Photochemistry of α-Keto-imines: a Novel Synthesis of Xylopinine[1]

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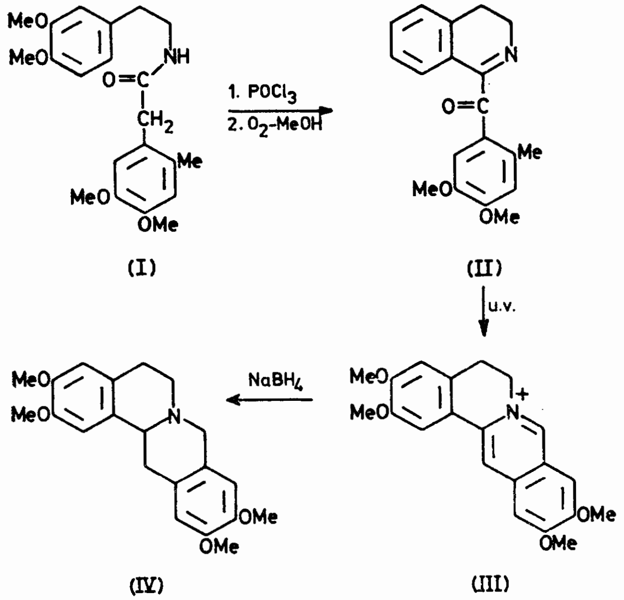
Summary Irradiation of 1-(2-methyl-4,5-dimethoxybenzoyl)-3,4-dihydro-6,7-dimethoxyisoquinoline in methanol gave a water soluble berberine salt which, on reduction with sodium borohydride, afforded (±)-xylopinine in 55% yield.

In contrast to α-diketones,[2] the photochemistry of α-keto-imines seems to have received little attention.[3] We were particularly interested in photoreactions of substrates like (II) because these could yield protoberberine-type alkaloids by the following steps:[4] (i) Norrish type II abstraction of a benzylic hydrogen† and cyclisation to a five-membered ring spiro compound; (ii) Norrish type I cleavage and an internal hydrogen abstraction by the formed acyl radical; (iii) ring closure of the resulting δ-amino aldehyde to a berberine salt.



Cyclisation of the amide[5] (I) with $POCl_3$ in toluene, followed by air oxidation in methanol gave the α-keto-imine (II) (60%) ($C_{21}H_{23}NO_5$, m.p. 154–155 °C, ν_{max} 1650 (C=O) and 1600 cm^{-1} (C=N). A 0·0054M solution of (II) in methanol‡ was irradiated (120 W high pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 15 h. The solvent was distilled off and the residue partitioned between ether and water. A small portion of the aqueous layer was made acidic with hydrochloric acid and chilled. The precipitated yellow solid was crystallised from methanol to give the berberinium chloride (III), $C_{21}H_{22}ClNO_4$, m.p. 206–208 °C, ν_{max} (Nujol) 1610 cm^{-1} ($C=N^+$), lit.[6] m.p. 207–208 °C. To the rest of the aqueous layer excess of sodium borohydride was added and the clear solution heated on a water bath for 1 h when almost pure (±)-xylopinine (IV) separated out as a white solid (55%, m.p. 155–156 °C). Its identity was confirmed by m.p. and t.l.c. comparison with an authentic sample.

We thank Professor M. Tomita for a sample of xylopinine.

(*Received*, 16*th May* 1978, *Com.* 529.)

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† The hydrogen may be abstracted by the carbonyl oxygen and transferred to the imine nitrogen or it may be abstracted directly by the latter.

‡ Irradiation in benzene or tetrahydrofuran led to complex mixtures from which the desired product could not be isolated.

[1] For previous paper in the series 'Studies in Synthetic Photochemistry,' see S. V. Kessar, Y. P. Gupta, A. Gainda, and A. Varsha, *Indian J. Chem.*, 1978, **16B**, 319.

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[4] Expected on the basis of known reactions of analogous α-diketones, N. K. Hamer, *J.C.S. Chem. Comm.*, 1977, 239; see also H. Irie, J. Fukudome, T. Ohmori, and J. Tanaka, *ibid.*, 1975, 63; H. Irie, K. Akgi, S. Tani, K. Yabusaki, and H. Yamane, *Chem. and Pharm. Bull. (Japan)*, 1973, **21**, 855.

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