

MR calcd. 33.7; *MR* found 33.7. The acid phthalate prepared from 1 g. of this product melted at 90–91.5° after several recrystallizations from petroleum ether.

The following properties were reported by Vavon and Horeau¹⁰ for the two isomers of 2-ethylcyclopentanol: *cis* isomer: b.p. 163°; n_D^{19} 1.4556; d_{18} 0.9198; acid phthalate m.p. 92°. *trans* isomer: b.p. 165°; n_D^{19} 1.4529; d_{18} 0.9149; acid phthalate m.p. 54.5–55°.

2-Ethylcyclopentanone.—Two grams of 2-ethylcyclopentanol obtained from the *trans*-3,5-dibromocyclopentene as described above was added dropwise with stirring to a solution of 3.6 g. of potassium dichromate and 3 cc. of sulfuric acid in 10 cc. of water. After completion of the reaction, the mixture was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether was removed and the residue was distilled at reduced pressure. One-half gram of 2-ethylcyclopentanone was obtained, b.p. 57° at 24 mm. The boiling point determined by the Siwoloboff micro method¹⁷ was 159° at 760 mm.; reported for 2-ethylcyclopentanone: 149°,¹⁸ 157–158°,¹⁰ 160–161°.¹⁹

A semicarbazone was prepared from this material, m.p. 178–179° after several recrystallizations from dilute ethanol. The semicarbazone prepared from an authentic sample of 2-ethylcyclopentanone (prepared by alkylation of 2-carbomethoxycyclopentanone^{10,19}) melted at 182°, and there was no depression of the melting point on admixture of these two semicarbazones.

Reaction of *trans*-3,5-Dibromocyclopentene with *n*-Octylmagnesium Bromide.—A Grignard reagent was prepared from 150 g. (0.78 mole) of redistilled *n*-octyl bromide and 20 g. of magnesium in 700 cc. of dry ether. Titration of an aliquot indicated that the resulting solution contained 0.65 mole of *n*-octylmagnesium bromide. A solution of 91 g. (0.40 mole) of *trans*-3,5-dibromocyclopentene in 100 cc. of ether was added slowly under nitrogen while stirring and cooling in a water-bath. There was marked evolution of heat and the reaction mixture became bright yellow in color. After complete addition, which required 4 hours, two liquid layers were observed, but after standing overnight, the flask contained a slushy suspension of white solid. The mixture was poured onto ice and the ether layer shaken with saturated ammonium chloride solution, saturated sodium carbonate and water. The ether solution was dried over anhydrous sodium sulfate, the ether was removed and the residue was distilled at reduced pressure. Four fractions were eventually obtained.

(1) The first fraction, 20 g. of *n*-octane, boiled below 20° at 10 mm. and was caught in the Dry Ice trap. On redistillation at atmospheric pressure this material had b.p. 125–126°; m.p. –57 to –54°, uncorrected; n_D^{20} 1.4002.

(2) The second fraction of 25 g., b.p. 100–110° at 1 mm., was a pale yellow liquid which darkened on standing. A

portion was crystallized several times from ether by cooling in Dry Ice to give a mass of long white needles. This material was then redistilled to give a colorless liquid, b.p. 86° at 0.5 mm.; n_D^{20} 1.4350; d_{20} 0.7748; m.p. 18°. This was demonstrated to be *n*-hexadecane by a mixed m.p. with an authentic sample, there being no depression.

(3) The third fraction of 10 g., b.p. 115–120° at 0.02 mm., was a yellow liquid which was crystallized from ether several times by cooling in Dry Ice and decanting. The residual ether was finally removed by protracted evacuation to give a colorless liquid, m.p. 17.5–18°; n_D^{20} 1.4592; d_{20} 0.8265. The b.p. at 2.5 mm. was 155°, from which it is calculated that the b.p. at atmospheric pressure would be approximately 355°. The b.p. calcd. for a dioctylcyclopentene by the method of boiling point numbers²⁰ is 362°. The analysis confirms the identity of this product as a dioctylcyclopentene, possibly the desired 3,5-di-*n*-octylcyclopentene.

Anal. Calcd. for $C_{21}H_{40}$: C, 86.22; H, 13.78. Found: C, 86.25; H, 13.83.

(4) The fact that the hexadecane fraction remaining after crystallization of a portion from ether darkened on standing led to the suspicion that it might contain a small amount of an octylbromocyclopentene. The b.p. calcd. for such a compound from b.p. numbers²⁰ is approximately 290° (hexadecane b.p. 287.5°). Repeated fractionations of this material at reduced pressure eventually produced a fraction with n_D^{20} 1.4600, boiling a fraction of a degree below the main fraction of hexadecane. This material was cooled in ice until mostly solid and the liquid portion was withdrawn to give 0.7 g. of pale yellow liquid, n_D^{20} 1.4721; d_{22} 1.027; *MR* calcd. for an octylbromocyclopentene 63.8; *MR* found 70.7. This material was still not pure, but the quantity was not sufficient to permit further purification.

Anal. Calcd. for $C_{13}H_{23}Br$: Br, 30.83. Found: Br, 25.58.

Summary

The reactions of *cis*- and *trans*-3,5-dibromocyclopentene with ethylmagnesium bromide gave hydrocarbon fractions shown to consist, in part at least, of 3,5-diethylcyclopentene, but which may contain 3,4-diethylcyclopentene also. Identical bromine containing fractions were also obtained from the two reactions. This material was demonstrated to be 3-ethyl-4-bromocyclopentene and is believed to be the *trans* isomer. Similar results were obtained on reaction of *trans*-3,5-dibromocyclopentene with *n*-octylmagnesium bromide.

(20) C. R. Kinney, *Ind. Eng. Chem.*, **32**, 559 (1940).

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(18) S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 713 (1909).

(19) F. H. Case and E. B. Reid, *THIS JOURNAL*, **50**, 3062 (1928).

[CONTRIBUTION FROM RESEARCH LABORATORY OF AEROJET ENGINEERING CORP.]

The Chemistry of Aliphatic Dinitro Compounds. I. The Michael Reaction¹

BY LEVONNA HERZOG, MARVIN H. GOLD AND RICHARD D. GECKLER

Aliphatic mononitro compounds are known to undergo Michael type condensations with compounds having an activated double bond.^{2–7} This reaction has now been extended to aliphatic gem-dinitro compounds.

(1) This work was performed under Contract N7onr-462, Task Order I with the Office of Naval Research.

(2) Kohler and Engelbrecht, *THIS JOURNAL*, **38**, 889 (1916); **41**, 764 (1919).

(3) Bruson and Riener, *ibid.*, **65**, 23 (1943).

(4) Kloetzel, *ibid.*, **70**, 3571 (1948).

(5) Leonard and Beck, *ibid.*, **70**, 2504 (1948).

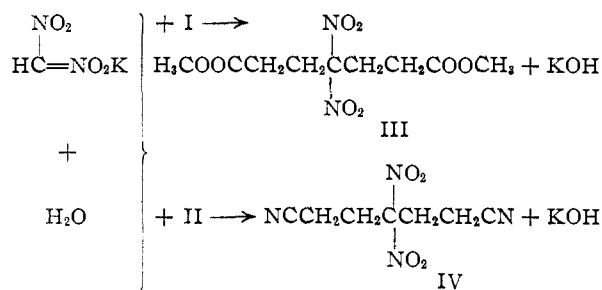
(6) Leonard and Shoemaker, *ibid.*, **71**, 1758–1876 (1949).

(7) Bruson, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 99.

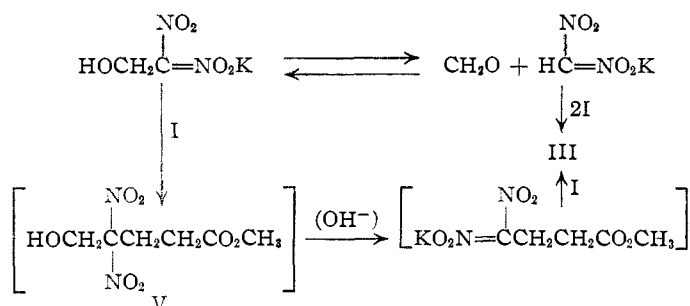
Potassium dinitromethane upon reaction with methyl acrylate (I) and acrylonitrile (II) gave dimethyl 4,4-dinitroheptanedioate (III) in 60% yield and 4,4-dinitroheptanedinitrile (IV) in 34% yield, respectively.

The reactions proceed readily in water solution at 35–45°. Aqueous potassium dinitromethane is sufficiently basic to effect the condensation without further addition of catalyst. Best results in the preparation of III were obtained when a 2.5-fold excess of methyl acrylate was used.

Potassium dinitroethanol underwent reaction with two molecules of methyl acrylate, in the same

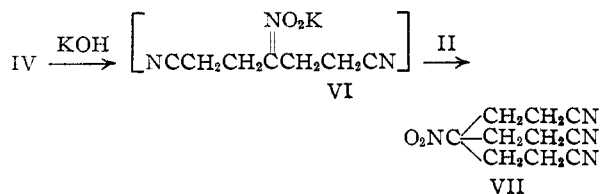


manner as potassium dinitromethane, to yield dimethyl 4,4-dinitroheptanedioate (III). This condensation can proceed either by the reaction of methyl acrylate with potassium dinitromethane, which is known to exist in equilibrium with potassium dinitroethanol in aqueous solution,⁸ or by the action of methyl acrylate on potassium dinitroethanol to yield methyl 4,4-dinitro-5-hydroxypentanoate (V). After spontaneous loss of formaldehyde, V can react with another molecule of methyl acrylate as shown by the equations



Klager⁹ has shown that when the *pH* of the reaction mixture is kept below 7, it is possible to isolate methyl 4,4-dinitro-5-hydroxypentanoate (V) which can then be made to react with another molecule of methyl acrylate to give dimethyl 4,4-dinitroheptanedioate. It is possible that the condensation proceeds by both of these paths simultaneously.

A by-product, tris-(2-cyanoethyl)-nitromethane (VII) was isolated in 12% yield from the reaction of potassium dinitromethane with acrylonitrile. During the condensation the base strength of the reaction mixture increased. Under the influence of the strong base one nitrogroup apparently was split from 4,4-dinitroheptanedinitrile (IV), and the resulting potassium 4-nitroheptanedinitrile (VI) then reacted with another molecule of acrylonitrile in the illustrated fashion



Another reaction of potassium dinitromethane and acrylonitrile was carried out where the *pH* was maintained below 8. Under these conditions,

as was expected, only 4,4-dinitroheptanedinitrile was isolated.

No analogous trisubstituted by-product was isolated from the reaction of methyl acrylate with potassium dinitromethane. The base formed during the Michael reaction was consumed by the hydrolysis of methyl acrylate, a process which is known to occur in alkaline solution at room temperature.¹⁰ The *pH* of the solution at the end of the condensation was 7.7 as compared with 9.3 in the case of the acrylonitrile reaction; apparently the solution was never sufficiently alkaline to effect the removal of a nitro group.

Dimethyl 4,4-dinitroheptanedioate (III) was hydrolyzed quantitatively to 4,4-dinitroheptanedioic acid (VIII) by refluxing with 18% hydrochloric acid. Inasmuch as few aliphatic dinitrocompounds had been synthesized previously, this compound was used as a starting material for the preparation of some new dinitrocompounds with varied functional groups. 4,4-Dinitroheptanedioyl chloride (IX) was prepared from VIII by cautious treatment with thionyl chloride. IX was converted by the action of a cold concentrated solution of sodium azide to 4,4-dinitroheptanedioyl azide (X), which rearranged readily to 3,3-dinitropentamethylene diisocyanate (XI) upon being warmed to 55° in chloroform solution. Treatment of XI with methanol yielded the corresponding urethan, dimethyl 3,3-dinitropentanedicarbamate (XII). By refluxing XII with concentrated hydrochloric acid, 3,3-dinitro-1,5-pentanediamine hydrochloride (XIII) was obtained. The free amine, 3,3-dinitro-1,5-pentanediamine darkened quickly upon exposure to air but appeared to be stable when stored for several weeks at -15° under nitrogen. The amine was characterized by diacetyl and dibenzoyl derivatives. Each of these conversions was carried out in yields exceeding 80%.

These nitro compounds, derived from dimethyl 4,4-dinitroheptanedioate, were all colorless and crystalline at room temperature and gave the expected functional group reactions.

Experimental¹¹

Potassium Dinitromethane and Potassium Dinitroethanol.—The method of Duden¹² was followed in the preparation of potassium dinitromethane and that of Duden and Ponndorf¹³ for potassium dinitroethanol.

Dimethyl 4,4-Dinitroheptanedioate (III). A. From **Potassium Dinitromethane.**—In a 200-ml. three-necked flask fitted with a stirrer, thermometer and dropping funnel was placed 8.1 g. (equivalent to 0.05 mole of dry salt) of damp potassium dinitromethane and 55 cc. of water. The temperature of the reaction mixture was kept at 35–45° while 23.2 g. (0.27 mole) of methyl acrylate was added during 1 hour, stirring was continued for an additional 3 hours. The reaction mixture which was at first bright yellow gradually became dark and at the end of the reaction was almost black. The mixture was extracted with ether, the ether extracts combined and treated with decolorizing charcoal. The ether was then evaporated and the residue crystallized from methanol. In this way 8.4 g. (60.4%) of colorless

(10) Williams and Sudborough, *J. Chem. Soc.*, **101**, 412 (1912).

(11) The microanalyses were carried out by Dr. A. Elek, Los Angeles, Calif.

(12) Duden, *Ber.*, **26**, 3003 (1893).

(13) Duden and Ponndorf, *ibid.*, **38**, 203 (1905).

(8) Duden and Ponndorf, *Ber.*, **38**, 2031 (1905).

(9) Dr. Karl Klager, private communication.

crystals m.p. 43.5–44.5¹⁴ were obtained. After one more crystallization the product melted at 44.5–45°.

Anal. Calcd. for C₉H₁₄O₈N₂: N, 10.07. Found: N, 9.91.

B. From Potassium Dinitroethanol.—The reaction was carried out in a manner identical to that described for potassium dinitromethane except that 10.7 g. (equivalent to 0.05 mole of dry salt) of damp potassium dinitroethanol was used in place of the potassium dinitromethane. The pH of the solution at the end of the reaction as measured with a Beckman pH meter was 7.7. The yield of crystallized dimethyl 4,4-dinitroheptanedioate was 8.05 g. (58%).

4,4-Dinitroheptanedinitrile (IV).—This preparation was carried out in the manner described for dimethyl 4,4-dinitroheptanedioate from potassium dinitromethane except that an equivalent quantity of acrylonitrile was used in place of methyl acrylate. The pH of the mixture at the end of the reaction was 9.3.

The reaction mixture was extracted with ether, which upon concentration deposited crude 4,4-dinitroheptanedinitrile in 28% yield. The product after treatment with decolorizing charcoal and crystallization from ethanol melted at 79°.

Anal. Calcd. for C₇H₉N₄O₄: N, 26.42. Found: N, 26.53.

The solid material which remained in the reaction mixture after the extraction was filtered and crystallized from ethanol, producing tris-(2-cyanoethyl)-nitromethane (VII) m.p. 110–113° in 12% yield. After another crystallization, this material melted at 114.5–116°, which agreed with the previously reported value.³ From the mother liquor a further quantity (7%) of 4,4-dinitroheptanedinitrile was obtained.

Anal. Calcd. for C₁₀H₁₂N₄O₂: C, 54.52; H, 5.50; N, 25.44. Found: C, 54.67; H, 5.58; N, 25.05.

B.—The reaction of potassium dinitromethane and acrylonitrile was also carried out where the pH was maintained below 8. To a mixture of 8.3 g. (0.057 mole) of potassium dinitromethane, 67 ml. of water, and 3 ml. of acetic acid was added 18 g. (0.34 mole) of acrylonitrile during 1 hour while the temperature was maintained at 30–40°. Stirring was continued at this temperature for 6 hours. The pH of the mixture as measured with a Beckman pH meter was 6. Dilute potassium hydroxide was added to the solution until it reached a pH of 7.7. Stirring was then continued for 8 more hours. The crystals which separated were isolated by filtration. In this way 3.4 g. (28.1%) of crude 4,4-dinitroheptanedinitrile was obtained. Extraction of the filtrate with ether yielded an additional 0.2 g. (1%) of product. No other material was isolated by evaporation of the mother liquor.

4,4-Dinitroheptanedioic Acid (VIII).—A mixture of 40 g. (0.14 mole) of dimethyl 4,4-dinitroheptanedioate and 350 cc. of 18% hydrochloric acid was refluxed until all of the acid was in solution, and then for an additional hour. Upon cooling the solution, the product crystallized to yield 27 g. of colorless plates, m.p. 139–140°. By concentration of the mother liquor, a second batch of crystals (7–8 g.) was recovered; total yield 95–97%. The acid was purified by recrystallization from water, m.p. 137° cor.

Anal. Calcd. for C₇H₁₀N₂O₈: N, 11.20; neut. equiv., 125.1. Found: N, 10.83; neut. equiv., 125.5.

4,4-Dinitroheptanedioyl Chloride (IX).—A mixture of 45 cc. of thionyl chloride which had been distilled over quinoline and 27 g. (0.1 mole) of 4,4-dinitroheptanedioic acid was heated cautiously. The temperature was maintained so as to keep the mixture bubbling gently (45–55°). After the acid had dissolved, the solution was refluxed for 2 hours. The solution was filtered while hot, through a fritted glass funnel and then cooled to –15°. The acid chloride separated from the solution in colorless crystals, m.p. 54–56°. Concentration of the mother liquor yielded an additional quantity of product; total yield 27 g. (95%). Recrystallization from thionyl chloride yielded crystals m.p. 57° (cor.).

A sample of 4,4-dinitroheptanedioyl chloride was converted quantitatively to dimethyl 4,4-dinitroheptanedioate by mixing with an excess of methanol.

4,4-Dinitroheptanedioyl Azide (X).—In a 100-ml. three-necked flask fitted with a thermometer, dropping funnel and stirrer was placed a solution of 9 g. (0.14 mole) of so-

dium azide dissolved in 24 cc. of water. A solution of 10 g. (0.035 mole) of 4,4-dinitroheptanedioyl chloride dissolved in 25 cc. of acetone was added from the dropping funnel with vigorous stirring. The temperature of the reaction mixture was kept at 5–10°. After the addition was complete the mixture was stirred for a half hour and then diluted with 10 cc. of water. The precipitated azide was filtered, washed with water until colorless, and then dried in a vacuum desiccator over calcium chloride. In this manner 9.5–10 g. (90–95%) of colorless crystals m.p. 68–69° (dec.) was obtained.

3,3-Dinitropentamethylene Diisocyanate (XI).—A solution of 10 g. (0.03 mole) of 4,4-dinitroheptanedioyl azide in 100 cc. of dry chloroform was heated gently until nitrogen was evolved at a moderate rate (45–50°). When the evolution of nitrogen had ceased the solution was refluxed for 15 minutes longer. The chloroform was then evaporated under vacuum and the residue crystallized from ether. When the ether solution was cooled below 0°, the product separated in colorless crystals. The isocyanate was then isolated by removal of the filtrate through a fritted filter stick in an apparatus that excluded moisture. A yield of 6.5–6.9 g. (80–85%) of product m.p. 37–38° was obtained. After further recrystallization the melting point was raised to 39.5° (cor.).

Anal. Calcd. for C₇H₈N₄O₆: C, 34.44; H, 3.33. Found: C, 34.07; H, 3.48.

Upon treatment of 3,3-dinitropentamethylene diisocyanate with aniline, the corresponding phenylurea was formed, m.p. 186–187° after crystallization from methanol-water solution.

Anal. Calcd. for C₁₀H₁₂N₆O₆: C, 52.76; H, 5.59. Found: C, 52.76; H, 5.27.

Dimethyl 3,3-Dinitropentanedicarbamate (XII) was prepared by dissolving 3,3-dinitropentamethylene diisocyanate in an excess of methanol. The reaction was attended by the evolution of heat. When the reaction was complete the methanol was evaporated and the residue crystallized from chloroform in colorless needles, m.p. 114°.

Anal. Calcd. for C₉H₁₆O₈N₄: C, 35.06; H, 5.23; N, 18.18. Found: C, 35.31; H, 5.20; N, 18.52.

3,3-Dinitro-1,5-pentanediamine dihydrochloride (XIII) was prepared by refluxing 10 g. (0.032 mole) of dimethyl 3,3-dinitropentanedicarbamate with 30 cc. of concd. hydrochloric acid for 16 hours. The solution was cooled and the precipitated amine hydrochloride filtered, to yield 8 g. of colorless crystals m.p. 225–230° (dec.).

3,3-Dinitro-1,5-pentanediamine was prepared from the hydrochloride by mechanically shaking an accurately weighed sample of amine hydrochloride with the theoretical amount of standard alcoholic sodium hydroxide for an hour. The alcohol was cooled to 0° and the precipitated sodium chloride filtered. The methanol was then evaporated leaving a colorless solid, m.p. 73–74°. After low temperature (–60 to –70°) crystallization from methylene chloride, colorless crystals m.p. 76–79° were obtained. This material became yellow after short exposure to the atmosphere. It was identified by means of derivatives.

N,N'-Diacetyl-3,3-dinitro-1,5-pentanediamine was prepared in the usual fashion from 3,3-dinitro-1,5-pentanediamine and acetic anhydride, m.p. 155–157° after crystallization from water.

Anal. Calcd. for C₉H₁₆O₆N₄: N, 20.28. Found: N, 20.40.

N,N'-Dibenzoyl-3,3-dinitro-1,5-pentanediamine was prepared from 3,3-dinitro-1,5-pentanediamine and benzoyl chloride in the manner of the Schotten-Baumann reaction; m.p. 145° after crystallization from methanol water (1:1).

Anal. Calcd. for C₁₉H₂₀O₆N₄: N, 13.99. Found: N, 14.12.

Summary

1. Potassium dinitromethane has been found to undergo the Michael-type condensation with two moles of methyl acrylate or acrylonitrile.

2. 4,4-Dinitroheptanedioic acid, 3,3-dinitropentamethylene diisocyanate, 3,3-dinitropentanediamine and several of their derivatives have been prepared.

(14) Melting points are uncorrected unless otherwise noted.