(24) S. E. Drewes and B. G. Riphagen, *J. Chem. Soc., Perkin Trans. 1*, 1908 (1974).
(25) S. E. Drewes and P. C. Coleman, *J. Chem. Soc., Perkin Trans. 1*, 2148 (1974).
(26) S. E. Drewes and P. C. Coleman, *J. Chem. Soc., Perkin Trans. 1*, 2578 (1974).
(27) S. E. Drewes and B. G. Riphagen, *J. Chem. Soc., Perkin Trans. 1*, 2574 (1976).
(28) W. A. Ehrhart, *J. Org. Chem.*, **33**, 2930 (1968).
(29) C. E. Berr, *J. Polym. Sci.*, **15**, 591 (1955).
(30) K. Frensch and F. Vogtle, *Tetrahedron Lett.*, 2573 (1977).
(31) E. Meraskentis and H. Zahn, *Chem. Ber.*, **103**, 3034 (1970).
(32) H. Zahn and J. E. Repin, *Chem. Ber.*, **103**, 3041 (1970).
(33) K. Sakamoto and M. Oki, *Bull. Chem. Soc. Jpn.*, **49**, 3159 (1976).
(34) For typical IR spectra, see Sadtler number 10550 for isophthalates, 28932 for 5-nitroisophthalates, 10552 for terephthalates, and 1265 for phthalates.
(35) For typical NMR spectra, see Sadtler number 10379M for isophthalates, 873M for 5-nitroisophthalates, 18746M for terephthalates, and 89M for phthalates.
(36) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).
(37) G. M. Bennett and R. L. Wain, *J. Chem. Soc.*, **138**, 1108 (1936).
(38) J. Arient and J. Marhan, *Collect. Czech. Chem. Commun.*, **28**, 1292 (1963).
(39) R. Fordyze, E. L. Lovell and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 1905 (1939).
(40) The hot hexane extractions were accomplished in a liquid–liquid extractor, modified so the portion of the apparatus containing the material to be extracted could be heated. Specific details for the further purification of products isolated in this manner are given under each compound in the Experimental Section.
(41) 1,8-Naphthaloyl dichloride was not very stable in a humid room.

New Synthetic Routes to *gem*-Dinitroalkanes and Derivatives[1a]

Clifford D. Bedford[1b] and Arnold T. Nielsen*

Organic Chemistry Branch, Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555

Received November 28, 1977

gem-Dinitroalkanes (**3**) have been prepared by reaction of nitro olefins with organolithium reagents, followed by treatment with tetranitromethane. 2-Alkoxy-*gem*-dinitroalkanes (**2**) are obtained similarly by employing alkoxides as the basic addend. The preparation of 1-bromo derivatives of **2** and their reaction with bases are described. The ^1H and ^{13}C NMR spectra of **2** and **3** are presented and discussed.

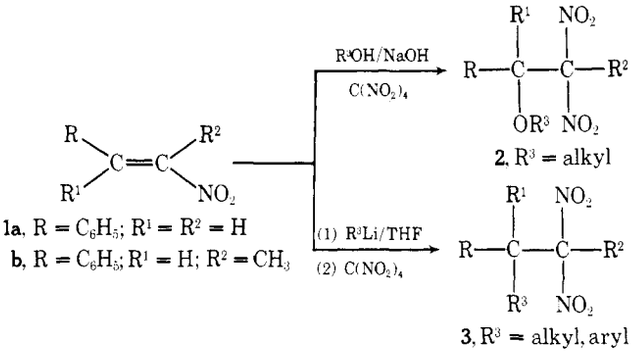
As part of a study of new synthetic routes to polynitro compounds we report a new method of preparing *gem*-dinitro compounds from nitro olefins and precursors. The principal known methods of preparation of these materials are the Kaplan–Shechter reaction (oxidative nitration of mononitroalkanes with silver nitrate),[2] the Ponzio reaction (nitration of an oxime to the pseudonitrole followed by oxidation),[3] the ter Meer synthesis (halogenation of mononitroalkanes and displacement of the halide by nitrite),[4] and alkylation of alkali metal salts of aliphatic polynitro compounds.[5] Each of these synthetic approaches has one or more shortcomings, such as low yield and/or limited scope. Terminal *gem*-dinitro compounds (1,1-dinitroalkanes) undergo reactions such as Michael condensations or Mannich reactions leading to other dinitro and polynitro materials.[6]

Recent synthesis programs in this laboratory have resulted in the facile preparation of several β-alkoxy-α,α-dinitroalkanes (*gem*-dinitro ethers) and *gem*-dinitroalkanes. Treatment of a nitro olefin (**1**) with tetranitromethane (TNM) in the presence of either an alkoxide or alkyllithium yields the corresponding *gem*-dinitro ether (**2**) or *gem*-dinitroalkane (**3**), respectively, Scheme I. The effects of alkyl substitution on the nitro olefin and various alcoholic media have been studied. A special feature of this synthesis is the introduction of two functional units in a one-pot reaction, allowing for the preparation of numerous *gem*-dinitro compounds, not easily accessible by known preparation routes.

The synthetic approach rests on well established experimental observations. Nitro olefins are excellent Michael acceptors and add numerous functional groups in a 1,2 fashion. Also, treatment of a nitronate anion with tetranitromethane, reacting as a nitronium ion source, results in the formation of dinitro and trinitro compounds.[7]

To establish the scope and limitations of this reaction with respect to addends several additions were conducted with ω-nitrostyrene (**1a**) and 2-nitro-1-phenyl-1-propene (**1b**).[8] In the preparation of dinitro ethers (**2**) alkoxides were generated

Scheme I

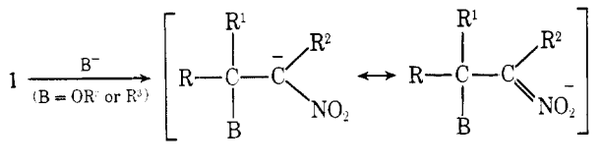


1a, R = C_6H_5; $R^1 = R^2 = H$
b, R = C_6H_5; $R^1 = H$; $R^2 = CH_3$

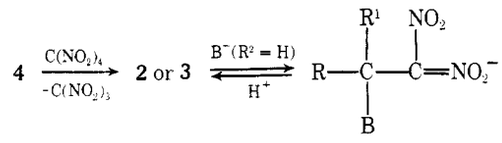
from an excess of the required alcohol by reaction with sodium metal or concentrated aqueous sodium hydroxide (2 mol equiv of base). A solution containing the nitro olefin (1 mol), tetranitromethane (1 mol), and the alcohol as solvent was then added slowly (0–10 °C). The dinitroalkanes (**3**) were prepared similarly in ether–tetrahydrofuran solvent at −40 °C by addition of alkyllithium reagents to the nitro olefin, followed by addition of tetranitromethane. The products were obtained as oils or low melting solids (70–90% yields of crude products). Yields of pure samples obtained by column chromatography were 20–60%. Results are summarized in Table I and indicate the versatility of the method.

The reaction is believed to proceed through anion **4**. Tetranitromethane reacts as the nitrating agent eliminating trinitromethide ion. Those 1,1-dinitroalkanes bearing an α hydrogen (**2a–d, 3a,b**) are present as their salts in the reaction mixture which must be acidified prior to workup to secure products.

Products were characterized and identified by examination of their ^1H and ^{13}C NMR spectra and infrared spectra (Tables II and III; see paragraph at end of paper about supplementary



4



2a–d;
3a, b anion

material). Products derived from ω-nitrostyrene (**2a–d; 3a,b**) in which $R^1 = R^2 = H$ are characterized by a ^1H NMR doublet near 6.3–6.4 δ (J = 9–10 Hz). Dinitromethane and 1,1-dinitroethane are the only *gem*-dinitro compounds for which ^{13}C data have been reported previously.[9] Chemical shift assignments reported in Table III were made with the assistance of ^1H pulse decoupled spectra and by comparison of the chemical shifts within a series. Assignments for the ring carbon atoms were given additional support by comparison of the ortho and meta aryl carbon shieldings in known monosubstituted benzenes. Although absolute assignments are unconfirmed, the magnitude and direction of the ortho and meta carbon atom chemical shifts, with respect to benzene, are consistent with other known carbon shieldings.[10] The *gem*-dinitro carbons are characterized by a very low field signal near δ 110–120. In all compounds the characteristic asymmetric and symmetric NO_2 stretching frequencies were observed in the infrared spectra near 1560 and 1300 cm^{-1}, respectively.

2-Acetoxynitroalkanes are convenient nitro olefin precursors[11] and may be employed in the *gem*-dinitroalkane synthesis. 2-Acetoxy-1-nitropentane with methanolic sodium hydroxide and tetranitromethane gave 1,1-dinitro-2-methoxypentane (**7**), in addition to some of the intermediate 1-nitro-2-methoxypentane (**6**). The nitro olefin **5** is readily generated in situ from the acetoxy compound by the attacking addend base. It was not possible to employ the nitro alcohol, 1-nitro-2-pentanol; much of the reactant was recovered unchanged.

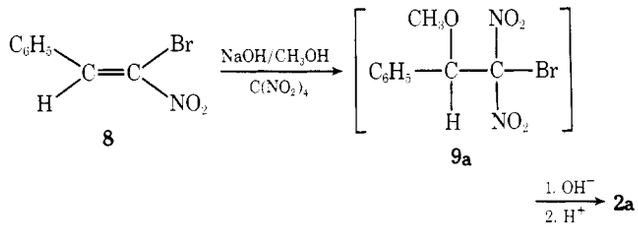
$CH_3CH_2CH_2CH(OAc)CH_2NO_2 \xrightarrow[-OAc^-]{CH_3O^-} CH_3CH_2CH_2CH{=}CHNO_2$ (**5**)

$5 \xrightarrow[C(NO_2)_4]{CH_3O^-} CH_3CH_2CH_2CH(OCH_3)CH_2NO_2$ (**6**) $+ CH_3CH_2CH_2CH(OCH_3)CH(NO_2)_2$ (**7**)

Reaction of 2-nitro-1-phenyl-1-propene with phenylmagnesium bromide, followed by tetranitromethane, failed to yield the desired 1,1-diphenyl-2,2-dinitropropane. The principal reaction product proved to be a bromo derivative, $C_{15}H_{14}BrNO_2$, 2-bromo-2-nitro-1,1-diphenylpropane; its structure is supported by ^1H and ^{13}C NMR, infrared, and mass spectra. Bromide oxidation by TNM had evidently occurred in the reaction leading ultimately to bromination of the intermediate nitronate anion (**4**) to form the isolated product.

An attempt to extend the reaction to Severin's reagent, $(CH_3)_2NCH{=}CHNO_2$,[12] by reaction with phenylmagnesium bromide and tetranitromethane, gave ω-nitrostyrene but no isolable *gem*-dinitro product.

The reaction between ω-bromo-ω-nitrostyrene (**8**), tetranitromethane, and methanolic sodium hydroxide revealed that introduction of nitro and methoxy groups had occurred, but the resulting bromo compound **9a** was unstable under the reaction conditions. Bromine displacement from the dinitro-substituted carbon occurred leading to **2a** anion and the only product isolated after acidification and workup was 1,1-dinitro-2-methoxy-2-phenylethane (**2a**, 60% yield).



8 **9a** **2a**

The scope of the new *gem*-dinitroalkane synthesis is believed to be potentially large. A wide variety of nitro olefins may be employed, with substituents alkyl, aryl, or H. Also, 2-acetoxy-1-nitroalkanes serve as convenient nitro olefin substitutes. Tetrasubstituted nitro olefins, although not examined in the present study, would be expected to react. *tert*-Butyllithium was the only organometallic addend employed which failed to yield an isolable product. Primary and secondary alkyl and aryl lithium reagents of wide variety would be expected to react normally. Alkoxides of low mo-

Table I. Properties and Yields of *gem*-Dinitro Compounds Prepared by Reactions of Scheme I

Nitro olefin 1	Addend R^3	Product, molecular formula[b]	Registry no.	Yield,[a] %	Bp/mp, °C
1a[f]	CH_3	**2a**, $C_9H_{10}N_2O_5$	65899-55-0	60	90 @ 0.7 mm
1a	CH_3CH_2	**2b**, $C_{10}H_{12}N_2O_5$	65899-56-1	44	29–30[c]
1a	$(CH_3)_2CH$	**2c**, $C_{11}H_{14}N_2O_5$	65899-57-2	38	*d*
1a	$CH_2{=}CHCH_2$	**2d**, $C_{11}H_{12}N_2O_5$	65899-58-3	37	*d*
1b[g]	CH_3	**2e**, $C_{10}H_{12}N_2O_5$	65899-59-4	42	53–55
1b	CH_3CH_2	**2f**, $C_{11}H_{14}N_2O_5$	65899-60-7	35	*d*
1b	$CH_3CH_2CH_2$	**2g**, $C_{12}H_{16}N_2O_5$	65899-61-8	20	*d*
1a	CH_3	**3a**, $C_9H_{10}N_2O_4$	65899-62-9	29	*d, e*
1a	$CH_3(CH_2)_3$	**3b**, $C_{12}H_{16}N_2O_4$	65899-63-0	45	*d*
1b	CH_3	**3c**, $C_{10}H_{12}N_2O_4$	65899-64-1	60	76–78

[a] Yields are of analytically pure samples; yields of initially isolated crude product were 70–90%. [b] Satisfactory analytical data (±0.3% for C, H, and N) and molecular weight data (±5%, by vapor osmometry in chloroform) for all compounds were submitted for review. [c] S. S. Novikov, V. M. Belikov, V. F. Dem'yanenko, and L. V. Lapshina, *Izv. Adad. Nauk SSSR, Otd. Khim. Nauk*, 1295 (1960), prepared **2b** by addition of ethanol to ω,ω-dinitrostyrene, bp 115–117 °C (3 mm); mp 31–32 °C. [d] The product was obtained analytically pure as an oil by column chromatography. [e] C. Lugercrantz, S. Forshult, T. Nilsson, and K. Torssell, *Acta Chem. Scand.*, **24**, 550 (1970), prepared **3a** by another method but gave no physical properties or details. [f] Registry no.: 102-96-5. [g] Registry no.: 705-60-2.

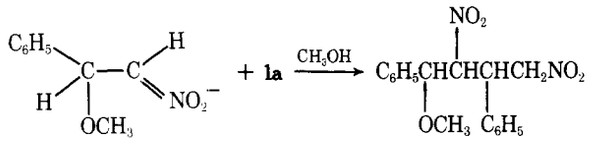
Table IV. Properties and Yields of 1-Bromo-1,1-dinitro Compounds (9)

Reactant dinitroalkane	Product, molecular formula[b]	Registry no.	Yield,[a] %	Mp, °C
2a	**9a**, $C_9H_9N_2O_5Br$	65899-65-2	91	41–43
2b	**9b**, $C_{10}H_{11}N_2O_5Br$	65899-66-3	74	*c*
2d	**9d**, $C_{11}H_{11}N_2O_5Br_3$	65899-67-4	85	*c*

[a] Yields are of analytically pure samples. [b] Satisfactory analytical data (±0.3% for C, H, N, and Br) and molecular weight data (±2% by vapor osmometry in chloroform) for all compounds were submitted for review. [c] The product was obtained analytically pure as an oil by column chromatography.

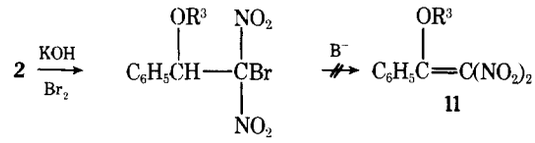
lecular weight are most convenient. Although alkoxides of C-4 and larger carbon content react, the workup and purification of product is made difficult by the low volatility of their alcohols. Phenoxide was not studied.

Interfering side reactions are few and present no problems in workup. 2-Alkoxy-1-nitroalkanes are present in small amounts in most product mixtures. A Michael addition of reactant nitro olefin leading to an alkoxy-substituted dimer is occasionally observed. In methanol solvent ω-nitrostyrene produced known[13] 2,4-dinitro-1,3-diphenyl-1-methoxybutane (**10**) in variable, low yield. With higher alcohols this side reaction is virtually absent.



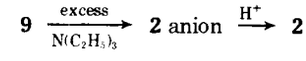
10

Acidic dinitro ethers **2a,b,d** were converted into their corresponding 1-bromo derivative (**9a,b,d**) by reaction with 10% KOH solution, followed by addition of bromine (Table IV). The alkyl compound **2d** afforded a tribromo derivative, **9d.** Treatment of **9** with triethylamine did not result in dehydrohalogenation to a dinitro olefin (**11**). Bromine attack by base occurred (as noted above) leading to **2** nitronate anion, which upon acidification gave reactant dinitro ether.



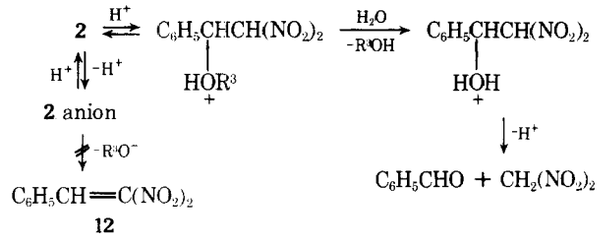
11

9a, $R^3 = CH_3$
b, $R^3 = C_2H_5$
d, $R^3 = CH_2BrCHBrCH_2$



2

Attempts to convert the acidic dinitro ethers **2a–d** to 1,1-dinitro olefins were unsuccessful. Treatment of **2a** with moist trifluoroacetic acid ultimately gave benzaldehyde and dinitromethane. With anhydrous trifluoroacetic acid the dinitro ether remained unchanged. The anions of acidic 1,1-dinitro ethers (**2a–d, 3a,b**) do not lose alkoxide ion to yield 1,1-dinitro olefins (**12**).



12

Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer grating spectrophotometer, Model 137. A Varian EM 360 or XL 100 nuclear magnetic resonance spectrometer was used for the scanning of proton and carbon spectra. Column chromatography was done on Woelm neutral silica gel with fluorescent indicator, "dry column chromatography grade." Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tenn.

Caution. All polynitro compounds are considered toxic and potentially explosive and should be handled with appropriate precautions. Tetranitromethane in hydrocarbon solvents forms an extremely hazardous mixture. In examples of preparation of acidic 1,1-dinitro compounds, the ether extracts must be washed six to ten times with 100-mL portions of water to remove the nitroform side product produced during the reaction. Insufficient washing may result in fume-offs upon concentration of the ether solutions.

The preparation of dinitro ethers employed two principal methods. These are illustrated in the preparations of **2a** and **2e.**

Method A: 1,1-Dinitro-2-methoxy-2-phenylethane (2a). To an ice-cold solution of 4 g (0.10 mol) of NaOH dissolved in 10 mL of water and 20 mL of methanol was added dropwise a solution containing 7.5 g (0.05 mol) of ω-nitrostyrene (**1a**) and 9.8 g (0.05 mol) of tetranitromethane dissolved in 50 mL of methanol. The temperature during addition was maintained at 0–10 °C. The resulting mixture was stirred at ambient temperature for 1 h after the addition was completed. The crude reaction mixture was then poured into 100 mL of water and acidified to pH 2 or less with concentrated HCl. The crude mixture was extracted twice with two 100-mL portions of diethyl ether, the combined ether extracts washed six to ten times with 100-mL portions of water, dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator at room temperature, affording 8.5 g (75% yield) of a reddish colored oil, essntially pure dinitro ether **2a** by NMR assay. The crude product was immediately dissolved in carbon tetrachloride to avoid possible fume-offs of residual nitroform, and chromatographed on 150 g of silica using carbon tetrachloride as eluent. The first fraction was analytically pure dinitro ether (**2a**), 6.8 g (60% yield). The same procedure was also used for the preparation of compounds **2b–d.**

Occasionally the NMR spectrum of the crude material indicated the presence of traces of a second component. Trituration with cyclohexane afforded a white crystalline solid, mp 145–152 °C, 1,3-dinitro-2,4-diphenyl-4-methoxybutane (**10**). Recrystallization from a benzene/cyclohexane mixture (1:9) afforded an analytically pure sample, mp 148–149 °C (lit.[13] mp 150–151 °C: NMR ($CDCl_3$) δ 7.40, 5 H, s, C_6H_5; 4.74, 5 H, m, CH_2, CH; 3.17, 3 H, s, CH_3.

Anal. Calcd for $C_{17}H_{18}N_2O_5$: C, 61.85; H, 5.45; N, 8.48; mol wt 330. Found: C, 61.87; H, 5.54; N, 8.29; mol wt 321 (osmometry $CDCl_3$).

Method B: 2,2-Dinitro-1-methoxy-1-phenylpropane (2e). To 1.15 g (0.05 mol) of sodium metal dissolved in 75 mL of methanol was added dropwise with cooling (0–10 °C) a solution of 4.0 g (0.025 mol) of 2-nitro-1-phenyl-1-propene (**1b**) and 4.9 g (0.025 mol) of tetranitromethane in 25 mL of methanol. The resulting solution was stirred at room temperature for 1 h. The product was isolated and purified as described under method A above, except that acidification prior to workup was omitted. Ultimately there was obtained 2.5 g (42%) of analytically pure, white crystalline **2e,** mp 53–55 °C. The same procedure was employed to prepare **2f,g.**

Reaction of ω-Bromo-ω-nitrostyrene with Tetranitromethane. To a solution of 0.8 g (0.02 mol) of NaOH dissolved in 10 mL of water and 20 mL of methanol was added dropwise with cooling (0–10 °C) a solution of 2.28 g (0.01 mol) of ω-bromo-ω-nitrostyrene[14] and 1.96 g (0.01 mol) tetranitromethane in 30 mL of methanol. The resulting solution was stirred for 1 h at room temperature after addition was complete. The crude mixture was then acidified with concentrated HCl to pH ~1 and purified as described in the preparation of **2a** above, yielding 1.5 g (60%) of **2a.** The NMR and infrared spectra were identical with authentic **2a.**

1,1-Dinitro-2-methoxypentane (7) and 2-Methoxy-1-nitropentane (6). To a solution of 2 g (0.05 mol) of NaOH in 5 mL of water and 10 mL of methanol was added with stirring and cooling (0–10 °C) a solution of 4.4 g (0.025 mol) of 2-acetoxy-1-nitropentane[15] and 4.9 g (0.025 mol) of tetranitromethane in 15 mL of methanol. The re-

sulting mixture was stirred for an additional hour, then acidified to a pH ~2 with concentrated HCl and stirred for an additional 30 min. The crude material, 2.8 g, was isolated as described in the preparation of **2a** above. The NMR spectrum showed starting material to be absent and the presence of three products: 1-nitro-1-pentene (**5**), 2-methoxy-1-nitropentane (**6**), and 1,1-dinitro-2-methoxypentane (**7**) in a 1:4:2 ratio, respectively. Nitro olefin **5** was readily identified by comparison of its NMR spectrum with an authentic sample of known **5**[15] prepared by base elimination of the acetate group from reactant 2-acetoxy-1-nitropentane; ($CDCl_3$) δ 7.25, m, $CH{=}CH_2$; 2.28, q, CH_2; 1.27, sextet, CH_2; 0.97, t, CH_3. Compound **6** was isolated by VPC on a 20% SE 52, $\frac{3}{8}$ in. column at 175 °C with a flow rate of 120 mL/min. Pure **6** was identified by NMR: ($CDCl_3$) δ 4.51, d, CH_2NO_2; 4.05, m, CH; 3.44, s, CH_3; 1.50, m, CH_2CH_2; 0.97, m, CH_3. Product **7** could not be isolated by VPC. The NMR spectrum of the crude mixture revealed the presence of the dinitromethine group of **7** by its characteristic peak at δ 6.4 (d, J = 7.0 Hz). In addition to the dinitromethine peak, a second methoxy peak at δ 3.55 was observed. The integral ratios between the two methoxy peaks (~1:2) corresponded to that of the dinitromethine and nitromethylene peaks (~1:4).

Decomposition of 2a with Trifluoroacetic Acid. A solution of 1,1-dinitro-2-methoxy-2-phenylethane **2a** in an equal volume of moist trifluoroacetic acid was allowed to stand at room temperature. The progress of the reaction was monitored by NMR. After 3 days no reactant **2a** remained and only the following peaks were observed: δ 10.0 (s, 1 H, CHO), 7.6 (m, 5 H, C_6H_5), 6.4 (s, 2 H, CH_2), and 4.0 (s, 3 H, CH_3O), corresponding to benzaldehyde (spectrum identical with authentic sample), dinitromethane (recorded value of 6.2 in CCl_4 solvent[16]), and methyl trifluoroacetate (spectrum identical with authentic sample). When a trifluoroacetic acid/trifluoroacetic anhydride mixture was used as solvent no reaction was observed after three days and the spectrum of **2a** remained unchanged.

The preparation of dinitroalkanes is illustrated in the following description: **2,2-dinitro-3-phenylbutane (3c).** To a solution of 4.03 g (0.025 mol) of 2-nitro-1-phenyl-1-propene (**1b**) dissolved in 30 mL of dry THF (cooled to −40 °C with an acetonitrile–dry ice bath) and under a positive nitrogen atmosphere was added with stirring 22 mL (0.05 mol) of a 5% ether solution of methyllithium. The resulting solution was stirred for 1 h at −40 °C followed by the addition of 4.9 g (0.025 mol) of tetranitromethane. The solution was then allowed to warm to room temperature and stirred an additional hour. The resulting product was isolated and purified as described in the preparation of **2a** above, yielding 3.4 g (60% yield) of an analytically pure white crystalline product (**3a**), mp 76–78 °C. A similar procedure was used for the preparation of **3a** and **3b.**

2-Bromo-2-nitro-1,1-diphenylpropane. A solution containing 0.05 mol of freshly prepared phenylmagnesium bromide in 40 mL of dry THF was cooled to 0 °C and 4.07 g (0.025 mol) of 2-nitro-1-phenylpropene was added. After stirring for 1 h at this temperature 3 mL (0.025 mol) of tetranitromethane was added and the solution was stirred for an additional hour. Workup analogous to the procedures described above for **2a** afforded, after chromatography, 2.5 g, 30% of an analytical sample of 2-bromo-2-nitro-1,1-diphenylpropane as a clear yellow oil: ^1H NMR ($CDCl_3$) δ 7.39 (s, 10, C_6H_5), 5.14 (s, 1, CH), 2.28 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ 138.38, 137.38, 130.01, 129.87, 128.99, 128.74, 128.35, 128.18 (C_6H_5), 101.67 (C_2), 61.80 (C_1), 30.72 (CH_3); IR (film) 1575, 1295, 1100, 814, 707 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.37; Br, 24.96; mol wt 320.195. Found: C, 56.19; H, 4.41; N, 4.43; Br 24.87; mol wt 320 (mass spectrum).

Reaction of 1-Nitro-2-dimethylaminoethylene with Phenylmagnesium Bromide and Tetranitromethane. To a solution of 1.16 g (0.01 mol) of 1-nitro-2-dimethylaminoethylene[12] dissolved in 20 mL of dry THF and cooled to 0 °C by an ice–salt bath was added 22 mL of 1 M solution of phenylmagnesium bromide in THF. The mixture was stirred for 15 min; 1.96 g (0.01 mol) of tetranitromethane was then added and the mixture was stirred for an additional 30 min and acidified with concentrated HCl. Following the usual workup procedure described above for **2a,** and after column chromatography on silica using $CHCl_3$ as eluent, 1.1 g of a mixture of benzaldehyde and ω-nitrostyrene (1:2 ratio) was obtained (materials identical with authentic samples).

1-Bromo-1,1-dinitro-2-methoxy-2-phenylethane (9a). To 1 g (4.4 mmol) of dinitro ether **2a** in 25 mL of a 1 N KOH solution was added 0.70 g (4.4 mmol) of bromine. The resulting mixture was stirred overnight at room temperature and extracted with two 75-mL portions of diethyl ether. The combined ether extracts were washed with two 100-mL portions of water, dried over anhydrous Na_2SO_4, and concentrated on a rotary evaporator leaving 1.23 g (91% yield) of crude **9a.** The crude material was chromatographed on 40 g of silica, using chloroform eluent, affording 1.1 g of an analytically pure oil which crystallized on standing, mp 41–43 °C. Similar procedures were used for the preparation of **9b,d,** except that 2 mol equiv of bromine was employed to obtain **9d.**

Reaction of 9a with Triethylamine. A sample of **9a** was dissolved in equal volumes of triethylamine and $CDCl_3$. The solution was allowed to stand at room temperature and the reaction was followed by NMR. The proton signal appearing at δ 5.46 gradually disappeared with the simultaneous growth of a new peak at 6.62 ppm. No further change was observed after 24 h; the material was then acidified with concentrated HCl. The NMR of the acidified material was identical with that of an authentic sample of **2a.**

Acknowledgment. The authors are indebted to R. A. Henry and D. W. Moore for technical assistance and helpful discussions.

Registry No.—5, 3156-72-7; **6,** 31236-66-5; **7,** 65899-68-5; **8,** 7166-19-0; **10,** 65899-69-6; tetranitromethane, 509-14-8; 2-acetoxy-1-nitropentane, 3428-90-8; 2-bromo-2-nitro-1,1-diphenylpropane, 65899-70-9; 1-nitro-2-dimethylaminoethylene, 1190-92-7; phenyl bromide, 108-86-1.

Supplementary Material Available: Proton NMR and IR spectral data for compounds **2a–g, 3a–c** and **9a,b,d** are presented in Table II. ^{13}C NMR data for compounds **2a–g** and **3a–c** are presented in Table III (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., Mar 17, 1978, Paper No. ORGN 203. (b) National Research Council Postdoctoral Research Associate, 1976–1978.
(2) (a) R. B. Kaplan and H. Shechter, *J. Am. Chem. Soc.*, **83,** 3535 (1961); (b) H. Feuer, *Tetrahedron,* **20** (Suppl. 1), 103 (1964); (c) C. M. Wright and D. R. Levering, *ibid.,* **19** (suppl. 1), 3 (1963).
(3) (a) J. R. Bull, E. R. H. Jones, and G. D. Meakins, *J. Chem. Soc.,* 2601 (1965); (b) S. S. Novikov, L. I. Khmel'nitskii, and O. V. Lebedev, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk,* 1783, 2019 (1960); (c) L. I. Khmel'nitskii, S. S. Novikov and O. V. Lebedev, *ibid.,* 477 (1961); (d) L. F. Fieser and W. von E. Doering, *J. Am. Chem. Soc.,* **68,** 2252 (1946); (e) J. L. Riebsomer, *Chem. Rev.,* **36,** 157 (1945).
(4) (a) H. Feuer, C. E. Colwell, G. Leston, and A. T. Nielsen, *J. Org. Chem.,* **27,** 3598 (1962); (b) E. ter Meer, *Justus Liebigs Ann. Chem.,* **181,** 1 (1876).
(5) (a) S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, *Izv. Adad. Nauk SSSR, Ser. Khim.,* 2725 (1976); (b) G. S. Hammond, W. Emmons, C. Parker, B. Graybill, J. Waters, and M. Hawthorne, *Tetrahedron,* **19,** (Suppl. 1), 177 (1963); (c) W. S. Reich, G. G. Rose and W. Wilson, *J. Chem. Soc.,* 1234 (1947).
(6) (a) E. E. Hamel, *Tetrahedron,* **19** (Suppl. 1), 85 (1963); (b) H. Feuer, G. Leston, R. Miller, and A. T. Nielsen, *J. Org. Chem.,* **28,** 339 (1963); (c) E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. React.,* **10,** 179 (1959).
(7) K. V. Altukhov and V. V. Perekalin, *Russ. Chem. Rev.,* **45,** 1052 (1976).
(8) (a) ω-Nitrostyrene was obtained from Aldrich Chemical Co. and used without further purification; (b) 2-nitro-1-phenyl-1-propene was prepared by the method described by H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.,* **15,** 8 (1950).
(9) E. T. Lippmaa, M. Ya. Myagi, Ya. O. Past, S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1006 (1971).
(10) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 197.
(11) (a) H. Feuer and R. Miller, *J. Org. Chem.,* **26,** 1348 (1961); (b) H. Feuer, R. Miller, and C. B. Lawyer, *ibid.,* **26,** 1357 (1961); (c) H. Feuer, A. Hirschfeld, and E. D. Bergmann, *Tetrahedron,* **24,** 1187 (1968).
(12) T. Severin, D. Scheel, and P. Adhikary, *Chem. Ber.,* **102,** 2966 (1969).
(13) J. Meisenheimer and F. Heim, *Chem. Ber.,* **38,** 466 (1905); *Justus Liebigs Ann. Chem.,* **355,** 260 (1907).
(14) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.,* **73,** 4664 (1951).
(15) E. Schmidt and G. Rutz, *Chem. Ber.,* **61,** 2142 (1928).
(16) W. Hofman, L. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.,* **86,** 554 (1964).