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PHOTOADDITION OF 2-PYRIDONES TO CONJUGATED DIENES.[1]†

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Abstract —— Irradiation of 2-pyridones with conjugated cyclic dienes gave [4+4]cycloaddition products. Irradiation with conjugated non-cyclic dienes afforded 2-substituted derivatives, probably derived from oxetane intermediate, together with the [2+2]cycloaddition products.

Our continuing interest in the photochemistry of nitrogen-carbonyl systems[2] prompted us to develop the photochemistry of 2-pyridones, a parent system of nitrogen-heteroaromatic carbonyl compounds. Photodimerization of 2-pyridones are well known as typical [4+4]cycloaddition of heterocycles.[3] Diels-Alder reaction of 2-pyridone occurs thermally with maleic anhydride.[4] Photo[2+2]-cycloaddition of 2-pyridone to olefins has already been reported.[5] We have also described photosensitized oxygenation of 2-pyridone which proceeds by way of photocycloaddition.[6]

To further explore these photochemical properties, we have examined cycloadditions of 2-pyridones with a diene system. Since photodimerization of 2-pyridones is regarded as [4+4]cycloaddition reaction of a conjugated diene component built into the molecules of 2-pyridones, we expected that 2-pyridones will undergo [4+4]cycloaddition with cyclic dienes. In the present paper we wish to report such intermolecular photoaddition reactions of 2-pyridones with conjugated dienes.

Irradiation of 2-pyridones of 1a-c in the presence of 10 equivalents of cyclopentadiene (2a), a typical conjugated cyclic diene, through a Pyrex filter with a 500 W high-pressure mercury lamp in acetonitrile, gave two types of intermolecular addition products 3 and 4 together with dimers or valence isomer of 2-pyridone as shown in Scheme 1 and Table I. As reported already in a

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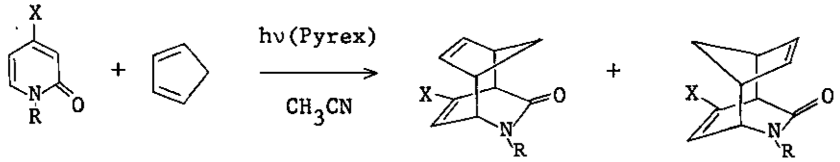
† Dedicated to Sir Derek Barton on the occasion of his 70th birthday.

preceding paper,[7] photolysis of 4-*tert*-butyl-2-pyridone gives a valence isomer. Even in the presence of large excess diene, 4-substituted 2-pyridones (1b and 1c) undergo the valence isomerization in competition with the [4+4]cycloaddition. Analytical and spectral data including an endo-absorption in the ultraviolet spectrum supported that these photoproducts 3a and 4a are [4+4]cycloadducts of 2-pyridones with cyclopentadiene. In the nmr spectra of 3a and 4a, H_{eq} of methylene of cyclopentene moiety of 3a showed its signal 0.4 ppm lower than that of H_{ax} (3a, H_{eq}: 2.53 and H_{ax}: 2.13 ppm. 4a, H_{eq}: 2.09 and H_{ax}: 1.93 ppm) by anisotropy effect of carbonyl group.



1 2a 3 4

a: R=H, X=H
b: R=H, X=Me
c: R=Me, X=*t*-Bu

Scheme 1

Table I. Photoaddition of 2a to 1

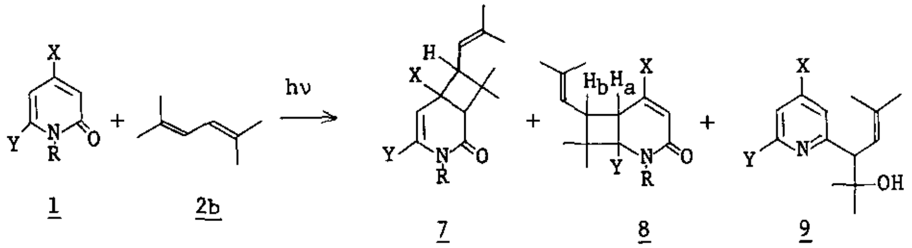
1	Time	Products Yields (%)			
	(h)	3	4	isomer*	dimer**
a	6	20	30	-	5
b	10	12	10	28	trace
c	10	6	20	45	-

* : valence isomer of Dewar pyridones.

**: [4+4]dimer of 2-pyridone.

Next, in order to examine a behavior of a conjugated non-cyclic diene to 1, 2,5-dimethyl-2,4-hexadiene (2b) was subjected to the photoreaction with 2-pyridones (1). Irradiation of 1a,b,d in the presence of 10 equivalents of 2b gave two kinds of cyclobutene derivatives 7, 8, and 2-substituted pyridine derivatives 9 (Scheme 2, Table II).

2,5-Dimethyl-2,4-hexadiene (2b) is known as a conjugated diene with s-*trans* conformation.[8] Yang *et al*. reported that photoaddition of a conjugated diene to aromatic hydrocarbon gave [4+4]adduct retaining *trans* configuration, and the *trans*-adduct from naphthalene with 2,5-dimethyl-2,4-hexadiene rearranged easily to a cyclobutane derivative by [3,3]-sigmatropic shift.[9] Although a direct pathway is possible to lead to the products 7, 8 by the [2+2]addition, a triplet



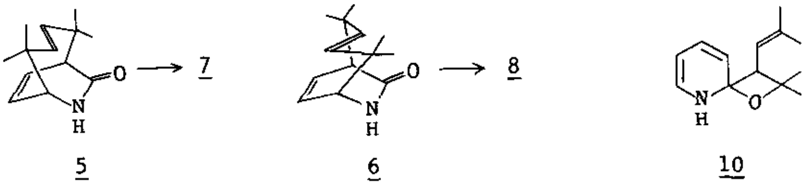
a: R=H, X=H, Y=H
b: R=H, X=Me, Y=H
d; R=H, X=Me, Y=Me

Scheme 2

Table II. Photoaddition of 2b to 1

1	Irradiation Time (h)	Products Yields (%)		
		7	8	9
a	8	14	17	28
b	13	8	trace	10
d	26	18	5	22

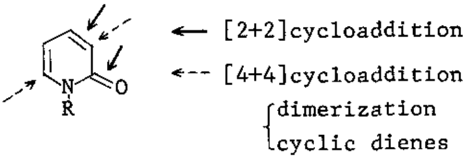
sensitization may be needed for the [2+2]photoaddition of 2-pyridone with olefin.[5] Formation of 7, 8 may be tentatively explained in terms of the [3,3]-sigmatropic rearrangement of the initially formed [4+4]adducts 5 and 6 to 7 and 8, respectively (Scheme 3).



Scheme 3

Based on the ^{1}H nmr coupling constants between H$_a$ and H$_b$ (J = 9 Hz for 7a, J = 10 Hz for 8a), the dimethylvinyl substituent is of cis-configuration to the six-membered ring. The structure of 2-substituted pyridine derivative 9 was confirmed by ir (disappearance of C=O and a new signal for O-H) and nmr (no decrease of aromatic protons, and low-field proton signal of α-proton of pyridine ring). Formation of 9 can be explained by initial oxetane (10) formation from 2b and the carbonyl group of 1, followed by oxetane ring cleavage and concomitant aromatization. Although dimerization[3] and addition to olefin[5] are well known in the photochemistry of 2-pyridone, the indirect evidence of the oxetane formation of the carbonyl group of 2-pyridone, presented in this report, is the first indication for the photoaddition of 2-pyridone to occur at the carbonyl site.[10a,c] Kaneko et al. have also reported independently that photoaddition of 2-quinolone derivatives with 2c gave the products apparently derived from oxetane.[10b,d]

Photoaddition reactions of olefins to 2-pyridone,[7] the simplest member of the nitrogen-carbonyl heteroaromatic family, is now summarized in Scheme 4. Cyclic dienes, including 2-pyridone itself, undergo the [4+4]addition at the C_3 and C_6 sites, whereas non-cyclic dienes may react toward the dual sites for the [2+2]addition.[10c]



Scheme 4

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