chloride,[3] warmed until no more nitric oxide was evolved (five minutes), and then distilled to dryness under reduced pressure. The residue was dissolved in 8 ml. of water and treated with excess sodium hydroxide. The mixture was boiled, copper oxide was removed, and the filtrate was shaken with 100 mg. of benzoyl chloride. Acidification gave a white precipitate which crystallized from toluene in the form of colorless prisms (100 mg., 71%), m. p. 149–150° alone or mixed with an authentic sample[1] of 1-benzoylpiperidine-4,β-propionic acid.

The author thanks Mr. Stanley T. Rolfson for the analyses reported in this paper.

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[3] Jones and Kenner, *J. Chem. Soc.*, 711 (1932).

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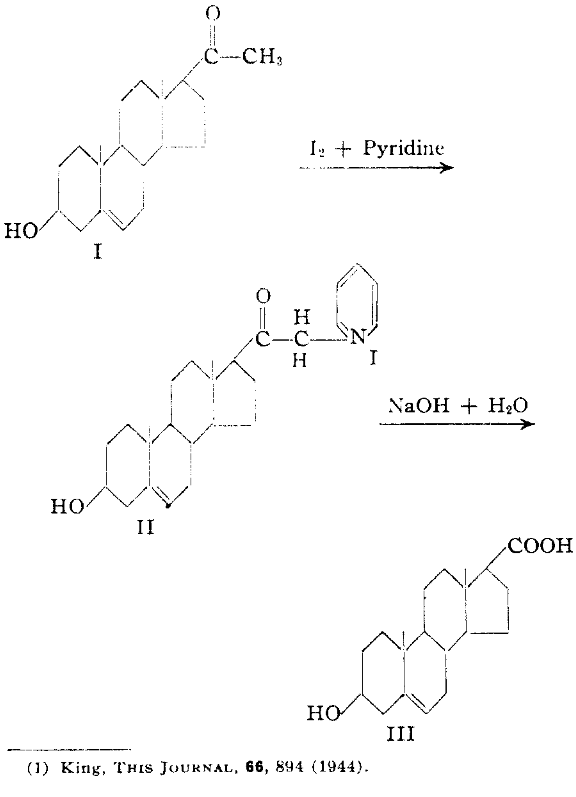
Preparation of 21-Pyridinium-3-β-hydroxy-5-pregnene-20-one Halides and 3-β-Hydroxy-5-androstene-17-carboxylic Acid

BY L. CARROLL KING

In a recent paper from this Laboratory the preparation of substituted β-ketoalkylpyridinium iodides by reaction of ketones with iodine and pyridine was reported.[1] This reaction has now been extended to 3-β-hydroxy-5-pregnene-20-one (I), which gave 21-pyridinium-3-β-hydroxy-5-pregnene-20-one iodide (II) in 50% yield. Alkaline decomposition of (II) or of the corresponding perchlorate yielded 93% of crude 3-β-hydroxy-5-androstene-17-carboxylic acid (III) from which the pure methyl ester was obtained (83% yield from II). The main reactions may be formulated as



Reich and Reichstein[2] obtained compounds of type II when a 21-halo-3-β-hydroxy-5-pregnene-20-one was treated with pyridine.

Experimental[3]

21-Pyridinium-3-β-hydroxy-5-pregnene-20-one Iodide (II).—A solution containing 3.12 g. of 3-β-hydroxy-5-pregnene-20-one in 75 ml. of pyridine was treated with 2.56 g. of iodine in a manner previously described.[1] The resulting relatively insoluble pyridinium iodide was separated from pyridine hydroiodide and crystallized from methanol; yield 3.053 g.; m. p. 248–250°.

Anal. Calcd. for $C_{26}H_{36}INO_2$: C, 59.91; H, 6.91. Found: C, 59.50; H, 6.83.

21-Pyridinium-3-β-hydroxy-5-pregnene-20-one Perchlorate.—This substance was prepared from the above pyridinium iodide as previously described.[1] The product was crystallized from methanol and apparently contains water of crystallization; m. p. 255–260° dec.

Anal. Calcd. for $C_{26}H_{36}ClNO_6\cdot{}^1/_2H_2O$: C, 62.07; H, 7.37. Found: C, 62.12; H, 7.04.

Methyl 3-β-Hydroxy-5-androstene-17-carboxylate.—To a suspension of 656 mg. of the above pyridinium iodide (II), or a corresponding quantity of the perchlorate, in water or 50% ethyl alcohol, 0.5 g. of sodium hydroxide was added. The mixture was heated for two hours on the steam-bath, acidified and the acidic fraction isolated. The crude 3-β-hydroxy-5-androstene-17-carboxylic acid, yield 400 mg., was of a light tan color and melted at 255–270°. On recrystallization from methanol or dioxane the melting point increased to 270–275°. The total crude product was then dissolved in methanol, a few drops of acetyl chloride added and the reaction mixture heated one hour. The methyl ester was recovered and crystallized from methanol; yield 332 mg.; m. p. 174–177°.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.83; H, 9.70. Found: C, 75.69; H, 9.37.

The above methyl 3-β-hydroxy-5-androstene-17-carboxylate was converted to the benzoate, m. p. 204–206°, and to the acetate, m. p. 153–154°.

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[1] King, THIS JOURNAL, **66**, 894 (1944).

[2] Reich and Reichstein, *Helv. Chim. Acta*, **22**, 1124 (1939).

[3] All melting points were observed on a Fisher–Jones melting point block. Carbon and hydrogen analyses by T. S. Ma.

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NEW COMPOUNDS

ω-Nitro-3-vinyl-pyrene

In the manner described for the preparation of nitrostyrene,[1] equimolecular amounts of 3-pyrene-aldehyde and nitromethane were condensed in the presence of methyl-alcoholic sodium hydroxide solution. Hydrochloric acid precipitated the ω-nitro-3-vinyl-pyrene as red crystals, which after recrystallization from a mixture of acetone and benzene had m. p. 177°.

Anal. Calcd. for $C_{18}H_{11}O_2N$: C, 79.1; H, 4.0. Found: C, 78.6; H, 3.9.

Alcoholic alkali gives a yellow solution, but the substance is not satisfactory as an indicator.

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[1] "Organic Syntheses," Coll. Vol. 1, p. 413.