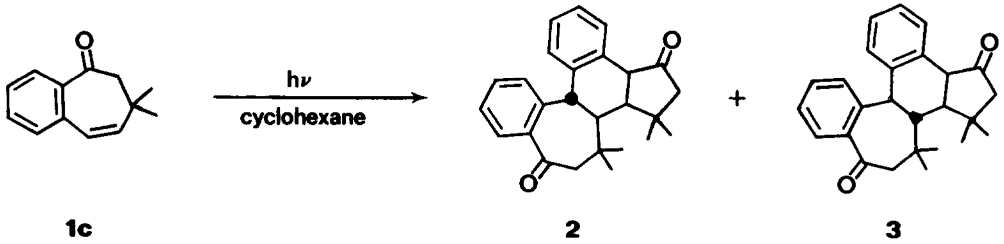
Tetrahedron Letters No. 40, pp 3447 - 3450, 1975. Pergamon Press. Printed in Great Britain.

TRAPPING OF A TRANS INTERMEDIATE IN THE PHOTODIMERIZATION OF A BENZO-2,4-CYCLOHEPTADIENONE

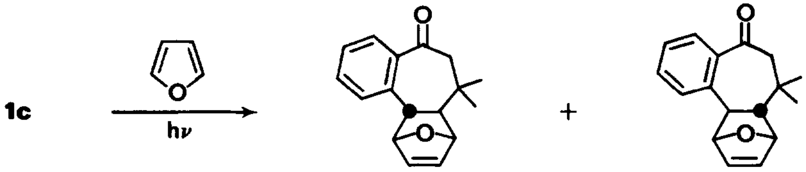
Harold Hart* and Mikio Suzuki
Department of Chemistry, Michigan State University
East Lansing, Michigan 48824, U.S.A.

(Received in USA 7 July 1975; received in UK for publication 28 August 1975)

Irradiation of 1c in cyclohexane gave two unusual photodimers, 2 and 3.[1] Despite the presence of four different chiral centers in the products, only the two stereoisomers shown were formed. Each product has a trans juncture between the six- and seven-membered rings. This suggested two possible mechanisms, the first step of which is either a photochemical $_{\pi}4s + {}_{\pi}2a$ cycloaddition, or the isomerization of 1c to a trans intermediate[2,3] which then undergoes a thermal $_{\pi}4s + {}_{\pi}2s$ cycloaddition; the 4π partner in either case is the styrene moiety in 1c (vide infra). We describe here a trapping experiment which supports the latter view.



Irradiation of a solution of 1c in furan (0.061M, Hanovia 450W lamp, Pyrex, 2 hr) gave no 2 or 3; instead, two crystalline furan adducts were isolated to which we assign structures 4 and 5.[4,5] The trans geometry of both adducts was apparent from their nmr spectra.[6] In

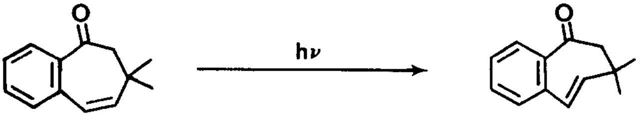


4 (52%)
mp 160-161°

5 (20%)
mp 171-172°

particular, the fact that in each isomer only one of the two ring juncture protons was coupled to an adjacent bridgehead proton (J_{ac} = 4 Hz in **4**, 0 Hz in **5**; J_{bd} = 0 Hz in **4**, 4 Hz in **5**)[6] showed that each adduct had only one exo proton.[3b,7] The fact that exo protons are deshielded relative to endo protons in these systems[3b,7a] allowed us to distinguish **4** from **5** [δH_a = 3.42 in **4** (exo), 2.78 in **5** (endo); δH_b = 2.08 in **5** (exo), 1.23 in **4** (endo)].[6] Finally, if the ring juncture protons in either adduct had been cis, the coupling constant J_{ab} would have been larger than was observed.[3b,8]

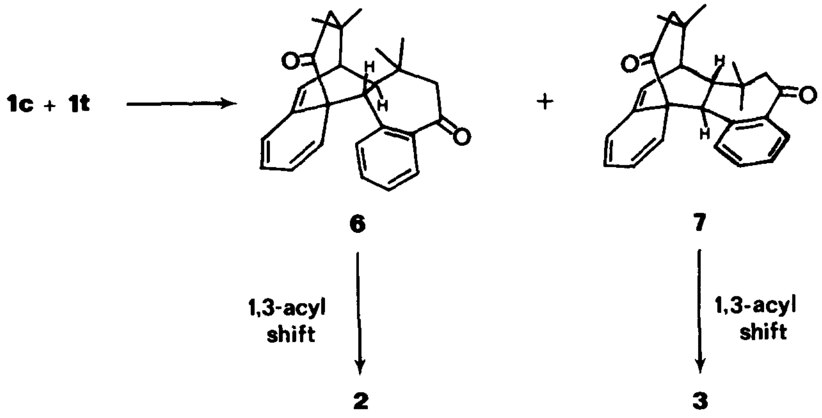
The different behavior of **1c** on irradiation in cyclohexane or in furan can be accounted for if the photoreaction in each case is the isomerization of **1c** to **1t**.[9] In furan, **1t** is



1c

1t

trapped by cycloaddition to give **4** and **5**, but in an inert solvent, **1t** is sufficiently reactive to add to the styrene moiety in **1c**. The resulting cycloadducts **6** and **7** then undergo a



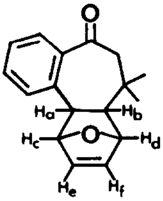
1,3-suprafacial acyl shift to re-aromatize, giving 2 and 3 respectively. In the following paper we present further evidence that cycloadducts such as 6 and 7 are formed in these photodimerizations.

Acknowledgement. We are indebted to the National Institutes of Health (GM-15997) for financial support.

References and Notes

1. H. Hart, T. Miyashi, D.N. Buchanan and S. Sasson, J. Am. Chem. Soc., 96, 4857 (1974).
2. For reviews on seven- and eight-membered ring ketones with a trans carbon-carbon double bond, see P.E. Eaton, Accounts Chem. Res., 1, 50 (1968); O.L. Chapman and D.S. Weiss, Organic Photochemistry, Marcel Dekker, Inc., New York, 3, 215 (1973); G. Köbrich, Angew. Chem., Int. Ed. Engl., 12, 464 (1973); G.L. Buchanan, Chem. Soc. Rev., 3, 41 (1974).
3. For papers on trans-cycloheptenones, see (a) E.J. Corey, M. Tada, R. LeMahieu and L. Libit J. Am. Chem. Soc., 87, 2051 (1965); (b) P.E. Eaton and K. Lin, ibid., 87, 2052 (1965); (c) H. Nozaki, M. Kurita and R. Noyori, Tetrahedron Lett., 2025 (1968); (d) H. Nozaki and M. Kurita, ibid., 3635 (1968).
4. All new compounds gave correct elemental analyses. All yields are of pure, isolated products.

5. Separated by column chromatography (silica gel 60, EM reagent, >230 mesh, CH_2Cl_2 eluent) in the sequence shown, and recrystallized from hexane.
6. A complete assignment of all methine protons was possible from 100 MHz spectra and europium shifted spectra. Chemical shifts, coupling constants (checked by decoupling) and dihedral angles as measured from models, are shown in the table.



	δ(ppm)			J,Hz		dihedral angle, °	
	4	**5**		**4**	**5**	**4**	**5**
H_a	3.42	2.78	ab	6	6	150	150
H_b	1.23	2.08	ac	4	0	55	100
H_c	5.43	5.43	bd	0	4	90	55
H_d	4.67	4.85	ce	1.5	2	20-30	15-20
H_e	6.20	6.53	df	2.0	1.5	20-30	15-20
H_f	6.35	6.27					

7. (a) F.A.L. Anet, Tetrahedron Lett., **25**, 1219 (1962); (b) R.R. Fraser, Can. J. Chem., **40**, 78 (1962).
8. P. Laszlo and P. von R. Schleyer, J. Am. Chem. Soc., **86**, 1171 (1964).
9. We cannot at present distinguish between a ground state **1t** and an excited state of **1c** which is twisted at the double bond so that it reacts as if it were a trans cycloalkene. Low temperature (-78°) irradiation of **1c** in ether followed by addition of furan when the light was removed failed to give **4** or **5** but we regard this result as indecisive. Irradiation of **1c** in methanol also gave **2** and **3**, so we feel that solvent polarity is not a major factor, and that the intermediates in cyclohexane and furan are probably identical.