carboxy-2,2-dimethyl-4-(aryl)-but-3-enoic acids (Vb–i) while (IIIa) produced (VIa) directly.

Conversion of the Dibasic Acids to the Corresponding Anhydrides (VIa–i). Acetic anhydride (10 mL) was added to the dibasic acid (1 g), refluxed for 5 h, and worked up as previously reported (*10*). The crude products were crystallized from hexane to give (*E*)-3-carboxy-2,2-dimethyl-4-(aryl)-3-enoic anhydrides (VIa–i).

Treatment of Half-Esters (IIb,c) with Acetic Anhydride and Sodium Acetate. A mixture of the half-ester (1 mol), freshly fused sodium acetate (2 mol), and excess of acetic acid and acetic anhydride was refluxed for 10–12 h and worked up as before (*10*). The products were crystallized from cyclohexane to produce the corresponding anhydrides (VIb,e).

Treatment of the Half-Ester (IIIa,c,e–i) with Concentrated Sulfuric Acid. The half-esters (IIIe–g) were added in portions to cold concentrated sulfuric acid (10 mL per 0.5 g) and left in ice for a period of 1 h. The mixture was poured into ice-cold water and the product was extracted with ether. The ethereal layer was washed with 5% sodium carbonate solution and then with cold water and finally dried (Na_2SO_4). Ether was evaporated, and the organic product was crystallized from petroleum ether (40–60 °C) or hexane to give methyl 3,4-dihydro-3,3-dimethyl-4-oxophenanthrene-2-carboxylate (VIIe), methyl 5-chloro-1,2-dihydro-2,2-dimethyl-1-oxonaphthalene-3-carboxylate (VIIf), and methyl 6-chloro-1,2-dihydro-2,2-dimethyl-1-oxonaphthalene-3-carboxylate (VIIg).

When the half-esters (IIIc,e,f,h,i) were treated with concentrated sulfuric acid and left overnight at room temperature, they produced 3,3-dimethyl-2-oxotetrahydrofurano-(4,5b)-6-methoxyindan-4-one (IXc), -(1,2d)-benzo[*e*]indan-3-one (IXe), -(4,5b)-8-chloroindan-4-one (IXf), -(4,5b)-6-chloroindan-4-one (IXh), and -(4,5b)-indan-4-one (IXi).

Treatment of the Anhydrides (VIc,f–i) with Anhydrous Aluminum Chloride. To a stirred solution of the anhydride in *sym*-tetrachloroethane (10 mL per 1 g anhydride), an excess amount of anhydrous aluminum chloride was added in one portion and stirring was continued for 6 h and the mixture was left overnight at room temperature. The material was poured into a mixture of ice and concentrated hydrochloric acid and the acidic product was extracted with ether. The ethereal layer was extracted with 10% carbonate solution, and the carbonate layer was acidified with cold dilute hydrochloric acid. The precipitated oxoindenyl acids (VIIIc,f–i) were extracted with ether, washed with cold water, dried (using Na_2SO_4), and filtered and the ether was distilled off. The oxoindenyl acids (VIIIc,f–i) obtained were crystallized from petroleum ether (bp 40–60 °C) to give 2-(6-methoxy-1-oxo-2-indenyl)- (VIIIc), 2-(4-chloro-1-oxo-2-indenyl)- (VIIIf), 2-(5-chloro -1-oxo-2-indenyl)- (VIIIg), 2-(6-chloro-1-oxo-2-indenyl)-2-methylpropanoic acids (VIIIh), and 2-methyl-2-(1-oxo-2-indenyl)-propanoic acid (VIIIi).

Cyclization of the Oxoindenyl Acids (VIIIc,f,h,i) with Concentrated Sulfuric Acid. The oxoindenyl acid was added in portions to cold concentrated sulfuric acid (10 ml per 0.5 g) and left overnight at room temperature. The mixture was poured into ice-cold water and the product was extracted with ether. The ethereal layer was washed with 5% sodium carbonate solutions and then cold water and finally dried (Na_2SO_4). Ether was evaporated and the remaining material was crystallized from petroleum ether (bp 40–60 °C) to give the ketonic lactones (IXc,f,h,i).

Registry No. Ia, 98-03-3; Ib, 1192-58-1; Ic, 123-11-5; Id, 135-02-4; Ie, 66-77-3; If, 89-98-5; Ig, 587-04-2; Ih, 104-88-1; Ii, 100-52-7; II, 49827-44-3; IIIa, 102696-75-3; IIIb, 102696-76-4; IIIc, 102696-77-5; IIId, 102696-78-6; IIIe, 102696-79-7; IIIf, 102696-80-0; IIIg, 102696-81-1; IIIh, 102696-82-2; IIIi, 102696-83-3; Vb, 102696-84-4; Vc, 102696-85-5; Vd, 102779-85-1; Ve, 102696-86-6; Vf, 102696-87-7; Vg, 102696-88-8; Vh, 102724-22-1; Vi, 102724-23-2; VIa, 102696-89-9; VIb, 102696-90-2; VIc, 102696-91-3; VId, 102696-92-4; VIe, 102696-93-5; VIf, 102696-94-6; VIa, 102696-95-7; VIh, 102696-96-8; VIi, 102696-97-9; VIIe, 102696-98-0; VIIf, 102696-99-1; VIIg, 102697-00-7; VIIIc, 102697-01-8; VIIIf, 102697-02-9; VIIIg, 102697-03-0; VIIIh, 102724-24-3; VIIIi, 102697-04-1; IXc, 102724-25-4; IXe, 102697-05-2; IXf, 102697-06-3; IXh, 102697-07-4; IXi, 102697-08-5.

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Polynitroalkyl Ethers by Direct Nitroalkylation

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The synthesis of symmetrical 3,3-dinitro and 3,3,3-trinitroalkyl ethers and of unsymmetrical ethers with one 3,3-dinitro or 3,3,3-trinitroalkyl group and one 2,2-dinitroalkyl group was accomplished by the reaction of the alcohols with triflic acid.

We were interested in synthesizing polynitro-substituted ethers such as **2** for a study of their properties such as melting point. There was no existing method for easily synthesizing such compounds. Although ethers with electron-withdrawing groups, such as nitro, in only one of the alkyl groups are readily accessible by the alkylation of the substituted alcohol (*1*), ethers with two polynitroalkyl groups have had to be synthesized indirectly (*2*). This usually involves alkylation of the polynitro alcohol with a group that can then be converted to a polynitro

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Table I. Polynitroalkyl Ethers Prepared according to Scheme I[a]

$$\underset{\mathbf{1}}{RC(NO_2)_2CH_2CH_2OH} + R'OH \rightarrow \underset{\mathbf{2}}{RC(NO_2)_2CH_2CH_2OR'}$$

	R	R′	method/conditions	yield, %	mp, °C	NMR (δ, $CDCl_3$)
3	CH_3	$CH_3C(NO_2)_2CH_2CH_2$	A; CF_3SO_3H; 20 h reflux	80	66–67	2.13 (s, 6 H), 2.80 (t, 4 H) 3.58 (t, 4 H)
4	F	$CF(NO_2)_2CH_2CH_2$	A; Nafion-H; 4 days reflux.	15	47.5–49	3.73 (t, 4 H), 3.06 (d of t, 4 H)
			B; 0.71 g 1, 3.2 equiv CF_3SO_3H; 60 °C 20 h	9		
5	NO_2	$C(NO_2)_3CH_2CH_2$	B; 1 g 1,[b] 3.9 equiv CF_3SO_3H; 65–70 °C 3 days	16	42.5–43	3.44 (t, 4 H), 3.92 (t, 4 H)
6	F	$CF(NO_2)_2CH_2$	B; 1 g 1, 2 equiv $CF(NO_2)_2CH_2OH$; 16.5 equiv CF_3SO_3H; 30–35 °C 7 days	20	48–49	3.18 (d of t, 2 H), 4.03 (t, 2 H), 4.65 (d, 2 H)
7	NO_2	$CH_3C(NO_2)_2CH_2$	B; 0.76 g 1, 2.9 equiv $CH_3C(NO_2)_2CH_2OH$; 11 equiv CF_3SO_3H; 70–75 °C 3 days	46	47.5–48.5	2.12 (s, 3 H), 3.40 (t, 2 H), 4.07 (t, 2 H), 4.33 (s, 2 H)
8	NO_2	$CF(NO_2)_2CH_2$	B; 1 g 1, 3 equiv $CF(NO_2)_2CH_2OH$; 21 equiv CF_3SO_3H; 65–70 °C 3 days	48	29–29.5	3.47 (t, 2 H), 4.18 (t, 2 H), 4.66 (d, 2 H)

[a] 3,3,3-Trinitropropanol was prepared by an adaption of the literature synthesis of 3,3,3-fluorodinitropropanol; see ref *3*.

group (such as through an oxime or a halide). We wish to report that polynitro ethers **2** can be synthesized by the reaction of the alcohols with triflic acid (as either catalyst or solvent depending on the alcohols) (Scheme I).

Scheme I

$$\underset{(\mathbf{1})}{RC(NO_2)_2CH_2CH_2OH} \xrightarrow{CF_3SO_3H} [RC(NO_2)_2CH_2CH_2OH_2^+ \rightleftarrows RC(NO_2)_2CH_2H_2^+ + H_2O]$$

$$\xrightarrow{R'OH} \underset{(\mathbf{2})}{RC(NO_2)_2CH_2CH_2OR'}$$

$$R = CH_3,\ F,\ NO_2$$

$$R' = \text{2,2-dinitroalkyl and 3,3-dinitroalkyl}$$

The reaction presumably proceeds through the carbonium ion or the protonated alcohol which then reacts with another molecule of alcohol (or a molecule of the second alcohol). The acid is also alkylated to give the triflate of the alcohol in varying amounts depending on the conditions.

Two methods were used for the synthesis of the symmetrical 3,3-dinitropropyl ethers: (A) refluxing a solution of the alcohol and a catalytic amount of triflic acid (or Nafion-H film cut into small pieces) with removal of the water via a reverse Dean-Stark trap; and (B) heating a mixture of alcohol and excess triflic acid. The unsymmetrical ethers were prepared by method B only. The conditions shown in Table I are the result of a limited investigation of the effects of varying reactant ratios, temperature, and reaction time on ether yields, and are not fully optimized.

The course of the reaction and the yields are strongly dependent on the reaction conditions. Ether formation competes with formation of the triflate of alcohol **1** and decomposition of alcohol **1**. The susceptibility to decomposition by triflic acid suprisingly increases in the order $R = CH_3 \ll NO_2 < F$. The ratio of triflic acid to alcohol **1** affects the ratios of the products.

Under the conditions of methods A and B 2,2-dinitropropanol alone did not undergo etherification. When the temperature was raised sufficiently to bring about a reaction, the *gem*-dinitro moiety was attacked with formation of carbonyl-containing species.

The 3,3,3-fluorodinitropropyl ether (**4**) was not obtained in preparatively useful yields by reaction of the triflate with alcohol. Ethers **4** and **6** could also not be made by the diazotization of 3,3,3-fluorodinitropropylamine in the presence of the appropriate alcohol. Thus, the reaction described here represents a unique approach to an otherwise not readily accessible series of polynitro compounds.

Experimental Section

Caution. Many of the compounds reported here are sensitive explosives and should be handled with appropriate care. Elemental analyses were obtained commercially. Satisfactory analyses were obtained for all compounds and were submitted for review. Melting points are uncorrected. ^1H NMR spectra were determined with a Varian EM 390 spectrometer. Chemical shifts are in parts per million from Me_4Si.

3,3-Dinitrobutyl Ether (3). A mixture of 3,3-dinitrobutanol (0.75 g) (prepared by adaption of the literature synthesis of 3,3,3-fluorodinitropropanol (*3*)), 1,2-dichloroethane (15 mL), and triflic acid (0.1 mL) was refluxed through a reverse Dean-Stark trap for 20 h and allowed to cool. The solution was washed with water, dried ($MgSO_4$), filtered, and freed of solvent to give an oil which soon solidified. Recrystallization from dichloromethane/hexane gave compound (**3**) (0.57 g, 80%).

3,3,3-Fluorodinitropropyl Ether (4). To dichloroethane (10 mL) was added Nafion-H (Type 117, obtained from DuPont Polymer Products Dept., Wilmington, DE) (3.1 g, cut into 1 × 2 mm pieces) and 3,3,3-fluorodinitropropanol (0.5 g) (*3*). The mixture was refluxed through a reverse Dean-Stark trap for 4 days. The catalyst was filtered off and washed with dichloromethane, and the solvent was removed from the combined organic solutions. The residue was extracted repeatedly with warm dichloromethane which on cooling gave compound (**4**) (0.07 g, 15%).

Polynitroalkyl Ethers by Method B; General Procedure. To the alcohol or mixture of alcohols under dry nitrogen was added dropwise with ice-cooling and stirring the appropriate amount of triflic acid. The mixture was maintained at temperature for the specified time (Table I), allowed to cool, and poured onto ice. Extraction with dichloromethane, washing the organic layer with saturated sodium bicarbonate solution and water, drying (Na_2SO_4), and removal of solvent gave the crude ether. Purification was by chromatography on Silica Gel 60 (EM Reagents) eluting with hexane and dichloromethane–hexane unless otherwise noted. All products were finally recrystallized from dichloromethane–hexane.

Registry No. **1** ($R = CH_3$), 102285-06-3; **1** (R = F), 36700-20-6; **1** ($R = NO_2$), 87695-55-4; **3**, 102285-07-4; **4**, 102285-08-5; **5**, 102285-09-6; **6**, 102285-10-9; **7**, 102285-11-0; **8**, 102285-12-1; $CF(NO_2)_2CH_2OH$, 17003-75-7; $CH_3C(NO_2)_2CH_2OH$, 918-52-5.

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