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 with 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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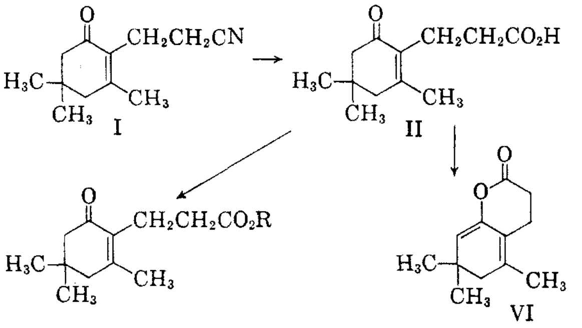
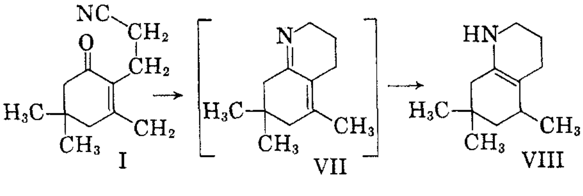
The base-catalyzed condensation of isophorone with acrylonitrile was reported by Bruson[1] to give mono-, di- and tricyanoethylation products. The structure of monocyanoethylated isophorone was shown to be 2-(2-cyanoethyl)-3,5,5-trimethyl-2-cyclohexeneone (I) by Julia.[2] Hydrolysis of I to the corresponding 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

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

(2) S. Julia, *Compt. rend.*, **237**, 913 (1953).

(3) R. Y. Lovina, N. P. Shusherina, and M. Y. Lurye, *J. Gen. Chem. U.S.S.R.*, **24**, 1423 (1954).

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

region, which would indicate hydrogen attached to a double bond, excludes consideration of the double bond at the 4 or 8 positions.

The infrared spectrum of the residual product obtained after warming VIII with water and a drop of hydrochloric acid shows new bands indicating the presence of ketone (5.90 μ), primary amine, (3.02 and 11.1μ) and imine (6.02 μ). These data are in accord with the presence of an equilibrium mixture of the expected products, the isomeric cyclic imine and its hydrolytic cleavage product, the amino ketone.

EXPERIMENTAL[5]

2-(2-Cyanoethyl)-3,5,5-trimethyl-2-cyclohexeneone (I). The method of Bruson,[1] modified by the use of sodium methylate as catalyst, gave a 20% yield of I (b.p. 129–131°/2.4 mm., n_D^{30} 1.4908, d_{20}^{20} 0.9920).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.40; H, 8.91; N, 7.34. Found: C, 75.42; H, 8.95; N, 7.38.

2-(2-Carboxyethyl)-3,5,5-trimethyl-2-cyclohexeneone (II). A mixture of 191 g. (1 mole) of I, 112 g. (2 moles) of potassium hydroxide and 1000 ml. of water was heated at reflux for 7 hr. The cooled mixture was then acidified with conc. hydrochloric acid to precipitate the product. Crystallization from heptane gave a 61% yield of refined II (m.p. 74.5–75.5°, reported[1] m.p. 76–77°).

2-(2-Carboallyloxyethyl)-3,5,5-trimethyl-2-cyclohexeneone (III). A mixture of 107 g. (0.51 mole) of II, 116 g. (2.0 moles) of allyl alcohol, 500 ml. of benzene, and 1.0 g. of *p*-toluenesulfonic acid was heated to reflux and the allyl alcohol-water-benzene azeotrope was taken off over a 5.5-hr. period. The reaction mixture was washed with 100 ml. of 20% aqueous sodium carbonate and then with 100 ml. of water. Distillation gave a 68% yield of III [b.p. 136°/1.7 mm., n_D^{30} 1.4861, d_{20}^{20} 1.0169. Infrared maxima at 3.24 μ ($CH_2{=}$), 5.8 μ (ester C=O), 6.03 μ (conj. ketone), 6.14 μ (conj. C=C), 7.24 and 7.32 μ [$(CH_3)_2C$], 8.7 μ (ester C—O—), 10.1 and 10.8 μ ($CH_2{=}C$)].

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 72.00; H, 8.80. Found: C, 71.61; H, 8.49.

2-(2-Carbo-"Oxo"-decyloxyethyl)-3,5,5-trimethyl-2-cyclohexeneone (IV). A mixture of 110 g. (0.52 mole) of II, 316 g. (2.0 moles) of Enjay Company "Oxo" decanol, 500 ml. of benzene, and 1.1 g. of *p*-toluenesulfonic acid was heated to reflux and water was removed as the benzene azeotrope over a 7-hr. period. The reaction mixture was washed with 10% aqueous sodium carbonate and then with water. Benzene was removed by distillation and IV was taken as residual dark oil in 99% yield [n_D^{30} 1.4739, d_{20}^{20} 0.9499. Infrared maxima at 5.80 μ (ester C=O). 6.03 (conj. ketone C=O), 6.13 μ (conj. C=C), 8.6 μ (ester C—O—), 14.4 μ (*cis* RCH=CHR')].

Anal. Calcd. for $C_{22}H_{38}O_3$: C, 75.5; H, 10.85. Found: C, 75.58; H, 10.87.

2-(2-Carbovinyloxyethyl)-3,5,5-trimethyl-2-cyclohexeneone (V). A mixture of 664 g. (3.15 moles) of II, 1376 g. (16 moles) of vinyl acetate, 10 g. of mercuric acetate, and 3.1 g. of conc. sulfuric acid was allowed to stand at ambient temperature for 72 hr. The catalyst was neutralized with 6 g. of anhydrous sodium acetate and the precipitate was removed by filtration. Distillation gave a 30% yield of V (b.p. 130°C./1.3 mm., n_D^{30} 1.4889).

Bromine titration of the vinyl group yielded a figure which was 102% of the calculated value. Infrared data was consistent with the assigned structure.

5,7,7-Trimethyl-3,4,6,7-tetrahydro-1,2-benzopyrone (VI). A mixture of 125 g. (0.596 mole) of II and 350 ml. of acetic anhydride was refluxed for 4 hr. during which time 105 ml. of distillate was removed. Distillation of the residual mixture gave 97 g., an 85% yield of VI [b.p. 125°/3.3 mm., n_D^{30} 1.5176, d_{20}^{20} 1.0571. Infrared maxima at 5.64 μ lactone C=O, strong), 6.1 μ (conj. C=C). Equivalent weight by saponification. Calcd.: 192. Found: 196].

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.1; H, 8.34. Found: C, 74.64; H, 8.12.

5,7,7-Trimethyl-1,2,3,4,5,6,7,8-octahydroquinoline (VIII). A mixture of 382 g. (2 moles) of I, 300 ml. of dioxane, 10 g. of wet Raney nickel (rinsed twice with dioxane), and 145 g. (8.5 moles) of anhydrous ammonia was hydrogenated in a stainless steel rocking autoclave at 160° and 1000 p.s.i.g. over a 5-hr. period. The cooled reaction mixture was filtered and fractionated to give 213 g., a 59% yield, of III [b.p. 85°/1.8 mm., n_D^{30} 1.5164, d_{20}^{20} 0.9495. Equivalent weight by perchloric acid in acetic acid titration. Calcd.: 179. Found: 179.5. Infrared maxima at 3.14 and 6.21 μ (—NH—), 6.12 μ (C=C), and 10.4 μ (—NH— out of plane)].

Anal. Calcd. for $C_{12}H_{21}N$: C, 80.4; H, 11.7; N, 7.84. Found: C, 80.6; H, 11.5; N, 7.95.

The *N*-phenylurea was prepared by treatment of VIII with phenyl isocyanate in ether and crystallized from ethanol (m.p. 115–116°).

Anal. Calcd. for $C_{19}H_{26}N_2O$: C, 76.6; H, 7.73; N, 9.40. Found: C, 77.0; H, 7.84; N, 9.75.

Hydrolysis of VIII. A mixture of 3.6 g. of VIII, 80 ml. of water, and one drop of conc. hydrochloric acid was warmed on steam bath overnight, cooled, and extracted with ether. The extract was dried over sodium sulfate and evaporated *in vacuo.* The residual oil, which quickly blackened on exposure to air, exhibited infrared maxima at 3.02 and 11.1 μ (—NH_2), 5.90 μ (C=O), 6.02 μ (C=N).

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[5] All temperatures are uncorrected.

Decomposition of Quaternary Salts. V. Stereospecificity in the Methadon Series

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Previous papers[1] in this series have shown that ketones of the methadon type give ethylidenetetrahydrofurans on pyrolysis of their quaternary salts. It has also been shown[2] that this reaction does not proceed by an olefinic intermediate since the optical isomers of isomethadon give optically active products. We now wish to report that the optically active forms of the ethylidenetetrahydrofurans are obtained when the optically active forms of methadon methiodide are decomposed. This would indicate that a concerted reaction takes place and that at no time is a carbonium ion formed. The most

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[1] Paper No. 4, S. J. Nelson, V. B. Fish, and N. R. Easton, *J. Am. Chem. Soc.*, **77**, 1908 (1955).

[2] N. R. Easton and V. B. Fish, *J. Am. Chem. Soc.*, **76**, 2836 (1954).