Synthesis of α,α,ω,ω-Tetranitroalkanes[1]

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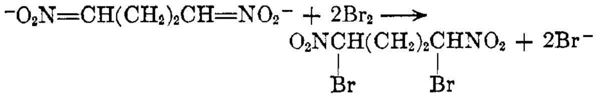
Preparations of 1,1,4,4-tetranitrobutane (I), 1,1,5,5-tetranitropentane (VI), and 1,1,6,6-tetranitrohexane (VII) are reported. 1,7-Dibromo-1,1,7,7-tetranitroheptane has been prepared from crude 1,1,7,7-tetranitroheptane (VIII). Compounds VI and VII were prepared by direct oxidative nitration of the corresponding α,ω-dinitroalkanes in 10 and 84% yield, respectively. Yields of I, VI, and VII of 49, 25, and 70%, respectively, were obtained when 1,4-dinitrobutane, 1,5-dinitropentane, and 1,6-dinitrohexane were first converted to the corresponding symmetrical bismethylol derivatives, the latter subjected to the oxidative nitration, and the resulting tetranitrodiols then demethylolated. 5-Hydroxymethyl-2,2,5-trinitro-1,6-hexanediol (XII) and 6-hydroxymethyl-2,2,6-trinitro-1,7-heptanediol (XV) were formed in low yields in the reactions leading to VI and VII. Compound I was prepared in 28% yield by the ter Meer reaction from 1,4-dibromo-1,4-dinitrobutane.

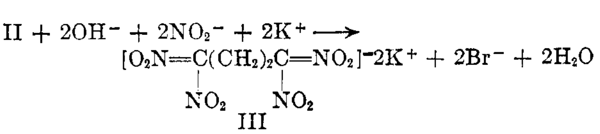
With the exception of 1,1,2,2-tetranitroethane[3] which is stable only as its disalt and the very unstable 1,1,3,3-tetranitropropane, the preparation of which has been reported recently,[4,5] α,α,ω,ω-tetranitroalkanes have not been reported in the literature. The present work describes methods of synthesizing the latter compounds from the now readily available α,ω-dinitroalkanes.[6]

At the outset of this investigation of ter Meer reaction,[7] by which 1,1-dinitroalkanes are prepared from 1-bromo-1-nitroalkanes, was studied as a route for preparation of 1,1,4,4-tetranitrobutane (I). Bromination of disodium 1,4-butanebisnitronate led to a 96% yield of 1,4-dibromo-1,4-dinitrobutane (II) consisting of a mixture of diastereoisomers, which could be separated into solid and liquid forms. Compound II (mixture of isomers) was treated with potassium nitrite and potassium hydroxide to form dipotassium 1,4-dinitrobutane-1,4-bisnitronate (III) as a precipitate. Acidification of the reaction mixture with dilute hydrochloric acid at 0°, gave no I. On the other hand, a 28% yield of I was realized after III was separated and a suspension of it in dry ether was treated with gaseous hydrogen chloride. This operation had to be carried out with great care because samples of the salt occasionally *exploded even while still wet.* The instability of the salt is probably due to impurities, for a sample of III obtained by demethylolating 2,2,5,5-tetranitro-1,6-hexanediol was found to be more stable (explosion point, 135–141°). Nevertheless, *great caution must be exercised at all times when handling III or other similar nitronate salts.*



$$^{-}O_2N{=}CH(CH_2)_2CH{=}NO_2^{-} + 2Br_2 \longrightarrow \underset{Br}{O_2NCH}(CH_2)_2\underset{Br}{CHNO_2} + 2Br^{-}$$

II



$$II + 2OH^{-} + 2NO_2^{-} + 2K^{+} \longrightarrow [O_2N{=}\underset{NO_2}{C}(CH_2)_2\underset{NO_2}{C}{=}NO_2]^{-}2K^{+} + 2Br^{-} + 2H_2O$$

III

$$III + 2HCl \xrightarrow{Et_2O} (O_2N)_2CH(CH_2)_2CH(NO_2)_2 + 2KCl$$

I

When 1,4-dinitro-1,1,4,4-tetrabromobutane was subjected to the ter Meer reaction[7] a 9% yield of I was realized; in addition, a small amount of fumaric acid was isolated. 2,5-Dibromo-2,5-dinitrocyclopentanone also underwent the ter Meer reaction to produce a 5% yield of I.

While this investigation was in progress, the oxidative nitration, an important new reaction for preparing *gem*-dinitro compounds, was made available to us by Dr. H. Shechter[4] several years prior to publication. The method generally gives excellent yields and has the added distinct advantage of avoiding the isolation of explosive nitronate salts, such as III. When applied directly to α,ω-dinitroalkanes, the reaction was successful with 1,5-dinitropentane (IV) and 1,6-dinitrohexane (V) affording 1,1,5,5-tetranitropentane (VI) and 1,1,6,6-tetranitrohexane (VII) in yields of 10 and 84%, respectively. The reaction evidently succeeded well with 1,7-dinitroheptane, but the crude 1,1,7,7-tetranitroheptane (VIII) obtained was an oil which could not be crystallized or distilled without decomposition; the material was converted into its crystalline dibromo derivative, 1,7-dibromo-1,1,-7,7-tetranitroheptane. Unfortunately, the direct oxidative nitration failed with 1,3-dinitropropane and 1,4-dinitrobutane.

$$[O_2N{=}CH(CH_2)_4CH{=}NO_2]^{-}2Na^{+} \xrightarrow[H_2O]{2NaNO_2 + 4AgNO_3} (O_2N)_2CH(CH_2)_4CH(NO_2)_2$$

VII

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[1] Taken, in part, from the Ph.D. theses of Charles E. Colwell (1950) and Gerd Leston (1952), Purdue University.

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[3] W. Will, *Ber.*, **47**, 961 (1914).

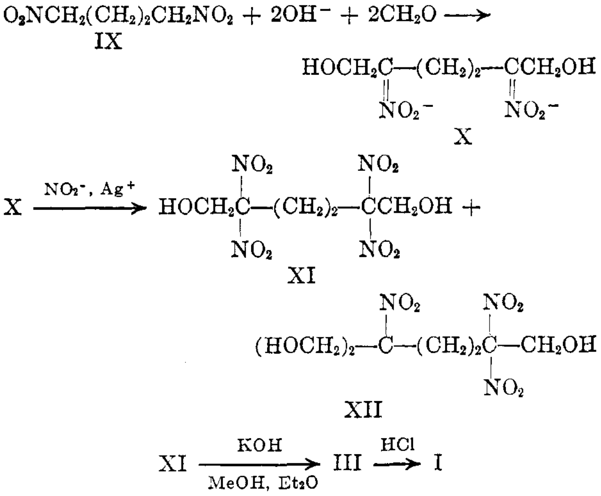
[4] R. B. Kaplan and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3535 (1961).

[5] K. Klager, J. P. Kispersky, and E. Hamel, *J. Org. Chem.*, **26**, 4368 (1961).

[6] H. Feuer and G. Leston, *Org. Syn.*, **34**, 37 (1954).

[7] E. ter Meer, *Ann.*, **181**, 1 (1876).

A modification of the direct oxidative nitration procedure involving formation of intermediate α,ω-dinitroalkanebisnitronate ions provided convenient syntheses of 1,1,4,4-tetranitrobutane (I) and 1,1,5,5-tetranitropentane (VI). The intermediate bismethylol derivatives were used since the oxidative nitration had been reported to proceed well with secondary nitro groups (2,2,4,4-tetranitropentane was readily obtained from 2,4-dinitropentane).[4] The following series of reactions was carried out with 1,4-dinitrobutane (IX), which led to 1,1,4,4-tetranitrobutane in 49% yield based on IX. Exactly two mole equivalents of formaldehyde per mole of IX were used in the preparation of X, and the latter was employed directly in the oxidative nitration step without isolation of its disalt. The 2,2,5,5-tetranitro-1,6-hexanediol (XI) containing a very small amount of XII was separated from silver by extraction with ether; the crude material could be used without recrystallization for the demethylolation step leading to III. Conveniently, the conversion of III to I with hydrogen chloride could be carried out in the same reaction vessel without isolating the explosive salt.



In a series of reactions similar to those above, 1,5-dinitropentane and 1,6-dinitrohexane were converted into the corresponding tetranitro derivatives. The reaction failed with 1,3-dinitropropane. Yields and melting points of the known α,α,ω,ω-tetranitroalkanes are summarized in Table I.

TABLE I

SYNTHESIS OF α,α,ω,ω-TETRANITROALKANES, $(O_2N)_2CH(CH_2)_nCH(NO_2)_2$

n	Cpd.	M.p., °C.	Per cent yield from $O_2NCH_2(CH_2)_nCH_2NO_2$ by oxidative nitration Direct	*Via* diol
0		Dec.[a,b]	..	..
1		13–15°, dec.[a,c]	0	0
2	I	87–88°[d]	0	49
3	VI	69–70°[e]	10	25
4	VII	66–68°[f]	84	70
5	VIII	Liquid[g]	(89)[g]	..

[a] Not prepared by oxidative nitration. [b] Free compound decomposes on attempted isolation; isolated as dipotassium salt.[3] [c] Decomposes above its melting point.[5] [d] Also prepared from 1,4-dibromo-1,4-dinitrobutane by the ter Meer reaction in 28% yield. [e] Was prepared in 85% yield from 2,2,6,6-tetranitro-1,7-heptanediol (XIII) by procedure d for compound I. *Anal.* Calcd. for $C_5H_8O_8N_4$: C, 23.83; H, 3.20; N, 22.22. Found: C, 24.20; H, 3.45; N, 21.85. [f] Was prepared in 95% yield from 2,2,7,7-tetranitro-1,8-octanediol (XIV) as compound VI. *Anal.* Calcd. for $C_6H_{10}O_8N_4$: C, 27.07; H, 3.79; 21.05. Found: C, 27.35; H, 3.98; N, 21.24. [g] The estimated yield of 89% represents the crude liquid product which could not be distilled without dec.; material isolated as its dibromo derivative.

The intermediates XI and its next higher homologs 2,2,6,6-tetranitro-1,7-heptanediol (XIII) and 2,2,7,7-tetranitro-1,8-octanediol (XIV) were each isolated and purified (yields 43, 29, and 75%, respectively); XI and XIV were characterized by diacetate derivatives. The demethylolation of the purified tetranitrodiols into the corresponding tetranitroalkanes proceeded in excellent yields (85–93%). Thus, the differences in over-all yields of I, VI, and VII (Table I) arise primarily in the previous steps. It is possible that the higher yield of XI relative to XIII may be due to an added stability of X (relative to its next higher homolog) which minimizes its demethylolation.[8,9]

5-Hydroxymethyl-2,2,5-trinitro-1,6-hexanediol (XII) and its next higher homolog, 6-hydroxymethyl-2,2,6-trinitro-1,7-heptanediol (XV), were isolated from the aqueous filtrates of the oxidative nitration step in yields of 0.46 and 6.4%, respectively. Structure XII was established by conversion to its triacetate and acetone ketal and that of XV by formation of a tribenzoate derivative. It was found that formation of XII occurred even when pure 2,5-dinitro-1,6-hexanediol was employed. By use of 5% excess formaldehyde in the methylolation step the yield of XII increased to 4%. Use of three mole equivalents of formaldehyde, one mole equivalent each of sodium nitrite and sodium hydroxide and two mole equivalents of silver nitrate per mole of 1,4-dinitrobutane led to 11% yield of XII in addition to 2,5-bis(hydroxymethyl)-2,5-dinitro-1,6-hexanediol (XVI) (21.5% yield).

The formation of trinitrotriols, such as XII, could arise by oxidative nitration of the anion of a dinitrotriol like 2,5-dinitro-2-hydroxymethyl-1,6-hexanediol (XVII). This process appears unlikely as the principal source of XII, however, because methylolation of 1,4-dinitrobutane gave no XVII under a variety of conditions.[8] A more likely route would appear to be methylolation of an intermediate trinitrodiol, *e.g.*, XVIII, under the favorable weakly alkaline conditions prevailing near the end of the oxidative nitration reaction. That the yield of the trinitrotriol XV (6.4%) is greater than

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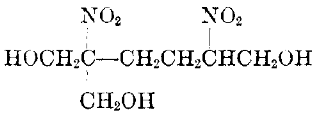
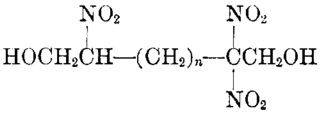
[8] Yields of symmetrical bismethylolation products derived from 1,5-dinitropentanebisnitronate ion are lower than those from 1,4-dinitrobutanebisnitronate ion. A detailed study of these reactions, including equilibria involved, has been reported; H. Feuer, A. T. Nielsen, and C. E. Colwell, *Tetrahedron*, in press.

[9] A. T. Nielsen, *Chem. Ind.* (London), 1358 (1957).



$HOCH_2\underset{CH_2OH}{\overset{NO_2}{C}}—CH_2CH_2\overset{NO_2}{C}HCH_2OH$

XVII



$HOCH_2\overset{NO_2}{C}H—(CH_2)_n—\underset{NO_2}{\overset{NO_2}{C}}CH_2OH$

XVIII ($n = 2$)
XIX ($n = 3$)

XII (0.46%) under the same conditions, while the yield of the tetranitrodiol XIII (29%) is less than XI (43%) suggests that XV is forming at the expense of XIII from a relatively lower concentration of the intermediate (XIX) and the relatively larger amount of formaldehyde present.

Three synthetic approaches to 1,1,4-trinitrobutane (XX) were tried, but no pure XX could be isolated. These were: (1) demethylolation of XII, (2) direct oxidative nitration of 1,4-dinitrobutane using one mole equivalent each of sodium hydroxide and sodium nitrite and two mole equivalents of silver nitrate, and (3) same as approach 2 with addition of one mole equivalent of formaldehyde prior to the oxidative nitration step (attempted synthesis of 2,2,5-trinitro-1-pentanol). In each instance work-up of the product mixtures ultimately led to oils which could not be purified or characterized.

Experimental

1,4-Dibromo-1,4-dinitrobutane (II).—Sodium methoxide (5.4 g., 0.1 g.-atom of sodium in 45 ml. of methanol) was added during 20 min. to 1,4-dinitrobutane[6,10] (14.8 g., 0.1 mole) in 260 ml. of anhydrous ether at 0° and stirring was continued for an additional hour. Bromine (35.2 g., 0.2 mole plus 10% excess) diluted with 40 ml. of chloroform was next added to the salt during 2 hr. at 0°, and the reaction was continued for another hour at 0°. Decanting the solution from the precipitate, extracting the precipitate with three 150-ml. portions of warm ether, combining the extracts with the original solution and evaporating *in vacuo* afforded 29.3 g. (96%) of a yellow liquid. Cooling the liquid in ice gave 12 g. of white solid, m.p. 58° after crystallization from methanol.

Anal. Calcd. for $C_4H_6O_4N_2Br_2$: C, 15.68; H, 1.96, N, 9.15. Found: C, 15.95; H, 2.13; N, 9.10.

The remaining liquid was distilled twice to give 15 g. of the other diastereoisomer; b.p. 149° (3 mm.); $n^{20}D$ 1.5340.

Anal. Found: C, 15.98; H, 1.99; N, 9.09.

1,1,4,4-Tetranitrobutane (I). (a) From 1,4-Dibromo-1,4-dinitrobutane (II).—Potassium hydroxide (2.63 g. of 85% assay, 0.04 mole) dissolved in 20 ml. of methanol was added in 30 min. at −5° to 0° to a mixture of 6.12 (0.02 mole) of 1,4-dibromo-1,4-dinitrobutane and 3.91 g. (0.04 mole) of 87% assay potassium nitrite dissolved in 15 ml. of methanol and 10 ml. of water. Stirring was maintained for 2 hr. and then the precipitated yellow salt was filtered, washed with 150 ml. of absolute ethanol and 75 ml. of dry ether, and resuspended *immediately* in 250 ml. of dry ether. *CAUTION: Do not allow the salt to dry due to danger of explosion.* Hydrogen chloride was then passed, at 0°, for 30 min. over the stirred suspension. Stirring for an additional hour, filtering, washing the inorganic salts with ether and evaporating the combined filtrate and washings *in vacuo* gave 1.4 g. of a soft solid. Recrystallization from chloroform afforded 0.66 g. (28%) of white 1,1,4,4-tetranitrobutane, m.p. 85–86.5°.

Anal. Calcd. for $C_4H_6O_8N_4$: C, 20.17; H, 2.54; N, 25.53. Found: C, 20.60; H, 2.08; N, 23.20.

(b) From 1,4-Dinitro-1,1,4,4-tetrabromobutane.—1,4-Dinitro-1,1,4,4-tetrabromobutane[11] (18.6 g., 0.04 mole) was dissolved in 200 ml. of methanol; potassium nitrite (8.0 g., 0.08 mole of 85% assay) dissolved in 80 ml. of water and 60 ml. of tetrahydrofuran was added (temperature −10°). While maintaining the temperature below −5°, potassium hydroxide (10.4 g., 0.18 mole of 85% assay) dissolved in 50 ml. of methanol was added, with stirring, during 10 min. The mixture was stirred overnight, allowing it to warm to 25°. After chilling to 0°, the yellow precipitate which formed was filtered and washed with methanol and ether. It was immediately suspended in absolute ether, the mixture chilled to 0°, and dry hydrogen chloride passed over the suspension until the yellow color disappeared. The mixture was then filtered, the residue washed thoroughly with ether, and the filtrate concentrated to dryness leaving a white solid (0.18 g.). Trituration of the residue with cold chloroform gave 0.14 g. of 1,1,4,4-tetranitrobutane, m.p. 80–84°.

The filtrate remaining after removal of the dipotassium salt (III) was concentrated to *ca.* 25 ml. by vacuum evaporation at 25°. The precipitate which formed was filtered and triturated with cold dilute methanol to yield 1.2 g. of slightly gummy crystals. Recrystallization from dilute methanol gave 1,1,4,4-tetranitrobutane, 0.35 g., m.p. 85–87° and 0.38 g., m.p. 75–80° (total yield of recrystallized I, 0.87 g., 9.1%). The above samples of I when mixed with an authentic sample showed no depression in melting point. Concentrating the combined mother liquors *in vacuo* and extracting the residue several times with ether gave 1.7 g. of oil, $n^{20}D$ 1.495–1.521, which was not identified.

The aqueous part, remaining after the ether extractions, was acidified with concentrated hydrochloric acid to pH 1 and evaporated to dryness at 25° *in vacuo*. This treatment gave 23.3 g. of a pale yellow residue which was extracted continuously with ether for 70 hr. There resulted 2.7 g. of a gummy residue which was extracted by heating on a steam bath first with 5 ml. of concentrated and then with 15 ml. of *N* hydrochloric acid. This treatment gave 0.35 g. of fumaric acid, m.p. 284–285° (sealed tube). When mixed with an authentic sample (m.p. 286–287°), the melting point was not depressed.

(c) From 2,5-Dibromo-2,5-dinitrocyclopentanone.[12]—A solution of 3.32 g. (0.01 mole) of 2,5-dibromo-2,5-dinitrocyclopentanone in 40 ml. of methanol was cooled to 0°. To the well stirred solution, a solution of potassium hydroxide (1.4 g., 0.21 mole, 86% assay) and potassium nitrite (2.1 g., 85% assay, 0.21 mole) in 5 ml. of water was added all at once. The temperature rose to 12° and the solution became orange; after stirring for 1 hr. at 0° a yellow solid precipitated. The precipitate was filtered, washed with methanol and ether, and resuspended in 50 ml. of ether. *CAUTION: A small portion of the dry salt exploded during the transfer, although a polyethylene spatula was used.*

A slow stream of gaseous hydrogen chloride was passed over the ether suspension at 0° for 0.5 hr.; the potassium chloride was then filtered. The ether filtrate was evaporated under reduced pressure, and the resulting oily solid was recrystallized from chloroform. The product, 1,1,4,4-tetranitrobutane, weighed 0.12 g. (5%), m.p. 84–87°;

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[10] H. Feuer and R. S. Anderson, *J. Am. Chem. Soc.*, **83**, 2960 (1961).

[11] K. Klager, *J. Org. Chem.*, **20**, 646 (1955).

[12] We are indebted to Dr. J. W. Shepherd for performing this experiment. The preparation of 2,5-dibromo-2,5-dinitrocyclopentanone has been described; H. Feuer, J. W. Shepherd, and C. Savides, *J. Am. Chem. Soc.*, **79**, 5768 (1957).

when mixed with an authentic sample the melting point was not depressed.

(d) **From 2,2,5,5-Tetranitro-1,6-hexanediol (XI).**—2,2,5,5-Tetranitro-1,6-hexanediol (14.8 g., 0.05 mole, m.p. 123–126°; see preparation below) was dissolved in 330 ml. of absolute ether and a solution of potassium hydroxide (7.9 g., 0.12 mole, 85% assay) in 50 ml. of methanol was added with stirring at −5° in 5 min. After stirring at 0° for 2 hr., dry hydrogen chloride was passed over the surface of the stirred suspension for 10 min. causing the yellow color to disappear. After continuous stirring at 0° for 3.5 hr., the potassium chloride residue was filtered and extracted with three 100-ml. portions of boiling ether. Evaporating the combined filtrate and extracts in vacuum gave 11.4 g. pale yellow crystals of I, m.p. 85–87°. Washing with cold 1 *N* hydrochloric acid afforded 10.63 g. (90%) of white I, m.p. 87–88°. When the reaction was carried out with crude IX, m.p. 115–123°, the yield of I was 87%.

2,2,5,5-Tetranitro-1,6-hexanediol (XI). (a) **From 1,4-Dinitrobutane (IX).**—1,4-Dinitrobutane (80.6 g., 0.545 mole) was added to a solution of sodium hydroxide (45 g., 1.10 moles, 98% assay) in 275 ml. of water and the mixture stirred for 2 hr. at 0°. Formalin (82 ml., 32.6 g. of formaldehyde, 1.09 moles) was added all at once causing the temperature to rise to 16°. After stirring the solution at 3° for 2 hr., 78 g. (1.12 moles, 98.6% assay) of sodium nitrite was added; then a solution of 380 g. (2.24 moles) of silver nitrate in 440 ml. of water was added all at once and the mixture stirred vigorously at 0° for 1 hr. Filtering the precipitate, drying *in vacuo* and continuous extraction in a Soxhlet apparatus with 640 ml. of dry ether for 20 hr. gave, after evaporating the solvent, 91 g. (56%) of crude 2,2,5,5-dinitro-1,6-hexanediol (IX), m.p. 115–123°. Recrystallizing a 15-g. aliquot of crude IX with 150 ml. of hot water containing a drop of concentrated hydrochloric acid gave 11.5 g. (equivalent to 43% yield) of pure IX, m.p. 126–127°.

Anal. Calcd. for $C_6H_{10}O_{10}N_4$: C, 24.17; H, 3.38; N, 18.79. Found: C, 23.97; H, 3.29; N, 18.85.

The aqueous part remaining after filtration of the silver and precipitate was extracted with three 150-ml. portions of ether. The extracts were dried and evaporated to yield 0.71 g. (0.45%) of **5-hydroxymethyl-2,2,5-trinitro-1,6-hexanediol (XII)**, m.p. 140–142° after recrystallization from water. When mixed with an authentic sample (see preparation below) the melting point was not depressed. When a 5% excess of formaldehyde was employed in the above procedure, the yield of XII increased to 4%.

(b) **From 1,1,4,4-Tetranitrobutane (I).**—A solution of 0.5 g. (2.1 mmoles) of I in 5 ml. of methanol was mixed with 0.34 g. of formalin (4.2 mmoles of formaldehyde) and the solution was stirred for 24 hr. at 25° after 4 drops of 4 *N* sodium hydroxide had been added. Extracting with ether, drying the extract with calcium sulfate, and evaporating the solvent *in vacuo* gave 0.35 g. (55% yield) of XI, m.p. 127–128°.

Anal. Calcd. for $C_6H_{10}O_{10}N_4$: C, 24.17; H, 3.38; N, 18.79. Found: C, 24.15; H, 3.32; N, 18.47.

1,6-Diacetoxy-2,2,5,5-tetranitrohexane, m.p. 89–90°, was obtained after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{10}H_{14}O_{12}N_4$: C, 31.41; H, 3.67; N, 14.66. Found: C, 31.02; H, 3.73; N, 14.30.

2-Hydroxymethyl-2,5,5-trinitro-1,6-hexanediol (XII).—1,4-Dinitrobutane (7.4 g., 0.05 mole) was added to a solution of 2 g. (0.05 mole) of sodium hydroxide dissolved in 40 ml. of water and the mixture stirred at 0° for 1.5 hr. until a clear solution resulted. Formalin (12.1 g. of 37%, 0.15 mole of formaldehyde) was added and the solution stirred for 1.5 hr. at 3°. Sodium nitrite (3.45 g., 0.05 mole) was then added and after 5 min., a solution of 17 g. (0.10 mole) of silver nitrate in 25 ml. of water was added all at once. After stirring for 1 hr., the mixture was filtered, washed with water, and dried to yield 21.0 g. of a silver-containing solid. This material was extracted continuously with ether for 33 hr. to yield, after evaporation of the ether, 4.38 g. of a white solid, m.p. 115–142°. Recrystallization from water gave 3.0 g. (21% crude XII), m.p. 132–144°; two more recrystallizations gave 1.4 g. (10%) of XII, m.p. 138–142°. The aqueous filtrate remaining after filtering the above silver-containing precipitate was extracted several times with ether. From the dried ether extracts there was isolated 2.0 g. of an oil mixed with some solid. Trituration of this material with ether gave an additional 0.15 g. (1%) of XII, m.p. 143–146°. The oily material remaining was not investigated.

Anal. Calcd. for $C_7H_{13}O_9N_3$: C, 29.68; H, 4.59; N, 14.84. Found: C, 29.15; H, 4.55; N, 14.41.

The residue (15.5 g.) remaining after continuous ether extraction of the original silver-containing solid was heated with water on the steam bath and *N* hydrochloric acid was added until no further precipitation of silver chloride occurred. The hot solution was filtered and the filtrate cooled to yield 2.9 g. (21.5%) of **2,5-bis(hydroxymethyl)-2,5-dinitro-1,6-hexanediol** (XVI) as white needles, m.p. 181–183° (m.p. reported,[8] 181–182°). The compound was converted into its tetraacetate derivative by reaction with acetic anhydride, m.p. 122–123° (m.p. reported,[8] 122–123°. When mixed with an authentic sample, m.p. 120°, the melting point was not depressed.

An attempt was made to prepare 1,1,4-trinitrobutane by demethylolating XII. A 2.83-g. (0.01 mole) sample of XII was suspended in 100 ml. of absolute ether. A solution of 4.0 g. (0.06 mole) of potassium hydroxide (85% assay) in 25 ml. of methanol was added at 3° and the resulting yellow suspension stirred for 5 hr. Dry hydrogen chloride gas was then passed into the cold (5°) solution for 15 min.; the solution was then filtered and the precipitate washed with ether. Evaporation of the ether gave a brown oily gum, which was extracted with dilute ethanol. Evaporation of the solvent gave a yellow oil (1.6 g.) which slowly decomposed at room temperature giving off oxides of nitrogen; attempts to purify it by distillation or crystallization were unsuccessful and the material was not investigated further.

5-Acetoxymethyl-1,6-diacetoxy-2,2,5-trinitrohexane, m.p. 79.5–80°, was obtained after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{13}H_{19}O_{12}N_3$: C, 38.14; H, 4.64; N, 10.26. Found: C, 37.77; H, 4.41; N, 10.01.

The acetone ketal of XII was prepared by warming an acetone solution of XII with boron trifluoride etherate on a steam bath for 5 min. A saturated solution of sodium bicarbonate was added and the precipitate which formed was filtered, washed with water and then with cold *N* hydrochloric acid. The product was purified by recrystallization from dilute ethanol to yield **5-(4-hydroxy-3,3-dinitrobutyl)-5-nitro-2,2-dimethyl-1,3-dioxan**, m.p. 143–144°.

Anal. Calcd. for $C_{10}H_{17}O_9N_3$: C, 37.15; H, 5.30; N, 13.00. Found: C, 37.30; H, 5.52; N, 13.17.

2,2,6,6-Tetranitro-1,7-heptanediol (XIII).—The same procedure was followed as for the preparation of XI by method a except that 0.5 mole of 1,5-dinitropentane[6,10] was employed. A total of 45 g. (28.8% yield) of XI, m.p. 94–95°, was obtained.

Anal. Calcd. for $C_7H_{12}O_{10}N_4$: C, 26.92; H, 3.84; N, 17.95. Found: C, 26.79; H, 3.96; N, 17.63.

Working up the aqueous filtrate of the oxidative nitration as in the isolation of XII gave an oil which crystallized slowly on standing for several days. Drying the mixture on a clay plate and recrystallizing four times with ethylene chloride gave 9.5 g. (6.4% yield) of **6-hydroxymethyl-2,2,6-trinitro-1,7-heptanediol (XV)**, m.p. 116.5–117°.

Anal. Calcd. for $C_8H_{15}O_9N_3$: C, 32.33; H, 5.09; N, 14.14. Found: C, 32.37; H, 4.99; N, 14.20.

6-Benzoxymethyl-1,7-dibenzoxy-2,2,6-trinitroheptane, m.p. 149–149.5°, was obtained after two recrystallizations from carbon tetrachloride containing Norit.

Anal. Calcd. for $C_{29}H_{27}O_{12}N_3$: C, 57.14; H, 4.43; N, 6.89. Found: C, 57.07; H, 4.24; N, 6.92.

2,2,7,7-Tetranitro-1,8-octanediol (XIV).—The procedure was the same as for the preparation of compound IX (method a) except that 8.8 g. (0.05 mole) of 1,6-dinitrohexane[8,10] was employed. This procedure afforded 14.7 g. (90% crude yield) of the diol, m.p. 140–157° dec. After two recrystallizations from dilute ethanol there was obtained 12.2 g. (75% yield) of the pure diol as feathery needles, m.p. 157–159° dec. The decomposition point depends on the rate of heating and the extent of subdivision of the sample; values ranging from 155–158° for a powdered sample to 164–166° for large crystals placed in the bath at 150° were obtained (capillary tube).

Anal. Calcd. for $C_8H_{14}O_{10}N_4$: C, 29.44; H, 4.29; N, 17.17. Found: C, 29.45; H, 4.40; N, 16.99.

1,8-Diacetoxy-2,2,7,7-tetranitroöctane, m.p. 93–94°, was obtained after two recrystallizations from dilute ethanol.

Anal. Calcd. for $C_{12}H_{18}O_{12}N_4$: C, 35.12; H, 4.39; N, 13.65. Found: C, 35.39; H, 4.23; N, 13.50.

1,1,6,6-Tetranitrohexane (VII). (a) From 1,6-Dinitrohexane (V).[13]—To a solution of 4.14 g. (0.1 mole; 97% assay) of sodium hydroxide in 50 ml. of water was added with stirring at 0–5° 8.8 g. (0.05 mole) of 1,7-dinitrohexane. After solution was attained, 6.9 g. (0.1 mole) of sodium nitrite was added all at once and after 15 min., a solution of 34 g. (0.1 mole) silver nitrate in 50 ml. of water was introduced. The reaction mixture immediately thickened and became dark in color. After continued stirring for 2 more hr. at 0°, the precipitate was filtered, washed with 100 ml. of water, and dried *in vacuo* for 48 hr. Continuous extraction of the dry solid with dry ether for 24 hr. and removal of the solvent *in vacuo* gave 11 g. (84% yield) of compound VII, m.p. 63–65°. Recrystallization with chloroform gave m.p. 66–67°; when mixed with compound VII prepared from XIV the melting point was undepressed.

(b) **From 1,6-Dibromo-1,1,6,6-tetranitrohexane.**[13]—To a solution of potassium iodide (6.3 g., 0.38 mole) in 150 ml. of 50% methanol was added 4.24 g. (0.01 mole) of 1,6-dibromo-1,1,6,6-tetranitrohexane (see preparation below). The mixture was stirred for 8 hr. at 26° and was then cooled and acidified with dilute hydrochloric acid and extracted with ether. The ether layer was washed with sodium thiosulfate solution, then reduced in volume to precipitate sulfur. The solution was filtered and the filtrate concentrated to dryness under reduced pressure, yielding 2.26 g. (85%) of 1,1,6,6-tetranitrohexane (VII), m.p. 64–65°. When mixed with an authentic sample, the melting point was not depressed.

1,6-Dibromo-1,1,6,6-tetranitrohexane.[13]—To a solution of 0.76 g. (0.0185 mole, 97% assay) sodium hydroxide in 150 ml. of water at 0–5° was added 2.0 g. (0.0075 mole) of 1,1,6,6-tetranitrohexane. The mixture was stirred until it became homogeneous; 2.5 g. (0.0138 mole) of bromine was then added dropwise, causing a yellow precipitate to form. The mixture was stirred for 2 hr. and then filtered. The product was crystallized first from hexane and then from aqueous ethanol to yield colorless crystals, m.p. 120–121°.

Anal. Calcd. for $C_6H_8N_4O_8Br_2$: C, 16.98; H, 1.88; N, 13.20. Found: C, 16.83; H, 2.03; N, 13.23.

1,7-Dibromo-1,1,7,7-tetranitroheptane.[13]—1,7-Dinitroheptane (9.5 g., 0.05 mole) was oxidatively nitrated by the same procedure employed with 1,6-dinitrohexane (VII) (procedure b, above) to yield 12.5 g. of a yellow oil, n^{20}_D 1.4800, believed to contain principally 1,1,7,7-tetranitroheptane (VIII); 89% yield calculated as (VIII). Attempts to crystallize the material failed. An attempted molecular distillation of the product resulted in its decomposition.

The crude 1,1,7,7-tetranitroheptane was converted into its dibromo derivative by the same procedure used for preparing 1,6-dibromo-1,1,6,6-tetranitrohexane (see above). The crude product was an oil which was first crystallized from hexane (m.p. 32–34°) and then from aqueous ethanol; m.p. 42.5–43°.

Anal. Calcd. for $C_7H_{10}N_4O_8Br_2$: C, 19.17; H, 2.28; N, 12.78. Found: C, 19.09; H, 2.40; N, 12.69.

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[13] We are indebted to Dr. R. Miller for carrying out this experiment.

Reactions of Acetylenes. II. Some Reactions of β-Ethynylcarboxylic Acids

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The alkylation of malonic esters with *tert*-acetylenic chlorides leads to substituted malonic esters, $HC\equiv C—C(R^1R^2)—C(R^3)(COOC_2H_5)_2$. These compounds have been used to prepare a wide variety of other products, notably saturated and unsaturated carboxylic acids, levulinic acids, pyrrolidones, pyrrolidines, and amines of novel structures. The facile hydration of the acetylenic group under alkaline conditions is pointed out.

The preparation[1] of 3,3-dimethyl-4-pentynoic acid (VI) from diethyl malonate in these laboratories some years ago suggested a reinvestigation and extension of the reaction involved. It is well known that sodiomalonic esters cannot be alkylated in the usual manner with *tert*-aliphatic halides since the latter are much too sensitive to elimination of hydrogen halide in strongly alkaline media. The *tert*-acetylenic halides $[R^1R^2C(Cl)\text{-}C\equiv CH]$, however, react in alkaline solutions by a unique mechanism[2,3] involving an electrophilic zwitterion-carbene, $(R^1R^2\overset{\oplus}{C}—C\equiv\overset{\ominus}{C} \longleftrightarrow R^1R^2C=C=C:)$, which has been shown to be capable of alkylating sterically hindered nucleophiles.[2]

In agreement with the earlier report[1] it has now been found that *tert*-acetylenic halides successfully alkylate sodiomalonic esters and their monoalkyl derivatives, thus providing a simple route to the

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