

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reactions of Propiolic Esters. II. Michael Addition to Certain Ketones¹BY W. E. BACHMANN, G. I. FUJIMOTO^{2a} AND E. K. RAUNIO^{2b}

The preceding paper³ described the addition of propiolic esters, $\text{HC}\equiv\text{CCOOR}$, in the presence of sodamide to the carbonyl group of cyclohexanone, 2-methylcyclohexanone, and 2-carboethoxy-2-methylcyclohexanone to form substituted acetylenic carbinols. The present paper describes the reaction of propiolic esters and sodamide with the three ketones, 1-tetralone, 6-methoxytetralone and 1-ketotetrahydrophenanthrene. The behavior of these ketones, in which the carbonyl group is attached to an aromatic nucleus, is entirely different from that of the purely alicyclic ketones. The semi-aromatic ketones added to the triple bond of the propiolic ester in Michael fashion to give β -substituted acrylic esters; carboalkoxyvinylation of the ketones took place analogous to cyanoethylation by acrylonitrile. The reaction is similar to the Michael addition of acetoacetic ester and of diethyl methylmalonate to ethyl propiolate.⁴ Thus, 1-tetralone and methylpropiolate in the presence of sodamide yielded the ester of β -(1-tetralone-2)-acrylic acid (Ia) and 6-methoxy-1-tetralone and ethyl propiolate gave the crystalline ethyl β -(6-methoxy-1-tetralone-2)-acrylate (Ib) in good yield. The structure of Ia was proved by saponification of the product of catalytic reduction to β -(1-tetralone-2)-propionic acid, which had been prepared recently⁵ by hydrolysis and decarboxylation of the products ob-

tained from 2-carbomethoxy-1-tetralone by cyanoethylation and by reaction with methyl β -bromopropionate. The Michael reaction with propiolic esters offers a new route to certain ketohydrophenanthrenes.⁵

The crystalline ethyl β -(1-ketotetrahydrophenanthrene-2)-acrylate (II) was obtained in 83% yield from 1-ketotetrahydrophenanthrene and ethyl propiolate. In accordance with its structure, the product possessed the properties of a vinylog of a β -ketoester. It formed a potassio derivative with alcoholic potassium hydroxide, from which the original ester was regenerated by addition of acid, and like 2-carbomethoxy-1-ketotetrahydrophenanthrene it was cleaved by hot aqueous alkali to 1-ketotetrahydrophenanthrene.

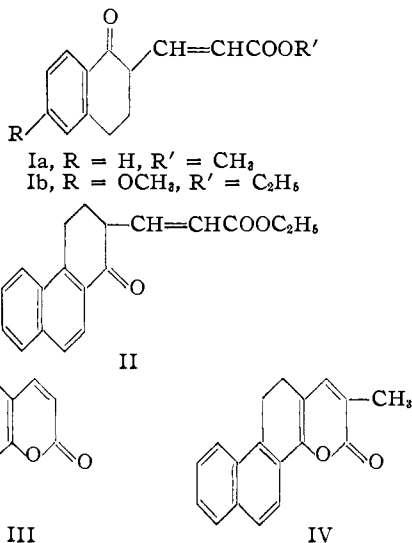
When II was heated with a mixture of acetic acid and hydrochloric acid in an attempt to hydrolyze the ester group, cyclization to the unsaturated lactone III took place. The potassio derivative of II reacted with methyl iodide to give a crystalline product which appears to be the methylated lactone IV. Both lactones, III and IV, underwent degradative cleavage with boiling alkali and yielded 1-ketotetrahydrophenanthrene. This result showed that the methyl group in the methylated product was not attached to the phenanthrene nucleus; the only logical position for the methyl group is that α to the ester group. By catalytic reduction II was converted into the substituted propionic ester from which β -(1-ketotetrahydrophenanthrene-2)-propionic acid was obtained by hydrolysis.

Experimental

Michael Addition of Propiolic Esters to 1-Tetralone and 6-Methoxytetralone.—A solution of 3 g. of 1-tetralone and 1.9 g. of methyl propiolate in 8 ml. of absolute ether was added to a suspension of sodamide prepared from 0.52 g. of sodium and 40 ml. of liquid ammonia; a brisk stream of ammonia was passed through the suspension during the addition of the ethereal solution. After the liquid ammonia had been evaporated with the aid of a water-bath, the mixture was treated with ice and dilute sulfuric acid, and the product was extracted into ether. The liquid product (4.15 g.) readily reduced dilute aqueous potassium permanganate.

A solution of 1 g. of the product in 25 ml. of acetic acid and 50 mg. of 10% palladium on charcoal catalyst was stirred under hydrogen until nearly a mole equivalent of hydrogen was absorbed. Hydrolysis of the reduced product gave 0.22 g. of crystalline β -(1-tetralone-2)-propionic acid; m. p. 108–110°, which did not depress the m. p. of an authentic specimen.⁵

In a similar manner condensation of 2 g. of 6-methoxy-1-tetralone with 1.15 g. of ethyl propiolate in the presence of sodamide yielded 2.6 g. of a solid product. After several recrystallizations from ethyl acetate-petroleum ether the ethyl β -(6-methoxy-1-tetralone-2)-acrylate (Ib) formed colorless needles; m. p. 90–92°. The formation of a 2,4-dinitrophenylhydrazone (m. p. 163°) was indicative of the presence of a carbonyl group.



(1) From the Ph.D. dissertations of G. I. Fujimoto and E. K. Raunio.

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(3) Bachmann and Raunio, *THIS JOURNAL*, **72**, 2530 (1950).

(4) Simonsen, *J. Chem. Soc.*, 97 (1913).

(5) Bachmann and Johnson, *THIS JOURNAL*, **71**, 3463 (1949).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.2; H, 6.6. Found: C, 70.2; H, 6.7.

1-Keto-1,2,3,4-tetrahydrophenanthrene and Ethyl Propiolate.—The reaction between 2 g. of the ketone, 1.04 g. of the propiolic ester and sodamide in liquid ammonia yielded a solid product after evaporation of the ammonia and addition of ice and dilute acid. A benzene solution of the product was washed with water and sodium bicarbonate and evaporated, and the residual solid was washed on a funnel with methanol; yield, 2.45 g. (83%); m. p. 111–113°. After several recrystallizations from ethanol, a sample of colorless ethyl β -(1-keto-1,2,3,4-tetrahydrophenanthrene-2)-acrylate (II) melted at 112–114°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 77.6; H, 6.1. Found: C, 77.6; H, 6.2.

The 2,4-dinitrophenylhydrazone after one recrystallization from ethanol and two from benzene formed orange-colored crystals; m. p. 204°.

Anal. Calcd. for $C_{25}H_{22}N_4O_6$: C, 63.4; H, 4.6; N, 11.8. Found: C, 63.9; H, 4.8; N, 11.0.

Addition of 5 ml. of a 2.5% solution of potassium hydroxide in absolute alcohol to a solution of 0.4 g. of II in 5 ml. of dry benzene and cooling the deep-red solution in an ice-bath precipitated 0.4 g. of fine orange-colored needles of the potassium derivative of II; the product was washed with benzene on a funnel until the washings were colorless. When the derivative was heated on a spatula, it burned without melting and left an ash. When an aqueous suspension of the derivative was acidified, II was recovered; m. p. 111–113°.

Formation of the Lactones.—A solution of 0.5 g. of ethyl β -(1-keto-1,2,3,4-tetrahydrophenanthrene-2)-acrylate in 13 ml. of acetic acid and 6 ml. of concentrated hydrochloric acid was heated on a steam-bath for twelve hours and then refluxed for three hours. Addition of the mixture to ice precipitated the lactone of β -(1-hydroxy-3,4-dihydrophenanthrene-2)-acrylic acid (III), which crystallized from methanol-ethyl acetate in pale-yellow needles; m. p. 188–190°. An analytical sample was sublimed at 140–180° and 0.1 mm.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.3; H, 4.8. Found: C, 82.4; H, 5.0.

When a mixture of 1 g. of II in 15 ml. of dry benzene was refluxed for one and one-half hours with 0.13 g. of sodium methoxide, the orange colored solid sodio derivative of II did not appear to be affected. After refluxing with 0.6 ml. of methyl iodide for several hours a clear solution resulted. After the cooled solution had been washed with water and aqueous potassium carbonate, the solvent was removed and the residual solid was washed with methanol. The compound (0.27 g.), presumably the lactone of α -methyl- β -(1-hydroxy-3,4-dihydrophenanthrene-2)-acrylic acid (IV), crystallized from ethyl acetate in orange-colored needles; m. p. 211–214°; mixed m. p. with III, 186–195° with sintering at 172–186°. The compound was recovered unchanged after being refluxed with

a mixture of acetic acid and hydrochloric acid for three hours.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.4; H, 5.3. Found: C, 82.5; H, 5.5.

Reduction of II.—A solution of 0.9 g. of II in 25 ml. of acetic acid absorbed a mole equivalent of hydrogen in the presence of 50 mg. of 10% palladium on charcoal in less than two hours. The product which was isolated was treated with Norit in ether; evaporation of the ether gave a liquid which crystallized on scratching. The ethyl β -(1-keto-1,2,3,4-tetrahydrophenanthrene-2)-propionate (0.83 g.) crystallized from methanol in colorless prisms; m. p. 67–68.5°. An analytical sample was evaporatively distilled at 110–120° and 0.1 mm.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 77.0; H, 6.8. Found: C, 77.1; H, 6.9.

Hydrolysis of 0.5 g. of the ester with aqueous potassium hydroxide and recrystallization of the resulting acid from aqueous alcohol and then from benzene gave 0.32 g. of β -(1-keto-1,2,3,4-tetrahydrophenanthrene-2)-propionic acid; m. p. 146–147° alone and when mixed with an authentic specimen which had been prepared by cyanoethylation of 1-keto-2-carbomethoxy-1,2,3,4-tetrahydrophenanthrene.⁶

Alkaline Cleavage of the Keto Esters and Lactones.—A mixture of 50 mg. of 1-keto-2-carbomethoxy-1,2,3,4-tetrahydrophenanthrene, 0.7 ml. of 40% aqueous sodium hydroxide and 1.6 ml. of methanol was refluxed on a steam-bath for two hours, the methanol was removed in a current of air, and the residue was digested with water and chloroform. From the chloroform solution 30 mg. of neutral product was isolated. By recrystallization from 60–75° petroleum ether with the aid of Norit, 20 mg. (63%) of 1-keto-1,2,3,4-tetrahydrophenanthrene was obtained; m. p. 94.5–96° alone and when mixed with an authentic specimen. Under identical conditions the ester of β -(1-ketotetrahydrophenanthrene-2)-acrylate gave a 53% yield of purified 1-ketotetrahydrophenanthrene. The ketone was obtained in 54–55% yields by cleavage of 50 mg. of the lactones, III or IV, with a boiling solution of 2 ml. of 40% sodium hydroxide and 5 ml. of methanol (three hours).

Summary

1-Tetralone, 6-methoxy-1-tetralone and 1-keto-1,2,3,4-tetrahydrophenanthrene, unlike purely alicyclic ketones, undergo a Michael reaction with propiolic esters in the presence of sodamide to give substituted acrylic esters. The reaction corresponds to carboalkoxyvinylolation of the ketone next to the carbonyl group.

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(6) Bachmann and Miller, results to be published soon.