Stereochemistry of the Photoisomerisation of 4-Methylenebicyclo[3,1,0]hex-2-enes to Spiro[2,4]hepta-4,6-dienes

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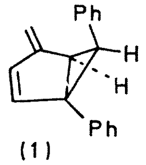
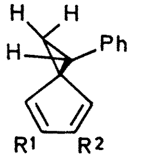
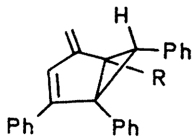
Summary The photochemical isomerisation of a 4-methylenebicyclo[3,1,0]hex-2-ene derivative to a spiro[2,4]-hepta-4,6-diene proceeds with a high degree of stereospecificity and is interpreted in terms of an excited state sigmatropic 1,5-shift followed by a thermal 1,5-shift.



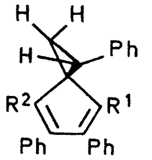
(1)



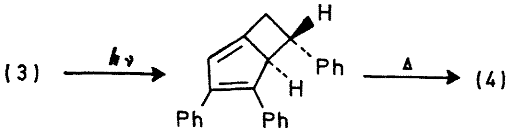
(2a) $R^1 = H, R^2 = Ph$
(2b) $R^1 = Ph, R^2 = H$



(3H) R = H
(3D) R = D



(4H) $R^1 = R^2 = H$
(4Da) $R^1 = D, R^2 = H$
(4Db) $R^1 = H, R^2 = D$



TABATA and HART[1] have recently described the photochemical conversion of a 4-methylenebicyclo[3,1,0]hex-2-ene (homofulvene) into a spiro[2,4]hepta-4,6-diene. In the course of the preparation of (1) by irradiation of 3,3-diphenyl-6-methylenecyclohexa-1,4-diene[2] we observed independently the formation of a mixture of secondary photoproducts. N.m.r. studies indicated that, apart from a small amount of material having an aromatic methyl group (not investigated further), they comprise a roughly 2:1 mixture of the spiroheptadienes (2a) and (2b), respectively.

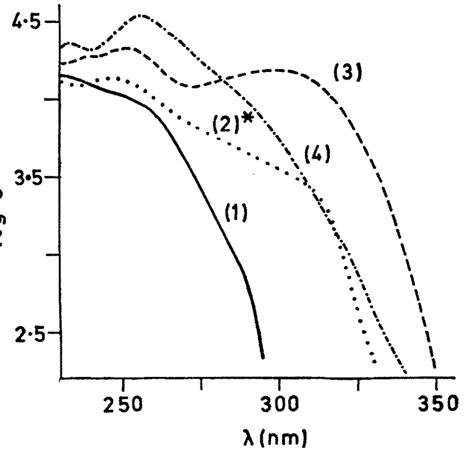


FIGURE (*asterisk denotes mixture of isomers*)

However, in view of reported photoisomerisations in the spiroheptadiene and related systems,[3] and the relative u.v. absorptions of (1) and (2) (Figure), it seemed possible that one isomer (2a) or (2b) was being formed stereospecifically from (1) and subsequently isomerised. Accordingly we prepared (3H) by Wittig reaction on the corresponding ketone[4] and assigned it the *exo*-configuration on the basis of the 4 Hz (*trans*) coupling between the cyclopropane protons compared with the 8·5 Hz (*cis*) in (1).[2] When a benzene solution of (3H) was irradiated through a Pyrex filter we obtained (4H) as the major product (85%). Under these conditions the Figure shows that relatively selective excitation of (3H) in the presence of (4H) should occur. We found that similar irradiation of the 5-deuterio-analogue (3D) to 60% conversion gave almost entirely (4Da) with a little (4Db) (< 5%); continued irradiation caused further scrambling of the deuterium label.

The structural assignments on (2) and (4) were made on the basis of u.v. and ^{1}H n.m.r. spectra. In particular the assignment of the stereochemical relationship of the 1-phenyl group to the protons 4-H and 7-H† was made on the basis of the expected shielding effect of the phenyl group on the *syn*-proton relative to the *anti*-proton.

The stereospecificity found is consistent with an allowed first excited state [1,5]-sigmatropic reaction with inversion, [π4s + σ2a]. This would give the strained bicyclo-[3,2,0]hepta-1,3-diene (5), which should undergo a ready isomerisation to (4) by a thermal [1,5]-sigmatropic reaction. On present evidence we feel this scheme is preferable to the tentative suggestion of Tabeta and Hart based on biradical intermediates. The aromatised products (like the aromatised compounds and methylenecyclohexadienes of Hart and others[1,6]) could arise independently.

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† Since submission of this communication a note has been published (H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 1970, **92**, 3474) describing investigations on a similar system whose observations and stereochemical assignments parallel ours but whose interpretation differs from that given here.

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