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Preliminary Note

Z–E photoisomerization of 3-methyl-3-penten-2-one. Evidence for non-radiative decay*

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Although the photochemistry of conjugated ketones has been extensively studied, it is remarkable that, as yet, there has been no report on the quantum efficiencies of *cis–trans* isomerization in a simple, aliphatic, α,β-unsaturated ketone [1]. Since the subject of non-radiative decay in conjugated carbonyl derivatives is of considerable current interest [1 - 3], both intrinsically as well as with respect to the photobiological properties of retinal [4], we report herein our results for direct irradiation in solution of 3-methyl-3-penten-2-one (I).

Both the E and Z isomers of I have been previously prepared stereochemically pure [5], and in contrast to 3-penten-2-one [3], are thermally stable in solution at room temperature. The two isomers are readily distinguished by i.r. spectroscopy [6], Z–I having three bands in the carbonyl/olefin region (1690, 1670, 1625 cm^{-1}), while E–I has only two (1670, 1645 cm^{-1}). We have also found n.m.r. useful, E–I having its vinyl proton (6.80 δ) downfield from that (5.84 δ) observed for Z–I, as one would expect [7].

E–I was obtained commercially (Chemical Samples Co.) and purified by vapour phase chromatography (v.p.c.) followed by molecular distillation. Irradiation of a pentane solution, either at 254 or 313 nm, gives rise to a single product detectable by v.p.c.; isolation and spectral analysis of this product verified that it was the Z-isomer. It was readily established that the photoisomerization is reversible (eqn. 1), and v.p.c. analysis of an E/Z mixture after prolonged photolysis at 313 nm demonstrated that all of the starting material could be accounted for by these two isomers:

(1)

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TABLE 1

Quantum efficiencies for photoisomerization of 3-methyl-3-penten-2-one

Starting isomer, M		Φ^a
E		
0.014		0.39
0.032		0.42
0.040		0.42
0.070		0.43
0.070		0.44
0.070		0.44
0.333		0.42[b]
	Av.	0.42 ± 0.02
Z		
0.034		0.40
0.034		0.41
	Av.	0.40_5

[a] In pentane solution, using, except where noted (footnote b), a medium pressure mercury lamp filtered to pass 313 nm irradiation. [b] This value was obtained using a 5 cm cylindrical cell with a flat quartz face; excitation was from a Hanovia high-pressure mercury—xenon arc passed through a Bausch and Lomb monochromator set at 313 nm.

The quantum efficiencies for E–Z isomerization were determined at 313 nm and are presented in Table 1.

All the data were obtained at low conversion (1 to 10%) and are corrected for back reaction. Uranyl oxalate actinometry was used for the E → Z determinations, and the E→Z reaction was then employed as a secondary actinometer for the Z→E measurements. It should be noted that the E→Z quantum efficiency remains effectively constant over a 23-fold change in concentration.

The validity of these data is supported by photostationary state measurements presented in Table 2. The photostationary state is related to the quantum efficiencies by:

TABLE 2

Photostationary state composition for 3-methyl-3-penten-2-one[a]

Initial composition (% Z)		Photostationary state (% Z)
59.7		46.0
49.2		44.5
44.6		44.6
39.3		44.5
	Av.	44.9 ± 0.07

[a] Pentane solution, 313 nm excitation.

$$\frac{[E]_{pss}}{[Z]_{pss}} = \frac{\epsilon_Z \Phi_{Z\rightarrow E}}{\epsilon_E \Phi_{E\rightarrow Z}} \qquad (2)$$

With $\epsilon_Z = 36$ and $\epsilon_E = 29$ at 313 nm, and the quantum efficiencies of Table 1, a photostationary state of 1.21 is predicted. This value is within experimental error of that observed (1.23 ± 0.04).

The significant aspect of these data is that $\Phi_{Z\rightarrow E}$ and $\Phi_{E\rightarrow Z}$ do not sum to unity! A sum of unity would be the consequence of a mechanism for photoisomerization which involved rapid, *complete* formation of a common, twisted intermediate [8], the simplest mechanism usually associated with olefins [8 - 10]. Thus, no matter which of the variety [8] of alternate mechanisms is operative, non-radiative decay (the molecule is non-fluorescent) at least partly competitive with twisting about the double bond, would seem to be a requisite. Similar conclusions have been reached for 3,5-heptadienone [1], and 2-carbomethoxy-2-butene [3]. For these molecules, the excited singlet state has been implicated in the non-sensitized irradiations. Though we cannot, at this time, assign with certainty the multiplicity of the reacting pentenone excited state, we have observed that piperylene (0.53 *M*) cannot quench the reaction. Quenching of the triplet portion of 2-carbomethoxy-2-butene photoisomerization has been shown to be feasible [3] and preliminary sensitization data place the pentenone triplet 10 - 15 kcal higher than that of piperylene. The ability of radiationless decay to compete with rapid twisting about the double bond in these conjugated carbonyl derivatives may be a consequence of enhanced internal conversion caused by the mixing of close-lying n,π^* and π,π^* singlets [3, 11], or of the finite barrier to rotation calculated for the (acrolein) n,π^* and π,π^* singlet and n,π^* triplet states [12]. The former proposal has been invoked recently to explain rapid internal conversion in coumarin [13].

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