[Contribution from the Organic Chemistry Division, U. S. Naval Ordnance Laboratory]

Michael Additions of Nitroform. I. Some Co-products in the Reaction with Methyl Acrylate[1a]

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In acidic media nitroform reacts with methyl acrylate to yield methyl 4,4,4-trinitrobutyrate (I). In near-neutral or alkaline media there were obtained in addition to I two unexpected co-products, dimethyl 4,4-dinitro-2-hydroxyheptanedioate (II) and the potassium salt of methyl 4,4-dinitro-2-butenoate (III). An analog of II, 5,5-dinitro-3-hydroxy-2,8-nonanedione (IV), was obtained in the reaction of potassium trinitromethide with methyl vinyl ketone. Proofs of structure of II and IV are described as is the synthesis by an independent method of 4,4-dinitro-2-hydroxyheptanedioic acid (V), the hydrolysis product of II.

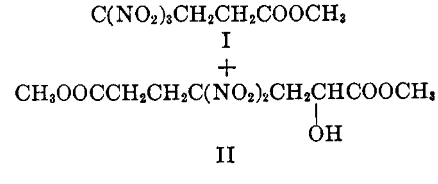
Nitroform, a strong *pseudo*-acid ($pK \sim 1$-2),[2] has been reported to undergo normal conjugate additions to a variety of unsaturated compounds including carboxylic acids,[3-5] esters,[3,4] nitriles,[3] amides,[6,7] aldehydes,[3] ketones,[3,8-11] and nitro compounds.[5,12-14] Unlike typical Michael additions of active methylene compounds[15] these reactions require no alkaline catalyst when carried out in nonaqueous solvents[4,6-14]; in aqueous systems optimal yields are achieved at pH values below 7 as with barbituric acid,[16,17] also a fairly strong *pseudo*-acid (pK 4.05). The latter effect is illustrated in Table I[18] for the reaction of nitroform with methyl acrylate.

TABLE I

EFFECT OF pH ON YIELD IN PREPARATION OF METHYL 4,4,4-TRINITROBUTYRATE, METHANOL–WATER, 60°

pH	Conditions	Yield, %
<1	Potassium salt in $3N$ HCl, 90 min.	39
1–2	Nitroform, no catalyst, 120 min.	80–90
1–2	Potassium salt, equimolar H_2SO_4, 90 min.	85
∼3.5	Potassium salt, large excess HOAc, 3 hr.	86
∼4.2	Potassium salt, HOAc–NaOAc buffer, 3 hr.	65
∼5	Potassium salt, trace H_2SO_4, 24 hr.	21

We wish now to report that under near-neutral or alkaline conditions these reactions may take a somewhat different course. Thus, when equimolar nitroform and sodium acetate (equals equimolar acetic acid and sodium trinitromethide) were allowed to react twenty-four hours at room temperature with a 200% molar excess of methyl acrylate in 33% aqueous methanol, the expected 1:1 adduct, methyl 4,4,4-trinitrobutyrate (I), was obtained in 56.5% yield. In addition, however, there was obtained 24.7% of an entirely unexpected co-product, dimethyl 4,4-dinitro-2-hydroxyheptanedioate (II). These were readily separable by virtue of I being relatively soluble in hot pentane, II relatively insoluble. A similar reaction in the absence of acetic acid, *i.e.*, potassium trinitromethide and 300% excess methyl acrylate in 50% methanol, yielded greater amounts of II (31.1%) relative to I (10.9%) together with still a third product (III, 34.4%)



$$Na^{+-}C(NO_2)_3 + CH_2{=}CHCOOCH_3 \xrightarrow[HOAc]{CH_3OH-H_2O} \underset{\text{I}}{C(NO_2)_3CH_2CH_2COOCH_3} + \underset{\text{II}}{CH_3OOCCH_2CH_2C(NO_2)_2CH_2\underset{\underset{OH}{|}}{C}HCOOCH_3}$$

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[1] (a) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, Abstracts, p. 56-O. (b) Present address, G.D./Advanced Products Dept., Chemicals Section, P. O. Box 6231, San Diego 6, Calif. (c) To whom all inquiries and further correspondence should be addressed.

[2] A. Hantzsch and A. Rickenberger, *Ber.*, **32**, 628 (1899).

[3] K. Schimmelschmidt, Ger. Patent **852,684**, October 16, 1952.

[4] H. Feuer, E. H. White, and S. M. Pier, *J. Org. Chem.*, **26**, 1639 (1961).

[5] M. B. Frankel, *Abstracts of Papers, Symposium on Nitroaliphatic Chemistry*, Purdue University, Lafayette, Ind., May 25–26, 1961, p. 13.

[6] H. Feuer and U. E. Lynch-Hart, *J. Org. Chem.*, **26**, 391 (1961).

[7] H. Feuer and U. E. Lynch-Hart, *J. Org. Chem.*, **26**, 587 (1961).

[8] S. S. Novikov, I. S. Korsakova, and M. A. Yatskovskaya, *Zhur. Obshchei Khim.*, **29**, 3343 (1959).

[9] S. S. Novikov, I. S. Korsakova, and N. N. Bulatova, *Zhur. Obshchei Khim.*, **29**, 3659 (1959).

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[11] S. S. Novikov, I. S. Korsakova, and M. A. Yatskovskaya, *Doklady Akad. Nauk S. S. S. R.*, **118**, 954 (1958).

[12] S. S. Novikov, K. K. Babievskii, and I. S. Korsakova, *Doklady Akad. Nauk S. S. S. R.*, **125**, 560 (1959).

[13] S. S. Novikov, I. S. Korsakova, and K. K. Babievskii, *Izv. Akad. Nauk S. S. S. R., Otdel Khim. Nauk*, 1847 (1959).

[14] J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960).

[15] E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, X, 179 (1959).

[16] M. J. Kamlet, *J. Am. Chem. Soc.*, **77**, 4896 (1955).

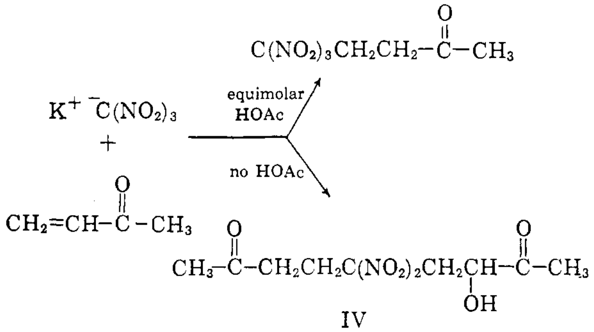
[17] M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **78**, 4556 (1956).

[18] Private communication, M. E. Hill of these laboratories.

which was ether-insoluble, water-soluble. In "absolute" methanol under like conditions III (48.2%) was the predominant product together with 23.3% I and 5.3% II. Also isolated was 24% potassium nitrite (based on initial nitroform)[19] The identity proof of III as the potassium salt of methyl 4,4-dinitro-2-butenoate and the formation of related compounds from acrylamide and acrylonitrile will be described in a subsequent paper.[20]

$$K^{+-}C(NO_2)_3 + CH_2{=}CHCOOCH_3 \xrightarrow[\text{or } CH_3OH]{CH_3OH\text{-}H_2O} I + II + \underset{\text{III}}{K^{+-}C(NO_2)_2CH{=}CHCOOCH_3} + KNO_2$$

An attempt to prepare the analog of II from equimolar nitroform and potassium acetate with methyl vinyl ketone led only to an almost quantitative yield of the normal 1:1 adduct, 5,5,5-trinitro-2-pentanone. Using potassium trinitromethide directly, however, gave the desired product, 5,5-dinitro-3-hydroxy-2,8-nonanedione (IV) in 18% yield.



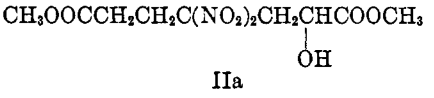
IV

Proof of structure. The molecular formula of II was readily established to be $C_7H_8N_2O_7(OCH_3)_2$ by elemental and methoxyl group analyses and by an x-ray molecular weight determination. Acid hydrolysis to an acidic compound (V), molecular formula $C_7H_{10}N_2O_7$, and neutral equivalent (found) 135.5, confirmed that II was a dicarboxylic ester.

The ultraviolet spectrum of II showed $\lambda_{max}^{CH_3OH}$ 278 mμ (ε 65.5). This indicated the absence of conjugated carbon-carbon unsaturation and served as strong evidence that both nitrogen atoms were present in nitro functions.[21] The failure of the compound to take up bromine under mild conditions in neutral media indicated that these nitro groups were part of an internal *gem* - dinitro function.

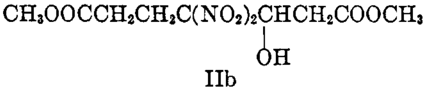
Attempts to methylate II with diazomethane or to acetylate it with acetic anhydride or ketene were unsuccessful as was an attempt to allow it to react it with phenyl isocyanate under milder conditions.[22] Under more vigorous conditions and in the presence of catalytic amounts of pyridine[23] II did form a phenylurethane in excellent yield. This confirmed the presence of a free but relatively unreactive hydroxyl group.

Its mode of formation from a one-carbon compound and the methyl ester of a three-carbon acid, coupled with the above evidence, led to the conclusion that II was the dimethyl ester of a seven-carbon straight chain hydroxydicarboxylic acid with a *gem*-dinitro group most probably in the 4-position. The alternative possibilities, depending on the positioning of the hydroxy group, were dimethyl 4,4-dinitro-2-hydroxyheptanedioate (IIa) or dimethyl 4,4-dinitro-3-hydroxyheptanedioate (IIb). These conclusions were shown to be valid



$$CH_3OOCCH_2CH_2C(NO_2)_2CH_2\underset{\displaystyle OH}{CH}COOCH_3$$

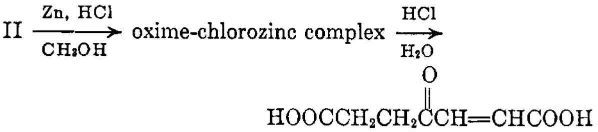
IIa



$$CH_3OOCCH_2CH_2C(NO_2)_2\underset{\displaystyle OH}{CH}CH_2COOCH_3$$

IIb

when, on reduction with zinc and ammonium chloride in methanol, II yielded the chlorozinc complex of an oxime which, on decomposition with hydrochloric acid, was converted to the known[24] 4-keto-2-heptenedioic acid (VI). The latter was characterized *per se* and as its dimethyl ester. Apparently the supposedly mild conditions of the acid decomposition had been sufficiently vigorous to effect dehydration in addition to hydrolysis.



$$II \xrightarrow[CH_3OH]{Zn,\ HCl} \text{oxime-chlorozinc complex} \xrightarrow[H_2O]{HCl} HOOCCH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH{=}CHCOOH$$

VI

Compound IV showed similar absorption characteristics in the ultraviolet.[21] It yielded both a crystalline phenylurethane and a mono(2,4-dinitrophenylhydrazone). By analogy with II, the possible structures for IV were 5,5-dinitro-3-hydroxy-2,8-nonanedione (IVa) and 5,5-dinitro-4-hydroxy-2,8-nonanedione (IVb). Although we were unable to effect an interconversion between II and IV or to

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[19] Spectrophotometric analysis of the reaction mixture also indicated the presence of 3.7% of unchanged nitroform anion and about 3% of a species whose spectrum, $\lambda_{max}^{dil.\ KOH}$ 377–378 mμ, suggested that it was the salt of a saturated 1,1-dinitro compound.

[20] Paper II in this series, M. J. Kamlet and L. A. Kaplan, in preparation.

[21] The molar absorbancy index for the $n \rightarrow \pi^*$ transition of saturated nitroaliphatic compounds near 280 mμ appears to be an additive function of the number of nitro groups, each group contributing 25–35 to this value, H. E. Ungnade, *J. Org. Chem.*, 22, 1088 (1957); V. I. Slovetsky, V. A. Shlyapochnikov, K. K. Babievskii, and S. S. Novikov, *Izv. Akad. Nauk S. S. S. R., Otdel Khim. Nauk*, 1675 (1960). The higher absorbancy index of IV, $\lambda_{max}^{CH_3OH}$ 279 (ε 129), may be due to contributions by the unconjugated carbonyl groups which absorb in the same region.

[22] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd ed., John Wiley and Sons, Inc., New York, 1948, p. 136.

[23] Hopkins and Williams Research Laboratory, *Organic Reagents for Organic Analysis*, Chemical Publishing Co., Inc., Brooklyn, N. Y., 1946, p. 76.

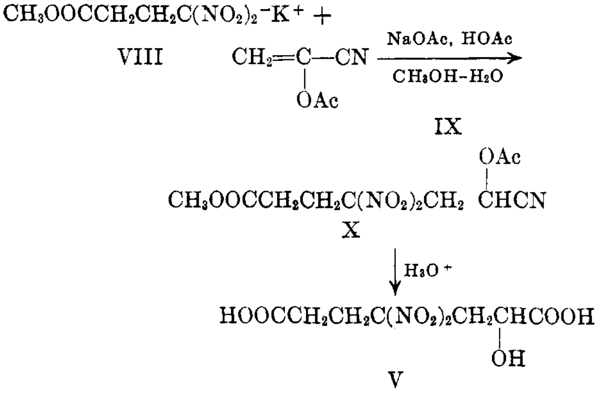
[24] W. Kota, *J. Chem. Soc. Japan*, **75**, 147 (1954).

derive from them a mutual derivative,[25] it seemed unlikely from their similar modes of formation that the positioning of the hydroxyl relative to the *gem*-dinitro group would differ between the two compounds.

Our preference for structures IIa and IVa for compounds II and IV was initially based on the following facts: (1) Compound IV gave a strong positive periodic acid test characteristic of α-hydroxy ketones.[26] (2) Although reduction of the hydroxy diester, II with sodium borohydride[27] or lithium aluminum hydride[28] did not give an analytically pure triol, the reduction product so obtained did give a strong positive periodic acid test characteristic of *vic*-glycols.[26] Structure IIa and not IIb, upon reduction would be expected to yield a *vic*-glycol.

Initial attempts to confirm the above structures by degradative procedures were unsuccessful,[29] although the oxidation of the dibasic acid V with sodium bismuthate in aqueous phosphoric acid[30] yielded 5-formyl-4-nitro-4-pentenoic acid. This result gave further support to the tentative assignment of structure IIa to compound II.

While the foregoing evidence favored the α-hydroxy ester structure IIa, confirmation of this assignment could only be made by independent synthesis of the dibasic acid V. Thus the reaction of potassium methyl 4,4-dinitrobutyrate with α-acetoxyacrylonitrile (IX) was effected under conditions similar to those which yielded II from nitroform and methyl acrylate. It was not possible to isolate the Michael adduct, methyl 6-acetoxy-6-cyano-4,4-dinitrohexanoate (X), as an analytically pure compound, but hydrolysis of the crude oil afforded a crystalline solid which proved to be a dibasic acid. Although analytical results agreed with those calculated for V, it was not possible to obtain a sharply melting sample, even after repeated crystallizations from assorted solvents. The best sample melted from 128.8 to 134.4°; a sample of V from hydrolysis of II had melting point 139–140°. The melting point of a mixture fell between the two; 129.5 to 138°. Infrared spectra of both samples of V were superimposable. X-ray interplanar spacings and intensities also showed the two products to be identical.



$$CH_3OOCCH_2CH_2C(NO_2)_2^-K^+ + \underset{\textstyle IX}{CH_2{=}\underset{OAc}{\overset{|}{C}}{-}CN} \xrightarrow[CH_3OH\text{-}H_2O]{NaOAc,\ HOAc}$$

VIII

$$CH_3OOCCH_2CH_2C(NO_2)_2CH_2\overset{OAc}{\overset{|}{C}}HCN$$

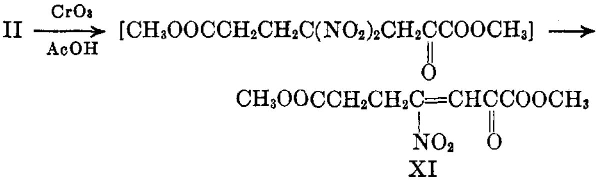
X

$$\Big\downarrow H_3O^+$$

$$HOOCCH_2CH_2C(NO_2)_2CH_2\underset{OH}{\underset{|}{C}}HCOOH$$

V

To investigate further the simultaneous oxidation-denitrosation reaction observed with sodium bismuthate and the hydroxy acid V (*vide supra*), the hydroxy ester II was oxidized with a cold solution of chromic anhydride in acetic acid. The resulting low-melting product proved to be a mononitro ketone (XI) from elemental analyses for both the ketone and its 2,4-dinitrophenylhydrazone and from the spectrum of the ketone, λ_{max}^{ether} (log ϵ) 249 mμ (3.86).[31]



$$II \xrightarrow[AcOH]{CrO_3} [CH_3OOCCH_2CH_2C(NO_2)_2CH_2\underset{O}{\underset{\|}{C}}COOCH_3] \longrightarrow$$

$$CH_3OOCCH_2CH_2\underset{NO_2}{\underset{|}{C}}{=}CH\underset{O}{\underset{\|}{C}}COOCH_3$$

XI

Oxidation of II with acid permanganate effected an almost quantitative conversion of the hydroxy ester to succinic acid. This oxidation can be depicted as following the same course as the chromic acid oxidation, with the ketone XI undergoing subsequent oxidative cleavage at the double bond to yield succinic acid. The same product, succinic acid, was obtained with the acid V, using either acid permanganate or chromic anhydride–acetic acid at slightly elevated temperatures. Though these simultaneous oxidation-denitrosations were unusual, they were not unexpected since facile denitrosation of polynitromethyl compounds under acidic conditions has been demonstrated to occur when a hydrogen atom alpha to the polynitromethyl group is rendered more acidic by the presence of a

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(25) An attempt to convert IV to V (the dibasic acid from II) by treatment with hypoiodide was frustrated by the instability of these compounds to the alkaline conditions of the iodoform reaction.

(26) Ref. 22, p. 56. Compounds II, V and 4,4-dinitro-5-hydroxyvaleric acid show negative results under similar conditions.

(27) Private communication, Prof. H. Shechter, Ohio State University.

(28) H. Feuer and T. J. Kucera, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

(29) Alkaline hydrolysis of II yielded only succinic acid. No evidence for the formation of methyl formylacetate (VII) or potassium methyl 4,4-dinitrobutyrate (VIII), the expected hydrolysis products of IIb were obtained. Under similar conditions 2,2,2-trinitroethanol reverts rapidly to formaldehyde and trinitromethide ion [J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.*, **77**, 496 (1955)]. Methyl 4,4-dinitro-5-hydroxyvalerate is deformylated to VIII [L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951)]. See also T. Hall, *Tetrahedron, in press.* In addition, the synthesis of structure IIb from the sodium enolate of VII and VIII in aqueous acetic acid was not realized.

(30) This reagent is reported to oxidatively decarboxylate α-hydroxy acids to aldehydes under these conditions. W. Rigby, *J. Chem. Soc.*, 1907 (1950). Simultaneous denitrosation also occurred in the present case.

(31) For comparison 2-nitro-2-butene shows $\lambda\lambda_{max}^{C_2H_5OH}$ (log $\epsilon\epsilon$) 234 (3.75), 242 (3.76), and 250 mμ (3.75) [E. A. Braude, E. R. H. Jones, and C. G. Rose, *J. Chem. Soc.*, 1104 (1947)].

second electron attracting group alpha to the hydrogen atom.[32]

EXPERIMENTAL[33] (CAUTION)[34]

Reaction of nitroform, sodium acetate, and methyl acrylate in methanol–water. A homogeneous solution of nitroform (60.4 g., 0.40 mole), sodium acetate trihydrate (54.4 g., 0.40 mole), and methyl acrylate (103.2 g., 1.20 moles) in 300 ml. methanol and sufficient water to bring the volume to 1000 ml. was stirred 24 hr. at room temperature during which time a deep orange color developed and the mixture separated into two phases. Addition of 100 ml. of ether to the lower phase and cooling in the freezer resulted in the precipitation of 20.4 g. of an off-white solid, m.p. 68–74°. The solvent was then stripped from the mother liquor *in vacuo* and the residual red oil extracted with four 250-ml. portions of boiling pentane which, upon cooling in Dry Ice-acetone, deposited a total of 58.6 g. of a progressively more colored product, m.p. 22–26°. The oily residue from these extractions, when taken up in ether and then chilled, deposited an additional 6.4 g. of the higher melting product, m.p. 72–74°.

Extraction of the upper phase of the original reaction mixture with 200 ml. of ether, washing the ether extract with water, drying over anhydrous calcium sulfate, and evaporating most of the solvent resulted in the recovery of a further 4.2 g. of the same product, m.p. 71–73°.

The combined lower melting crudes (61.9%), recrystallized from pentane, yielded 53.6 g. (56.5%) of pure *methyl 4,4,4-trinitrobutyrate* (I), m.p. 27–28° (lit.[35] 26°), λ_{max}^{hexane} (log ϵ) 279 mμ (1.94). The combined higher melting crudes (26.4%) were recrystallized from pentane-ether yielding 29.1 g. (24.7%) of *dimethyl 4,4-dinitro-2-hydroxyheptanedioate* (II) as chunky white equant crystals, m.p. 74.6–76.3°. A further recrystallization from ether gave the analytical sample, m.p. 75.6–76.4°, $\lambda_{max}^{CH_3OH}$ (log ϵ) 278 (1.82).

Anal. Calcd. for $C_9H_{14}N_2O_9$: C, 36.80; H, 4.79; N, 9.52; OCH_3, 21.14; mol. wt., 294. Found: C, 36.90, 37.17; H, 4.54, 4.77; N, 9.30, 9.36; OCH_3, 21.41, 21.77; mol. wt. (x-ray), 289.

The *phenylurethane of* II was prepared by refluxing 2.94 g. (0.01 mole) of II with 11 g. of phenyl isocyanate and two drops of pyridine in 25 ml. carbon tetrachloride. Two crops of crude product totalling 4.8 g., m.p. 59–65° were collected and recrystallized from carbon tetrachloride to yield 2.5 g. of tiny white needles, m.p. 78.5–80°; a second recrystallization from pentane–ether afforded the analytical sample as clusters of white bars, m.p. 80.5–82.5°.

Anal. Calcd. for $C_{16}H_{19}N_3O_{10}$: C, 46.50; H, 4.60; N, 10.16; OCH_3, 15.01. Found: C, 46.57, 46.73; H, 4.48, 4.73; N, 9.91, 10.13; OCH_3, 14.79, 15.15.

Reaction of potassium trinitromethide with methyl acrylate in methanol–water. A suspension of 179.3 g. (0.95 mole) of potassium trinitromethide in 1000 ml. of 50% methanol-water containing 304 g. (4.0 mole) of methyl acrylate was stirred several hours at 5–10°, then overnight at room temperature during which time the salt dissolved and the red solution separated into two phases. Five hundred milliliters of ether was added, the mixture stirred an additional 15 min., and the phases allowed to separate. The aqueous phase was extracted with a further two 250-ml. portions of ether.

The combined ether extracts, washed with three 200-ml. portions of water, dried over calcium sulfate, decolorized with charcoal, concentrated, and chilled in the freezer, deposited 36.0 g. of II, m.p. 71.5–74°. By stripping the excess methyl acrylate *in vacuo* an additional 24.8 g. of crude II, m.p. 68–71°, was recovered together with a red oil. Fractional extraction of the oil with successive portions of hot pentane as above yielded 25.2 g. (10.9%) of I, m.p. 25–27°, and 3.3 g. of an unresolvable oil. The pentane extractions left a residue 25.1 g. of crystalline II, m.p. 67–72°.

The aqueous washes were combined with the original aqueous phase and evaporated to dryness *in vacuo* leaving as a residue 69.1 g. of mixed orange and white crystals. The residue was suspended in 500 ml. ether and the mixture refluxed 1 hr. and filtered. Evaporation of the ether solution afforded a further 8.8 g. of II, m.p. 73–74°. Recovery of II totalled 94.7 g. (34.4%).

The material remaining after the final ether extraction was recrystallized from water to give 57.1 g. (27.0%)[36] of pure *potassium methyl 4,4-dinitro-2-butenoate* (III) as thick orange hexagonal plates, $\lambda\lambda_{max}^{H_2O}$ (log $\epsilon\epsilon$) 326, 398 mμ (4.24, 3.98).

Anal. Calcd. for $KC_5H_5N_2O_6$: K, 17.14; C, 26.31; H, 2.19; N, 12.29. Found: K, 17.31; C, 26.39, 26.19; H, 2.53, 2.65; N, 12.82, 12.46.

Acid Hydrolysis of II. A suspension of 5.88 g. (0.02 mole) of II in 50 ml. constant-boiling hydrochloric acid was refluxed 17 hr. during which time solution took place. The solution was concentrated to 15 ml. and cooled to precipitate a granular solid which was taken up in ether, dried over magnesium sulfate, added to petroleum ether, and cooled whereupon 3.76 g. of white crystalline solid, m.p. 139–140.8°, precipitated. Extraction of the aqueous mother liquor with ether and similar treatment furnished 1.04 g. of the same material, m.p. 139.2–140.2° (total 93%). The analytical sample of *4,4-dinitro-2-hydroxyheptanedioic acid* (V), m.p. 140–141°, was obtained by recrystallization of the combined crudes from ether–hexane.

Anal. Calcd. for $C_7H_{10}N_2O_7$: C, 31.60; H, 3.79; N, 10.54; neut. equiv., 133. Found: C, 32.11, 32.33; H, 3.80, 3.62; N, 10.36, 10.23, neut. equiv., 135.6.

Reaction of nitroform, sodium acetate, and methyl vinyl ketone in methanol–water. Methyl vinyl ketone (42.0 g., 0.60 mole) was added to a solution of 30.2 g. (0.20 mole) nitroform and 27.2 g. (0.20 mole) sodium acetate trihydrate in 450 ml. of 33% aqueous methanol with stirring and cooling. An exothermic reaction immediately ensued with the separation of a second phase which after 90 min. solidified. After stirring overnight the solid was filtered off (45 g., m.p. 34–47°) and extracted with successive portions of hot 10:1 pentane–ether. These were combined, concentrated, and cooled to furnish 34.0 g. (77%) of *5,5,5-trinitro-2-pentanone*, m.p. 43–45°.

Reaction of potassium trinitromethide with methyl vinyl ketone in methanol–water. Dropwise addition of methyl vinyl ketone (105 g., 1.50 moles) with stirring and cooling to a suspension of 67.3 g. (0.375 mole) of potassium trinitromethide at such a rate that the temperature did not exceed 10° required 1 hr. (CAUTION).[37] The salt dissolved and the solution turned black during the first 45 min.

After stirring overnight 250 ml. of water was added and the solution extracted with four 250-ml. portions of ether (a little sodium chloride was added to break the emulsion).

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[32] M. J. Kamlet, L. A. Kaplan, and J. C. Dacons, *J. Org. Chem.*, **26**, 4371 (1961).

[33] All melting points are uncorrected. Microanalyses were performed by Prof. Mary Aldridge, Dept. of Chemistry, American University, Washington, D. C., and by Prof. Kathryn Gerdeman, Dept. of Chemistry, Univ. of Maryland, College Park, Md., Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer or on a Beckman Model DU using 1-cm. quartz cells.

[34] Many of the compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

[35] K. Schimmelschmidt, Hunter Report BIOS 1919, 22/IG, July 3, 1946.

[36] Spectrophotometric analysis of the initial aqueous solution indicated that III was formed in 34.4% total yield.

[37] The reaction is quite exothermic. An earlier attempt in which the temperature was not controlled resulted in a vigorous *fume-off*.

The combined extracts were dried over anhydrous magnesium sulfate, treated with charcoal, pentane added, and concentrated to yield three crops of impure product totalling 16.6 g. (16.9%), m.p. 96–106°. Recrystallization of 15.0 g. of this material from hexane gave 13.5 g. of *5,5-dinitro-3-hydroxy-2,8-nonanedione* (IV) as chunky, white equant crystals, m.p. 109.2–110.4°. A further recrystallization from ether gave the analytical sample as fine white bars, m.p. 111.8–112.8° $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ (log ϵ) 279 mμ (2.11).

Anal. Calcd. for $C_9H_{14}N_2O_7$: C, 41.25; H, 5.34; N, 10.68. Found: C, 41.37, 41.21; H, 5.34, 5.36, N, 10.14, 10.18.

The *phenylurethane of IV*, prepared as with II, was formed in almost quantitative yield and had m.p. 220–223° dec. This was recrystallized from ethanol to give glistening white crystals, m.p. 226–227° dec.

Anal. Calcd. for $C_{16}H_{19}N_3O_8$: C, 50.40; H, 4.99; N, 11.01. Found: C, 50.60, 50.70; H, 4.98, 4.88; N, 11.03, 11.18.

The *2,4-dinitrophenylhydrazone of* IV was prepared by the method of Shriner and Fuson.[38] This procedure led to a mixture of products, m.p. 120–126°, probably containing both the mono and bis derivatives. Fractional crystallization from methanol and then from methanol–water gave a small amount of a product melting at 102 to 115° and a larger quantity of a *mono(2,4-dinitrophenylhydrazone) of* IV, m.p. 206–206.5° dec. Recrystallization of the latter from ether–pentane did not change the melting point.

Anal. Calcd. for $C_{15}H_{18}N_6O_{10}$: C, 40.72; H, 4.07; N, 18.99. Found: C, 40.88, 41.01; H, 3.69, 3.87; N, 18.87, 19.01.

Zinc–ammonium chloride reduction of II. Portionwise addition of 14.7 g. (0.05 mole) of II to a stirred suspension of 6.6 g. (0.10 mole) of powdered zinc and 2.6 g. (0.05 mole) of ammonium chloride in 75 ml. of methanol caused the temperature to rise to 65° with almost complete solution of the zinc. The solution was refluxed 10 min., cooled to 5°, and the precipitated *oxime-chlorozinc complex* (15.9 g.) filtered off, washed with ether, and dried.

Addition of this material to 4*N* hydrochloric acid gave gas evolution and a blue-green solution from which, on continued standing, a blue oil separated. On stirring overnight the oil redissolved and the blue color disappeared. Prolonged continuous extraction of the solution with ether followed by evaporation of the ether and drying of the viscous residue over sulfuric acid gave 3.4 g. of a hygroscopic gummy semisolid. This material was dissolved in a minimal amount of hot water and allowed to stand 7 days in the refrigerator whereupon 0.85 g. of a tan solid, m.p. 179–180°, separated. A single crystallization from water (charcoal) gave pure *4-keto-2-heptenedioic acid* (VI) as tiny white platelets, m.p. 184–185° (lit.[2] 186°), neut. equiv. 86.8 (calcd. 86).

The *dimethyl ester of* VI, prepared by refluxing a methanolic hydrogen chloride solution and removing the solvent, melted at 100–102° (lit.[24] 102–103°).

Mild chromic acid oxidation of II. A solution of 10.0 g. (0.10 mole) of chromic anhydride in 20 ml. of acetic acid and 10 ml. of water was added dropwise to a cooled, stirred solution of 14.7 g. (0.05 mole) of II in 150 ml. acetic acid at such a rate that the temperature did not exceed 20°. The addition required 35 min., and stirring was continued for an additional hour after which time the solution was diluted with 150 ml. of water and 20 ml. of concd. hydrochloric acid and extracted with two 500-ml. portions of ether. The combined extracts were washed with water and dried over anhydrous magnesium sulfate; the ether was stripped off at atmospheric pressure and the acetic acid *in vacuo*.

The residual oil was taken up in ether and the solution chilled to precipitate two crops, totalling 4.1 g., of chunky yellow crystals, m.p. 25.5–26.5°. A single crystallization from ether gave the analytical sample of *dimethyl 2-keto-4-nitro-3-heptenedioate* (XI), m.p. 26.0–26.5°, $\lambda_{\text{max}}^{\text{ether}}$ (log ϵ) 249 mμ (3.86).

Anal. Calcd. for $C_9H_{11}NO_7$: C, 44.10; H, 4.49; N, 5.72; OCH_3, 25.30. Found: C, 44.24, 44.14; H, 4.51, 4.64; N, 5.25, 5.54; OCH_3, 26.07, 26.23.

The *mono(2,4-dinitrophenylhydrazone) of* XI[38] melted at 143.2–143.8° after a single recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{15}N_5O_{10}$: C, 42.38, H, 3.53; N, 16.46. Found: C, 42.33, 42.27; H, 3.39, 3.45; N, 16.70.

Permanganate oxidation of II. One-fiftieth mole of II in 100 ml. of 10% sulfuric acid decolorized 240 ml. of normal potassium permanganate solution or 12 equiv. per mole. The colorless solution was concentrated to 100 ml. and continuously extracted overnight with ether. Evaporation of the ether left 2.30 g. (97.5%) of *succinic acid*, m.p. 179–180°, mixture m.p. with authentic sample 182–184°.

Sodium bismuthate oxidation of V. An equimolar amount of sodium bismuthate was added to a well stirred solution of 5.32 g. (0.02 mole) of V in 100 ml. of 33% phosphoric acid. The mixture, initially chocolate in color, began to lighten immediately and was allowed to stir 20 hr. after which time it was filtered to remove inorganic salts. The filtrate was added to a solution of 2.97 g. (0.015 mole) of 2,4-dinitrophenylhydrazine in 0.5*N* of methanolic hydrogen chloride and allowed to stand 2 hr. during which time a dark red solid precipitated (2.40 g.). This material was dried and leached with boiling ethyl acetate–chloroform, leaving as a residue the *2,4-dinitrophenylhydrazone of 5-formyl-4-nitro-4-pentenoic acid*, a carmine red solid, m.p. 227–229°.

Anal. Calcd. for $C_{12}H_{11}N_5O_8$: C, 40.80; H, 3.12; N, 19.83. Found: C, 40.96, 40.95; H, 2.77, 2.88; N, 20.17, 19.86.

Alkaline degradation of II, *spectrophotometric studies.* A 2.00×10^{-3} molar solution of II in 0.1*N* aqueous sodium hydroxide showed no evidence of the high intensity absorption at ~380 mμ which is characteristic of the anion of methyl 4,4-dinitrobutyrate.[39] Immediately upon solution the spectrum showed a low intensity maximum at 390 mμ (ϵ 75)[40] and a shoulder at 280 mμ (ϵ 175). After 24 hr. these were overshadowed by a maximum which had appeared at 287 mμ (ϵ 230), while after 6 days the spectrum showed twin maxima at 291 and 320 mμ (ϵ 170 and 160).

Isolation of product. Ten grams of II required about 40 min. to dissolve in 50 ml. of 4*N* sodium hydroxide. Acidification of the amber solution with hydrochloric acid caused evolution of nitrous fumes. Stripping the solvent left a gummy solid which was taken up in ether. The sodium chloride was filtered off and the solution was dried over magnesium sulfate and concentrated. The residual oil, taken up in ethyl acetate, decolorized, and allowed to evaporate slowly, deposited 100 mg. of a gummy white solid, m.p. 147–161°. A single recrystallization from ethyl acetate furnished nicely formed white crystals (2.3%), m.p. 177–179°; mixture m.p. with authentic *succinic acid*, 179–181°.

From similar reactions carried out in the presence of *p*-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine no crystalline products were isolable.

Independent synthesis of V. To a mixture of 23.0 g. (0.10 mole) of potassium methyl 4,4-dinitrobutyrate (VIII) in 200 ml. of water containing 0.10 mole each of sodium acetate and acetic acid was added 22.2 g. (0.20 mole) of α-acetoxyacrylonitrile in 100 ml. of methanol. The mixture was stirred 20 hr. after which time it had turned orange-red, and an oil had separated. The mixture was extracted with ether, and the combined ether extracts were washed thoroughly with 10% sodium carbonate solution, dried over anhydrous magnesium sulfate, and concentrated.

About five grams of a viscous oil remained which could not be crystallized. It was therefore hydrolyzed directly by refluxing with 50 ml. of constant-boiling hydrochloric

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(38) Ref. 22, p. 143.

(39) The potassium salt of methyl 4,4-dinitrobutyrate shows $\lambda_{\text{max}}^{\text{dil. KOH}}$ (log ϵ) 379 mμ (4.22) [D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961)].

(40) Values of ϵ are based on the initial concentration of II. They have no meaning in terms of the actual products in solution.

acid. After an 8-hr. period no oil remained, and the solution was filtered hot to remove suspended particles of carbon, treated with Norit and evaporated to dryness *in vacuo.* The residual solid was thoroughly extracted with 250 ml. of ether, the ether extract dried over anhydrous magnesium sulfate, again treated with Norit, concentrated to about 100 ml., and hexane added till slight clouding was observed. On cooling the solution a white crystalline solid separated, m.p. 120–125°; on admixture with a sample of V from hydrolysis of II, m.p. 122–127°.

The crude *4,4-dinitro-2-hydroxyheptanedioic acid* was recrystallized from acetonitrile–heptane–benzene to yield a slightly higher melting sample, m.p. 128–131°; and again from ethyl acetate–benzene to give a sample melting at 128.8–134.4°. The latter, on admixture with the sample of V from hydrolysis of II, melted from 129.5 to 138°.

Anal. Calcd. for $C_7H_{10}N_2O_9$: C, 31.60; H, 3.79; N, 10.54. Found: C, 31.99, 32.04; H, 3.79, 3.85; N, 10.09, 9.80.

Evidently the sample of V prepared in this way was contaminated by a small amount of impurity which could not readily be removed by crystallization. Infrared spectra of both samples of V were superimposable and x-ray diffraction patterns confirmed that they were indeed identical.

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Directive Influences in Olefin Formation

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In the formation of olefin mixtures by elimination reactions of 3-heptyl derivatives, bimolecular processes (chloride plus base, quaternary ammonium hydroxide plus heat, or alcohol with sulfuric or phosphoric acid) give 55–66% of 2-heptene and 45–34% of 3-heptene, but monomolecular processes (pyrolysis of hydrogen phthalate, xanthate, or amine oxide, and probably aluminum oxide dehydration) give 43–48% of 2-heptene and 57–52% of 3-heptene. These results are most easily explained by electronic effects in the first group, and by steric effects in the second group. Dehydration of 2,4-dimethyl-3-hexanol with sulfuric or phosphoric acid gives 58–60% of 2,4-dimethyl-2-hexene and 42–40% of the 3-hexene, which is in accord with the results of the 3-heptyl series, but the bromide and base give only 51% of the 2-hexene: pyrolyses of the acetate and hydrogen phthalate give high (100 and 75%) proportions of the 2-hexene, but aluminum oxide yields only 49%. Pyrolysis of 2,5-dimethyl-3-hexyl acetate gives 68% of 2,5-dimethyl-3-hexene.

The formation of olefins by elimination reactions is a synthetic process of long standing, but more than one product is usually observed. The pyrolytic cis eliminations have been covered in a recent review[2] dealing with esters, xanthates, amine oxides, and other starting materials. Other elimination reactions such as the action of strong acids on alcohols, bases on halides, and pyrolysis of quaternary ammonium hydroxides have been the basis of the formulation of the Hofmann[3] and Saytzeff[4] rules. Despite the prolonged attention granted such reactions it cannot be said that all factors are well understood.[5]

In this paper eliminations have been studied in which, for the most part, there is no obvious difference in predictions based on either Hofmann or Saytzeff rules. This would apply either to the 3-heptyl or to the 2,4-dimethyl-3-hexyl derivatives, but in the case of the pyrolysis of 2,5-dimethyl-3-hexyl acetate there was potential steric hindrance so located that the normally favored elimination might yield the minor quantity of product.

Dehydration of 3-heptanol with sulfuric acid gave an olefin mixture in which the 2-heptene: 3-heptene ratio was 60.4:39.6. Dehydration of the 3-heptanol with phosphoric acid gave the product ratio 55.0:45.0. Refluxing 3-chloroheptane with methanolic potassium hydroxide gave 62.8:37.2. Heating 3-heptyltrimethylammonium hydroxide gave 65.8:34.2. These are all reactions best interpreted as proceeding by concerted mechanisms, and the favored product in each case is 2-heptene. This should be the more stable isomer on the basis of hyperconjugation, although no difference in stability is apparent in available data.[6]

Pyrolysis of 3-heptyl methyl xanthate gave an olefin mixture in which the 2-heptene:3-heptene ratio was 46.7:53.3. 3-Heptyldimethylamine oxide gave a ratio of 44.8:55.2. 3-Heptanol over alumina gave 47.5:52.5 and pyrolysis of 3-heptyl hydrogen phthalate gave 42.6:57.4. These reactions all involve a cyclic intramolecular transition state if one can assume that the 3-heptanol-alumina dehydra-

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(1) Du Pont Fellow, 1957–58.

(2) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(3) A. W. Hofmann, *Ann.*, **79**, 11 (1851).

(4) A. Saytzeff, *Ann.*, **179**, 296 (1875).

(5) See, for example, E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, New York, 1959, p. 472.

(6) R. R. Dreisbach, *Physical Properties of Chemical Compounds—II* (Number 22 of the Advances in Chemistry Series), American Chemical Society, Washington, D. C., (1959), p. 247–250.