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THE PHOTOINTERCONVERSION OF CYCLOHEPTATRIENES AND BICYCLO(3,2,0)HEPTA-2,6-DIENES: THE ROLE OF SINGLET AND TRIPLET STATES AND THE POSSIBLE INTERMEDIACY OF CIS, TRANS, CIS-CYCLOHEPTATRIENES.

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The light induced rearrangements of the bicyclo(3,2,0)hepta-2,6-dienes 1 and 2 to the same quadricyclene derivative 3 have been reported.[1] These are the only recorded photoreactions of this di-π-methane system[2] despite the numerous examples of its production by the photochemical isomerisation of cycloheptatrienes.[3-5] This latter reaction is generally directionally specific, only one of the two possible dienes being formed from cycloheptatrienes in which 1,4- and 3,6-ring closures are not equivalent. Semi-empirical rules based on the electronic nature of the substituents have been put forward for predicting the direction in which ring closure can occur.[4] In this communication we report experiments which concern both the apparent general absence of photoreactivity of the bicyclic dienes and the ring closure mechanisms available to the cycloheptatrienes.

The cycloheptatriene 4 can be prepared as a minor product of the thermal decomposition of ethyl diazoacetate in anisole.[6] Treatment of 4 with methanolic HCl gives clean conversion to 6. The structures of 4 and 6 follow from spectral data.[6]

Irradiation1) of a 0.005M nitrogen purged benzene solution of 4 in pyrex resulted in clean total conversion after 1.5 hours to 7 (65%) and 8 (35%). Similar treatment of 6 gave clean total conversion to 8 after 2 hours. The structures of these products follow from spectral data.[6] The formation of 8 from 4 presumably involves two

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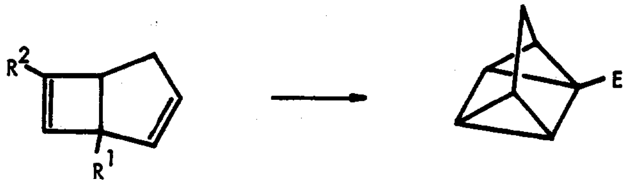
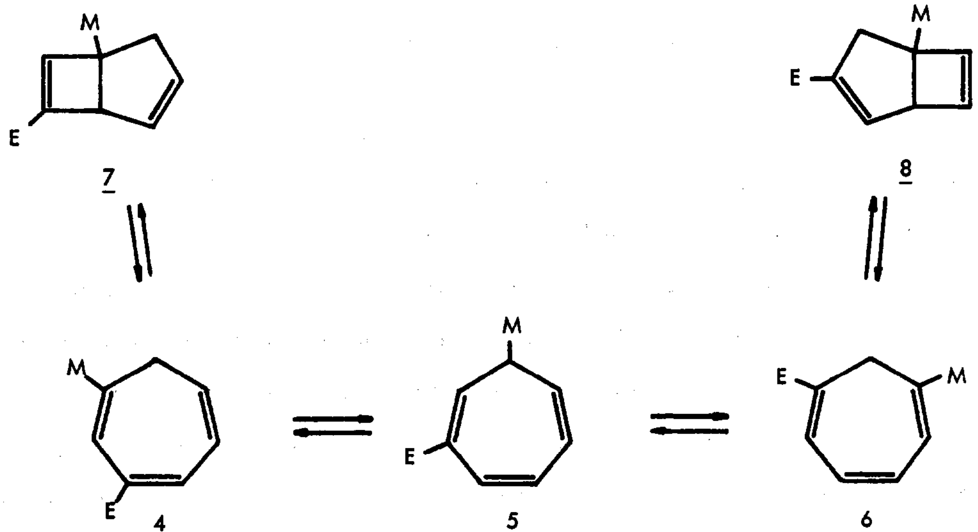
1) 100w medium pressure mercury arc.



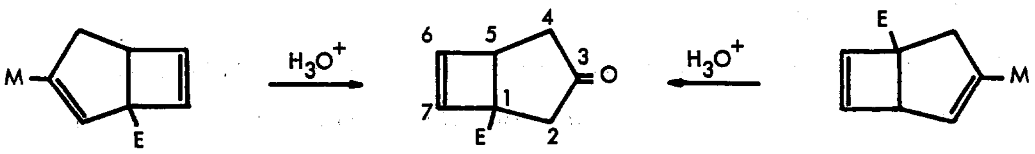
$\underline{1}$ R^1=E; R^2=H

$\underline{2}$ R^1=H; R^2=E

$\underline{3}$



$\underline{7}$ $\underline{8}$ $\underline{4}$ $\underline{5}$ $\underline{6}$



$\underline{9}$ $\underline{11}$ $\underline{10}$

M = MeO-; E = EtO_2C-

1,7-hydrogen shifts to give 6 via the intermediacy of 5 followed by ring closure. Clearly ring closure is totally specific in each case. In 6 the substituents have the same directive effect and 8 would be the predicted product;[4] the effect of the methoxy function is dominant in 4.

On further irradiation of the photoproducts 7 and 8 slow but clean and complete conversion (75-90 hours) to an approximately 1:1 mixture of 9 and 10, the alternative ring closure products of 4 and 6 respectively, took place in each case. The instability of 9 and 10 with respect to hydrolysis and their identical g.l.c. behaviour made resolution of the mixture impossible. The structures of the components follow from the n.m.r. spectrum of the total photoproduct [τ (CCl_4); 3.63 (d; 3Hz) and 3.93 (d; 3Hz), 3.67 (d; 3Hz) and 3.87 (d; 3Hz), 2 cyclobutene olefinic AB systems;[2] 5.38 (t; ~1.5Hz) and 5.51 (q; ~ 2Hz), 2 enol ether β-olefinic protons; 6.45 (s) and 6.47 (s), 2 enol ether methoxy groups] and the virtually quantitative hydrolysis of this mixture to a single product, the ketone 11. The structure of the latter follows from the following data: ν_{max} ($CHCl_3$): 1749 (5-ring ketone) and 1723 (CO_2Et). τ ($CDCl_3$): 3.77 (d; 3Hz) and 3.83 (d; 3Hz), C(6) and C(7) AB;[2] 6.44 (d; 9Hz), 7.45 (q; 17 and 9Hz) and 7.78 (d; 17Hz), C(4) and C(5) ABX;[2] 7.08 (d; 18Hz) and 7.59 (d; 18Hz), C(2) AB; 5.82 (q; 7Hz) and 8.72 (t; 7Hz), CO_2Et.

These results show that the bicyclic dienes 7 and 8 are able to open photochemically to the corresponding cycloheptatrienes 4 and 6 which then interconvert via 1,7-hydrogen shifts. This reversibility of ring closure provides a ready explanation of the apparent general lack of photoreactivity of bicyclo(3,2,0)hepta-2,6-dienes; the ring opening reaction will in many instances be a "hidden" process due to the position of the photostationary state. In the present case the enol ethers 9 and 10 accumulate in the photomixture due to their inability to compete in pyrex for the available light.[3]

In order to obtain information concerning the mechanism of formation of 7,8,9 and 10 a series of sealed pyrex ampoules containing degassed and non-degassed 0.007M benzene solutions of 4 and 6 were irradiated on a conventional "merry-go-round" apparatus and the reactions monitored by n.m.r. and g.l.c. A typical set of product compositions after 95 hours is shown in the table over.

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[2] In such systems the ring junction protons do not couple with the cyclobutene olefinic protons.[7]

[3] On irradiation in quartz 9 and 10 rapidly polymerise.

Expt.	Starting Material	Products (%)[4] 7	8	9	10
	degassed				
1	4	14	18	18	50
2	6	14	22	6	58
	non-degassed				
3	4	35	65	0	0
4	6	23	77	0	0

The complete absence of the enol ethers 9 and 10 on irradiation in the presence of oxygen indicates strongly that they arise via triplet excited states.[5] The singlet reactions (experiments 3 and 4) lead to the establishment of a photostationary state between 7,4,5,6 and 8 which strongly favours 7 and 8. In the absence of oxygen chemical reaction of triplet states takes place leading to 9 and 10.

It is reasonable to assume that the triplet states from which 9 and 10 arise are those of either (a) the cycloheptatrienes 4 and 6 or (b) the bicyclic dienes 7 and 8.[6]

(a) Cycloheptatriene exists in the ground state as a pair of interconverting "boat-like" conformers.[8] In the first excited state the barriers to rotation about the central and terminal bonds of the π-system will be lowered; SCF-CI calculations by Simmons[9] indicate that in all cis hexatrienes the central bond order is significantly lower than the terminal bond orders in both the S_1 and T_1 states, the difference being greatest for T_1. In addition the ground state of cycloheptatriene is stabilised by suprafacial pericyclic interaction;[10] the first excited state, solely in terms of pericyclic stabilisation should prefer a geometry allowing formation of a Möbius-like array[11] via 1,6-antarafacial interaction. These factors suggest the possibility that relaxation of the spectroscopic singlet of a cycloheptatriene involving twisting about the C(3)-C(4) bond leads to a non-spectroscopic singlet of C_2-symmetry (cf. 12). In contrast to the spectroscopic singlet this would possess the ideal geometry for 1,4- or 3,6-ring closure to a bicyclic diene (cf. 12). Intersystem crossing from such a singlet could lead to a triplet capable of crossing, at least in part, to a ground state cis, trans, cis-cycloheptatriene. Such a species (13 and 14 from 4 and 6 respectively) would rapidly ring close via the thermally allowed conrotatory mode[12] to give one or both possible bicyclic dienes.

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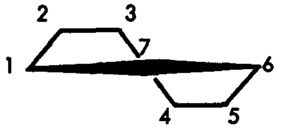
[4] Estimated from g.l.c. and n.m.r.

[5] On irradiation of non-degassed benzene solutions of 9 and 10 decay to unidentified oxidation products occurred. The fact that aerated solutions of 7 and 8 do not similarly decay on irradiation is further evidence that 9 and 10 are not formed under these conditions.

[6] Sensitisation experiments have not as yet allowed a distinction between these possibilities to be made.



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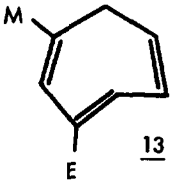

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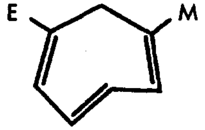

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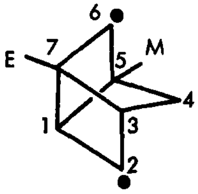
(b) In a bicyclo(3,2,0)hepta-2,6-diene the atomic orbitals which are involved in the C(3)-C(4) π-overlap of the corresponding cycloheptatriene are orthogonal. During the opening of a triplet excited state electron repulsion may well cause this relationship to be maintained, again resulting ultimately in collapse, at least in part, to a *cis, trans, cis*-cycloheptatriene.

Any 7 or 8 formed by ring closure of 13 or 14 would be "recycled" to eventually give 9 or 10.

Although we favour one or other of the mechanisms outlined above for the formation of 9 and 10, a process involving the direct rearrangement of 7 and 8 via tricyclic biradicals of type 15[7] cannot be excluded. However, the initial 3,7 π-bridging required would be atypical of singlet and triplet di-π-methane photochemistry.[2]



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Baldwin and Kaplan[13] have recently suggested that the *thermal* interconversions of some bicyclo(3,2,0)hepta-2,6-dienes proceed via intermediate *cis, trans, cis*-cycloheptatrienes rather than through an antarafacial-antarafacial Cope transition state.

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[7] Biradical 15, the result of C(3)-C(7) bridging in 7 would yield 9 on cleavage of the C(1)-C(5) bond.

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