[Contribution from Research Laboratory of Aerojet Engineering Corp.]

THE CHEMISTRY OF ALIPHATIC DINITRO COMPOUNDS. II. METHYL δ-HYDROXY-γ,γ-DINITROVALERATE[1]

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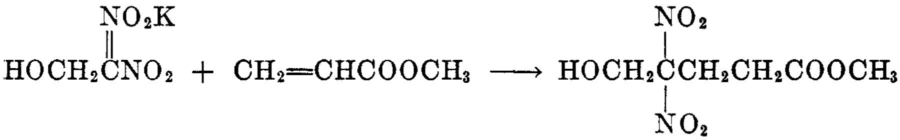
The Michael reaction of potassium dinitromethane and potassium dinitroethanol with two moles of methyl acrylate has been described by Herzog, Gold, and Geckler (1). It has been found that under suitable conditions, potassium dinitroethanol can be made to react with one mole of methyl acrylate to form methyl δ-hydroxy-γ,γ-dinitrovalerate (I).

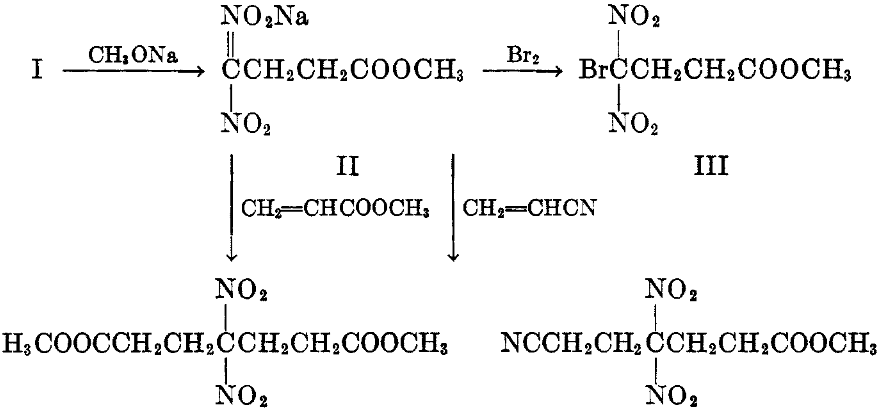


$$HOCH_2\overset{\overset{NO_2K}{\|}}{C}NO_2 + CH_2{=}CHCOOCH_3 \longrightarrow HOCH_2\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}CH_2CH_2COOCH_3$$

I

In order to stop the reaction at this stage, it is necessary to use equivalent quantities of the two reactants and to carry out the reaction at pH 5–6 by means of a buffer such as sodium acetate.

Duden and Ponndorf (2) showed that dinitro alcohols, such as 2,2-dinitroethanol, exist in equilibrium with the dinitroparaffin and formaldehyde. The elimination of formaldehyde is favored by the addition of base, which shifts the equilibrium to form the corresponding *aci*-salts. Therefore by treatment of I with a base, the *aci*-sodium salt of methyl γ,γ-dinitrobutyrate (II) was formed. Because of the difficulty of purifying II, it was characterized as the corresponding bromide, methyl γ-bromo-γ,γ-dinitrobutyrate (III).



$$\text{I} \xrightarrow{CH_3ONa} \underset{\underset{NO_2}{|}}{\overset{\overset{NO_2Na}{\|}}{C}}CH_2CH_2COOCH_3 \xrightarrow{Br_2} Br\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}CH_2CH_2COOCH_3$$

II III

II $\xrightarrow{CH_2=CHCOOCH_3}$ $H_3COOCCH_2CH_2\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}CH_2CH_2COOCH_3$

II $\xrightarrow{CH_2=CHCN}$ $NCCH_2CH_2\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}CH_2CH_2COOCH_3$

IV

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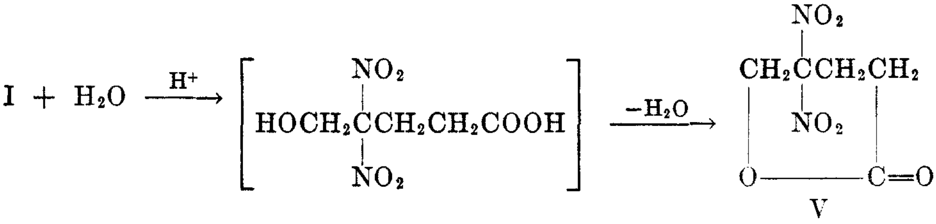
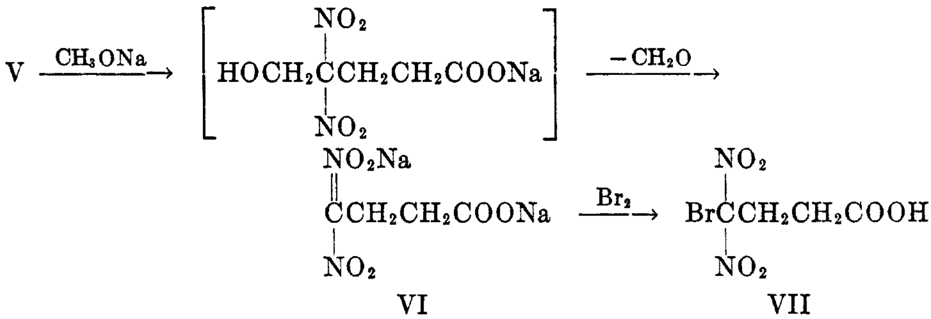
II was also found to be capable of undergoing the Michael reaction. Treatment of II with methyl acrylate or with acrylonitrile yielded dimethyl 4,4-dinitroheptanedioate or methyl 6-cyano-4,4-dinitrohexanoate (IV) respectively.

Upon heating methyl δ-hydroxy-γ,γ-dinitrovalerate with 18% hydrochloric acid, γ,γ-dinitro-δ-valerolactone (V) was formed.



The structure of V was proved in the following manner:



Lactones upon treatment with base normally suffer ring opening with the formation of salts of ω-hydroxy acids. Thus, V upon hydrolysis with sodium methoxide would be expected to lead to the sodium salt of 5-hydroxy-4,4-dinitrobutyrate. However, in the presence of excess sodium methoxide the molecule was further degraded with the elimination of formaldehyde and disodium γ,γ-dinitrobutyrate (VI) was formed. VI was characterized by conversion to the corresponding bromo acid, γ-bromo-γ,γ-dinitrovaleric acid (VII).

EXPERIMENTAL

Methyl δ-hydroxy-γ,γ-dinitrovalerate (I). In a three-necked flask fitted with a stirrer, thermometer, and dropping-funnel were placed 34.8 g. of potassium dinitroethanol and 100 cc. of water. During five minutes 17 g. of methyl acrylate was added to the mixture. The reaction mixture was kept well agitated while a solution of 12 g. of acetic acid and 12 g. of water was added during one hour. The temperature of the reaction mixture did not exceed 30°. After three hours, almost all of the yellow potassium salt had disappeared. The solution which had become brown was stirred for three more hours and then allowed to stand overnight. The product was extracted with ether. The ether was washed with saturated sodium chloride solution, sodium bicarbonate solution, and then again with saturated sodium chloride solution. Upon evaporation of the ether, 8.94 g. (20.1%) of crude methyl δ-hydroxy-γ,γ-dinitrovalerate remained, n_{D}^{24} 1.4738. The compound cannot be distilled in a high vacuum without some decomposition.

aci-Sodium salt of methyl γ,γ-dinitrobutyrate (II). Using similar equipment, 57.2 g. of methyl δ-hydroxy-γ,γ-dinitrovalerate was dissolved in 150 cc. of methanol. A solution of

16 g. of sodium methoxide in 80 cc. of methanol was added dropwise while the reaction mixture was kept at 0–10°. A yellow-brown precipitate formed during the addition. The precipitate was washed with methanol and ether. In this way 36 g. (60%) of bright yellow crystals of the *aci*-sodium salt of methyl γ,γ-dinitrobutyrate was obtained.

This salt was characterized by conversion to *methyl γ-bromo-γ,γ-dinitrobutyrate* (III). Into a solution of 4.28 g. of the *aci*-sodium salt of methyl γ,γ-dinitrobutyrate in 25 cc. of water was slowly dropped 3.2 g. of bromine. The yellow solution turned reddish brown, then colorless, and a yellow oil separated. The mixture was extracted with ether, this was washed with water, and dried over sodium sulfate. The ether was evaporated and the residue distilled in an air-bath at 110–120°/2 mm.; 5.15 g. (95%) of colorless liquid which crystallized on cooling, m.p. 17–18° was collected.

Anal. Calc'd for $C_5H_7BrN_2O_6$: C, 22.15; H, 2.60; N, 10.34; Br, 29.49.
Found: C, 22.37; H, 2.68; N, 10.49; Br, 29.58, 29.92.

Methyl 6-cyano-4,4-dinitrohexanoate (IV). In the usual apparatus were placed 15 g. of the damp *aci*-sodium salt of methyl γ,γ-dinitrobutyrate (equivalent to 12 g. of dry salt) and 25 cc. of water. To this was added 9 g. of acrylonitrile with stirring. The reaction mixture was then heated to 45–50° for eight hours. The yellow solution gradually turned brown and an oily phase separated. The solution was at *p*H 8 at the end of the reaction. The mixture was extracted with ether, and the ether evaporated, leaving 7.8 g. of dark brown oil. The oil was dissolved in 10 cc. of methanol and cooled in a Dry Ice-acetone bath to induce crystallization. After treatment with decolrizing charcoal, one more crystallization from methanol and one from ether, colorless crystals, m.p. 50° were obtained.

Anal. Calc'd for $C_8H_{11}N_3O_6$: C, 39.19; H, 4.51.
Found: C, 40.08; H, 4.55.

Dimethyl 4,4-dinitroheptanedioate. A mixture of 4.28 g. of the sodium salt of methyl γ,γ-dinitrobutyrate, 1.70 g. of methyl acrylate, and 10 cc. of water was stirred for 6 hours and then allowed to stand overnight. The mixture was extracted with ether and the extract dried with sodium sulfate. After evaporation of the solvent, 2.78 g. (45%) of dimethyl 4,4-dinitroheptanedioate was obtained. The melting point, 46°, agreed with that reported previously (1) and a mixed melting point with an authentic sample showed no depression.

γ,γ-Dinitro-δ-valerolactone (V). A mixture of 8.93 g. of methyl γ,γ-dinitro-δ-hydroxyvalerate and 45 cc. of 18% hydrochloric acid (1:1) was heated for 30 minutes on a steam-bath. The oil which at first was insoluble dissolved slowly. The solution was then extracted with ether and the ether solution washed until neutral with saturated sodium chloride and sodium bicarbonate solution. The ether was evaporated and the residue distilled in an air-bath at 130–135°/0.005 mm. After redistillation 3.2 g. of a nearly colorless liquid was obtained which was crystallized from absolute ether by cooling in a Dry Ice-acetone mixture, m.p. 78–79°.

Anal. Calc'd for $C_6H_6N_2O_6$: C, 31.59; H, 3.18; N, 14.74.
Found: C, 31.85; H, 3.19; N, 15.24.

Disodium γ,γ-dinitrobutyrate (VI). A solution of 52 g. of γ,γ-dinitro-δ-valerolactone in methanol was placed in the usual apparatus and 33.7 g. of sodium methoxide dissolved in 170 cc. of methanol was added while the temperature was kept at 0–10°. After stirring for 30 minutes the precipitated brown sodium salt was washed with methanol and ether. In this way 46 g. (75%) of yellow crystalline material was obtained. Recrystallized from methanol, it was found to decompose at 197°.

Anal. Calc'd for $C_4H_4N_2Na_2O_6$: N, 12.62. Found: N, 13.73.

γ-Bromo-γ,γ-dinitrobutyric acid (VII). Into a solution of 4.44 g. of disodium γ,γ-dinitrobutyrate dissolved in 25 cc. of water was dropped, with good agitation, 3.2 g. of bromine. The brown solution became colorless, and then changed to the color of bromine. The mixture was extracted twice with ether. The ether solution was dried over sodium sulfate and evaporated. The residue was distilled in an air-bath at 150°/2 mm.; yield, 1.5 g. of colorless liquid which crystallized on standing. After recrystallization from ether-hexane and then from water, the product melted at 88–89°.

Anal. Calc'd for $C_4H_5BrN_2O_6$: C, 18.69; H, 1.96; N, 10.90; Br, 31.10.
Found: C, 18.99; H, 2.01; N, 11.26; Br, 31.06, 31.29.

SUMMARY

1. Methyl δ-hydroxy-γ,γ-dinitrovalerate has been prepared. Treatment of this compound with base yielded the *aci*-sodium salt of methyl γ,γ-dinitrobutyrate which was amenable to the Michael reaction.

2. Treatment of methyl δ-hydroxy-γ,γ-dinitrovalerate with acid yielded γ,γ-dinitrovalerolactone.

3. Some derivatives of these compounds have been prepared.

AZUSA, CALIFORNIA

REFERENCES

(1) HERZOG, GOLD, AND GECKLER; In press.
(2) DUDEN AND PONNDORF, *Ber.*, **38**, 2031 (1905).