phase chromatographic analysis of the distillate (2-foot column of 10% Carbowax 6000 on Haloport F at 100° C. and a helium flow rate of 54 cc. per minute) was made by reference to a standard calibration curve in which the concentrations of known mixtures of the amino alcohols had been plotted.

The ring opening was allowed to proceed to the extent of 96.8% before exposure to hydroxide ion. This means that base-catalyzed ring opening could not have exceeded 3.2%. For the other compounds the maximum is less than 10%.

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Reaction of Bis(2,2,2-trinitroethyl) Formal with Potassium Cyanide

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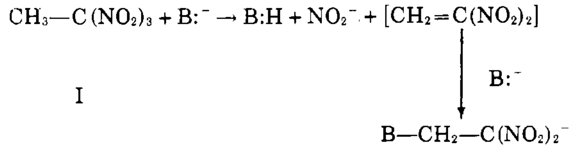
Bis(2,2,2-trinitroethyl) formal reacts with methanolic potassium cyanide to yield dipotassium bis(1-cyano-2,2-dinitroethyl) formal as the main product, together with minor amounts of the corresponding amide-nitrile and diamide. Some properties and reactions of these materials are described.

THE REACTION of 1,1,1-trinitroethane (I) with a variety of nucleophiles yields β-substituted 1,1-dinitroethane salts. Examples include the formation of potassium 3,3-dinitropropionitrile from the reaction of potassium cyanide with I (*7*), potassium methyl 2,2-dinitroethyl ether from potassium methoxide (*6*), potassium ethyl 2,2-dinitroethyl ether from potassium ethoxide (*6*) or ethanolic potassium hydroxide (*2*), potassium ethyl 2-carbethoxy-4,4-dinitrobutyrate from potassium diethyl malonate (*9*), and the zwitterionic salts, ammonium, dimethylammonium, trimethylammonium, guanidinium, and piperidinium *N*-(2-nitroethyl-2-nitronate) from I and the corresponding amines (*3, 9*). Zeldin and Shechter (*9*) have suggested that the reactions proceed through the attack of the base at the β-hydrogen, leading to elimination of nitrous acid and the formation of 1,1-dinitroethylene (never isolated), which serves as a substrate for subsequent Michael addition of the nucleophile.



$$\begin{tikzcd} CH_3-C(NO_2)_3 + B:^- \arrow[r] & B{:}H + NO_2^- + [CH_2=C(NO_2)_2] \arrow[d, "B:^-"] \\ & B-CH_2-C(NO_2)_2^- \end{tikzcd}$$

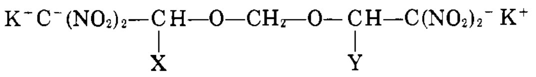
I

To the best of our knowledge, the literature contains no mention of similar reactions on polynitroaliphatics other than I.

We wish, therefore, to record the closely analogous reactions of bis(2,2,2-trinitroethyl) formal (II) with potassium cyanide in methanol to yield dipotassium bis(1-cyano-2,2-dinitroethyl) formal (III) as the main product (62%). Also formed were minor amounts of the amide-nitrile, IV, and the diamide, V, these hydrolysis products of III probably arising from small amounts of water in the "absolute" methanol.

$$C(NO_2)_3CH_2-O-CH_2-O-CH_2C(NO_2)_3 \xrightarrow{KCN,\ MeOH} HCN + KNO_2 +$$

II

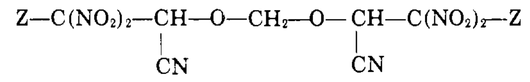


$$K^-C^-(NO_2)_2-\underset{X}{CH}-O-CH_2-O-\underset{Y}{CH}-C(NO_2)_2^-K^+$$

III, X = Y = CN
IV, X = CN, Y = CONH$_2$
V, X = Y = CONH$_2$

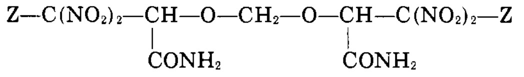
The dinitrile, III, decomposes slowly in aqueous acid and undergoes hydrolysis in aqueous base, but is relatively stable at intermediate pH's. Its separation from IV and V was readily effected by adding the crude product mixture to water and stirring. Initially an amorphous yellow tar was formed, but this soon turned nicely crystalline as III was transformed to its relatively insoluble monohydrate and IV and V dissolved. In hot aqueous alkali, III was converted in high yield to V, which precipitated as the dihydrate. When isolation and purification of III were sidestepped—i.e., the crude product mixture added directly to hot aqueous alkali—II was converted to V in 80% overall yield.

Attempts in aqueous or nonaqueous media to convert the dinitrile salt to its conjugate diacid, VI, were frustrated by spontaneous decomposition of the latter. A dibromo derivative, VII, was readily obtained, however, by bromination of an ether suspension of III. In the case of the diamide salt, by way of contrast, the conjugate diacid, VIII, which precipitated on acidification of a concentrated aqueous solution of V, was stable, but attempts at bromination led to decomposition. Stable dimethylol derivatives, IX and X, were also obtained by treatment of III and V with formaldehyde and mineral acid; yields were 70 and 84%, respectively.



$$Z{-}C(NO_2)_2{-}\underset{CN}{CH}{-}O{-}CH_2{-}O{-}\underset{CN}{CH}{-}C(NO_2)_2{-}Z$$

VI, Z = H
VII, Z = Br
IX, Z = CH_2OH



$$Z{-}C(NO_2)_2{-}\underset{CONH_2}{CH}{-}O{-}CH_2{-}O{-}\underset{CONH_2}{CH}{-}C(NO_2)_2{-}Z$$

VIII, Z = H
X, Z = CH_2OH

As anticipated (*1*), the dimethylol derivatives underwent rapid and quantitative deformylation in dilute aqueous alkali; ultraviolet spectra of III and IX in such media were identical, as were spectra of V, VIII, and X. Ultraviolet absorption maxima were at 349 mμ for III and at 355.5 mμ for V, representing hypsochromic displacements of 14 and 7.5 mμ, respectively, relative to bis(2,2-dinitroethyl) formal dianion, which exhibits λ_{max} (log ε) = 363 mμ (4.52). These shifts on β-substitution by cyano and carbamyl are in directions and of magnitudes such as would be predicted from spectra-structure relationships in the 1,1-dinitrocarbanion series (*4*).

Infrared spectra of III, V, VII, and VIII, reported and interpreted in detail in an earlier paper (*5*), were also completely consistent with the assigned structures.

EXPERIMENTAL

CAUTION!. The compounds described herein are explosive in nature and appropriate precautions should be taken in their handling. Further, appreciable amounts of hydrogen cyanide are generated in the preparation of III. This combination of explosive and toxic gas hazards dictates extreme care in designing and carrying out experiments.

Dipotassium Bis(1-cyano-2,2-dinitroethyl) Formal Monohydrate (III). Addition of 74.8 grams (0.20 mole) of bis(2,2,2-trinitroethyl) formal (*8*) to 2500 ml. of stirred methanol containing 65.0 grams (1.0 mole) of potassium cyanide resulted in immediate solution, followed within one minute by the separation of a yellow precipitate. After stirring the mixture 3½ hours at room temperature, the crude product was filtered, washed with methanol and with ether, and air dried. It amounted to 68.5 grams and showed $\lambda_{max}^{H_2O}$ 350 mμ. After six days in the refrigerator, the mother liquor deposited a further 7.1 grams, $\lambda_{max}^{H_2O}$ 351.5 mμ.

For separation of the dinitrile from amide-nitrile and diamide, advantage was taken of its lesser solubility in water. Portionwise addition of the first crop to 200 ml. of water with stirring led initially to formation of an amorphous tar, which on continued stirring again turned crystalline. After 30 minutes of stirring, the mixture was filtered and the product washed with methanol and with ether. Thus was obtained 53.0 grams (61.8%) of III, $\lambda_{max}^{H_2O}$ (log ε) 349 mμ (4.48). A single recrystallization from water gave the analytical sample as small pale yellow equant crystals, $\lambda_{max}^{H_2O}$ (log ε) 349 mμ (4.49). Anal. Calcd. for $K_2C_7H_4N_6O_{10}\cdot H_2O$: C, 19.60; H, 1.40; N, 19.60. Found: C, 19.74, 19.85; H, 1.12, 1.32; N, 19.54, 19.53.

A second crop (3.0 grams), obtained on cooling the above aqueous mother liquor, was combined with the second crop from the original reaction mixture and converted to pure diamide as follows. The material was dissolved in 150 ml. of hot 3% aqueous potassium hydroxide, the solution filtered hot, 15 grams of potassium acetate added, and the solution cooled, whereupon it deposited 7.2 grams (7.4%) of dipotassium bis(1-carbamyl-2,2-dinitroethyl) formal dihydrate (V), $\lambda_{max}^{H_2O}$ (log ε) 355.5 mμ (4.48). A single recrystallization from water gave the analytical sample as small well-formed yellow platelets with unchanged spectrum. Anal. Calcd. for $K_2C_7H_8N_6O_{12}\cdot 2H_2O$: C, 17.41; H, 2.49; N, 17.41. Found: C, 17.40, 17.62; H, 2.38, 2.53; N, 17.02, 17.09.

A similar run, wherein the total crude product was converted to diamide by dissolving in 1000 ml. of hot 3% aqueous potassium hydroxide and adding 100 grams potassium acetate before cooling, led to V in 80% over-all yield.

Bis(1-cyano-2-bromo-2,2-dinitroethyl) Formal (VII). A stirred suspension of 1.2 grams of III in 50 ml. of ether was treated with bromine until the color was no longer dispersed. The mixture was filtered from potassium bromide, cyclohexane was added, and the solution was concentrated to yield 0.76 gram of product as clusters of fine white platelets, m.p. 132–33° C. Anal. Calcd. for $C_7H_4Br_2N_6O_{10}$: C, 17.08; H, 0.81; N, 17.08; Br, 32.55; mol. wt., 492. Found: C, 16.79, 17.14; H, 0.72, 0.82; N, 17.40, 17.10; Br, 32.67, 32.81; mol. wt., 493, 501.

Bis(1-cyano-2,2-dinitro-3-hydroxypropyl) Formal (IX). Two grams of paraformaldehyde was stirred with 50 ml. of hot water containing 2 ml. of concentrated hydrochloric acid to depolymerize. The solution was filtered hot and 2.0 grams of III was added. This dissolved immediately, and soon thereafter the product began to precipitate, 1.28 grams (70%), m.p. 119–23° C. (dec.). Recrystallization from ether-cyclohexane afforded 1.15 grams of IX as clusters of white platelets, m.p. 137–38° C. (dec.), $\lambda_{max}^{dil\ Na_2CO_3}$ (log ε) 349 mμ (4.49). A further recrystallization from ether-cyclohexane gave the analytical sample, m.p. 138.5–39° C. (dec.) Anal. Calcd. for $C_9H_{10}N_6O_{12}$: C, 27.40; H, 2.54; N, 21.30. Found: C, 27.89, 27.70; H, 2.57, 2.78; N, 20.89.

When a similar procedure was applied to 2.9 grams of V, 2.16 grams (84%) of bis(1-carbamyl-2,2-dinitro-3-hydroxypropyl) formal (X) was obtained. Two recrystallizations from methanol-benzene gave the analytical sample, m.p. 153.5–54° C. (frothing), $\lambda_{max}^{dil\ Na_2CO_3}$ (log ε) 355.5 mμ (4.48). Anal. Calcd. for $C_9H_{14}N_6O_{14}$: C, 25.12; H, 3.27; N, 19.50; mol. wt., 430. Found: C, 24.91, 25.22; H, 3.21, 3.01; N, 18.62, 18.73; mol. wt. 423, 429.

Bis(1-carbamyl-2,2-dinitroethyl) Formal (VIII). The diamide, V, 1.24 grams, was dissolved in 25 ml. of hot water, the solution cooled to 30° C., 4 ml. of concentrated hydrochloric acid added, and the solution allowed to stand, which led to precipitation of VIII as fine white needles, 0.91 gram (92%), m.p. 119–19.5° C. (dec.), $\lambda_{max}^{dil\ KOH}$ (log ε) 355.5 mμ (4.48). Anal. Calcd. for $C_7H_{10}N_6O_{12}$: C, 22.69; H, 2.70; N, 22.69. Found: C, 22.42, 22.69; H, 2.58, 2.49; N, 22.23, 22.22.

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