Photoreactions of 4-Methylenebicyclo[3,2,0]hept-2-enes

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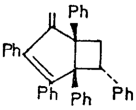
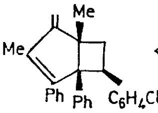
Summary 4-Methylenebicyclo[3,2,0]hept-2-enes are shown to undergo photofragmentation reactions from the excited singlet state and, depending on the substitution pattern, may undergo rearrangement to norbornene derivatives from both singlet and triplet states.

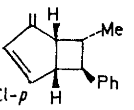
THERE have been reported several studies on the photochemical behaviour of rigid *s-trans*-1,3 dienes.[1,2] Our interest in such systems arose from the novel photorearrangement of 4-methylenebicyclo[3,1,0]hex-2-enes to spiro[2,4]hepta-4,6-dienes,[3,4] the mechanistic details of which remain unsettled. Since the related 4-methylenebicyclo[3,2,0]hept-2-ene system has not previously been studied we investigated the behaviour of some substituted derivatives.



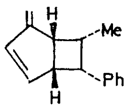
(I)



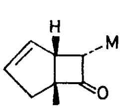
(II)



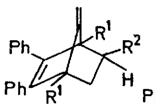
(IIIa)



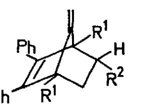
(IIIb)



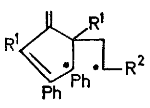
(IV)



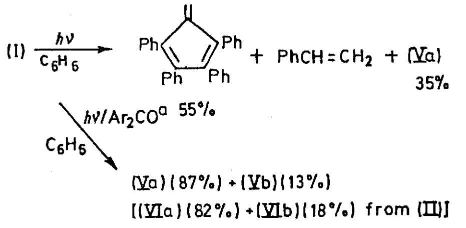
(Va) $R^1 = R^2 = Ph$
(VIa) $R^1 = Me$, $R^2 = C_6H_4{\cdot}Cl$



(Vb) $R^1 = R^2 = Ph$
(VIb) $R^1 = Me$, $R^2 = C_6H_4{\cdot}Cl$



(VII)



Compounds (I) and (II) were readily accessible from the reaction of the appropriate ketones[5] with methylenetriphenylphosphorane while the epimers (IIIa) and (IIIb) were obtained (several stages) from *endo*-7-methylbicyclo[3,2,0]hept-2-en-6-one (IV).[6] Details of this latter synthesis together with the stereochemical assignments—based on the use of $Eu(DPM)_3$ shift reagent[7]—will be given in the full paper.

Irradiation ($\lambda > 313$ nm) of (I) in benzene gave 1,2,3,4-tetraphenylfulvene, styrene, and the norbornene derivative (Va), together with a small amount of an unidentified product. Qualitatively similar behaviour was shown by (II) except that both epimers of the norbornene (VIa,b) were formed. However, when (IIIa) or (IIIb) were irradiated ($\lambda > 220$ nm) in pentane no products of the norbornene types were formed and only fulvene and propenylbenzene were formed along with polymeric material. Although there was observed a slow interconversion of the *cis*- and *trans*-isomers of propenylbenzene under the conditions of photolysis, we found by extrapolating to zero conversion that (IIIa) gave exclusively *trans*-propenylbenzene whereas (IIIb) gave the *cis*-isomer with *ca.* 5% of the *trans*-isomer. A similar photofragmentation has been observed with some 11,12-disubstituted-[4,4,2]propella-2,4-dienes.[8]

The photosensitised reaction of (I) was far more efficient than the direct and gave solely the epimers (Va) and (Vb) in the ratio 7:1 with no fragmentation. Compound (II) also gave products from a 1,3 shift with (VIa) as the major isomer, indicating that the triplet reaction is not stereospecific and probably proceeds by way of the triplet biradical (VII).

Since the photosensitised reaction gives no fragmentation products from (I), (II), or (IIIa,b) we conclude that this fragmentation arises from the excited singlet state. The high degree of stereospecificity indicates that a concerted process may be occurring but the evidence does not enable us to distinguish between a $_{\sigma}2_{s} + _{\sigma}2_{s}$ process and a *retro*-Diels–Alder reaction of "hot" norbornene products from a 1,3 shift. For both (I) and (II) the formation of norbornene

[a] Michlers ketone as photosensitiser for (I); benzophenone for (II).

products proceeds far more efficiently from the triplet state than from the singlet. This contrasts with that expected on the grounds that the free rotor effect of the *exo*-methylene group should more efficiently deactivate the excited triplet.[9]

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