°C; ^{1}H NMR δ 6.74 (1 H, H-5), 3.06 (2 H, H-1), 2.45, 2.03, 2.28, 2.23 (3 H, 3 H, 3 H, 6 H, CH$_3$); ^{13}C NMR δ 144.5, 139.2, 138.0, 135.1, 134.1, 129.1, 126.3 (all q), 126.9 (C-6), 40.9 (C-1, 20.3, 18.1, 14.8 (2 C), 14.0 (CH$_3$). Anal. Calcd for C$_{14}$H$_{18}$: C, 90.3; H, 9.7. Found: C, 89.8; H, 9.7.

3,4,5,6,7-Pentamethyl-1H-indene (12b). This indene was prepared as for **12d** using 1.00 g of **1b**: yield 0.80 g (88%); mp (after sublimation) 133–34 °C (lit.[13] mp 104 °C); ^{1}H NMR δ 6.15 (br, 1 H, H-2), 3.17 (br, 2 H, H-1), 2.53 and 2.29 (3 H, 9 H, CH$_3$ on C-4, -5, -6, -7), 2.41 (m, $J_{1,3}$ and $J_{2,3}$ ~ 1 Hz, 3 H, CH$_3$ at C-3); ^{13}C NMR δ 142.1, 141.9, 140.5, 133.7, 131.6, 129.0, 127.5 (q), 129.7 (C-2), 36.6 (C-1, 19.1 (2 C), 16.4 (2 C), 15.9 (CH$_3$). Anal. Calcd for C$_{14}$H$_{18}$: C, 90.3; H. 9.7. Found: C, 90.2; H, 9.4.

3,4,5,7-Tetramethyl-1H-indene (12a). This indene was prepared as for **12b**, except that 100% H$_2$SO$_4$ was used and the ion solution was kept at 20 °C for 4 h before quenching. From 1.00 g (5.3 mmol) of alcohol **1a**, there was obtained 0.40 g (47%) of **12a**, purified in this case by sublimation of the crude residue (0.1 mm, bath 45 °C): mp 59–60 °C; ^{1}H NMR δ 6.90 (1 H, H-6), 6.23 (br, 1 H, H-2), 3.16 (br, 2 H, H-1), 2.52, 2.34, 2.32 (all 3 H, CH$_3$ at C-4, -5, -7), 2.42 (m, 3 H, CH$_3$ at C-3); ^{13}C NMR δ 143.0, 135.1, 129.7, 127.3 (all q), 130.3 and 127.8 (CH aromatic), 35.6 (C-1), 20.1, 18.5, 18.1, 14.7 (CH$_3$). Anal. Calcd for C$_{13}$H$_{16}$: C, 90.7; H, 9.3. Found: C, 90.8; H, 9.2.

2,3,4,5,5,6,7-Heptamethyl-5H-indene (13). The cation solution described for the preparation of **2e**, using 0.50 g (2.2 mmol) of the alcohol **1e**, was allowed to warm to 20 °C, resulting after 2 h in the formation of cation EH$^+$. After quenching in the usual way, the crude residue was purified by sublimation, yield 0.30 g of red crystals (65%), mp 42–43 °C (some decomposition occurs during the purification since the yield of the nearly pure crude product is virtually quantitative). The compound slowly polymerizes on contact with air. **13:** ^{1}H NMR δ 6.00 (1 H, H-3), 2.32, 2.04, 1.94, and 1.87 (all sharp 3 H singlets, CH$_3$ at C-3, -4, -6, -7),

2.20 (d, $J = 1$, CH$_3$ at C-2), 1.13 (6 H, C-5 CH$_3$'s); ^{13}C NMR δ 150.6, 140.0, 138.5, 135.2, 133.1, 123.4, 121.2 (all q), 120.1 (CH alkene), 44.4 (q, C-5), 23.9 (2 C, CH$_3$'s on C-5), 15.7, 14.8, 14.5, 13.9, 13.3 (CH$_3$); electronic spectrum (acetonitrile), 220 nm, 248, 253, 265, 420 (ϵ_{max} 13100, 21900, 19700, 5600, 1060). Anal. Calcd for C$_{16}$H$_{22}$: C, 89.7; H, 10.3. Found: C, 88.9; H, 10.5.

Electronic Spectra of Cations BH$^+$ and EH$^+$ from Alcohol 1e. Cation BH^+ was prepared at 0 °C in 96% H$_2$SO$_4$. The spectrum was recorded at 5.2 °C [λ_{max} 483 nm, 351, 313, 260 (ϵ_{max} 9350, 4600, 5000, 15200, respectively)]. On warming to 20 °C, the rearrangement of BH$^+$ to EH$^+$ slowly takes place. The spectrum of EH$^+$ shows λ_{max} 380 nm, 352 (ϵ_{max} 11850, 25200). On leaving cation EH$^+$ for 24 h at 20 °C, there was no change in the spectrum.

Kinetic Measurements. The first-order rate constants shown in Table II were obtained by ^{1}H NMR integration of the area decrease of a reactant peak and the accompanying increase of a product peak. The temperature calibration and other NMR details follows that given previously.[14]

Registry No. **1a**, 74705-62-7; **1a·AH$^+$**, 84012-09-9; **1a·CH$^+$**, 84012-07-7; **1a·DH$^+$**, 84000-52-2; **1b**, 84000-28-2; **1b·BH$^+$**, 84000-48-6; **1b·DH$^+$**, 84000-53-3; **1c**, 84000-29-3; **1c·AH$^+$**, 84012-08-8; **1c·BH$^+$**, 84000-49-7; **1c·CH$^+$**, 84000-46-4; **1c·DH$^+$**, 84000-54-4; **1d**, 84000-30-6; **1d·BH$^+$**, 84000-50-0; **1d·DH$^+$**, 84000-56-6; **1e**, 84000-31-7; **1e·BH$^+$**, 84000-51-1; **1e·EH$^+$**, 84000-47-5; **2d**, 84000-32-8; **2e**, 84000-33-9; **3d**, 84000-35-1; **3e**, 84000-34-0; **4d**, 84000-36-2; **4e**, 84000-37-3; **5e**, 84000-38-4; **6d**, 84000-40-8; **6e**, 84000-39-5; **7d**, 84000-42-0; **7e**, 84000-41-9; **12a**, 84000-44-2; **12b**, 84000-43-1; **12c**, 36230-98-5; **12d**, 21866-46-6; **13**, 84000-45-3.

(13) Heilbrunn, A. G.; Marechal, E. *C. R. Acad. Sci., Ser. C* **1972**, *274*, 1069.

(14) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of 1,1,1-Trimethylolethane Trinitrate

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The kinetics for the alkaline homogeneous hydrolysis of 1,1,1-trimethylolethane trinitrate (MTN) in 95% ethanol–water with sodium hydroxide concentrations between 0.25 and 2.1 M and temperatures between 50.0 and 60.0 °C have been investigated. One mole of MTN was found to react with 3 mol of base and to hydrolyze by a series of consecutive and competitive bimolecular and internal cyclization reactions involving three nitrate ester intermediates to form the cyclic alcohol ether 3-methyl-3-oxetanemethanol (AE) as the final major product with only trace amounts of the expected trialcohol 1,1,1-tris(hydroxymethyl)ethane (TA). MTN and its intermediates showed good second-order rate constants for the expression $-d(\text{MTN})/dt = k_1(\text{MTN}) = k_2(\text{B}^-)(\text{MTN})$, where k_1 is the first-order rate constant with excess base, B$^-$. Relative k_2 values in 95% ethanol–water, 95% methanol–water, and water were found to be 1.0, 0.1, and 0.01, respectively. Hydrolysis kinetics and product formation for each nitrate ester intermediate have been determined, and an overall hydrolysis mechanism for MTN is presented.

Introduction

Highly energetic nitrate esters such as nitroglycerine (NG) and 1,1,1-trimethylolethane trinitrate (MTN) are widely used in propellant and explosive compositions. It is essential, therefore, that a thorough knowledge of their chemical reactions be known, including hydrolytic stability, for safety as well as environmental concerns. An excellent historical summary of the alkaline hydrolyses of nitrate

esters has been presented by Urbanski[1] with 24 references covering work from 1885 through 1955. None of these investigations, however, included MTN. Baker and coworkers' kinetic studies of the alkaline hydrolyses of nitrate esters are classic[2-4] and led to the conclusion that three

(1) T. Urbanski, "Chemistry and Technology of Explosives", Pergamon Press, New York, 1965, pp 7–18.

major reactions were involved. These were (a) nucleophilic substitution on carbon to give the parent alcohol, (b) β-hydrogen elimination to yield olefin and nitrate ions, and (c) α-hydrogen elimination to yield the corresponding carbonyl compound and nitrite ions. Cristol and co-workers[5] suggested that nucleophilic attack on nitrogen could also occur to produce nitrate ions and the corresponding alcohol, while Anbar and co-workers[6] showed with ^{18}O-labeled water that nitrate esters could react under alkaline conditions to yield products derived from a mixture of carbon–oxygen and nitrogen–oxygen fission reactions. In 1968 Fraser[7] compared the alkaline hydrolyses of 18 mono-, di-, and trinitrate esters in 90% ethanol–water by measuring the decrease in base concentration with time. Initial second-order rate constants were derived on the assumption that the rates for the disappearance of base and nitrate ester were equivalent. Although MTN was studied in one run, no product analyses were reported.

In 1979 alkaline hydrolysis kinetic studies as well as product analyses were made on the two mononitrate ester isomers of glycerine and the two dinitrate ester isomers of glycerine as well as NG itself.[8] The alkaline hydrolysis of NG was found to be complex, and surprisingly, no mono- or dinitrate ester isomers of glycerine were observed. The isomerization of the 2-glyceryl mononitrate ester to the 1-glyceryl mononitrate ester as well as the isomerization of 1,2-glyceryl dinitrate ester to the 1,3-glyceryl dinitrate ester under basic conditions were intriguing. The internal cyclization of 1,3-glyceryl dinitrate to the epoxide, glycidyl nitrate (although not observed in NG hydrolysis), is closely related to two internal cyclized products resulting from the alkaline hydrolysis of MTN. We now report our kinetics results concerning the formation of these products from MTN under basic conditions and suggest a possible mechanism for their formation.

Experimental Section

Materials. 1,1,1-Tris(hydroxymethyl)ethane (TA) and ethyl nitrate (EN) were obtained commercially (Eastman) and used without further purification. 1,1,1-Trimethylolethane trinitrate (MTN) was prepared by mixed-acid nitration of TA and checked for purity by TLC, VPC, and GC/CI MS. 1,1,1-Trimethylolethane dinitrate (MA) and 1,1,1-trimethylolethane mononitrate (DA) were produced from the photolytic decomposition of MTN in another study and were separated and purified by column chromatography. Purity was checked by TLC and GC/CI MS, and properties were compared to literature values.[9] 3-Methyl-3-oxetanemethanol (AE) was prepared and purified from TA and diethyl carbonate by the pyrolysis of the corresponding carbonate ester according to Pattison's procedure.[10]

3-Methyl-3-oxetanemethyl nitrate (NE) was prepared from the alkaline hydrolysis of MTN. A total of 0.0894 mol (22.8 g) of MTN in 100 mL of ethanol in a 250-mL beaker was treated with 12 mL of 50% aqueous sodium hydroxide (0.228 mol) in 50 mL of ethanol. The mixture was boiled down to 100 mL to remove EN; another

(2) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

(3) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1208 (1952).

(4) J. W. Baker and A. J. Neale, *J. Chem. Soc.*, 3225 (1954).

(5) S. J. Cristol, B. Franzus, and A. Shadan, *J. Am. Chem. Soc.*, 77, 2512 (1955).

(6) M. Anbar, I. Dostrovsky, D. Samuel, and A. D. Yoffe, *J. Chem. Soc.*, 3603 (1954).

(7) R. T. M. Fraser, Explos. Res. Develop. Estab., Waltham Abbey, Engl., Report No. ERDE 4/R/68, (obtainable from U.S. Clearinghouse, Fed. Sci. Tech. Inform. U.S. Govt. Res. Develop. Rep. 1968, 68 (23), No. AD-675917; Also, R. T. M. Fraser, *Chem. Ind.* (*London*), 33, 1117–8 (1968).

(8) C. Capellos, W. J. Fisco, C. Rabaudo, V. D. Hogan, J. Campisi, F. X. Murphy, T. C. Castorina, and D. H. Rosenblatt, Technical Report ARLCD-TR-79022, Aug 1979, U.S. Army Armament Research and Development Command, Dover, NJ.

(9) T. Urbanski, ref 1, pp 198–199.

(10) D. B. Pattison, *J. Am. Chem. Soc.*, 79, 3455–6 (1957).

50 mL of ethanol was added, and the mixture was again boiled down to 100 mL. The mixture was then cooled in an ice bath, and 9.98 g of salt (after drying) were filtered off. LC analysis showed 0.014 mol (15.7%) of DA and 0.0022 mol (2.5%) of MA, while GC analysis showed 0.0375 mol (42%) of NE in the filtrate. The ethanol was evaporated and the residue extracted with benzene. Benzene was removed by vacuum distillation, and 3.0 g of a clear liquid was collected, bp 52–54 °C (1–2 mm Hg). The product was purified by redistillation and showed a single peak in the LC trace. Proof of structure for NE was obtained by GC/CI MS, NMR, and elemental analysis. Mass spectra showed m/z 148 (P + 1) and was obtained with a Finnigan 4000 gas chromatograph/EI CI mass spectrometer with a 6 ft by $^1/_4$ in. glass column packed with 3.5% Dexsil 300 on 80/100 HP Chromosorb W AWDMCS: methane flow, 20 mL/min; injection temperature, 190 °C; column, 100 °C for 3 min, then programmed 20 °C/min to 150 °C. The ^1H and ^{13}C NMR spectra were run on a Varian XL-200 spectrometer (referenced to Me$_4$Si) in benzene-d_6 solvent. The ^1H spectrum showed peaks at δ 0.79 (s, 3), 3.84 (s, 2), 3.91 (d, 2), and 4.03 (d, 2). The ring protons were geminally coupled, J_{AB} = 6.0 Hz. At high resolution the lower field doublet was observed to be a doublet of quartets where the $J_{AB'}$ long-range coupling was 0.33 Hz and the higher field doublet was only broadened. The ^{13}C NMR spectrum showed δ 20.0 (methyl), 38.0 (quaternary), 77.0 (CH$_2$ONO$_2$), 79.0 (ring CH$_2$'s), where a noise off resonance spectrum allowed assignment of ^{13}C multiplicities. Anal. Calcd: C, 40.90; H, 6.13; N, 9.53. Found: C, 40.94, 41.05; H, 6.17, 6.23; N, 9.42, 9.31.

Analysis. AE and TA concentrations were determined with a gas chromatograph (Hewlett-Packard, Model 5830A) using dual 6 ft by $^1/_8$ in. SS columns packed with 60/80 Tenax GC (Supelco, Inc.): column temperature, 185 °C; He flow, 35 mL/min; injection temperature, 190 °C; FID temperature, 300 °C; attenuation, X512. Under these conditions, a 1.0-μL injection of a standard ethanolic solution containing 0.0142 M AE and 0.0155 M TA gave the following retention times and peak heights: 1.45 m (42 mm) and 5.88 m (26 mm), respectively. Peak heights were used to calculate AE and TA unknown concentrations by comparison to standards of known concentrations.

MTN, MA, DA, NE, and EN concentrations were determined with a liquid chromatograph (Hewlett-Packard, Model 1084A), equipped with a variable-wavelength detector (HP Model 1030) and a variable-volume injector with a 10-μm RP-8 column, 25 cm × 4.6 mm i.d. at 40 °C: eluent, 43% methanol–water (v/v); flow, 1.0 mL/min; detector wavelength, 220 nm; attenuation, 0.0128 AU/cm. Under these conditions the following retention times and relative molar height responses were obtained: DA (3.81 m, 0.86), NE (5.30 m, 0.68), EN (5.84 m, 0.89), MA (7.98 m, 1.36), and MTN (16.5 m, 1.00). A 50-μL injection of a 2.39 × 10⁻⁴ M MTN aqueous solution gave a peak height of 61.9 mm and an area count of 300 400. Peak heights were used to calculate MTN, MA, DA, NE, and NE concentrations by comparison to standards of known concentrations.

Nitrate and nitrite ion concentrations were determined with an ion chromatograph (Dionex, Model 10) with a 3 mm by 500 mm anion separator column, a 3 mm by 150 mm precolumn, and a 6 mm by 250 mm anion suppressor column: eluent, 0.003 M sodium bicarbonate–0.0024 M sodium carbonate in distilled water; flow rate, 2.3 mL/min; sensitivity, 3 μmho, full scale. Under these conditions, a 100-μL injection of a mixture of 4.33 × 10⁻⁴ M nitrate and 9.00 × 10⁻⁴ M nitrite ions had the following retention times and peak heights: nitrite (5.4 m, 175 mm); nitrate (13.8 m, 149 mm). Peak heights were used to calculate nitrite and nitrate ion concentrations by comparison to standards of known concentrations.

Acetate and formate ion concentrations were determined by using 0.005 M borax as eluent under the conditions outlined for the nitrite–nitrate ion analyses. A 100-μL injection of a mixture of 1.75 × 10⁻³ M acetate and 1.33 × 10⁻³ M formate ions gave the following retention times and peak heights: acetate (4.6 m, 134 mm); formate (6.4 m, 141 mm).

Kinetics. Stock ethanolic solutions of sodium hydroxide and MTN were thermostated separately in 10-mL volumetric flasks in a constant temperature bath held to ±0.05 °C at least 0.5 h before a run. Concentrations of stock solutions were chosen so that on mixing, the final base concentration was at least 10 times

Table I. Product Distribution: Base Hydrolysis of MTN in 95% Ethanol-Water at 55 °C

time, min	concentration, M						
	NaOH	MTN	MA	DA	NE	TA	AE
0	1.83	0.43	0	0	0	0	0
31.8		0.023	0.37	0.046	0.064		
78.8		0	0.20	0.089	0.13		
1122.7	0.70		0	0.027	0.043	0.0082	0.31
2194.8	0.59			0	0.0054	0.021	0.35

Scheme I

$$CH_3C(CH_2ONO_2)_3 \longrightarrow CH_3C(CH_2ONO_2)_2CH_2OH \longrightarrow CH_3C(CH_2ONO_2)(CH_2OH)_2 \longrightarrow CH_3C(CH_2OH)_3$$

MTN   MA   DA   TA
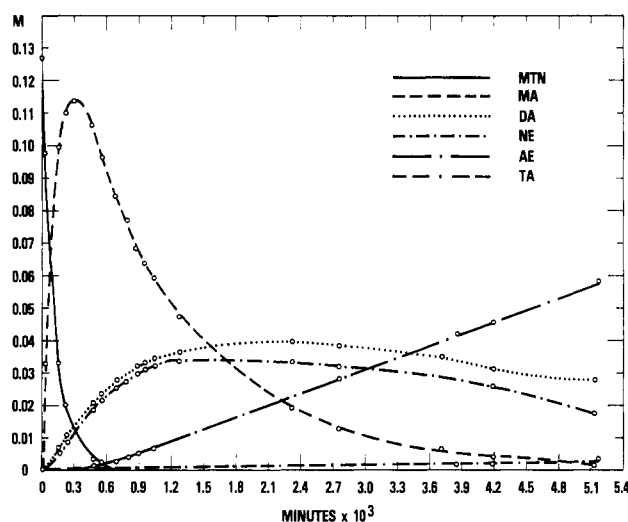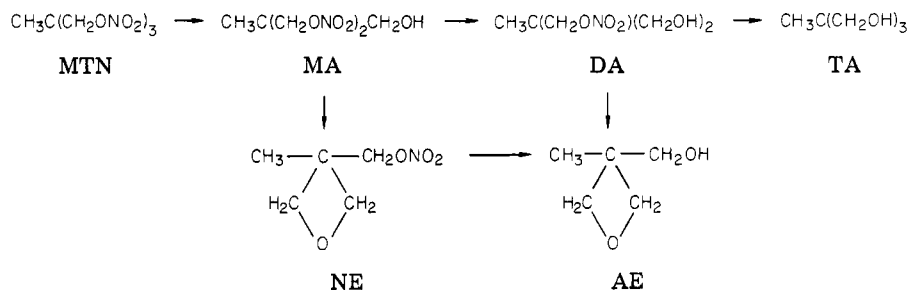

NE   AE

Figure 1. Alkaline hydrolysis of MTN in 95% methanol–water at 55 °C.

the MTN concentration. Appropriate aliquots were taken with time by means of a micropipet and added to a known volume of water so that the resulting concentration of MTN was between 2×10^{-5} and 2×10^{-4} M. Times were obtained with an automatic timer (Precision Scientific Co., Chicago). Hydrolysis kinetics for MA, DA, NE, and EN were determined in a similar manner. Base concentrations were determined by standard acid titration of an aliquot of the reaction solution at the conclusion of a run. IC analyses were made directly on the diluted aqueous samples. LC analyses were made on a 1–2-mL portion of the diluted sample after adjusting the pH to 7–8 by the addition of small portions of solid potassium dihydrogen phosphate. GC analyses of AE resulting from the basic hydrolyses of DA and NE were determined on appropriately diluted aqueous solutions with time after adjusting the pH to 7–8 with solid potassium dihydrogen phosphate.

Results and Discussion

The major reactions in the basic hydrolysis of metriol trinitrate (MTN) were found to produce the three nitrate ester intermediates MA, NE, and DA with the formation of two stable alcohols, AE and TA, as final products. In one scale-up run, Table I, AE was formed in 81.8% yield while TA was formed in 4.9% yield. Figure 1 shows the hydrolysis of 0.128 M MTN in 0.760 M sodium hydroxide in 95% methanol–water at 55 °C as a function of time. The overall hydrolysis of MTN may be shown as in

Table II. Solvent Effects: Basic Hydrolysis of MTN at 55 °C

solvent	$10^{-3}k_2{}^a$
95% ethanol-water	1.27
95% methanol-water	0.12
water	0.013^b

a Second-order rate constant calculated from $k_2 = k_1/$ (NaOH), L mol^{-1} s^{-1}. b Extrapolated value from Arrhenius plot from values of k_2 at three temperatures: 0.021×10^{-3} (60 °C); 0.34×10^{-3} (90 °C); 0.72×10^{-3} (100 °C).

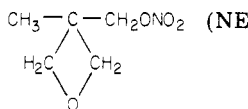**Table III. Solvent Effects: Activation Parameters for the Basic Hydrolysis of MTN**

solvent	$\Delta H^{\ddagger a}$	$\Delta F^{\ddagger a}$	$\Delta S^{\ddagger b}$
water	20.8	27.1	−17.8
95% ethanol–water	25.0	23.5	+4.6

a kcal mol^{-1}. b cal deg^{-1}.

Scheme I. Basic hydrolysis kinetics of MTN as well as each nitrate ester intermediate will be considered separately. Referring to Figure 1, we see that after 5170 min, MTN was completely hydrolyzed and produced the following equilibrium concentrations and molar yields based on MTN: 1.9×10^{-3} M MA (1.5%); 2.1×10^{-2} M NE (16.5%); 4.1×10^{-2} M DA (31.8%); 5.8×10^{-2} M AE (45.5%); 3.0×10^{-3} M TA (2.3%). During hydrolysis the concentration of sodium hydroxide had decreased from 0.760 to 0.452. From these data, the ratio moles of base consumed/moles of nitrate groups reacted was found to be 0.97. Since the hydrolysis of MTN was found to be approximately 10 times faster in ethanol than in methanol and 100 times faster than in water, Table II, the hydrolysis kinetics of MTN and its intermediates were carried out in 95% ethanol–water. The activation parameters for the basic hydrolysis of MTN in 95% ethanol–water and in water are shown in Table III. These data support a mechanism for charge dispersal in the activated complex created in the transition state by a reaction between an ion and a neutral molecule. Reaction rates in the polar solvent, water, would be expected to proceed at a slower rate than in the nonpolar solvent, ethanol.[11]

(11) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, (1959), p 184; also E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

Table IV. Kinetic Data: Base Hydrolysis of MTN and Intermediates in 95% Ethanol-Water at 55 °C

compd	$(NaOH)^a$	$10^{-4}k_1{}^b$	$10^{-3}k_2{}^c$	rel rate^d
$CH_3C(CH_2ONO_2)_3$ (MTN)	0.6454	8.28	1.34	1.00
	0.9604^e	12.3	1.28	
$CH_3C(CH_2ONO_2)_2CH_2OH$ (MA)	0.2553	0.66	0.25	0.19
	0.4429	1.03	0.23	
	1.014^f	1.5	0.15	
$CH_3C(CH_2ONO_2)(CH_2OH)_2$ (DA)	0.6454	0.25	0.039	0.029
	0.7354^g	0.28	0.038	
	2.075	0.69	0.033	
$CH_3{-}\underset{H_2C\diagdown_{O}\diagup CH_2}{\overset{|}{C}}{-}CH_2ONO_2$ (NE)	0.3707	0.16	0.043	0.032
	0.5959^h	0.26	0.043	
	1.620	1.05	0.064	
$CH_3CH_2ONO_2$ (EN)	0.6454	0.14	0.022	0.016
	1.863^i	0.46	0.025	

^{a} (NaOH) $\gg$ (compound). ^{b} First-order rate constant, k_1 = $1/t \ln (C_0/C_t)$, s^{-1}. ^{c} Second-order rate constant, $k_2 = k_1/$ (NaOH), L mol^{-1} s^{-1}. ^{d} Relative k_2 values. ^{e} MTN = 1,1,1-trimethylolethane trinitrate; see Table V. ^{f} MA = 1,1,1-trimethylolethane dinitrate; see Table VI. ^{g} DA = 1,1,1-trimethylolethane mononitrate; see Table VII. ^{h} NE = 3-methyl-3-oxetanemethyl nitrate; see Table IX. ^{i} EN = ethyl nitrate; see Table VIII.

Table V. Hydrolysis of 1,1,1-Trimethylolethane Trinitrate (MTN) in 95% Ethanol-Water at 55 °C

time, min	$M \times 10^{-2}$						
	MTN^a	EN	MA	NO_2^-	NO_3^-	NE	DA
0	2.44	0	0	0	0	0	0
0.75	2.34	0.073	0.11	<0.030	<0.080	<0.010	<0.005
2.80	1.93	0.30	0.34	0.077	0.123	<0.01	<0.005
7.10	1.49	0.69	0.74	0.217	0.369	0.028	0.013
12.5	0.97	1.01	1.05	0.463	0.534	0.063	
18.9	0.60	1.25	1.25	0.650	0.739	0.120	
30.1	0.28	1.48	1.34	0.860	1.07	0.270	0.20
41.4	0.13	1.68	1.32	1.05	1.23	0.41	0.26
52.0	0.054	1.72	1.22	1.10	1.27	0.50	0.37
73.3	0.010	1.78	0.98	1.13	1.40	0.66	0.44
93.1	0.005	1.75	0.80	1.16	1.64	0.75	
137.8		1.78	0.49	1.30	1.93	0.87	0.60
161.6		1.75	0.38	1.31	2.10	0.89	0.65
1208.9^b		0.48	0.02	1.93	4.19	0.04	0.095

^{a} (NaOH) = 0.9604 M. ^{b} Found 0.87 × 10^{-2} M AE, 3-methyl-3-oxetanemethanol, at conclusion of run.
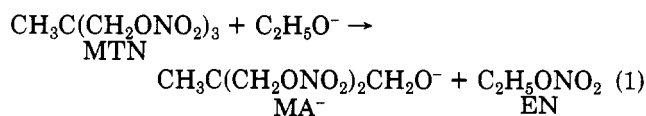
In Table IV are listed the first- and second-order rate constants, k_1 and k_2, for MTN and its hydrolysis intermediates as a function of base concentration in 95% ethanol-water at 55 °C. Ethyl nitrate (EN) is included since it is formed during hydrolysis and undergoes base hydrolysis itself. The k_2 values were calculated from the expression $k_2 = k_1/[NaOH]$, where $k_1 = 1/t \times \ln (C_0/C_t)$ and is the pseudo-first-order rate constant for the disappearance of the particular compound whose concentrations initially and at time t are C_0 and C_t, respectively. In water the base ion would be OH$^-$, while in 95% ethanol-water the base ion present would be expected to be largely $C_2H_5O^-$. With the sodium hydroxide concentration represented by B$^-$, the rate expression for the disappearance of MTN is given by $-d(MTN)/dt = k_1(MTN) = k_2(B^-)$-(MTN), and B$^- \gg$ MTN.

The order with respect to base concentration for MTN was found to be 1.0 and was calculated from the expression $(NaOH)_1{}^x/(NaOH)_2 = k_{1\text{-}1}/k_{1\text{-}2}$, where $k_{1\text{-}1}$ and $k_{1\text{-}2}$ are the first-order rate constants at base concentrations $(NaOH)_1$ and $(NaOH)_2$, respectively. The fairly close agreement of the k_2 values of the other compounds also indicate a first-order dependency on base concentration with notable exceptions for MA and NE at base concentrations greater than 1 M.
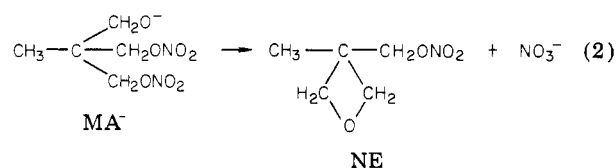
Table V shows the hydrolysis of 2.44 × 10^{-2} M MTN in 0.9604 M NaOH in 95% ethanol-water at 55 °C and the formation of the nitrate ester intermediates MA, NE, and DA with time. The formation of ethyl nitrate (EN) as well as NO$_3^-$ and NO$_2^-$ are also included. These data lend

support to the following relationships in the early stages of MTN hydrolysis: $-d(MTN)/dt = +d(MA)/dt = +d$-$(EN)/dt$. After 30.1 min, MTN was 89% hydrolyzed with the formation of 62% MA, 12.5% NE, and 9.3% DA, which accounts for 94% of the organic fractions from MTN. From 30.1 min to 137.8 min, the MA concentration decreased by 0.85 × 10^{-2} M, while the NO$_3^-$ concentration increased by 0.86 × 10^{-2} M, and the NE concentration increased by 0.60 × 10^{-2} M. These results indicate the following reactions:

(1) Nucleophilic attack by ethoxide ion on nitrogen to form ethyl nitrate and 1,1,1-trimethylolethane dinitrate anion, MA$^-$.

$$CH_3C(CH_2ONO_2)_3 + C_2H_5O^- \rightarrow$$
$$\underset{MTN}{}$$
$$\underset{MA^-}{CH_3C(CH_2ONO_2)_2CH_2O^-} + \underset{EN}{C_2H_5ONO_2} \quad (1)$$

(2) Internal cyclization of 1,1,1-trimethyolethane anion (MA$^-$) to form the cyclic ether nitrate, 3-methyl-3-oxetanemethyl nitrate (NE), and nitrate ion.

$$\underset{MA^-}{CH_3{-}\underset{CH_2ONO_2}{\overset{CH_2O^-}{C}}{-}CH_2ONO_2} \longrightarrow \underset{NE}{CH_3{-}\underset{H_2C\diagdown_O\diagup CH_2}{\overset{|}{C}}{-}CH_2ONO_2} + NO_3^- \quad (2)$$

After 137.8 min, MTN was completely hydrolyzed for a total loss of 7.32 × 10^{-2} M nitrate moities, while a total of

Table VI. Hydrolysis of 1,1,1-Trimethylolethane Dinitrate (MA) in 95% Ethanol–Water at 55 °C

time, min	M × 10⁻³						product ratio conversion [b]		
	MA[a]	DA	EN	NE	NO₃⁻	NO₂⁻	NO₃⁻/ NE	EN/ DA	(DA + NE)/ (−MA)
0	9.14	0	0	0	0	0			
15.5	8.05	0.36	0.32	0.95	1.1	0.04	1.1	0.9	1.2
23.8	7.30	0.49	0.40	1.3	1.4	0.06	1.1	0.8	1.0
30.7	7.00	0.69	0.52	1.6	1.6	0.15	1.0	0.8	1.1
39.9	6.42	0.84	0.65	2.0	2.0		1.0	0.8	1.0
55.8	5.76	0.98	0.95	2.7	2.8	0.21	1.0	1.0	1.1
83.7	4.57	1.3	1.3	3.6	3.4	0.29	0.9	1.0	1.1
186.5[c]	1.91	1.8	2.0	4.8	5.4	0.75	1.1	1.1	0.9

[a] (NaOH) = 1.014 M. [b] Ratio of sum of products DA and NE to moles of MA reacted. [c] GC/FI analysis showed presence of 1.0 × 10⁻³ M 3-methyl-3-oxetanemethanol (AE) and 0.05 × 10⁻³ M 1,1,1-tris(hydroxymethyl)ethane (TA).

Table VII. Hydrolysis of 1,1,1-Trimethylolethane Mononitrate (DA) in 95% Ethanol–Water at 55 °C

time, min	M × 10⁻³					product ratio conversion [b]			
	DA[a]	AE	EN	NO₃⁻	NO₂⁻	NO₃⁻/ AE	NO₂⁻/ −DA	EN/ −DA	AE/ −DA
0	15.6	0	0	0	0				
115.9	13.4	1.58	0.23	2.09	0.18	1.3	0.082	0.10	0.72
281.5	9.66	4.40	0.46	5.27	0.34	1.2	0.057	0.07	0.74
1314.2	1.72	10.4	0.46	11.8	0.85	1.1	0.061	0.03	0.75

[a] (NaOH) = 0.7354 M. [b] Ratio of products formed to moles of DA reacted.

7.46 × 10⁻² M nitrite and nitrate moities (102%) were distributed among the products as follows: MA (13.4%); NE (11.9%); DA (8.2%); EN (24.3%); NO₃⁻ (26.3%); NO₂⁻ (17.7%). The formation of nitrite ions indicates the occurrence of side reactions.

The results in Table VI show the simultaneous formation of 1,1,1-trimethylolethane mononitrate (DA) and 3-methyl-3-oxetanemethyl nitrate (NE) from the hydrolysis of 9.14 × 10⁻³ M MA in 1.014 M NaOH in 95% ethanol-water at 55 °C. These data lend support to the kinetic relationships (a) -d(MA)/dt = +d(DA)/dt + d(NE)/dt, (b) +d(NE)/dt = +d(NO₃⁻)/dt, and (c) +d(DA)/dt = +d(EN)/dt, and suggest the following reactions:

(3) Competitive internal cyclization and nucleophilic attack by ethoxide ion on the nitrogen of MA (eq 3).
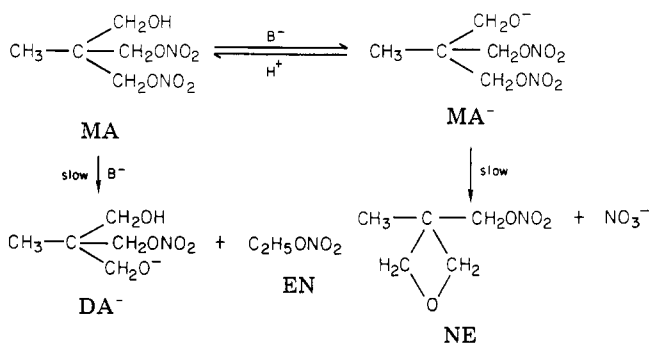
The molar yield of NO₂⁻ formed from the available nitrate groups in MA was found to increase from 1.8% at 15.5 min to 5.2% at 186.5 min at the point where MA was 79% hydrolyzed. At the same time, the molar yields of intermediates and end products were as follows: DA (24%); NE (66%); AE (13%); TA (0.7%). The total molar concentrations of intermediates and end products formed were 7.65 × 10⁻³ M, which is reasonably close to the 7.23 × 10⁻³ M decrease observed for MA. These results also indicate that the side reactions leading to NO₂⁻ formation are relatively small.

The hydrolysis of 15.6 × 10⁻³ M 1,1,1-trimethylolethane mononitrate (DA) with 0.7354 M NaOH in 95% ethanol-water at 55 °C is shown in Table VII. These data suggest the following kinetic relationships: -d(DA)/dt =

Scheme II
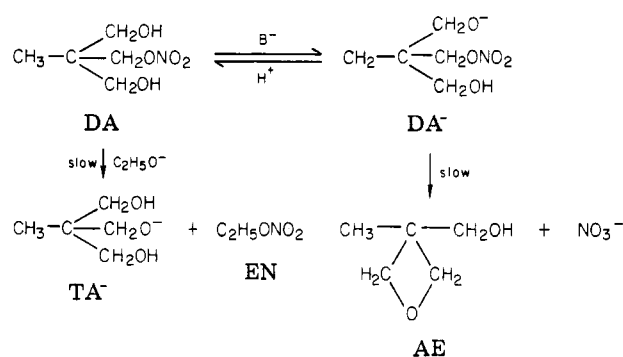
+d(AE)/dt = +d(NO₃⁻)/dt. Again, as with MA, the yields of NO₂⁻ are relatively small. The yield of NO₂⁻ ion formed from DA was found to be 6.6 ± 1.3 molar percent over the entire hydrolysis range. The end product, TA, was too dilute to be detected by GC/FI under the conditions of this experiment. However, if it is assumed that the formation of TA parallels the formation of EN just as the formation of DA parallels the formation of EN in the hydrolysis of MA (Table VI), an estimation of the amount of TA may be made. On this basis, after 281.5 min the molar decrease of DA was 5.94 × 10⁻³ M (38% DA hydrolysis), while the molar increases for AE and TA were 4.40 × 10⁻³ and 0.46 × 10⁻³ M, respectively, and together account for 82 mol % of the organic products from DA hydrolysis. A side reaction, possibly occurring by proton abstraction from the methylene linkage to produce both NO₂⁻ and NO₃⁻ ions, is suggested for the missing 18 mol % of the DA hydrolysis reaction. This is supported by the somewhat larger NO₃⁻ concentration compared to the AE concentration. On the basis of these data, the major hydrolysis paths for DA appear to be similar to MA hydrolysis, as shown in Scheme II. Since the ratio EN/DA was observed to decrease with time (Table VI), it could be argued that the formation of NO₂⁻ came from the hydrolysis of EN. However, the contribution of NO₂⁻ from the hydrolysis of EN would be expected to be small on the basis of the data in Table VIII. With the data from Table VIII and the k_2 value for EN hydrolysis, Table 4, the

Table VIII. Hydrolysis of Ethyl Nitrate (EN) in 95% Ethanol–Water at 55 °C

| time, min | M × 10⁻² | | | conversion[b] | |
	EN^a	NO_3^-	NO_2^-	$NO_3^-/$ −EN	$NO_2^-/$ −EN
0	5.84	0	0		
59.0	4.97	0.80	0.03	0.92	
121.4	4.22	1.50	0.03	0.92	0.01
193.0	3.48	2.13	0.06	0.90	0.02
239.1	2.88	2.46	0.13	0.83	0.04

^{a} (NaOH) = 1.863 M. ^{b} Ratio of products formed to moles of EN reacted.

concentration of NO_2^- formed from EN in 281.5 min was calculated to be 0.045 × 10⁻³ M and is only about 5% of the total NO_2^- formed.

The results of the hydrolysis of 3.31 × 10⁻² M 3-methyl-3-oxetanemethyl nitrate (NE) with 0.5959 M NaOH in 95% ethanol–water at 55 °C are shown in Table IX. The molar conversion to 3-methyl-3-oxetanemethanol (AE) was 64 ± 8% over the entire hydrolysis range. The formation of AE and ethyl nitrate (EN) may be explained by nucleophilic attack by ethoxide ion on nitrogen:
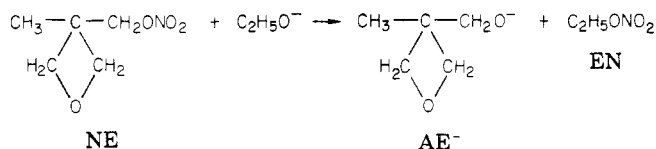
Ethyl nitrate (EN) does not increase appreciably, since $k_2(EN)/k_2(NE) \simeq 0.5$ (Table IV). Also, the major formation of NO_2^- must come from NE directly since the expected formation of NO_2^- from EN would be small (Table VIII). Proton abstraction from the methylene linkage of NE could lead to the formation of NO_2^- ion (oxygen–nitrogen fission) and the corresponding cyclic aldehyde or of NO_3^- ion (carbon–oxygen fission) and an electron-deficient organic fragment that undergoes rearrangement. Most likely both these processes are occurring simultaneously. The formation of 0.25 × 10⁻² M formate ion and 0.09 × 10⁻² M acetate ion along with a number of other

unidentified peaks in the IC analysis of the NE hydrolysate after 682.8 min indicates extensive rearrangement. In addition, base-aldehyde condensation reactions would be expected to produce complex products. Indeed, the base hydrolysis of NE produced deep yellow to brown solutions whose color intensity increased with time.

Finally, some mention should be made of the cyclization reactions of MA and DA (Tables VI and VII), whose rates undoubtedly depend on the concentrations of MA^- and DA^-, respectively. The concentrations of MA^- and DA^- in 95% ethanol–water depend on the following equilibria:

$$MA + B^- \rightleftharpoons MA^- + BH$$

$$DA + B^- \rightleftharpoons DA^- + BH$$
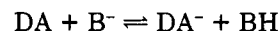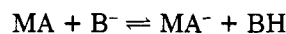
where B^- is the base ion concentration in 95% ethanol–water (mainly $C_2H_5O^-$) and BH is the solvent concentration. Ignoring the solvent, the following equilibria constants may be written: $K_{MA} = MA^-/(MA)(B^-)$; $K_{DA} = DA^-/(DA)(B^-)$. From the data shown in Table VI, it is apparent that since -MA = +NE + DA, then, -d(MA)/dt = d(NE)/dt + d(DA)/dt. But, -d(MA)/dt = k_1(MA), where k_1 is the first-order rate constant for the disappearance of MA in excess base, Table IV. Furthermore, d(NE)/dt = k_{1NE}(MA) and d(DA)/dt = k_{1DA}(MA) so that $k_1 = k_{1NE} + k_{1DA}$, where k_{1NE} and k_{1DA} are the first-order rate constants for the formation of NE and DA. During the reaction between MA and base, the ratio NE/DA was found to be fairly constant at a particular base concentration, Table X. Since NE/DA = d(NE)/dt ÷ d(DA)/dt, it follows that NE/DA = k_{1NE}/k_{1DA}. The values of k_1, k_{1NE}, and k_{1DA} as a function of base concentration in 95% ethanol–water at 55 °C are given in Table X. The second-order rate constant k_{2DA} for the formation of DA from MA, where $k_{2DA} = k_{1DA}/(NaOH)$, is also given. Now, on the assumption that the first-order rate constant for the formation of NE, k_{1NE}, is proportional to the MA^- ion concentration, a value of K_{MA} = 1.8 L mol⁻¹ was calculated from the k_{1NE} values at various NaOH concentrations (Table X) by iterative techniques. The fraction MA ionized at a particular NaOH strength, x, was calculated from the expression $x = K_{MA}(NaOH)/[1 + K_{MA}(NaOH)]$. The

Table IX. Hydrolysis of 3-Methyl-3-oxetanemethyl Nitrate (NE) in 95% Ethanol–Water at 55 °C

| time, min | M × 10⁻² | | | | | conversion[b] | | | |
	NE^a	EN	AE	NO_2^-	NO_3^-	AE/ −NE	EN/ −NE	$NO_2^-/$ −NE	$NO_2^-/$ −NE
0	3.31	0	0	0	0				
189.2	2.46	0.35	0.43	0.35	0.23	0.50	0.41	0.41	0.27
308.3	2.08	0.40	0.84	0.57	0.33	0.68	0.33	0.46	0.26
377.5	1.89	0.43	1.06	0.69	0.35	0.74	0.30	0.48	0.25
483.9	1.51	0.43	1.21	0.83	0.46	0.67	0.24	0.46	0.26
557.6	1.34	0.44	1.28	0.93	0.49	0.65	0.22	0.47	0.25
682.8	1.08	0.45	1.54	1.06	0.58	0.69	0.20	0.47	0.26

^{a} (NaOH) = 0.5959 M. ^{b} Ratio of products formed to moles of NE reacted.

Table X. Kinetic Data for the Competitive Formation of 3-Methyl-3-oxetanemethyl Nitrate (NE) and 1,1,1-Trimethylolethane Mononitrate (DA) from 1,1,1-Trimethylolethane Dinitrate (MA)

$NaOH^a$	MA^b	NE/ DA^c	$k_1{}^d$	$k_{1NE}{}^e$	$k_{1DA}{}^f$	$k_{2DA}{}^g$	fraction of MA^h ionized, x	$k_{1NE}/$ x^i
0.2553	9.14	4.0	0.66	0.53	0.13	0.50	0.31	1.71
0.4429	1.38	2.9	1.03	0.77	0.26	0.58	0.44	1.75
1.014	9.14	2.6	1.50	1.08	0.42	0.42	0.65	1.66

^{a} M, 95% ethanol–water, 55 °C. ^{b} M × 10⁻³. ^{c} Product molar ratios over 85% reaction of MA from at least eight points, ±0.1. ^{d} First-order rate constant for disappearance of MA. ^{e} First-order rate constant for the rate of formation of NE. ^{f} First-order rate constant for the rate of formation of DA. ^{g} Second-order rate constant for the rate of formation of DA; $k_{2DA} = k_{1DA}/(NaOH)$. ^{h} $x = K_{MA}(NaOH)/[1 + K_{MA}(NaOH)]$, where $K_{MA} = (MA^-)/(MA)(NaOH) = 1.8$ L mol⁻¹. ^{i} s⁻¹ × 10⁻⁴.

data in Table X show a first-order base dependency for the conversion of MA to DA, as well as a base-equilibrium-controlled rate dependency for cyclization of MA⁻ to form NE.

Although a similar type study for the conversion of 1,1,1-trimethylolethane mononitrate (DA) to 3-methyl-3-oxetanemethanol (AE) and 1,1,1-tris(hydroxymethyl)-ethane (TA) was not accomplished due to the difficulty in reliably analyzing small amounts of TA in the DA hydrolysis runs, the data presented in Tables I and VII lend support to a similar type process. In this regard, it is of interest to compare the ratio of the first-order rate constants for the cyclization of MA to NE and the cyclization of DA to AE, i.e., k_{1NE}/k_{1AE}, at 0.7354 M NaOH in 95% ethanol–water at 55 °C. From the data in Table X, k_{1NE} = 9.7 × 10⁻⁵ s⁻¹ at 0.7354. Since DA was converted to AE in 74 mol % yield, Table VII, k_{1AE} = 0.74 k_1(DA), where k_1(DA) is the first-order rate constant for base reaction with DA, Table IV. From these data, k_{1NE}/k_{1AE} = 4.6. Since these rate constants were calculated at the same base

concentration, and since it is assumed that K_{MA} and K_{DA} are not too different, this ratio is suprisingly close to a value of 4.0, which would be expected statistically for a nucleophilic cyclization displacement where MA⁻ has twice as many nitrate groups as DA⁻. On the basis of these results, one might very well speculate that the spiral dioxetane
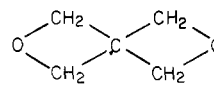
would be formed as a major product from the alkaline hydrolysis of the tetranitrate ester, pentaerythrol tetranitrate (PETN).

Ionicity in Anionic Photoexcited States. The Effect of the Covalent Character of the Carbon–Metal Bond on the Photochemical Ring Opening of Cyclopropyl Anions

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Although 1-cyano- and 1-carbomethoxy-substituted *trans*-2,3-diphenylcyclopropyllithiums ring open to the corresponding allyllithiums upon photoexcitation, the analogous 1-vinyl- and 1-bromo-substituted cyclopropyllithiums do not. Shifts of the oxidative peak potential in the cyclic voltammetric scans of the photoreactive cyclopropyllithiums imply that they exist as ion pairs at low temperature in THF solution. The importance of the ionic charater of the carbon–metal bond in determining the efficiency of photorearrangement is also implied by MNDO reaction path calculations.

Although several carbanionic photorearrangements are known,[1] the identity of those factors which control anionic photoreactivity are still poorly understood. Previous work has shown, for example, that electron ejection can so dominate the chemistry of anionic excited states that intramolecular rearrangement becomes a pathway of negligible importance.[2] An obvious factor which may significantly influence the reactivity patterns of alkali metal salts of hydrocarbons is the degree of covalency of the carbon–metal bond. We report here studies of substitutent effects on the photoreactivity and the ionicity of the carbon–metal bond in a series of cyclopropyl anions, species which have previously been shown to rearrange with the stereochemistry anticipated from orbital topological considerations.

Previous work in our laboratory has established that several cyclopropyllithiums (1a and 1b) undergo photochemical ring opening at low temperatures by a net disrotatory pathway (eq 1),[3] and the reverse photoreaction,

1a, X = CN
b, X = CO₂Me
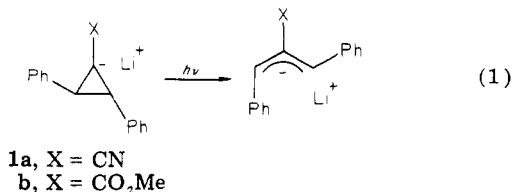
i.e., the photocyclization of cinnamylmagnesium bromide to the corresponding cyclopropylmagnesium bromide, has been described.[4] It was therefore surprising to find in this study that the related organolithiums 1c and 1d were completely photostable (eq 2). (The unsubstituted com-

1c, X = vinyl
d, X = Br
e, X = H
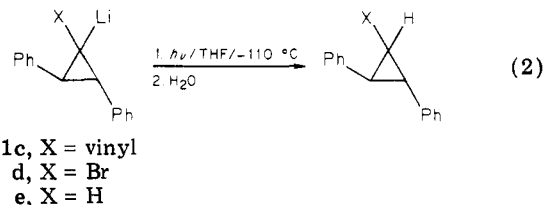
pound 1e proved to be insufficiently stable to test for photoreactivity.) Since those systems which did photorearrange bore strongly electron-withdrawing substituents, the carbon–lithium bond would be expected to be highly polarized, i.e., to possess substantial ionic character.

Results

The cyano- and carbomethoxy-substituted cyclopropyllithiums 1a and 1b were prepared by treatment of the corresponding cyclopropanes with lithium diisopropyl amide (LDA) as described previously.[5] After a D₂O quench at –78 °C in THF in the absence of light, C-deu-

(1) Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.
(2) Fox, M. A.; Singletary, N. J. *J. Org. Chem.* **1982**, *47*, 3412. Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531.
(3) Fox, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 4008.
(4) Yogev, A.; Cohen, S. *J. Am. Chem. Soc.* **1976**, *98*, 2013.
(5) Newcomb, M.; Ford, W. T. *J. Am. Chem. Soc.* **1974**, *96*, 2968.