## Short Communication

Valence photoisomerization of 1-ethoxycarbonyl-1 H-azepine: excited state energetics and multiplicity

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The general importance of photochemical valence isomerization (I → II) 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 Id → IId. The absorption, photosensitization and quenching data fortuitously combine to provide quantitative information which is normally unavailable in the absence of triene luminescence:

a) X = CH_2
b) X = O
c) X = NR
d) X = NCO_2Et
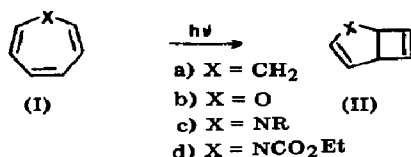
Irradiation of Id in the region of n, π^* absorption [2] gave IId in high yield. Quantum yields for isomerization in solution with and without additives are shown in Table 1. The lack of quenching by diene and cyclo-octatetraene (for which a very low triplet energy has been calculated [3]), along with the lack of sensitization in experiments where sensitizers absorbed >75% of the light, implicate a singlet excited state for valence isomerization of Id.

That a triplet state of Id 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 [Id] gave $k_q \tau = 56 \pm 8$ and $2.3 \pm 0.5 \times 10^5 \ M^{-1}$, respectively. Using triplet lifetimes of valerophenone (8.0×10^{-9} s) [4] and biacetyl (4.6×10^{-4} s) [5], quenching constants are calculated ($k_q = 7.0 \times 10^9$ and $5.2 \times 10^8 \ M^{-1} \ s^{-1}$, respectively).

Photolysis of Id in benzene near its onset of absorption using an argon ion laser (457.9 mm) gave IId with a quantum yield of 0.013 ± 0.004
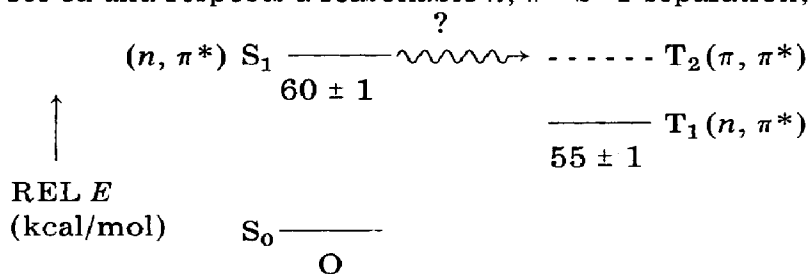
TABLE 1

Quantum yields for photoisomerization Id → IId

[3]	Solvent	Additive (M)	Φ^a
0.08	cyclohexane	- - - -	0.010
0.09	diglyme	- - - -	0.013
0.10	benzene	- - - -	0.013
0.03	n-propyl bromide	- - - -	0.013
0.08	benzene	cyclo-octatetraene (0.11)	0.014
0.10	benzene	diene[b] (0.02 - 0.08)	0.012
0.10	benzene	fluorenone (0.9) (53)[c]	<0.003[d]
0.09	benzene	benzophenone (1.0) (69)[c]	<0.003[d]
0.007	benzene	valerophenone (0.4) (72)[c]	<0.003[d]

[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.

(ferrioxalate actinometry). Luminescence of Id was not observed in benzene at room temperature or in an EPA glass at 77 °K.

The reactivity of S_1 and the unreactivity of T_1 for Id complete an excited state stucture–reactivity pattern already in evidence for Ia [1a, b] and Ib [1e]. The data further allow the relative location of states for Id on the basis of the following: (1) the effectiveness of laser emission (61 kcal/Einstein) at a wavelength which must be near the O–O transition; (2) the quenching of valerophenone photoelimination at near the diffusion controlled rate [6] (requiring E_T (Id) <70 kcal/mol); and (3) the quenching of biacetyl (E_T = 55 - 56 kcal/mol) phosphorescence at a rate short of the diffusion limit [6]. The following Jablonski diagram is consistent with the data for Id and respects a reasonable n, π^* S–T separation;

$$(n, \pi^*)\ S_1 \overset{?}{\underset{60 \pm 1}{\text{———}\rightsquigarrow}} \cdots \cdots T_2(\pi, \pi^*)$$

$$\underset{55 \pm 1}{\text{———}}\ T_1(n, \pi^*)$$

REL E
(kcal/mol) S_0 ———
                    O

Importantly, a very low lying triplet (E_T <50 kcal/mol), either of a planar, "resonance" stabilized $8e$ variety, as suggested for $4N$ cyclic hydrocarbon pi systems [3] or similar to Ia (E_T = 47 kcal/mol [1b] does not obtain for Id. However, a π, π^* triplet at 60 kcal/mol or less seems likely if Id be diene-like [7]. This raises the possibility of an intrinsically rapid [8] 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, Id was no more than 1/10 as efficient in sensitizing the dimerization of 1,3-cyclohexadiene (E_T = 51 - 52 kcal/mol [7]) 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 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.

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