Infrared spectra. The infrared spectra of the compounds listed in Table I were recorded from a potassium bromide disk on a Perkin-Elmer, Model 21, recording spectrophotometer with sodium chloride optics. Other spectra were taken on the above instrument or a Baird Associates infrared spectrophotometer.

Acknowledgment. The authors wish to thank Dr. F. E. Cislak, Reilly Tar & Chemical Co., Indianapolis, Ind., for a generous gift of 2- and 4-picoline *N*-oxide.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, AEROJET-GENERAL CORP.]

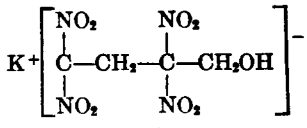
The Preparation and Reactions of 1,1,3,3-Tetranitropropane[1]

K. KLAGER, J. P. KISPERSKY, AND E. HAMEL

Received April 11, 1961

1,1,3,3-Tetranitropropane has been prepared by deformylation of aqueous potassium *aci*-2,2,4,4-tetranito-1-butanol (I). The alcohol I was prepared by partial acidification of potassium *aci*-2,2-dinitroethanol. 1,1,3,3-Tetranitropropane is a low-melting unstable solid which in the form of its dipotassium salt was found to undergo reactions typical of terminal *gem*-dinitro groups. It reacted as a bifunctional compound upon condensation with formaldehyde, yielding 2,2,4,4-tetranitro-1,5-pentanediol; with methyl acrylate, however, it reacted as a monofunctional compound, yielding only methyl potassium *aci*-4,4,6,6-tetranitrohexanoate.

Herzog, Gold, and Geckler[2] described a new method for the preparation of potassium *aci*-2,2-dinitroethanol and a subsequent paper dealt with the reactions of this compound with α,β-unsaturated carbonyl compounds and formaldehyde.[3] Duden and Pondorf[4] had previously reported that the acidification of potassium dinitroethanol with excess mineral acid, in addition to the gases nitrogen, nitric oxide, nitrogen dioxide, carbon monoxide and carbon dioxide, gave a poor yield of a crystalline compound of unknown structure having the empirical formula $C_6H_2N_4O_7$. We have found that upon partial acidification, potassium *aci*-2,2-dinitroethanol is converted into potassium *aci*-2,2,4,4-tetranitro-1-butanol (I). The

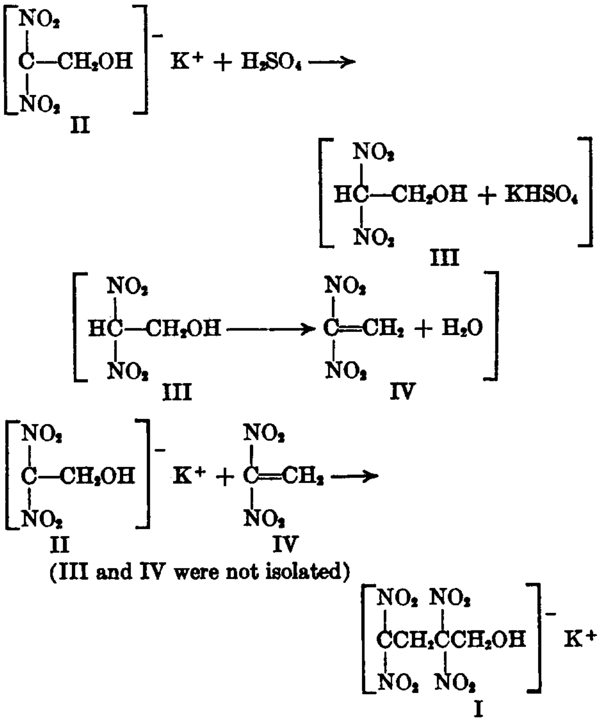


$$K^+\left[\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2OH\right]^-$$

I

facile formation of the 1,1,3,3-tetranitropropane structure stimulated a study of the influence of *p*H upon the yield of I from aqueous potassium *aci*-2,2-dinitroethanol solutions. From this study it was concluded that the optimum conditions were a *p*H of 4, 20°, and two and one-half hours' reaction time. Under these conditions, potassium *aci*-2,2-dinitroethanol was converted into I in 70% yield. The crystalline compound reported by Duden and Pondorf[4] was not isolated under these conditions.

The formation of I can be explained by the following reaction scheme:



$$\underset{II}{\left[\underset{NO_2}{\overset{NO_2}{C}}-CH_2OH\right]^-}K^+ + H_2SO_4 \longrightarrow \underset{III}{\left[H\underset{NO_2}{\overset{NO_2}{C}}-CH_2OH + KHSO_4\right]}$$

$$\left[\underset{III}{H\underset{NO_2}{\overset{NO_2}{C}}-CH_2OH} \longrightarrow \underset{IV}{\underset{NO_2}{\overset{NO_2}{C}}=CH_2} + H_2O\right]$$

$$\underset{II}{\left[\underset{NO_2}{\overset{NO_2}{C}}-CH_2OH\right]^-}K^+ + \underset{IV}{\underset{NO_2}{\overset{NO_2}{C}}=CH_2} \longrightarrow \underset{I}{\left[\underset{NO_2}{\overset{NO_2}{C}}CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH\right]^-}K^+$$

(III and IV were not isolated)

The potassium salt (II) was partially converted, at a *p*H of 4, into 2,2-dinitroethanol (III). Elimination of water from III would give 1,1-dinitroethylene (IV), which as an α,β-unsaturated nitro compound would react with II in a Michael addition-type reaction forming potassium tetranitro-1-butanol (I). The formation of 1,1-dinitroethylene as a reactive intermediate has been postulated in similar reactions.[5,6]

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[1] This work was performed under a contract with the Office of Naval Research.

[2] L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).

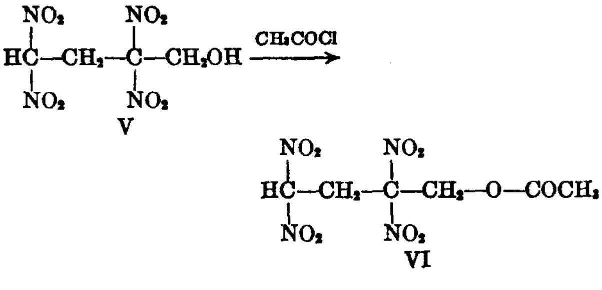
[3] K. Klager, *J. Org. Chem.*, **16**, 161 (1951).

[4] P. Duden and G. Pondorf, *Ber.*, **38**, 2031 (1905).

[5] M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958).

[6] L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957).

Potassium *aci*-2,2,4,4-tetranitro-1-butanol (I) was used as a starting material for the preparation of compounds containing the 1,1,3,3-tetranitropropane structure. Acidification with mineral acid converted I to 2,2,4,4-tetranitro-1-butanol (V), m.p. 32–33°. It is an unstable compound which was found to decompose at refrigerator temperature yielding oxalic acid.

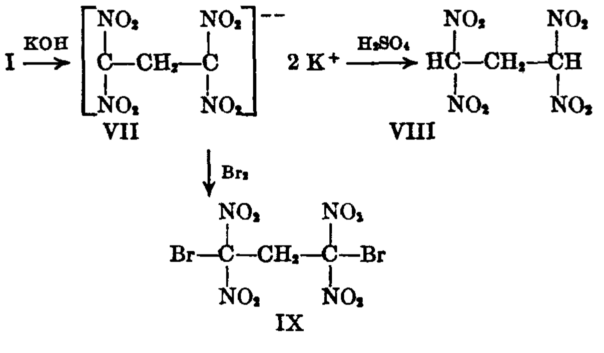


$$HC(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2OH \xrightarrow{CH_3COCl} HC(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2{-}O{-}COCH_3$$

V

VI

Acetylation of V with acetyl chloride yielded the stable crystalline acetate (VI), m.p. 58–59°, which was previously obtained by a different procedure.[5] Treating I with aqueous potassium hydroxide caused deformylation with the formation of dipotassium *aci*-1,1,3,3-tetranitropropane (VII). Acidification of VII with cold dilute sulfuric yielded 1,1,3,3-tetranitropropane (VIII), m.p. 13–15°. It is a very unstable compound which readily decomposes above its melting temperature. Bromination of VII gave the stable compound 1,3-dibromo-1,1,3,3-tetranitropropane (IX), m.p. 67–68°. The dibromo compound is the most characteristic derivative of the 1,1,3,3-tetranitropropane structure; traces of tetranitropropane salts may be detected by bromination. In a similar manner chlorination of VII yielded 1,3-dichloro-1,1,3,3-tetranitropropane, m.p. 35°.



$$I \xrightarrow{KOH} 2K^+\left[C(NO_2)_2{-}CH_2{-}C(NO_2)_2\right]^{--} \xrightarrow{H_2SO_4} HC(NO_2)_2{-}CH_2{-}CH(NO_2)_2$$

$$VII \xrightarrow{Br_2} Br{-}C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}Br$$

VII

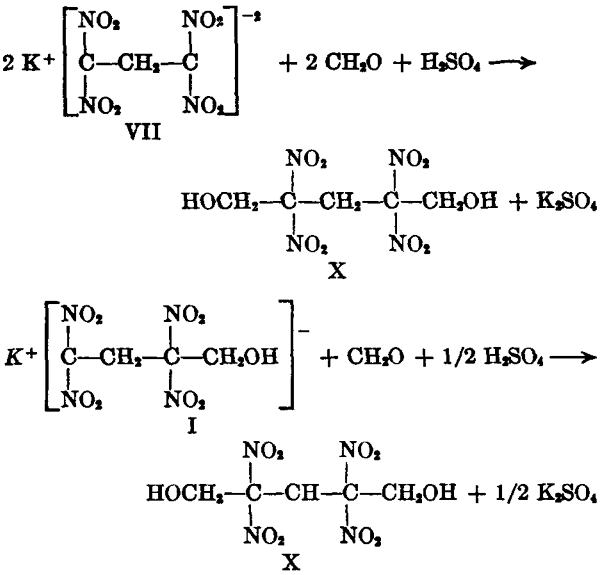
VIII

IX

Treating the dibromide (IX) with alkali iodides or cyanides yielded the corresponding dibasic salts of 1,1,3,3-tetranitropropane (VII).[7]

Inasmuch as VIII has two acidic hydrogen atoms it should exhibit reactions of both a mono- and bifunctional reagent. With one mole of formaldehyde both VII and VIII formed the unstable 2,2,4,4-tetranitro-1-butanol (V). Treating either VII or VIII with two moles of formaldehyde and mineral acid gave 2,2,4,4-tetranitro-1,5-pentanediol (X), an unstable crystalline compound, m.p. 95–97° dec.

However, X was more conveniently prepared by the acidification of I in the presence of formaldehyde.



$$2K^+\left[C(NO_2)_2{-}CH_2{-}C(NO_2)_2\right]^{-2} + 2\,CH_2O + H_2SO_4 \longrightarrow HOCH_2{-}C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2OH + K_2SO_4$$

$$K^+\left[C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2OH\right]^- + CH_2O + 1/2\,H_2SO_4 \longrightarrow HOCH_2{-}C(NO_2)_2{-}CH{-}C(NO_2)_2{-}CH_2OH + 1/2\,K_2SO_4$$

VII

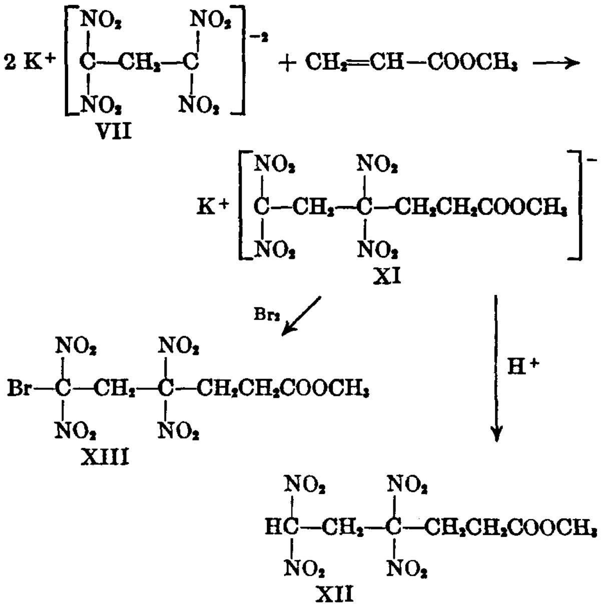
X

I

X

2,2,4,4-Tetranitro-1,5-pentanediol (X) could be quantitatively titrated as a dibasic acid.

Dipotassium *aci*-1,1,3,3-tetranitropropane (VII) was found to condense with conjugated unsaturated carbonyl compounds but only as a monofunctional reagent. With methyl acrylate VII gave methyl potassium *aci*-4,4,6,6-tetranitrohexanoate (XI).



$$2K^+\left[C(NO_2)_2{-}CH_2{-}C(NO_2)_2\right]^{-2} + CH_2{=}CH{-}COOCH_3 \longrightarrow K^+\left[C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2CH_2COOCH_3\right]^-$$

$$XI \xrightarrow{Br_2} Br{-}C(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2CH_2COOCH_3$$

$$XI \xrightarrow{H^+} HC(NO_2)_2{-}CH_2{-}C(NO_2)_2{-}CH_2CH_2COOCH_3$$

VII

XI

XIII

XII

Acidification of the salt (XI) with sulfuric acid converted it into methyl 4,4,6,6-tetranitrohexanoate (XII), a stable crystalline compound, m.p. 36–37°. Bromination of the potassium salt of methyl 4,4-6,6-tetranitrohexanoate, gave methyl 6-bromo-4,4,6,6-tetranitrohexanoate (XIII). All attempts to

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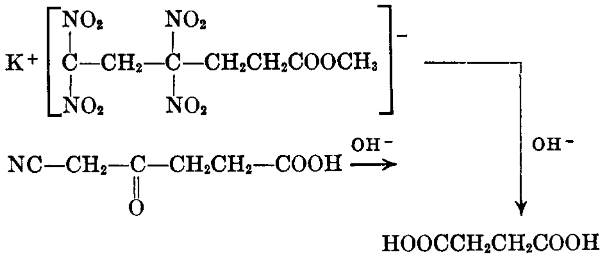
(7) K. Klager, *Anal. Chem.*, **23**, 534 (1951).

force the condensation of dipotassium *aci*-1,1,3,3-tetranitropropane with two moles of methyl acrylate, or the condensation of methyl potassium *aci*-4,4,6,6-tetranitrohexanoate with methyl acrylate or acrylonitrile, caused degradation yielding oils of low nitrogen content. The same result was obtained when methyl 4,4,6,6-tetranitrohexanoate was treated with methyl acrylate in the presence of an organic base such as Triton B or triethylamine. These results are in contrast with those obtained when formaldehyde was added to VII with the rapid formation of the 2:1 adduct X. This behavior may be due to steric factors. Molecular models of I and XI show that the carbon atom bearing the terminal *gem*-dinitro group in XI is shielded considerably by the bulk of the methyl propionate portion of the molecule whereas little shielding is provided by the hydroxymethyl portion of I.

Treating the potassium salt, XI, with hot aqueous alkali followed by acidification, resulted in the evolution of carbon dioxide and nitric oxide. From the aqueous solution, there was isolated succinic acid. The portion of the molecule containing the nitro groups was oxidatively degraded to a carboxyl group, forming succinic acid. A similar alkaline treatment of 5-cyano-4-ketovaleric acid also yielded succinic acid.[8]



EXPERIMENTAL[9]

Dipotassium aci-1,1,3,3-tetranitropropane (VII). (*A*) *From potassium aci-2,2-dinitroethanol.* Potassium *aci*-2,2-dinitroethanol[2] (200 g.) was added to 500 ml. of water and cooled to 20°. Seventy-five milliliters of 30% sulfuric acid was added dropwise to the suspension giving a *p*H of 4.2. The temperature was kept between 18–21° by means of external cooling. After 2.5 hr., a color change from yellow to orange was observed. The mixture was then cooled to 0° and 20% aqueous potassium hydroxide was added dropwise until a *p*H of 9–10 was attained. The precipitated salt was filtered and washed with ice water, 50% methanol, and finally methanol. Recrystallization from water at 75–80° gave 225 g. (yield 75%) of salt, m.p. 274° dec.

Anal. Calcd. for $C_3H_2K_2N_4O_8$: C, 12.00; H, 0.67; N, 18.65. Found: C, 12.52; H, 1.01; N, 20.02.

(B) *From 1,3-dibromo-1,1,3,3-tetranitropropane* (IX). A solution of 11.7 g. of 1,3-dibromo-1,1,3,3-tetranitropropane in 50 ml. of methanol was cooled to 0–10°. To this was slowly added a solution of 4 g. of potassium cyanide in 15 ml. of water and 6 ml. of methanol. After 30 min. the salt which precipitated was filtered. There was obtained 9.2 g. (yield 91%) of salt, m.p. 274° dec.

When sodium cyanide was used, the disodium salt of 1,1,3,3-tetranitropropane was obtained.

In place of the alkali cyanides, the corresponding iodides may be used if the conversion is carried out in methanol solution.

1,1,3,3-Tetranitropropane (VIII). To a suspension of 5 g. of dipotassium *aci*-1,1,3,3-tetranitropropane in 20 ml. of water cooled to 0° was added portionwise, a solution of 2 g. of sulfuric acid in 12 ml. of water. The salt was converted to a yellow, oily solid. The product was collected on a precooled funnel, and quickly recrystallized from ethyl chloride at Dry Ice temperature. The yellow solid melted at 13–15° dec.

Anal. Calcd. for $C_3H_4N_4O_8$: C, 16.08; H, 1.78; N, 25.00. Found: C, 16.05; H, 2.56; N, 23.70.

Although the analytical value for nitrogen is poor, it is considered satisfactory for a compound of such poor thermal stability.

1,3-Dibromo-1,1,3,3-tetranitropropane (IX). A suspension of 38 g. of dipotassium *aci*-1,1,3,3-tetranitropropane (containing 30% methanol) in 200 ml. of water was cooled to 0°, and 8 ml. of bromine added dropwise until an excess of bromine was noticeable. The white precipitate which formed was recrystallized from boiling hexane giving 21.2 g. (yield 71%); m.p. 66–67°.

Anal. Calcd. for $C_3H_2Br_2N_4O_8$: C, 9.42; H, 0.52; Br, 41.85; N, 14.66. Found: C, 9.97; H, 0.93; Br, 42.01; N, 14.31.

1,3-Dichloro-1,1,3,3-tetranitropropane. A solution of 3 g. of dipotassium *aci*-1,1,3,3-tetranitropropane in 100 ml. of water was cooled to 0° and a slow stream of chlorine was introduced. A colorless oil was obtained which soon crystallized. The product was recrystallized from hexane at Dry Ice–acetone temperature. A white crystalline solid, 2.2 g. (yield 75%), was obtained; m.p. 35–35.5°.

Anal. Calcd. for $C_3H_2Cl_2N_4O_8$: C, 12.30; H, 0.69; N, 19.12. Found: C, 12.56; H, 0.74; N, 19.62.

Potassium aci-2,2,4,4-tetranitro-1-butanol (I). A solution of potassium *aci*-2,2-dinitroethanol (480 g., containing 30% methanol) in 1200 ml. of water was cooled to 18–20°. One hundred and thirty-six milliliters of 30% sulfuric acid was added dropwise over a period of 30 min. until the *p*H of the solution was 4.0 to 4.2. After 2 hr., the mixture was cooled to 3° and filtered. The product was immediately washed with 1 l. of methanol and stored in the refrigerator. There was obtained 240 g. (dry basis) (yield 63%) of salt; m.p. 110° dec.

2,2,4,4-Tetranitro-1-butanol (V). Potassium *aci*-2,2,4,4-tetranitro-1-butanol (5.84 g.) was suspended in 30 ml. of water, and 5 ml. of 30% sulfuric acid was added at room temperature. The aqueous solution was extracted twice with methylene chloride, yielding 3.55 g. of yellow viscous oil. The oil was crystallized from methylene chloride at Dry Ice-acetone temperature giving 2.79 g. (yield 55%) of 2,2,4,4-tetranitro-1-butanol; m.p. 35–36°.

Anal. Calcd. for $C_4H_6N_4O_9$: C, 18.90; H, 2.48; N, 22.05. Found; C, 18.89; H, 2.46; N, 23.10.

2,2,4,4-Tetranitro-1-butyl acetate (VI). To a solution of crude 2,2,4,4-tetranitro-1-butanol (3.35 g.) in 5 ml. of methylene chloride was added a solution of 2 g. of acetyl chloride in 5 ml. of methylene chloride and the mixture was brought to reflux. After 1.5 hr. the solution was evaporated and the oily residue which remained (3.51 g.) was crystallized from methylene chloride at −70 to −80° yielding the acetate, 2.85 g. (yield 73%); m.p. 58–59°.

Anal. Calcd. for $C_6H_8N_4O_{10}$: C, 27.33; H, 2.72; N, 18.92; Equiv. wt. 296. Found: C, 24.62; H, 2.89; N, 18.50; Equiv. wt. 297, 298.

2,2,4,4-Tetranitro-1,5-pentanediol (X). Potassium *aci*-2,2,4,4-tetranitro-1-butanol (125 g. containing 20% methanol) was added to 300 ml. of water, and 28.8 ml. of formalin. The slurry was cooled to 5° and 70 ml. of 30% sulfuric acid added dropwise over a period of 30 min. After an additional 30 min. at 0 to 5°, 20 ml. more of 30% sulfuric acid was added dropwise at a rapid rate. The cooling bath was removed and the solution was allowed to gradually warm up to 20° over

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(8) J. Thiele and H. Landers, *Ann.*, **369**, 310 (1909).

(9) Microanalyses are by Elek's Microanalytical Laboratory, Los Angeles, Calif. Melting points are uncorrected.

a 2-hr. period. After an additional 2 hr. at this temperature the resulting mixture was extracted with four 150-ml. portions of ether. The ether was dried and distilled *in vacuo* leaving a residue of 85 g. of product. The solid was recrystallized from chloroform giving 35 g. (yield 35%) of white 2,2,4,4-tetranitro-1,5-pentanediol; m.p. 97–99° dec.

Anal. Calcd. for $C_5H_8N_4O_{10}$: C, 21.13; H, 2.84; N, 19.07. Found: C, 21.55; H, 3.26; N, 19.02.

Methyl potassium aci-4,4,6,6-tetranitrohexanoate (XI). To a solution of 100 g. of damp (20%) methanol) dipotassium *aci*-1,1,3,3-tetranitropropane in 200 ml. of water was added 80 g. of methyl acrylate at room temperature. After 2 hr. at 45–50° the mixture was refluxed (70–72°) until all the starting material disappeared. The mixture was allowed to stand overnight and the crystals which separated were filtered, washed with ice water, 50% methanol and methanol giving 47 g. (yield 49%) of salt; m.p. 140° dec.

Anal. Calcd. for $C_7H_9N_4O_{10}K$: C, 24.14; H, 2.61; N, 16.09. Found: C, 23.79; H, 2.62; N, 17.02.

Methyl 4,4,6,6-tetranitrohexanoate (XII). To 4 g. of XI in 50 ml. of water at 60° was added 30% sulfuric acid to a *p*H of 2. The resulting suspension was extracted with methylene chloride. Evaporation of the solvent gave 3.2 g. of a resinous residue which was crystallized from isopropyl ether at Dry Ice-acetone temperature; m.p. 36–37°.

Anal. Calcd. for $C_7H_{10}N_4O_{10}$: C, 27.10; H, 3.25; N, 18.06; equiv. wt., 310. Found: C, 27.75; H, 3.58; N, 17.90; equiv. wt., 317.

Methyl 6-bromo-4,4,6,6-tetranitrohexanoate (XIII). Bromine was added dropwise to a suspension of 1 g. of XI in 30 ml. of water until the bromine color persisted. A yellow oil precipitated, which soon crystallized. Extraction with ether gave a crude product which was recrystallized from hexane at −70°. The bromide, 0.8 g. (yield 72%), m.p. 65–66°, exhibited a depression when mixed with authentic 1,3-dibromo-1,1,3,3-tetranitropropane (m.p. 66–67°) to 45°.

Anal. Calcd. for $C_7H_9N_4O_{10}Br$: C, 21.06; H, 2.31; N, 14.04; Br, 20.60. Found: C, 21.07; H, 2.24; N, 14.35; Br, 19.79; 19.68.

Reaction of XI *with aqueous potassium hydroxide.* Methyl potassium *aci*-4,4,6,6-tetranitrohexanoate (10.5 g.) was dissolved in 105 ml. of water, heated to 70°, and 25 ml. of 20% aqueous potassium hydroxide was added. The color changed from yellow to deep red and after 2.5 hr. the color turned orange. Upon cooling to room temperature and acidification with 30% sulfuric acid, a vigorous gas evolution occurred (carbon dioxide, nitric oxide, nitrogen dioxide and probably nitrous oxide were liberated). The solution was extracted with ether for 7 hr. and the residue (2.6 g.) from the ether extract, m.p. 188–189°, was sublimed *in vacuo*. Succinic acid, 2.4 g. (yield 67%), was obtained which did not show a depression when mixed with authentic succinic acid, m.p. 188–189°.

Anal. Calcd for $C_4H_6O_4$: equiv. wt. 59.05. Found: equiv. wt. 59.01.

AZUSA, CALIF.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY]

Reactions of Polynitroalkanes with Hot Mineral Acids

MORTIMER J. KAMLET, LLOYD A. KAPLAN, AND JOSEPH C. DACONS

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On refluxing with constant boiling hydrochloric acid, 1-nitroalkanes and 1,1-dinitroalkanes are converted to carboxylic acids with the same carbon skeleton. The internal *gem*-dinitro function is stable to these conditions as is the terminal trinitromethyl group except when alpha to an activated methylene group. With compounds of the latter type the chain is degraded by one carbon atom and a carbonyl group is formed.

Hot mineral acids convert primary nitroalkanes to hydroxamic acids and thence to the corresponding carboxylic acids. The transformation is known as the Victor Meyer reaction.[1] Secondary nitroalkanes are generally stable to hot mineral acids in their *normal*-forms, but may readily be hydrolyzed to carbonyl compounds under substantially milder conditions if first converted to the *aci*-forms by formation and neutralization of their alkali salts (Nef reaction[2]). We wish now to describe the effect of Victor Meyer reaction conditions on terminal and internal *gem*-dinitroalkanes and on terminal trinitroalkanes and their derivatives.

We have observed that when 1-(2,4-dinitrophenyl)-3-nitropropane or 1,1-dinitro-3-(2,4-dinitrophenyl)propane was suspended in constant boiling hydrochloric acid and the mixture heated to reflux, complete solution ensued within several hours. In either case the same product, 2,4-dinitrohydrocinnamic acid precipitated in fair yield when the solution was cooled.

In the former instance hydroxylamine hydrochloride could be isolated from the mother liquor; this represents a typical example of the Victor Meyer reaction. The latter case, however, exemplifies a new type of chemical transformation. Although the eventual product is the same as with the mononitro compound, the hydroxamic acid is not an intermediate, and a somewhat different mechanism probably applies.

The reaction appears to be general for 1,1-dinitro compounds and their salts. Thus, in refluxing hydrochloric acid, α,α,*m*-trinitrotoluene was converted to *m*-nitrobenzoic acid (80%), potassium 4,4-dinitrobutyramide to succinic acid (80%), potassium methyl 4,4-dinitrobutyrate to succinic acid (73%), potassium 4,4-dinitro-2-butenamide to fumaric acid (34%), and potassium methyl 4,4-dinitro-2-butenoate to fumaric acid (10%). With 1,1-dinitro-3-phenylpropane the anticipated hydrocinnamic acid was not obtained. Instead 1-indanone, which

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[1] T. W. J. Taylor and W. Baker, *Sidgwick's Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1945, pp. 230–236.

[2] For an excellent review of the Nef reaction see W. E. Noland, *Chem. Revs.*, 55, 137 (1955).