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THE PHOTOCHEMISTRY OF BICYCLO-[3, 2, 0]-HEPTA 2, 6-DIENES. I.

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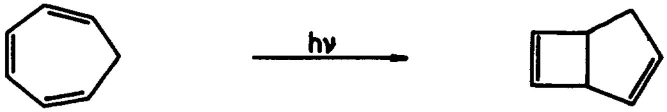
The photochemical conversion of cycloheptatriene (1) to bicyclo-[3, 2, 0]-hepta-2, 6-diene (2) is well documented (1, 2) and a large number of derivatives of 1 have been converted into the corresponding bicyclic compounds (3, 4, 5, 6, 7). However in all reported cases, photochemically induced rearrangement of the bicyclic diene system was not observed. We wish to report our preliminary results concerning the photochemistry of the bicyclic ester 3[1]. Irradiation of a 0.012M solution of 3 in benzene (Hanovia medium pressure mercury arc, quartz vessel) for 2.5 hours resulted in virtually quantitative conversion to two isomeric esters in a ratio of 4:1. The absence of olefinic proton signals in its NMR. spectrum showed the major isomer to be tetracyclic. Structure 4[2], the consequence of direct cycloaddition of the two double bonds in 3 could be excluded for this photoproduct since the 6- or 7- carboethoxy isomer[1] of 3, under the same conditions, was equally readily converted to the same mixture (identical NMR. spectra and GLC. characteristics).



1   2

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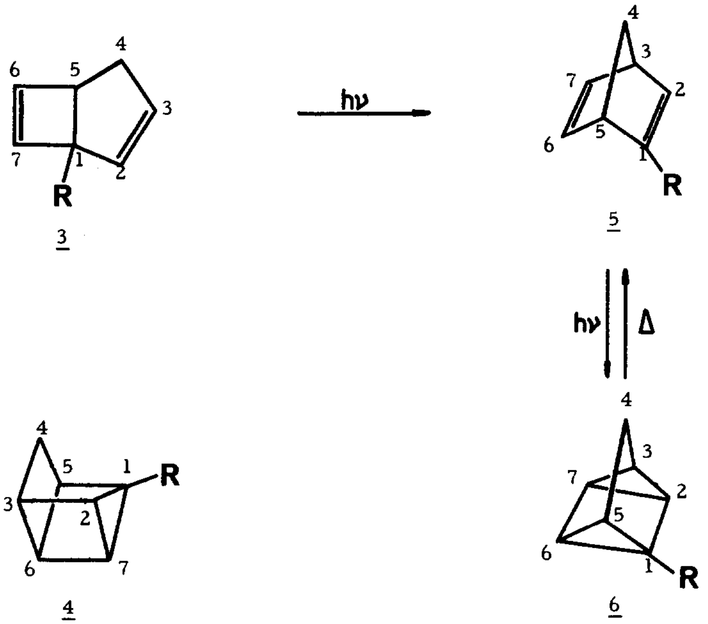
[1] Details concerning the preparation and ground state chemistry of this compound will be described in a later paper.

[2] For the sake of clarity the numbering system applied to 4, 5 and 6 corresponds to that of 3 rather than to their conventional systematic systems.



R= $-COOC_2H_5$

The quadricyclene structure 6[2] was in fact established for this photoproduct from its facile quantitative thermal converstion (170°; 115 minutes in benzene) to the bicyclo-[2, 2, 1]-hepta-2, 5-diene derivative 5[2] (8) (cf. references 9 and 10) which was also shown by GLC. analysis[3] to be identical to the minor product in the photolysis mixture. Irradiation of 5 under conditions identical to those employed for 3 resulted in 80 per cent conversion to 6 within 15 minutes (cf. references 9, 10, 11). The structure of 5 was conclusively established from spectral data, particularly from its NMR. spectrum (Fig. 1).

Irradiation of 3 in ether similarly lead to formation of 5 and 6 at a comparable rate to that in benzene solution. However, in ether solution these products undergo further photochemical transformations which are under investigation.

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3) Control experiments showed that 5 was not formed by thermolysis of 6 under the GLC. conditions used.

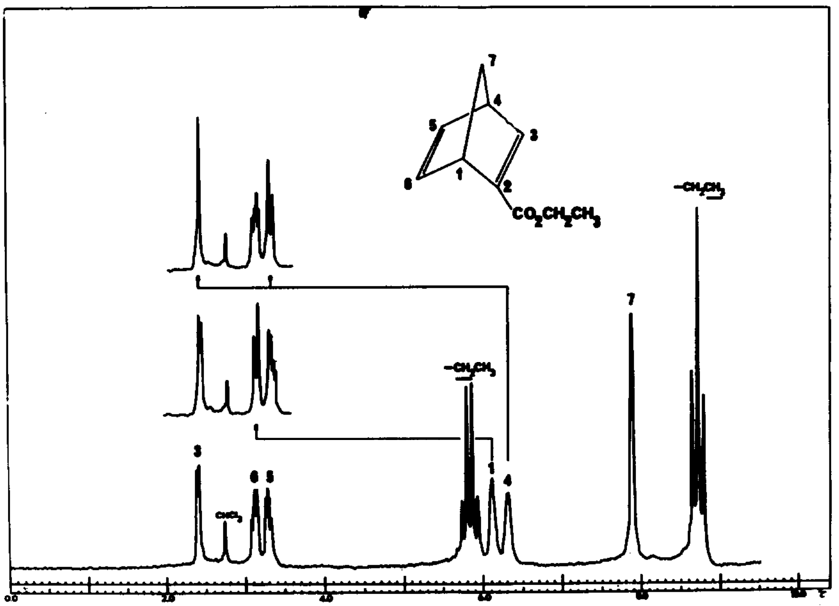
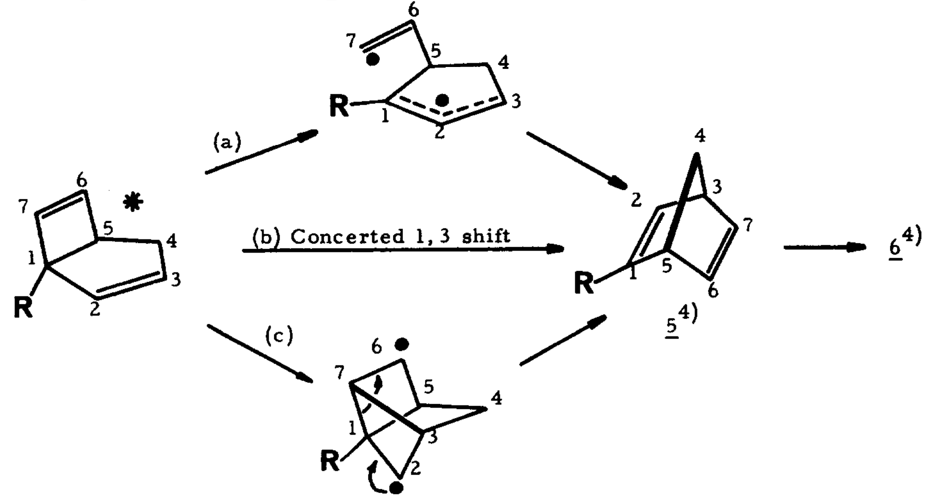


Fig. 1. 100 Mc. NMR. spectrum of 5 (conventional numbering) in $CDCl_3$.

Three mechanisms for the formation of 6 from 3 appear worthy of consideration (Scheme 1), each involving 5 as an intermediate which is subsequently converted to 6. Mechanisms (a) and (c) both involve biradical intermediates and could proceed via either singlet or triplet excited states of 3. Mechanism (b) proceeding via a singlet state is



Scheme 1. (R= -COOC$_2$H$_5$)

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[4] All compounds discussed are racemic.

attractive in that it would involve a concerted, symmetry allowed (12), 1,3 migration with retention of configuration of C(7) from C(1) to C(3). This would then represent the photochemical counterpart of Berson's thermal 1,3 carbon migration with inversion in the bicyclo-[3,2,0]-hept-2-ene series (13).

Work is in progress to establish the exact nature of the participating excited state of 3 and to distinguish between the proposed possible mechanisms for its transformation to 5.

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