at −78° over a period of 2 hours to maleic anhydride (700 g.) kept at 130°. The excess maleic anhydride was removed by vacuum distillation and the brittle brown glassy solid residue was reprecipitated from tetrahydrofuran as an amorphous powder (31 g.). The powder softened at about 60–70° and dissolved slowly in warm 10% aqueous KOH to form a somewhat viscous solution. The polymer was reprecipitated by the addition of HCl. The infrared spectrum of this material was similar to that obtained *via* co-condensation of maleic anhydride and pyrolyzed *p*-xylene.[10]

Anal. Calcd. for the 1:1 copolymer of *p*-xylylene with maleic acid, $C_{12}H_{12}O_4$: C, 65.41; H, 5.49. Found: C, 66.2, 66.3; H, 5.62, 5.74.

A small sample was converted in good yield to terephthalic acid by oxidation with $KMnO_4$ in aqueous NaOH to confirm the assigned linear configuration of the polymer.

Copolymers of *p*-xylylene with diethyl maleate, diethyl fumarate, acrylonitrile, *n*-octyl acrylate and styrene were also prepared using this procedure to afford thermoplastic polymers that softened in the range 60–150°.

Copolymerization of *p*-Xylylene and Chloranil.—*p*-Xylylene (0.04 mole) in toluene (500 cc.) at −78° was added slowly to 0.1 mole of chloranil dissolved in 400 cc. of *p*-xylene kept at 95–100°. A highly swollen, gelatinous solid (2.5 g.) was obtained. After continuous extraction with hot *p*-xylene for 3 hours, the white insoluble residue contained 32.9% chlorine corresponding to a molar ratio of *p*-xylylene:chloranil of 1.8:1. The material softened at 195–200° and was completely soluble in tetrachloroethane.

ST. PAUL 9, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Action of Alkali on 3,4-Phenacylidene-3-acetylcoumarin

BY S. WAWZONEK AND C. E. MORREAL[1,2]

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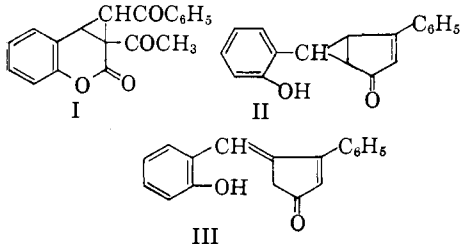
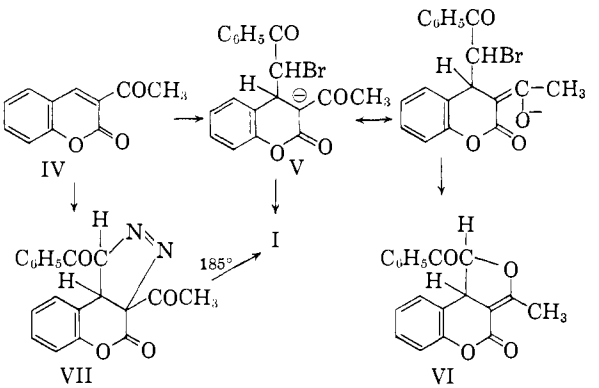
The structure of 3,4-phenacylidene-3-acetylcoumarin prepared by the alkaline condensation of 3-acetylcoumarin with phenacyl bromide has been confirmed by its synthesis from 3-acetylcoumarin and diazoacetophenone. Alkaline treatment of this compound gave 3-phenyl-4-*o*-hydroxybenzal-2-cyclopenten-1-one as reported by Widman. Proof of this structure is the conversion of its methyl ether to 5-*o*-methoxybenzal-4-phenyl-3-cyclopenten-1,2-dione. Cleavage of this diketone gave β-phenyl-α-*o*-methoxybenzalglutaconic acid which was identical with a sample prepared by the alkaline condensation of β-phenylglutaconic acid with *o*-methoxybenzaldehyde.

3,4-Phenacylidene-3-acetylcoumarin (I), which has been prepared by the reaction of 3-acetylcoumarin with phenacyl bromide in the presence of sodium ethoxide[3] is converted by 10% sodium hydroxide into a new compound to which structure



II was first assigned and then later structure III.[3] Since the only evidence offered for structure III was the formation of salicylic acid in the oxidation with potassium permanganate, compound III was considered worthy of further investigation.

3,4-Phenacylidene-3-acetylcoumarin (I) was prepared successfully according to Widman's directions.[3] This reaction probably proceeds by a Michael addition of the phenacyl bromide anion directly to 3-acetylcoumarin (IV) followed by an intramolecular alkylation of the resultant ion (V) rather than by the alkylation of the ethyl α-acetylcoumarinate anion as proposed by Widman. Cyclization of the ion V can proceed in two ways; C-alkylation would give 3,4-phenacylidene-3-acetylcoumarin (I), whereas O-alkylation would form the dihydrofuran VI. The latter possibility was eliminated by the infrared spectra, which gave an absorption peak at 9.85μ in the region reported for cyclopropane rings,[4] and by synthesis from 3-acetylcoumarin and diazoacetophenone. The intermediate pyrazoline VII gave the desired product upon heating at 185°.



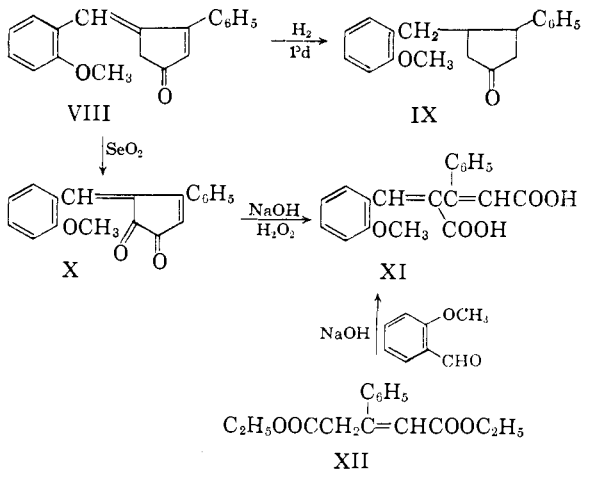
Treatment of 3,4-phenacylidene-3-acetylcoumarin (I) with alkali gave a product which from its reactions proved to be 3-phenyl-4-*o*-hydroxybenzal-2-cyclopenten-1-one (III) as reported by Widman. To facilitate further study this compound was converted into its methyl ether VIII with dimethyl sulfate and alkali. This ether (VIII) added two moles of hydrogen and gave 4-*o*-methoxybenzyl-3-phenylcyclopentanone (IX) which formed an oxime. Condensation of the methylene group in VIII with *o*-methoxybenzaldehyde to a di-*o*-methoxybenzal derivative was not successful. 3-Phenyl-4-*o*-methoxybenzal-2-cyclopenten-1-one (VIII), however, could be oxidized to 5-*o*-methoxybenzal-4-phenyl-3-cyclopenten-

(1) Abstracted in part from the Ph.D. Thesis of C. E. Morreal, June, 1959.

(2) Allied Chemical Corporation Fellow, 1957–1958.

(3) O. Widman, *Ber.*, **51**, 533, 907 (1918).

(4) F. J. Piehl and W. G. Brown, THIS JOURNAL, **75**, 5023 (1953).

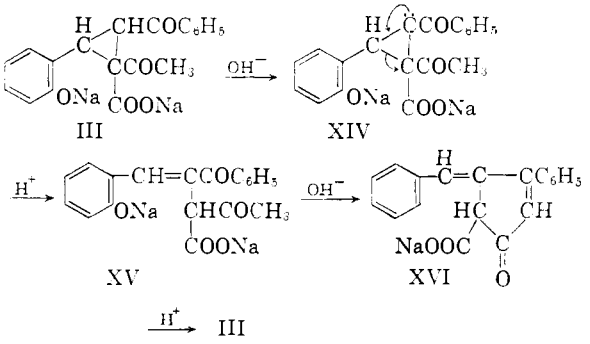


1,2-dione (X). The α-diketone structure was indicated by the formation of a phenazine when X was treated with *o*-phenylenediamine.

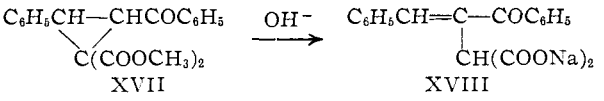
Cleavage of the diketone X with hydrogen peroxide in alkali gave β-phenyl-α-*o*-methoxybenzalglutaconic acid (XI). This product was identical with a sample synthesized by the alkaline condensation of diethyl β-phenylglutaconate (XII)[5] with *o*-methoxybenzaldehyde.

The synthesis of the diketone X from 4-phenyl-3-cyclopenten-1,2-dione, which was prepared from 3-phenyl-2-cyclopenten-1-one[6] was not successful; the diketone failed to give the desired product when treated with *o*-methoxybenzaldehyde in the presence of base.

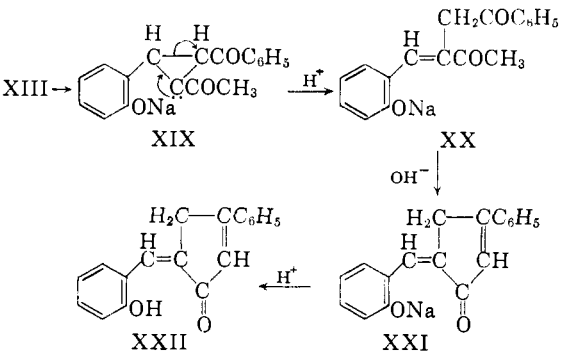
The formation of 3-phenyl-4-*o*-hydroxybenzal-2-cyclopenten-1-one (II) from the action of alkali on 3,4-phenacylidene-3-acetylcoumarin points to the abstraction of a proton by the hydroxide ion from the carbon atom of the cyclopropane ring attached to the benzoyl group.



The resulting anion XIV undergoes a reverse Michael reaction and forms XV. The coumarin ring probably opens prior to the cleavage. A similar sequence of reactions probably occurs in the action of alkali of 1,1-dicarbomethoxy-2-benzoyl-3-phenylcyclopropane[7] (XVII).



If decarboxylation occurred in XIV prior to this abstraction of a proton, the anion XIX could result and give rise to the isomeric 3-phenyl-5-*o*-methoxybenzal-2-cyclopenten-1-one (XXI). The methyl ether of this compound was synthesized by the condensation of 3-phenyl-2-cyclopenten-1-one with *o*-methoxybenzaldehyde and found to be different from the product prepared from 3,4-phenacylidene-3-acetylcoumarin (I).



Experimental[8]

3,4-Phenacylidene-3-acetylcoumarin (I).—Diazoacetophenone[9] (7.8 g.) in benzene (10 ml.) was added to a solution of 3-acetylcoumarin (10 g.) in benzene (10 ml.) and the resulting solution was allowed to stand at 25° for two days. During this period the solution became red and the white pyrazoline VII precipitated. Two crystallizations from ethanol gave white needles (12.7 g.) melting at 182°.

Anal. Calcd. for $C_{19}H_{14}N_2O_4$: C, 68.26; H, 4.22. Found: C, 68.08; H, 4.14.

The pyrazoline VII (5 g.) upon heating for 5 minutes at 185° gave a red solid which was recrystallized twice from absolute ethanol. The 3,4-phenacylidene-3-acetylcoumarin (I) (2.0 g.) obtained melted at 187°. A mixture with a sample prepared from 3-acetylcoumarin and phenacyl bromide showed no depression. The infrared absorption spectra of the two compounds were superimposable and gave an absorption peak at 9.85 μ in the region reported for cyclopropane rings.[4]

Widman[3] reported a melting point of 184° for this compound.

4-*o*-Hydroxybenzal-3-phenyl-2-cyclopenten-1-one (III) was prepared by the directions of Widman[3] and melted at 204°. The literature[3] reports 202°.

4-*o*-Methoxybenzal-3-phenyl-2-cyclopenten-1-one (VIII).—4-*o*-Hydroxybenzal-3-phenyl-2-cyclopenten-1-one (III) (10 g.) in 20% sodium hydroxide (50 ml.) was treated dropwise at 0–10° with dimethyl sulfate (4.8 g.) with rapid stirring. The orange product after six crystallizations from absolute ethanol gave fine needles (9.6 g.) with an orange-red tinge, m.p. 127°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.35; H, 5.74.

4-*o*-Methoxybenzyl-3-phenylcyclopentanone (IX).—4-*o*-Methoxybenzal-3-phenyl-2-cyclopenten-1-one (VIII) (10 g.) in absolute ethanol (100 ml.) was hydrogenated at 45 pounds pressure in the presence of Adams platinum catalyst (0.1 g.). Removal of the alcohol gave 4-*o*-methoxybenzyl-3-phenylcyclopentanone (IX) (8.0 g.) boiling at 164° (0.02 mm.) and melting at 74–75°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.31; H, 7.20.

The oxime melted at 144.5° after two crystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.25; H, 7.16. Found: C, 77.10; H, 6.87.

5-*o*-Methoxybenzal-4-phenyl-3-cyclopenten-1,2-dione (X).—4-*o*-Methoxybenzal-3-phenyl-2-cyclopenten-1-one (VIII)

(5) S. Ruhemann, *J. Chem. Soc.*, **75**, 248 (1899).
(6) W. Borsche and W. Menz, *Ber.*, **41**, 194 (1908).
(7) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1406 (1917).
(8) Melting points and boiling points are not corrected.
(9) F. Arndt and J. Amende, *Ber.*, **61**, 1123 (1928).

(5 g.) in methanol (50 ml.) was refluxed with a solution of selenium dioxide (2 g.) in water (5 ml.) for 15 hours. The resulting red solution after removal of the selenium gave upon evaporation a red oil. Traces of selenium and selenium dioxide were removed by refluxing the oil with acetone (50 ml.) for one hour and filtering. Concentration of the acetone to 25 ml. gave orange-yellow crystals of the diketone (2.0 g.) melting at 164°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.47; H, 4.99.

The phenazine prepared by refluxing the diketone X (0.5 g.) in absolute ethanol (10 ml.) with *o*-phenylenediamine (0.2 g.) for 30 minutes formed long yellow needles with a greenish tinge, m.p. 163°, yield 0.4 g. A mixture with the diketone started to melt at 120°.

Anal. Calcd. for $C_{25}H_{18}N_2O$: C, 81.30; H, 5.46. Found: C, 81.48; H, 5.44.

β-Phenyl-α-*o*-methoxybenzalglutaconic Acid (XI).—The diketone X (1 g.) and 30% hydrogen peroxide (1 ml.) in ethanol (25 ml.) were treated with 20% sodium hydroxide (5 drops) and allowed to stand for 30 minutes. The resulting solution was poured into water (50 ml.) and extracted twice with 25-ml. portions of ether. The alkaline layer upon acidification gave β-phenyl-α-*o*-methoxybenzalglutaconic acid (XI) melting at 229–230° after four crystallizations from an alcohol–benzene mixture; yield 0.5 g.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97. Found: C, 70.03; H, 4.95.

A solution of diethyl β-phenylglutaconate[5] (XII, 2.0 g.), *o*-methoxybenzaldehyde (1.0 g.) and sodium methoxide (1.0 g.) in methanol (20 ml.) was refluxed for 2 hours. Acidification gave a quantitative yield of β-phenyl-α-*o*-methoxybenzalglutaconic acid (XI) melting at 229–230° after recrystallization from an ethanol–benzene mixture. This sample did not depress the melting point of the product obtained by the cleavage of the diketone X and had similar infrared spectra.

5-Isonitroso-3-phenyl-2-cyclopenten-1-one.—A solution of 3-phenyl-2-cyclopenten-1-one[6] (4.5 g.), butyl nitrite (4.4 g.) and concentrated hydrochloric acid (2 ml.) in ethanol (50 ml.) was refluxed for 30 minutes and allowed to stand for one hour. The resulting crystals after five crystallizations from absolute ethanol gave 5-isonitroso-3-phenyl-2-cyclopenten-1-one (3.0 g.) melting at 203°.

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85. Found: C, 69.72; H, 4.98.

4-Phenyl-3-cyclopenten-1,2-dione.—5-Isonitroso-3-phenyl-2-cyclopenten-1-one (10 g.) in acetic acid (50 ml.) was refluxed with 37% formaldehyde (50 ml.) and concentrated hydrochloric acid (2 ml.) for 30 minutes and allowed to stand overnight. The solution was diluted with water (300 ml.) and extracted twice with chloroform (100 ml.). Removal of the chloroform gave orange crystals which were recrystallized four times from benzene; m.p. 185°, yield 1.4 g.

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.43; H, 4.83.

Equimolar amounts of the diketone and *o*-methoxybenzaldehyde in ethanol when refluxed with either 10% sodium hydroxide or sodium ethoxide gave a black tar.

5-*o*-Methoxybenzal-3-phenyl-2-cyclopenten-1-one.—3-Phenyl-2-cyclopenten-1-one[6] (5 g.) and *o*-methoxybenzaldehyde (4.3 g.) were refluxed with 10% sodium hydroxide (5 ml.) in ethanol (15 ml.) for 2 hours. The mixture after acidification gave 5-*o*-methoxybenzal-3-phenyl-2-cyclopenten-1-one (5.0 g.) which after six crystallizations from ethanol melted at 152–153°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83. Found: C, 81.93; H, 6.00.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Cyclization of N-Chlorodialkylamines

BY S. WAWZONEK AND T. P. CULBERTSON[1,2]

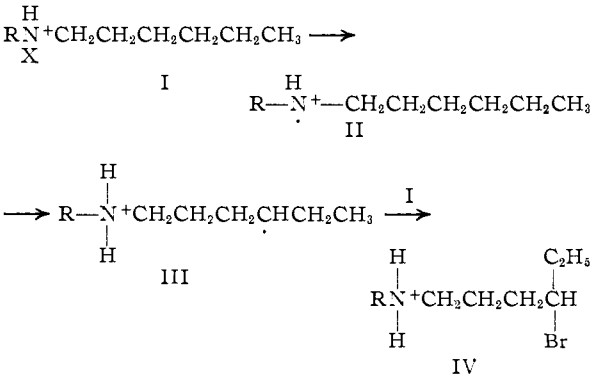
RECEIVED JUNE 4, 1959

Ethylamylamine, methylhexylamine and dihexylamine have been cyclized through their N-chloro derivatives and the resulting tertiary amines have been examined by gas chromatography. Ethylamylamine gave pure 1-ethyl-2-methylpyrrolidine. Methylhexylamine gave a mixture consisting of 80% 1-methyl-2-ethylpyrrolidine and 20% 1-methyl-2-methylpiperidine. Dihexylamine gave 95.6% 1-hexyl-2-ethylpyrrolidine and 4.4% 1-hexyl-2-methylpiperidine.

Secondary aliphatic amines can be converted into pyrrolidines by heating[3] or irradiating[4] the N-bromo or N-chloro derivative in sulfuric acid and treating the resulting solution with alkali. In all the examples of simple aliphatic amines studied only pyrrolidines are reported as final products even when the alkyl groups are extended beyond four carbon atoms.

In the mechanism proposed[4] the ring size depends on the alkyl halide formed during the irradiation of the N-haloamine. This intermediate is a direct consequence of the hydrogen abstraction step II → III.

Factors determining which hydrogen is abstracted are the stereo configuration of the carbon chain and the relative stability of the carbon free radical formed. The steric factor is the sole one involved in the synthesis of the bicyclic amines, N-methylgranatanine[5] and quinuclidines[6] by this method; piperidine ring formation is favored over that of pyrrolidine rings.



(1) Abstracted in part from the Ph.D. Thesis of T. P. Culbertson, February, 1959.

(2) Ethyl Corporation Fellow, 1957–1958.

(3) (a) G. H. Coleman and G. E. Goheen, THIS JOURNAL, **60**, 730 (1938); (b) G. H. Coleman, G. Nicholas and T. F. Martens, *Org. Syntheses*, **25**, 14 (1945).

(4) S. Wawzonek and T. P. Culbertson, THIS JOURNAL, **81**, 3367 (1959).

(5) S. Wawzonek and P. J. Thelen, *ibid.*, **72**, 2118 (1950).

(6) S. Wawzonek, M. F. Nelson, Jr., and P. J. Thelen, *ibid.*, **73**, 2806 (1951).