

ether extract was washed twice with 3% HCl solution, then with distilled water until free of acid, and finally dried over anhydrous sodium sulfate. Evaporation of the solvent yielded the reduced peroxide concentrate consisting of methyl monohydroxy-9-octadecynoate: hydrogen absorption value, 1.96 moles/mole; hydroxyl, 1.02 moles/mole.

Anal. Calcd. for $C_{19}H_{34}O_3$: C, 73.51; H, 10.97. Found: C, 73.42; H, 10.88.

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Reaction of 1,5-Dinitropentane with Methyl Vinyl Ketone

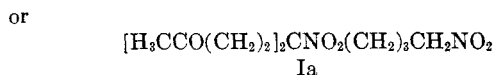
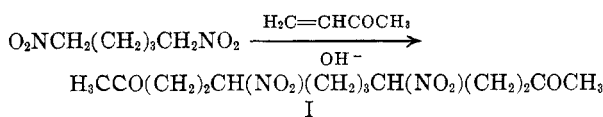
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Michael-type condensations of aliphatic mono-nitro and *gem*-dinitro compounds with compounds having an activated double bond have been studied by many investigators.²⁻⁴ However, the literature is void of this reaction with α,ω -dinitro compounds.

This communication deals with the reaction of 1,5-dinitropentane and methyl vinyl ketone, in the presence of a sodium hydroxide catalyst. The reaction was carried out in different solvents and under a variety of conditions. In all runs, besides intractable oils, a solid was obtained which analyzed correctly for a di-addition product. The maximum refined yield of 25% resulted when the reaction was carried out in 90% ethanol at 50° for 20 hr.

Two di-addition products might arise from this reaction, the symmetrical adduct I and the unsymmetrical one (Ia).



Proof that 5,9-dinitro-2,12-tridecanedione (I) had formed was obtained by (1) the Nef⁵ reaction, (2) the red-white-and-blue test,⁶ (3) infrared spectra, and (4) the bromination product.

(1) From the M.S. Dissertation of Clayton N. Aguilar, Purdue University, May 1956.

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

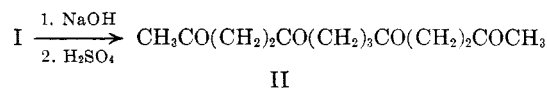
(3) H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951). Previous pertinent publications are cited in this paper.

(4) E. D. Bergman and R. Corett, *J. Org. Chem.*, **21**, 107 (1956).

(5) J. U. Nef, *Ann.*, **280**, 263 (1894).

(6) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 399, (1948).

The Nef reaction of the disodium salt of I gave in 28% yield a white nitrogen-free solid II, which was unstable to light and air at room temperature. The infrared spectrum of II showed a strong absorption peak at 5.93 μ , characteristic of the carbonyl group and no maxima for nitro groups. Since tertiary nitro groups are not affected in the Nef reaction, structure Ia is eliminated.



When II was reacted with semicarbazide a new compound was obtained, the nitrogen analysis of which gave a low value for the expected tetrasemicarbazone and a high value for a disemicarbazone. It is possible that not all of the carbonyl groups in II had reacted, and it is believed that the product obtained constituted a mixture of semicarbazones. Attempts to form an oxime of II yielded only gummy materials. Treatment of II with 2,4-dinitrophenylhydrazine in sulfuric acid yielded the 2,4-dinitrophenylhydrazone of acetone (III) and some unreacted II. It is believed that III arose from the oxidation of II to acetoacetic acid, followed by decarboxylation.

The presence of secondary nitro groups in the addition product I was further confirmed by the blue color which resulted from the red-white-and-blue reaction. The presence of a primary nitro group would have been indicated by a red color, and a tertiary nitro group is not affected by this test.

The infrared spectrum of the di-addition product exhibited absorption maxima for the carbonyl group at 5.88 μ and the nitro group at 6.50 μ (asym. stretching) and 7.39 μ (sym stretching). These findings are also in agreement with structure I, because according to the studies of Brown,⁷ a structure such as Ia should show splitting of the nitro bond in the asymmetric stretching vibration.

Additional evidence for I resulted from its bromination in the presence of two or less-than-two equivalents of base. A dibromo compound was obtained in 61% yield, the analysis and infrared spectrum of which agreed with the expected 5,9-dibromo-5,9-dinitro-2,12-tridecanedione (IV). As expected, IV was insoluble in base and gave a negative red-white-and-blue test.⁸ Its infrared spectrum showed a maximum at 5.84 μ for the car-

(7) J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(8) A referee has suggested that besides structures I and Ia, the compounds $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CO}(\text{CH}_2)_3\text{CH}(\text{NO}_2)(\text{CH}_2)_3\text{CH}_2\text{NO}_2$ (V) and $\text{CH}_3\text{COCH}(\text{CH}_2\text{CH}_2\text{COCH}_2)\text{CH}_2\text{CH}(\text{NO}_2)(\text{CH}_2)_3\text{CH}_2\text{NO}_2$ (VI), derived from an abnormal Michael addition, should be considered. Although in addition reactions of nitro paraffins to methyl vinyl ketone such self-condensations of the ketone have never been reported in the literature, this possibility cannot be ruled out *a priori*. However, the insolubility of the dibromo derivative IV in base, together with the negative color test, is evidence that IV is not a derivative of V or VI.

bonyl group, and at 6.46 μ (asym. stretching) and 7.32 μ (sym. stretching) for the nitro group.

EXPERIMENTAL

5,9-Dinitro-2,12-tridecanedione. To 0.05 mole (8.10 g.) of 1,5-dinitropentane,⁹ 50 ml. of 90% aqueous ethanol, eight drops of 13% methanolic sodium hydroxide, and 0.12 mole (9.90 g.) of 85% methyl vinyl ketone were added with stirring. The reaction mixture was gradually heated and kept at 50 \pm 2°, with continuous stirring, for 20 hr., after which it was cooled and acidified to a pH of four with *N* hydrochloric acid. The acidified reaction mixture was chilled and the solid that separated out was collected by filtration. The crude product, m.p. 61–72°, weighed 5.15 g. Crude yield, 34%. Careful recrystallization from ethyl acetate gave pure *5,9-dinitro-2,12-tridecanedione*, m.p. 77.5–78.5°, representing 73% by weight of the crude taken for purification. Refined yield, 25%.

Anal. Calcd. for C₁₃H₂₂N₂O₆: C, 51.64; H, 7.34; N, 9.21. Found: C, 51.80, 51.88; H, 7.35, 7.50; N, 9.57, 9.63.

The *disemicarbazone* of the refined product was prepared. The derivative melted at 180.0–180.5° (dec.), after one recrystallization from aqueous tetrahydrofuran.

Anal. Calcd. for C₁₅H₂₈N₄O₆: C, 43.26; H, 6.78; N, 26.91. Found: C, 43.48, 43.30; H, 6.84, 7.03; N, 26.70, 26.79.

2,5,9,12-Tridecanetetrone (II). A solution of 2.7 g. (approximately 27 mmoles) of sulfuric acid in ten ml. of water was cooled down to 0–5° with an ice bath. The solution of the disodium salt, previously prepared by allowing a mixture of 0.9 g. (3 mmoles) of *5,9-dinitro-2,12-tridecanedione*, 20 ml. of methanol, 10 ml. of water, and 9.0 ml. of 2*N* methanolic sodium hydroxide (approximately 18 mmoles of sodium hydroxide) to stand 1.5 hr., was added to the acid solution, with stirring, over a 15-min. period. The mixture was chilled and filtered to give the first crop of solid, which was 0.6 g. of sodium sulfate. The liquor was evaporated, rechilled, and filtered to yield a second crop of solid, which was the crude product weighing 0.2 g. (28%). Recrystallization from aqueous ethanol gave *2,5,9,12-tridecanetetrone*, m.p. 106–107° (dec.). The compound was unstable to light and air at room temperature.

Anal. Calcd. for C₁₃H₂₀O₄: C, 64.98; H, 8.39. Found: C, 64.95, 65.02; H, 8.43, 8.46.

Reaction of II with semicarbazide. By following the procedure of Shriner, Fuson, and Curtin¹⁰ and employing 0.5 g. of II, 0.1 g. of a solid was obtained which after several recrystallizations from aq. ethanol melted at 211–214° (dec.).

Anal. Calcd. for C₁₇H₃₂N₁₂O₄ (tetrasemicarbazone): N, 35.88; for C₁₅H₂₆N₆O₄ (disemicarbazone): N, 23.71. Found: N, 26.50, 26.71.

Reaction of II with 2,4-dinitrophenylhydrazine. The procedure of Shriner, Fuson, and Curtin¹⁰ was followed. The reaction mixture was filtered and the solid, after several recrystallizations from aq. ethanol melted at 125.5–126.5°. It was identified as the semicarbazone of acetone. A mixed melting point determination with an authentic sample gave no depression.

The above filtrate deposited on cooling a solid which was unreacted II.

5,9-Dibromo-5,9-dinitro-2,12-tridecanedione. A solution consisting of 1.8 g. (6 mmoles) of *5,9-dinitro-2,12-tridecanedione*, 60 ml. of methanol, 10 ml. of water, and 6.0 ml. of 2*N* methanolic sodium hydroxide (approximately 12 mmoles of sodium hydroxide) was cooled to 3° with an ice bath. Then 9.0 g. of bromine was added with stirring, and

the mixture was removed from the ice bath and allowed to stand for 5 min. The excess bromine and some solvent were stripped off and the mixture was chilled and filtered to give 1.7 g. (61%) of *5,9-dibromo-5,9-dinitro-2,12-tridecanedione*, m.p. 65.5–66.5°. Recrystallization from carbon tetrachloride gave a refined product, m.p. 65.5–66.0°.

Anal. Calcd. for C₁₃H₂₀Br₂N₂O₆: C, 33.93; H, 4.38; N, 6.09; Br, 34.74. Found: C, 33.81, 33.72; H, 4.18, 4.25; N, 6.00, 6.26; Br, 34.51, 34.69.

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Alkali-Resistant Hemicellulose in Luffa Cellulose¹

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This work was undertaken to investigate the relationship of the alkali-resistant hemicellulose and cellulose in the skeletal substance of the dishcloth gourd (*Luffa cylindrica*). In 1927³ its constituents were reported to be cellulose, lignin, hemicellulose, and small amounts of mannan and galactan. An analysis of its constituents is shown in Table I.

TABLE I

ANALYSIS OF LUFFA CONSTITUENTS	
alpha-Cellulose	62.8%
Pentosan	19.5%
Lignin	12.1%
Uronic anhydride	6.7%

Table II indicates that alcohol extraction, delignification with chlorine dioxide (sodium chlorite in acid solution), and alkali extraction were found to be a proper sequence of procedures for cellulose evaluation. The skeletal structure of the gourd was completely disintegrated by using the above sequence. The completion of disintegration was observed by the changes in the physical state of the gourd upon chemical treatment. When the other sequences in Table II were used, disintegration was incomplete. If the disintegration is incomplete, some hemicellulose originally trapped in the cellulose would not be separated. There appears to be some alcohol-soluble compound serving as a cementing agent to bind cellulose and hemicellulose together to a certain extent. It is possible that the alcohol-soluble constituent might be affected by the chemical treatments, particularly chlorine dioxide or alkali, so as to become less soluble in alcohol, rendering

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(3) S. Masuda, *Cellulose Industry*, **3**, 321 (1927).

(9) H. Feuer and G. Leston, *Org. Syntheses*, **34**, 39 (1954).

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, New York, 1956, p. 218.