

Novel Type of Transformation of a 2*H*-Azirine in the Presence of Fe₂(CO)₉

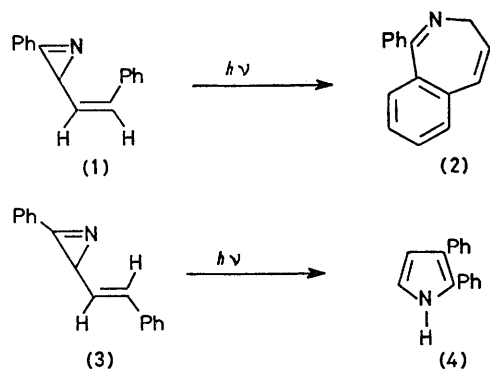
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Summary Upon treatment with Fe₂(CO)₉ in dry benzene, (*Z*)-2-phenyl-3-(2,3-diphenyl-2*H*-azirin-2-yl)acrylophenone leads, *inter alia*, to 2,3,5,6-tetraphenylpyridine, a novel transformation which implies loss of an oxygen atom.

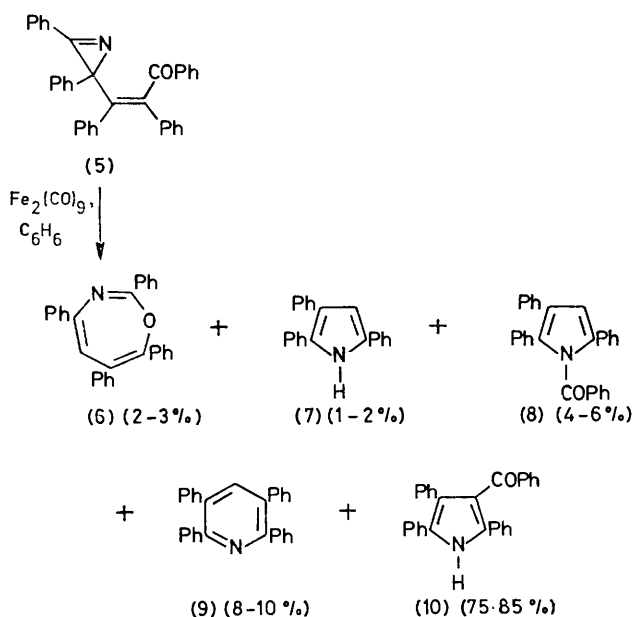
THE thermal behaviour and photochemistry of 2*H*-azirines have been extensively investigated during the last 20 years.¹ Recently Padwa has observed an unusual intramolecular photocyclization which takes place during the irradiation of the (*Z*)-3-phenyl-2-styryl-2*H*-azirine (**1**). The result of

this photolysis, which gives rise to 1-phenyl-3H-2-benzazepine (2), is in striking contrast with the photochemistry of the (*E*)-isomer (3) which leads to the 2,3-diphenylpyrrole (4)^{2,3} (Scheme 1).



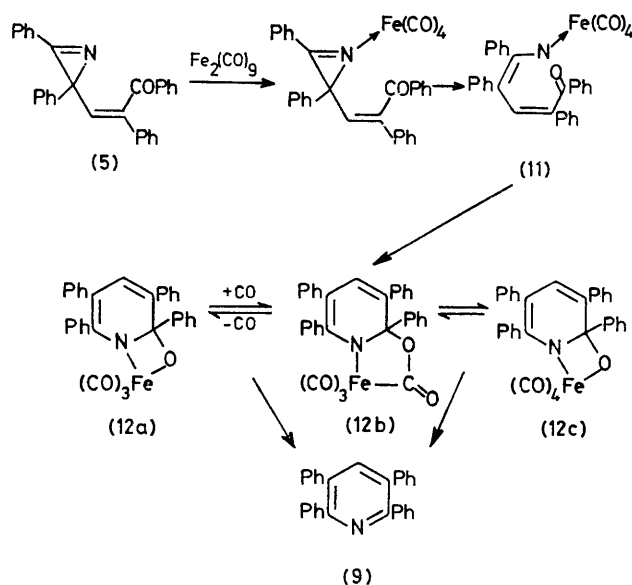
SCHEME 1

In an investigation of the chemical properties of various (*Z*)-vinylazirines, the tetraphenylazirine (5), which is the only known stable (*Z*)-ketovinylazirine,⁴ was treated with Fe₂(CO)₉ in dry benzene. (Scheme 2). The formation



SCHEME 2

of the products (6), (7), (8), and (10) is not surprising since these compounds have already been found in the reaction mixture obtained after treatment of (5) with Mo(CO)₆ in anhydrous tetrahydrofuran (THF).⁵ The unexpected isolation of the pyridine (9) is of interest. Its formation is best explained by the mechanism in Scheme 3.



SCHEME 3

This mechanism is purely speculative since no intermediates have been isolated. Initial complexation of (5) followed by a C-N bond cleavage may account for the formation of (11) as suggested by Alper.^{6,7} Cyclization and ligand migration could then lead to structures (12) which collapse to give (9).⁸

A somewhat similar transformation of an azirine into a pyridine has been reported by Padwa who observed the thermal transformation of 2-methyl-3-phenyl-2H-azirine-2-propionaldehyde into 3-methyl-2-phenylpyridine.⁹ However, his proposed mechanism, involving successive 1,4- and 1,5-hydrogen transfer, cannot account for the formation of (9) from (5).

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¹ For recent reviews on the chemistry of azirines, see: V. Nair and K. H. Kim, *Heterocycles*, 1977, **7**, 353; P. Gilgen, H. Heimgartner, H. Schmid, and H. J. Hansen, *ibid.*, 1977, **6**, 143; A. Padwa, *Accounts Chem. Res.*, 1976, **9**, 371.

² A. Padwa, J. Smolanoff, and A. Tremper, *Tetrahedron Letters*, 1974, **29**; *J. Amer. Chem. Soc.*, 1975, **97**, 4682; *J. Org. Chem.*, 1976, **41**, 543.

³ J. P. Le Roux, J. C. Cherton, and P. L. Desbene, *Compt. rend.*, 1975, **280**, 37.

⁴ Two other (*Z*)-ketovinylazirines have been described by Mukai but both are unstable compounds: T. Mukai, T. Kumagai, and O. Seshimoto, *Pure and Appl. Chem.*, 1977, **49**, 287.

⁵ F. Bellamy, to be published.

⁶ H. Alper and J. E. Prickett, *J.C.S. Chem. Comm.*, 1976, 191.

⁷ H. Alper, J. E. Prickett, and S. Wollowitz, *J. Amer. Chem. Soc.*, 1977, **99**, 4330.

⁸ For somewhat analogous mechanisms see: G. D. Annis and S. V. Ley, *J.C.S. Chem. Comm.*, 1977, 581; R. Aumann, K. Fröhlich, and H. Ring, *Angew. Chem.*, 1974, **86**, 309; Y. Becker, E. Eisenstadt, and Y. Shvo, *Tetrahedron*, 1978, **34**, 799.

⁹ A. Padwa and N. Kamigata, *J. Amer. Chem. Soc.*, 1977, **99**, 1871.