Tetrahedron Letters Vol.21, pp2737-2740
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0040-4039/80/0708-2737$02.00/0

INTERMOLECULAR PHOTOADDITION INVOLVING 1,4-TRANSFER OF CYANO GROUP. 3
PHOTOADDITION OF 2-CYANOPYRIDINE TO OLEFINS[1]

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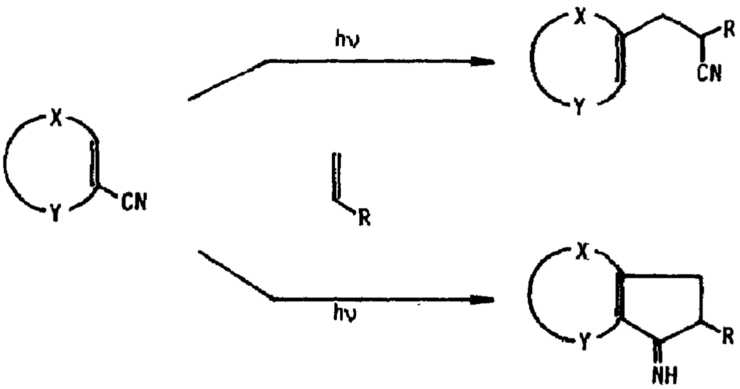
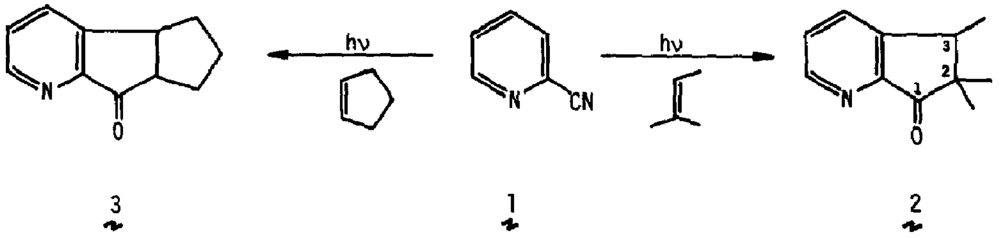
Summary: Photoreaction of 2-cyanopyridine with 2-methyl-2-butene and cyclopentene provided the corresponding annelated ketones 2 and 3, respectively, whereas photoreaction with 1-trimethylsilyloxycyclopentene afforded the "ene" product 8.

In a previous paper we have reported a new type of photoannelation in which an α,β-unsaturated nitrile such as 6-cyanouracil undergoes (3 + 2) addition with alkenes, in competition with the 1,4-transfer of a cyano group (Eq. 1).[2] It has also been shown that these processes are solvent- and temperature-dependent.[2a] In order to know the generality and the synthetic scope of this novel photoannelation, we have examined the photoreaction of a number of α,β-unsaturated nitriles with olefins. We report herein a preliminary result on the photoaddition of 2-cyanopyridine to olefins.[3]



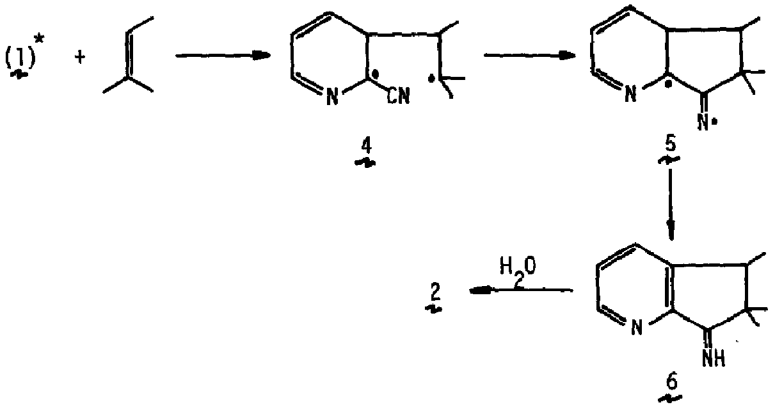
(Eq. 1)



Irradiation of 2-cyanopyridine (1, 20 mM) and 2-methyl-2-butene (50 mM) in acetonitrile with a 10-W low-pressure mercury lamp (Vycol filter) for 6 h produced a colored solution. Removal of the solvent followed by preparative TLC (silica gel, CHCl$_3$-ethyl acetate; 10 : 3) provided 2 (16%).[4] Irradiation of 1 (27 mM) and cyclopentene (75 mM) in acetonitrile under the same conditions followed by similar workup gave the tricyclic product 3 (36%).[4] The structures of the photoproducts were assigned on the basis of spectral data (Table 1).[5] Under the conditions 3-cyanopyridine or 4-cyanopyridine did not react with these olefins.

The formation of 2 and 3 may be reasonably rationalized by assuming 1,4-biradical intermediates as proposed in a previous paper.[2a] The biradical intermediate 4 may close to cyclic iminium species 5 and subsequent disproportionation of 5 would yield 6 which on workup produces 2 (Scheme 1). The present reaction provides a useful method for the synthesis of annelated pyridines. However, the photoreaction has some serious limitations. For example, photoreaction of 1 with monosubstituted olefins such as 1-hexene and vinyl acetate did not yield the adducts, whereas irradiation of 1 with enol ether 7 afforded a different type of product, 8 (20%), presumably via an "ene" reaction.[6] In contrast to the case of 6-cyanouracil,[2a] photoreaction of 1 with alkynes afforded neither rearranged adducts nor (3 + 2) adducts. We are continuing to explore the scope and limitation of the photoaddition of unsaturated nitriles.

Scheme 1



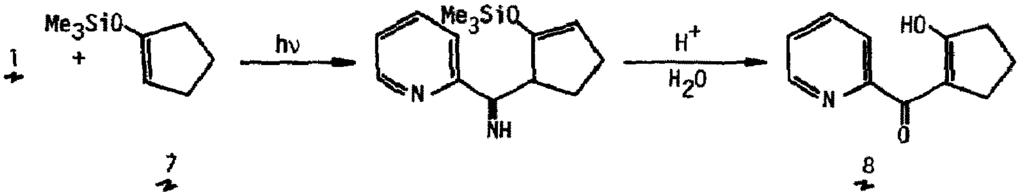


Table 1. Spectral data of the photoproducts[a]

Compound	
2	Viscous oil; ^{1}H NMR (CCl_4) δ 1.03 (s, 3 H), 1.20 (s, 3 H), 1.31 (d, 3 H, J = 7 Hz), 3.03 (q, 1 H, J = 7 Hz), 7.33 (dd, 1 H, J = 8, 5 Hz), 7.79 (dd, 1 H, J = 8, 1 Hz), 8.63 (dd, 1 H, J = 5, 1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 20.4 (q), 24.2 (q), 42.7 (d), 48.2 (s), 127.5 (d), 133.5 (d), 150.7 (d), 151.4 (s), 152.0 (s), 209.8 (s); IR (neat) 1715 cm^{-1}.
3	Bp 130 - 135 °C/20 mmHg; ^{1}H NMR (CCl_4) δ 1.50 - 2.40 (m, 6 H), 2.98 (m, 1 H), 3.74 (m, 1 H), 7.34 (dd, 1 H, J = 8, 5 Hz), 7.80 (dd, 1 H), J = 8, 1 Hz), 8.65 (dd, 1 H, J = 5, 1 Hz); ^{13}C NMR ($CDCl_3$) δ 24.8 (t), 30.6 (t), 32.5 (t), 41.4 (d), 50.8 (d), 127.7 (d), 134.4 (d), 150.4 (d), 152.8 (s), 153.9 (s), 208.5 (s); IR (neat) 1710 cm^{-1}.
8	Mp 120 - 123 °C; ^{1}H NMR ($CDCl_3$) δ 1.91 (m, 2 H), 2.41 (t, 2 H, J = 7 Hz), 2.86 (t, 2 H, J = 7 Hz), 7.36 - 7.90 (m, 3 H), 8.69 (m, 1 H), 9.5 - 10.5 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.3 (t), 29.7 (t), 38.9 (t), 103.4 (s), 123.3 (d), 124.2 (d), 136.2 (d), 149.3 (d), 151.5 (s), 152.6 (s), 185.1 (s); IR (KBr) 3400, 1660, 1630, 1610 cm^{-1}.

[a] Satisfactory elemental analyses and mass spectral data were obtained.

Acknowledgments: This work was supported by a Grant-in-Aid for Scientific Research from t
Ministry of Education and the Yamada Science Foundation.

References and Notes

1. Photoinduced Reactions. 125.
2. (a) I. Saito, K. Shimozono, and T. Matsuura, *J. Am. Chem. Soc.*, in press; (b) I. Saito, K. Shimozono, T. Matsuura, K. Fukuyama, and Y. Katsube, submitted to *Teterahedron Lett*.
3. Photoaddition of cyanopyridines, see (a) T. Caronna, S. Morrocchi, and P. Traldi, *J. C. S Chem. Commun.*, 64 (1979); (b) Y. Ito and T. Matsuura, *J. Org. Chem.*, **44**, 41 (1979).
4. A considerable amount of polymeric products derived from the alkene has been observed.
5. The regiochemistry of **2** was confirmed by the chemical shift of C-3 carbon (δ 42.7, double and the fragmentation pattern of the mass spectrum.
6. An analogous "ene" reaction by photoexcited nitriles, see T. S. Cantrell, *J. Org. Chem.*, **42**, 4238 (1977).

(Received in Japan 11 April 1980)