[Contribution from the Department of Chemistry, Carnegie Institute of Technology]

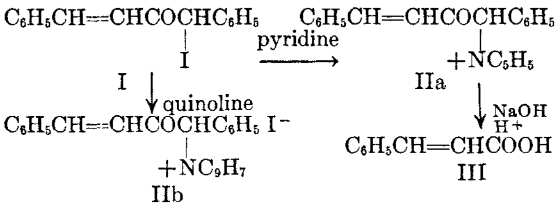
The Degradation of a Derivative of Benzyl Styryl Ketone to *trans*-Cinnamic Acid[1]

DAVID I. SAPPER[2] AND PHILIP L. SOUTHWICK

Received September 21, 1955

The degradation of an iodine derivative of benzyl styryl ketone, 1,4-diphenyl-1-iodo-3-butene-2-one, to *trans*-cinnamic acid was successfully accomplished by treating the iodo ketone with pyridine and subsequently treating the resulting pyridinium salt with aqueous ethanolic sodium hydroxide. Reaction of the iodo ketone with quinoline in a similar manner gave the corresponding quinolinium salt. Both of the quaternary salts, 1-(1,4-diphenyl-2-keto-3-butenyl)pyridinium iodide and 1-(1,4-diphenyl-2-keto-3-butenyl)quinolinium iodide, were also prepared directly from benzyl styryl ketone by treatment of that compound with iodine and pyridine or quinoline according to a procedure introduced by King.[3]

In connection with another problem[4] it was desired to degrade an iodine derivative of benzyl styryl ketone, 1,4-diphenyl-1-iodo-3-butene-2-one (I),[4] to cinnamic acid (III). The degradation was accomplished by conversion of the iodo ketone into the corresponding pyridinium salt (IIa), followed by cleavage of this salt with sodium hydroxide.

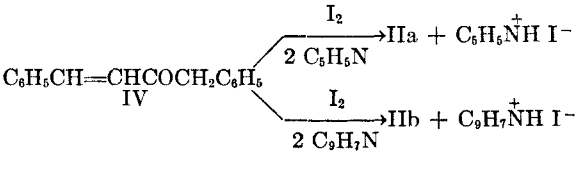


$$\begin{tikzcd}
\underset{\mathrm{I}}{C_6H_5CH{=}CHCO\underset{\mathrm{I}}{C}HC_6H_5} \arrow[r, "\text{pyridine}"] \arrow[d, "\text{quinoline}"] & \underset{\mathrm{IIa}}{C_6H_5CH{=}CHCO\underset{+NC_5H_5}{C}HC_6H_5\ I^-} \arrow[d, "\text{NaOH}", "\text{H}^+"'] \\
\underset{\mathrm{IIb}}{C_6H_5CH{=}CHCO\underset{+NC_9H_7}{C}HC_6H_5\ I^-} & \underset{\mathrm{III}}{C_6H_5CH{=}CHCOOH}
\end{tikzcd}$$

An analogous degradation of an α-haloalkyl aryl ketone had been observed by Bamberger[5] and had since been utilized or studied by a number of other investigators.[3,6–15] It had apparently, not, however, been applied to an α'-halogen derivative of an α,β-unsaturated ketone. Although the fact that the carbonyl group of such a ketone is part of a conjugated system suggested that the alkaline cleavage might fail, no such difficulty was in fact encountered, and the degradation was accomplished in reasonably good yield.

The iodo ketone (I) was found to react readily with both pyridine and quinoline to yield the crystalline quaternary ammonium salts, 1-(1,4-diphenyl-2-keto-3-butenyl)pyridinium iodide (IIa) and 1-(1,4-diphenyl-2-keto-3-butenyl)quinolinium iodide (IIb). When the pyridinium iodide IIa was heated with aqueous ethanolic sodium hydroxide, it was converted in 58% yield to *trans*-cinnamic acid. Benzyl pyridinium iodide would be the other anticipated product from the alkaline degradation, but no attempt was made to isolate it from the reaction mixture. The fact that *trans*-cinnamic acid was obtained in the degradation suggests that the starting iodo ketone (I) has the *trans* configuration.

King[3] has shown that the pyridinium iodides from aryl alkyl ketones can be synthesized in good yields by allowing one mole of the ketone to react with one mole of iodine and two moles of pyridine. This reaction has been extended to other tertiary amines and to several types of ketones[10–13,16] but not previously to an α,β-unsaturated ketone. In the present investigation benzyl styryl ketone (IV) was found to react readily with iodine and either pyridine or quinoline to yield 62% of IIa and 45% of IIb respectively. The presence of



$$\begin{tikzcd}
 & \mathrm{IIa} + C_6H_5\overset{+}{N}H\ I^- \\
\underset{\mathrm{IV}}{C_6H_5CH{=}CHCOCH_2C_6H_5} \arrow[ur, "I_2", "2\ C_5H_5N"'] \arrow[dr, "I_2", "2\ C_9H_7N"'] & \\
 & \mathrm{IIb} + C_9H_7\overset{+}{N}H\ I^-
\end{tikzcd}$$

the conjugated unsaturation evidently did not seriously complicate the reaction. The ketone derivatives were easily separated from the hydriodides of pyridine and quinoline by washing the mixture

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[1] This paper is based on a portion of a thesis submitted by David I. Sapper in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, July 1952. The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell Grant in support of this work.

[2] Research Corporation Fellow, 1951–1952. Present address: Yerkes Research Laboratory, E. I. du Pont de Nemours and Co., Inc., Buffalo 7, N. Y.

(3) King, *J. Am. Chem. Soc.*, **66**, 894 (1944).

(4) Southwick and Sapper, *J. Org. Chem.*, **19**, 1926 (1954).

(5) Bamberger, *Ber.*, **20**, 3338 (1887).

(6) Schmidt and Van Ark, *Archiv. Pharm.*, **238**, 331 (1900).

(7) Babcock, Nakamura, and Fuson, *J. Am. Chem. Soc.*, **54**, 4407 (1932).

(8) Babcock and Fuson, *J. Am. Chem. Soc.*, **55**, 2946 (1933).

(9) Krohnke, *Ber.*, **66**, 604 (1933); **68**, 1177 (1935); **70**, 864 (1937).

(10) King, *J. Am. Chem. Soc.*, **66**, 1612 (1944).

(11) King, McWhirter, and Barton, *J. Am. Chem. Soc.*, **67**, 2089 (1945).

(12) King and McWhirter, *J. Am. Chem. Soc.*, **68**, 717 (1946).

(13) King, McWhirter, and Rowland, *J. Am. Chem. Soc.*, **70**, 239 (1948).

(14) Pearson and Dillon, *J. Am. Chem. Soc*, **70**, 1933 (1948).

(15) Pearson and Sandy, *J. Am. Chem. Soc.*, **73**, 931 (1951).

(16) Hartwell and Kornberg, *J. Am. Chem. Soc.*, **68**, 868 (1946); **68**, 1131 (1946).

with cold water, which readily dissolved the more soluble hydriodides.

EXPERIMENTAL[17,18]

1-(1,4-Diphenyl-2-keto-3-butenyl)pyridinium iodide. (*A*) *Reaction of 1,4-diphenyl-1-iodo-3-butene-2-one with pyridine.* Crude unsolidified iodo ketone[4] (10.5 g., 0.03 mole) was dissolved in 20 ml. of ethanol and 2.4 g. (0.03 mole) of pyridine was added. After several hours a tan crystalline material was made to separate by adding ether to the solution. The product was filtered and dried. The yield was 4.5 g. (35%), m.p. 177° with decomposition. Recrystallization from ethanol and water gave yellow plates, m.p. 178° with decomposition.

Anal. Calc'd for $C_{21}H_{18}INO$: C, 59.00; H, 4.24; N, 3.28. Found: C, 59.00; H, 3.97; N, 3.30.

(*B*) *Reaction of benzyl styryl ketone with iodine and pyridine.* Benzyl styryl ketone[4] (5 g., 0.0225 mole) and 5.7 g. (0.0225 mole) of iodine were warmed in 30 ml. of pyridine for two hours on a steam-bath. The mixture was allowed to stand at room temperature overnight. Some ethanol was added, and the mixture was cooled in a Dry Ice chest for two hours. The tan product which separated from the mixture was removed by filtration, washed twice with cold water, and dried. The yield was 6 g. (62.4%), m.p. 175–178°. Recrystallization from ethanol gave yellow plates, m.p. 178° with decomposition. This substance did not depress the melting point of the substance obtained from the reaction of 1,4-diphenyl-1-iodo-3-butene-2-one with pyridine.

1-(1,4-Diphenyl-2-keto-3-butenyl)quinolinium iodide. A mixture of 2 g. (0.009 mole) of benzyl styryl ketone, 2.3 g. (0.009 mole) of iodine, and 15 ml. of quinoline was heated on a steam-bath for 20 minutes and then was allowed to stand at room temperature for 12 hours. After adding 15 ml. of ether, the mixture was placed in a Dry-Ice chest for several hours. A gum-like substance separated. The solution was decanted, and 10 ml. of warm ethanol was added to the residue. On cooling, a lemon-yellow precipitate separated. It was filtered, washed once with cold water, and dried. The yield was 2 g. (45%), m.p. 176° with decomposition. Recrystallization from aqueous ethanol gave orange needles or prisms, m.p. 182° with decomposition.

Anal. Calc'd for $C_{25}H_{20}INO$: N, 2.93. Found: N, 2.96.

The same product was obtained when 1,4-diphenyl-1-iodo-3-butene-2-one (I) was treated with quinoline in ethanol solution.

Reaction of 1-(1,4-diphenly-2-keto-3-butenyl)pyridinium iodide with sodium hydroxide. When 1.5 g. (0.035 mole) of the pyridinium iodide (IIa) was dissolved in 20 ml. of 50% aqueous ethanol and 1.5 g. of sodium hydroxide was added, an immediate red coloration appeared. The mixture was heated on a steam-bath for one hour, during which time it turned dark brown. After standing overnight, the solution was diluted with water and acidified with hydrochloric acid. The product which separated was filtered, washed once with cold water, and dried. The yield was 0.3 g. (58%) of a substance soluble in cold dilute sodium bicarbonate solution and melting at 127–132°. Recrystallization from hot water yielded a sample melting at 131–132° which did not depress the melting point of an authentic sample of *trans*-cinnamic acid.

PITTSBURGH 13, PA.

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[17] Microanalyses by Drs. G. Weiler and F. B. Strauss, Oxford, England.

[18] Melting points are corrected.