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THE PHOTOCHEMISTRY OF CYCLOHEPTATRIENES - DIRECTIVE EFFECT OF SUBSTITUENTS ON RING CLOSURE

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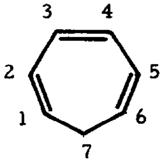
The light induced conversions of cycloheptatrienes to bicyclo-[3, 2, 0]-hepta 2, 6-dienes are well known (1-11). Such reactions generally proceed via excited singlet states and have been interpreted after Woodward and Hoffmann (12) as symmetry allowed electrocyclic processes. What has remained unclear is the fact that substituted cycloheptatrienes which may give two possible bicyclic dienes apparently in all cases close highly selectively to give only one product.[1] In certain cases steric factors have been invoked in an attempt to rationalise this specificity (6, 7, 8, 10). This will be commented on later.

It appeared unlikely to us that steric factors were the cause of the selectivity observed, a much more probable culprit in an unsymmetrical system being the charge distribution in the excited state. This paper is an attempt to show that this is the case by rationalising the published observations along with some of our own in a manner which allows the prediction of direction of ring closure in any particular instance.

If polarisation is present in the excited state then for the reaction we are concerned with polarisation in a 1, 4 or 3, 6 sense (cf. 1) will be important. We shall assume that ring closure occurs in the most polarised direction, i.e. if 1, 4- is greater than 3, 6-polarisation then C(1) will bond to C(4).



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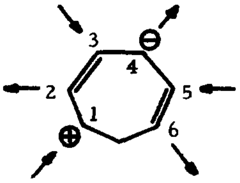
[1] In one case (4c) 3% of the alternative product is reported to be also formed (5).

In order to decide on the direction of polarisation we can consider the two extreme cases 2 and 3 where complete charge separation has occurred,2) in a 1,4 sense in 2 and in



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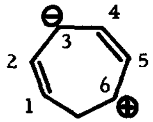

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a 3,6 sense in 3. If one is more stable than the other it would be expected to contribute more to the structure of the excited state, which would result in the excited molecule being polarised preferentially in that sense.

In 2 the arrows show the required nature (electron donating or withdrawing) of a substituent at each carbon atom if it is to stabilise the 1,4 polarised species (2) with respect to the 3,6 polarised species (3). The opposite type of substituent would destabilise 2 with respect to 3. The effect of substituents at positions 1,3,4 and 6 would obviously be greater than that of those at positions 2 and 5.

The results from this analysis are as follows:

1) An electron donating substituent at positions 1,3 or 5 or an electron withdrawing substituent at positions 2,4 or 6 will result in 1,4 ring closure.

2) For 3,6 ring closure the opposite applies.

3) If the influence of a 1,3,4 or 6 substituent is opposed by the influence of a 2 or 5 substituent then the former will be expected to direct ring closure.3)

To our knowledge there are no examples of cycloheptatriene ring closure which violate these conclusions. In Table I are listed the cycloheptatrienes taken from the literature and our own work (8, 12, 14 and 16) (13, 14) which have been successfully ring closed. All fit nicely into the proposed scheme.

It should be noted that the structure of 7 has not been conclusively established.

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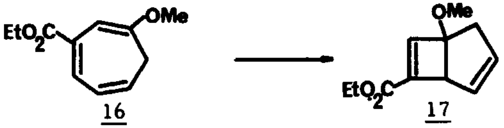
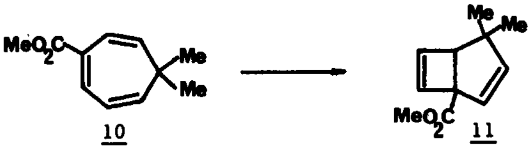
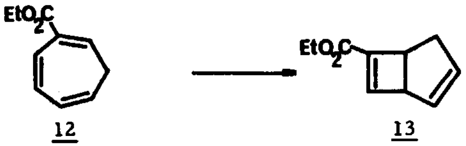
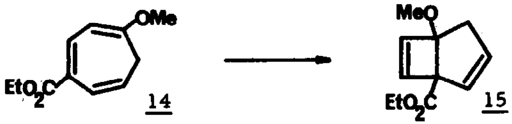
2) The molecule is considered as polarised in the direction shown (positive end at C(1) or C(6)) since this is in accord with the experimental results.

3) This is assuming that the substituents have comparable directive influences.

Table I

	Ref.		Ref.
 4 → 5	3, 5	 16 → 17	14
R = a) OMe, b) SMe, c) NMe_2			
 6 → 7 ?	3	 18 → 19	11
 8 → 9	9, 13	 20 → 21	6, 10
 10 → 11	4[4)]	 22 → 23	7, 10
 12 → 13	9, 13	 24 → 25	8, 10
 14 → 15	14	 26 → 27	8, 10

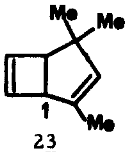
4) Chapman in fact suggests a charge separated intermediate in this particular case.

Irradiation of 6 results in the formation of three bicyclic isomers (3), one of which, 5a, comes from 4a. For the remaining pair, assuming the specificity generally observed, experimental evidence (3) favours the formation of 7 from 6 and of the 2-methoxy bicyclic diene from the 2-methoxy cycloheptatriene. We are at present attempting to confirm this.

We have ring closed 14 in which the methoxyl and ester functions are assisting each other directionally (14). Although it ring closes in the expected manner it does so extremely slowly compared with 8 and with 16 in which the substituents oppose each other. This is almost certainly due to steric compression involved in bringing the methoxyl and ester groups together at the ring junction in 15. However none of the alternative unhindered product is formed. In other words although steric factors may influence the efficiency of ring closure electronic factors determine the direction. In the case of 16 the directive effect of the methoxyl must exceed that of the ester function.

The formation of 15 and particularly that of 19[5)] appear to rule out steric requirements as the controlling factor in direction of ring closure.

Of particular interest are the methylated cycloheptatrienes 20, 22, 24, and 26. Jones and Jones have stated (6, 7, 8, 10) that the direction of ring closure in these cases can be most readily explained on steric grounds. From what has gone before we doubt this. In addition we find the steric arguments used by these authors far from conclusive. In



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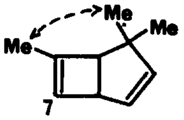

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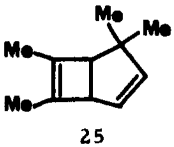

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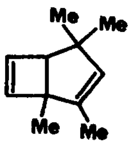

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5) Mukai (11) has postulated a doubly benzylic biradical intermediate for this reaction. Some degree of 1,4-polarisation with charge delocalised over the phenyl rings appears to be an equally attractive explanation.

particular it is argued that 23 is formed from 22 because in the alternative 28, methyl-methyl interactions as shown, raise the energy of the system (7, 10). It is then claimed that conversion of 24 to 25 rather than 29 is to be expected on steric grounds (8, 10). We find it difficult to accept the necessary conclusion that introduction of an additional methyl group at C(1) in 23 to give 29 and at C(7) in 28 to give 25 must reverse the relative stabilities.

The reactions of 20, 22, 24 and 26 agree with the polarisation concept. The cases of 20 and 22 are straight forward. Electron donating groups at C(3) and C(2) result in 1, 4 and 3, 6 ring closure respectively. In 24 the 3 substituent influence will dominate resulting in 1, 4 ring closure. In 26 the 1 and 6 methyl groups will counteract each other leaving the directing influence of the electron donating methyl at C(2) which results in 3, 6 closure.

All the results to date are consistant with the ring closing species being polarised in one of the directions shown in 2 and 3. This suggests that in those cases where n,π^* or π,π^* states may be involved, reaction is proceeding via the latter.

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