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REPORT DOCUMENTATION PAGE

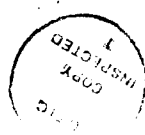
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 16 February 1990	3. REPORT TYPE AND DATES COVERED Journal Article	
4. TITLE AND SUBTITLE Direct Polynitroaliphatic Alcohol Addition to Alkenes. 1. Synthesis of New 2-Fluoro-2,2-dinitroethyl Acetals and Ethers			5. FUNDING NUMBERS	
6. AUTHOR(S) Robert E. Cochoy, Raymond R. McGuire and Scott A. Shackelford				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Frank J. Seiler Research Laboratory USAF Academy Colorado 80840-6528			8. PERFORMING ORGANIZATION REPORT NUMBER FJSRL-JR-90-0003	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Bolling AFB DC 20332			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION UNLIMITED			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This paper reports the first direct, one-step addition of FDNEOH to certain unsaturated hydrocarbons to form new 2-fluoro-2,2-dinitroethoxy acetal and ether compounds in high yield. These nonaqueous mercury salt catalyzed Markovnikov additions with FDNEOH are achieved under the mild, neutral reaction conditions. The scope and limitations of this new polynitroaliphatic reaction as a complementary alternative to other polynitroaliphatic syntheses are discussed. (S) ←				
14. SUBJECT TERMS			15. NUMBER OF PAGES 6	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT NONE	

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Published in Journal of Organic Chemistry, February 16, 1990, 1401-1406, by the American Chemical Society



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**Direct Polynitroaliphatic Alcohol Addition to Alkenes. 1. Synthesis of New 2-Fluoro-2,2-dinitroethyl Acetals and Ethers<sup>1</sup>**

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Received July 31, 1989

Acetal- and ether-compounds containing the 2-fluoro-2,2-dinitroethoxy structure represent an important class of energetic compounds for potential use in formulated propellant and explosive materials, but, their synthesis routes are severely limited. This limitation results from the inherent instability of the *gem*-2,2-dinitroaliphatic alcohol structure in alkaline or acidic solution<sup>4</sup> and from the very weak nucleophilic properties exhibited by this class of alcohol reactants.<sup>5-7</sup> Therefore, the usual alkaline or acidic conditions for converting alcohols into acetals or ethers cannot be used with *gem*-2,2-dinitroaliphatic alcohols like 2-fluoro-2,2-dinitroethanol (FDNEOH) because deformylation occurs, producing formaldehyde and either

(1) McGuire, R. R.; Cochoy, R. E.; Shackelford, S. A. US Patent 4,424,398, Jan 3, 1984.

(2) Present address: Lawrence Livermore National Laboratory, P.O. Box 808 (Code L-282), Livermore, CA 94550.

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(4) Coburn, M. D. *Synthesis* 1977, 570.


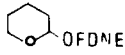
(5) Cochoy, R. E.; McGuire, R. R. *J. Org. Chem.* 1972, 37, 3041-3042.

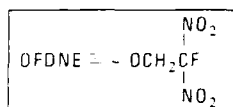
(6) Shipp, K. G., Hill, M. E., Kamlet, M. J. *NOLTR* 62-68, April 1962.

(7) Adolph, H. G.; Kamlet, M. J. *J. Org. Chem.* 1968, 34, 45-50.

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Table I. 2-Fluoro-2,2-dinitroethanol Catalytic Addition to Unsaturated Hydrocarbons

reactant	solvent	products	prod. no.	catalyst	% yield	prod. distribution
HC - COCH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_3\text{C} - \text{COCH}_2\text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>1</u>	Hg(OCOCH <sub>3</sub> ) <sub>2</sub>	95	<u>2</u> FOUND ONLY
			AND			ONCE IN A MIXTURE OF
		$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_2\text{C} = \text{COCH}_2\text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>2</u>			<u>1</u> (73%) AND <u>2</u> (27%)
	CCl <sub>4</sub>		<u>3</u>	---	100	---
H <sub>2</sub> C = CHOCH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_3\text{C} - \text{CHOCH}_2\text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>4</u>	HgSO <sub>4</sub>	73	---
H <sub>2</sub> C = CHOFDNE	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_3\text{C} - \text{CHOFDNE} \\   \\ \text{OFDNE} \end{array}$	<u>5</u>	HgSO <sub>4</sub>	61	---
$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C} = \text{CCH}_2\text{CH}_2\text{CH}_3 \end{array}$	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C} - \text{CCH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>6</u>	HgSO <sub>4</sub>	74	---
				Hg <sub>2</sub> SO <sub>4</sub>	58	--
H <sub>2</sub> C = CHCH = CH <sub>2</sub>	CCl <sub>4</sub>	$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_2\text{C} = \text{CHCH} - \text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>7</u>	HgSO <sub>4</sub>	53	<u>7</u> (77%)
			AND			AND
		$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_3\text{CCH} = \text{CHCH}_2 \\   \\ \text{OFDNE} \end{array}$	<u>8</u>			<u>8</u> (23%)
H <sub>2</sub> C = CHOCH = CH <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_2\text{C} = \text{CHOCH} - \text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>9</u>	HgSO <sub>4</sub>	70	SEE TABLE III
			AND	OR		
		$\begin{array}{c} \text{OFDNE} \\   \\ \text{H}_3\text{C} - \text{CHOCH} - \text{CH}_3 \\   \\ \text{OFDNE} \end{array}$	<u>10</u>	Hg <sub>2</sub> SO <sub>4</sub>	74	SEE TABLE III

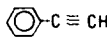
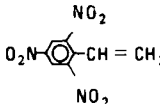




the 2-fluoro-2,2-dinitromethyl anion (FC(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>) or 2-fluoro-2,2-dinitromethane (FC(NO<sub>2</sub>)<sub>2</sub>H). In spite of this chemical instability, some 2-fluoro-2,2-dinitroethoxy-substituted esters, formals, ethers, amines, and oximes have been synthesized using FDNEOH,<sup>5-13</sup> synthesis strategies included Michael additions, Mannich condensations, and trifluoroacetic anhydride condensation. Indirect approaches using trifluoromethanesulfonate (triflate) ester intermediates recently expanded polynitroaliphatic ether syntheses<sup>11-13</sup> and sometimes permit a one-pot procedure. This paper reports the first direct, one-step addition of FDNEOH to certain unsaturated hydrocarbons to form new 2-fluoro-2,2-dinitroethoxy acetal and ether compounds in high yield. These nonaqueous mercury salt catalyzed Markovnikov additions with FDNEOH are achieved under the mild, neutral reaction conditions. The scope and limitations of this new polynitroaliphatic reaction as a complementary alternative to other polynitroaliphatic syntheses are discussed.

### Results and Discussion

Direct addition of weakly nucleophilic 2-fluoro-2,2-dinitroethanol (FDNEOH) to unsymmetrically substituted hydrocarbons by mercury salt catalysis proved to be a general one-step method when the carbon-carbon double

Table II. Alkynes/Alkenes Resistant to 2-Fluoro-2,2-dinitroethanol Catalytic Addition at the Milder Ambient Pressure Conditions

$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C} = \text{CC} \equiv \text{CH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C} = \text{CC} \equiv \text{CH} \end{array}$	
$\text{N} \equiv \text{CCH}_2\text{C} \equiv \text{CH}_3$	HOCH <sub>2</sub> C ≡ CCH <sub>2</sub> OH	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{HOCC} \equiv \text{CCOH} \end{array}$
$\begin{array}{c} \text{O} \\    \\ \text{H}_2\text{C} = \text{CHOCCF}_3 \end{array}$	H <sub>2</sub> C = CH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	H <sub>2</sub> C = CHBr
		

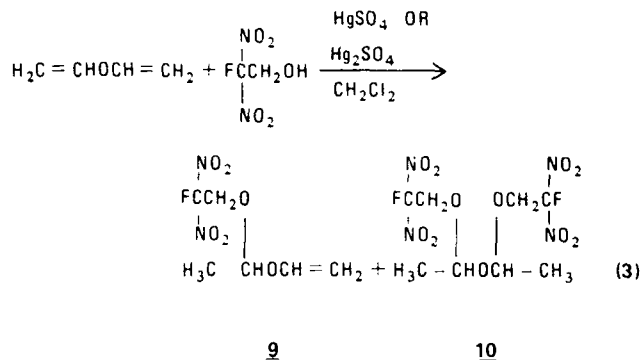
or triple bond is activated by an electron-donating atom or substituent. Mercury(II) sulfate, mercury(I) sulfate, mercury(II) acetate, red mercury(II) oxide, and phenylmercury(II) chloride all catalyzed this addition reaction, but generally, the two sulfate salts produced the best results. While this reaction system is similar to the mercury-catalyzed solvomercuration-demercuration olefin additions reported for the more common aliphatic alcohols,<sup>14</sup> it differs because the poorly nucleophilic FDNEOH forms Markovnikov acetal and ether derivatives in CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub> solvent without requiring an alkaline sodium boro-

- (8) Grakauskas, V.; Baum, K. *J. Org. Chem.* 1969, 34, 3927-3930.  
 (9) Adolph, H. G. *J. Org. Chem.* 1971, 36, 806-809.  
 (10) Grakauskas, V. *J. Org. Chem.* 1972, 38, 2999-3004.  
 (11) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* 1973, 38, 3673-3677.  
 (12) Chapman, R. D.; Andreshak, J. L.; Shackelford, S. A. *J. Org. Chem.* 1988, 53, 3771-3775.  
 (13) Chapman, R. D.; Andreshak, J. L.; Herrlinger, S. P.; Shackelford, S. A.; Hildreth, R. A.; Smith, J. P. *J. Org. Chem.* 1986, 51, 3792-3798.

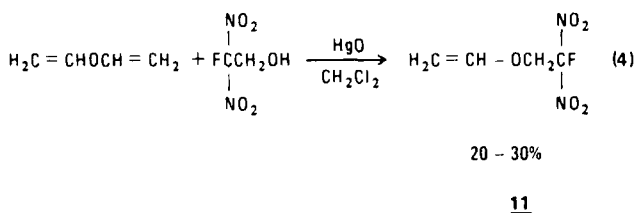
- (14) (a) Brown, H. C.; Geoghegan, P. J., Jr., *J. Am. Chem. Soc.* 1967, 89, 5646-5647. (b) Brown, H. C.; Kurek, J. T.; Rei, M. H.; Thompson, K. L. *J. Org. Chem.* 1985, 50, 1171-1174, and references therein.



7 (77%) and 1,4-adduct, 1-(2-fluoro-2,2-dinitroethoxy)-but-2-ene, 8 (23%). No diadduct products were found with butadiene; this contrasts with divinyl ether, which produces both monoadduct 9 and diadduct 10 products (eq 3).



The addition of FDNEOH to divinyl ether (DVE) proceeds under milder conditions in refluxing  $\text{CH}_2\text{Cl}_2$  solvent over 16 h with either mercury(II) or mercury(I) sulfate catalysis. The product distribution of 9 versus 10 is easily varied by the DVE/FDNEOH stoichiometry used. A detailed GLPC/MS analysis of the crude oil isolate of 2:1 DVE/FDNEOH stoichiometry using mercury(II) sulfate catalyst reveals the increasing retention time-product distribution: 2-fluoro-2,2-dinitroethyl vinyl ether (11) (6%), monoadduct 9 (70%), ethyl vinyl ether adduct 4 (3%), bis(2-fluoro-2,2-dinitroethyl) ethyl acetal 5 (1%), and the diadduct 10 (20%). The diadduct 10 appears as two overlapping peaks in the 30-m capillary HP SE-30 column and apparently represents a diastereomeric pair caused by the two asymmetric carbon atoms on each side of the bridging oxygen atom. The diastereomer of lower GLPC retention time predominates (56 to 44%) regardless of the DVE/FDNEOH reactant stoichiometry. This diastereomeric mixture apparently causes the  $^1\text{H}$  NMR spectrum of 10 to give a multiplet resembling a pentet for the single hydrogen ( $\delta$  5.07) on each asymmetric carbon; theoretically, a quartet is expected. The three minor products 4, 5, and 11 all result from minor competing transesterification reaction pathways like that shown in eq 4. Under different



reaction conditions, the competing transesterification illustrated by eq 4 alternatively can become the exclusive reaction pathway and produce polynitroalkyl vinyl ethers by reaction of DVE with various  $\beta$ -substituted 2,2-dinitro alcohols.<sup>17,18</sup> DVE contains ethanol as a stabilizer (4%) even when purified, and the minor transesterification reaction between DVE and the ethanol stabilizer produces the intermediate ethyl vinyl ether that adds FDNEOH to form 4. Similarly, FDNEOH produces a trace of 11, and some 11 continues adding FDNEOH to yield 5. Such transesterification reactions are known in mercury(II)-catalyzed reactions between vinyl ethers and the more

Table III. 2,2,2-Fluorodinitroethanol/Divinyl Ether Mono- and Diadduct Product Percentages

DVE/FDNEOH	catalyst <sup>a</sup>	% 9	% 10	anal. method
0.75	A	18	82	isoltd wt
0.93	A	27	73	$^1\text{H}$ NMR
0.99	A	36	64	GLPC/MS
1.00	B	37	63	$^1\text{H}$ NMR
2.00	B	68	32	$^1\text{H}$ NMR
2.00	A	63	37	$^1\text{H}$ NMR
2.00	A	60	40	GLPC/MS
2.00	A	78	22	GLPC/MS
2.00	B	59	47	isoltd wt

<sup>a</sup> A,  $\text{HgSO}_4$ ; B,  $\text{Hg}_2\text{SO}_4$ .

common nucleophilic alcohols.<sup>19</sup> Depending upon reaction stoichiometry, either the monoadduct product 9 or the diadduct 10 selectively predominates. Essentially, a 1:1 DVE/FDNEOH molar ratio with either mercury(I) or mercury(II) sulfate catalyst produces twice as much diadduct 10 as monoadduct 9, while a 2:1 DVE/FDNEOH ratio reverses this distribution. Table III provides a more detailed correlation of 9 and 10 product distribution as a function of reactant ratio, catalyst used, and product analysis method. A 3:1 DVE/FDNEOH reactant stoichiometry provides no significant increase in the monoadduct 9.

While a change from mercury(II) to mercury(I) sulfate catalysis has little effect upon product distribution of the DVE and FDNEOH addition (Table III), altering the mercury salt anion displays a marked impact. Mercury(II) acetate catalyzes ambient temperature addition of FDNEOH to ethoxyacetylene and provides a high yield of the bis(2-fluoro-2,2-dinitroethyl) ethoxy ethyl orthoester 1, but little reaction occurs with DVE. Refluxing 40 h in  $\text{CH}_2\text{Cl}_2$ , less than 15% reaction occurs between DVE and FDNEOH with  $\text{Hg}(\text{OAc})_2$  catalyst. Analysis by GLPC/MS reveals only two minor reaction products, the vinyl ether 11 (3%) and the DVE monoadduct 9 (5%), plus unreacted alcohol (85%) and product 4 (7%) from the ethanol stabilizer. No trace of the diastereomeric diadduct 10 was observed even though some monoadduct 9 forms. Phenylmercury(II) chloride, which produces the orthoester 1 with ethoxyacetylene, also yields no appreciable amount of 9, 10, or 11 with DVE and FDNEOH even when reacted 68 h at room temperature followed by 5-h reflux in  $\text{CH}_2\text{Cl}_2$  solvent. Catalysis of the reaction between DVE and FDNEOH by red mercury(II) oxide in refluxing  $\text{CH}_2\text{Cl}_2$  produces only a transesterification reaction in which 11 is the exclusive product;<sup>18</sup> a 20–30% isolated yield indicates that the reaction does not proceed to completion (eq 4). This incomplete transesterification initially is driven by the elimination of the ethenol structural fragment from the DVE molecule to form ethenol's acetaldehyde tautomer as a reaction byproduct.<sup>18</sup> Reflux beyond 20 h fails to improve the yield of 11 and product degradation occurs. This important reaction can be driven to completion by modifying the reaction conditions and much higher yields of 11 result.<sup>17,18</sup> This reaction modification and the scope this novel transesterification are addressed in a future paper.

### Conclusions

Markovnikov-directed additions of the weakly nucleophilic 2-fluoro-2,2-dinitroethanol (FDNEOH) to a variety of reactive unsaturated hydrocarbons is achieved by mercury salt catalysis under neutral, nonaqueous reaction

(17) Shackelford, S. A.; McGuire, R. R.; Cochoy, R. E. US Patent 4,426,540, Jan 17, 1984.

(18) Shackelford, S. A.; Cochoy, R. E.; Loving, B. A.; McGuire, R. R. *FJSRL-TR-77-0018*, Dec 1977.

(19) Watanbe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* 1957, 79, 2828–2833.

conditions. This finding expands the scope of potentially available 2-fluoro-2,2-dinitroethoxy acetal and ether compounds that suffer from severe limitations in possible synthetic strategies. Both the product yield or the specific 2-fluoro-2,2-dinitroalkoxy compound produced can depend upon the FDNEOH/alkene reactant stoichiometry or the specific mercury salt catalyst used. Under overnight ambient pressure reflux in  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$  solvent, unsaturated hydrocarbons must possess an electron-donating substituent or oxygen atom at its  $\text{C}_2$  or vinylic position. Otherwise, addition of the poor FDNEOH nucleophile fails to occur; but, more stringent reaction conditions in a sealed Paar pressure bottle may extend this reaction to less reactive alkynes and alkenes as shown by butadiene's reaction with FDNEOH. Demonstration of the subject reaction further opens the possibility of producing analogous new energetic acetal and ethers using other weakly nucleophilic 2,2-dinitroalkyl-substituted alcohols that also are subject to the facile deformylation reaction under alkaline or acidic conditions.

### Experimental Section

**General.** The divinyl ether (DVE) used was purchased from PCR, Inc., Gainesville, FL,<sup>20</sup> and initially was used without further purification. Later purchases came from Marshallton Research Laboratory, Winston-Salem, NC. In later reactions, the ethanol stabilizer was enriched by DVE evaporation. The ethanol stabilizer was reduced to 4% ( $^1\text{H}$  NMR analysis) by two distillations (7 in. Vigreux column), the second over  $\text{CaH}_2$ . Other alkenes and alkynes were distilled only when necessary. The 2-fluoro-2,2-dinitroethanol (FDNEOH) was purchased from the Naval Surface Warfare Center/White Oak Laboratory, Silver Spring, MD, as a 30% by-weight solution in  $\text{CH}_2\text{Cl}_2$  solvent.<sup>21</sup> Prior to use, the  $\text{CH}_2\text{Cl}_2$  was removed by rotary evaporation to yield a slightly yellow oil. (Caution! The FDNEOH during solvent removal goes through a sensitivity maximum between 30% solution and neat compound; this operation should be conducted behind appropriate shielding.) The viscous FDNEOH was vacuum distilled in a short path column (bp 36.0–38.8 °C at 0.1 mmHg). Caution! FDNEOH can be explosive under the proper stimulus and also causes severe burns to the skin. Proper shielding and skin protection should be used when handling it or when working up reactions containing this reagent. The distilled FDNEOH always contained a trace of 2-fluoro-2,2-dinitroethyl methyl formal. The mercury(I) and -(II) sulfate catalysts were obtained from J. T. Baker Chemical Co. ("Baker Analyzed" reagent) as was the red mercury(II) oxide. Mercury(II) acetate came from Fisher Scientific Co. (A.C.S. grade). Neutral aluminum oxide used in the purification and workup was "Baker Analyzed" purity (pH 6.9–7.4 water slurry). The  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  solvents were MCB spectrometric grade. Nuclear magnetic resonance  $^1\text{H}$  spectra were taken either on a Varian A-60, T-60, or JOEL FXQ90 instrument ( $\text{CDCl}_3$  solvent and TMS internal reference). Infrared spectra were obtained as a neat liquid film (NaCl plates) on a Beckman IR-20 spectrophotometer. Mass spectra were taken on a Dupont 21-491 double focusing mass spectrometer or with a Hewlett Packard 5985 GC/MS system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Addition of 2-Fluoro-2,2-dinitroethanol to Unsaturated Aliphatic Compounds (General Procedure).** The alkene/alkyne was weighed into  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$  solvent contained in an appropriate-sized round-bottom flask with a Teflon-coated stir bar. FDNEOH was added to the stirred solution; then, the solid  $\text{Hg}(\text{I})$  or  $-(\text{II})$  salt catalyst was added. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite filled drying tube. The reaction was sometimes stirred at room temperature, but usually required reflux for 16–19 h. Reaction so-

lution filtration and the solvent removal by rotary evaporation followed. The remaining oil was taken up in 1–3 mL of  $\text{CCl}_4$  and was eluted through a short neutral aluminum oxide column to remove unreacted FDNEOH. This column was prepared by packing 2.5 g of aluminum oxide slurried in  $\text{CCl}_4$  into a 15-mL "course" glass sintered Buchner funnel.  $\text{CCl}_4$  removal afforded the addition product(s). Vacuum distillation provided further product purification.

**Addition of 2-Fluoro-2,2-dinitroethanol to Ethoxyacetylene (Products 1 and 2).** A flask charged with 1.05 g (15 mmol) of distilled ethoxyacetylene, 25 mL of  $\text{CH}_2\text{Cl}_2$ , 3.08 g (20 mmol) of FDNEOH, and 100 mg of mercury(II) acetate was stirred overnight at room temperature (ca. 16 h). Solvent removal and filtration of the resulting oil through 23 g of alumina (pH = 7.2) with  $\text{CH}_2\text{Cl}_2$ , followed by  $\text{CH}_2\text{Cl}_2$  removal, afforded 3.59 g (95%) of clear yellow oil 2. Vacuum distillation (molecular still), 90 °C/0.05 mm for 4 h, gave 3.26 g of less pure oil: density 1.42 g/mL; NMR (dd, 4.64, 4 H) with  $J_{\text{vic-HF}} = 17$  Hz, (q, 3.57, 2 H), (s, 1.54, 3 H), (t, 1.22, 3 H); IR (neat film)  $\text{cm}^{-1}$  2990, 2950, 2900 (sat. CH), 1600, 1310 ( $\text{NO}_2$ ). Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{N}_4\text{O}_5\text{F}_2$ : C, 25.4; H, 3.20; N, 14.8; F, 10.1. Found: C, 25.4; H, 3.19; N, 14.7; F, 10.1. In one experiment, 27% vinyl acetal 2 was obtained by distillation (48 °C/0.2 mm) of the crude oil mixture with 1: NMR (dd, 4.94, 2 H) with  $J_{\text{vic-HF}} = 16.5$  Hz (q, 3.96, 2 H), (q, 3.57, 2 H), (t, 1.33, 3 H).

**Addition of 2-Fluoro-2,2-dinitroethanol to 3,4-Dihydropyran (Product 3).** A flask charged with 1.00 g (11.9 mmol) of 3,4-dihydropyran, 10 mL of  $\text{CCl}_4$ , and 1.00 g (6.5 mmol) of FDNEOH was stirred under reflux for 17 h.  $\text{CCl}_4$  solvent removal afforded 1.56 g (100%) of light yellow oil: NMR (m, 4.82, 1 H), (dd, 4.70, 2 H), (m, 3.72, 2 H), (m, 1.68, 6 H).

**Addition of 2-Fluoro-2,2-dinitroethanol to Ethyl Vinyl Ether (Product 4).** A flask charged with 2.15 g (30 mmol) of ethyl vinyl ether, 25 mL of  $\text{CH}_2\text{Cl}_2$ , and 3.08 g (20 mmol) of FDNEOH was cooled with stirring in an ice bath before 200 mg of  $\text{HgSO}_4$  was added. The solution was stirred for 16 h at room temperature. Workup gave 4.65 g of crude oil; vacuum distillation through a 6-in. Vigreux column at 34–35 °C/0.10 mm yielded 3.29 g (73%) of product 4 as a colorless oil: NMR (q, 4.92, 1 H), (dd, 4.60, 2 H) with  $J_{\text{vic-HF}} = 18$  Hz, (m, 3.60, 2 H), (m, 1.26, 6 H); IR (neat film)  $\text{cm}^{-1}$  2995, 2940, 2900 (sat. CH), 1600, 1315 ( $\text{NO}_2$ ); mass spectrum, characteristic  $m/e$  225 ( $\text{M} - 1$ ), 211, 183, 181, 155, 134, 91, 77, 73, 45 (base), 30, 29. Anal. Calcd for  $\text{C}_5\text{H}_{11}\text{N}_2\text{O}_5\text{F}$ : C, 31.9; H, 4.87; N, 12.4; F, 8.41. Found: C, 31.9; H, 4.69; N, 12.2; F, 8.35.

**Addition of 2-Fluoro-2,2-dinitroethanol to 2-Fluoro-2,2-dinitroethyl Vinyl Ether (Product 5).** A flask charged with 1.50 g (8.3 mmol) of 2-fluoro-2,2-dinitroethyl vinyl ether,<sup>18</sup> 20 mL of  $\text{CH}_2\text{Cl}_2$ , 1.28 g (8.3 mmol) of FDNEOH, and 250 mg of  $\text{HgSO}_4$  was stirred under reflux for 24 h. The isolated crude oil was molecular distilled at 68.0–68.4 °C/0.2 mm to yield 1.71 g (61%) of product 5. Colorless oil with a density = 1.55 g/mL: NMR (q, 5.02, 1 H), (dd, 4.64, 4 H) with  $J_{\text{vic-HF}} = 17$  Hz, (d, 1.43, 3 H); IR ( $\text{cm}^{-1}$ ) 3000, 2950, 2900 (sat. CH), 1600, 1310 ( $\text{NO}_2$ ); mass spectrum,  $m/e$  333 ( $\text{M} - 1$ ), 319, 181, 147, 133, 91, 75, 73, 57, 45, 44, 30 (base), 29. Anal. Calcd for  $\text{C}_4\text{H}_9\text{N}_4\text{O}_{10}\text{F}_2$ : C, 21.6; H, 2.40; N, 16.8; F, 11.4. Found: C, 21.6; H, 2.5; N, 16.6; F, 11.2.

**Addition of 2-Fluoro-2,2-dinitroethanol to 2-Methyl-1-pentene (Product 6).** (a) A flask charged with 2.52 g (30 mmol) of 2-methyl-1-pentene, 25 mL of  $\text{CH}_2\text{Cl}_2$ , 3.08 g (20 mmol) of FDNEOH, and 200 mg of  $\text{HgSO}_4$  was stirred under reflux for 16 h. The purple solution yielded 2.95 g of crude product. Vacuum distillation at 47–48 °C/0.2 mm (6-in. Vigreux column) gave 3.51 g (74%) of nearly colorless oil 6. Redistillation, 45 °C/0.2 mm, was done with a 12-in. glass bead column: NMR (dd, 4.42, 2 H), (s amid a mult, 1.17, 13 H); IR ( $\text{cm}^{-1}$ ) 2970, 2940, 2880 (sat. CH), 1600, 1315 ( $\text{NO}_2$ ). Anal. Calcd for  $\text{C}_7\text{H}_{15}\text{N}_2\text{O}_5\text{F}$ : C, 40.4; H, 6.36; N, 11.8; F, 7.98. Found: C, 40.4; H, 6.37; N, 11.7; F, 7.76.

(b) A flask charged with 1.00 g (12 mmol) of 2-methyl-1-pentene, 20 mL of  $\text{CH}_2\text{Cl}_2$ , 1.85 g (12 mmol) of FDNEOH, and 550 mg of  $\text{Hg}_2\text{SO}_4$  was stirred under reflux for 48 h. Workup gave 1.58 g of purple oil (58%) 6: NMR (dd, 4.42, 2 H), (s amid a mult, 1.17, 14 H).<sup>22</sup>

(20) Divinyl ether is no longer available from this source. Later, quantities were obtained from Marshallton Research Laboratory, P.O. Box 11646, Winston-Salem, NC 27106.

(21) This material is available from Fluorochem, Inc., 680 S. Ayon Ave., Azusa, CA 91702.

(22) This integration should be 13 H; the product possesses a slight unidentified impurity.

**Addition of 2-Fluoro-2,2-dinitroethanol to 1,3-Butadiene (Products 7 and 8).** A Paar pressure bottle charged with 40 mL of  $\text{CCl}_4$  was cooled in an ice bath before 4.2 g (7.8 mmol) of 1,3-butadiene was bubbled into the solvent. Next, 3.08 (2.0 mmol) of 2-fluoro-2,2-dinitroethanol and 100 mg of  $\text{HgSO}_4$  were added to the Paar bottle. The bottle, stoppered with a Teflon-brand wrapped rubber stopper, was shaken at 55 °C for 16 h. The reaction product was then washed through 23 g of alumina (pH = 7.2) with  $\text{CCl}_4$ . The  $\text{CCl}_4$  was removed; the product was again filtered through 23 g of alumina with a  $\text{CCl}_4$  wash.  $\text{CCl}_4$  removal provided 4.05 g of light reddish brown oil. Vacuum distillation (6-in. Vigreux column) at 35 °C/0.10 mm gave 2.19 g (53%) of light yellow oil. The distillate contained mainly the 1,2-adduct 7 with some 1,4-adduct 8. Distillation (51.0–51.5 °C/1.6 mm) (12-in. glass bead column) provided nearly pure (90%) 1,2-adduct 7; the 1,4-adduct would not distill even with a diethyl succinate pot chaser. Analytical samples of the two adducts were obtained by preparative GLPC (8 ft. by  $\frac{1}{2}$  in. 20% Dow 710 silicon oil column) at 148 °C. **1,2-Adduct 7:** NMR (m, 5.55, 3 H), (dd, 4.48, 2 H) with  $J_{\text{vic-HF}} = 18$  Hz, (pent, 4.02, 1 H), (d, 1.25, 3 H); IR ( $\text{cm}^{-1}$ ) 3090 (=CH), 2990, 2930, 2890 (sat. CH), 1600, 1310 ( $\text{NO}_2$ ). Anal. Calcd for  $\text{C}_5\text{H}_9\text{N}_2\text{O}_5\text{F}$ : C, 34.6; H, 4.36; N, 13.5; F, 9.13. Found: C, 34.85; H, 4.39; N, 13.3; F, 9.16. **1,4-Adduct 8:** NMR (m, 5.62, 2 H), (dd, 4.49, 2 H) with  $J_{\text{vic-HF}} = 18$  Hz, (d, 1.76, 3 H); IR ( $\text{cm}^{-1}$ ) 3010 (=CH), 2985, 2960, 2920, 2870 (sat. CH), 1600, 1315 ( $\text{NO}_2$ ). Anal. Calcd for  $\text{C}_5\text{H}_9\text{N}_2\text{O}_5\text{F}$ : C, 34.6; H, 4.36; N, 13.5; F, 9.13. Found: C, 34.85; H, 4.39; N, 13.6; F, 8.71.

**Addition of 2-Fluoro-2,2-dinitroethanol to Divinyl Ether (Products 9 and 10).** (a) A flask charged with 1.05 g (15 mmol) of divinyl ether (DVE), 25 mL of  $\text{CH}_2\text{Cl}_2$ , 3.08 g (20 mmol) of FDNEOH, and 200 mg of  $\text{HgSO}_4$  was stirred under reflux for 16 h. Short-path vacuum distillation (43.2–43.4 °C/0.3 mmHg) of the isolated oil afforded 0.4 g (12%) of monoadduct 9. The pot residue was taken up in  $\text{CCl}_4$  and passed through a short alumina (pH = 7.2) column.  $\text{CCl}_4$  removal gave 2.20 g (58%) of pure diadduct 10, density = 1.42 g/mL. **Diadduct 10:** NMR (pent, 5.07, 2 H), (dd, 4.57, 4 H) with  $J_{\text{vic-HF}} = 18$  Hz, (d, 1.39, 6 H); IR ( $\text{cm}^{-1}$ ) 3000, 2940 (sat. CH), 1600, 1310 ( $\text{NO}_2$ ); mass spectrum, characteristic  $m/e$  181 (higher GLPC diastereomer), 147, 133, 119, 105, 91, 75, 73, 45 (base), 44, 30, 29. Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{N}_4\text{O}_{11}\text{F}_2$ : C, 25.4; H, 3.20; N, 14.8; F, 10.1. Found: C, 25.6; H, 3.20; N, 14.7; F, 10.0.

(b) DVE (2.10 g, 30.0 mmol), FDNEOH (2.31 g, 15.0 mmol),

and 200 mg of  $\text{HgSO}_4$  in 25 mL of  $\text{CH}_2\text{Cl}_2$  refluxed 16 h produced 3.28 g of crude oil product. GC/MS analysis revealed the following crude product distribution: 11 (6%), 9 (70%), 4 (3%), 5 (1%), and 10 (20%). Prolonged or gradual heating during distillation causes apparent polymerization of 9.

(c) A flask charged with 2.0 g (28.6 mmol) of DVE, 60 mL of  $\text{CH}_2\text{Cl}_2$ , 2.2 g (14.3 mmol) of FDNEOH, and 750 mg of  $\text{Hg}_2\text{SO}_4$  was stirred under reflux for 26 h. Workup produced 2.63 g of crude oil containing both monoadduct 9 and diadduct 10. Short-path vacuum distillation afforded 1.29 g (40%) of monoadduct 9. The pot residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and eluted through a short alumina column.  $\text{CH}_2\text{Cl}_2$  removal gave 0.91 g (34%) of diadduct 11. **Monoadduct 9:** NMR (dd, 6.36, 1 H), (q, 5.14, 1 H), (dd, 4.62, 2 H) with  $J_{\text{vic-HF}} = 18$  Hz, (m, 4.50, 2 H), (d, 1.40, 3 H); IR ( $\text{cm}^{-1}$ ) 3120, 3070 (=CH), 3000, 2945 (sat. CH), 1645 (C=C), 1600, 1315 ( $\text{NO}_2$ ); mass spectrum, characteristic  $m/e$  181, 134, 105, 91, 87, 71, 45 (base), 44, 43, 30, 29. Anal. Calcd for  $\text{C}_5\text{H}_9\text{N}_2\text{O}_5\text{F}$ : C, 32.2; H, 4.05; N, 12.5; F, 8.48. Found: C, 32.0; H, 3.98; N, 12.5; F, 8.31.

**Acknowledgment.** We are deeply indebted to Dr. H. G. Adolph and Dr. M. J. Kamlet (deceased Feb 1988), NSWC/WOL, for their helpful technical discussions and encouragement. Mr. J. L. Pflug (FJSRL) provided extensive  $^1\text{H}$  NMR and GLPC/mass spectral analyses; Dr. Clay M. Sharts (SDSU) and Dr. John E. Marlin (FJSRL) provided helpful manuscript comments, and Mrs. Linda Pukajilo (FJSRL) aided in manuscript preparation. The Air Force Office of Scientific Research through Dr. D. L. Ball, Director of Chemical and Atmospheric Sciences, generously provided financial support.

**Registry No.** 1, 88934-30-9; 2, 124618-93-5; 3, 124618-94-6; 4, 124618-95-7; 5, 124618-96-8; 6, 88934-26-3; 7, 88934-28-5; 8, 88934-29-6; 9, 88934-27-4; ( $\pm$ )-10, 124618-97-9; *meso*-10, 124618-98-0; 11, 52483-76-8; FDNEOH, 17003-75-7; DVE, 109-93-3;  $\text{H}_2\text{C}=\text{CHOFDNE}$ , 52483-76-8;  $\text{EtOC}\equiv\text{CH}$ , 927-80-0;  $\text{EtOCH}=\text{CH}_2$ , 109-92-2;  $\text{H}_2\text{C}=\text{C}(\text{Me})\text{CH}_2\text{CH}_2\text{CH}_3$ , 763-29-1;  $\text{H}_2\text{C}=\text{CHC}=\text{H}=\text{CH}_2$ , 106-99-0;  $\text{Hg}(\text{OAc})_2$ , 1600-27-7;  $\text{HgSO}_4$ , 7783-35-9;  $\text{Hg}_2\text{SO}_4$ , 7783-36-0;  $\text{HgO}$ , 21908-53-2; 3,4-dihydropyran, 110-87-2.