Photoinitiated Substitution Reactions of 4-Cyanopyridine and 2-Cyanoquinoline with 2,3-Dimethylbut-2-ene

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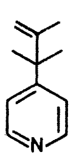
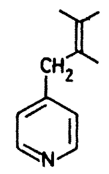
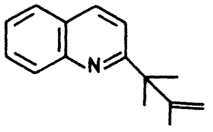
Summary Substitution of the cyano group occurs when either 4-cyanopyridine or 2-cyanoquinoline is irradiated at 254 nm with 2,3-dimethylbut-2-ene, leading to (**1**) and (**2**) or (**3**) and (**4**), respectively, without forming cyclic photoadducts.

THE photoaddition of alkenes to benzene is well known,[1] and reactions between alkenes and 1- and 2-naphthonitrile[2] and 9-cyanophenanthrene[3] have also been reported. However, very little is known about the photoreactions of alkenes with heteroaromatic bases. Haszeldine *et al.*,[4] only recently reported that the photoreaction of alkenes with pentafluoropyridine, unlike pyridine, yielded bicyclic and tricyclic photoadducts.

We now report preliminary results of our study of the photoinitiated substitution reactions of 2,3-dimethylbut-2-ene with either 4-cyanopyridine or 2-cyanoquinoline. Irradiation of a deaerated solution of 4-cyanopyridine in 2,3-dimethylbut-2-ene (molar ratio 1:2) at 80 °C for 50 h, in a Model RPR 100 Rayonet photochemical reactor equipped with low pressure lamps, gave (**1**) and (**2**)† (2:1 ratio) in 20% overall yield. Similarly, irradiation of a deaerated solution of 2-cyanoquinoline in 2,3-dimethylbut-2-ene, under the same conditions for 24 h, gave (**3**) and (**4**)† (1:1 ratio) with an overall yield of 5%.


(1)


(2)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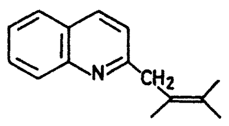
(4)

A mechanism for the reaction involving electron transfer from the π system of the olefin to the π system of the heteroaromatic base, similar to that generally suggested for the photoreaction of alkenes with benzene,[1] could be envisaged. However, in our opinion, the fact that no photocyclisation, but only photosubstitution, occurs is consistent with a monophotonic hydrogen photoabstraction from the olefin by the $n\pi^*$ excited state of the heterocyclic base[5] followed by cross dimerisation of the two radicals and elimination of HCN.[6] A similar mechanism is reported for the photoreaction of methyl benzoate and 2,3-dimethylbut-2-ene.[7]

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† The i.r., n.m.r., and mass spectra fully support the assigned structures.

[1] D. Bryce-Smith and A. Gilbert, Tetrahedron Report No. 40, *Tetrahedron*, 1977, **33**, 2459.

[2] J. J. Cullough, R. C. Miller, and W. S. Wu, *Canad. J. Chem.*, 1977, **55**, 2909.

[3] K. Mizuro, C. Pac, and H. Sakuri, *J. Amer. Chem. Soc.*, 1974, **96**, 2993.

[4] M. G. Barlow, D. E. Brown, and R. N. Haszeldine, *J.C.S. Chem. Comm.*, 1977, 669.

[5] A. Castellano, J. P. Catteau, and A. Lablache-Combier, *Tetrahedron*, 1975, **31**, 2255.

[6] For other examples of cyanide substitution on heteroaromatic bases see: T. Caronna, S. Morrocchi, and B. M. Vittimberga, *Chimica e Industria*, 1976, **58**, 548; N. Hata, I.Ono and H. Hirose, *Bull. Chem. Soc. Japan*, 1973, **46**, 942; B. M. Vittimberga, T. Caronna, and S. Morrocchi, Abstracts, Amer. Chem. Soc. Nat. Meeting, Chicago 1977.

[7] T. S. Cantrell, *J.C.S. Chem. Comm.*, 1973, 468.