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Photocycloadditions of 4-Methoxy-2-pyridone to Olefins and Synthesis of 1,2-Dihydrocyclobuta[c]pyridin-3(4*H*)-ones

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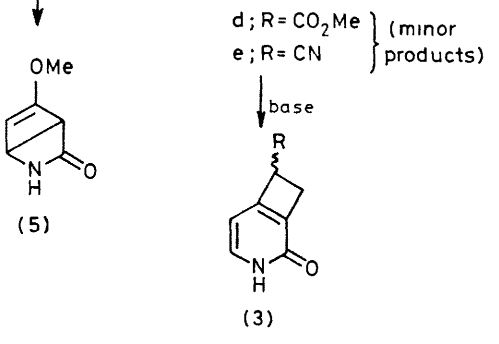
Summary Irradiation of 4-methoxy-2-pyridone (**1**) in acetone in the presence of electron-rich alkenes afforded the 3-azabicyclo[4.2.0]oct-4-en-2-ones (**2a**—**c**) as the major products, whereas photolyses in the presence of electron-deficient alkenes led to the 2-azabicyclo[4.2.0]-oct-4-en-3-ones (**4a**, **b**) as the major products; base treatment of the former adducts gave rise to the novel 1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-ones (**3a**—**c**).

RECENTLY, we reported that irradiation of 4-methoxy-2-quinolone in an appropriate solvent in the presence of olefins afforded [2+2] cycloadducts in quantitative yields and that these products may be transformed to the then unknown 1,2-dihydrocyclobuta[*c*]quinolin-3-ones by base treatment.[1] Extension of this work has led us to the unique photocycloadditions of 4-methoxy-2-pyridone (**1**) to olefins giving either 3-azabicyclo[4.2.0]oct-4-en-2-ones (**2a**—**c**)† or 2-azabicyclo[4.2.0]oct-4-en-3-ones (**4a**, **b**)† as the major products, depending upon the kind of olefin used. These cycloadditions were observed only when acetone was used as a solvent and the use of other solvents (*e.g.*, alcohols, ether, dichloromethane) afforded only the photo-2-pyridone[2] (**5**),† irrespective of the presence or absence of olefins in the photolyses.



Irradiation of a 5 mM solution of 4-methoxy-2-pyridone[3] (**1**) in acetone containing 50—100 mol. equiv. of isobutene yielded a cycloadduct[4] in 94·7% yield. The structure of the compound (**2a**), formed by cycloaddition between the 3,4-double bond of (**1**) and the olefin, was assigned from its n.m.r. spectrum (1-H, tt, *J* 10·0 and 1·5 Hz).‡ Other electron-rich alkenes formed the same type of adducts (**2b**, **c**)‡ as mixtures of two stereoisomers in which the *syn*-isomers always predominated over the *anti*-isomers.

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† All new compounds gave satisfactory combustion and/or mass spectrometric analysis and spectroscopic data consistent with the assigned structures.

‡ Decoupling experiments showed that the larger couplings corresponded to vicinal couplings and the smaller couplings were due to long-range couplings with NH and 5-H.

Base treatment of these adducts (**2a**—**c**) afforded 1-substituted 1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-ones (**3a**—**c**)‡ in high yields.

TABLE. Photocycloadditions of (**1**) to electron-rich or -deficient alkenes.[a]

	syn M.p./°C (yield/%)	*anti* M.p./°C (yield/%)
(**2a**)	183—184 (94·7)	
(**2b**)	126—127 (55·6)	Oil (trace)
(**2c**)	106—108 (66·6)	Oil (12·7)
(**4a**)[b]	185—187 (35·1)	Oil (5·5)
(**4b**)[c]	223—225 (20·6)	200—202 (17·8)

[a] Only major regioisomers are shown. [b] A mixture of *syn*- and *anti*-isomers of (**2d**) was also obtained in 8·7% yield. [c] *syn*-(**2e**) (m.p. 161—162 °C, 11·4%) and *anti*- (**2e**) (m.p. 140—142 °C, 9·2%) were also obtained.

Interestingly, photolyses of (**1**) in the presence of electron-deficient alkenes were found to give a new type of adduct (**4a,b**) as the major product, formed by cycloaddition between the 5,6-double bond of (**1**) and the alkenes, again mixtures of the *syn*- and *anti*-stereoisomers were obtained, and the adducts of type (**2**) became the minor products. Each of the (**4**)-type adducts shows the 4-H n.m.r. signal as a singlet at δ 5·1—5·5 and so could be distinguished from the (**2**)-type adducts which show the 4-H and 5-H as a set of doublets at δ *ca.* 6·4 and 4·9.[5]

These results clearly indicate that the photo-2-pyridone (**5**) is formed from the S_1 state, whereas the cycloadducts (**2**) and (**4**) are formed from the T_1 state.

In conclusion, this method provides not only a convenient synthetic route to the previously unknown 1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-ones[6] (**3**) but also direct chemical proof for the participation of a triplet state of an α-oxoazine in the cycloaddition to olefins.

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[1] C. Kaneko and T. Naito, *Chem. Pharm. Bull.*, 1979, **27**, 2254. See also C. Kaneko, T. Naito, and M. Somei, *J. Chem. Soc., Chem. Commun.*, 1979, 804.

[2] The photo-2-pyridone (**5**) was obtained as a stable compound (m.p. 94—95 °C) and reverted to (**1**) when refluxed for 6 h in *o*-dichlorobenzene. For the formation of some photo-2-pyridones, see E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, 1964, **86**, 950; R. C. De Selm and W. R. Schleigh, *Tetrahedron Lett.*, 1972, 3563.

[3] K. Takeda and K. Igarashi, *Shionogi Kenkyusho Nempo*, 1951, **1**, 1.

[4] Cycloadditions forming type (**2**) adducts from 4-unsubstituted 2-pyridones have been reported: K. Somekawa, T. Simou, K. Tanaka, and S. Kumamoto, *Chem. Lett.*, 1975, 45.

[5] Stereoselective formation of [2+2] adducts having *cis*-ring junctions from the photocycloadditions of 2-quinolones to olefins has been reported and explained by the steric constraints due to the double bond and the amide function in the pyridone system (G. R. Evanega and D. L. Fabiny, *J. Org. Chem.*, 1970, **35**, 1757; O. Buchardt, J. J. Christensen, and N. Harrit, *Acta Chem. Scand., Ser. B*, 1976, **30**, 189). Complete regio- and stereo-chemistries of each adduct (**2**) or (**4**) were determined by n.m.r. spectroscopy using the decoupling technique. The key factor in the stereochemical assignments is the fact that long range coupling (1—2 Hz) between 1-H and 7-H for both types of adducts (**2**) and (**4**) is observed only if these two protons are *cis* oriented on the cyclobutane ring.

[6] 1,2-Dihydrocyclobuta[*c*]pyridine has been synthesized recently: R. P. Thummel and D. K. Kohli, *J. Org. Chem.*, 1978, **43**, 4882; J. M. L. Riemann and W. S. Trahanovsky, *Tetrahedron Lett.*, 1977, 1867.