

4-(Trinitromethyl)tetrahydro-2-furanol and 4-(Fluorodinitromethyl)tetrahydro-2-furanol *via* Lactone Reduction with Borane. The Preparation of *cis/trans*-2-Polynitroalkoxy-4-polynitromethyltetrahydrofurans

Michael E. Sitzmann\* and William H. Gilligan

Naval Surface Weapons Center, White Oak Laboratory,  
10901 New Hampshire Avenue,  
Silver Spring, Maryland 20903-5000  
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Normally borane reduces lactones too rapidly to allow the isolation of intermediates but 4-(trinitromethyl)tetrahydro-2-furanol and 4-(fluorodinitromethyl)tetrahydro-2-furanol are isolated in 72 and 36% yield from the reduction of 4-hydroxy-3-(trinitromethyl)butyric acid,  $\gamma$ -lactone and 4-hydroxy-3-(fluorodinitromethyl)butyric acid,  $\gamma$ -lactone with borane-tetrahydrofuran complex. The preparation of 2-polynitroalkoxy-4-polynitromethyltetrahydrofurans from the 2-furanols is described.

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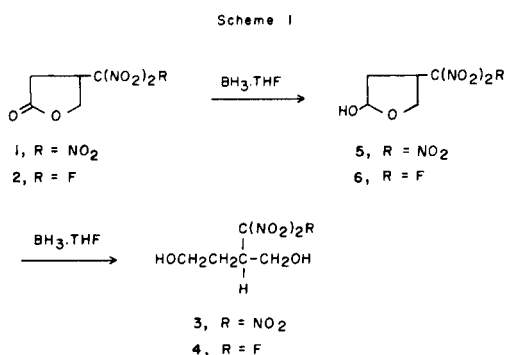
### Introduction

During attempts to reduce 4-hydroxy-3-(trinitromethyl)butyric acid,  $\gamma$ -lactone (**1**) and 4-hydroxy-3-(fluorodinitromethyl)butyric acid,  $\gamma$ -lactone (**2**) with borane-tetrahydrofuran complex to the corresponding diols [2-(trinitromethyl)butane-1,4-diol (**3**) and 2-(fluorodinitromethyl)butane-1,4-diol (**4**)], we discovered that the reaction could be controlled to provide the intermediate 2-furanols, 4-(trinitromethyl)tetrahydro-2-furanol (**5**) and 4-(fluorodinitromethyl)tetrahydro-2-furanol (**6**) (Scheme I). The isolation of 2-furanols under these conditions is unusual since borane normally converts lactones to diols too rapidly to allow the

*cis* and *trans* isomers were separated by column chromatography in order to determine the melting points and amounts of the two isomers.

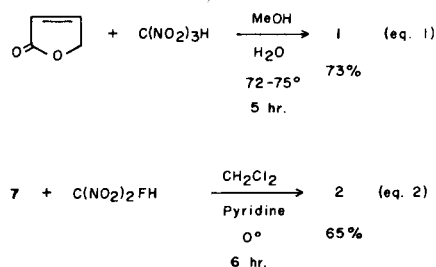
### Results and Discussion.

The required lactones (**1** and **2**) were prepared by the Michael addition of trinitromethane and fluorodinitromethane to  $\gamma$ -crotonolactone (**7**) (eq. 1 and eq. 2). Trinitromethane added to the unsaturated lactone **7** upon heating in aqueous methanol but under similar conditions fluorodinitromethane did not react. However, in methylene chloride solution with pyridine present to ionize the fluorodinitromethane, good yields of **2** were obtained.



isolation of intermediates [1]. Because borane reduces lactones so rapidly, a more selective borane, disiamyl borane, is used for the controlled partial reduction of lactones [1]. This reagent, however, did not reduce **1** or **2** to the 2-furanols.

The 2-furanols (**5** and **6**) were reacted with polynitroalcohols to produce *cis/trans*-2-polynitroalkoxy-4-polynitromethyltetrahydrofurans. The *cis/trans* mixtures are liquids or low melting solids and are of interest as energetic plasticizers or low melting solid additives. The

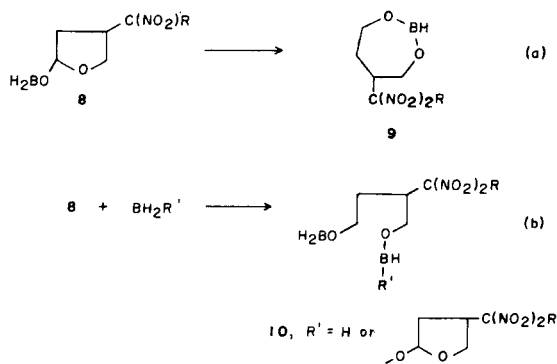


The reduction of **1** and **2** with borane-tetrahydrofuran complex to give the diols **3** and **4** was slow [2] and tlc indicated the presence of three materials which were shown to be the starting lactone (highest  $R_f$ ), the 2-furanol (intermediate  $R_f$ ) and the diol (lowest  $R_f$ ). By controlling the temperature and reaction time, the amount of 2-furanol relative to starting lactone and diol was increased. Thus reduction of **1** with borane-THF at 0° for 4 hours gave a 72% yield of **5**. Under the same conditions **2** gave only a 36% yield of **6**.

Attempts to improve the yield of **6** with shorter reaction times were not successful because although shorter reaction times did give less diol, the amount of unreacted lac-

tone increased with little change in the amount of 2-furanol. Similarly, varying the amount of borane-tetrahydrofuran complex did not lead to better yields of **6**. The amount of unreacted lactone changed but the diol was always formed in greater amounts than the 2-furanol. That **5** can be obtained in appreciably greater yield than **6** is apparently due to the slower conversion of the 2-furanol intermediate (**8**) to diol when  $R = \text{NO}_2$  than when  $R = \text{F}$  thereby allowing a buildup of **8** when  $R = \text{NO}_2$ . The conversion of **8** to diol can occur by two mechanisms (Scheme II): (a) the ring oxygen in **8** can migrate to boron to produce **9**; (b) **8** can react with active boranes to form **10** [3]. However, the experimental evidence does not clearly suggest which mechanism is operating.

Scheme II



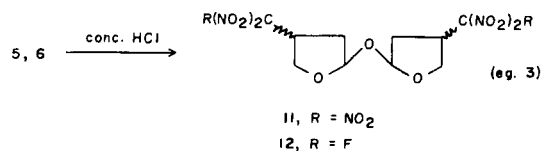
The inductive effect of the trinitromethyl group is not much different than that of the fluorodinitromethyl group with the  $\sigma^*$  parameters being 4.5 and 4.4, respectively [4,5]. However, the trinitromethyl group does have greater steric requirements than the fluorodinitromethyl group and it is possible that this steric effect accounts for the difference in the rate of conversion of **8** to diol for  $R = \text{NO}_2$  versus  $R = \text{F}$ .

Lactones **1** and **2** could not be reduced to the 2-furanols with disiamyl borane [1] or 9-borabicyclo[3.3.1]nonane [6]. In both cases reaction occurred with the evolution of hydrogen but only trace amounts of the 2-furanols and diols were formed. A similar reaction involving evolution of hydrogen with a nitro compound (nitrobenzene) has been observed for these boranes [1,6].

*cis/trans* Isomers of the 2-furanols are possible but apparently only one isomer is formed. The 2-furanols (**5** and **6**) show only one spot by tlc and have sharp melting points. By contrast the products from reaction of the 2-furanols with polynitroalcohols (described below) are produced as *cis/trans* mixtures.

Heating **5** and **6** with concentrated hydrochloric acid did not lead to opening of the 2-furanol ring but instead gave the respective bis ether (**11** and **12**) (eq. 3). Tlc in-

dicated that **11** and **12** were mixtures of isomers. The predominant isomer was separated by fractional crystallization and identified.



Heating the 2-furanols (**5** and **6**) with polynitroalcohols (**13-15**) in the presence of an acid catalyst with azeotropic removal of water gave *cis/trans*-2-polynitroalkoxy-4-polynitromethyltetrahydrofurans (**16-21**) in excellent yields (Scheme III, Table I). Products **16-21** show two spots on a tlc plate (methylene chloride as developer)

Scheme III

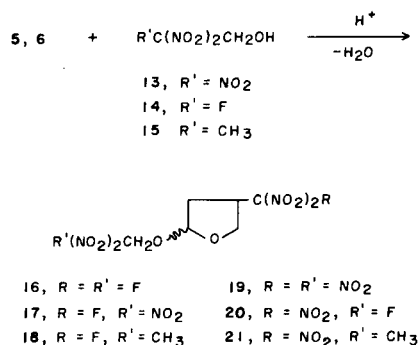


TABLE I

*cis/trans*-2-Polynitroalkoxy-4-polynitromethyltetrahydrofurans

Compound	$R_1$	$R_2$	% yield	<i>cis/trans</i>	Mp °C	
					<i>cis</i>	<i>trans</i>
<b>16</b>	F	F	96	35/65	25-26	19-20
<b>17</b>	F	$\text{NO}_2$	94	30/70	96-97	60-61
<b>18</b>	F	$\text{CH}_3$	100	30/70	55-56	[a]
<b>19</b>	$\text{NO}_2$	$\text{NO}_2$	73	15/85	[b]	75-77
<b>20</b>	$\text{NO}_2$	F	88	30/70	70-71	68-69
<b>21</b>	$\text{NO}_2$	$\text{CH}_3$	93	30/70	69-70	64-65

[a] The *trans* isomer was an oil which could not be crystallized. [b] The *cis* isomer was not separated and characterized.

with the upper spot (larger  $R_F$ ) in appreciably higher concentration. The two products corresponding to the tlc spots were separated by column chromatography and all data collected on the separated products consistently indicate that the product with the larger  $R_F$  is the *trans* isomer and the one with the smaller  $R_F$  is the *cis* isomer.

The amount of *trans* isomer formed was generally about twice that of the *cis* isomer. This is consistent with the fact that the less sterically crowded *trans* isomer would be expected to be formed in the greater amount.

The *cis* isomer has both electron withdrawing groups on the same side of the ring and should have a greater dipole moment than the *trans* isomer. This is consistent with the fact that each *cis* isomer has a smaller  $R_f$  and a higher melting point than its corresponding *trans* isomer.

The nmr data also support the structure assignment of the *cis* and *trans* isomers. The isomers exhibit chemical shifts in the region 2.8 to 2.0 ppm for the two hydrogens at the 3-position of the tetrahydrofuran ring. For the *trans* isomer the chemical shifts of these two hydrogens are only slightly different and often overlap to form a complex multiplet. By contrast, these same two hydrogens in each *cis* isomer exhibit a much greater difference in chemical shift. One hydrogen has a chemical shift higher and the other has a chemical shift lower than the two hydrogens in the *trans* isomer. This is consistent with the *cis* and *trans* structure assignment since in the *cis* isomer the hydrogen on the same side of the ring as both electron withdrawing groups would be deshielded to give a higher chemical shift and the other hydrogen with no electron withdrawing groups on its side of the ring would be shifted in the opposite direction. Each of these two hydrogens in the *trans* isomer has an electron withdrawing group on its side of the ring and thus the chemical shifts are not much different.

## EXPERIMENTAL

**Caution!** The compounds described herein are energetic materials and should be handled with care. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The nmr spectra were determined on a Varian EM-390 spectrometer and the chemical shifts are relative to tetramethylsilane. The melting points are uncorrected.

### 4-Hydroxy-3-(trinitromethyl)butyric Acid, $\gamma$ -Lactone (1).

A mixture of 7.5 g (0.089 mole) of  $\gamma$ -crotonolactone [7], 56.7 g (0.124 mole) of 33% aqueous trinitromethane and 32 ml of methanol was stirred in an oil bath at 72-75° for 5 hours. The mixture was then cooled in an ice bath to precipitate an oil which turned to a solid and was removed by filtration and washed with cold water to give 13.7 g, mp 103-105°. The water wash precipitated more oil from the filtrate. After extraction into methylene chloride, the oil was crystallized from methanol-water to give an additional 1.55 g of product [total yield of 15.25 g (73%)]. Recrystallization from methanol-water raised the mp to 105-106°; nmr (deuteriomethylene chloride):  $\delta$  2.74-3.36 (m, 2H), 4.25-4.60 (m, 2H), 4.75-4.97 (m, 1H); ir (potassium bromide): 1775 (shoulder at 1787) (C=O), 1600, 1590 (NO<sub>2</sub>) cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>8</sub>: C, 25.54; H, 2.14; N, 17.87. Found: C, 25.63; H, 2.13; N, 17.81.

### 4-Hydroxy-3-(fluorodinitromethyl)butyric Acid, $\gamma$ -Lactone (2).

A solution containing 16.5 g (0.196 mole) of  $\gamma$ -crotonolactone [7] and 31.8 g (0.256 mole) of fluorodinitromethane in 100 ml of methylene chloride (protected by a drierite drying tube) was stirred in an ice bath while 30.8 ml of pyridine was added in 3 ml portions over 5 minutes. The

solution was stirred at ice bath temperature for 3 hours before an additional 8.9 ml of pyridine was added in 3 portions over 2 minutes. After an additional 3 hours at 0°, the solution was poured into a solution containing 85 ml of concentrated hydrochloric acid diluted with 170 ml of water. The mixture was stirred vigorously at ambient temperature for 15 minutes before the methylene chloride layer was separated, washed with water and dried over sodium sulfate. Removal of the methylene chloride gave 28.4 g of tan solid which was dissolved in 120 ml of hot chloroform. The hot solution was stirred with 10 g of silica gel 60, then filtered and the silica gel was washed with 120 ml of hot chloroform. Hexane was added to the filtrate (at room temperature) to the cloud point. Cooling to -15° gave 21.9 g of white crystals, mp 58-60°. A second crop (4.6 g, mp 57-59°) raised the yield to 26.5 g (65%); nmr (deuteriochloroform):  $\delta$  2.55-3.14 (m, 2H), 3.97-4.88 (m, 3H); ir (potassium bromide): 1800, 1766 (C=O), 1609, 1600 (shoulder) (NO<sub>2</sub>) cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>FO<sub>6</sub>: C, 28.86; H, 2.42; N, 13.46; F, 9.13. Found: C, 28.95; H, 2.45; N, 13.18; F, 9.12.

### 2-(Trinitromethyl)butane-1,4-diol (3).

A 1 M solution of borane-tetrahydrofuran complex (10 ml, 10 mmoles) was stirred under a nitrogen atmosphere in a cold water bath (15°) while 2.1 g (8.94 mmoles) of 4-hydroxy-3-(trinitromethyl)butyric acid,  $\gamma$ -lactone was added. The solution was stirred at 25° for 1 hour and then at 35-37° for 3 days before it was cooled to room temperature and 1 ml of water was slowly added dropwise. Most of the tetrahydrofuran was removed and the residue was stirred with ether. The insoluble material (boric acid) was removed by filtration and the ether filtrate was extracted twice with water to remove remaining boric acid. The ether was removed to give 2.10 g (98%) of an oil which was essentially pure by tlc. An analytical sample was obtained by chromatography on silica gel 60 with methylene chloride-acetone (80/20) as eluent; nmr (deuteriomethylene chloride):  $\delta$  1.90-2.12 (m, 2H), 2.44 (broad OH), 3.60 (broad m, 1H), 3.93 (t, 2H), 4.23 (d, 2H); ir (film): 3700-3050 (OH), 1600 (NO<sub>2</sub>) cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>8</sub>: C, 25.11; H, 3.79; N, 17.57. Found: C, 25.00; H, 3.86; N, 17.34.

### 2-(Fluorodinitromethyl)butane-1,4-diol (4).

To a 1 M solution of borane-tetrahydrofuran complex (5 ml, 5 mmoles) stirred under a nitrogen atmosphere in an ice bath was added 1.0 g (4.8 mmoles) of 4-hydroxy-3-(fluorodinitromethyl)butyric acid,  $\gamma$ -lactone. The solution was then held in a water bath at 25-28° for 24 hours before 1 ml of water was slowly added dropwise. The solution was poured into 15 ml of water and extracted with ether to give 1.02 g (100%) of an oil which was essentially pure by tlc. Chromatography on silica gel 60 using methylene chloride-acetone (80/20) as eluent gave an analytical sample; nmr (deuteriochloroform):  $\delta$  1.70-1.93 (m, 2H), 2.36 (OH), 3.34-3.97 (m, 5H); ir (film): 3700-3050 (OH), 1605 (NO<sub>2</sub>) cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>FO<sub>6</sub>: C, 28.31; H, 4.28; N, 13.21; F, 8.96. Found: C, 28.04; H, 4.44; N, 12.81; F, 8.50.

### 4-(Trinitromethyl)tetrahydro-2-furanol (5).

A 1 M solution of borane-tetrahydrofuran complex (39 ml, 0.039 mole) was stirred in an ice bath under a nitrogen atmosphere. 4-Hydroxy-3-(trinitromethyl)butyric acid,  $\gamma$ -lactone (11.0 g, 0.0468 mole) was added and the solution was kept at 0° for 4 hours before 8 ml of water was slowly added dropwise. The mixture was stirred at 25° for 1 hour and then was poured into 80 ml of water. Extraction with ether (80 ml, then 2 x 25 ml) gave 12.3 g of a semisolid which was chromatographed on silica gel 40 (methylene chloride as eluent) to give 8.0 g (72%) mp 76-78°. Crystallization from chloroform raised the melting point to 79-80°; nmr (deuteriomethylene chloride):  $\delta$  2.30-2.57 (m, 2H), 2.86 (m, 1H), 3.97-4.69 (m, 3H), 5.70 (m, 1H); ir (potassium bromide): 3410 (OH), 1625, 1595 (NO<sub>2</sub>) cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O<sub>8</sub>: C, 25.32; H, 2.98; N, 17.72. Found: C, 25.40; H, 3.10; N, 17.38.

Compound 5 has also been reported as the product from trinitromethane and butyne-1,4-diol but no yield was given [8].

## 4-(Fluorodinitromethyl)tetrahydro-2-furanol (6).

To 50 ml (0.05 mole) of a 1 *M* solution of borane-tetrahydrofuran complex stirred in an ice bath under a nitrogen atmosphere was added 12.5 g (0.06 mole) of 4-hydroxy-3-(fluorodinitromethyl)butyric acid,  $\gamma$ -lactone. The reaction solution was held at 0° for 4.5 hours before 10 ml of water was slowly added dropwise. The mixture was stirred at 20° for 30 minutes and was poured into 100 ml of water and extracted with ether (100 ml, then 2 x 25 ml). The combined ether extracts were dried over sodium sulfate and the solvent was removed to give 12.8 g of oil which was shown by tlc analysis to be a mixture of starting  $\gamma$ -lactone, the desired 2-furanol (6) and the diol, 2-(fluorodinitromethyl)butane-1,4-diol (4). Chromatography on silica gel 60 (methylene chloride, then 3%, 6% and 20% acetone as eluent) separated the oil into 1.2 g of  $\gamma$ -lactone, 4.45 g (36%) of 6 (mp 71-74°) and 5.9 g of diol. Crystallization of 6 from chloroform raised the melting point to 73-75°; nmr (deuteriochloroform):  $\delta$  2.00-2.39 (m, 2H), 2.90 (d, 1H), 3.90-4.56 (m, 3H), 5.73 (m, 1H); ir (potassium bromide): 3370 (OH), 1597 (NO<sub>2</sub>) cm<sup>-1</sup>.

Anal. Calcd. for C<sub>8</sub>H<sub>8</sub>FN<sub>2</sub>O<sub>6</sub>: C, 28.58; H, 3.36; F, 9.04; N, 13.33. Found: C, 28.64; H, 3.30; F, 9.05; N, 13.28.

## bis[4-(Trinitromethyl)tetrahydro-2-furyl] Ether (11).

A mixture of 0.80 g (3.4 mmoles) of 4-(trinitromethyl)tetrahydro-2-furanol and 8 ml of concentrated hydrochloric acid was stirred in an oil bath at 75-77° for 16 hours. The dark colored solid was removed and stirred with a small amount of ether. The ether insoluble product was stirred with 10 ml of boiling 1,2-dichloroethane and some dark insoluble solid was removed by filtration. The filtrate was treated with charcoal and refiltered before the solvent was removed to give 0.47 g of white solid (mp 144-151°) which was shown by tlc to contain several products (presumably isomers). The solid was dissolved in 5 ml of hot 1,2-dichloroethane and the solution was cooled to room temperature to give crystals, mp 153-155°; nmr (deuterioacetone):  $\delta$  2.47, 2.57 (pair of d, 4H), 4.20-4.75 (m, 6H), 5.68 (m, 2H).

Anal. Calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>6</sub>O<sub>15</sub>: C, 26.32; H, 2.65; N, 18.42. Found: C, 26.06; H, 2.65; N, 18.11.

## bis[4-(Fluorodinitromethyl)tetrahydro-2-furyl] Ether (12).

A mixture of 0.36 g (1.7 mmoles) of and 6 ml of concentrated hydrochloric acid was stirred in an oil bath at 70-72° for 7 hours before it was cooled and the insoluble solid (0.18 g, mp 107-117°) was removed by filtration. Tlc showed the product was a mixture of several compounds which are presumably isomers. The product was dissolved in 20 ml of boiling ether and the solution was cooled to 5° to give 0.11 g of crystals, mp 123-124°; nmr (deuteriomethylene chloride):  $\delta$  2.18 (m, 4H), 3.85-4.38 (m, 6H), 5.59 (m, 2H).

Anal. Calcd. for C<sub>10</sub>H<sub>11</sub>F<sub>2</sub>N<sub>4</sub>O<sub>11</sub>: C, 29.86; H, 3.01; F, 9.45; N, 13.93. Found: C, 29.82; H, 3.01; F, 9.46; N, 14.04.

*cis/trans*-2-(2-Fluoro-2,2-dinitroethoxy)-4-(fluorodinitromethyl)tetrahydrofuran (16).

A flask containing a mixture of 1.25 g (6 mmoles) of 4-(fluorodinitromethyl)tetrahydro-2-furanol, 1.85 g (12 mmoles) of 2-fluoro-2,2-dinitroethanol, 0.18 g (0.95 mmole) of *p*-toluenesulfonic acid monohydrate and 10 ml of 1,2-dichloroethane was attached to a reverse Dean Starke trap and immersed in an oil bath and held at 105-110° for 2 hours. The cooled mixture was poured onto a silica gel 60 column (60 g) and eluted with methylene chloride to give 1.99 g (96%) of 16 as the *cis/trans* mixture (oil). Part of the oil (1.0 g) was rechromatographed on silica gel 60 (125 g) using 50/50 methylene chloride-hexane as eluent (with a gradual increase to 70/30) to separate the *cis* and *trans* isomers. The ratio of *cis* to *trans* product is 35/65.

The *cis* isomer had mp 25-26°; nmr (deuteriochloroform):  $\delta$  2.00, 2.17 (pair of d, 1H), 2.40-2.75 (m, 1H), 3.77-4.98 (m, 5H), 5.40 (d, 1H).

The *trans* isomer had mp 19-20°; nmr (deuteriochloroform):  $\delta$  2.00-2.48 (m, 2H), 3.70-4.30 (m, 3H), 4.42-4.97 (m, 2H), 5.40 (d, 1H).

Anal. Calcd. for C<sub>7</sub>H<sub>8</sub>F<sub>2</sub>N<sub>4</sub>O<sub>10</sub>: C, 24.29; H, 2.33; F, 10.98; N, 16.19. Found for *cis* isomer: C, 24.46; H, 2.43; F, 10.59; N, 15.78. Found for

*trans* isomer: C, 24.34; H, 2.29; F, 10.70; N, 16.31.

*cis/trans*-2-Polynitroalkoxy-4-polynitromethyltetrahydrofurans (17-21).

Compounds 17-21 were prepared by procedures essentially identical to that used for 16 except that silica gel 40 was used instead of silica gel 60 for those which contain the trinitromethyl moiety (17, 19, 20, 21).

*cis/trans*-2-(2,2,2-Trinitroethoxy)-4-(fluorodinitromethyl)tetrahydrofuran (17).

The product was obtained in 94% yield and the ratio of *cis* to *trans* isomer was 30/70.

The *cis* isomer had mp 96-97°; nmr (deuteriochloroform):  $\delta$  2.02, 2.19 (pair of d, 1H), 2.43-2.78 (m, 1H), 3.69-4.55 (m, 3H), 4.67-5.03 (m, 2H), 5.50 (d, 1H).

The *trans* isomer had mp 60-61°; nmr (deuteriochloroform):  $\delta$  2.07-2.52 (m, 2H), 3.72-4.45 (m, 3H), 4.67-5.03 (m, 2H), 5.58 (m, 1H).

Anal. Calcd. for C<sub>7</sub>H<sub>8</sub>FN<sub>3</sub>O<sub>12</sub>: C, 22.53; H, 2.16; F, 5.09; N, 18.77. Found for *cis* isomer: C, 22.66; H, 2.21; F, 5.17; N, 18.44. Found for *trans* isomer: C, 22.43; H, 2.23; F, 4.88; N, 18.53.

*cis/trans*-2-(2,2-Dinitropropoxy)-4-(fluorodinitromethyl)tetrahydrofuran (18).

The yield of product was 100% and the ratio of the *cis* to *trans* isomer was 30/70.

The *cis* isomer had mp 55-56°; nmr (deuteriochloroform):  $\delta$  1.93-2.23 (s and m overlap, 4H), 2.37-2.79 (m, 1H), 3.62-4.06 (m, 2H), 4.19-4.59 (m, 3H), 5.31 (d, 1H).

The *trans* isomer was obtained as an oil which could not be crystallized; nmr (deuteriochloroform):  $\delta$  2.00-2.37 (s and m overlap, 5H), 3.75-4.60 (m, 5H), 5.33 (m, 1H).

Anal. Calcd. for C<sub>8</sub>H<sub>11</sub>FN<sub>4</sub>O<sub>10</sub>: C, 28.08; H, 3.24; F, 5.55; N, 16.37. Found for *cis* isomer: C, 28.29; H, 3.27; F, 5.31; N, 16.24. Found for *trans* isomer: C, 28.18; H, 3.30; F, 5.45; N, 16.10.

*cis/trans*-2-(2,2,2-Trinitroethoxy)-4-(trinitromethyl)tetrahydrofuran (19).

The product was isolated in 73% yield and the ratio of *cis* to *trans* isomer was 15/85.

The *cis* isomer was not separated and characterized.

The *trans* isomer had mp 75-77°; nmr (deuteriochloroform):  $\delta$  2.52, 2.60 (pair of d, 2H), 3.94-5.22 (m, 5H), 4.47 (m, 1H).

Anal. Calcd. For C<sub>7</sub>H<sub>8</sub>N<sub>6</sub>O<sub>14</sub>: C, 21.01; H, 2.02; N, 21.00. Found: 21.02; H, 2.01; N, 20.84.

*cis/trans*-2-(Fluoro-2,2-dinitroethoxy)-4-(trinitromethyl)tetrahydrofuran (20).

The yield of product was 88% and the ratio of *cis* to *trans* isomer was 30/70.

The *cis* isomer had mp 70-71°; nmr (deuteriochloroform):  $\delta$  2.22, 2.38 (pair of d, 1H), 2.61-2.95 (m, 1H), 3.68-4.93 (m, 5H), 5.37 (d, 1H).

The *trans* isomer had mp 68-69°; nmr (deuteriochloroform):  $\delta$  2.50 (m, 2H), 3.86-4.91 (m, 5H), 5.36 (m, 1H).

Anal. Calcd. for C<sub>7</sub>H<sub>8</sub>FN<sub>3</sub>O<sub>12</sub>: C, 22.53; H, 2.16; F, 5.09; N, 18.77. Found for *cis* isomer: C, 22.62; H, 2.17; F, 5.03; N, 18.58. Found for *trans* isomer: C, 22.54; H, 2.35; F, 5.06; N, 18.49.

*cis/trans*-2-(2,2-Dinitropropoxy)-4-(trinitromethyl)tetrahydrofuran (21).

A 93% yield of product was obtained and the ratio of *cis* to *trans* isomer was 30/70.

The *cis* isomer had mp 69-70°; nmr (deuteriochloroform):  $\delta$  2.08-2.38 (s and m overlap, 4H), 2.60-2.96 (m, 1H), 3.66-4.58 (m, 5H), 5.36 (d, 1H).

The *trans* isomer had mp 64-65°; nmr (deuteriochloroform):  $\delta$  2.22 (s, 3H), 2.41, 2.51 (pair of d, 2H), 3.88-4.61 (m, 5H), 5.37 (m, 1H).

Anal. Calcd. for C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>O<sub>12</sub>: C, 26.03; H, 3.00; N, 18.97. Found for *cis* isomer: C, 26.22; H, 3.02; N, 18.82. Found for *trans* isomer: C, 26.05; H, 3.07; N, 18.67.

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## REFERENCES AND NOTES

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- [2] The complete conversion of **1** to **3** required three days at slightly elevated temperatures. A similar conversion of **2** to **4** was appreciably faster requiring only approx. one day. The yields in both cases were essentially quantitative.
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- [8] A. H. Neeley and R. K. Frantz, U. S. Patent 3,123,212 (1965); *Chem. Abstr.*, **64**, 6619b (1966). Compound **5** was unexpectedly obtained when trinitromethane and butyne-1,4-diol were heated in the presence of mercuric nitrate-nitric acid as catalyst. Fluorodinitromethane will not react similarly to give **6** because it is a much weaker acid ( $pK_a = 7.7$ ) [9] than trinitromethane ( $pK_a = 0$ ) [10] and will not ionize in the presence of nitric acid to add to the butyne-1,4-diol. [Note that fluorodinitromethane will not add to  $\gamma$ -crotonolactone (**7**) to give **2** unless pyridine is present to produce ionization (see experimental section). Fluorodinitromethane anion is unstable and therefore the reaction is kept at  $0^\circ$ .]
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