evaporation of the ligroin (b.p. 90–120°) leachings yielded about 1 g. of *N-hydroxymethyl-N,N'-methylenebisdodecanamide* (IIa) as a colorless wax which melted at 106–106.5° after two crystallizations from alcohol and drying *in vacuo* at 55°.

Anal. Calcd. for $C_{26}H_{52}N_2O_3$: C, 70.86; H, 11.89. Found: C, 71.08; H, 11.82.

IIa gave a positive Eegriwe test, liberated formaldehyde at 220° and depressed the melting point of Ia by 23°. Three attempts to repeat this reaction, two using 1-naphthyl isocyanate from a different source (Matheson Coleman & Bell), and one employing purified isocyanate, b.p. 153.0–153.5°/20 mm., gave only colorless, low-melting mixtures in which no IIa could be detected; infrared evidence indicated that a good deal of unchanged Ia was present.

N-Hydroxymethyl-N,N'-methylenebisdodecanamide (IIa) was also obtained from Ia under Schotten-Bauman conditions.[4] When 10% aqueous potassium hydroxide (10 ml.) and benzoyl chloride (1 ml.) were added with shaking to *N*-hydroxymethyldodecanamide (1.0 g.) a vigorous reaction occurred. After cooling the colorless slurry was shaken mechanically for 1 hr. at room temperature. The solid was filtered and crystallized twice from 95% alcohol and once from chloroform. Evaporation of the chloroform mother liquors gave a solid, which was recrystallized from 100% alcohol to yield 80 mg. of colorless IIa, m.p. 104–105°, which proved to be identical with IIa from the aforedescribed reaction by mixed melting point and infrared spectrum (16 peaks checked).

N,N'-Methylenebisdodecanamide (III) has been prepared from lauroyl chloride in 20% yield[12] and, it has been claimed in the patent literature, from lauronitrile in "excellent" yield.[13] Using a variation of a convenient method of Einhorn,[4] a mixture of lauramide (1 g.), 36% aqueous formaldehyde (2 ml.), 5% sulfuric acid (1 ml.), and ethylene dichloride (10 ml.) was heated to reflux for 1.5 hr., cooled, filtered, and washed with water. The crude product, m.p. 145–148° (0.6 g., 57%), recrystallized from ethanol as colorless crystals, m.p. 155–156° (lit. 156–157°,[12] 154–155°[13]), infrared absorption (see Fig. 1) at 3310, 3055, 1633, 1553, 1535, 1128, and 863 cm.$^{-1}$, in apparent agreement with the literature.[12]

Anal. Calcd. for $C_{25}H_{50}O_2N_2$: N, 6.82. Found: N (Kjeldahl), 6.78.

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Bromination Products of Mesitylglyoxal and Configuration of the Corresponding Monoximes

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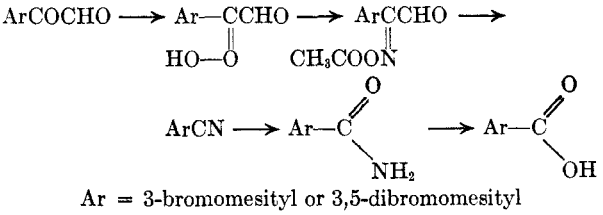
In the light of the behavior of benzene, toluene, the xylenes, and mesitylene toward bromine in polar solvents,[2,3] we decided to investigate phenylglyoxal and mesitylglyoxal under similar conditions.

(1) In partial fulfillment of the requirements for the M.S. degree.

(2) P. B. D. de la Mare and P. N. Robertson, *J. Chem. Soc.*, 279 (1943).

(3) R. Oda and K. Tumura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **33**, No. 728, 129 (1937).

In both aqueous methanol and aqueous acetic acid, mesitylglyoxal underwent both mono- and dibromination, and the products proved to be identical with those obtained by Fuson *et al.*,[4,5] whereas phenylglyoxal did not undergo bromination. In aqueous acetic acid, both more rapid bromination and higher yields resulted than in aqueous methanol. Gray and Fuson[6] characterize the monoxime of mesitylglyoxal in terms of molecular formula and physical properties. We decided to investigate the configurations of the mono- and dibromoglyoxal monoximes. Thus we prepared the monoximes, acetylated them, and subjected the acetates to treatment with dilute aqueous sodium hydroxide.[7] These oximino esters underwent cleavage and not hydrolysis, thus indicating that they were of the α-configuration, and in terms of the products, that the oximino groups had replaced the ketocarbonyl oxygens.



Ar = 3-bromomesityl or 3,5-dibromomesityl

EXPERIMENTAL

Mesitylglyoxal and phenylgalyoxal were prepared according to the method of Gray and Fuson.[6]

Phenylglyoxal did not undergo bromination in aqueous methanol or aqueous acetic acid.

3-Bromomesitylglyoxal. To a 200-cc. 2-necked round bottom flask equipped with a mechanical stirrer, was added 5.3 g. (0.03 mole) of mesitylglyoxal dissolved in the minimum volume of cold methanol or glacial acetic acid. To this solution water was added to incipient cloudiness, followed by a few drops of the chosen solvent to give a clear solution. To the prepared solution 4.8 g. (0.03 mole) of bromine was added dropwise with vigorous stirring. The color of the bromine disappeared very rapidly. After the addition of the bromine, stirring was continued for some time. Finally enough water was added to produce slight turbidity, and the contents of the flask were chilled overnight. A pale yellow crystalline substance was obtained which when recrystallized from methanol exhibited the same physical and chemical properties as the compound obtained by Fuson and Soper.[4] A boiling aqueous solution of the glyoxal to which a few drops of methanol were added, on cooling, deposited the colorless hydrate. Both the glyoxal and its hydrate upon oxidation with alkaline hydrogen peroxide gave 3-bromomesitoic acid,[8] melting and mixed melting point with an authentic sample at 168°.

3,5-Dibromomesitylglyoxal was prepared by the same method as 3-bromomesitylglyoxal by using 2 moles of

(4) R. C. Fuson and Q. F. Soper, *J. Org. Chem.*, **9**, 193 (1944).

(5) R. C. Fuson, C. H. McBurney, and W. E. Holland, *J. Am. Chem. Soc.*, **61**, 3246 (1939).

(6) A. R. Gray and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 739 (1934).

(7) R. P. Barnes and A. H. Blatt, *J. Am. Chem. Soc.*, **57**, 1330 (1935).

(8) P. R. Shildneck and R. Adams, *J. Am. Chem. Soc.*, **53**, 347 (1931).

bromine per mole of mesitylglyoxal. It was obtained as the hydrate, exhibiting physical and chemical properties identical with those of the compound obtained by Fuson *et al.*,[5] yielding an identical semicarbazone, mesitylglycolic acid, and 3,5-dibromomesitoic acid.

The α-ketoxime of 3-bromomesitylglyoxal. An aqueous solution of 2.5 g. of hydroxylamine hydrochloride and 4 g. of sodium acetate in 10 cc. of water was prepared and heated to 40°. To this aqueous solution was added 2.5 g. of 3-bromomesitylglyoxal dissolved in 10 cc. of alcohol. The solution was warmed and shaken. In a few minutes a crystalline solid began to separate. When the reaction appeared to be complete, the mixture was chilled, filtered, washed first with water and finally twice with alcohol. On recrystallization from dilute alcohol, white crystals were obtained which melted at 135–136°.

Anal. Calcd. for $C_{11}H_{12}O_2BrN$: C, 48.89; H, 4.44. Found: C, 49.00; H, 4.49.

The α-ketoxime acetate of 3-bromomesitylglyoxal. A cold solution of 1.5 g. of the ketoxime in 5.5 cc. of acetic anhydride was shaken for about 1 hr. On chilling, pale yellow crystals separated. Upon filtering, drying, and recrystallization from methanol, white crystals melting at 87–88° were obtained.

Anal. Calcd. for $C_{13}H_{14}O_3BrN$: C, 50.00; H, 4.48. Found: C, 49.60; H, 4.56.

The α-ketoxime of 3,5-dibromomesitylglyoxal. This oxime was prepared in the same manner as the monobromooxime. It was obtained as white crystals, melting at 202–203°.

Anal. Calcd. for $C_{11}H_{11}O_2Br_2N$: C, 37.82; H, 3.15. Found: C, 37.99; H, 3.49.

The α-ketoxime acetate of 3,5-dibromomesitylglyoxal. This oxime acetate was prepared in the same manner as the monobromooxime acetate.

Anal. Calcd. for $C_{13}H_{13}O_3Br_2N$: C, 39.90; H, 3.33. Found: C, 39.72; H, 3.10.

Cleavage of the oxime acetates of the bromoglyoxals. One half g. of each of the oxime acetates was dissolved in 10 cc. of alcohol and shaken for several hours with 30 cc. of cold aqueous 5% sodium hydroxide. The solutions were diluted with water and extracted with ether. The ether was evaporated and the residues refluxed for several hours with 30% sodium hydroxide. The solutions were acidified witb dilute hydrochloric acid and extracted with ether. The ethereal solutions were washed with water and dried over anhydrous sodium sulfate. Upon filtration and concentration by evaporation, each solution yielded a white crystalline solid. The monobromooximeacetate yielded 3-bromomesitoic acid and the dibromooxime acetate yielded 3,5-dibromomesitoic acid. Each acid was identified by comparison with an authentic sample.

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Some Derivatives of Cyanoethylated Isophorone

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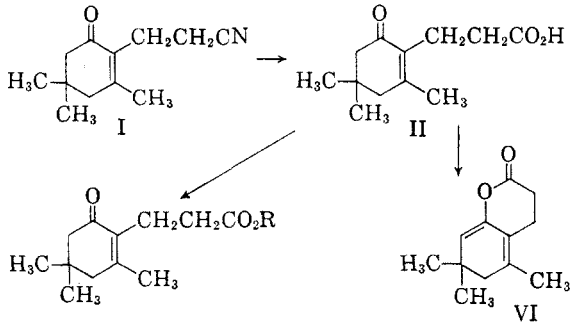
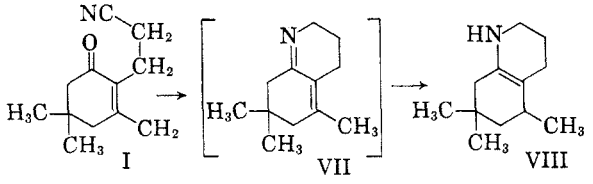
The base-catalyzed condensation of isophorone with acrylonitrile was reported by Bruson[1] to give mono-, di- and tricyanoethylation products. The structure of monocyanoethylated isophorone was shown to be 2-(2-cyanoethyl)-3,5,5-trimethyl-2-cyclohexeneone (I) by Julia.[2] Hydrolysis of I to the corresponding acid (II)[1,2] and preparation of the methyl ester[2] appear to be the extent of utilization of this readily available keto nitrile. Herein is reported the synthesis of the allyl (III) decyl (IV), and vinyl (V) esters of II by conventional methods, as well as its conversion to the enol-lactone (VI) by dehydration with acetic anhydride. Similar dehydrations of 5-keto acids have been reported by Russian workers[3] to give monounsaturated enol-lactones.



	R,
III	$-CH_2CH=CH_2$
IV	$-C_{10}H_{21}$
V	$-CH=CH_2$

We also report a further transformation of I to an octohydroquinoline system. Hydrogenation of I over Raney nickel in ammoniacal dioxane gave the novel cyclic enamine (VIII) in 59% yield. Reductive cyclization of 5-keto nitriles has been reported previously by Nazarov[4] to yield a saturated material.

A possible mode of formation of VIII may involve initial reduction and cyclodehydration to VII followed by 1,4-addition of hydrogen. It is not surprising that the resulting hindered internal double bond is resistant to further reduction.



The general structure of VIII has been assigned on the basis of elemental analysis, acid equivalent, *N*-phenylurea derivative, and infrared spectrum. That the double bond is in the fully substituted position is indicated by very intense infrared bands at 6.12 and 6.21μ, which correspond to double bond and secondary amine absorptions, respectively, and are intensified as a result of interaction of the unshared pair of electrons on nitrogen with the double bond. Lack of absorption in the 12.4μ

(1) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **75**, 3585 (1953).

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(4) N. Nazarov, G. A. Shvekhgeimer, and V. A. Rudenko, *J. Gen. Chem. U.S.S.R.*, **24**, 325 (1954).