

PRIMARY AND SECONDARY PHOTOCHEMISTRY OF α -TROPOLONE METHYL ETHER

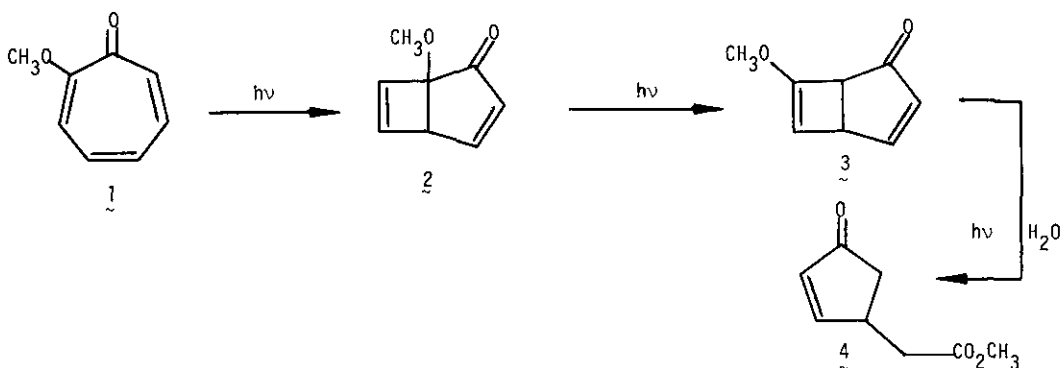
Dedicated to Professor T. Nozoe who did so much for the chemistry of troponeid compounds on the occasion of his 77th birthday.

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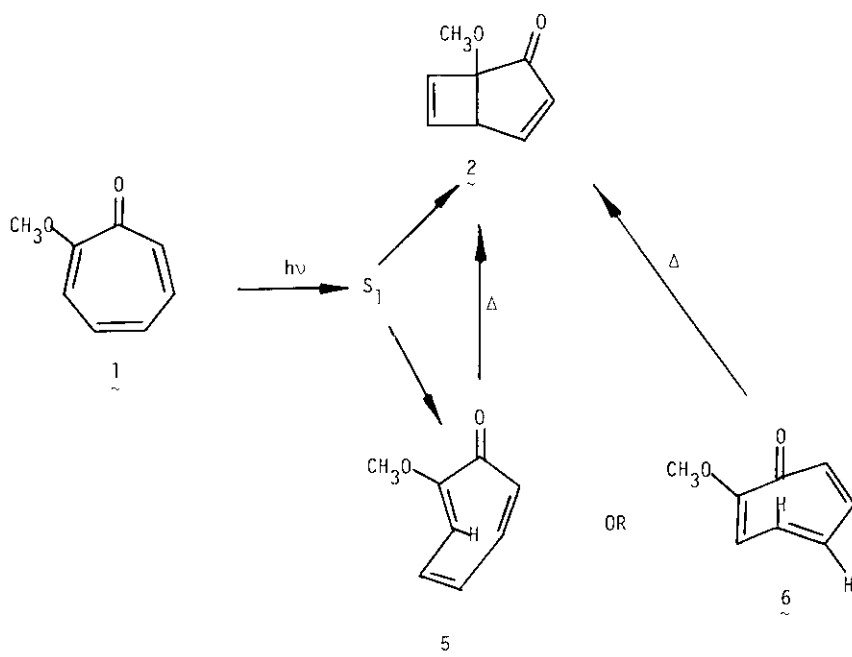
Abstract The photoisomerization of α -tropolone methyl ether to 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one proceeds via the S_1 state. Irradiation of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one gives 6-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one and 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one. The 6-methoxy product is formed via α -cleavage in the T_1 state. The 7-methoxy product is formed in a process involving a deep-seated skeletal rearrangement. The first step in this rearrangement involves formation of *cis,cis*-2-methoxybicyclo[2.1.0]pent-2-en-5-yl ketene from the S_1 state of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one. The ketene intermediate is converted to 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one by a facile Cope rearrangement which proceeds rapidly above 233K.

Irradiation of α -tropolone methyl ether (1) in aqueous solution has been shown to give in sequence 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (2), 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (3), and methyl 4-oxo-2-cyclopentenylacetate (4).¹ It is the details of these three photochemical

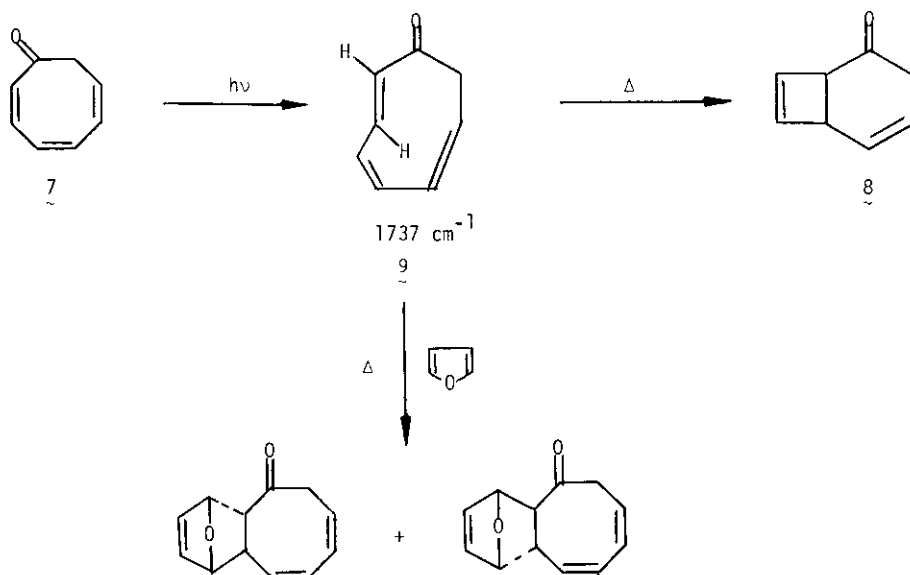


processes which form the content of the present manuscript.

Irradiation (290 ± 15 nm) of α -tropolone methyl ether (0.01-0.10 M) in *t*-butyl alcohol gives 2 with a quantum yield of 0.051 (< 2% conversion). The reaction is not quenched by di-*tert*-butyl nitroxide at concentrations up to 0.5 M. Attempts to photosensitize the reaction using 254 nm light and either acetophenone (E_T 74 kcal/mole, k_{ic} 10^{11} sec⁻¹) or benzophenone (E_T 69 kcal/mole, k_{ic} 10^{10} sec⁻¹) were unsuccessful. The triplet energy of α -tropolone methyl ether is ~ 49 kcal/mole in EPA.² The negative quenching and sensitization data suggest that the formation of 2 involves orbital symmetry allowed bridging in the S_1 state of α -tropolone methyl ether or *cis-trans* isomerization of one of two double bonds (5 and 6) followed by orbital symmetry allowed thermal closure. The photoisomerization of 2,4,6-cyclooctatrien-1-one (7) to 8 proceeds via a



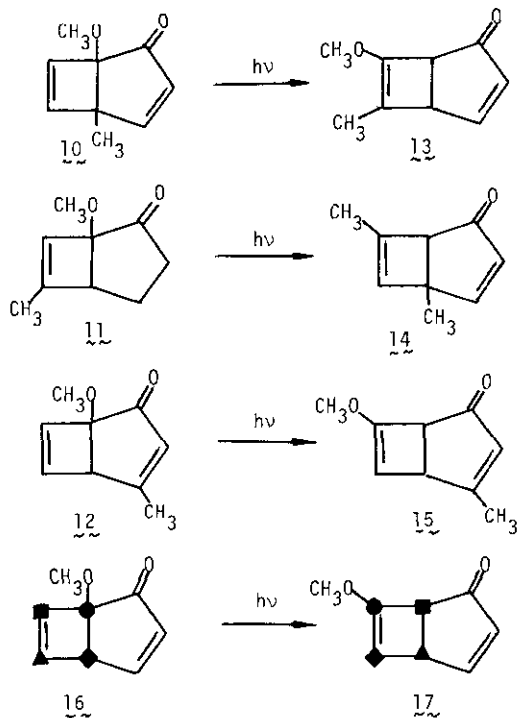
highly strained trans-double bond intermediate (9).³ A process involving a tropolone ring with a



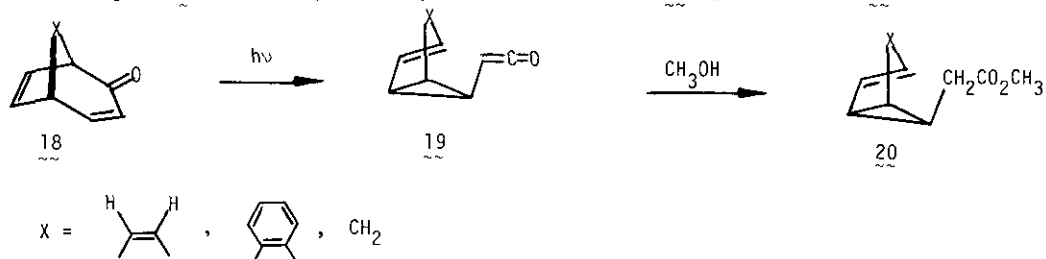
trans-double bond thus must be seriously considered. The photoisomerization of α -tropolone methyl ether unfortunately does not occur at low temperatures, and the methods used to observe 9 are therefore not applicable.

The photochemical transformation of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (2) to 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (3) involves a fascinating rearrangement. When alkyl derivatives of 2 (10-12) are irradiated, a deep-seated skeletal rearrangement is disclosed.^{3,4} It is clear from the product structures (13-15) that the bridgehead carbons exchange places with the

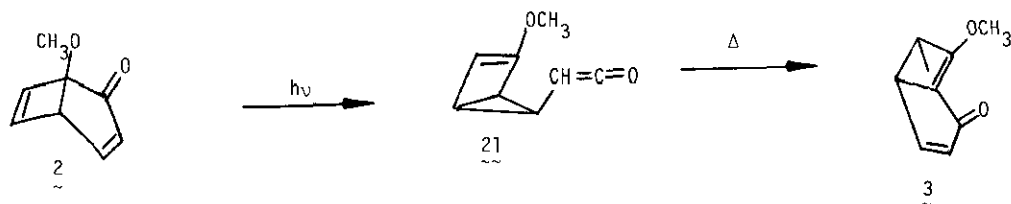
cyclobutene olefin carbons. This transformation is shown schematically as 16 \rightarrow 17. Irradiation of 2 at 77K reveals initial formation of an intermediate which has infrared bands characteristic



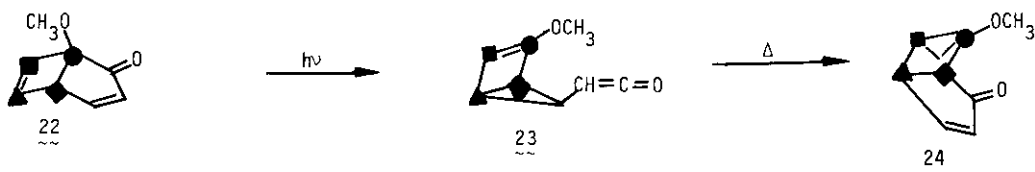
of a ketene (2118 cm^{-1}) and an enol ether double bond ($1620, 825\text{ cm}^{-1}$).⁶ Warming the intermediate above 233K, gives 3. A variety of bridged bicyclic ketones (18) give ketenes (19) by the same



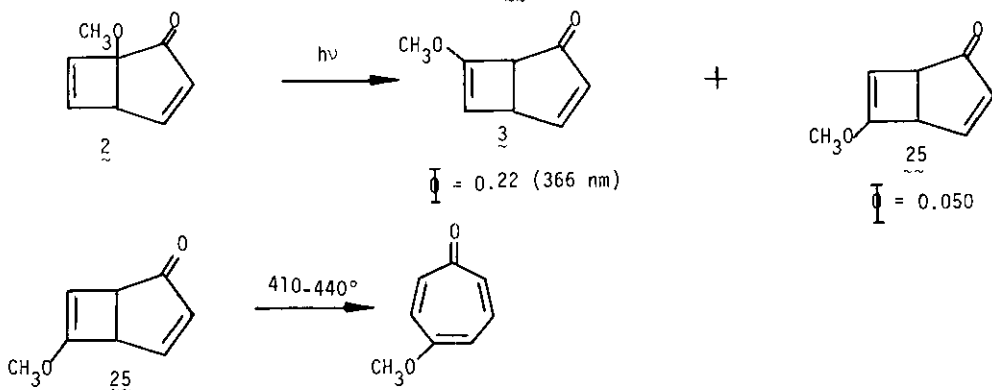
process.^{6,7} These ketenes are kinetically more stable than the ketene derived from 2, and can be characterized by nmr spectroscopy and trapping as the esters (20).⁶ It is thus reasonable to assign structure 21 to the ketene derived from 2. Compound 21 is a *cis*-divinylcyclopropane, a bicyclo[2.1.0]pentene, an enol ether, and a ketene. The facile Cope rearrangement which transforms



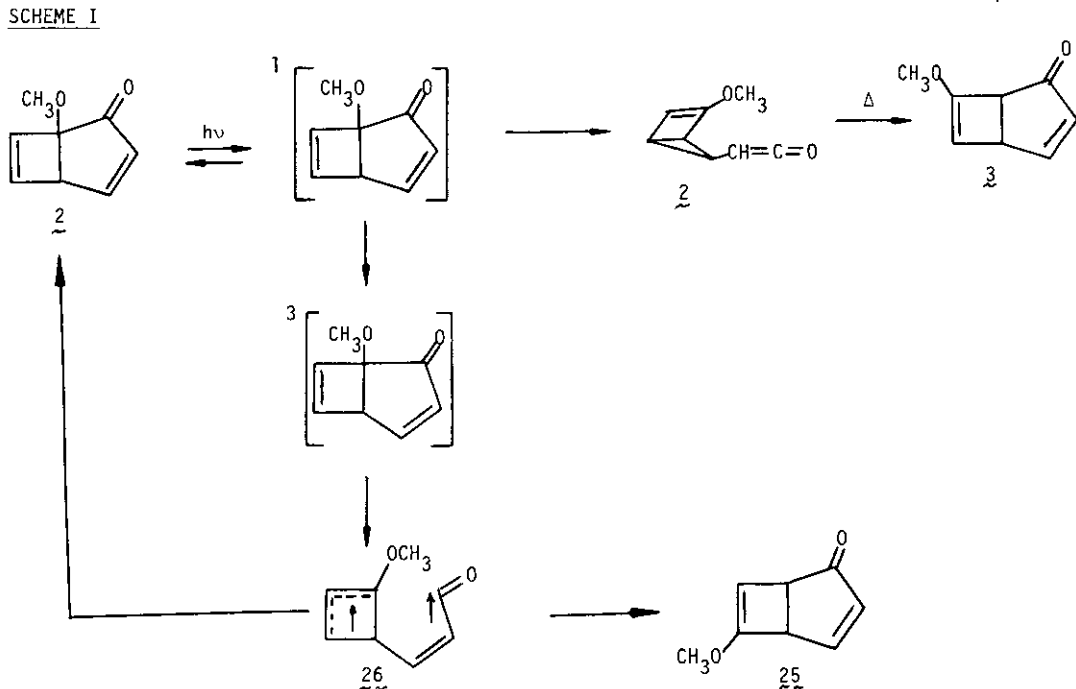
it to 3 is not surprising. This Cope rearrangement also accounts for the skeletal rearrangement (22-24).



A second product is formed in the irradiation of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (2). This product has been identified by spectroscopy⁸ and pyrolysis to γ -tropolone methyl ether as 6-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (25). A variety of photosensitizers (acetophenone,

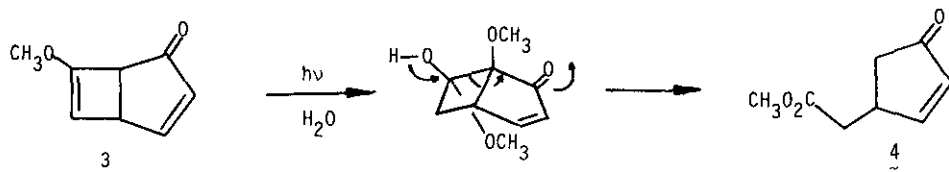


benzophenone, thioxanthone, and Michler's ketone) gave increased yields of 25 and di-*tert*-butyl nitroxide quenched formation of 25 (slope = 3.59) but not formation of 3. These results are consistent with the mechanism shown in Scheme I. The ketene (21) is derived from the S_1 state



of 2. Formation of 21 competes with intersystem crossing to the T_1 state of 2 which cleaves to the triplet biradical 26. This biradical can give 2 or 25.

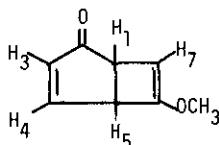
The final stage in the conversion of 1 to 4 involves a photochemical hydration of a double bond in 3. The details of this process are not known.



Acknowledgment. This research was supported by grant CHE 75-10939 from the National Science Foundation.

Notes and References

1. W.G. Dauben, K. Koch, S.L. Smith, and O.L. Chapman, *J. Am. Chem. Soc.*, 1963, 85, 2616; *ibid.*, 1961, 83, 1768.
2. R. Croteau and R.M. Leblanc, *Photochem. and Photobiol.*, 1978, 28, 33.
3. O.L. Chapman, L.L. Barber, and J.D. Lassila, *J. Am. Chem. Soc.*, 1968, 90, 2449.
4. S.L. Smith, Ph.D. Thesis, Iowa State University, Ames, Iowa.
5. O.L. Chapman and J.D. Lassila, *J. Am. Chem. Soc.*, 1968, 90, 2449
6. O.L. Chapman, M. Kane, J.D. Lassila, R. Loeschen, and H.E. Wright, *J. Am. Chem. Soc.*, 1969, 91, 6856.
7. A.S. Kende, Z. Goldschmidt, and P.T. Izzo, *J. Am. Chem. Soc.*, 1969, 91, 6858; J. Ciabattoni, J.E. Crowley, and A.S. Kende, *ibid.*, 1969, 89, 2778.
8. Compound 25 shows $\nu_{C=O}$ 1705, $\nu_{C=C}$ 1635 (enol ether) cm^{-1} ; parent ion m/e 136 (40% of base peak); H_1 3.04 δ (sextet, $J_{13} = 1.2$ Hz, $J_{17} = 1.2$ Hz, $J_{15} = 2.8$ Hz), H_3 6.11 δ (octet, $J_{34} = 6$ Hz, $J_{13} = 1.2$ Hz, $J_{35} = 0.5$ Hz), H_4 7.63 δ (octet, $J_{34} = 6$ Hz, $J_{47} = 0.4$ Hz, $J_{45} = 2.8$ Hz), H_5 3.97 δ (sextet, $J_{45} = 2.8$ Hz, $J_{15} = 2.8$ Hz, $J_{35} = 0.5$ Hz), H_7 4.82 δ (broad doublet, J_{47}



= 0.4 Hz, $J_{17} = 1.2$ Hz), OCH_3 3.63 δ (singlet, 3H).

Received, 16th January, 1979