12

OFFICE OF NAVAL RESEARCH

Contract N00014-67-A-0280-0003

Sponsored by the
Advanced Research Projects Agency
ARPA Order No. 2721

TECHNICAL REPORT NO. 4

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

by

G. Jones, II and L.J. Turbini

Prepared for publication
in the
Journal of Photochemistry

Department of Chemistry
Boston University
Boston, Massachusetts 02215

December 1, 1976

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Porjects Agency of the U.S. Government.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE ⑨		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 4, 1 Jul 74 –	2. GOVT ACCESSION NO. 31 May 75,	3. RECIPIENT'S CATALOG NUMBER
4. ~~TITLE (and Subtitle)~~ ⑥ Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine: Excited State Energetics and Multiplicity.		5. TYPE OF REPORT & PERIOD COVERED Technical, 7/1/74-5/31/75
		6. PERFORMING ORG. REPORT NUMBER
7. ~~AUTHOR(s)~~ ⑩ Guilford/Jones, II and Laura J./Turbini		8. ~~CONTRACT OR GRANT NUMBER(s)~~ ⑮ N00014-67-A0280-0003, W ARPA Order-2721
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Boston University Boston, Massachusetts 02215		10. ~~PROGRAM ELEMENT, PROJECT, TASK~~ AREA & WORK UNIT NUMBERS ARPA Order No. 2721/1-4-74 Program Code No. 4F10
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	DODAAD Code N00014	12. REPORT DATE December 1, 1976
		13. NUMBER OF PAGES 4
14. ~~MONITORING AGENCY NAME &~~ ADDRESS (if different from Controlling Office) ⑪ 1 Dec 76 ⑫ 6p.		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of Photochemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Valence photoisomerization, excited state configuration and multiplicity, photochemistry or heterocycles.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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 luminescence, but excited state energies can be estimated from absorption and sensitization data (S_1 = 60 kcal/mol, T_1 = 55 kcal/mol).

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

401003

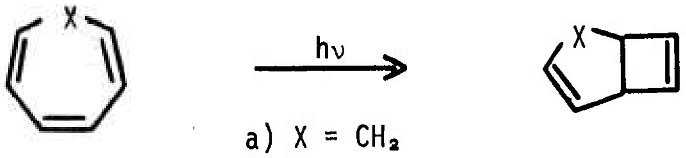
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

4/B

VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE.
EXCITED STATE ENERGETICS AND MULTIPLICITY.

Guilford Jones, II* and Laura J. Turbini
Department of Chemistry, Boston University
Boston, Massachusetts 02215

The general importance of photochemical valence isomerization **1** → **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** → **2d**. 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

1 **2**

Irradiation of **1d** in the region of n,π* absorption[2] gave **2d** in high yield. Quantum yields for isomerization in solution with and without additives are

Table. Quantum Yields for Photoisomerization **1d** → **2d**.

[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	cyclooctatatraene (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.

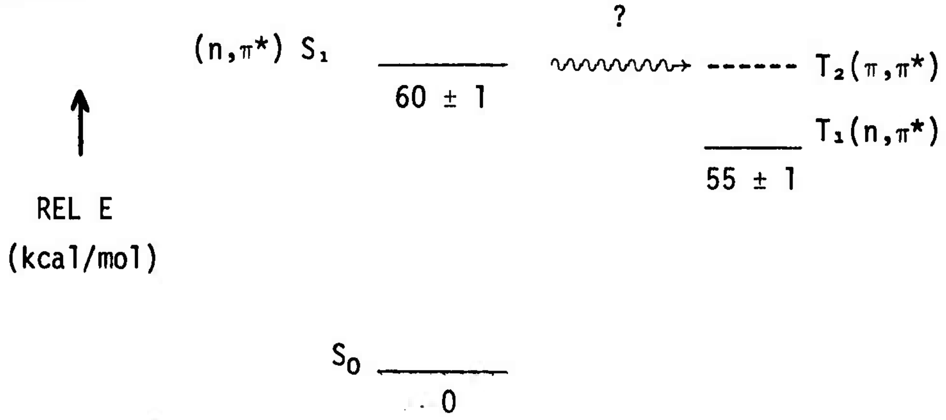
---

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 **1d**.

That a triplet state of **1d** 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 [**1d**] gave $k_q\tau = 56 \pm 8$ and $2.5 \pm 0.3 \times 10^5$ M^{-1}, respectively. Using triplet lifetimes of valerophenone (8.0×10^{-9} sec)[4] and biacetyl (4.6×10^{-4} sec)[5], quenching constants are calculated ($k_q = 7.0 \times 10^9$ and 5.3×10^8 $M^{-1}sec^{-1}$, respectively).

Photolysis of **1d** 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 S_1 and the unreactivity of T_1 for **1d** complete an excited state structure - reactivity pattern already in evidence for **1a**[1a,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 (**1d**) <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 **1d** and respects a reasonable n, π* S - T separation.



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 **1a** (E_T = 47 kcal/mol[1b]) does not obtain for **1d**. However, a π,π* triplet at 60 kcal/mol or less seems likely if **1d** 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, **1d** 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 **1d** 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

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR.

REFERENCES

(1) (a) L.B. Jones and V.K. Jones, *Forstschritte der Chem. Forschung*, **13**, 307 (1969); (b) R. Srinivasan, *Adv. in Photochem.*, **4**, 113 (1966); (c) L.A. Paquette in "Nonbenzenoid Aromatics," vol. 1, J.P. Snyder, Ed., Academic Press, N.Y., p. 249 (d) L.A. Paquette and J.H. Barrett, *J. Amer. Chem. Soc.*, **88**, 1718 (1966); (e) J.M. Holouka and P.D. Gardner, *ibid.*, **89**, 6390 (1967).

(2) L.A. Paquette, D.E. Kuhla, J.H. Barrett, and R.J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).

(3) N.C. Baird, *J. Amer. Chem. Soc.*, **94**, 4941 (1972).

(4) P.J. Wagner and A.E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7495 (1972).

(5) N.J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

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

(7) R.E. Kellogg and W.T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

(8) M.A. El-Sayed, *Accounts Chem. Res.*, **4**, 23 (1971).

(9) For details concerning triplet counting (nmr method), see S.G. Cohen, G.A. Davis, and W.D.K. Clark, *J. Amer. Chem. Soc.*, **94**, 869 (1972).