STEREOSELECTIVITY AND REGIOSELECTIVITY OF THE PHOTOCYCLOADDITION OF

2-METHYL-2,4-HEXADIENE AND ACETONE.

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Until recently (2), 1,3-dienes were considered to be photochemically inert toward cyclo-
addition with alkanones. It is now clear that triplet ketones can cycloadd to 1,3-dienes,
although inefficiently, if energy transfer to the diene (inducing diene isomerization and/or
dimerization) is exothermic (3). More importantly, from both the standpoint of synthetic and
mechanistic studies, singlet alkanones are quenched by 1,3-dienes, and cycloaddition products,
not cis-trans-isomerization, are observed (4). We report here results of a study of the photo-
cycloaddition of acetone to 2-methyl-2,4-hexadiene (1).

Barltrop and Carless (5) have reported that irradiation of solutions of acetone and 1,3-
dienes (butadiene, isoprene, 2,3-dimethylbutadiene and 2,5-dimethyl-2,4-hexadiene) leads to the
formation of oxetanes. No data on the stereoselectivity of oxetane formation were given in this
report, but (a) butadiene was reported to yield a 2-vinyl oxetane and a 3-vinyl oxetane in 2%
and 8% yield, respectively and (b) isoprene was reported to yield a mixture of 2- and 3-vinyl
oxetanes in about 20% yield (in an unspecified ratio). Dowd, et al. (6) reported that 3-methyl-
ene-cyclobutanone adds to cis- and trans-1,3-pentadiene stereospecifically, but with only modest
regioselectivity. Since the photoreactions of cyclobutanone are somewhat atypical relative to
other alkanones (7), we felt study of the stereoselectivity and regioselectivity of a more
representative alkanone-diene system (Scheme I) was warranted. In particular, this system
offers the possibility of eight isomeric oxetanes as products.

Irradiation of solutions of trans-I in acetone leads to formation of four of the oxetanes,
2, 3, 4, and 6. In addition, isomerization of the diene is observed. Table I summarizes a
study of the yields of 2-6 and cis-I as a function of concentration of trans-I. It is apparent
that at high (≈2M) concentrations of trans-I, the reaction is stereospecific, since only trans-
oxetanes are formed. The regioselectivity with respect to formation of 2- or 3- alkenyl
oxetanes strongly favors the formation of the 3-alkenyl oxetane. However, within the experi-

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mental error, no regioselectivity is found with regard to which double bond of trans-I undergoes 2+2 addition to acetone. Finally, the occurrence of trans-cis isomerization decreases markedly as the concentration of trans-I is increased. This result suggests that most (and possibly all) of the significant isomerization is due to incomplete trapping of singlet acetone, thereby allowing formation of triplet acetone which sensitizes trans-cis isomerization. Barltrop and Carless (5) and Yang et al. (4b) have presented evidence that the major, if not the exclusive, path for oxetane formation is via the addition of alkanone singlets to 1,3-diene. Stern-Volmer quenching of the fluorescence of acetone with trans-I leads to a $k_{\text{q}}^F \Gamma_F$ value of 0.58 M$^{-1}$ ($k_{\text{q}}^F = \text{rate of fluorescence quenching}, \Gamma_F = \text{fluorescence lifetime}$). A plot of $1/\phi_{\text{ox}}$ versus $1/[1,3\text{-diene}]$ is linear with a slope of 14M and intercept of 6.6. Interpretation of the slope and intercept in terms of a Stern-Volmer analysis, yields a limiting $\phi_{\text{ox}}$ of 0.15 ($\phi_{\text{ox}}$ if the total oxetane formation), and a value of $k_{\text{q}}^{\text{ox}}$ of 0.47M$^{-1}$, in excellent agreement with the value from fluorescence quenching. Independent measurement of $\Gamma_F$ by the single photon counting method (8) allows us to evaluate $k_{\text{q}}^F = 2.7 \times 10^8$ M$^{-1}$ sec$^{-1}$.

In summary, we conclude that (1) singlet acetone adds stereospecifically to trans-I; (2) regiospecificity is achieved with respect to formation of 3-alkenyl oxetane (no 2-alkenyl oxetane is observed); (3) no regiospecificity is achieved with respect to formation of 2,2-dimethyl or 2-methyl oxetane; (4) acetone singlet sensitized trans to cis-I isomerization does not occur efficiently; (5) the rate constant for fluorescence quenching is the same, within the experimental error, as the rate constant for the interaction leading to oxetane formation.
Table I. Quantum Yields of Formation of Oxetanes and cis-1.\textsuperscript{a}

<table>
<thead>
<tr>
<th>[trans-1]</th>
<th>%\textsuperscript{a,b}</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>cis-1</th>
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<tr>
<td>3.9M</td>
<td>70</td>
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<td>0.049</td>
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<td>c</td>
<td>0.2</td>
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<td>55</td>
<td>0.037</td>
<td>0.036</td>
<td>c</td>
<td>c</td>
<td>0.5</td>
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<td>40</td>
<td>0.028</td>
<td>0.029</td>
<td>c</td>
<td>c</td>
<td>-----</td>
</tr>
<tr>
<td>0.61M</td>
<td>30</td>
<td>0.018</td>
<td>0.020</td>
<td>c</td>
<td>c</td>
<td>-----</td>
</tr>
<tr>
<td>0.24M</td>
<td>10</td>
<td>0.006</td>
<td>0.006</td>
<td>c</td>
<td>c</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

(a) 6.8M acetone. Excitation 313 nm. Actinometer valerophenone in benzene (acetophenone assumed to be 0.33). Values extrapolated to zero conversion.

(b) Approximate % of the acetone singlets trapped. Calculated from the measured $\tau_F$ and $k_q^F$ values (see text).

(c) Trace amounts (<5% of 2 or 3) in all cases.

Scheme I.

\[ \text{trans-1} \overset{h\nu}{\rightarrow} \text{cis-1} \]

\[ \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \]
REFERENCES

1. Molecular Photochemistry. LII. Paper LII. Nicholas J. Turro and Peter Lechtken, J. Am. Chem. Soc., 94, 0000 (1972). The authors thank the Air Force Office of Science Research (Grant AFOSR-70-1848) for their generous support of this work. K.D. thanks the SRC for a NATO Fellowship.


   (b) N.C. Yang, M.H. Hui and S. Bellard, ibid., 4056 (1971).


