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PHOTOCHEMISTRY OF SUBSTITUTED CYCLOHEPTATRIENES: CHANGE IN DIRECTION OF RING CLOSURE ON REACTION VIA AN UPPER EXCITED STATE

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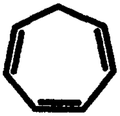
The light-induced ring closure of cycloheptatrienes to bicyclo(3,2,0)hepta-2,6-dienes (1 → 2) has been extensively studied from the point of view of product analysis.[1-8] In all reported cases the state involved in ring closure is thought to be the lowest excited singlet and for unsymmetrical cycloheptatrienes only one of the two possible bicyclic products is produced. We have interpreted this directional specificity in terms of the polarisation present in the S_1 state and the effect of substituents on this polarisation.[1] Our intuitive approach has since received theoretical support.[9,10]



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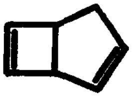
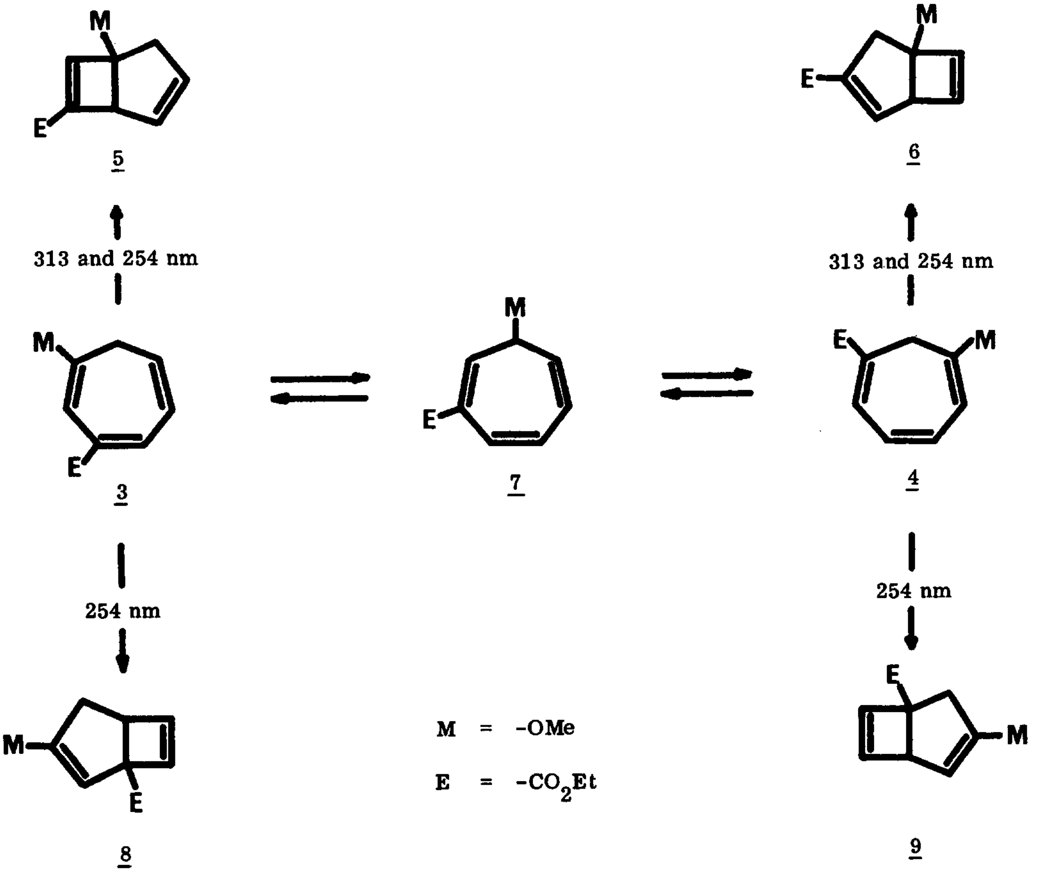


2

We report here cases in which the selectivity is wavelength dependent and indicates that reaction via an upper excited state may proceed, at least in part, and possibly exclusively in the opposite direction to that taken by S_1.

The cycloheptatrienes 3 and 4 show two absorption bands in the ultraviolet (Fig. 1). Irradiation in the long wavelength band (5×10^{-3}M in cyclohexane, 313 nm[12]) results in exclusive isomerisation to the 'normal' bicyclic products 5 and 6 which are produced on similar irradiation in benzene.[11] In the case of 4 the photochemical reversibility of the ring closure reaction results in the product of ∼ 20% of 5 at complete conversion, presumably via the intermediacy of 7 and 3.[11]

In contrast irradiation of 3 or 4 in the short wavelength band (5×10^{-3}M in cyclohexane, 254 nm[13]) results in the production of both possible bicyclic dienes in equivalent amounts.[14] In Fig. 2 is shown the initial production of 6 and 9 from 4 under conditions where the latter absorbs all of the incident 254 nm light. Clearly both bicyclic dienes are products of excitation of 4. The change in the rate of production of 6 reflects the



M = -OMe

E = $-CO_2Et$

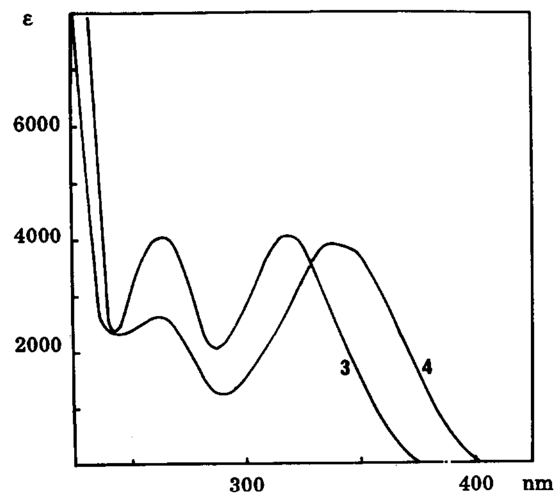


Fig. 1 Ultraviolet spectra of 3 and 4 in Ethanol.

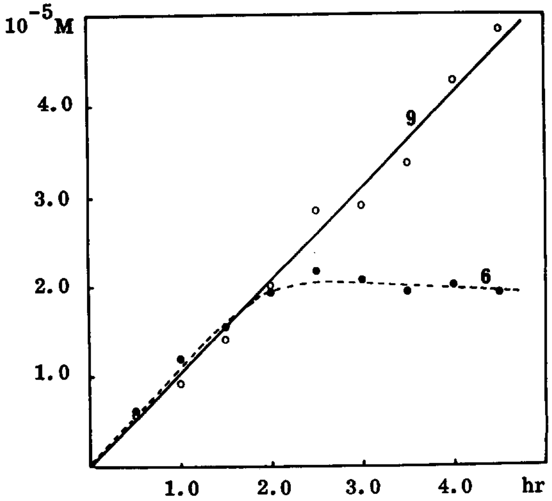


Fig. 2 Production of 6 and 9 on Irradiation of 4 (5×10^{-3}M) at 254 nm in Cyclohexane.

greater ability of this $\alpha\beta$-unsaturated ester to compete for the light. This results in the back reaction to give 4 becoming significant.

All of the above reactions are insensitive to oxygen.

Wavelength dependent photochemistry of acyclic E- and Z-hexa-1,3,5-trienes has been described previously.[15] In these cases ground state conformational factors coupled with extinction coefficient differences in the various conformers contributing to the ground-state equilibrium were put forward to explain the wavelength dependence. Such factors cannot be of consequence in the cases of 3 and 4. The simplest explanation of the data is that on excitation into the short wavelength band both 3 and 4 undergo chemical reaction, at least in part, from their S_2 states. The fact that on irradiation at 313 nm 4 gives 6 exclusively, whereas at 254 nm 6 and 9 are initially produced in equal amounts, means that the minimum amount of ring closure product which does not arise *via* S_1 on 254 nm irradiation is $\sim$ 50% and the process would then be directionally specific. If however no product arises *via* S_1 the process shows no directional specificity. Since the electron distributions in S_2 and S_1 are bound to be different, it is understandable that these species should exhibit different selectivities towards ring closure.

An alternative explanation involves the mode of relaxation of the spectroscopic S_2 state produced by photon absorption. In a simple hexatriene excitation from ψ_3 to ψ_5 would weaken the C(1)-C(2) and C(5)- C(6) but not the C(3)-C(4) bond with respect to rotation. Relaxation by twisting about the terminal double bond could therefore lead to cross-over to a ground-state *trans,cis,cis*-cycloheptatriene which would immediately ring close *via* the allowed conrotatory mode. Once *cis-trans* isomerisation had occurred, the ring-closure would necessarily be directionally specific and it is conceivable that in product analysis we are witnessing the effect of substituents on the selectivity of *cis-trans* isomerisation from S_2. An identical argument can be applied to a short-lived T_2 state.

Calculations are in progress in an effort to establish both the electronic configurations and the charge distributions of the various excited states of 3 and 4 and related systems. It is hoped that these will help to clarify the nature of the above photochemical processes. Wavelength manipulations of the kind described could be of value to the synthetic chemist and with this in mind work on other substituted cycloheptatrienes is in progress.

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12. Medium pressure mercury arc in pyrex; filter solution of 0.02M potassium chromate in 1% aqueous potassium carbonate.
13. Low pressure mercury arc, no transmission below 200 nm.
14. In the case of 3, conversion to 4 results in production of 6 and 9 as well.
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