PHOTOADDICTION OF 2-PYRIDONES TO CONJUGATED DIENES.\textsuperscript{1†}

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Our continuing interest in the photochemistry of nitrogen-carbonyl systems\textsuperscript{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.\textsuperscript{3} Diels-Alder reaction of 2-pyridone occurs thermally with maleic anhydride.\textsuperscript{4} Photo[2+2]-cycloaddition of 2-pyridone to olefins has already been reported.\textsuperscript{5} We have also described photosensitized oxygenation of 2-pyridone which proceeds by way of photocycloaddition.\textsuperscript{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

\textsuperscript{†}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.

\[ \text{hv(Pyrex) \quad \text{CH}_3\text{CN} \quad \rightarrow \quad X^2 + X^3} \]

\[
\begin{align*}
\text{1} & \quad X \\
\text{2a} & \quad R=H, \quad X=H \\
\text{3} & \quad R=H, \quad X=Me \\
\text{4} & \quad R=Me, \quad X=t-Bu
\end{align*}
\]

**Scheme 1**

Table I. Photoaddition of 2a to 1

<table>
<thead>
<tr>
<th>1</th>
<th>Time (h)</th>
<th>Products</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6</td>
<td>3 20 30 4 5</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>10</td>
<td>12 10 28 trace</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>10</td>
<td>6 20 45</td>
<td></td>
</tr>
</tbody>
</table>

*: valence isomer of Dewar pyridones.


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

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a: \( R=H, \ X=H, \ Y=H \)  
b: \( R=H, \ X=Me, \ Y=H \)  
c: \( R=H, \ X=Me, \ Y=Me \)  

**Scheme 2**

<table>
<thead>
<tr>
<th>Table II. Photoaddition of 2b to 1</th>
</tr>
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<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>----</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>d</td>
</tr>
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sensitization may be needed for the [2+2]photoaddition of 2-pyridone with olefin. 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).

Based on the \( ^1H \) 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 \( \alpha \)-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 and addition to olefin 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.\textsuperscript{10a,c} Kaneko et al. have also reported independently that photoaddition of 2-quinolone derivatives with 2c gave the products apparently derived from oxetane.\textsuperscript{10b,d}

Photoaddition reactions of olefins to 2-pyridone,\textsuperscript{7} the simplest member of the nitrogen-carbonyl heteroaromatic family, is now summarized in Scheme 4. Cyclic dienes, including 2-pyridone itself, undergo the \([4+4]\) addtion at the \(\text{C}_3\) and \(\text{C}_6\) sites, whereas non-cyclic dienes may react toward the dual sites for the \([2+2]\) addition.\textsuperscript{10c} Scheme 4

REFERENCES


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