After the solution had cooled, 2.65 g. (53%) of the methyl ether acetate of *threo*-1,2-diphenylethylene glycol (VIII), m.p. 64–65°, was obtained.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.10; H, 6.55.

Hydrolysis of the Methyl Ether Acetate of *threo*-1,2-Diphenylethylene Glycol (VIII).—A solution of 0.5 g. of VIII and 20 ml. of 10% alcoholic sodium hydroxide was refluxed two hours on a steam-bath. The reaction mixture was cooled, diluted with 200 ml. of water and the solution extracted with ether. The ether layer was dried with sodium sulfate and evaporated to dryness. The residue was recrystallized from petroleum (b.p. 30–60°) and yielded 0.35 g. (83%) of the methyl ether of *threo*-1,2-diphenylethylene glycol (X), m.p. 53–54°.

Preparation of the Methyl Ether of *threo*-1,2-Diphenylethylene Glycol (X).—The method of Curtin[15] was used with the following modifications. Potassium sand was made from 0.36 g. (9.31 milliatoms) of potassium metal in 50 ml. of dry benzene in a nitrogen atmosphere. A solution of 2 g. (9.31 millimoles) of *threo*-1,2-diphenylethylene glycol[16] in 50 ml. of dry benzene was added. Hydrogen was evolved rapidly for the first 30 minutes and the reaction mixture was stirred four hours longer in a nitrogen atmosphere, after which time 20 ml. of methyl iodide was rapidly added. The mixture was stirred, refluxed for three hours and allowed to stand overnight. The solvent was then evaporated and the residue treated with 100 ml. of water and the aqueous suspension steam distilled. The steam distillate was extracted with ether, dried with sodium sulfate and evaporated to dryness. The oily residue was dissolved in petroleum ether (30–60°) from which crystallized 1 g. (47%) of X, m.p. 53–54°. A mixed m.p. with the product from saponification of VIII was undepressed.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 78.91; H, 7.07. Found: C, 78.68; H, 7.03.

Acetylation of the Methyl Ether of *threo*-1,2-Diphenylethylene Glycol (X).—To 0.2 g. of monomethyl ether (X) from the above preparation in 10 ml. of dry pyridine was added 10 ml. of acetic anhydride. The solution was allowed to stand at room temperature for two days and poured onto ice. Ammonium hydroxide was added to destroy the excess acetic anhydride and the reaction mixture extracted with ether. The ether extract was dried with sodium sulfate, evaporated to dryness, and recrystallized from 95% ethanol to yield 0.2 g. (85%) of VIII, m.p. 64–65°. A mixed m.p. with the product obtained from the hydrogenation of VII was undepressed.

Preparation of the Methyl Ether Acetate of *erythro*-1,2-Diphenylethylene Glycol.—Benzoin methyl ethyl was reduced with lithium aluminum hydride[17] to give the monomethyl ether of the *meso*-glycol,[18] m.p. 101–102°, in 95% yield. To 6.0 g. of this monomethyl ether in 30 ml. of dry pyridine was added 10 g. of acetic anhydride and the solution heated for 5 hours on the steam-bath. After the resulting solution was poured onto ice, the solid was recrystallized from alcohol to give a quantitative yield of the *erythro*-acetate methyl ether, m.p. 59–60°. A mixed melting point with the product from hydrogenation of VII was depressed, m.p. 48–53°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; OCH_3, 11.48. Found: C, 75.25; H, 6.81; OCH_3, 11.54.

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[15] D. Y. Curtin, E. E. Harris and E. K. Meislich, THIS JOURNAL, **74**, 2901 (1952).

[16] Prepared according to the method of S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946).

[17] *Cf.* the procedure of W. G. Dauben, R. A. Micheli and J. F. Eastham, *ibid.*, **74**, 3852 (1952).

[18] J. C. Irvine and J. Weir, *J. Chem. Soc.*; 1384 (1907).

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Action of Oxidizing Agents on Salts of Nitroalkanes. I. Oxidative Dimerization[1,2,3]

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Oxidation of *s*-alkanenitronates with either cationic or anionic oxidants results, in general, in simultaneous formation of *vic-t*-dinitroalkanes and ketones. Oxidants which effect these reactions are: persulfates, ferricyanides, hydrogen peroxide, bromates, silver nitrate and ammoniacal cupric chloride; reaction occurs most rapidly and highest yields of *vic*-dinitroalkanes are obtained with persulfates. Oxidation of alkaline solutions of 2-nitropropane with potassium permanganate yields acetone. Nitroethane, a primary nitroalkane, upon oxidation with persulfates gives 3,4,5-trimethylisoxazole. The action of cationic or anionic oxidants on a *s*-alkanenitronate is believed to involve transfer of one electron to the oxidant; the resulting nitroalkyl radicals may then dimerize to *vic*-dinitroalkane or be converted into ketone and nitric oxide (or its oxidized products).

Electrolysis of salts of primary and secondary nitro compounds results in formation of *vicinal* dinitroalkanes[4]; Pearson and Evans[4e] report that anodic oxidation of aqueous sodium 2-propanenitronate also yields acetone (65%) and nitric oxide along with 2,3-dimethyl-2,3-dinitrobutane (15%). With the chemical oxidants: nitrogen dioxide,[5a] air[5b] or hydrogen peroxide,[5b] sodium 2-propanenitronate is converted to 2,3-dimethyl-2,3-dinitrobutane in low yield.

In order to obtain additional information concerning the nature and yields of products from oxidation–reduction reactions of this type, an investigation has been made of the actions of various chemical oxidants on salts of primary and secondary nitroalkanes. The mononitro compounds investigated are 2-nitropropane, 2-nitrobutane, nitrocyclohexane and nitroethane; the oxidizing agents are: sodium or ammonium persulfates, hydrogen peroxide, potassium ferricyanide, ferric chloride, silver nitrate, sodium bromate, ammoniacal cupric chloride and potassium permanganate.

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[1] A portion of this research was abstracted from a thesis submitted by Ralph B. Kaplan to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1950.

[2] Financial support for much of this research was provided by the Office of Naval Research.

[3] The term oxidative dimerization is used to describe processes involving transfer of one electron from an anion that result in pairing of the resulting oxidized intermediates.

[4] (a) N. J. Zelinsky, *J. Russ. Phys. Chem. Soc.*, **26**, 610 (1894); (b) C. Ulpiani and O. Gasparini, *Gazz. chim. ital.*, **32**, II, 242 (1902); (c) C. D. Nenitzescu, *Ber.*, **62**, 2669 (1929); (d) C. D. Nenitzescu and D. A. Isacescu, *ibid.*, **63**, 2484 (1930); (e) R. Pearson and W. V. Evans, *Trans. Electrochem. Soc.*, **84**, 173 (1943); (f) C. T. Bahner, U. S. Patent 2,485,803, October 25, 1949.

[5] (a) C. G. Goebel, Ph.D. Thesis, Purdue University, 1944; (b) C. S. Coe, E. C. Attané and T. F. Doumani, U. S. Patent 2,465,974, March 29, 1949.

Oxidation of alkaline solutions of secondary nitro compounds with sodium persulfate results in formation of *vic*-dinitroalkanes and ketones (equations 1 and 2): 2,3-dimethyl-2,3-dinitrobutane (51–62%) and acetone (8–27%), 3,4-dimethyl-3,4-dinitrohexane (37%) and 2-butanone (48%), and 1,1′-dinitrobicyclohexyl (26–30%) and cyclohexanone (66.5%) are obtained readily from salts of 2-nitropropane, 2-nitrobutane and nitrocyclohexane at 0–5°.

$$2RR—C{=}NO_2^- + S_2O_8^{=} \xrightarrow{H^+} RRC(NO_2)C(NO_2)RR + 2SO_4^{=} \quad (1)$$

$$RR—C{=}NO_2^- + 2S_2O_8^{=} + 2H_2O \xrightarrow{H^+} RR—C{=}O + 4H^+ + NO_3^- + 4SO_4^{=} \quad (2)$$

Attempts to convert 1,1-dinitroethane and trinitromethane to 2,2,3,3-tetranitrobutane and hexanitroethane failed.

Oxidation of the 2-propanenitronate (1 equivalent)–persulfate (2–4 equivalents) system occurs very slowly at 0–5° at *p*H's above 9.4; in the *p*H range 9.4–7.2, formation of *vic*-dinitroalkane is accelerated, and reactions are essentially complete in two to four hours.[6] The alkalinity of the mixtures decreases rapidly during oxidation (see equations 1 and 2), and, unless the solutions are buffered or alkali is added, the mixtures finally become acidic; the nitroalkane is then either regenerated, decomposed into ketone[7] (the Nef reaction) or converted into pseudonitrole by reaction with nitrous acid[8] (from nitrite ion formed during oxidation). In general, the yield of coupled product is decreased and that of ketone is increased if the oxidations are effected with dilute reagents or at elevated temperatures.

Reactions accompanying the coupling process in alkaline medium produce ketone, hydrogen ion and nitrite ion; nitrite ion is also oxidized to nitrate by persulfate (equation 2). Reaction of sodium 2-propanenitronate and sodium persulfate in which the *p*H is controlled between 7.9–8.2 by continuous addition of sodium hydroxide results in formation of 2,3-dimethyl-2,3-dinitrobutane (17–20%) and acetone (8–27%); the presence of nitrite ion and sodium 2-propanenitronate was established by acidifying the mixture; 2-nitro-2-nitrosopropane[8] was isolated in 10–11% yield. Under identical conditions, alkaline solutions of 2-nitropropane in the absence of oxidizing agents yield only traces of acetone (see Experimental); it is concluded, therefore, that formation of ketone (equation 2) during oxidation occurs simultaneously with oxidative dimerization (equation 1) and does not result primarily by the Nef reaction.[7]

The primary nitro compound, nitroethane, undergoes rapid reaction with persulfates in alkaline medium to yield, ultimately, 3,4,5-trimethylisoxazole; no direct evidence was obtained for the formation of 2,3-dinitrobutane. Interpretation of these results must be deferred until further investigation of this reaction can be made since nitroethane is also converted to 3,4,5-trimethylisoxazole by alkali.[9] It has been found previously, however, that anodic oxidation of aqueous sodium ethanenitronate does yield 2,3-dinitrobutane, 2-nitro-2-butene and 3-nitro-2-butanol.[4f]

In general, the anionic oxidants studied other than persulfates are inferior in effecting oxidative dimerization of secondary nitroalkanes. Oxidation of the 2-propanenitronate anion occurs slowly with excess hydrogen peroxide. The reaction is acid-catalyzed and at *p*H 8.0–4.2 yields 2,3-dimethyl-2,3-dinitrobutane (8–15%) and acetone (−55%) (equations 3 and 4). With potassium ferricyanide as oxidant (*p*H 9.4–7.0) at 25°, the coupled product (6–15%) is formed very rapidly (*p*H 9.4–7.0) (equation 5) along with acetone (36–55%), nitrite and nitrate ions, and 2-nitropropane. With alkaline potassium permanganate, oxidation of sodium 2-propanenitronate occurs almost instantaneously to yield acetone[10] (> 90%); no coupled product is obtained. Oxidative dimerization (3–6%) of salts of 2-nitropropane is effected slowly by alkaline bromates; even though the action of this oxidant is accelerated by acids, it is the most ineffective of the anionic oxidants studied.

$$2RRC{=}NO_2^- + H_2O_2 + 2H^+ \longrightarrow RRC(NO_2)C(NO_2)RR + 2H_2O \quad (3)$$

$$RRC{=}NO_2^- + 2H_2O_2 \xrightarrow{H^+} RRC{=}O + NO_3^- + 2H_2O \quad (4)$$

$$2(CH_3)_2C{=}NO_2^- + 2Fe(CN)_6^{\equiv} \longrightarrow (CH_3)_2C(NO_2)C(NO_2)(CH_3)_2 + 2Fe(CN)_6^{\overline{\equiv}} \quad (5)$$

Cationic oxidants may also effect oxidative dimerization of primary and secondary nitroalkanes; in general, however, reactions are slower and give lower yields than those in which persulfates are used. Silver salts of primary nitro compounds have been previously shown to decompose thermally into silver and the corresponding *vic*-dinitro compounds.[11] Present extension of this reaction to secondary nitroalkanes reveals that the ketone from the nitroalkane is produced along with *vic*-dinitroalkane. Decomposition of aqueous mixtures of silver nitrate and sodium 2-propanenitronate at 0–5° results in formation of acetone (30%), 2,3-dimethyl-2,3-dinitrobutane (11%) (equations 6 and 7) and 2-nitropropane (> 30%). Similarly, decomposition of aqueous cupric 2-propanenitronate occurs slowly at 100° to yield acetone (90%) and 2,3-dimethyl-2,3-dinitrobutane (4.5%). Ferric 2-propanenitronate is more stable than the corresponding silver or copper salt; upon being heated in water, it decomposes slowly into acetone and 2-nitro-2-nitrosopropane.

$$2(CH_3)_2C{=}NO_2Ag \longrightarrow (CH_3)_2C(NO_2)C(NO_2)(CH_3)_2 + 2Ag \quad (6)$$

$$(CH_3)_2C{=}NO_2Ag \longrightarrow (CH_3)_2C{=}O + [NO] + Ag \quad (7)$$

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[6] In many experiments yields of coupled product greater than 40% were obtained in 10–15 minutes.

[7] J. U. Nef, *Ann.*, **280**, 263 (1894); M. Konovalov, *Ber.*, **29**, 2193 (1896); E. F. Degering and K. Johnson, *J. Org. Chem.*, **8**, 10 (1943).

[8] V. Meyer, *Ann.*, **175**, 120 (1875).

[9] W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **77**, 1262 (1900).

[10] *Cf.* S. S. Nametkin and E. I. Pozdynakova, *J. Russ. Phys. Chem. Soc.*, **45**, 1420 (1913); S. S. Nametkin and A. M. Khukhrikova, *ibid.*, **47**, 425 (1915).

[11] A. Angeli, V. Castellana and R. Ferrero, *Atti accad. Lincei*, **18**, 38 (1909); *C. A.*, **4**, 1739 (1910); A. Angeli and L. Alessandri, *Atti accad. Lincei*, **19**, I, 784 (1910); *C. A.*, **4**, 2634 (1910); *cf.*, G. B. Brown and R. L. Shriner, *J. Org. Chem.*, **2**, 376 (1938).

On the basis of the present study, it is suggested that oxidation of secondary alkanenitronates (equations 8–10) with anionic oxidants proceeds through transfer of one electron and involves nitroalkyl radicals as intermediates; similar postulates have been made to account for formation of *vic*-dinitroalkanes[4c,4d,4e] and carbonyl compounds[4e] by anodic oxidation of alkanenitronates.[12] Oxidation of a nitronate with cationic oxidants (silver and copper ions) may involve similar processes since the metallic alkanenitronate is formed, decomposition of which (equation 11, one electron transfer possibly involving the complex ion of the metal alkanenitronate) can yield the metal and the nitroalkyl radical.

$$\mathrm{RRC{=}NO_2^- + H^+ \ldots Oxidant \longrightarrow RR\dot{C}{-}NO_2 + H\text{-}Oxidant} \qquad (8)$$

$$\mathrm{2RR\dot{C}{-}NO_2 \longrightarrow RRC(NO_2)C(NO_2)RR} \qquad (9)$$

$$\mathrm{RR\dot{C}NO_2 \longrightarrow RRC{=}O + \cdot NO}^{13} \qquad (10)$$

$$\mathrm{RRC{=}NO_2Ag \longrightarrow RR\dot{C}{-}NO_2 + Ag} \qquad (11)$$

A study has been initiated of other possible methods for generating nitroalkyl radicals in order to determine if they dimerize to *vicinal* dinitroalkanes and decompose into carbonyl compounds as postulated in equations 9 and 10.[14] Nenitzescu and Isacescu[4d] have proposed that radicals are intermediates in the decomposition of 9-iodo-9-nitrofluorene and phenyliodonitromethane into iodine and 9,9′-dinitro-9,9′-bifluorene and 1,2-dinitro-1,2-diphenylethane; in the present investigation, the decomposition of 2-iodo-2-nitropropane (see Experimental) was conducted in non-aqueous systems to determine if similar reactions occur. In refluxing methanol, photolytic decomposition of 2-iodo-2-nitropropane yields acetone and traces of 2,3-dimethyl-2,3-dinitrobutane; at 250°, in the absence of a solvent, acetone is the principal product. It appears, therefore, that the difference in type of products obtained from decomposition of 9-iodo-9-nitrofluorene, phenyliodonitromethane and 2-iodo-2-nitropropane may possibly be related to the relative stabilities of the intermediate radicals.

Experimental

The Action of Various Oxidizing Agents on Sodium 2-Propanenitronate. Sodium Persulfate.—A mixture of ammonium persulfate (4.5 g., 0.02 mole) and sodium acetate (4.0 g., 0.05 mole) in water (15 ml.) was added to a solution of 2-nitropropane (0.89 g., 0.01 mole) in 10% sodium hydroxide (5 ml.) at 0–5°. Precipitation of a white solid occurred rapidly at *p*H 9.4–7.2. After 6 hours the mixture was filtered to obtain 2,3-dimethyl-2,3-dinitrobutane (0.47 g., 0.0267 mole) in 53% yield, m.p. and mixed m.p. with an authentic sample 209–210°, lit. 209°.[15] Distillation of the slightly acidic filtrate yielded acetone (13.9%) and 2-nitropropane (> 10%); acetone was isolated as its 2,4-dinitrophenylhydrazone (0.33 g., 0.00139 mole), m.p. 126° from ethanol-water, lit. 126–128°,[16] mixed m.p. no depression. Oxidative dimerization of 2.5 moles of 2-nitropropane gave 2,3-dimethyl-2,3-dinitrobutane and acetone in 55–62% and 8–11% yields, respectively. The yield of 2,3-dimethyl-2,3-dinitrobutane (51–58%) was not reduced greatly by using sodium 2-propanenitronate and ammonium persulfate in equimolar quantities. In general, yields of product were increased by using very concentrated reagents. Sodium persulfate may be used directly; aqueous solutions of the commercial product are acidic and were made slightly alkaline before being added to the reaction mixture. If the buffer was omitted, the yield of coupled product was reduced to 28%. The products may become contaminated with 2-nitro-2-nitrosopropane at the later stages of reaction. Formation of the pseudonitrole may be minimized by addition of urea to the reaction mixture; however, the yields of 2,3-dimethyl-2,3-dinitrobutane are lowered. Oxidation systems in which the mole ratio of 2-nitropropane to sodium chloride was 1:3 did not yield 2-chloro-2-nitropropane (yield of 2,3-dimethyl-2,3-dinitrobutane, 33%).

An experiment was conducted as described previously (0.02 mole of 2-nitropropane); however, when the *p*H of the reaction mixture dropped from 9.4 to 7.9, 10% sodium hydroxide was added dropwise over a 3.5-hour period to maintain the *p*H between 7.9–8.2. The mixture was made very alkaline with 50% sodium hydroxide and then filtered to isolate 2,3-dimethyl-2,3-dinitrobutane (0.3 g., 17.1% yield). The aqueous filtrate was extracted with ethyl ether (C.P., 3 20-ml. portions); the ether extracts were added to 2,4-dinitrophenylhydrazine (3 g.) in aqueous sulfuric acid (60 ml. in 250 ml. of water). After evaporation of the ether, crude acetone 2,4-dinitrophenylhydrazone (1.89 g., m.p. 117–124°) was isolated. The yield of derivative, after recrystallization from 95% ethanol, was 27% (1.29 g., 0.00532 mole) based on 2-nitropropane, m.p. 123–124°, lit. 126–128°.[16] The remaining aqueous filtrate, upon acidification with 6 *N* acetic acid, evolved oxides of nitrogen, and yielded 2-nitro-2-nitrosopropane (10%), m.p. 75–76° (blue melt, dec.), lit. 75–76°.[8]

A series of experiments was conducted to determine the extent of decomposition of sodium 2-propanenitronate into acetone (the Nef reaction) at 0–5° at *p*H 10.4–6.8 in the absence of persulfates. The previous experiments were repeated; however, ammonium persulfate was omitted and dilute acetic acid was added very slowly over a 4-hour period to maintain the *p*H of the mixture from 7.7–8.1. No acetone was obtained, as evidenced by failure to form a 2,4-dinitrophenylhydrazone, by extraction of the mixture with ethyl ether. Similarly, distillation of an aqueous solution of sodium 2-propanenitronate (2.05 g., 30 ml., *p*H 10.4), adjusted to *p*H 6.8 at 0–5° with dilute acetic acid, resulted in recovery of 2-nitropropane. The yield of acetone, isolated as a 2,4-dinitrophenylhydrazone, was much less than the yields obtained in the oxidations.

Potassium Ferricyanide.—An aqueous solution of potassium ferricyanide (27 g. in 120 ml., 0.082 mole) was rapidly added to a stirred mixture of 2-nitropropane (8.9 g., 0.01 mole), sodium hydroxide (4 g., 0.1 mole) and sodium acetate (8.9 g.) in water (30 ml.) at 25°. The *p*H of the red-brown solution dropped continuously and, after 6.5 minutes, was lowered from 9.4 to 8.2. Precipitation of 2,3-dimethyl-2,3-dinitrobutane was essentially complete at *p*H 8.5. After 85 minutes, the solution was yellow-red in color and had a *p*H of 7.1; no gases were evolved during oxidation. The mixture was filtered immediately to give 2,3-dimethyl-2,3-dinitrobutane (0.82 g., 0.00466 mole) in 11.4% yield, m.p. 211°, lit. 209°.[15] The filtrate contained nitrite and 2-propanenitronate ions and acetone; upon acidification of an aliquot portion, oxides of nitrogen were evolved and 2-propanepseudonitrole was formed. Distillation of the filtrate (*p*H 7.1) yielded acetone and 2-nitropropane; acetone was isolated as a 2,4-dinitrophenylhydrazone (10.7 g., 0.045 mole) in 54.9% yield, m.p. 126°, lit. 126–128°.[16] The amount of regenerated 2-nitropropane was not determined.

The yields of 2,3-dimethyl-2,3-dinitrobutane obtained with potassium ferricyanide as oxidant ranged from 6–15% and were not affected greatly by excess sodium hydroxide or potassium ferricyanide or by lowering the temperature of reaction to 5°.

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[12] These oxidation reactions are similar to the Kolbe synthesis of alkanes by electrolysis of salts of carboxylic acids[12a] and the formation of diethyl tetramethylsuccinate by reaction of persulfates with ethyl isobutyrate or alkaline solutions of ethyl dimethylmalonate.[12b] (a) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London E. C. 4, 1948, p. 142; (b) F. Fichter and J. Heer, *Helv. Chim. Acta*, **18**, 1276 (1935).

[13] Decomposition of a secondary nitroalkyl radical (neglecting any hydrolytic process) may yield the ketone and nitric oxide, a stable free radical; nitric oxide is further oxidized to nitrite and nitrate ions.

[14] H. Barker has demonstrated in This Laboratory that decomposition of acetyl peroxide in 2-nitropropane results in formation of 2,3-dimethyl-2,3-dinitrobutane.

[15] L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

[16] N. R. Campbell, *Analyst*, **61**, 391 (1936).

Hydrogen Peroxide.—Hydrogen peroxide (30 ml., 30%) was added rapidly to a stirred solution of 2-nitropropane (1.80 g., 0.02 mole) in 10% sodium hydroxide (12 ml.) at 5–10°. The *p*H of the solution dropped from 12.8 to 9.3 upon addition of peroxide. Glacial acetic acid was added until the solution had a *p*H of 5.4. Concentrated hydrochloric acid (37%) was then slowly added; the solution became light yellow. When the *p*H of the mixture reached 4.8, precipitation of 2,3-dimethyl-2,3-dinitrobutane began. In 4 hours, reaction was essentially complete (*p*H 4.5), and the solution became colorless. Filtration of the mixture yielded 2,3-dimethyl-2,3-dinitrobutane (0.48 g., 0.00167 mole) in 8.7% yield, m.p. 209°, no depression by an authentic sample. Distillation of the residue yielded acetone in 55% yield; the ketone was isolated as its 2,4-dinitrophenylhydrazone (2.63 g., 0.011 mole), m.p. 126°. Yields of 2,3-dimethyl-2,3-dinitrobutane ranged from 8–15% in these experiments and, in general, were improved by increasing the concentration of reagents.

Mixtures of 2-nitropropane dissolved in excess sodium hydroxide and hydrogen peroxide remained homogeneous for over 24 hours; upon addition of acid, precipitation of 2,3-dimethyl-2,3-dinitrobutane occurred. The coupled product (8–15% yield) was slowly produced (24 hours) at *p*H's between 6.5–8.0; however, the reaction rate was greatly accelerated at *p*H's between 4.5–5.5. In one experiment, 2,3-dimethyl-2,3-dinitrobutane was produced in the *p*H range of 0–1.

Silver Nitrate.—An aqueous solution of silver nitrate (25.5 g., 0.15 mole, in 79 ml. of water, 0–5°) was rapidly added to a stirred solution of 2-nitropropane (13.35 g., 0.15 mole) and sodium hydroxide (6.0 g., 0.15 mole) in water (90 ml.) at 0° in diffused light. A white salt precipitated which decomposed gradually to yield silver. The mixture was stirred for 12 hours; the silver precipitated in large gray crystalline lumps. The aqueous mixture was filtered (165 ml.); acetone was isolated in 30% yield as a 2,4-dinitrophenylhydrazone (0.66 g., 0.00277 mole from 10-ml. aliquot), m.p. 126°, lit. 126–128°.[16] The silver deposit and the aqueous filtrate were extracted with ethyl ether; evaporation of the ether extract gave 2-nitropropane (> 30% yield), 2,3-dimethyl-2,3-dinitrobutane (crude yield 1.77 g.; from ethanol 1.47 g., 0.00835 mole, 11.1% yield, m.p. 209°) and a low-melting, oily-white solid (unidentified). In a similar experiment in which silver 2-propanenitronate was prepared at 25° and the mixture was refluxed for 30 minutes, acetone, 2,3-dimethyl-2,3-dinitrobutane and 2-nitropropane were obtained in 25, 9.7, and >40% yields, respectively.

Sodium Bromate.—Sodium bromate (1.5 g., 0.01 mole) in water (7 ml.) was added to an aqueous solution of sodium 2-propanenitronate (1.11 g., 0.01 mole in 4 ml.); dilute hydrochloric acid was added until the *p*H of the mixture was 8.9. After 10 days at room temperature the solution was filtered to yield 2,3-dimethyl-2,3-dinitrobutane (0.05 g., 2.85×10^{-4} mole, 5.7%), m.p. 209°. The alkaline filtrate, when distilled into 2,4-dinitrophenylhydrazine, yielded traces of acetone 2,4-dinitrophenylhydrazone. The *p*H of the distillation residue was 11.4. Reactions conducted under similar conditions at *p*H's of 10.1 and 10.8 gave 2,3-dimethyl-2,3-dinitrobutane in 4.5 and 3.1% yields, respectively.

Cupric Ammonium Hydroxide.—Cupric chloride dihydrate (4.25 g., 0.025 mole) in 5 *N* ammonium hydroxide (15 ml.) was added to 2-nitropropane (4.5 g., 0.05 mole) in aqueous sodium hydroxide (2.3 g., 0.057 mole in 20 ml.). The mixture was stored for 12 hours at 25–30°. The homogeneous blue solution was refluxed for 2 hours during which time copper was deposited. The mixture was cooled and extracted with ether; evaporation of the ether extract gave 2,3-dimethyl-2,3-dinitrobutane (0.2 g.) in 4.5% yield, m.p. 208°. Excess alkali reduced the yield of coupled product; when 100% excess sodium hydroxide was used, no 2,3-dimethyl-2,3-dinitrobutane was formed. The yields of acetone from similar experiments ranged from 75–90%.

Reaction of Sodium 2-Butanenitronate and Sodium Persulfate.—A solution of 2-nitrobutane (1.03 g., 0.01 mole) in 10% sodium hydroxide (6 ml.) was added to a mixture of ammonium persulfate (2.3 g., 0.01 mole), sodium acetate (1.0 g., 0.012 mole) and water (6 ml.) at 0–5°. After 6 hours, the solution was filtered to obtain 3,4-dimethyl-3,4-dinitrohexane (0.20 g., 0.002 mole), white crystalline plates, in 40% yield, m.p. 76–77°, recrystallized from petroleum ether, m.p. 79.5–80°, lit. 79–80°.[17] Distillation of the slightly acidic filtrate into 2,4-dinitrophenylhydrazine solution yielded 2-butanone 2,4-dinitrophenylhydrazone (1.21 g., 0.0048 mole) in 48% yield; recrystallized from chloroform–ethanol, m.p. 110–111°, lit. 111° (115°).[18]

If the time of reaction is extended, the products become oily; as reaction proceeds, the *p*H of the mixture is decreased, and, if the mixture becomes strongly acidic, 3,4-dimethyl-3,4-dinitrohexane becomes contaminated with 2-butanepseudonitrole. Oxidative dimerization of 2-nitrobutane was conducted under alkaline conditions in the absence of buffer by continuously adding sodium hydroxide to the reaction mixture; the yield of 3,4-dimethyl-3,4-dinitrohexane in this experiment was 38.2%.

Reaction of Sodium Cyclohexanenitronate and Sodium Persulfate.—A solution of ammonium persulfate (2.3 g., 0.01 mole) and sodium acetate (1.0 g., 0.012 mole) in water was added rapidly at 0–5° to nitrocyclohexane (1.39 g., 0.0109 mole) in 10% sodium hydroxide. After 6 hours at 0–5°, the mixture was filtered to yield 1,1′-dinitrobicyclohexyl (0.20 g., 7.8×10^{-4} mole), white shiny plates, in 14.3% yield, m.p. 214° (darkening) –220° (dec.), lit. 217°.[19] The slightly acidic filtrate was distilled into 2,4-dinitrophenylhydrazine (3.0 g., in 50 ml. of concd. sulfuric acid and 200 ml. of water); cyclohexanone was obtained in 66.5% yield as a 2,4-dinitrophenylhydrazone (1.85 g., 0.00665 mole), m.p. 161–162° from chloroform–ethanol (1:3), lit. 162°.[16] The residue from distillation was very acidic. 1,1′-Dinitrobicyclohexyl was obtained in 26–30% yield by using the procedure described for 2-nitropropane and 2-nitrobutane in which sodium hydroxide was added at a rate such that the reaction mixture was maintained slightly alkaline.

Decomposition of 2-Iodo-2-nitropropane (a).—2-Iodo-2-nitropropane (2 g., 0.093 mole), b.p. 38–40° (2–3 mm.), dissolved in C.P. methanol (30 ml.) rapidly liberated iodine when exposed to sunlight. The solution was placed in a silica flask and then refluxed for 36 hours while illuminated with a 275-watt sun lamp (Westinghouse, R.S.). The mixture was distilled until much of the methanol had been removed; additional methanol (30 ml.) was added to the tarry residue and the distillation was continued. The distillate, after decolorization with sodium thiosulfate, was added to 2,4-dinitrophenylhydrazine (3 g.); acetone 2,4-dinitrophenylhydrazone (0.68 g., 0.0286 mole) was obtained in 31% yield, m.p. 125–127°. The residue from distillation, when decolorized with aqueous sodium thiosulfate, yielded traces of 2,3-dimethyl-2,3-dinitrobutane, m.p. 208–210°.

(b).—2-Iodo-2-nitropropane (5 g., 0.232 mole) was added dropwise into a silica flask at 250–270°. Liberation of iodine and oxides of nitrogen occurred very rapidly during pyrolysis; as the iodine concentration in the flask began to increase, the mixture was heated carefully to prevent violent decomposition. After the residue from the pyrolysis was steam distilled, the aqueous condensate was combined with the condensate obtained from pyrolysis and then distilled into 2,4-dinitrophenylhydrazine. The acetone obtained from the pyrolysis was isolated as a 2,4-dinitrophenylhydrazone, m.p. 127°, yield 12.7% (0.70 g., 0.0294 mole).

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[17] I. Bevad and A. Pirinsky, *Ber.*, **39**, 1231 (1906). 3,4-Dimethyl-3,4-dinitrobutane may exist in *meso* and D,L-modifications; the structure of the product obtained in these experiments has not been determined.

[18] C. F. H. Allen, THIS JOURNAL, **52**, 2957 (1930).

[19] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **42**, 586 (1910); *Chem. Zentr.*, **81**, II, 1376 (1910).