PRIMARY AND SECONDARY PHOTOCHEMISTRY OF α-TROPOLONE METHYL ETHER

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

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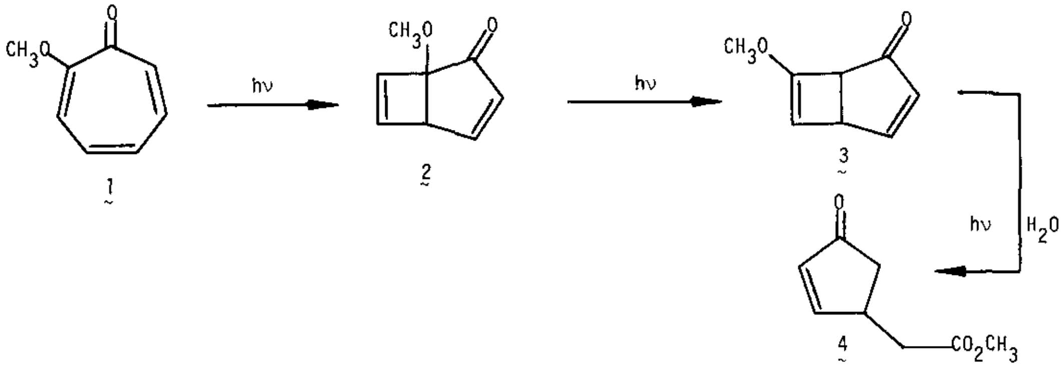
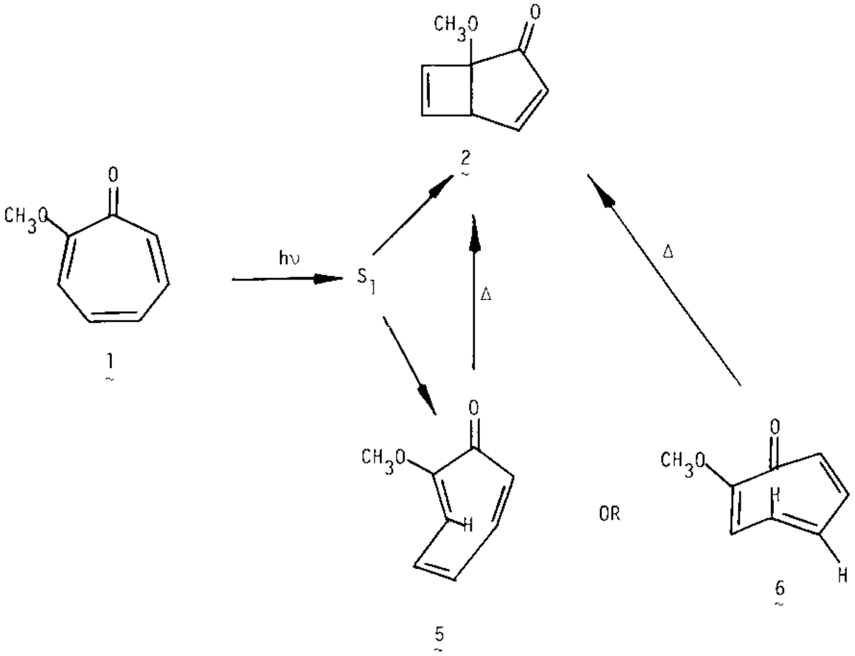
Abstract The photoisomerization of α-tropolone methyl ether to 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one proceeds *via* the S_1 state. Irradiation of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one gives 6-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one and 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one. The 6-methoxy 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-methoxybicylo[3.2.0]hepta-3,6-dien-2-one by a facile Cope rearrangement which proceeds rapidly above 233K.

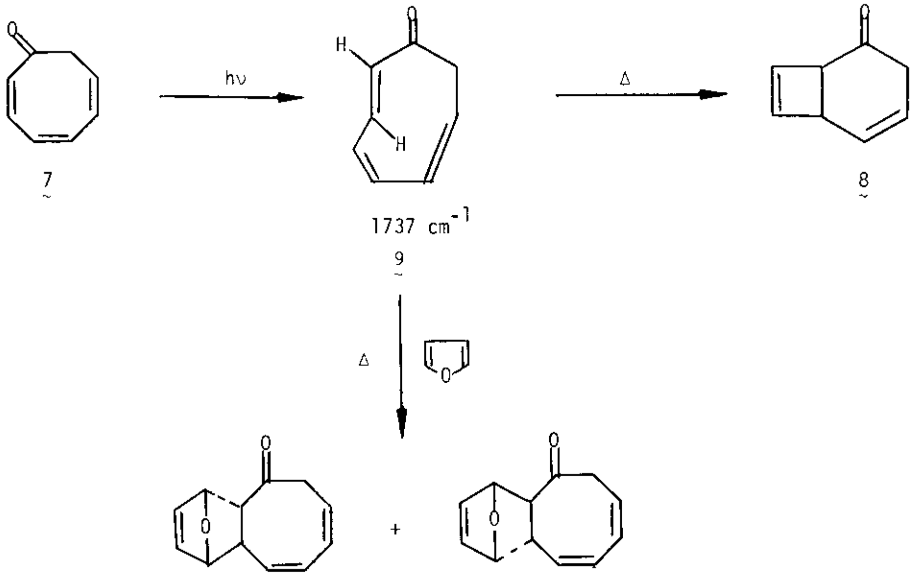
Irradiation of α-tropolone methyl ether (**1**) in aqueous solution has been shown to give in sequence 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**2**), 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**3**), and methyl 4-oxo-2-cyclopentenylacetate (**4**).[1] It is the details of these three photochemical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



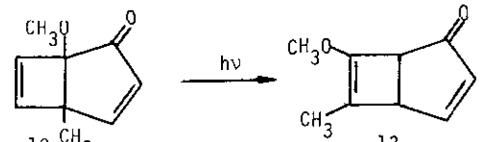
Irradiation (290 ± 15 nm) of α-tropolone methyl ether (0.01-0.10 M) in *t*-butyl alcohol gives **2** with a quantum yield of 0.051 (< 2% conversion). The reaction is not quenched by di-*tert*-butyl nitroxide at concentrations up to 0.5 M. Attempts to photosensitize the reaction using 254 nm light and 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 $\sim$ 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 ⟶ 17. Irradiation of 2 at 77K reveals initial formation of an intermediate which has infrared bands characteristic



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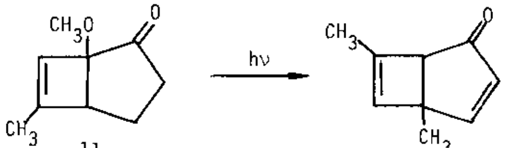

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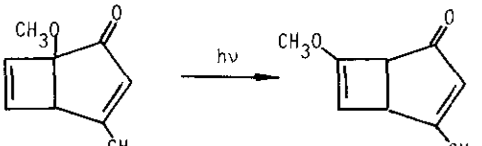

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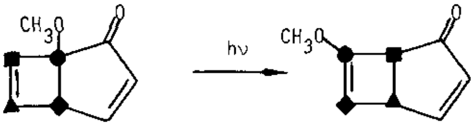
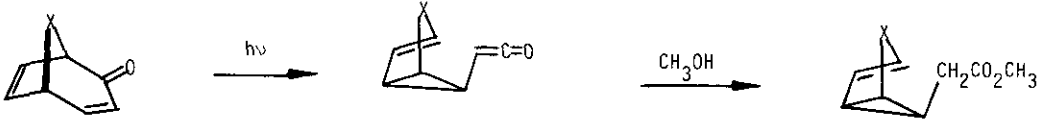
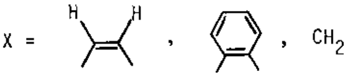


16 17

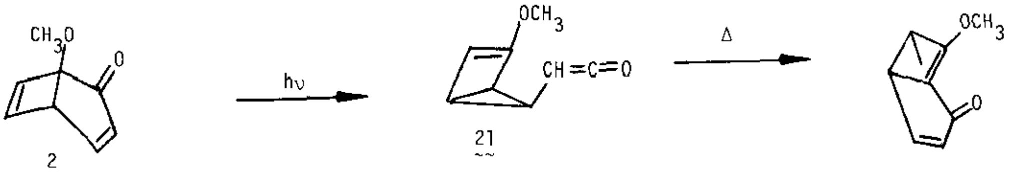
of a ketene (2118 cm^{-1}) and an enol ether double bond (1620, 825 cm^{-1}).[6] Warming the intermediate above 233K, gives 3. A variety of bridged bicyclic ketones (18) give ketenes (19) by the same



18 19 20

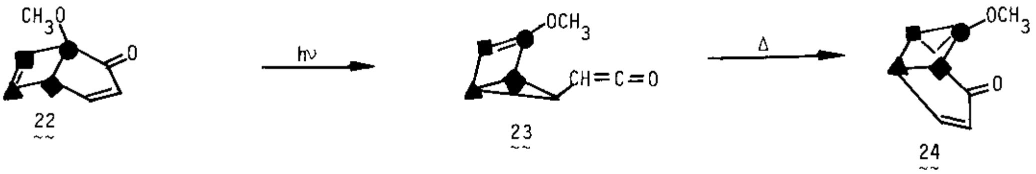


process.[6,7] These ketenes are kinetically more stable than the ketene derived from 2, and can be characterized by nmr spectroscopy and trapping as the esters (20).[6] It is thus reasonable to assign structure 21 to the ketene derived from 2. Compound 21 is a cis-divinylcyclopropane, a bicyclo[2.1.0]pentene,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

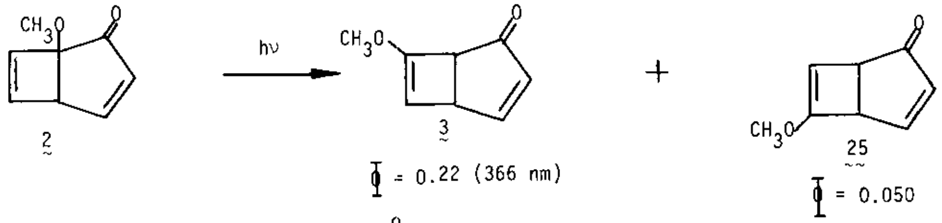


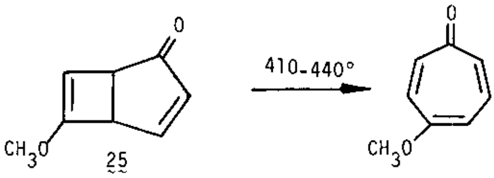
2 21 3

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

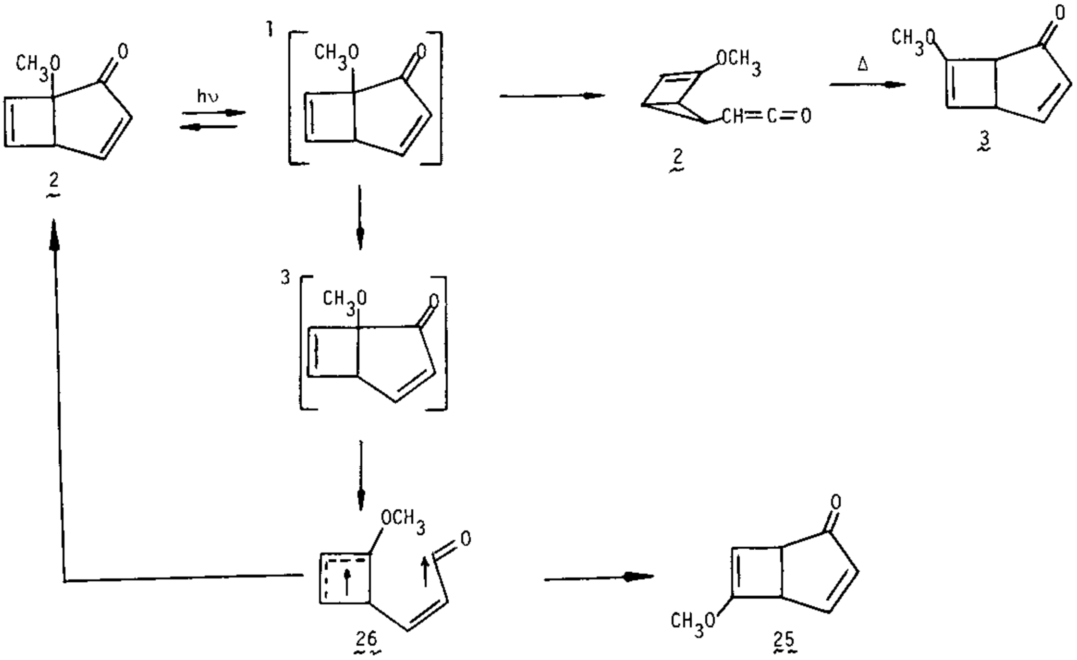


A second product is formed in the irradiation of 1-methoxybicylo[3.2.0]hepta-3,6-dien-2-one (2). This product has been identified by spectroscopy[8] and pyrolysis to γ-tropolone methyl ether as 6-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (25). A variety of photosensitizers (acetophonone, benzophenone, 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



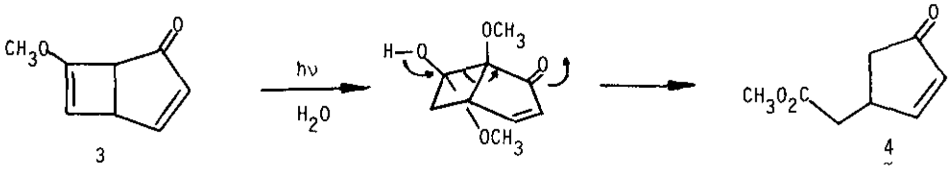


SCHEME I



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.



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Notes and References

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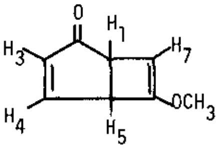
8. Compound 25 shows ν_{CO} 1705, $\nu_{C=C}$ 1635 (enol ether) cm^{-1}; parent ion m/e 136 (40% of base peak); H_1 3.04 δ (sextet, J_{13} = 1.2 Hz, J_{17} = 1.2 Hz, J_{15} = 2.8 Hz), H_3 6.11 δ (octet, J_{34} = 6 Hz, J_{13} = 1.2 Hz, J_{35} = 0.5 Hz), H_4 7.63 δ (octet, J_{34} = 6 Hz, J_{47} = 0.4 Hz, 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).

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