possesses a characteristic absorption band at 4.72 μ (53% transmission), 5.13 μ (6% transmission) and 5.62 μ (27% transmission), respectively, where the other components absorb very little. However, the small peak at 4.93 μ (93% transmission) in the 2-pentyne spectrum which is characteristic of the triple bond[39] lies at a wave length at which both 1-pentyne and 1,2-pentadiene have comparable absorption, and the compounds are otherwise so similar that no wave length suitable for determination of the 2-pentyne was found. However, this compound has the highest boiling point and is readily determined by analytical distillation. This was done in several cases, but for most experiments the 2-pentyne was determined by difference.

It was found by attempting to analyze known mixtures that solutions of 1-pentyne or 1,2-pentadiene in 2-pentyne failed to follow Beer's law, the departure being greater in the case of the allene. Therefore, a series of known solutions were prepared and measured at the characteristic wave length, graphs were prepared showing the variation of absorption with composition, and the composition of the unknown mixtures was determined by reference to these graphs. A comparison of the composition of two known mixtures of the three components made up by weight with the results of spectral analysis gave a percentage error of about 4% when about 10% of each minor component was present. The results of analyses of equilibrium mixtures by the infrared method and by analytical distillation with a Podbielniak Hyd-Robot Column[40] were in agreement at least within 1% in absolute values, but the percentage error was somewhat larger because only 1 to 4% of 1-pentyne and 1,2-pentadiene were present. The percentage error of the distillation method when applied to a known mixture containing about 10% of each minor component was 5 to 10% for these components but only 1 to 1.5% for 2-pentyne.

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[39] Wotiz and Miller, THIS JOURNAL, 71, 3441 (1949).

[40] We wish to thank Mr. C. K. Hewes, Chief Chemist, for allowing us to use the distillation equipment of the Richfield Oil Corporation in this work.

LOS ANGELES, CALIFORNIA RECEIVED AUGUST 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Condensation of 1,1-Dinitroethane with Electronegatively Substituted Unsaturated Compounds. The Synthesis of 3,3-Dinitro-1-butene[1,2]

BY HAROLD SHECHTER AND LAWRENCE ZELDIN

The base-catalyzed condensation of 1,1-dinitroethane with electronegatively substituted unsaturated compounds results in the formation of substituted *gem*-dinitro compounds. The preparations of methyl 4,4-dinitropentanoate, 5,5-dinitro-2-hexanone, 2,2,4-trinitropentane, 4,4-dinitro-1-pentanal and methyl 3,3-dinitro-*n*-butyl sulfone by this procedure are described. Addition occurs rapidly at or below room temperature; however, the reaction is reversed at elevated temperatures. The stability of the secondary *gem*-dinitroalkane structure has been investigated. 3,3-Dinitro-1-butene has been synthesized in an over-all yield of 41% by (1) hydrolysis of methyl 4,4-dinitropentanoate to yield 4,4-dinitropentanoic acid, (2) preparation of silver 4,4-dinitropentanoate, (3) reaction of silver 4,4-dinitropentanoate with bromine to yield 3,3-dinitro-1-bromobutane and (4) dehydrohalogenation of 3,3-dinitro-1-bromobutane to produce 3,3-dinitro-1-butene.

An investigation of the base-catalyzed condensation reaction of acidic dinitroalkanes and electronegatively substituted unsaturated compounds has been inaugurated as a general method for the synthesis of substituted *gem*-dinitro compounds. The addition of mononitroalkanes to α,β-unsaturated esters,[3] α,β-unsaturated ketones,[4] acrylonitrile,[5] nitroölefins[6] and vinyl sulfones[7] has been effected in the presence of metal alkoxide and amine catalysts. During this investigation, it was reported that reaction of potassium dinitromethane with methyl acrylate and acrylonitrile yielded dimethyl 4,4-dinitroheptanedioate and 4,4-dinitroheptanedinitrile,[8] respectively.

The present paper describes the base-catalyzed addition of 1,1-dinitroethane to various representative α,β-unsaturated compounds in either aqueous, diethyl ether or dioxane media. In the majority of the experiments, benzyltrimethylammonium hydroxide (Triton B) in diethyl ether or dioxane was used as catalyst because it offered high efficiency in low concentration; however, the potassium salt of 1,1-dinitroethane was used advantageously in aqueous solution. The addition reactions occur readily at or below room temperature and appear to be more rapid than the analogous condensations of mononitroalkanes. In two examples (see Experimental), addition was complete within 7 hours at room temperature.

The α,β-unsaturated compounds employed were methyl acrylate, methyl vinyl ketone, 2-nitropropene, acrolein and methyl vinyl sulfone; the products obtained were methyl 4,4-dinitropentanoate (72%), 5,5-dinitro-2-hexanone (95%), 2,2,4-trinitropentane (93%), 4,4-dinitro-1-pentanal (74%) and methyl 3,3-dinitro-*n*-butyl sulfone (23%), respectively. The first four products are pale-green, viscous oils possessing a faint musk-like odor; methyl 3,3-dinitro-*n*-butyl sulfone is an odorless, white solid. All of these compounds are thermally stable, as evidenced by their distillation at temperatures of 97–146°.[9] In the presence of bases, however, distillation results in reversal of reaction and decomposition of the reactants. The products are stable in strong acids, even at high temperatures (130–140°), and in strong bases at room temperature. The secondary *gem*-dinitro grouping is not affected rapidly by alkaline potassium permanganate; oxidation of 4,4-dinitro-1-pentanal to 4,4-dinitropentanoic acid occurred readily with this reagent.

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[1] This research was supported by the Office of Naval Research.

[2] Taken in part from a thesis to be submitted by Lawrence Zeldin to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

[3] E. P. Kohler and H. Engelbrecht, THIS JOURNAL, **41**, 764 (1919).

[4] E. P. Kohler, *ibid.*, **38**, 889 (1916); M. C. Kloetzel, *ibid.*, **69**, 2271 (1947).

[5] H. A. Bruson and T. W. Riener, *ibid.*, **65**, 23 (1943); G. D. Buckley, T. J. Elliott, F. G. Hunt and A. Lowe, *J. Chem. Soc.*, 1505 (1947).

[6] A. Lambert and H. A. Piggott, *ibid.*, 1489 (1947).

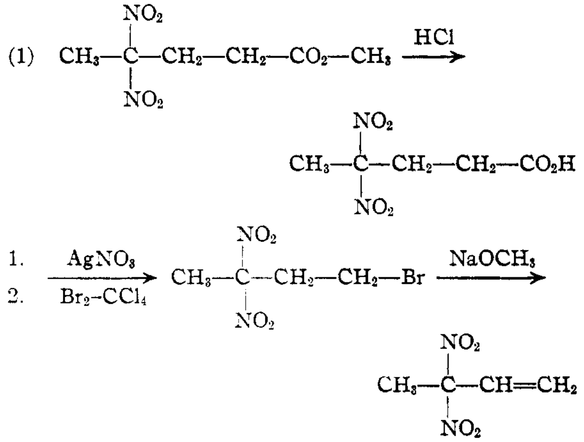
[7] G. D. Buckley, J. D. Charlish and J. D. Rose, *ibid.*, 1514 (1947).

[8] L. Herzog, M. H. Gold and R. D. Geckler, Abstracts of Papers, 118th Meeting of the American Chemical Society, Chicago, Illinois, p. 25N.

[9] In addition to the value reported in the experimental section, methyl 4,4-dinitropentanoate was distilled without decomposition at 145–146° (8 mm.).

The efficiency of the base-catalyzed addition reactions of primary *gem*-dinitroalkanes with α,β-unsaturated compounds to effect carbon-alkylation in preference to oxygen-alkylation is indeed striking since reaction of alkylating or acylating agents with acidic *gem*-dinitroalkanes usually results in the formation of derivatives of the alkyl nitronitronic acid.[10] It appears, therefore, that electronegatively substituted unsaturated compounds are reagents of such weak cationoid character that the difference in binding energy of the anion produced by carbon-alkylation over that from oxygen-alkylation is sufficient to outweigh the collision and entropy factors which favor oxygen-alkylation.[11]

3,3-Dinitro-1-butene, the first olefin of its type to be prepared, was synthesized (Equation (1)) by: (1) hydrolysis of methyl 4,4-dinitropentanoate with concentrated hydrochloric acid to yield 4,4-dinitropentanoic acid (98% yield), (2) preparation of silver 4,4-dinitropentanoate (100% yield), (3) reaction of silver 4,4-dinitropentanoate with bromine in anhydrous carbon tetrachloride[12] to yield 3,3-dinitro-1-bromobutane (81% yield) and (4) dehydrobromination of 3,3-dinitro-1-bromobutane with alcoholic sodium methoxide to yield 3,3-dinitro-1-butene (60% yield).



$$(1)\quad CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-CO_2-CH_3 \xrightarrow{HCl} CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-CO_2H$$

$$\xrightarrow[2.\ Br_2-CCl_4]{1.\ AgNO_3} CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-Br \xrightarrow{NaOCH_3} CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH{=}CH_2$$

This unusual vinyl compound is a colorless, practically odorless liquid. It can be stored for long periods of time without decomposition and is stable toward light and heat. The compound decolorizes a bromine–tetrachloroethane solution very slowly.

Experimental

Reagents.—1,1-Dinitroethane[13] was prepared from 1-chloro-1-nitroethane, potassium nitrite and potassium hydroxide, b.p. 55–57° (4 mm.), n^{20}_D 1.4345, yield 41%. Commercial methyl acrylate, methyl vinyl ketone (85% aqueous azeotrope), acrolein (97.4% aqueous azeotrope), and methyl vinyl sulfone were used without further purification or removal of inhibitors. 2-Nitropropene was prepared from 2-nitro-1-propanol[14] by the procedure of Buckley and Scaife,[15] b.p. 52–54° (80 mm.); yield 48%.

Methyl 4,4-Dinitropentanoate.—A solution of potassium hydroxide (12.3 g., 0.22 mole) in water (130 ml.) was added slowly to a stirred mixture of 1,1-dinitroethane (25.1 g., 0.21 mole) and water (50 ml.) at 15°. The yellow potassium salt of 1,1-dinitroethane formed partially precipitated from the solution. Methyl acrylate (51.6 g., 0.60 mole) was added to the aqueous suspension of potassium 1,1-dinitroethane over a 2-hour period. After the mixture had been stirred for 4 hours and the oily layer had been separated, glacial acetic acid (10 g., 0.167 mole) was added to partially neutralize the aqueous layer. Additional methyl acrylate (8.5 g., 0.10 mole) was added, and the solution was stirred at room temperature for 11 hours. The solution was extracted with diethyl ether; the ether extracts were combined with the oily layer and then dried with a saturated sodium chloride solution. Distillation of the product, after removal of the solvent, yielded methyl 4,4-dinitropentanoate (30.8 g., 72% conversion, b.p. 94–97° (0.6–0.7 mm.), n^{20}_D 1.4556, d^{20}_{20} 1.3078; *MR*D (calcd.), 42.80; *MR*D (found), 42.80.

Anal. Calcd. for $C_6H_{10}N_2O_6$: C, 34.95; H, 4.89; N, 13.59. Found: C, 35.25; H, 4.71; N, 13.71.

4,4-Dinitropentanoic Acid.—Methyl 4,4-dinitropentanoate (42.8 g., 0.207 mole) was hydrolyzed in 3 hours in a refluxing solution of 37% hydrochloric acid (200 ml.) and water (180 ml.). After charcoal was added, the hot solution was filtered. On cooling, transparent needles of 4,4-dinitropentanoic acid separated. The solid was filtered, washed with water, and dried on a porous plate. The aqueous solution was extracted with ether and the extracts were evaporated to dryness to yield additional product. The total yield of 4,4-dinitropentanoic acid was 39.1 g. (98%); m.p. 97.4–99.2° after recrystallization from hot water.

Anal. Calcd. for $C_5H_8N_2O_6$: C, 31.25; H, 4.20; N, 14.58; neut. equiv., 192. Found: C, 31.57; H, 3.91; N, 14.56; neut. equiv., 194.

3,3-Dinitro-1-bromobutane.—The potassium salt of 4,4-dinitropentanoic acid was prepared by adding 4,4-dinitropentanoic acid (35.2 g., 0.183 mole) to a solution of potassium hydroxide (11.7 g., 0.186 mole) in water (130 ml.). The solution was heated to boiling, as was a solution of silver nitrate (32.7 g., 0.193 mole) in water (70 ml.). The two solutions were poured simultaneously, while hot, into boiling water (60 ml.) and the resulting slurry was vigorously stirred. After being cooled in the dark, the gray silver 4,4-dinitropentanoate was filtered, and dried to constant weight in a vacuum oven at 60–65° (2 days). The yield of silver salt was 55.0 g. (100%).

The silver salt was dispersed in stirred carbon tetrachloride (300 ml. anhydrous). Dry bromine (30.0 g., 0.188 mole) in carbon tetrachloride (40 ml.) was added dropwise at room temperature. When the addition was completed, the mixture was warmed to 60°, whereupon rapid evolution of carbon dioxide commenced. After the initial carbon dioxide evolution ceased, the solution was refluxed for 1 hour, then cooled and filtered. The silver bromide (33.5 g., 97.4%) obtained was dried in a stream of dry air. The filtrate was decolorized with 3% aqueous sodium thiosulfate (70 ml.). The solvent was removed under vacuum and the residual oil distilled to yield 3,3-dinitro-1-bromobutane (33.5 g., 80.5% conversion), b.p. 92–93° (2.4 mm.), n^{20}_D 1.4962, d^{20}_{20} 1.6803; *MR*D (calcd.) 39.68; *MR*D (found), 39.48.

Anal. Calcd. for $C_4H_7N_2O_4Br$: C, 21.16; H, 3.11; N, 12.34; Br, 35.29. Found: C, 21.18; H, 3.04; N, 12.27; Br, 35.32.

3,3-Dinitro-1-butene.—A solution of sodium methoxide (3.3 g., 0.061 mole) in methanol (30 g.) was added dropwise (1.5 hours), with stirring, to 3,3-dinitro-1-bromobutane (11.4 g., 0.05 mole) at room temperature. Stirring was continued for another 1.5 hours. The reaction mixture was then extracted with a mixture of water (50 ml.) and ether (200 ml.). The aqueous layer was separated, extracted once with ether, acidified with nitric acid, and reacted with excess silver nitrate. The silver bromide formed was filtered and dried at 120° for 24 hours; the yield was 9.7 g. (quantitative).

After the combined ether extracts had been evaporated under vacuum, the residue was distilled to yield 3,3-dinitro-1-butene (4.4 g., 60.3% conversion), b.p. 59.0–59.5° (4.5 mm.), n^{20}_D 1.4535, d^{20}_{20} 1.2480; *MR*D (calcd.), 31.45; *MR*D (found), 31.68.

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(10) J. U. Nef, *Ann.*, **280**, 263 (1894); P. Duden, *Ber.*, **26**, 3008 (1893).

(11) A. J. Birch, "The Labile Molecule," Discussions of The Faraday Society, No. 2, 1947, p. 251; M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 104.

(12) J. Kleinberg, *Chem. Revs.*, **40**, 386 (1947); A. Lüttringhaus and D. Schade, *Ber.*, **74**, 1565 (1941).

(13) H. W. Jacobson, Ph.D. thesis, Purdue University, 1942.

(14) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

(15) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.88; H, 4.13; N, 19.18. Found: C, 32.92; H, 3.89; N, 19.15.

2,2,4-Trinitropentane.—2-Nitropropene (8.7 g., 0.10 mole) was added dropwise in one hour to a stirred solution of 1,1-dinitroethane (48.0 g., 0.40 mole), 40% aqueous benzyltrimethylammonium hydroxide (1.0 ml.) and dioxane (35 ml.) at 5–10°. The mixture was stirred at room temperature for 90 hours and then poured into water (100 ml.); hydrochloric acid (2 *N*) was added until the solution became acidic. The organic layer was separated and the aqueous layer was extracted with ether. The organic-ether fractions were washed with distilled water (30 ml.) and saturated sodium chloride solution (2 × 25 ml.). After the ether had been removed at atmospheric pressure, vacuum distillation of the residue in an atmosphere of nitrogen yielded 1,1-dinitroethane (25.5 g.), b.p. 59–61° (5 mm.), and 2,2,4-trinitropentane (19.3 g., 93.2% conversion), b.p. 107–108° (0.8 mm.), n^{20}_{D} 1.4699, d^{20}_{20} 1.3715; MR_{D} (calcd.), 42.15; MR_{D} (found), 42.12.

Anal. Calcd. for $C_5H_9N_3O_6$: C, 28.99; H, 4.38; N, 20.29. Found: C, 28.91; H, 4.37; N, 20.31.

5,5-Dinitro-2-hexanone.—Methyl vinyl ketone (13.2 g. of an 85% azeotropic solution, 0.16 mole) was added slowly (1 hour) at 10° to a stirred solution of 1,1-dinitroethane (19.2 g., 0.16 mole), 40% aqueous benzyltrimethylammonium hydroxide (1.0 ml.) and dioxane (35 ml.). Stirring was continued for an additional 65 hours at room temperature. The solution was then poured into water (100 ml.) and acidified with 2 *N* hydrochloric acid. The organic product was extracted with methylene chloride. After removal of the solvent, distillation yielded 5,5-dinitro-2-hexanone (29.8 g., 95% conversion), b.p. 109–110° (1.3 mm.), n^{20}_{D} 1.4607, d^{20}_{20} 1.2638; MR_{D} (calcd.), 41.17; MR_{D} (found), 41.26.

Anal. Calcd. for $C_6H_{10}N_2O_5$: C, 37.89; H, 5.30; N, 14.73. Found: C, 38.06; H, 4.96; N, 14.74.

The semicarbazone was prepared in 98% yield by the procedure of Shriner and Fuson.[16a] After recrystallization from hot methanol, the white crystals melted at 192.5–193°.

Anal. Calcd. for $C_7H_{13}N_5O_5$: C, 34.01; H, 5.30; N, 28.33. Found: C, 34.14; H, 5.29; N, 28.30.

The *p*-nitrophenylhydrazone[16b] was prepared in 90% yield. The orange needles melted at 146–147° after recrystallization from hot ethanol.

Anal. Calcd. for $C_{12}H_{15}N_5O_6$: C, 44.31; H, 4.67; N, 21.53. Found: C, 44.35; H, 4.66; N, 21.60.

4,4-Dinitro-1-pentanal.—A solution of acrolein (8.4 g. of a 97.4% azeotrope, 0.5 mole) in ether (60 ml.) was added over a 4-hour period to a stirred solution of benzyltrimethylammonium hydroxide (40% in water, 1.0 ml.), 1,1-dinitroethane (18.0 g., 0.15 mole) and diethyl ether (60 ml.) at room temperature. The reaction mixture was stirred for an additional 3 hours. The mixture was then extracted with 2 *N* hydrochloric acid (2 × 60 ml.) and the ether solution was dried by extraction with a saturated sodium chloride solution. After the solvent had been removed, the residue was distilled to yield 4,4-dinitro-1-pentanal (19.1 g., 74.3% conversion), b.p. 97–97.5° (0.8 mm.), n^{20}_{D} 1.4650, d^{20}_{20} 1.3284; MR_{D} (calcd.), 36.54; MR_{D} (found), 36.65. The red tarry residue (polymer) weighed 4.7 g. (18% yield).

Anal. Calcd. for $C_5H_8N_2O_5$: C, 34.09; H, 4.58; N, 15.91. Found: C, 34.14; H, 4.46; N, 15.67.

The semicarbazone[16a] was obtained in minute white crystals from hot methanol, m.p. 154.5–155.5°; yield 100%.

Anal. Calcd. for $C_6H_{11}N_5O_5$: C, 30.90; H, 4.76; N, 30.03. Found: C, 31.22; H, 4.48; N, 30.00.

The red ***p*-nitrophenylhydrazone**[16b] was recrystallized from hot ethanol, m.p. 141–142°; yield 90%.

Anal. Calcd. for $C_{11}H_{13}N_5O_6$: C, 42.44; H, 4.21; N, 22.50. Found: C, 42.41; H, 4.36; N, 22.70.

4,4-Dinitropentanoic Acid.—4,4-Dinitro-1-pentanal (1.05 g., 0.006 mole) was oxidized with alkaline potassium permanganate. The manganese dioxide and excess permanganate were dissolved, after acidification with sulfuric acid, in aqueous sodium bisulfite. The aqueous solution was extracted with ether. The solvent was evaporated on a steam-bath and Skellysolve F was added to the residue. 4,4-Dinitropentanoic acid precipitated as white needles (1.09 g., 95% conversion); m.p. 98.5–100.5° after recrystallization from Skellysolve F; neut. equiv. (calcd.), 192; neut. equiv. (found), 195.

The melting point of this product was not depressed by the addition of 4,4-dinitropentanoic acid prepared from methyl 4,4-dinitropentanoate.

Methyl 3,3-Dinitro-*n*-butyl Sulfone.—Methyl vinyl sulfone (21.2 g., 0.20 mole) was slowly added (1 hour) to a stirred solution of 1,1-dinitroethane (24.0 g., 0.20 mole), benzyltrimethylammonium hydroxide (40% aqueous solution, 2.0 ml.) and dioxane (30 ml.) at 10°. The solution was stirred for 65 hours, then neutralized with aqueous hydrochloric acid (70 ml., 1.5 *N*). The organic product was extracted with ether; the ether extracts were washed with a saturated solution of sodium chloride. After the solvent was removed, petroleum ether (60–90°) was added to the residual oil. On shaking, white crystals of methyl 3,3-dinitro-*n*-butyl sulfone separated. The solid was filtered and dried; the yield was 8.9 g. (19.7% conversion). After recrystallization from hot benzene, the product melted at 76–78°.

Anal. Calcd. for $C_5H_{10}N_2O_6S$: C, 26.55; H, 4.46; N, 12.39; S, 14.17. Found: C, 26.77; H, 4.20; N, 12.05; S, 14.35.

After the filtrate had been concentrated under vacuum, potassium hydroxide (10% in methanol) was added. The yellow salt formed was filtered and dried to yield potassium 1,1-dinitroethane (4.5 g., 15% recovery). The yield of methyl 3,3-dinitro-*n*-butyl sulfone, based on 1,1-dinitroethane consumed, was 23%.

COLUMBUS 10, OHIO

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(16) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, (a) procedure 13, p. 170, (b) procedure 14, p. 171, John Wiley and Sons, Inc., New York, N. Y.