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THE PHOTOCHEMISTRY OF BICYCLO(3,2,0)HEPTA-2,6-DIENES: THE FORMATION OF A TETRACYCLO(3,2,0,0,^{2,7}0,^{3,6})HEPTANE

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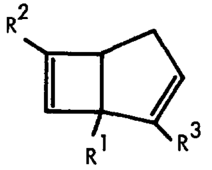
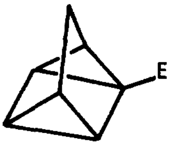
The light induced conversions of the 1- and 6-ethoxycarbonylbicyclo(3,2,0)hepta-2,6-dienes 1 and 2 (E = CO_2Et) to the same quadricyclene derivative (3) have been reported.[1] We wish to describe here the strikingly different behaviour of the 2-ethoxycarbonyl-isomer (4). Irradiation of a 0.009M benzene solution of 4 in quartz 1) resulted in complete disappearance of starting material after 5.25 hours. Approximately 50% of the product was polymeric. The remainder consisted of a 3:1 mixture of two tetracyclic isomers of 4 which were isolated by preparative g.l.c. The minor isomer was identified as the quadricyclene ester 3 by comparison of its n.m.r. spectrum with that of an authentic specimen. The major product contains the alternative homoprismane ring system and has been identified as 1-ethoxycarbonyltetracyclo(3,2,0,0,^{2,7}0,^{3,6})heptane (5). Apart from the ester triplet and quartet the n.m.r. spectrum contains signals due to seven protons which occur between 6.4 and 8.2 τ (Fig. 1). These chemical shifts are not typical of protons on a three membered ring and the only structure compatible with this spectrum is 5 which contains only two cyclopropane protons. These are



1 R^1=E; R^2=R^3=H
2 R^1=R^3=H; R^2=E
4 R^1=R^2=H; R^3=E



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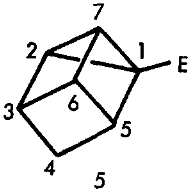

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1) 100 w medium pressure mercury arc.

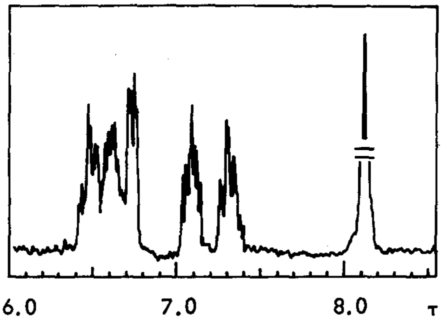
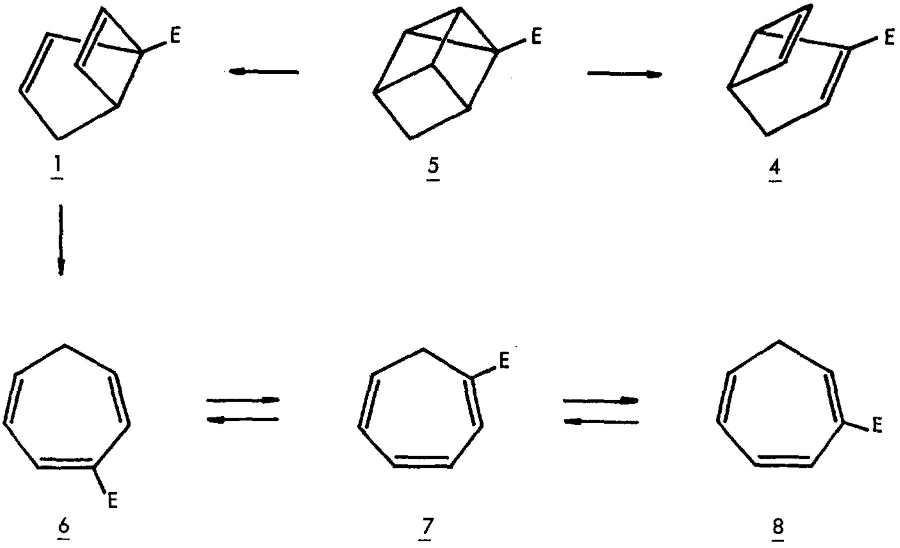


Fig. 1. The ring proton signals in the n.m.r. spectrum of 5.

deshielded by the electron withdrawing ester function and resonate at 7.08 and 7.30 τ.2) The C(4) methylene group gives rise to a finely split triplet signal (J = 1 Hz) at 8.12 τ and the three methine protons at C(3), C(5) and C(6) resonate between 6.40 and 6.80 τ.



Scheme 1 (E = CO_2Et)

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2) The corresponding protons in 3 give rise to signals at 7.61 and 7.76 τ.[2]

The structure of 5 was confirmed by its thermolysis to the two possible bicyclo(3,2,0)hepta-2,6-dienes 1 and 4 (Scheme 1). At the relatively high temperature of 205° a 0.013M benzene solution of 5 required 11.5 hours for total conversion.[3)] The diene 1 undergoes further reaction at this temperature to give the cycloheptatriene 6[4)] which equilibrates with 7 and 8 via 1,5-hydrogen shifts.[1b] The table below shows the composition of the thermolysis mixture at different conversions of 5.[5)]

Conversion of 5 (%)	Products (%)			
	1	4	7	(6 + 8)*
30	8	15	1	6
95	2	48	22	24
100	1	48	27	24

*One peak under g.l.c. conditions used.

Irradiation of 4 in ether[1)] again gives 5 and 3 together with a third unidentified product. The latter is stable to these conditions whereas 5 and 3 decay to unknown products. The conversion of 1 and 2 to 3 is much faster than that of 4 to 5 and 3 in both benzene and ether. The reactions of 1 and 2 proceed via singlet states in ether and partly via triplet sensitisation in benzene.[2] However, preliminary experiments show that the photoconversion of 4 in ether is quenched by oxygen, thus indicating the participation of a triplet excited state. The formation of 5 is therefore probably not the consequence of a concerted 2 + 2 cycloaddition reaction.

Recently Prinzbach et al[4] have reported that both direct and sensitised excitation of the tricyclic ester 9 (E = CO_2Me) gives the homoprismane derivative 10. However, the structure 9 was not unambiguously established.[5] A comparison of the spectral data quoted for 9[5] with those of 2 and the norbornadiene ester 11 (E = CO_2Et) strongly suggests that the correct structure for the tricyclic ester is 12.[6)] The anticipated photoproduct would then be the quadricyclene derivative 13.[7)] The position of the ester function in 9

[3)] Conversion of 3 to the corresponding norbornadiene is complete after 2 hours at 175°.[1]

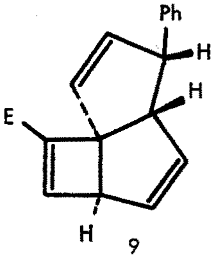
[4)] An authentic sample of 1 yielded 33% of 6 after 0.5 hours at 200°C.

[5)] Products were identified by g.l.c. comparison with authentic samples on four different columns and by photolysis in pyrex to known photoproducts in the cases of 6,7 and 8.[3]

[6)] For example, the chemical shifts (τ) and structures of the olefinic n.m.r. signals of 11 and the corresponding signals for the tricyclic ester and 2 (all in C_6D_6) are as follows (*denotes additional fine coupling).

	11	tricyclic ester	2
H_3	2.44 (q; 3 and 1Hz)	2.68 (q; 3 and 1Hz)	3.14 (s)
H_6	3.16 (q; 5 and 3Hz)*	3.07 (d; 5.2Hz)	4.4-4.64
H_5	3.47 (q; 5 and 3Hz)*	3.48 (q; 5.2 and 3Hz)	4.4-4.64

[7)] Evidence for the structure of the pentacyclic photoproduct was not presented.[4]



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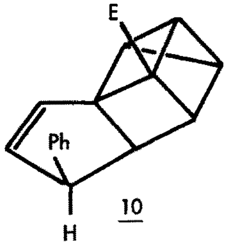

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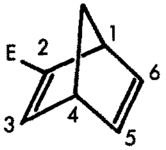

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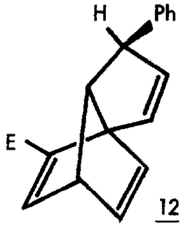

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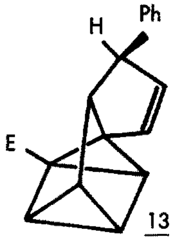

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corresponds to that in 2 rather than in 4. In the light of the known photoconversion of 2 to 3[1] the product of photolysis of 9 could in any case be 13 rather than 10.

The production of homoprismanes of type 5 is now the third known light induced reaction of bicyclo(3,2,0)hepta-2,6-dienes, the others being quadricyclene formation[1] and ring opening.[6]

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