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Syntheses and Ring-opening Reactions of 5-Alkoxy- and 5-Acetoxy-3-oxo-2-azabicyclo[2.2.0]hex-5-enes

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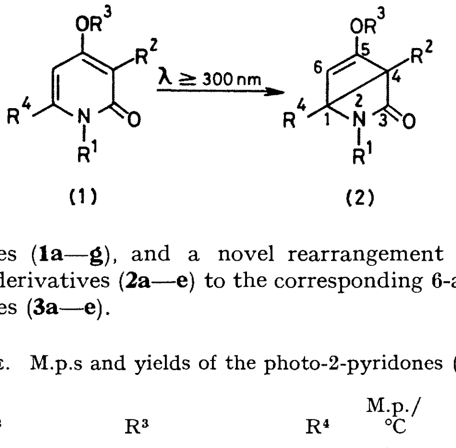
Summary The efficient photochemical synthesis of 5-alkoxy- and 5-acetoxy-3-oxo-2-azabicyclo[2.2.0]hex-5-enes (**2a**—**e** and **f**,**g**), and a new rearrangement reaction of the former compounds (**2a**—**e**) to 6-alkoxy-2-pyridones (**3a**—**e**), are reported.

Corey and Streith first synthesized *N*-methyl-photo-2-pyridone *via* low temperature photoisomerization of a dilute solution of *N*-methyl-2-pyridone.[1] Although the relatively high stability of the photo-2-pyridones, including the parent compound 3-oxo-2-azabicyclo[2.2.0]hex-5-ene, was later demonstrated by two research groups,[2,3] the syntheses of these photo-2-pyridones have been hampered owing to concomitant and more efficient formation of the photodimers.[1–5]

De Selms *et al.*[2] reported a high-yield formation of the corresponding photo-2-pyridone by irradiation of recinine (3-cyano-4-methoxy-1-methyl-2-pyridone) with no dimer detected, and speculated that this exceptional photochemical behaviour of recinine might have some significance in phytological photosynthesis. Previously, we reported that irradiation of 4-methoxy-2-pyridone in acetone in the presence of olefins gave the intermolecular [2 + 2] cycloadducts with no dimer formation.[6] These two experiments seem to suggest an inability of the 4-alkoxy-2-pyridones to photodimerize and, hence, the selective and high-yield formation of the photo-2-pyridones by irradiation of compounds (**1**) in an appropriate transparent solvent. Experiments along these lines have led us to find an efficient route to the 5-alkoxy- and 5-acetoxy-derivatives (**2a**—**e** and **2f**,**g**) of 3-oxo-2-azabicyclo[2.2.0]hex-5-ene from the 4-oxygenated 2-pyridones (**1a**—**g**), and a novel rearrangement of the 5-alkoxy derivatives (**2a**—**e**) to the corresponding 6-alkoxy-2-pyridones (**3a**—**e**).



(**1**) (**2**)

Table. M.p.s and yields of the photo-2-pyridones (**2**).

	R^1	R^2	R^3	R^4	M.p./ °C	Yield/ %
a;	Me	H	Me	H	Oil	81·9
b;	H	H	Me	H	94—95	83·4
c;	H	H	$CH_2CH{=}CH_2$	H	42—43	80·0
d;	H	H	$[CH_2]_2CH{=}CH_2$	H	38—41	92·0
e;	H	H	CH_2Ph	H	122—124	89·8
f;	H	$CH_2CH{=}CH_2$	COMe	H	92—94	85·5
g;	H	H	COMe	Me	Oil	88·5

Syntheses were carried out by irradiation of 10^{-2}—10^{-3} M ethereal solutions (other transparent solvents can also be used)† with Pyrex filtered irradiation from a high-pressure mercury arc lamp (Toshiba 400P) and the products (**2a**—**g**) were isolated by direct recrystallization or column chromatographic separation of the concentrated residue. No photodimer was obtained from any of these 4-oxygenated

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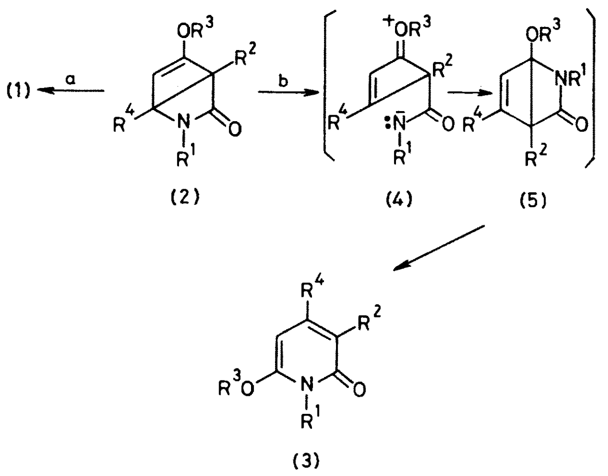
† In these solvents, the cycloadducts of pyridones (**1**) with olefins were not obtained.

2-pyridones (**1a**—**g**), and hence the photo-2-pyridones (**2a**—**g**) were obtained as the sole product in very high yields.

These photo-2-pyridones (**2**) are all liquids or low melting solids and were characterized by acceptable mass (molecular ions and substituted cyclobutadiene cations as the major fragment ions), i.r. (absorptions at 1725—1765 cm^{-1}: β-lactam carbonyl), and n.m.r. spectra.[‡]

Thermal reactions of the photo-2-pyridones so far reported have been limited to cycloreversion leading to the original 2-pyridones (*e.g.*, path a).[2,3] However, it was found that, while the 5-acetoxy derivatives (**2f,g**) reverted selectively to 4-acetoxy-2-pyridones (**1f,g**) irrespective of the conditions employed, thermolysis of the 5-alkoxy derivatives (**2a**—**e**) above 80 °C caused concomitant formation of both 4- and 6-alkoxy-2-pyridones[7] (**1** and **3**), the yield ratio of which was dependent upon the solvent employed. Thus, for example, while (**2e**) afforded 4-benzoyloxy-2-pyridone (**1e**) (24·0%) and its 6-isomer (**3e**) (20·8%) in addition to recovered (**2e**) (45·4%) after refluxing in benzene for 60 h, the same two pyridones were obtained in the respective yields of 20·2 and 57·9% by refluxing in acetonitrile (30 h), with 6·5% recovery of (**2e**). Preferential formation of the 6-alkoxy-2-pyridones (**3a**—**e**) compared to the 4-isomers (**1a**—**e**) was also observed in acetone (sealed tube at 100 °C), but not in *o*-dichlorobenzene (reflux). These facts[§] imply the intermediacy of zwitterionic species (**4a**—**e**) in the rearrangement of (**2a**—**e**) to (**3a**—**e**). In accordance with this explanation,[¶] the addition of AgBF$_4$[8] to these reaction media led to almost selective formation of the 4-alkoxy-2-pyridones (**2a**—**e**).



Since these 4-oxygenated 2-pyridones never photodimerize under any condition,[**] a general synthetic route to photo-2-pyridones having an oxygen function at the 5-position seems to be established.

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[‡] N.m.r. spectra were measured in CDCl$_3$: δ (**2b**), 3·18 (s, 1- and 4-H), 3·80 (s, Me), 5·00 (s, 6-H), and 6·37br (s, NH); δ (**2f**) 2·17 (s, Me), 4·13 (s, 1-H), 5·73 (s, 6-H), 6·80br (s, NH), and allyl group signals.

[§] The presence of the alkoxy-function at the 5-position of (**2a**—**e**) may facilitate the heterolytic cleavage of the C(1)–N(2) bond to give (**4**). The weaker electron-donating character of the acetoxy-function is probably not enough to accelerate this cleavage. Dielectric constants (ϵ) for these aprotic solvents (MeCN, acetone, *o*-dichlorobenzene, and benzene) are 37·5, 20·7, 9·93, and 2·28, respectively.

[¶] In order to verify the proposed mechanism, photochemical conversion of (**3b**) into (**5b**) was examined under the same conditions as for the conversion of (**1**) into (**2**). However, within a comparable irradiation period, the starting pyridone was recovered and neither the photopyridone nor the dimer was detected.

[**] The photolyses of (**1**) under sensitization conditions also did not produce any photodimer.[6]

[1] E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, 1964, **86**, 950.
[2] R. C. De Selms and W. R. Schleigh, *Tetrahedron Lett.*, 1972, 3563.
[3] H. Furrer, *Chem. Ber.*, 1972, **105**, 2780.
[4] E. C. Taylor, R. O. Kan, and W. W. Paudler, *J. Am. Chem. Soc.*, 1961, **83**, 4484.
[5] Y. Nakamura, T. Kato, and Y. Morita, *J. Chem. Soc., Chem. Commun.*, 1978, 620.
[6] H. Fujii, K. Shiba, and C. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1980, 537.

[7] The structures of the 6-alkoxy-2-pyridones (**3a**—**e**) were asigned from their n.m.r. spectra *e.g.*, δ (**3e**) 5·73 (dd, 5-H), 6·16 (dd, 3-H), and 7·32 (dd, 4-H) ($J_{3,4}$ 8·6, $J_{4,5}$ 7·6, and $J_{3,5}$ 0·9 Hz), and benzyl signals at 5·07 (s) and 7·25br (s). The compound (**3b**) obtained from (**2b**) was identical with an authentic sample: A. R. Katritzky, F. D. Popp, and J. D. Rowe, *J. Chem. Soc.* (*B*), 1966, 562.

[8] Metal species such as AgBF$_4$ are known to promote orbital-symmetry forbidden disrotatory opening in molecules such as Dewar benzene: J. Wristers, L. Brener, and R. Pettit, *J. Am. Chem. Soc.*, 1970, **92**, 7499; W. Sleger, R. Case, J. S. McKennis, and R. Pettit, *ibid.*, 1974, **96**, 287.