Scheme III

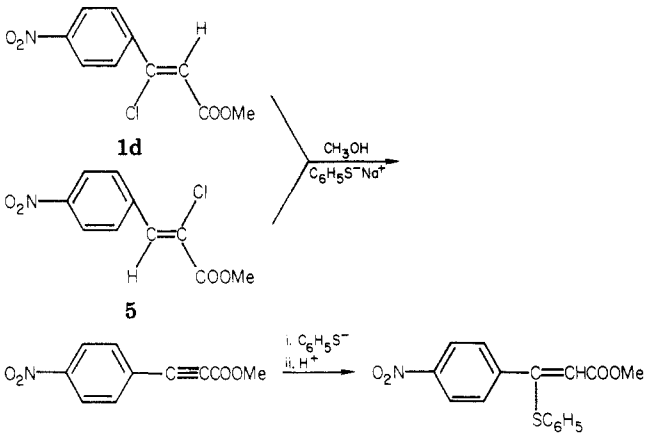

Table IV

compd	mp, °C	% yield	λ_{max},[a] nm (ϵ)	ν(C=O, CS), cm^{-1}
3a	63-65	88	260 (10 000)	1700, 660
3b	63-64	86	286 (4590)	1715, 650
3c	66-70	90	269 (5500)	1730, 630

[a] In ethanol.

Reaction of Para-Substituted Methyl Phenylpropiolates with Sodium Thiophenoxide in Absolute Methanol. Para-substituted phenylpropiolic acids were prepared by the dehydrobromination of the corresponding dibromide with 35% alcoholic potassium hydroxide. The methyl esters were synthesized by the reaction of the corresponding acids with absolute methanol in presence of dry hydrogen chloride. The addition experiments were carried out by treating the appropriate para-substituted methyl phenylpropiolate (0.5–1 g) dissolved in absolute methanol with an equivalent amount of sodium thiophenoxide under a nitrogen atmosphere for 3 days at 50 °C. The mixture was poured into ice-cold water, and the precipitated solid was filtered and crystallized from the appropriate solvent. Table IV lists the properties of the products from the reaction of para-substituted phenylpropiolates **3a–c** with thiophenoxide ion in methanol.

Kinetic Measurements. The rates of reaction were determined by following the rates of liberation of chloride ion by the electrometric method as previously reported.[1,15] Most reactions were followed to 80% completion, and in all cases the infinity titer was found to agree with the calculated value.

Acknowledgment. We are grateful to Professor Dr. B. Thomas of York University, England, for running and interpreting the mass spectra.

Registry No. 1a, 56377-29-8; **1b**, 56377-28-7; **1c**, 56377-31-2; **1d**, 56377-30-1; **2a**, 34875-03-1; **2b**, 78089-36-8; **2c**, 78089-37-9; (*E*)-**2d**, 78089-38-0; (*Z*)-**2d**, 78089-39-1; **3a**, 4891-38-7; **3b**, 7515-16-4; **3c**, 7515-18-6; (*E*)-**4a**, 34875-13-3; (*E*)-**4b**, 78089-40-4; (*E*)-**4c**, 78089-41-5; **5**, 14898-20-5; **6**, 78089-42-6; sodium thiophenoxide, 930-69-8; thiophenoxide(1–), 13133-62-5.

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

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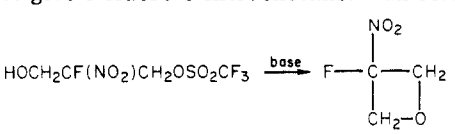
Displacement reactions of the tosylates derived from 2-fluoro-2-nitro-1,3-propanediol, 2-fluoro-3-hydroxy-2-nitro-1-propyl *p*-toluenesulfonate and 2-fluoro-2-nitro-1,3-propylene di-*p*-toluenesulfonate, were studied. Direct substitution products were obtained with these tosylates and sodium azide and 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-nitroethyl)malonate and dimethyl (2-fluoro-3-hydroxy-2-nitropropyl)malonate.

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 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.

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

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

(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.

0022-3263/81/1946-3816$01.25/0

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]

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow{KOH} HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OTs + HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OTs$$

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 intramolecular 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]

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow[Me_2SO]{NaN_3} HOCH_2CF(NO_2)CH_2N_3$$

$$TsOCH_2CF(NO_2)CH_2OTs \xrightarrow[Me_2SO]{NaN_3} N_3CH_2CF(NO_2)CH_2N_3$$

$$HOCH_2CF(NO_2)CH_2OTs \xrightarrow[Me_2SO]{LiBr} HOCH_2CF(NO_2)CH_2Br$$

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-nitro alcohols 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

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

of 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. Deformylation 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]

Scheme I

$$HOCH_2CF(NO_2)CH_2OTs \rightleftharpoons {}^-OCH_2CF(NO_2)CH_2OTs$$

$${}^-OCH_2CF(NO_2)CH_2OTs \underset{CH_2O}{\overset{-CH_2O}{\rightleftharpoons}} {}^-O_2N{=}CFCH_2OTs$$

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

$$NO_2CF{=}CH_2 + {}^-OCH_2CF(NO_2)CH_2OTs \longrightarrow {}^-O_2N{=}CFCH_2OCH_2CF(NO_2)CH_2OTs \xrightarrow{CH_2O} \xrightarrow{H^+} HOCH_2CF(NO_2)CH_2OCH_2CF(NO_2)CH_2OTs$$

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 in situ 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

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

conditions the ditosylate reacted much more slowly, and only decomposition resulted. Similarly, reaction of the monotosylate with an excess of dimethyl sodiomalonate in tetrahydrofuran at room temperature gave dimethyl (2-fluoro-2-nitroethyl)malonate 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 equiv of the malonate salt, followed

$$HOCH_2CF(NO_2)CH_2OTs + {}^-CH(CO_2Me)_2 \xrightarrow{THF} HCF(NO_2)CH_2CH(CO_2Me)_2 \xrightarrow{CH_2O} HOCH_2CF(NO_2)CH_2CH(CO_2Me)_2$$

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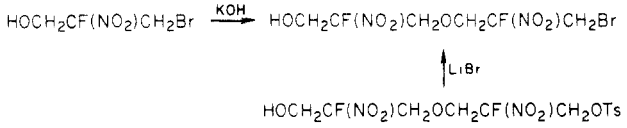
by the addition of 2 equiv of formaldehyde, dimethyl (2-fluoro-3-hydroxy-2-nitropropyl)malonate was obtained in 24% yield.

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.

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 nucleophilic 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; ^1H 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 ($OSO_2C_6H_4CH_3$-*p*), 1020 cm^{-1} (CF).

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 × 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 × 50 mL), and the resulting solution was washed with cold 2 M HCl (2 × 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; ^1H 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 ($OSO_2C_6H_4CH_3$-*p*), 1010 cm^{-1} (CF).

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 × 10 mL) to give 0.2 g of 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; ^1H 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_2OSO_2, 7.40 (m, 4 H, C_6H_4); ^{19}F NMR (acetone) ϕ 140.6 (quintet, J = 16 Hz, 1 F, $C(F)(NO_2)CH_2OSO_2C_6H_4CH_3$-*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 ($SO_2C_6H_4CH_3$-*p*), 1030 cm^{-1} (CF).

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; ^1H 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, $CF(NO_2)CH_2OS$); IR (CH_2Cl_2) 3650 (OH), 1585, 1360 (NO_2), 1380, 1200, 1180 ($SO_2C_6H_4CH_3$-*p*) 1040 cm^{-1} (CF).

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 × 10 mL). The methylene chloride solution was washed with water (2 × 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 ^1H NMR) contaminated with small amounts of monotosylate and Me_2SO: ^1H 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), 1585, 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; ^1H NMR (acetone-d_6) δ 4.13 and 4.42 (s and AB q, 2 H, CH_2OH), 5.30 and 5.53 (s and AB q, 2 H, CH_2N), 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).

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

1,3-Diazido-2-fluoro-2-nitropropane. 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 × 20 mL). The methylene chloride solution was washed with water (5 × 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 ^1H NMR, ^{19}F NMR, and IR spectra to be identical with the material obtained previously.[2]

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

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 × 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 × 15 mL) and ether (2 × 14 mL), acidified to pH 6, and extracted again with ether (2 × 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, CH_2OH); ^{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} (CF).

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-nitroethyl)malonate. 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 × 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–nitroethyl)malonate, 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, $CHCO_2CH_3$), 3.77 (s, 6 H, CO_2CH_3), 5.53 and 6.33 (d, t, J = 6 and 47 Hz, 1 H, $HCFNO_2$); ^{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} (CF).

Anal. Calcd for $C_7H_{10}FNO_6$: 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-nitropropyl)malonate. Dimethyl malonate (0.277 g, 2.0 mmol) was added dropwise at 0 °C 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 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 × 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-nitropropyl)malonate: ^{1}H NMR ($CDCl_3$) δ 2.93 (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, CH), 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} (CF).

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 × 10 mL). The ethyl acetate solution was dried and the 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 ($CDCl_3$) δ 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 Me_2SO was heated at 100 °C for 16 h. The reaction mixture was cooled, diluted with 10 mL of water, and extracted with ether (3 × 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 comparison of ^{1}H NMR, ^{19}F NMR, and IR spectra with the above material.

Registry No. 2-Fluoro-3-hydroxy-2-nitro-1-propyl toluenesulfonate, 78328-82-2; 2-fluoro-2-nitro-1,3-propylene di-*p*-toluenesulfonate, 78328-83-3; 2-fluoro-2-nitro-1,3-propanediol, 4776-99-2; 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl *p*-toluenesulfonate, 78328-84-4; 11-hydroxy-2,6,10-trifluoro-2,6,10-trinitro-4,8-dioxa-1-undecyl *p*-toluenesulfonate, 78328-85-5; 3-azido-2-fluoro-2-nitro-1-propanol, 78328-86-6; 1-(2-fluoro-3-hydroxy-2-nitropropyl)-4(5)-carboxy-1,2,3-triazole, 78328-91-3; 1,3-diazido-2-fluoro-2-nitropropane, 75233-65-7; 3-bromo-2-fluoro-2-nitro-1-propanol, 75233-70-4; 2-fluoro-3-methoxy-2-nitro-1-propanol, 78328-87-7; dimethyl (2-fluoro-3-hydroxy-2-nitropropyl)malonate, 78328-88-8; dimethyl malonate, 108-59-8; dimethyl (2-fluoro-2-nitroethyl)malonate, 78328-89-9; 7-bromo-2,6-difluoro-2,6-dinitro-4-oxaheptan-1-ol, 78328-90-2.