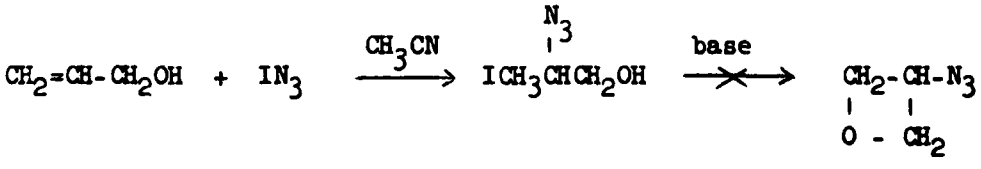


The greatest obstacle to scale-up of the preparation of 3-azidooxetane was the final step, the displacement of the tosylate with azide.

The reaction was previously carried out in hexamethylphosphoramide (HMPA), at 87°C, and the azide was obtained in 50% yield.[3] This solvent is highly toxic, and not readily available in large quantities. Furthermore, a small amount of solvent codistills with the product, necessitating a potentially hazardous redistillation. Other solvents were therefore examined. The reaction was also found to take place in sulfolane, but the yield of 3-azidooxetane was only 30%. The use of triethylene glycol as the solvent required a higher reaction temperature, 160°C, but the reaction could be run under vacuum and the product removed as it was formed. Pure 3-azidooxetane was obtained in this way in 55% yield. Polyethylene glycols are inexpensive, nontoxic and widely available.



Another potential route to 3-azidooxetane is based on the reported[7] addition of iodine azide to primary olefins to give secondary azides. The application of this reaction to allyl alcohol afforded 2-azido-3-iodo-1-propanol in 98% yield. β-Iodoazides are known to undergo HI elimination with strong base to give vinyl azides[7], but in this case it was hoped that oxetane ring closure would predominate. However, no 3-azidooxetane was formed with potassium t-butoxide in t-butanol or ether, with DBU in methylene chloride, or with aqueous sodium hydroxide.



B. Experimental

3,3-Dinitrooxetane. A solution of 0.390 g (3.8 mmol) of 3-nitrooxetane and 0.310 g (4.4 mmol) of sodium nitrite in 4.4 mL of methanol and 4.4 mL of 1.0 M aqueous potassium hydroxide was added to a stirred mixture of 1.50 g (8.8 mmol) of silver nitrate in 3.0 mL of water and 15 mL of ether. After the reaction mixture was stirred for 2 h, 3 mL of a saturated sodium chloride solution was added and stirring was continued for 20 min. The reaction mixture was then filtered through celite and the filter cake was washed with ether. The aqueous solution was extracted with more ether (2 x 15 mL) and the combined ether solutions were dried and evaporated in vacuo to give 0.330 g of a solid residue. Preparative TLC (CH_2Cl_2) gave 0.180 g (32.0%) of analytically sure 3,3-dinitrooxetane: mp 70-71°C; ^1H NMR ($CDCl_3$) δ 5.27 (s); IR(CH_2Cl_2) 1580, 1330 ($-NO_2$), 1000 cm^{-1} (oxetane); d = 1.65.

Anal. Calcd for $C_3H_4N_2O_5$: C, 24.34; H, 2.72; Found: C, 24.54; H, 2.80.

Reaction of 3,3-Dinitrooxetane with Trifluoromethanesulfonic Acid. Trifluoromethanesulfonic acid (0.030 mL, 0.33 mmol) was added to a solution of 0.044 g (0.3 mmol) of 3,3-dinitrooxetane in 0.5 mL of $CDCl_3$. The reaction was followed by NMR. In 24 h, 46% of the oxetane had been converted to 2,2-dinitro-3-hydroxy-1-propyl triflate. After 13 days, NMR indicated an 87% conversion of the oxetane to the corresponding monotriflate. Properties of this triflate are described in Appendix A.

Attempted polymerization of 3,3-Dinitrooxetane with Phosphorous Pentafluoride. Phosphorous pentafluoride was bubbled for several minutes

into a solution of 0.074 g (0.50 mmol) of 3,3-dinitrooxetane in 1.4 mL of methylene chloride. After the solution was stirred for 10 minutes, the reaction was quenched by the addition of 1 mL of methanol. The 3,3-dinitrooxetane was recovered quantitatively.

3-Chloro-2-hydroxy-1-propyl acetate. Epichlorohydrin (187 g, 2.0 mol) was added dropwise over a 75 min period to a mechanically stirred suspension of 10.0 g (0.062 mol) of anhydrous ferric chloride in 138 mL (2.4 mol) of glacial acetic acid at 0-10°C. After the addition was completed, the reaction mixture was stirred one h and was allowed to stand at room temperature for 2 days. Anhydrous sodium acetate (5.1 g, 0.062 mol) was added and excess acetic acid was then removed in vacuo. The mixture was diluted with 200 mL of methylene chloride and filtered through celite. The solution was washed with 10% potassium carbonate and dried over potassium carbonate and sodium sulfate. Removal of the methylene chloride in vacuo gave 275 g of crude 3-chloro-2-hydroxy-1-propyl acetate, and an additional 9 g was recovered by extracting the potassium carbonate solution with methylene chloride (93% crude yield). This material was used without purification in the subsequent step. ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H, $-COCH_3$); 3.80 (m, 6 H, $-CH_2CH(OH)CH_2-$); IR (film) 3500 (-OH); 1735 cm^{-1} ($-COCH_3$).

3-Chloro-2-(1-ethoxyethoxy)-1-propyl acetate. A solution of 30.5 g (0.20 mol) of 3-chloro-2-hydroxy-1-propyl acetate, 22 g (0.30 mol) of ethyl vinyl ether, and 7.5 g (0.030 mol) of pyridinium p-toluenesulfonate in 150 mL of methylene chloride was stirred at room temperature for 6 h. The solution was then washed with 75 mL of water, dried and stripped of

solvent *in vacuo* to give 44.0 g (98.0%) of 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate: ^{1}H NMR ($CDCl_3$) δ 1.05-1.37 (overlapping t and d, 6 H, $-CH_2\underline{CH_3}$ and $-CH\underline{CH_3}$); 2.07 (s, 3 H, $-COCH_3$); 3.53 and 4.12 (m, 7 H, $-CH_2CHCH_2-$ and $\underline{CH_2}CH_3$); 4.72 (q, J=4 Hz, 1 H, $-\underline{CH}CH_3$); IR (film) 1740 cm^{-1} ($-COCH_3$). The unpurified product was used in the next step.

3-(1-Ethoxyethoxy)oxetane. A mixture of 33.7 g (0.15 mol) of 3-chloro-2-(1-ethoxyethoxy)propyl acetate and 18 g (0.45 mol) of sodium hydroxide in 45 mL of water was heated at reflux for 21 h. The reaction mixture was then cooled to room temperature and extracted with 150 ml of 2:1 methylene chloride-ether and 100 mL of 1:1 methylene chloride-ether. The solution was dried and solvent was removed to give 19.0 g of crude 3-(1-ethoxyethoxy)oxetane: ^{1}H NMR ($CDCl_3$) δ 1.00-1.40 (overlapping t and d, 6 H, $-CH_2\underline{CH_3}$ and $-CH\underline{CH_3}$); 3.52 (q, J=4 Hz, 2 H, $-\underline{CH_2}CH_3$), 4.60 (m, 6 H, $\underline{CH_2}CH\underline{CH_2}O$ and $-\underline{CH}CH_3$); IR (film) 980 cm^{-1} (oxetane).

3-Hydroxyoxetane. A. A solution of 15.0 g of crude 3-(1-ethoxyethoxy)oxetane and 0.58 g (2.3 mmol) of pyridinium p-toluenesulfonate in 75 mL of methanol was heated at reflux for 16 h. The methanol was removed *in vacuo* and the residue was extracted with ether (50 mL and 10 mL). Removal of the ether *in vacuo* left 7.0 g of crude 3-hydroxyoxetane, which did not contain significant impurities on the basis of ^{1}H NMR and GC. Vacuum distillation afforded 3.7 g of 3-hydroxyoxetane, bp 63-68°C (4.0 mm). The overall yield of distilled 3-hydroxyoxetane from epichlorohydrin was 39.4%.

B. A solution of 805 g of crude 3-tetrahydropyranyloxyoxetane and 30.2 g (0.12 mol) of pyridinium p-toluenesulfonate in 4 L of methanol was heated at

reflux for 23 h. The methanol was removed in vacuo and the residue was extracted with ether (2000 mL and 100 mL). The ether was removed in vacuo, and vacuum distillation of the residue gave 172.7 g of 3-hydroxyoxetane: bp 65-70°C (5.0 mm). The overall yield of 3-hydroxyoxetane from epichlorohydrin was 46.7%.

3-Oxetyl Tosylate. A solution of 19.2 g (0.10 mol) p-toluenesulfonyl chloride in 100 mL of ether was added dropwise over 30 min to a mechanically stirred solution of 7.4 g (0.10 mol) of 3-hydroxyoxetane, 10.9 g (0.11 mol) of triethylamine, and 6.1 g (0.050 mol) of 4-dimethylaminopyridine in 100 mL of ether. The resulting suspension was stirred for 16 h and was then filtered. The solvent was removed in vacuo and a solution of the residue in 30 mL of methylene chloride was applied to a 100 g silica gel column. Elution with 700 mL of 3:1 methylene chloride-ethyl acetate afforded 20.0 g (87.7%) of 3-oxetyl tosylate. Most of the product was eluted with the first 250 mL of solvent.

3-Azidooxetane. A suspension of 2.30 g (0.010 mol) of 3-oxetyl tosylate and 0.70 g (0.10 mol) of sodium azide in 5 mL of triethylene glycol was heated at 160°C (40 mm) to effect the distillation of 0.550 g (55.5%) of 3-azidooxetane.

Poly(3-azidotrimethylene ether). To a solution of 0.212 g (2.1 mmol) of 3-azidooxetane in 1.0 mL of methylene chloride cooled with an ice-bath, was added 0.025 mL (0.2 mmol) of freshly distilled boron trifluoride etherate. After 4.5 h, the resulting yellow solution was quenched with 1.0 mL of pH 7.0 phosphate buffer. The resulting emulsion was broken by

the addition of methylene chloride and water. The organic phase was dried and solvent was removed. The residue was dissolved in 4 mL of methylene chloride, and 16 mL of hexane was added to precipitate the polymer. The precipitate, a viscous oil was dried under vacuum to give 0.092 g (43.4%) of poly(3-azidotrimethylene ether): ^{1}H NMR ($CDCl_3$) δ 3.63 (s); IR (CH_2Cl_2) 3650 (-OH); 2150 cm^{-1} ($-N_3$); mol wt (VPO, ethyl acetate, 35°C) 2100; functionality by the silylation method was 2.0.

2-Azido-3-iodo-1-propanol. A solution of 4.08 g (25 mmol) of iodine monochloride in 5 mL of dry acetonitrile was added dropwise over 17 min to a stirred suspension of 3.28 g (50 mmol) of sodium azide in 15 mL of acetonitrile at -5°C. After 10 min, 1.16 g (20 mmol) of freshly distilled allyl alcohol was added. The reaction mixture was stirred for 16 h and was then poured into 50 ml of water. The resulting mixture was extracted with ether (3 x 20 mL). The ether solution was washed with 30 mL of 10% sodium thiosulfate solution and then with 30 mL of saturated sodium chloride solution. The solution was dried and solvent was removed in vacuo to give 4.46 g (98.1%) of 2-azido-3-iodo-1-propanol: ^{1}H NMR ($CDCl_3$) δ 3.25 (d, J=4 Hz, 2 H, $-\underline{CH_2}OH$); 3.77 (m, 4 H, $-CH_2CH(N_3)-$ and -OH); IR (CH_2Cl_2) 3650 (-OH); 2150 cm^{-1} ($-N_3$).

Stability of poly(3-azidotrimethylene ether). The neat polymer was heated 1 hour at 90°C and then 15 min at 100°C without any loss of the azide group as determined by IR. However, heating the neat polymer 15 min at 125°C effected a 17% loss of the azide group and heating 15 min at 145°C effected a 27% loss of the azide group. The analysis was carried out by

recording the IR spectrum of the polymer in CH_2Cl_2 and then removing the solvent. The neat polymer was heated for the specified period, cooled, and diluted quantitatively with methylene chloride. The IR spectrum was then redetermined. Heating neat 3-azidooxetane for 1 h at 150°C did not effect any loss of the azido group.

III. Miscellaneous

A. Discussion

In the preceding report,[3] an improved synthesis of 1-fluoro-1-nitroethylene was described, consisting of the selective hydrolysis of diethyl fluoronitromalonate to 2-fluoro-2-nitroethanol, followed by dehydration. The dehydration reagents that were tried were acetic anhydride-

$$(EtOC)_2CFNO_2 \xrightarrow[2)\ H^+]{1)\ K_2CO_3,\ CH_2O,\ -15^\circ C} HCFNO_2CH_2OH \longrightarrow CH_2{=}CFNO_2$$

potassium acetate, phthalic anhydride and dicyclohexyl carbodiimide. Yields were low and poorly reproducible by all three methods, and the product was not pure.

Subsequently, improved results were obtained by heating the alcohol with alumina at 135-140°C under vacuum. A mixture of 2-fluoro-2-nitroethylene and water was collected, and simple distillation gave the olefin consistently in 15-20% yield.

$$CHFNO_2CH_2OH \xrightarrow[\Delta]{Al_2O_3} CFNO_2{=}CH_2$$

Attempts to polymerize this olefin were unsuccessful. Amine bases such as pyridine or DBU in ether or methylene chloride resulted in rapid decomposition at 0°. Potassium carbonate or sodium bicarbonate give decomposition product with loss of fluoride ion. Free radical initiators (di-t-butyl peroxide, AIBN) also gave unstable products that lost fluoride. Heating the neat olefin resulted in detonation at 100°C. The olefin gave a Diels-Alder adduct with 2,3-dimethylbutadiene.

As an in-situ source of 1-fluoro-1-nitroethylene for Michael reactions, 2-fluoro-2-nitroethyl acetate was found to be useful. Diethyl sodiomalonate as well as lithio 2-nitropropane gave the corresponding adducts.

$$(EtOC)_2CHNa + HFCNO_2CH_2OCOCH_3 \longrightarrow (EtOC)_2CHCH_2CHFNO_2$$

$$(CH_3)_2CNO_2Li + HFCNO_2CH_2OCOCH_3 \longrightarrow (CH_3)_2CNO_2CH_2CHFNO_2$$

Some additional work was also carried out on the polymerization of fluorodinitroethyl glycidyl ether, with the objective of preparing difunctional hydroxyl terminated oligomers with a molecular weight of several thousand. In the preceding report period[3] hydrated triflic acid was used to prepare difunctional oligomers with molecular weights of 1200 to 1800, along with nonfunctional cyclic materials. Further work with this system did not provide higher molecular weight products.

The triethylaluminum-water catalyst system has been used commercially to produce very high molecular weight polymers from epoxides. We have attempted to use relatively large amounts of these catalysts to produce

polymers with controlled molecular weights.

A triethylaluminum-water catalyst (2:1 ratio) provided the best results, and mobile products with molecular weights as high as 30,000 were obtained. However, the catalyst efficiency was not readily reproducible, and the polymer functionality was generally 1.0 or less. Similar results were obtained with triethylaluminum-ethylene glycol.

B. Experimental

1-Fluoro-1-nitroethylene. A 500 mL flask containing a stirring bar, 30 g (0.33 mol) of 2-fluoro-2-nitroethanol and 150 g of neutral activated alumina was connected to a rotary evaporator with a -80° exit trap. The flask was rotated for 30 min at ambient conditions and then for 4 h at 135-140°C under vacuum (105 mm Hg). A mixture of product and water collected in the trap. The lower layer was separated, and was filtered through sodium sulfate in a Pasteur pipette. Distillation with a short path still gave 3.7 g (15% yield) of 1-fluoro-1-nitroethylene, bp 72-78°C.

1,2-Dimethyl-4-fluoro-4-nitrocyclohexene. A sealed tube containing 0.1 g of 1-fluoro-1-nitroethylene and 0.5 mL of 2,3-dimethyl-1,3-butadiene was heated at 80-90°C for 2.5 h. The mixture was diluted with methylene chloride and filtered through silica gel. Solvent and excess olefin were removed under vacuum. The residue showed a single GC peak: ^{1}H NMR ($CDCl_3$) δ 2.00-3.43 (m, 6 H, ring) and 1.67 (s, 6 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 124.2 (m).

Diethyl 2-Fluoro-2-nitroethylmalonate. To a solution of 5.0 mmol of diethyl sodiomalonate in 20 mL of 1:1 tetrahydrofuran-methylene chloride was added 0.302 g (2.0 mmol) of 2-fluoro-2-nitroethyl acetate, and the

mixture was stirred 18 h. The mixture was poured into cold 1 N HCl and the product was extracted with methylene chloride. The solution was dried over magnesium sulfate and solvent was removed. Silica gel flash chromatography (3/4" x 12" column, methylene chloride-ethyl acetate) gave 0.15 g (30%) of colorless oil: IR (film) 1740 and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.02 (d, t, J= 50, 6 Hz, 1 H, $\underline{CH}FNO_2$), 4.23 (q, J=8 Hz, 4 H, $\underline{CH_2}CH_3$), 3.60 (t, J=7 Hz, 1 H, $\underline{CH}(CO_2Et)_2$, 2.37-3.07 (m, 2 H, $\underline{CH_2}CHF$), and 1.30 (t, J=8 Hz, 6 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 147.1 (m).

1-Fluoro-3-methyl-1,3-dinitrobutane. To a slurry of 0.475 g (5.0 mmol) of lithio 2-nitropropane in 5 ml of tetrahydrofuran at 0° was added 0.302 g (2.0 mmol) of 2-fluoro-2-nitroethyl acetate. The mixture was stirred 18 h at room temperature, and was then quenched with 20 mL of cold 0.5 N HCl. Extraction with methylene chloride gave an oil. Flash chromatography (3/4" x 12" silica gel column, CH_2Cl_2) gave the adduct (38%): ^1H NMR ($CDCl_3$) δ 6.37 and 5.53 (d of AB quartets, J=5,4 Hz, 1 H, $\underline{CH}FNO_2$), 2.5-3.17 (m, 2 H, $\underline{CH_2}CHF$) and 1.77 (s, 6 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 144.5 (m).

Polymerization of Fluorodinitroethyl Glycidyl Ether with Triethylaluminum-Water. To a stirred mixture of 0.3 ml of methylene chloride and 0.9 µL (0.05 mmol) of water under nitrogen was added 0.05 mL (0.10 mmol) of 25% triethylaluminum in hexane. In 10 min 0.29 mL (2.0 mmol) of fluorodinitroethyl glycidyl ether was added, and the resulting solution was stirred for 60 h at ambient temperature. Acetonitrile (5 mL) and 0.5 mL of 10% aqueous ammonium chloride were added and the mixture was stirred for 15 min. The product was dried over magnesium sulfate and solvent was removed. NMR indicated

that 78% of the epoxide was consumed. Flash chromatography (3/4" x 12" silica gel column) yielded 0.063 g of monomer (200 mL methylene chloride eluent), 0.236 g (63% yield) of polymer with a VPO molecular weight of 1180 (300 mL of 4:1 methylene chloride-ethyl acetate) and 0.061 g of polymer with a molecular weight of 4,442. Functionality of the polymer fractions was 1.0 by silylation.

References

1. Fluorochem Report ONR-1-7, January 1978.
2. Fluorochem Report ONR-2-1, March 1979.
3. Fluorochem Report ONR-2-2, March 1980.
4. Smart, J.; Chladek, S. Coll. Czech. Chem. Comm., 1966, 31, 2978. Eaton, P.E.; Cooper, G.F.; Johnson, R.C.; Mueller, R.H. J. Org. Chem., 1972, 37, 1947.
5. Miyashita, N.; Yashikoshi, A.; Grieco, P.A. J. Org. Chem., 1977, 42, 3772.
6. Steglich, W.; Hofle, G. Angew. chem. internat. Ed., 1969, 8, 981.
7. Fowler, F.W.; Hassner, A.; Levy, L.A. J. Am. Chem. Soc., 1967, 89, 2077.

Appendix A

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Reactions of 2-Fluoro-2-nitro-1,3-propanediol. Trifluoromethanesulfonates and 3-Fluoro-3-nitrooxetane[1]

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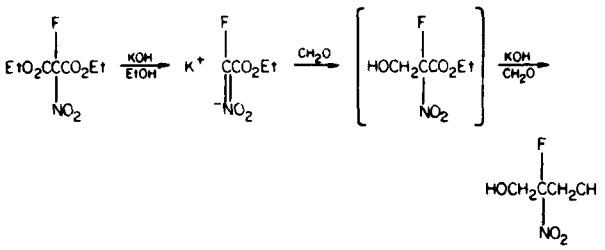
The reaction of diethyl fluoronitromalonate with base and formaldehyde provided a convenient synthesis of 2-fluoro-2-nitro-1,3-propanediol. This diol reacted with triflic anhydride to give 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate and 2-fluoro-2-nitro-1,3-propylene ditriflate. The monotriflate reacted with base to give 3-fluoro-3-nitrooxetane. The ditriflate underwent displacement reactions with sodium azide, 2-fluoro-2,2-dinitroethanol, and methanol. Reactions of 3-fluoro-3-nitrooxetane with strong acids resulted in ring opening to give 3-substituted 2-fluoro-2-nitropropanols. The oxetane was polymerized with phosphorus pentafluoride. Triflates derived from 2,2-dinitro-1,3-propanediol and 2-(hydroxymethyl)-2-nitro-1,3-propanediol did not cyclize.

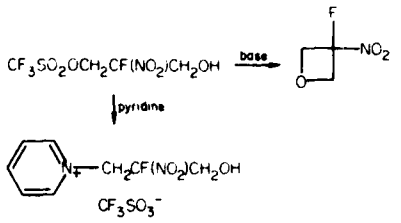
Primary 2-nitro and 2,2-dinitro alcohols readily undergo the reverse Henry reaction under basic conditions to give nitronate salts and formaldehyde.[2] This reaction is markedly inhibited by a fluorine α to nitro as a manifestation of the "fluorine effect" or the destabilization of a nitronate salt by an α fluorine.[3] Thus, 2-fluoro-2,2-dinitroethanol can be alkylated under basic conditions,[4-6] and 2-fluoro-2-nitro-1,3-propanediol has even been reported to give a stable dialkoxide salt. In order to explore further the chemistry of 2-fluoro-2-nitro-1,3-propanediol, we have developed an improved method for its preparation, and the present paper describes reactions of its trifluoromethanesulfonates (triflates).

(1) This work was supported by the Office of Naval Research.
(2) Feuer, H.; Bachman, G. B.; Kispersky, J. P. *J. Am. Chem. Soc.* **1951**, *73*, 1360.
(3) Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 4761. Hine, J.; Mahone, L. G.; Liotta, C. L. *Ibid.* **1967**, *89*, 5911.
(4) Adolph, H. G.; Kamlet, M. J. *J. Org. Chem.* **1969**, *34*, 45.
(5) Grakauskas, V.; Baum, K. *J. Org. Chem.* **1969**, *34*, 3927.
(6) Grakauskas, V. *J. Org. Chem.* **1970**, *35*, 3030.

Scheme I



Scheme II



Triflates have been used previously[7] to alkylate polynitro alcohols that could not be alkylated by other reagents. One objective of this work was to utilize both the stability of 2-fluoro-2-nitro alcohols under basic conditions and the high reactivity of triflates in displacement reactions to synthesize 3-fluoro-3-nitrooxetane. Two nitrooxetanes were reported previously, and only one had a nitro group on the ring; the reaction of 2-(hydroxymethyl)-2-nitro-1,3-propanediol with phosphorus pentachloride was reported to give 3-(chloromethyl)-3-nitrooxetane[8] as a minor byproduct. The other reported nitrooxetane, 3,3-bis(nitromethyl)oxetane was obtained from 3,3-bis(iodomethyl)oxetane and silver nitrite.[9]

2-Fluoro-2-nitro-1,3-propanediol was first synthesized by fluorination of the nitronate salt of 2,2-dimethyl-5-nitro-1,3-dioxane and subsequent acid hydrolysis of the dioxane.[10] The fluorination of the nitronate salt of 2-nitro-1,3-propanediol was also reported to afford 2-fluoro-2-nitro-1,3-propanediol, but a dilute (1:50) fluorine–nitrogen mixture and prolonged reaction times were used.[11] We were unable to carry out this fluorination on a useful scale because of ignition at the fluorine inlet.

A much more facile direct fluorination gives diethyl fluoronitromalonate from diethyl nitromalonate in high yield, and hydrolysis of this product has been shown to give ethyl fluoronitroacetate.[12] These reactions provide the basis for a convenient preparative route to 2-fluoro-2-nitro-1,3-propanediol. A solution of diethyl fluoronitromalonate in ethanol was treated with 1 equiv of potassium hydroxide below −10 °C and then with 2 equiv of aqueous formaldehyde. Hydrolysis, decarboxylation, and formylation took place in situ to give 2-fluoro-2-nitro-1,3-propanediol. The crude diol could not be recrystallized easily, and the high pot temperatures needed for distillation resulted in some decomposition. However, silylation of the crude diol enabled convenient purification by distillation, and the silyl groups were readily removed with refluxing methanol. A 71% yield of 2-fluoro-2-nitro-1,3-propanediol was obtained in this way from diethyl fluoronitromalonate (Scheme I).

The desired triflates were prepared from the above alcohol by conventional procedures, with the predominant product determined by the stoichiometry. A twofold excess of 2-fluoro-2-nitro-1,3-propanediol reacted with triflic anhydride and pyridine to give a 79% yield of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate and a 9% yield of 2-fluoro-2-nitro-1,3-propylene ditriflate. When only 1 equiv of the diol was used, the yields of monotriflate and ditriflate were 52% and 28%, respectively. Reaction of the diol with 2 equiv of both triflic anhydride and pyridine afforded the ditriflate in 76% yield (eq 1).

$$HOCH_2CF(NO_2)_2CH_2OH \xrightarrow[\text{pyridine}]{(CF_3SO_2)_2O} CF_3SO_2OCH_2CF(NO_2)CH_2OH + CF_3SO_2OCH_2CF(NO_2)CH_2OSO_2CF_3 \quad (1)$$

The cyclization of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate proved to be a surprisingly facile reaction and gave 3-fluoro-3-nitrooxetane, the first fully characterized oxetane with a nitro group on the ring. Thus the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base, in methylene chloride solution at room temperature, provided a 62% isolated yield of 3-fluoro-3-nitrooxetane. Similar yields (NMR) were obtained with potassium hydroxide or potassium carbonate in aqueous dioxane, with triethylamine in chloroform, and with potassium methoxide in methanol. The latter reaction gave no evidence of methoxide displacement of the triflate group. Pyridine, however, did not effect cyclization, but underwent N-alkylation to give 2-fluoro-3-hydroxy-2-nitro-1-propylpyridinium triflate (Scheme II).

Displacement reactions of 2-fluoro-2-nitro-1,3-propylene ditriflate were also studied. Sodium azide in dimethyl sulfoxide at room temperature gave a quantitative yield of 1,3-diazido-2-fluoro-2-nitropropane, identified spectrally and by conversion to the bis(triazole) derivative with propiolic acid (eq 2). Similarly, the reaction of the di-

$$CF_3SO_2OCH_2CF(NO_2)CH_2OSO_2CF_3 \xrightarrow[Me_2SO]{NaN_3} N_3CH_2CF(NO_2)CH_2N_3 \quad (2)$$

triflate with 2-fluoro-2,2-dinitroethanol in dioxane–formalin afforded a 22% yield of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane (eq 3). The ditriflate

$$CF_3SO_2OCH_2CF(NO_2)CH_2OSO_2CF_3 + FC(NO_2)_2CH_2OH \xrightarrow[CH_2O]{KOH} FC(NO_2)_2CH_2OCH_2CF(NO_2)CH_2OCH_2CF(NO_2)_2 \quad (3)$$

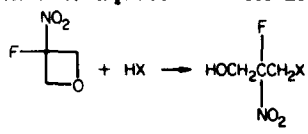
underwent rapid decomposition with methanolic potassium methoxide at room temperature, but with refluxing methanol containing suspended sodium sulfate, a 32% yield of 1,3-dimethoxy-2-fluoro-2-nitropropane and a 16% yield of 2-fluoro-3-methoxy-2-nitro-1-propyl triflate were obtained. Sodium sulfate has been used previously as a mild acid scavenger in triflate reactions[7] (eq 4).

$$CF_3SO_2OCH_2CF(NO_2)CH_2OSO_2CF_3 \xrightarrow[Na_2SO_4]{CH_3OH} CH_3OCH_2CF(NO_2)CH_2OCH_3 + CF_3SO_2OCH_2CF(NO_2)CH_2OCH_3 \quad (4)$$

Ring opening of 3-fluoro-3-nitrooxetane occurred with strong acids. Concentrated hydrochloric acid, hydrobromic acid, and anhydrous triflic acid gave 3-chloro-2-fluoro-2-nitro-1-propanol, 3-bromo-2-fluoro-2-nitro-1-propanol, and

(7) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.
(8) Kleinfeller, H. *Chem. Ber.* **1929**, *62*, 1582. The only evidence in support of the structural assignment was elemental analysis.
(9) Nielsen, A. T.; Finnegan, W. G. *Tetrahedron* **1966**, *22*, 925.
(10) Kissinger, L. W.; Benziger, T. M.; Rohwer, R. K. *Tetrahedron, Suppl.* **1964**, 320.
(11) Eremenko, L. T.; Oreshko, G. V. *Izv. Adad. Nauk SSRR, Ser. Khim.* **1969**, 380.
(12) Adolph, H. G.; Oesterling, R. E.; Sitzman, M. E. *J. Org. Chem.* **1968**, *33*, 4296.

2-fluoro-3-hydroxy-2-nitro-1-propyl triflate, respectively (eq 5). With 50% aqueous sulfuric acid, 2-fluoro-2-

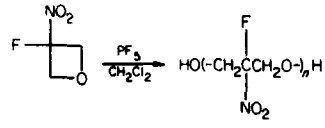


(5)

X = Cl, Br, CF_3SO_3

nitro-1,3-propanediol was obtained. The oxetane did not react, however, with glacial acetic acid at 80 °C, with triflic anhydride in ether at room temperature, or with methanolic strong acids.

Cationic polymerizations of oxetanes are inhibited by electron-withdrawing substituents,[13] and polymerizations of examples with substituents comparable to those of 3-fluoro-3-nitrooxetane have not been reported. An effective catalyst for oxetane polymerizations has been reported to be phosphorus pentafluoride.[14] Reaction of an excess of this catalyst with 3-fluoro-3-nitrooxetane in methylene chloride at room temperature resulted in rapid polymerization (eq 6). A polymeric diol precipitated, which had



(6)

a molecular weight of 2500 (vapor-phase osmometer).

The importance of fluorine in the cyclization of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate to give 3-fluoro-3-nitrooxetane was shown by reactions of nonfluorine-containing analogues. The reaction of 2,2-dinitro-1,3-propanediol with equimolar amounts of pyridine and triflic anhydride *in ether* gave a 47% yield of 2,2-dinitro-3-hydroxy-1-propyl triflate and a 14% yield of 2,2-dinitro-1,3-propylene ditriflate. Similarly, 2-(hydroxymethyl)-2-nitro-1,3-propanediol gave 3-hydroxy-2-(hydroxymethyl)-2-nitro-1-propyl triflate and 2-(hydroxymethyl)-2-nitro-1,3-propylene ditriflate. Both 2,2-dinitro-3-hydroxy-1-propyl triflate and 3-hydroxy-2-(hydroxymethyl)-2-nitro-1-propyl triflate underwent decomposition with potassium carbonate or triethylamine under the conditions that were used to prepare 3-fluoro-3-nitrooxetane. Aqueous sodium bicarbonate and 2,2-dinitro-3-hydroxy-1-propyl triflate gave 2,2-dinitro-1,3-propanediol.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. A Varian 920 gas chromatograph was used for GLC separations, and a Mechrolab 301A vapor osmometer was used for molecular weight determinations. Previously described safety precautions for nitro compounds[15,16] were observed.

2-Fluoro-2-nitro-1,3-propanediol. A solution of 3.3 g (0.05 mol) of 85% potassium hydroxide in 35 mL of ethanol was added over 15 min to a solution of 11.3 g (0.05 mol) of diethyl fluoronitromalonate[12] in 35 mL of ethanol at −12 to −27 °C. After 30 min, 8.5 mL (0.11 mol) of formalin (37%) was added. The reaction mixture was allowed to warm to room temperature over 1 h and was stirred an additional 2 h. The starting material was consumed completely on the basis of NMR spectra. The reaction mixture was then filtered and the solvent was removed in vacuo. To the residue were added 100 mL of ether and 15 mL (0.15 mol) of pyridine. The ether solution was then decanted, and the remaining orange gum was extracted with 50 mL of acetonitrile. To the combined acetonitrile and ether solutions was added 25 mL (0.15 mol) of trimethylsilyl chloride, and the reaction mixture was then refluxed for 5.5 h and stirred overnight at room temperature. Distillation of the solution gave 10.07 g (70.7%) of 1,3-bis(trimethylsiloxy)-2-fluoro-2-nitropropane: bp 82–83 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 18 H, $SiMe_3$), 3.85 and 4.13 (s and AB q pattern, 4 H, CH_2); ^{19}F NMR ($CDCl_3$) ϕ 141.2 (quintet, J = 16 Hz); IR (CH_2Cl_2) 1575, 1360 (NO_2), 1130, 860 ($SiMe_3$), 1090 cm^{-1} (CF). Anal. Calcd for $C_9H_{22}NFSi_2O_4$: C, 38.13; H, 7.82. Found: C, 37.74; H, 7.87.

A solution of the above compound in 100 mL of methanol was refluxed for 4 h and solvent was then removed in vacuo to afford 4.91 g (70.6%) of 2-fluoro-2-nitro-1,3-propanediol: mp 86–87 °C (lit.[11] mp 86–87 °C); ^{1}H NMR (acetone d_6) δ 3.95 (s), 4.23 (AB quartet), 4.80 (t, J = 6 Hz, 2 H, OH); ^{19}F NMR (acetone-d_6) ϕ 145.6 (quintet, J = 16 Hz); IR (CH_2Cl_2) 3620 (OH), 1575, 1335 (NO_2), 1040 cm^{-1} (CF). An AB quartet and a singlet have been observed previously for CH_2CFNO_2 in the ^{1}H NMR spectrum.[17]

2-Fluoro-3-hydroxy-2-nitro-1-propyl Triflate. A solution of 10.9 mL (0.065 mol) of triflic anhydride in 210 mL of ether was added dropwise to a solution of 17.4 g (0.124 mol) of 2-fluoro-2-nitro-1,3-propanediol and 6.0 mL (0.074 mol) of pyridine in 210 mL of ether. The reaction temperature was kept below 26 °C. After the reaction mixture was stirred for 16 h, the precipitate that formed was filtered and washed with ether (2 × 40 mL). Removal of the ether in vacuo left 26.2 g of a white solid, which was partitioned between 300 mL of methylene chloride and 60 mL of water. The methylene chloride solution was washed with 30 mL of water, dried over sodium sulfate, and chromatographed on a 125-g silica gel column (methylene chloride). Elution with a total of 500 mL of methylene chloride gave 2.2 g (8.9%) of ditriflate. Further elution with 500 mL of 9:1 methylene chloride–ethyl acetate afforded 13.26 g (78.9%) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate. Recrystallization from methylene chloride–petroleum ether at −10 °C gave an analytical sample: colorless hygroscopic solid; mp 29–30 °C; ^{1}H NMR ($CDCl_3$) δ 2.65 (br s, 1 H, OH), 4.10 (d, J = 14 Hz, 2 H, CH_2OH), 5.07 (AB q, J = 14 Hz, 2 H, $CH_2OSO_2CF_3$); ^{19}F NMR ($CDCl_3$) ϕ 72.0 (s, 3 F, SO_2CF_3), 139.4 (quintet, J = 14 Hz, 1 F, O_2NCF); IR (CH_2Cl_2) 3625 (OH), 1580, 1350 (NO_2), 1420, 1220, 1140, 900 (SO_2CF_3), 1000 cm^{-1} (CF).

Anal. Calcd for $C_4H_5F_4NSO_6$: C, 17.22; H, 1.86; N, 5.17. Found: C, 17.82; H, 1.75; N, 5.31.

The combined aqueous layers were extracted with ethyl acetate (3 × 100 mL) to give 8.70 g of 2-fluoro-2-nitro-1,3-propanediol.

2-Fluoro-2-nitro-1,3-propylene Ditriflate. A solution of 1.39 g (0.010 mol) of 2-fluoro-2-nitro-1,3-propanediol and 1.8 mL (0.022 mol) of pyridine in 10 mL of chloroform was added dropwise at 0–5 °C to a solution of 5.8 g (0.02 mol) of triflic anhydride in 10 mL of chloroform. After 3 h, the reaction mixture was washed with ice–water (2 × 10 mL) and the chloroform solution was dried over sodium sulfate. The solvent was removed in vacuo, and the residue was chromatographed on a 64-g silica gel column (methylene chloride). Elution with a total of 300 mL of methylene chloride afforded 2.80 g (75.5%) of 2-fluoro-2-nitro-1,3-propylene ditriflate. Recrystallization from methylene chloride–petroleum ether gave an analytical sample: mp 57–58 °C; ^{1}H NMR ($CDCl_3$) δ 4.93 (d, J = 14 Hz); ^{19}F NMR ($CDCl_3$) ϕ 71.8 (s, 6 F, SO_2CF_3), 136.7 (quintet, J = 14 Hz, 1 F, O_2NCF); IR (CH_2Cl_2) 1595, 1320 (NO_2), 1420, 1220, 1140, 900 (OSO_2CF_3), 1005 cm^{-1} (CF).

Anal. Calcd for $C_5H_4F_7NS_2O_8$: C, 14.90; H, 1.00; N, 3.47. Found: C, 15.30; H, 0.91; N, 3.61.

3-Fluoro-3-nitrooxetane. A solution of 3.1 mL (0.0207 mol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 18 mL of methylene chloride was added dropwise to a solution of 5.42 g (0.020 mol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate in 36 mL of methylene chloride. After 75 min, the reaction mixture was chromatographed on a 30-g silica gel column (methylene chloride) to give 2 g of crude product. Vacuum distillation afforded 1.486 g (61.4%) of 3-fluoro-3-nitrooxetane. An analytical sample was obtained by preparative GC (12% QF-1 on Chromasorb W, 100 °C): bp 31 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 4.97 (sextet); ^{19}F NMR ($CDCl_3$) ϕ 127.7 (quintet, J = 14 Hz); IR (CH_2Cl_2) 1575, 1345 (NO_2), 1000 cm^{-1} (CF); $n_D^{24.5}$ 1.4281.

(13) Pruckmayer, G. In "High Polymers"; Frisch, K. C., Ed.; Wiley-Interscience: New York, 1972; Vol. XXVI, p 74.
(14) Campbell, T. W.; Foldi, V. S. *J. Org. Chem.* **1961**, *26*, 4654.
(15) Grakauskas, V.; Baum, K. *J. Org. Chem.* **1968**, *33*, 3080.
(16) Kamlet, M. J.; Adolph, H. G. *J. Org. Chem.* **1968**, *33*, 3073.
(17) Baum, K. *J. Org. Chem.* **1970**, *35*, 846.

Anal. Calcd for $C_3H_4FNO_3$: C, 29.76; H, 3.33; N, 11.58. Found: C, 30.13; H, 3.35; N, 12.07.

The use of the silica gel column for the removal of the DBU triflic acid salt was employed as the salt was not easily extracted from methylene chloride by water. The refractive index of the distilled oxetane was the same as that of the sample isolated by GC.

1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane. To a solution of 1.545 g (10.0 mmol) of 2-fluoro-2,2-dinitroethanol (FDNE) in 15 mL of 2:1 dioxane–formalin was added 0.665 g (10.0 mmol) of potassium hydroxide (85%). The yellow solution was cooled with an ice bath to 22 °C, and 1.013 g (2.5 mmol) of 2-fluoro-2-nitro-1,3-propylene ditriflate was then added. The temperature of the reaction mixture rose to 32 °C over 6 min, and the pH dropped from 11 to 8. After 1 h the solvent was removed in vacuo, and to the residue were added 5 mL of water and 25 mL of 1:1 carbon tetrachloride-methylene chloride. The water layer was extracted with two 12-mL portions of this solvent, and the combined organic solution was then washed with water (4 × 25 mL), and dried over sodium sulfate. Removal of solvent in vacuo gave 0.64 g of a 3:1 mixture of the di- and monoethers (^{19}F NMR). Chromatography on 25 g of silica gel (2:1 methylene chloride–petroleum ether) gave 0.222 g (21.6%) of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane; crystallization from methylene chloride–petroleum ether afforded an analytical sample: mp 52 °C; ^1H NMR (9:1 $CDCl_3$–acetone-d_6) δ 4.2 (d, J = 16 Hz, 4 H, $CH_2CFNO_2CH_2$), 4.70 (d, J = 16 Hz, 4 H, $CH_2CF(NO_2)_2$); ^{19}F NMR (9:1 $CDCl_3$–acetone-d_6) ϕ 109.4 (br m, 2 F, $CF(NO_2)_2$), 138.7 (quintet, J = 16 Hz, 1 F, $CFNO_2$); IR (CH_2Cl_2) 1600, 1320 cm^{-1} (NO_2); d_{25} 1.709.

Anal. Calcd for $C_7H_8F_3N_5O_{12}$: C, 20.45; H, 1.96; N, 17.03. Found: C, 20.47; H, 1.90; N, 16.70.

1,3-Diazido-2-fluoro-2-nitropropane. A solution of 0.407 g (1.0 mmol) of 2-fluoro-2-nitro-1,3-propylene ditriflate in 5.5 mL of dimethyl sulfoxide was stirred at room temperature for 22 h with 0.225 g (3.3 mmol) of sodium azide. The reaction mixture was then diluted with 50 mL of water and extracted with methylene chloride (3 × 17 mL). The methylene chloride solution was washed with water (5 × 25 mL) and dried over sodium sulfate. Removal of the methylene chloride in vacuo afforded 0.195 g (100%) of 1,3-diazido-2-fluoro-2-nitropropane: ^1H NMR ($CDCl_3$) δ 3.87 (d, J = 16 Hz); ^{19}F NMR ($CDCl_3$) ϕ 133.8 (quintet, J = 16 Hz); IR ($CDCl_3$) 2150 (N_3), 1580, 1320 (NO_2) cm^{-1}.

A solution of 0.184 g of 1,3-diazido-2-fluoro-2-nitropropane and 0.159 g (2.27 mmol) of propiolic acid in 1.0 mL of chloroform was allowed to stand at room temperature for 54 h. The resulting precipitate was washed with chloroform to give 0.234 g of 1,3-bis[1-(4-(or 5-)-carboxy-1,2,3-triazolo)]-2-fluoro-2-nitropropane. An analytical sample was crystallized from acetone–carbon tetrachloride: mp 163–170 °C; ^1H NMR (acetone-d_6) δ 5.77 (m, 4 H, CH_2), 7.73 (s, 2 H, CO_2H) and 8.57 (s, 2 H, Ar); ^{19}F NMR (acetone-d_6) ϕ 134.0 (quintet, J = 16 Hz).

Anal. Calcd for $C_9H_8FN_7O_6$: C, 32.84; H, 2.45; N, 29.78. Found: C, 32.44; H, 2.65; N, 29.21.

1,3-Dimethoxy-2-fluoro-2-nitropropane. A mixture of 1.55 g (3.8 mmol) of 2-fluoro-2-nitro-1,3-propylene ditriflate, 31 mL of methanol, and 3.1 g of sodium sulfate was refluxed for 24 h. The reaction mixture was filtered and solvent was removed in vacuo to give 0.649 g of a yellow liquid. Chromatography on silica gel (1:1 methylene chloride–hexane) afforded 0.169 g (15.5%) of 2-fluoro-3-methoxy-2-nitro-1-propyl triflate: ^1H NMR ($CDCl_3$) δ 3.42 (s, 3 H, OCH_3), 3.92 (d, J = 15 Hz, 2 H, CH_2OCH_3), 4.95 (d, J = 15 Hz, 2 H, $CH_2OSO_2CF_3$); ^{19}F NMR ($CDCl_3$) ϕ 72.9 (s, 3 F, SO_2CF_3), 138.0 (quintet, J = 15 Hz, 1 F, $CFNO_2$). A 0.203-g (32.1%) sample of 1,3-dimethoxy-2-fluoro-2-nitropropane was also obtained: ^1H NMR ($CDCl_3$) δ 3.40 (s, 6 H, OCH_3), 3.73 and 4.03 (s and AB q pattern, 4 H, CH_2); ^{19}F NMR ($CDCl_3$) ϕ 138.6 (quintet, J = 16 Hz); IR (CH_2Cl_2) 1580, 1360 cm^{-1} (NO_2).

Anal. Calcd for $C_5H_{10}FNO_4$: C, 35.93; H, 6.03; N, 8.38. Found: C, 36.22; H, 6.24; N, 8.34.

2-Fluoro-3-hydroxy-2-nitro-1-propylpyridinium Triflate. To a solution of 0.271 g (1.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate in 2.7 mL of ether was added 0.081 mL (1.0 mmol) of pyridine. After the reaction mixture was stirred for 8 days at room temperature, ^{19}F NMR of the ether solution indicated that a small amount of the original monotriflate still remained. The ether was decanted from the viscous oil that had precipitated. The oil was washed with 2 mL of ether and with 20 mL of methylene chloride, leaving 0.316 g (90.3%) of 2-fluoro-3-hydroxy-2-nitro-1-propylpyridinium triflate: ^1H NMR (acetone-d_6) δ 4.33 (d, J = 16 Hz, 2 H, CH_2OH), 5.35 (1 H, OH), 5.75 (d, J = 16 Hz, 2 H, $CH_2NC_5H_5$); ^{19}F NMR (acetone-d_6) ϕ 78.0 (s, 3 F, SO_2CF_3), 137.5 (quintet, J = 16 Hz, 1 F, $FCNO_2$).

3-Chloro-2-fluoro-2-nitro-1-propanol. To 0.242 g (2.0 mmol) of 3-fluoro-3-nitrooxetane was added 1.0 mL (12 mmol) of concentrated HCl. After being allowed to stand for 30 min at room temperature, the reaction mixture was diluted with 4 mL of water and extracted with ethyl acetate (3 × 5 mL). The ethyl acetate solution was dried over potassium carbonate, and the solvent was then removed in vacuo to give 0.304 g (96.5%) of 3-chloro-2-fluoro-2-nitro-1-propanol. Chromatography on silica gel (9:1 methylene chloride–ethyl acetate) afforded an analytical sample: ^1H NMR ($CDCl_3$) δ 3.08 (br s, 1 H, OH), 4.05 (d, J = 16 Hz, 2 H, $CH_2OH(Cl)$), 4.12 (d, J = 16 Hz, 2 H, $CH_2Cl(OH)$); ^{19}F NMR ($CDCl_3$) ϕ 137.4 (quintet, J = 16 Hz); IR (CH_2Cl_2) 3630 (OH), 1580, 1360 cm^{-1} (NO_2).

Anal. Calcd for $C_3H_5NFClO_3$: C, 22.87; H, 3.20; N, 8.89. Found: C, 22.59; H, 3.41; N, 8.70.

3-Bromo-2-fluoro-2-nitro-1-propanol. To 0.363 g (3.0 mmol) of 3-fluoro-3-nitrooxetane was added 1.5 mL (13.5 mmol) of 48% HBr. After 1 h at room temperature, the reaction mixture was extracted with ether (3 × 10 mL). The ether extract was dried over sodium sulfate and potassium carbonate, and solvent was then removed in vacuo to give 0.564 g (93.1%) of 3-bromo-2-fluoro-2-nitro-1-propanol. Chromatography on silica gel (9:1 methylene chloride–ethyl acetate) afforded an analytical sample: ^1H NMR ($CDCl_3$) δ 3.25 (br t, 1 H, OH), 3.85 (d, J = 16 Hz, 2 H, CH_2Br), 3.92 (AB q, J = 16 Hz, 2 H, CH_2OH); ^{19}F NMR ($CDCl_3$) ϕ 134.0 (quintet, J = 16 Hz); IR (CH_2Cl_2) 3630 (OH), 1580, 1360 cm^{-1} (NO_2).

Anal. Calcd for $C_3H_5NFBrO_3$: C, 17.84; H, 2.50; N, 6.93. Found: C, 17.70; H, 2.53; N, 6.98.

Polymerization of 3-Fluoro-3-nitrooxetane. Phosphorus pentafluoride was bubbled into a solution of 0.121 g (1.0 mmol) of 3-fluoro-3-nitrooxetane in 1.2 mL of methylene chloride. Within a few minutes a solid had precipitated. The addition of PF_5 was stopped, and 0.2 mL of methanol was added. The solid was then filtered, washed well with methylene chloride, and air-dried to afford 0.100 g (82.6%) of poly(3-fluoro-3-nitrotrimethylene ether): mp 233–235 °C; ^1H NMR (Me_2SO-d_6) δ 4.03 (AB q, J = 16 Hz); ^{19}F NMR (Me_2SO-d_6) ϕ 139.8 (m); mol wt (vapor-phase osmometer, DMF, 60 °C) 2500.

2,2-Dinitro-3-hydroxy-1-propyl Triflate and 2,2-Dinitro-1,3-propylene Ditriflate. A solution of 1.7 mL (0.010 mol) of triflic anhydride in 15 mL of ether was added dropwise over a 9-min period at 12–18 °C to a solution of 1.66 g (0.010 mol) of 2,2-dinitro-1,3-propanediol and 0.81 mL (0.010 mol) of pyridine in 15 mL of ether. The mixture was stirred for 2 h at room temperature, and the resulting precipitate was filtered and washed with ether. Removal of ether in vacuo gave 3.0 g of a yellow liquid, which was dissolved in 20 mL of methylene chloride, washed with water, dried over sodium sulfate, and stripped of solvent. The residue was chromatographed on 60 g of silica gel. Elution with 100 mL of methylene chloride and 50 mL of 95:5 methylene chloride–ethyl acetate gave 0.607 g (14.0%) of 2,2-dinitro-1,3-propylene ditriflate. Crystallization from methylene chloride–petroleum ether gave an analytical sample: mp 54–55 °C; ^1H NMR ($CDCl_3$) δ 5.26 (s); ^{19}F NMR ($CDCl_3$) ϕ 72.0 (s); IR (CH_2Cl_2) 1590, 1305 (NO_2), 1425, 1220, 1140, 930 (OSO_2CF_3), 1000 cm^{-1} (CF).

Anal. Calcd for $C_5H_4N_2F_6S_2O_{10}$: C, 13.96; H, 0.94; N, 6.51. Found: C, 14.00; H, 1.02; N, 6.29.

Further elution with 9:1 methylene chloride–ethyl acetate afforded 1.4 g (46.8%) of 2,2-dinitro-3-hydroxy-1-propyl triflate. Crystallization from methylene chloride–petroleum ether gave an analytical sample: mp 43–44 °C; ^1H NMR ($CDCl_3$) δ 2.76 (br s, 1 H, OH), 4.52 (s, 2 H, CH_2OH), 5.21 (s, 2 H, $CH_2OSO_2CF_3$); ^{19}F NMR ($CDCl_3$) ϕ 72.4 (s); IR (CH_2Cl_2) 3620 (OH), 1585, 1320 (NO_2), 1420, 1220, 1140, 840 (OSO_2CF_3), 995 cm^{-1} (CF).

Anal. Calcd for $C_4H_5N_2F_3SO_8$: C, 16.11; H, 1.69; N, 9.40. Found: C, 16.27; H, 1.68; N, 9.67.

3-Hydroxy-2-(hydroxymethyl)-2-nitro-1-propyl Triflate and 2-(Hydroxymethyl)-2-nitro-1,3-propylene Ditriflate. A

solution of 1.9 mL (11.0 mmol) of triflic anhydride in 15 mL of 9:1 ether–ethyl acetate was added dropwise over 15 min at 18–21 °C with ice-bath cooling to a solution of 1.51 g (10.0 mmol) of 2-(hydroxymethyl)-2-nitro-1,3-propanediol and 0.90 mL (11.0 mmol) of pyridine in 30 mL of 1:1 ether–ethyl acetate. The mixture was stirred at room temperature for 1 h, and the resulting precipitate was filtered and washed with ether. Sovent was removed, and the residue wash chromatographed on 111 g of silica gel (4:1 methylene chloride–ethyl acetate) to give 0.671 g (16.2%) of 2-(hydroxymethyl)-2-nitro-1,3-propylene ditriflate. Crystallization from methylene chloride–petroleum ether gave an analytical sample: mp 56–57 °C; ^{1}H NMR ($CDCl_3$) δ 2.70 (br s, 1 H, OH), 4.05 (s, 2 H, CH_2OH), 4.90 (s, 4 H, $CH_2OSO_2CF_3$); ^{19}F NMR ($CDCl_3$) ϕ 72.4 (s); IR (CH_2Cl_2) 3600 (OH), 1570, 1355 (NO_2), 1420, 1220, 1150, 830 (OSO_2CF_3), 980 cm^{-1} (CF).

Anal. Calcd for $C_5H_5F_6NSO_9$: C, 17.36; H, 1.70; N, 3.37. Found: C, 18.59; H, 1.75; N, 3.64.

Continued elution afforded 1.258 g (44.4%) of 3-hydroxy-2-(hydroxymethyl)-2-nitro-1-propyl triflate. Crystallization from methylene chloride–petroleum ether gave an analytical sample: mp 72–73 °C; ^{1}H NMR (acetone-d_6) δ 4.03 (s, 4 H, CH_2OH), 4.47 (s, 2 H, OH), 5.10 (s, 2 H, $CH_2OSO_2CF_3$); ^{19}F NMR (acetone-d_6) ϕ 74.8 (s); IR ($CDCl_3$) 3610, 3380 (OH), 1560, 1360 (NO_2), 1420, 1225, 1150, 870, (OSO_2CF_3), 980 cm^{-1} (CF).

Anal. Calcd for $C_5H_6F_3NSO_7$: C, 21.21; H, 2.85; N, 4.95. Found: C, 21.02; H, 2.81; N, 4.76.

Registry No. 2-Fluoro-2-nitro-1,3-propanediol, 4776-99-2; 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate, 70187-43-8; 2-fluoro-2-nitro-1,3-propylene ditriflate, 75233-63-5; 3-fluoro-3-nitrooxetane, 70187-44-9; 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-fluoro-2-nitropropane, 75233-64-6; 1,3-diazido-2-fluoro-2-nitropropene, 75233-65-7; 1,3-dimethoxy-2-fluoro-2-nitropropane, 75233-66-8; 2-fluoro-3-hydroxy-2-nitro-1-propylpyridinime triflate, 75233-68-0; 3-chloro-2-fluoro-2-nitro-1-propanol, 75233-69-1; 3-bromo-2-fluoro-2-nitro-1-propanol, 75233-70-4; poly(3-fluoro-3-nitromethylene ether), 75232-62-1; 2,2-dinitro-3-hydroxy-1-propyl triflate, 75233-71-5; 2,2-dinitro-1,3-propylene ditriflate, 75233-72-6; 3-hydroxy-2-(hydroxymethyl)-2-nitro-1-propyl triflate, 75233-73-7; 2-(hydroxymethyl)-2-nitro-1,3-propylene ditriflate, 75247-60-8; diethyl fluoronitromalonate, 680-42-2; 1,3-bis(trimethylsiloxy)-2-fluoro-2-nitropropane, 75233-74-8; triflic anhydride, 358-23-6; FDNE, 17003-75-7; propiolic acid, 471-25-0; 1,3-bis[1-(4-(or 5-)-carboxy-1,2,3-triazolo)]-2-fluoro-2-nitropropane, 75232-63-2; 2-fluoro-3-methoxy-2-nitro-1-propyl triflate, 75233-75-9; 2-(hydroxymethyl)-2-nitro-1,3-propanediol, 126-11-4.

Reactions of 2-Fluoro-2-nitro-1,3-propanediol. p-Toluenesulfonates.[1]

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Abstract

Displacement reactions of the tosylates derived from 2-fluoro-2-nitro-1,3-propanediol, 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate and 2-fluoro-2-nitro-1,3-propylene di-p-toluenesulfonate, were studied. Direct substitution products were obtained with these tosylates and sodium azide, and with the monotosylate and lithium bromide. The monotosylate reacted under more strongly basic conditions to give products rationalized on the basis of the intermediate formation of 1-fluoro-1-nitroethylene. The monotosylate and potassium hydroxide gave a dimeric and a trimeric ether under conditions that did not affect the ditosylate. The monotosylate, but not the ditosylate gave a methyl ether with potassium methoxide. Dimethyl sodiomalonate and the monotosylate gave dimethyl 2-fluoro-2-nitroethylmalonate and dimethyl 2-fluoro-3-hydroxy-2-nitropropylmalonate.

We have recently developed an improved synthesis of 2-fluoro-2-nitro-1,3-propanediol and investigated the reactions of its triflate derivatives.[2] The monotriflate cyclized under mild conditions in the presence of a variety of bases to give 3-fluoro-3-nitrooxetane.[2] In connection with this work, we

$$HOCH_2CF(NO_2)CH_2OSO_2CF_3 \xrightarrow{\text{base}} F\text{-}C(NO_2)(CH_2\text{-}O)\text{-}CH_2$$

have examined the reactions of the corresponding tosylates. The tosylate group is a more commonly used leaving group for oxetane ring closures,[3] but in this system cyclization did not occur, and a different reaction course was followed.

The desired tosylates were prepared from 2-fluoro-2-nitro-1,3-propanediol by conventional procedures. The reaction of an excess of diol and pyridine with p-toluenesulfonyl chloride in refluxing chloroform afforded a 78% yield of 2-fluoro-3-hydroxy-2-nitro-1-propyl tosylate and a 10% yield of 2-fluoro-2-nitro-1,3-propylene ditosylate, whereas an excess of p-toluenesulfonyl chloride in pyridine gave the ditosylate in 67% yield.

$$HOCH_2CF(NO_2)CH_2OH \xrightarrow[TsCl]{\text{Pyridine}} TsOCH_2CF(NO_2)CH_2OH + TsOCH_2CF(NO_2)CH_2OTs$$

Although the monotosylate was consumed within minutes in a reaction with potassium hydroxide at room temperature, no 3-fluoro-3-nitrooxetane was detected. A solid product was obtained in 34% yield identified as 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl tosylate, the monotosylate of the dimeric ether. In addition, an 18.5% yield of the corresponding trimeric

ether was obtained. Under the same conditions, the oxetane was obtained from the corresponding triflate reaction.[2]

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow{KOH} HOCH_2CF(NO_2)CH_2\text{-}O\text{-}CH_2CF(NO_2)CH_2OTs$$
$$+ \; HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OTs$$

Superficially, this reaction appears to be a simple intermolecular nucleophilic displacement. One cannot rationalize, however, why, if the same mechanism is operating, there is a complete reversal from an intermolecular to an intramolcular reaction depending on whether the leaving group is tosylate or triflate. Furthermore, the tosylate groups of 2-fluoro-2-nitro-1,3-propylene ditosylate would be expected to have similar reactivity to that of the monotosylate. For this reason, a competition experiment was conducted in which an equimolar mixture of the monotosylate and the ditosylate was treated with base. The monotosylate was converted to the above dimer but all of the ditosylate was recovered.

Other displacement reactions of both the monotosylate and the ditosylate required much more severe conditions, but both compounds displayed similar reactivity. Neither compound reacted with sodium azide in dimethyl sulfoxide at room temperature. At 55° C, however, the monotosylate gave a 52% yield of 3-azido-2-fluoro-2-nitro-1-propanol, isolated as the triazole derivative from reaction with propiolic acid. Similarly, the ditosylate at 65°C gave a 97% yield of 1,3-diazido-2-fluoro-2-nitropropane. The monotosylate reacted at 100° C with lithium bromide in dimethyl sulfoxide to give an 80% yield of 3-bromo-2-fluoro-2-nitro-1-propanol, obtained previously from the oxetane.[2]

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow[DMSO]{NaN_3} HOCH_2CF(NO_2)CH_2N_3$$

$$TsOCH_2CF(NO_2)CH_2OTs \xrightarrow[DMSO]{NaN_3} N_3CH_2CF(NO_2)CH_2N_3$$

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow[DMSO]{LiBr} HOCH_2CF(NO_2)CH_2Br$$

The extreme reactivity of the monotosylate in the dimerization reaction compared to its reactivity and that of the ditosylate in the other displacement reactions thus indicates that the mechanism of the dimerization is not simple nucleophilic displacement. A key factor permitting the synthesis of 3-fluoro-3-nitrooxetane is the inhibition of deformylation by fluorine.[4] Nonfluorinated 2-nitroalcohols are deformylated readily by base,[5] and nitronate salts with leaving groups at the β position, are converted to olefins.[6] If deformylation is involved in the dimerization of

$$HOCH_2C(NO_2)RCH_2X \xrightarrow{OH^-} {}^-O_2NCRCH_2X \xrightarrow{X^-} O_2NCR{=}CH_2$$

the monotosylate, the reaction should be suppressed by mass action if formaldehyde is added. It was found, in fact, that when the dimerization experiment was repeated with formalin added to the reaction mixture, 33% of the monotosylate starting material was recovered after a 25 min reaction

period. Without the added formaldehyde, the reaction was complete in 5 min. These results are consistent with the mechanism, shown in Scheme I. Defor-

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Scheme I

$$HOCH_2CF(NO_2)CH_2OTs \xrightleftharpoons{OH^-} {}^{\ominus}OCH_2CF(NO_2)CH_2OTs$$

$${}^{\ominus}OCH_2CF(NO_2)CH_2OTs \xrightleftharpoons[CH_2O]{-CH_2O} {}^{\ominus}O_2N{=}CFCH_2OTs$$

$${}^{\ominus}O_2N{=}CFCH_2OTs \longrightarrow NO_2CF{=}CH_2 + {}^{\ominus}OTs$$

$$NO_2CF{=}CH_2 + {}^{\ominus}OCH_2CF(NO_2)CH_2OTs \longrightarrow {}^{\ominus}O_2N{=}CFCH_2OCH_2CF(NO_2)CH_2OTs$$

$$\xrightarrow{CH_2O} \xrightarrow{H^+} HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OTs$$

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formylation and elimination of tosylate would give 1-fluoro-1-nitroethylene, and Michael addition of the salt of the original monotosylate to 1-fluoro-1-nitroethylene, followed by recombination of the resulting nitronate salt with formaldehyde would give the observed dimeric ether. The trimeric ether would be formed similarly by the addition of this dimeric product to more 1-fluoro-1-nitroethylene. There is precedent for the addition of alcohols to nitroolefins,[7] and the preparation of 1-fluoro-1-nitroethylene has been reported.[8]

On the other hand, the reactions of the monotosylate and the ditosylate

with bromide and azide ion appear to proceed by a direct displacement mechanism. These reagents are apparently insufficiently basic to generate 1-fluoro-1-nitroethylene. Likewise, the cyclization of the monotriflate to the oxetane takes place by nucleophilic displacement. In this case the ring closure is attributed to the ability of the more reactive leaving group[9] to undergo intramolecular displacement faster than deformylation.

That treatment of the monotosylate with base results in the <u>in situ</u> generation of 1-fluoro-1-nitroethylene was further supported by trapping with other nucleophiles. Thus, the monotosylate reacted with potassium methoxide in methanol at room temperature to give 2-fluoro-3-methoxy-2-nitro-1-propanol in 35% yield. Under these conditions the ditosylate reacted much more slowly, and only decomposition resulted. Similarly, reaction of the monotosylate

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow{KOCH_3} HOCH_2CF(NO_2)CH_2OMe$$

with an excess of dimethyl sodiomalonate in tetrahydrofuran at room temperature gave dimethyl 2-fluoro-2-nitroethylmalonate in 29% yield. The formaldehyde generated in the reaction is apparently trapped by the excess malonate salt. When this reaction was carried out with only 2 equivalents of the malonate salt, followed by the addition of 2 equivalents of formaldehyde, dimethyl 2-fluoro-3-hydroxy-2-nitropropylmalonate was obtained in 24% yield.

$$HOCH_2CF(NO_2)CH_2OTs + \ominus CH(CO_2Me)_2 \xrightarrow{THF} H\text{-}CF(NO_2)CH_2CH(CO_2Me)_2$$

$$\xrightarrow{CH_2O} HOCH_2CF(NO_2)CH_2CH(CO_2Me)_2$$

Bromide as a leaving group would be expected to behave more like tosylate than triflate in these reactions. Indeed, the reaction of 3-bromo-2-fluoro-2-nitro-1-propanol with base gave an oil, not readily purified for analysis, with the spectral properties expected for 7-bromo-2,6-difluoro-2,6-dinitro-4-oxaheptan-1-ol. The same product was obtained independently by the reaction of the dimeric tosylate with lithium bromide.

$$HOCH_2CF(NO_2)CH_2Br \xrightarrow{KOH} HOCH_2CF(NO_2)CH_2\text{-}O\text{-}CH_2CF(NO_2)CH_2Br$$

$$\uparrow LiBr$$

$$HOCH_2CF(NO_2)CH_2\text{-}O\text{-}CH_2CF(NO_2)CH_2OTs$$

Thus, compounds of the structure $HOCH_2CF(NO_2)CH_2X$ undergo three different modes of reaction, depending on the nature of the leaving group and the nucleophilic reagent. With the highly reactive triflate leaving group, oxetane ring closure takes place with a variety of bases. With the less reactive tosylate leaving group, weakly basic nucleophilie reagents result in direct displacement products, but strongly basic reagents result in deformylation and elimination to give 1-fluoro-1-nitroethylene in-situ. Michael adducts of this olefin are isolated.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. Previously described safety precautions for nitro compounds[10] were observed.

2-Fluoro-3-hydroxy-2-nitro-1-propyl p-Toluenesulfonate. A solution of 1.91 g (10 mmol) of p-toluenesulfonyl chloride in 28 mL of chloroform was added dropwise over 2.5 h to a refluxing solution of 2.78 g (20 mmol) of 2-fluoro-2-nitro-1,3-propanediol[2] and 1.6 mL (20 mmol) of pyridine in 28 mL of chloroform. The reaction mixture was then heated at reflux for 5 h, cooled, and washed with 10 mL of water, two 10 mL portions of 1.0 M HCl, and then with 10 mL of water. The chloroform solution was dried and evaporated to give 2.6 g of a white solid, which was recrystallized from methylene chloride-petroleum ether to give 1.6 g of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate. Recrystallization gave an analytical sample: mp 88-89°C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H, CH_3), 2.90 (br s, 1 H, -OH), 4.00 (d, J= 16 Hz, 2 H, $-CH_2OH$), 4.52 (d, J=16 Hz, 2 H, $-CH_2OTs$), 7.40 (m, 4 H, Ph); ^{19}F NMR ($CDCl_3$) ϕ 138.8 (quintet, J=16 Hz); IR (CH_2Cl_2) 3620 (-OH), 1585 ($-NO_2$), 1380, 1195, 1180 ($-OSO_2-C_6H_4CH_3-p$), 1020 cm^{-1} (C-F).

Anal. Calcd for $C_{10}H_{12}FNSO_6$: C, 40.96; H, 4.12; N, 4.78. Found: C, 40.77; H, 4.11; N, 4.57.

The mother liquor was chromatographed on silica gel (methylene chloride-ethyl acetate) to give 0.44 g (10.0%) of the corresponding ditosylate and an additional 0.68 g (2.28 g combined yield; 77.8%) of the monotosylate. The first water extract and the first acid extract were combined and extracted

with ethyl acetate (3 x 20 mL) to recover 1.3 g of 2-fluoro-2-nitro-1,3-propanediol.

2-Fluoro-2-nitro-1,3-propylene Di-p-toluenesulfonate. A solution of 6.10 g (32 mmol) of p-toluenesulfonyl chloride in 20 mL of pyridine was added dropwise over 15 min to a stirred solution of 1.12 g (8 mmol) of 2-fluoro-2-nitro-1,3-propanediol in 20 mL of pyridine. After 17 h, the reaction mixture was poured into 240 mL of ice water. The resulting solid precipitate was filtered and washed with water and petroleum ether. The combined aqueous layers were extracted with methylene chloride (2 x 50 mL), and the resulting solution was washed with cold 2 M HCl (2 x 50 mL) and with water (50 mL), dried and stripped of solvent to give 0.3 g of a viscous liquid. The solid and liquid were combined and crystallized from ethanol to give 2.40 g (67.1%) of 2-fluoro-2-nitro-1,3-propylene di-p-toluenesulfonate. Recrystallization from ethanol afforded an analytical sample: mp 90-91°C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 6 H, CH_3), 4.47 (d, J=16 Hz, 4 H, $-CH_2-$), 7.43 (m, 8 H, Ph); ^{19}F NMR ($CDCl_3$) ϕ 136.8 (quintet, J=16 Hz); IR (CH_2Cl_2) 1590 ($-NO_2$), 1380, 1195, 1180 ($-OSO_2-C_6H_4CH_3-p$), 1010 cm^{-1} (C-F).

Anal. Calcd for $C_{17}H_{18}FNS_2O_8$: C, 45.63; H, 4.06; N, 3.13. Found: C, 45.64; H, 4.17; N, 3.17.

Reaction of 2-Fluoro-3 hydroxy-2-nitro-1-propyl p-Toluenesulfonate with Potassium Hydroxide. A solution of 0.293 g (1.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate in 2.0 mL of dioxane and 1.5 mL of 0.67 M potassium hydroxide was stirred at room temperature for 25 min. The resulting orange solution was extracted with ethyl acetate (3 x 10 mL)

to give 0.2 g a yellow residue. Flash chromatography[11] (9:1 methylene-chloride-ethyl acetate) gave 0.070 g (34%) of 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl-p-toluenesulfonate. Crystallization from methylene chloride-petroleum ether gave an analytical sample: mp 89-90°C; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H, CH_3), 4.03 (d, J=16 Hz, 7 H, $-CH_2-$ and -OH), 4.43 (d, J=16 Hz, 2 H, $-CH_2O-SO_2$, 7.40 (m, 4 H, C_6H_4); ^{19}F NMR (acetone) ϕ 140.6 (quintet, J=16 Hz, 1 F, $C(F)(NO_2)-CH_2O-SO_2C_6H_4CH_3-_p$), 142.2 (quintet, J=16 Hz, 1 F, $C(F)(NO_2)-CH_2OH$); IR (CH_2Cl_2) 3625 (-OH), 1580 ($-NO_2$), 1380, 1195, 1180 ($-SO_2-C_6H_4CH_3-_p$), 1030 cm^{-1} (C-F).

Anal. Calcd for $C_{13}H_{16}F_2N_2SO_9$: C, 37.68; H, 3.89; N, 6.76. Found: C, 37.62; H, 3.83; N, 6.61.

Further elution with 4:1 methylene chloride-ethyl acetate gave 0.033 g (18.5%) of 11-hydroxy-2,6,10-trifluoro-2,6,10-trinitro-4,8-dioxa-1-undecyl p-toluenesulfonate. Crystallization from methylene chloride-hexane gave an analytical sample: mp 93-94°C; ^{1}H NMR (acetone-D_6) δ 2.45 (s, 3 H, CH_3), 3.97-4.90 (m, 12 H, $-CH_2-$), and 7.47 (m, 4 H, C_6H_4); ^{19}F NMR (acetone - D_6) ϕ 140.2 (br m, 2 F, $HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2O-$), 142.0 (br m, 1 F, $-CF(NO_2)CH_2OC_6H_4$); IR (CH_2Cl_2) 3650 (-OH), 1585, 1360 ($-NO_2$), 1380, 1200, 1185 (-OTs), 1040 cm^{-1} (C-F).

Anal. Calcd for $C_{16}H_{20}F_3N_3SO_{12}$: C, 35.89; H, 3.77; N, 7.85. Found: C, 35.94; H, 3.83; N, 7.92.

3-Azido-2-fluoro-2-nitro-1-propanol. A solution of 0.293 g (1.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate and 0.069 g (1.0 mmol) of sodium azide in 3 mL of dimethyl sulfoxide was heated at 55°C for

66 h. The reaction mixture was then cooled, diluted with 18 mL of water, and extracted with methylene chloride (3 x 10 mL). The methylene chloride solution was washed with water (2 x 10 mL), dried and evaporated to give 0.11 g of a yellow oil consisting of 3-azido-2-fluoro-2-nitro-1-propanol (51.8% yield by ^{1}H NMR) contaminated with small amounts of monotosylate and DMSO. ^{1}H NMR ($CDCl_3$) δ 3.90 (d, J=16 Hz, 2 H, $-CH_2OH$), 4.00 (d, J=16 Hz, 2 H, $-CH_2N_3$); ^{19}F NMR ($CDCl_3$) ϕ 137.0 (quintet, J=16 Hz); IR (CH_2Cl_2) 2150 ($-N_3$), 5185, 1380 cm^{-1} ($-NO_2$).

The crude azide and 0.050 g, (0.7 mmol) of propiolic acid were dissolved in 0.6 mL of chloroform. After several days 0.077 g of 1-(2-fluoro-3-hydroxy-2-nitropropyl)-4-(or 5-)-carboxy-1,2,3-triazole was isolated by filtration. Recrystallization from acetonitrile-carbon tetrachloride gave an analytical sample: mp 175-177°C; ^{1}H NMR (acetone-D_6) δ 4.13 and 4.42 (s and AB q, 2 H, $-\underline{CH_2}OH$), 5.30 and 5.53 (s and AB q, 2 H, $-CH_2-N$), 7.25 (br s, 1 H, $-CO_2H$), 8.38 (s, 1 H, triazole); ^{19}F NMR (acetone-D_6) ϕ 139.2 (quintet, J=16 Hz).

<u>Anal.</u> Calcd for $C_6H_7FN_4O_5$: C, 30.78; H, 3.01. Found: C, 30.59; H, 3.22.

<u>1,3-Diazido-2-fluoro-2-nitropropane</u>. A solution of 0.447 g (1.0 mmol) of 2-fluoro-2-nitro-1,3-propylene ditosylate and 0.20 g (3.0 mmol) of sodium azide in 5 mL of dimethyl sulfoxide was heated at 65°C for 20 h. The reaction mixture was then cooled, diluted with 45 ml of water, and extracted with methylene chloride (3 x 20 mL). The methylene chloride solution was washed with water (5 x 30 mL), dried and stripped of solvent to give 0.184 g

(97.4%) of 1,3-diazido-2-fluoro-3-nitropropane, which was shown by ^{1}H NMR, ^{19}F NMR, and IR to be identical with the material obtained previously.[2]

3-Bromo-2-fluoro-2-nitro-1-propanol. A solution of 0.897 g (3.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate and 0.800 g (9.0 mmol) of lithium bromide (dried overnight at 135°C) in 9 mL of dimethyl sulfoxide was heated at 100°C for 16 h. No monotosylate remained (^{19}F NMR). The reaction mixture was cooled, diluted with 81 mL of water, and extracted with methylene chloride (3 x 30 mL) to give 1.16 g of yellow liquid. Flash chromatography[11] (silica gel, 9:1 methylene chloride-ethyl acetate) afforded 0.486 g (80.2%) of 3-bromo-2-fluoro-2-nitro-1-propanol, identical with an authentic sample.[2]

2-Fluoro-3-methoxy-2-nitro-1-propanol. To 20 mL of a 1.0 M solution of potassium methoxide in methanol was added 2.93 g (10.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate. The mixture was stirred for 30 min and the resulting precipitate was filtered and washed with methanol. Solvent was removed from the combined methanol solutions and the residue was dissolved in 10 mL of water. The aqueous solution was extracted with methylene chloride (3 x 15 mL) and ether (2 x 14 mL), acidified to pH 6, and extracted again with ether (2 x 15 mL). The combined organic solutions were then dried and evaporated. Chromatography on 45 g of silica gel (methylene chloride-ethyl acetate) afforded 0.538 g (35.2%) of 2-fluoro-3-methoxy-2-nitro-1-propanol. Vacuum distillation gave an analytical sample: bp 92-93°C (0.27 mm); ^{1}H NMR ($CDCl_3$) δ 2.92 (br s, 1 H, -OH), 3.43 (s, 3 H, $-OCH_3$), 3.77 and 4.05 (s and AB quartet, 2 H, $-CH_2OCH_3$), 3.93 and 4.20 (s and AB quartet, 2 H, $-\underline{CH_2}OH$);

^{19}F NMR ($CDCl_3$) ϕ 140.4 (quintet, J=16 Hz); IR (CH_2Cl_2) 3630 (-OH), 1570, 1355 ($-NO_2$), 1060 cm^{-1} (C-F).

Anal. Calcd for $C_4H_8FNO_4$: C, 31.39; H, 5.27; N, 9.15. Found: C, 31.50; H, 5.01; N, 8.95.

Dimethyl 2-Fluoro-2-nitroethylmalonate. Dimethyl malonate (1.53 g, 11 mmol) was added dropwise with stirring to a suspension of 10 mmol of sodium hydride in 10 mL of dry tetrahydrofuran at 0°C, and 0.586 g (2.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate was added to the resulting gel. A homogeneous solution formed in 10 min that slowly became viscous. After 17 h, 10 mL of 1.0 M HCl was added slowly with cooling, and the product was extracted with ethyl acetate (2 x 20 mL). The ethyl acetate solution was dried and solvent was removed, and the residue was extracted with methylene chloride. Chromatography of the extract (50 g of silica gel, methylene chloride-ethyl acetate) gave 0.130 g (29.1%) of dimethyl 2-fluoro-2-nitroethylmalonate, a viscous oil: ^1H NMR ($CDCl_3$) δ 2.35-3.10 (m, 2 H, CH_2), 3.63 (t, J=8 Hz, 1 H, $\underline{CH}CO_2CH_3$), 3.77 (s, 6 H, CO_2CH_3), 5.53 and 6.33 (d,t, J=6 and 47 Hz, 1 H, H-$CFNO_2$); ^{19}F NMR ($CDCl_3$) ϕ 145.9 (d,t, J=20 and 48 Hz); IR (CH_2Cl_2) 1740 (CO_2CH_3), 1580, 1360 ($-NO_2$), 1065 cm^{-1} (C-F).

Anal. Calcd for $C_7H_{10}FNO_6$: Found: C, 37.68; H, 4.52; N, 6.28. Found: C, 37.82; H, 4.49; N, 6.12.

Dimethyl 2-Fluoro-3-hydroxy-2-nitropropylmalonate. Dimethyl malonate (0.277 g, 2.0 mmol) was added dropwise at 0° to a suspension of sodium hydride (2.0 mmol) in 10 mL of dry tetrahydrofuran, and 0.293 g (1.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate was added. The

mixture was stirred at room temperature for 21 h and 0.1 mL (2 mmol) of formalin was then added. The reaction mixture was then cooled to 0°C and 10 mL of 1.0 M HCl was added dropwise. The resulting solution was extracted with ethyl acetate (2 x 20 mL), and the ethyl acetate solution was dried and evaporated. Flash chromatography[11] (9:1 methylene chloride-ethyl acetate) of the residue gave 0.062 g (24.5%) of analytically pure dimethyl 2-fluoro-3-hydroxy-2-nitropropylmalonate: ^{1}H NMR ($CDCl_3$) δ2.93 (br s, 1 H, -OH), 2.72 and 3.02 (d of d, J=7 and 18 Hz, 2 H, $CFCH_2$, 3.53 (t, J=7 Hz, 1 H, C-H), 3.72 and 3.73 (s, 6 H, CO_2CH_3), 3.90 and 4.17 (s and AB quartet, 2 H, $-CH_2OH$); ^{19}F NMR ($CDCl_3$) ϕ 134.8 (quintet, J=18 Hz); IR (CH_2Cl_2) 3620 (-OH), 1740 ($-CO_2CH_3$), 1570, 1350 ($-NO_2$), 1080 cm^{-1} (C-F).

Anal. Calcd for $C_8H_{12}FNO_7$: C, 37.95; H, 4.78; N, 5.53. Found: C, 37.81; H, 4.77; N, 5.46.

7-Bromo-2,6-difluoro-2,6-dinitro-4-oxaheptan-1-ol. A. A 1.0 M potassium hydroxide solution (2.0 mL) was added to a solution of 0.404 g (2.0 mmol) of 3-bromo-2-fluoro-2-nitro-1-propanol[2] in 2.0 mL of dioxane. The resulting orange solution was stirred at room temperature for 30 min and was then extracted with ethyl acetate (3 x 10 mL). The ethyl acetate solution was dried and solvent was removed. Flash chromatography[11] of the residue on silica gel (9:1 methylene chloride-ethyl acetate) afforded 0.101 g (31.3%) of 7-bromo-2,6-difluoro-2,6-dinitro-4-oxaheptan-1-ol: ^{1}H NMR ($CDCl_3$) 3.75-4.38 (m, 8 H, $-CH_2-$), 2.60 (br s, 1 H, -OH); ^{19}F NMR ($CDCl_3$) ϕ 131.2 (quintet, J=16 Hz, 1 F, $CF(NO_2)-CH_2Br$), 139.6 (quintet, J=16 Hz, 1 F, $CF(NO_2)-CH_2OH$; IR (CH_2Cl_2) 3640 (-OH), 1580 and 1355 cm^{-1} ($-NO_2$).

B. A solution of 0.111 g (0.27 mmol) of 2,6-difluoro-7 hydroxy-2,6-dinitro-

4-oxa-1-heptyl p-toluenesulfonate and 0.050 g (0.6 mmol) of dry lithium bromide in 1.1 mL of dry DMSO was heated at 100°C for 16 h. The reaction mixture was cooled, diluted with 10 mL of water and extracted with ether (3 x 10 mL). Flash chromatography of the residue on silica gel (9:1 methylene chloride-ethyl acetate) afforded 0.060 g (69.3%) of 7-bromo-2, 6-difluoro-2,6-dinitro-4-oxaheptan-1-ol, which was identical by ^{1}H NMR, ^{19}F NMR, and IR with the above material.

References

1. This work was supported by the Office of Naval Research.
2. Berkowitz, P.T.; Baum, K. J. Org. Chem., 1980, 45, 4853.
3. Balsamo, A.; Ceccarelli, G.; Crotti, P.; Macchia, F. J. Org. Chem., 1975, 40, 473. Rowland, A.T.; Drawbaugh, R.S.; Dalton, J.R. J. Org. Chem., 1977, 42, 487.
4. Adolph, H.G.; Kamlet, M.J. J. Am. Chem. Soc., 1966, 88, 4761. Hine, J.; Mahone, L.G.; Liotta, C.L. J. Am. Chem. Soc., 1967, 89, 5911.
5. Feuer, H.; Bachman, G.B.; Kispersky, J.P. J. Am. Chem. Soc., 1951, 73, 1360.
6. Melton, J.; McMurry, J.E. J. Org. Chem., 1975, 40, 2138. Ville, J. Bull. Soc. Chim. Fr., 1959, 1407. Carroll, F.I.; Kepler, V.A. Can. J. Chem., 1966, 44, 2909.
7. Lambert, A.; Scaife, C.W.; Wilder-Smith, A.E. J. Chem. Soc., 1947, 1474. Hopff, H.; Capaul, M. Helv. Chim. Acta., 1960, 43, 1904.
8. Eremenko, L.T.; Oreshko, G.V. Izv. Akad. Nauk. SSSR, Ser Khim., 1969, 724.

9. Hansen, R.L. J. Org. Chem., 1965, 30, 4322. Streitwieser Jr, A.; Wilkins, C.L.; Kiehlmann, E. J. Am. Chem. Soc., 1968, 90, 1598. Mun Su, T.; Silwinski, W.F.; Schleyer, P. von R. J. Am. Chem. Soc., 1969, 91, 5386.

10. Grakauskas, V.; Baum, K. J. Org. Chem., 1968, 33, 3080. Kamlet, M.J.; Adolph, H.G. J. Org. Chem., 1968, 33, 3073.

11. Still, W.C.; Kahn, M.; Mitra, A. J. Org. Chem., 1978, 43, 2923.

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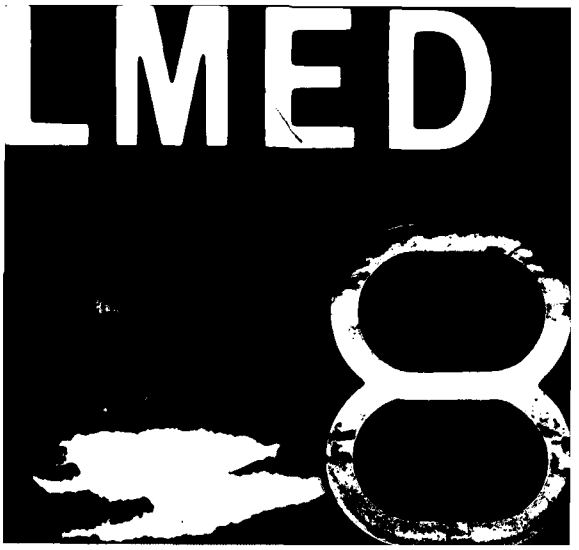
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