VALENCE PHOTOCISMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE:
EXCITED STATE ENERGETICS AND MULTIPLICITY

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Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine: Excited State Energetics and Multiplicity.

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SUPPLEMENTARY NOTES
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KEY WORDS
Valence photoisomerization, excited state configuration and multiplicity, photochemistry or heterocycles.

ABSTRACT
Photolysis of 1-ethoxycarbonyl-1H-azepine in solution at 325-385 nm gives a valence isomer with a quantum efficiency of 0.013. Valence photoisomerization cannot be driven with triplet photosensitizers nor can it be quenched by a triplet quenchers. The isomerization can be carried out using laser excitation at 458 nm. The azepine does not luminesce, but excited state energies can be estimated from absorption and sensitization data (\( S_1 = 60 \text{ kcal/mol}, T_1 = 55 \text{ kcal/mol} \)).
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The general importance of photochemical valence isomerization $1 \rightarrow 2$ for systems related to 1,3,5-cycloheptatriene is well recognized.\(^1\) Quantitative studies directed to the identification of excited states responsible for isomerization and the general location of states for the cyclic trienes are rare. We supply here such detail concerning the previously reported\(^{1d}\) isomerization $1d \rightarrow 2d$. The absorption, photosensitization and quenching data fortuitously combine to provide quantitative information which is normally unavailable in the absence of triene luminescence.

\[
\begin{align*}
\text{hv} & \quad \text{a)} \quad X = \text{CH}_3 \\
& \quad \text{b)} \quad X = \text{O} \\
& \quad \text{c)} \quad X = \text{NR} \\
& \quad \text{d)} \quad X = \text{NCO}_2\text{Et}
\end{align*}
\]

Irradiation of $1d$ in the region of n,II* absorption\(^2\) gave $2d$ in high yield. Quantum yields for isomerization in solution with and without additives are
Table. Quantum Yields for Photoisomerization $^1\text{d} \rightarrow ^2\text{d}$.

<table>
<thead>
<tr>
<th>[3]</th>
<th>Solvent</th>
<th>Additive (M)</th>
<th>$\Phi^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>cyclohexane</td>
<td>----</td>
<td>0.010</td>
</tr>
<tr>
<td>0.09</td>
<td>diglyme</td>
<td>----</td>
<td>0.013</td>
</tr>
<tr>
<td>0.10</td>
<td>benzene</td>
<td>----</td>
<td>0.013</td>
</tr>
<tr>
<td>0.03</td>
<td>n-propyl bromide</td>
<td>----</td>
<td>0.013</td>
</tr>
<tr>
<td>0.08</td>
<td>benzene</td>
<td>diene$^b$ (0.02-0.08)</td>
<td>0.012</td>
</tr>
<tr>
<td>0.10</td>
<td>benzene</td>
<td>fluorenone (0.9) (53)$^c$</td>
<td>&lt;0.003$^d$</td>
</tr>
<tr>
<td>0.09</td>
<td>benzene</td>
<td>benzophenone (1.0) (69)$^c$</td>
<td>&lt;0.003$^d$</td>
</tr>
<tr>
<td>0.007</td>
<td>benzene</td>
<td>valerophenone (0.4) (72)$^c$</td>
<td>&lt;0.003$^d$</td>
</tr>
</tbody>
</table>

$^a$Rayonet reactor (325 - 385 nm), 30 ± 1°C, valerophenone actinometer, estimated error ± 15%.
$^b$2,4-dimethyl-2,5-hexadiene ($E_T < 58$ kcal/mol).
$^c$Sensitizer $E_T$, kcal/mol.
$^d$Upper limit corrected for azepine absorption.

shown in the Table. The lack of quenching by diene and cyclooctatetraene (for which a very low triplet energy has been calculated$^3$), along with the lack of sensitization in experiments where sensitizers absorbed >75% of the light, implicate a singlet excited state for valence isomerization of $^1\text{d}$.

That a triplet state of $^1\text{d}$ is available was inferred from its quenching behavior. Conventional Stern-Volmer analysis of the quenching of valerophenone photoelimination$^4$ and biacetyl phosphorescence in benzene as a function of $[\text{d}]$ gave $k_q = 56 ± 8$ and $2.5 ± 0.3 \times 10^5 \text{ M}^{-1}$, respectively. Using triplet lifetimes of valerophenone ($8.0 \times 10^{-9}$ sec)$^4$ and biacetyl ($4.6 \times 10^{-4}$ sec)$^5$, quenching constants are calculated ($k_q = 7.0 \times 10^9$ and $5.3 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$, respectively).

Photolysis of $^1\text{d}$ in benzene near its onset of absorption using an argon ion laser (457.9 nm) gave 2d with a quantum yield of 0.013 ± 0.004 (ferrioxalate
actinometry). Luminescence of 1d was not observed in benzene at room temperature or in an EPA glass at 77°K.

The reactivity of S1 and the unreactivity of T1 for 1d complete an excited state structure - reactivity pattern already in evidence for 1a1a, b and 1b.1e

The data further allow the relative location of states for 1d on the basis of the following (1) the effectiveness of laser emission (61 kcal/Einstein) at a wavelength which must be near the 0-0 transition (2) the quenching of valerophenone photoelimination at near the diffusion controlled rate,6 (requiring \( E_T(\text{1d}) < 70 \text{ kcal/mol} \)); and (3) the quenching of biacetyl (\( E_T = 55 - 56 \text{ kcal/mol} \)) phosphorescence at a rate short of the diffusion limit.6 The following Jablonski diagram is consistent with the data for 1d and respects a reasonable \( n, \pi^* \) S - T separation.

\[
\begin{array}{c}
\text{(n,}\pi^*) \text{ S}_1 \quad ? \\
\uparrow \quad \text{REL E (kcal/mol)} \\
\text{60} \pm 1 \\
\text{T}_1(\pi,\pi^*) \quad \text{55} \pm 1 \\
\text{T}_0(n,\pi^*) \quad \text{0}
\end{array}
\]

Importantly, a very low lying triplet (\( E_T < 50 \text{ kcal/mol} \)), either of a planar, "resonance" stabilized 8e variety, as suggested for 4N cyclic hydrocarbon \( \pi \) systems,3 or similar to 1a (\( E_T = 47 \text{ kcal/mol} \)) does not obtain for 1d. However, a \( \pi,\pi^* \) triplet at 60 kcal/mol or less seems likely if 1d be diene-like.7 This raises the possibility of an intrinsically rapid8 intersystem crossing to an unreactive triplet manifold which would account in part for the low isomerization quantum yield and the lack of quenching by a heavy atom solvent (n-PrBr).

Triplet counting experiments did not confirm the efficient formation of a reasonably
long lived triplet. Thus, 1d was no more than 1/10 as efficient in sensitizing the dimerization of 1,3-cyclohexadiene \( (E_T = 51 - 52 \text{ kcal/mol}) \) compared with benzophenone under parallel irradiation conditions. Intersystem crossing remains a possibility however, if the resulting triplet be very short lived or if energy transfer be insufficiently exothermic.\(^6\)

The assignment and location of states for \( \text{Id} \) provide important reference points for the heterocyclic trienes generally. In addition, the indirect photochemical and photophysical methods employed here may be extendable to such systems with somewhat unusual chromophores where detection of luminescence may be impossible.

ACKNOWLEDGEMENT

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REFERENCES


(6) The bimolecular encounter rate is calculated from the Debye equation to be \( 1.8 \times 10^{10} \) (benzene, 30°); for a discussion of diffusion limited quenching constants and the exothermicity necessary in energy transfer, see P.J. Wagner and I. Kochvar, *J. Amer. Chem. Soc.*, 90, 2232 (1968) and ref. cited therein.

