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Photodehydrogenation of Substituted Pyrrolidines
Hydrogen Transfer Induced by Benzophenone

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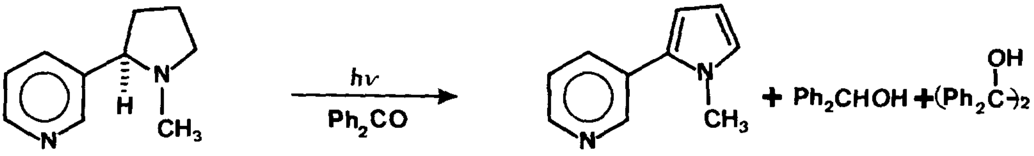
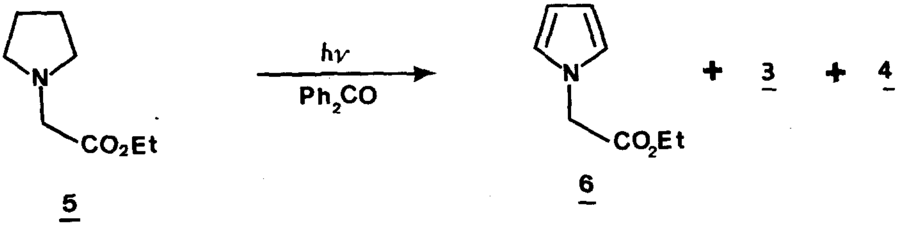
When excited in their $^3(n, \pi^*)$ excited states, ketones are able to abstract hydrogen from carbon atoms bearing heteroatom substituents. Several groups have studied the photochemical oxidation of amines (1) and amides (2) in the presence of benzophenone and found that aromatization of 5-membered ring amines occurs under these conditions. For example, when nicotine is irradiated in the presence of dyes, the pyrrolidine moiety is oxidized to a pyrrole (3a). Similarly, photolysis of imidazolines in acetone produces dehydrogenation and formation of the corresponding imidazoles (3b).

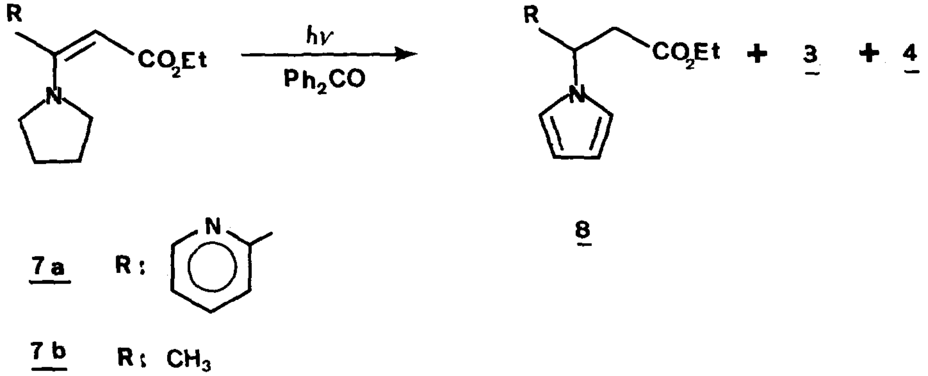
Consistent with these observations, we have found that irradiation at 254 nm of a benzene solution of nicotine (10^{-2}M) containing benzophenone 10^{-1}M provides nicotyrine 2 (40%), benzhydrol 3, benzopinacol 4, and some uncharacterized polymeric material. Similarly, irradiation of 5 under identical conditions gives 6 (4). In neither of these cases were any products detected which would have resulted from coupling of benzhydryl and α-pyrrolidino radicals.



1 2 3 4

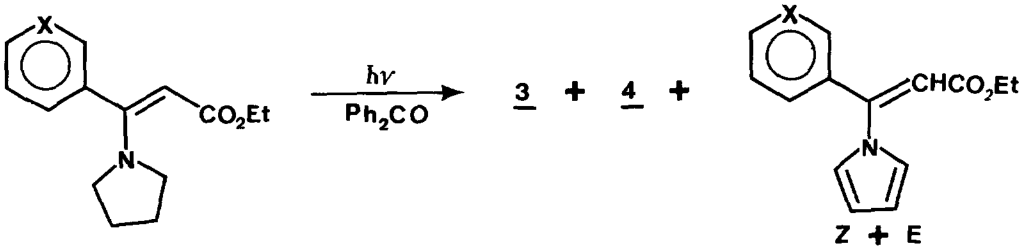
In striking contrast to these results, irradiation at 254 nm (or 366 nm) of a solution of 7a in benzene (or acetonitrile) containing benzophenone leads to 3, 4 and 8a (50%) (5). Likewise, 8b (30%) is the major product obtained from 7b in similar conditions. Thus, in these cases oxidation of the pyrrolidino substituent is accompanied by reduction of the conjugated carbon-carbon double bond (6).





It is well known that excited pyridines, quinolines (7) and carboxylic esters (8) are able to abstract hydrogen atoms. In order to determine if 8 is obtained from the triplet excited state of 7 or from a chemically induced sensitization, we have irradiated 7a in the presence of p-methoxyacetophenone (E_T = 74 kcal) a photosensitizer whose ability to abstract hydrogen is very low (9). Since 7a is recovered almost quantitatively from this experiment, we conclude that 8a results from chemical sensitization by benzophenone.

This hydrogen transfer process seems to be very sensitive to molecular structure. For example when 7c or 7d are irradiated in the presence of benzophenone the conjugated double bond in 7 is not reduced and 3, 4 and 9 are the main products of the reaction. However, in order to effect both oxidation of the pyrrolidine moiety and reduction of the acrylic group in this reaction, it does seem necessary for the pyrrolidine group to be β to the ester substituent. Thus, irradiation of 10 in the presence of benzophenone only



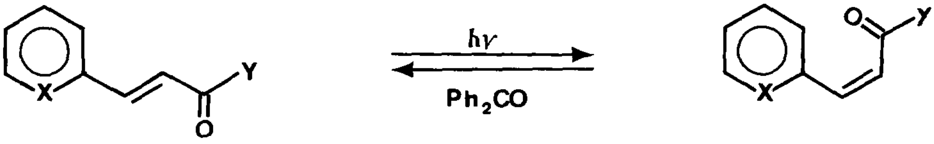
7c : X = N

7d : X = CH

9c 50%

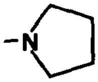
9d >30%

leads to Z ⇄ E isomerization following energy transfer from the sensitizer. Furthermore, no reduction is observed when 10a is irradiated in N-methylpyrrolidine in the presence of an aromatic ketone.



10 E

10 Z

	X	Y
10a	CH	OC_2H_5
b	N	OC_2H_5
c	N	

These results confirm the facile photodehydrogenation of the pyrrolidino substituent and show that hydrogen transfer can be induced by benzhydryl radicals. The mechanistic details of these reactions are currently under investigation.

Acknowledgements

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References:

1) S.G. Cohen, A. Parola and G.H. Parsons Chem. Rev. 73, 141 (1973)
2) J.C. Gramain, R. Remuson and Y. Troin J.C.S. Chem. Comm. 194 (1976)
3) a) Y. Hubert-Brierre, D. Herlem and F. Khuong-Huu Tetrahedron 31, 3049 (1975)
   b) T. Matsuura, Y. Ito and I. Saito Bull. Chem. Soc. Japan 46, 3805 (1973)
4) All the new compounds show spectroscopic and analytical properties (IR. UV. NMR mass spectra and/or microanalysis) which are in agreement with the proposed structures.
5) In benzene, benzophenone (0.1 M) is absorbing more than 63% of the light. The remaining of the light is absorbed by the solvent when excitation is carried out at 254 nm. We have found that similar results are obtained for 7a when the excitation is carried out at 366 nm and when benzophenone is replaced by acetophenone.
6) Reduction of multiple bonds through a chemical sensitization by a ketone has been described. For examples see :
   a) A. Padwa and M. Dharan Tetrahedron Letters 1053 (1972)
   b) J.M. Hornback, G.S. Proehl and I.J. Starner J. Org. Chem. 40, 1077 (1975)
   c) J.C. Pacifici and Q. Irick Tetrahedron Letters 2207 (1969)
7) a) A. Castellano and A. Lablache-Combier Tetrahedron 2303 (1971)
   b) S. Caplain, A. Castellano, J.P. Catteau and A. Lablache-Combier Tetrahedron 3541 (1971)
   c) G. Allan, A. Castellano, J.P. Catteau and A. Lablache-Combier Tetrahedron 4687 (1971)
   d) F.R. Stermitz and W.H. Huang J. Amer. Chem. Soc. 92, 1446 (1970)
   e) M. Saeki, N. Toshima and H. Hirai Bull. Chem. Soc. Japan 48, 476 (1975)
   f) E.C. Alexander and R.J. Jackson Jr. J. Amer.Chem. Soc. 98, 1609 (1976).
8) For example:
   a) F. Fukui, K.I. Senda, Y. Shigemitsu and Y. Odaira, J. Org. Chem. 37, 3176 (1972)
   b) J.E. Gano J.C.S. Chem. Comm. 1491 (1971)
   c) J.E. Gano Tetrahedron Letters 2549 (1969)
   d) A.A. Scala and G.E. Hussey J. Org. Chem. 36, 598 (1971)
   e) M.J. Jorgenson and S. Patumtevapibal Tetrahedron Letters 489 (1970)
9) a) N.C. Yang, D.S. Mc Clure, S.L. Murov, J.J. Houser and R. Dusenbery J. Amer. Chem. Soc., 89, 5466 (1967)
   b) P.J. Wagner Pure and Applied Chem. 49, 259 (1977).

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