Photoreactions of Substituted 4-Methylenebicyclo[3.2.0]hept-2-enes

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Photolysis of several 7-aryl-substituted derivatives of 4-methylenebicyclo[3.2.0]hept-2-ene leads to fragmentation to fulvenes and styrenes in a process which shows high stereoselectivity and proceeds exclusively from the excited singlet state. In certain cases rearrangement to derivatives of 7-methylenebicyclo[2.2.1]hept-2-ene may also occur from both excited singlet and excited triplet states but with different stereoselectivity from the two states. Quantum yield measurements show that the latter rearrangement proceeds far more efficiently from the triplet state than the singlet and the relevance of this to current views on the free rotor effect of the *exo*-methylene group is considered.

THE photochemical rearrangement of 4-methylenebicyclo[3.1.0]hex-2-enes (1) to spiro[2.4]hepta-4,6-dienes has been reported both by us [1] and by other authors.[2,3] While this rearrangement has been shown to proceed in a stereospecific manner this does permit a clear choice between the various mechanistic possibilities. Further, no very obvious analogues of this system have been studied other than the corresponding ketones whose behaviour is quite different. Several bicyclo[3.1.0]hex-2-ene derivatives may undergo a stereospecific [1,3] shift from the excited singlet state [4] and there have been numerous studies on cyclohexenes and cyclohexadienes bearing an *exo*-methylene group in conjugation.[5-7] Since none of these systems is closely related to (1) we chose to examine the behaviour of some 4-methylenebicyclo[3.2.0]hept-2-enes. The present compounds possess the same chromophore as (1) and, in addition, have relatively weak σ bonds attached to the five-membered ring. On the other hand the structural constraints should preclude a concerted [1,5] shift such as we postulated as the initial step in the rearrangement of (1). Although the related ketones (2) and (3) [8] have been shown to undergo a non-stereospecific [1,3] shift on irradiation giving bicyclo[2.2.1]hept-2-en-7-ones there is doubt as to the exact nature of the excited states involved and they are not obviously comparable with the dienes studied here.

Compounds (4) and (5) were prepared by reaction of the appropriate ketones (2) and (3) [8] with methylenetriphenylphosphorane. We have assumed the configurations proposed by Cookson and his co-workers for these ketones but, in the case of (3), were able to obtain supplementary evidence to support this assignment

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[1] N. K. Hamer and M. E. Stubbs, *Chem. Comm.*, 1970, 1013.

[2] T. Tabata and H. Hart, *Tetrahedron Letters*, 1969, 4929.

[3] H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 1971, **93**, 3662.

[4] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, 1972, **94**, 3647.

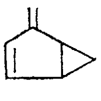
[5] W. G. Dauben and J. S. Ritscher, *J. Amer. Chem. Soc.*, 1970, **92**, 2925; W. G. Dauben and C. Suter, *ibid.*, p. 7408.

[6] H. E. Zimmerman, P. Hacket, D. F. Juers, J. M. McCall, and B. Schroder, *J. Amer. Chem. Soc.*, 1971, **93**, 3653.

[7] H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, 1969, **91**, 5307.

[8] R. C. Cookson and D. C. Warrell, *J. Chem. Soc. (C)*, 1967, 1391.

using Eu(dpm)$_3$ shift reagent.[9] Unfortunately (2) does not complex with the reagent, presumably for steric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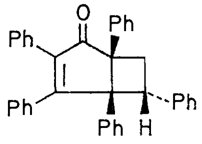
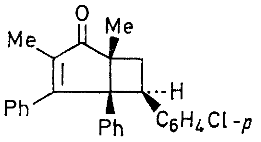

(2)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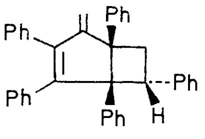
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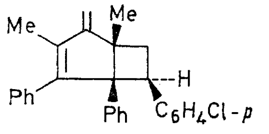
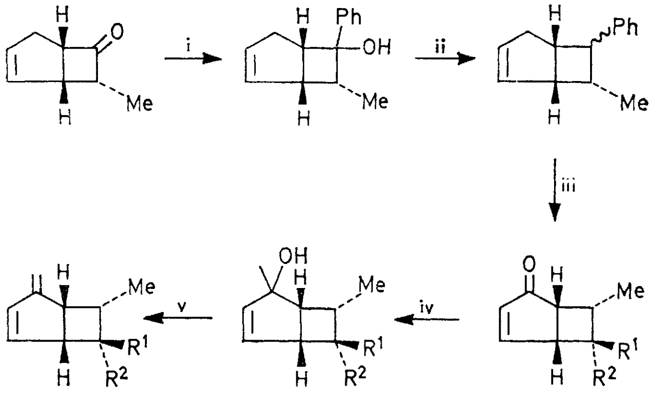

(5)

reasons. The preparation of other suitably substituted bicyclo[3.2.0]hept-3-en-2-one precursors for the required dienes presented difficulties. While compounds of this structure are reported to be formed by photolysis of amino- or alkoxy-tropones [10] this does not appear to be so for simple alkyl- or aryl-tropones. Moreover experiments on 1,4,5,6,7-pentamethylbicyclo[3.2.0]hepta-3,6-dien-2-one [11] suggested that selective hydrogenation of the C(6)–C(7) double bond was difficult to achieve. We therefore adopted the sequence shown in the Scheme



(11a,b) (10a,b) (9)

a; R^1 = Ph R^2 = H

b; R^1 = H R^2 = Ph

SCHEME Reagents: i, PhMgBr; ii, Na–NH$_3$; iii, O$_2$–$h\nu$-sensitiser, Cu(OAc)$_2$-pyridine; iv, LiMe; v, p-CH$_3$C$_6$H$_4$SO$_3$H

which permits a reasonably flexible route to the introduction of substituents into the four-membered ring. Addition of phenylmagnesium bromide to (6) [12] (from cyclopentadiene and methylketen) gave almost exclusively the alcohol (7) which on subsequent reduction gave a mixture of the two epimers of (8) in similar amounts. Photosensitised oxygenation of (8) with singlet oxygen,[13] although slow, gave after treatment with cupric acetate good conversions into the required ketones (9a and b). These were separated and their configurations deduced by ^{1}H n.m.r. spectroscopy using the shift reagent (see Appendix). However in larger scale preparations it proved more convenient to defer the separation of the epimers until the final step. Unexpectedly neither ketone underwent the required Wittig reaction although it did appear that the intermediate betaine was formed but failed to eliminate (similar divergent behaviour among structurally similar ketones has been observed in Wittig reactions on some bicyclo[3.1.0]hex-3-en-2-ones).[6] Methyl–lithium did however add stereoselectively (presumably *exo*) to (9a and b) to give the corresponding alcohols (10a and b). These underwent acid catalysed dehydration at very different rates (a factor of the order of 10^2) which provided a relatively simple separation of the epimers (11a and b).

RESULTS

On direct irradiation compounds (4), (5), and (11a and b) gave mainly fragmentation to the appropriate fulvenes and styrenes. The yields are shown in Table 1 along with the quantum yields for this inefficient process. Although there was slow interconversion of *cis*- and *trans*-propenylbenzene under the irradiation conditions used for (11a and b) we were able to show by extrapolation from studies of low conversions that (11a) gave solely *trans*-propenylbenzene whereas (11b) gave 94% *cis* and 6% *trans*. Also formed from (4) and (5) [but not from (11a and b)] were the substituted 7-methylenebicyclo[2.2.1]hept-2-ene derivatives (12a) and (13a and b), identified by comparison with authentic samples independently synthesised. From examination of the behaviour of mixtures of the appropriate fulvenes and styrenes under similar conditions we showed that these two were primary photoproducts.

The triplet reactions of (5) and (11a and b) were examined using benzophenone as sensitiser but owing to substrate absorption it was necessary to use Michler's ketone for (4).[14] Under these conditions no fragmentation of (4) or (5) was observed but very efficient conversion into mixtures of (12a and b) and (13a and b) respectively. In contrast (11a and b) were almost inert and, even after prolonged irradiation in the presence of the sensitiser, gave no identifiable monomeric products. Using the photosensitised isomerisation of *trans*-stilbene as actinometer [15] we determined the quantum yield for the isomerisation of (4) to be 0·50.* Table 2 shows the isomer distribution of (12) and

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* The value for the quantum yield in benzophenone-sensitised isomerisation of *trans*-stilbene given in this paper has since been revised.[16] However, this revision is not very substantial and we have used the quoted value for Michler's ketone.

[9] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641; J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, 1972, **94**, 5325.

[10] T. Nozoe, T. Hirai, T. Kobayashi, and H. Hayashi, *Tetrahedron Letters*, 1970, 3501.

[11] H. N. Junker, W. Schafer, and H. Niedenbruck, *Chem. Ber.*, 1967, **100**, 2508.

[12] J. Jaz and E. Denis, *Bull. Soc. chim. belges*, 1966, **75**, 845.

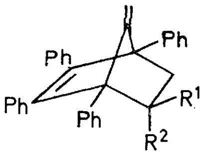
[13] C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104; K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

[14] P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 1971, **8**, 245.

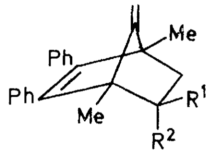
[15] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Conncell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[16] D. Valentine and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 3449.

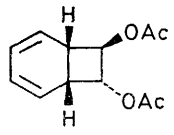
(13) from the photolysis of (4) and (5) and also the behaviour of these products under the reaction conditions.



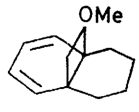
(12)
a; R^1 = Ph R^2 = H
b; R^1 = H R^2 = Ph



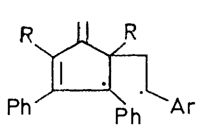
(13)
a; R^1 = p-ClC_6H_4 R^2 = H
b; R^1 = H R^2 = p-ClC_6H_4



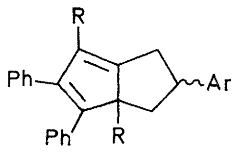
(14)



(15)



(16)
a; R = Ar = Ph
b; R = Me Ar = p-ClC_6H_4



(17)
a; R = Ar = Ph
b; R = Me Ar = p-ClC_6H_4

We estimated the primary triplet photoproducts distribution (12a)/(12b) to be 7 : 1 and (13a)/(13b) to be 4·8 : 1.

TABLE 1

Direct irradiations

Compound	(4)	(5)	(11a)	(11b)
Solvent	Benzene	Benzene	Pentane	Pentane
Wavelength (nm)	313	313	>220	>200
Fulvene yield (%)	55	45	*a*	*a*
Quantum yield	0·008 ± 0·001	0·009 ± 0·002		
Styrene yield (%)	40	38	60[b] (*trans*)	67[b] (94% *cis*, 6% *trans*)
Methylenenorbornene products [yield (%)]	(12a) (40)[c] (12b) (<1)	(13a) (30) (13b) (25)		

[a] Fulvene detected but could not be accurately estimated. [b] 30% Polymeric material also formed. [c] 10% Additional, unidentified product also formed.

TABLE 2

Photosensitised irradiations

Compound	(4)	(12a)	(12b)	(5)	(13a)	(13b)
Irradiation time (min)	5[a]	25[a]	25[a]	50[b]	50[b]	50[b]
Product composition (%)	(4) 48			(5) 33		
	(12a) 46	93		(13a) 55	90	15
	(12b) 6	7	100	(13b) 12	10	85

[a] Substrate (0·0008M) with Michler's ketone (0·0025M). [b] Substrate (0·004M) with benzophenone (0·02M); this was conducted in a different apparatus so that irradiations times are not comparable between the two sets.

There was no evidence either here or in the direct irradiation experiments that (4) or (5) underwent epimerisation at C(7).

Attempts to investigate the direct irradiation products from (4) and (5) in the presence of potential triplet quenchers (oxygen and 9,10-dibromoanthracene) were unsuccessful. Part of the difficulty arises from the low triplet energies of these compounds (E_T *ca.* 200 kJ mol^{-1}) [17] which is very restrictive on the choice of possible quenchers which do not absorb appreciably in the region of the substrate. The other, and more serious difficulty, arises from the very low quantum yields from the direct reaction giving complications from side reactions (particularly with oxygen as quencher) involving the quencher and substrate.

DISCUSSION

The photofragmentation to styrenes and fulvenes appears to be a general reaction of the excited singlet state of these 7-aryl-4-methylenebicyclo[3.2.0]hept-2-enes. It appears from the high degree of stereoselectivity in the elimination from (11a) and (11b) that either a concerted process $[\sigma_{2s} + \sigma_{2s}]$ or possibly a biradical intermediate, whose rate of breakdown is fast compared with rotation about the C(6)–C(7) bond, is involved. There are relatively few fragmentations of this type reported and all previous ones [18,19] involve the aromatisation of a cyclohexadiene system in the process. In the case of (14) [18] it was shown that the fragmentation proceeded from the triplet state whereas the elimination of methyl vinyl ether from (15),[19] which shows comparable stereoselectivity to the present cases, is probably a singlet reaction. While it is not possible to exclude fragmentation by a retro-Diels–Alder reaction of 'hot' (12) and (13) it seems unlikely in view of the complete absence of such products from the photosensitised reactions. Further, although (12a) underwent a slow thermal elimination of this type in refluxing benzene (13a and b) were inert even in refluxing xylene. Also, the absence of any products of the norbornene type from (11a and b) argues against their involvement.

Tables 1 and 2 show that the epimer ratios of (12) and (13) from direct irradiation are very different from those on photosensitisation. Since the limit of detection of

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[17] N. C. Baird, *Mol. Photochem.*, 1970, **2**, 53.

[18] W. H. Laarhoven, T. J. H. M. Cuppen, and R. J. Nivard, *Tetrahedron*, 1970, **26**, 1069; R. A. Caldwell, *J. Org. Chem.*, 1969, **34**, 1886.

[19] L. A. Paquette and G. C. Thompson, *J. Amer. Chem. Soc.*, 1972, **94**, 7127.

(12b) was *ca.* 1% we propose that the singlet rearrangement of (4) is a stereospecific [1,3] shift [20,21] and the <15% of (12) can arise from the triplet reaction. It is quite possible that the singlet reaction of (5) is also stereospecific if it is allowed that here 60—65% of reaction proceeds from initial decay to the excited triplet which seems reasonable since the chlorine atom will assist intersystem crossing. It is however, unfortunate that this point which might in principle be settled from studies with suitable triplet quenchers must, for the reasons given earlier, remain in question.

The preferential formation of the *exo*-isomers (12a) and (13a) from both (4) and (5), despite the fact that the latter differ in configuration, indicates clearly that the triplet reactions proceed through relatively long-lived biradicals (16) which undergo preferred ring closure *via* a five-membered transition state. This process is expected to be much more ready than formation of the four-membered transition state [leading to epimerisation at C(7)] or the alternative five-membered transition state [leading to (17)] since both these will involve the development of considerable angle strain.

Finally we draw attention to the remarkable efficiency of the triplet reaction of (4) and (5) compared to the singlet reaction. This contrasts with almost all previous studies on cyclic olefins bearing an *exo*-methylene group in conjugation where the triplet state rearranges, if at all, with much lower quantum efficiency than the singlet. The reason for this lack of reactivity has generally been attributed to the free rotor effect of the *exo*-methylene group resulting in efficient dissipation of the excitation energy.[22] Our results indicate that either this supposition is incorrect or that steric hindrance by the vicinal substituents in (4) and (5) prevents this occurring. While on this view the lack of reactivity of the triplets of (11a and b) becomes understandable we would point out that Goldschmidt and Kende [23] have reported an example of a diene triplet reaction which is more efficient than the singlet reaction (although less strikingly so than here) and in which steric hindrance effects are probably small.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a Varian HA 100 (100 Hz) spectrometer for solutions in deuteriochloroform unless otherwise stated. U.v. absorbances were measured in 95% ethanol on a Unicam SP 500/2 spectrometer.

Chromatography.—T.l.c. and preparative layer chromatography (p.l.c.) were carried out on plates coated with Merck silica gel GF 254; silver nitrate-impregnated plates were prepared by immersing these in a solution of silver nitrate (10%) in acetonitrile followed by drying at 100°. Column chromatography was carried out on alumina (Woelm; neutral) partially deactivated by addition of water (10% w/w) and on silica gel (Fisons).

Solvents and Reagents.—The solvents used for photolysis were AnalaR grade degassed under N_2 prior to use. Other solvents were purified and dried by reported procedures. Michler's ketone was recrystallised three times from methanol prior to use and benzophenone was recrystallised from ethanol. *trans*-Stilbene was recrystallised from ethanol and sublimed and *cis*-stilbene was purified by column chromatography on silica gel. After purification the latter contained <0·1% of the *trans*-isomer. *cis*-Propenylbenzene was prepared by biacetyl-photosensitised isomerisation of the *trans*-isomer; [24] both isomers were purified by g.l.c. and contained <0·5% of the isomeric impurity.

endo-4-*Methylene*-1,2,3,5,7-*pentaphenylbicyclo*[3.2.0]*hept*-2-*ene* (4).—To a solution of methylenetriphenylphosphorane [from methyl triphenylphosphonium bromide (8·7 g) and butyl-lithium (23 mmol)] in dry tetrahydrofuran (300 ml) was added in portions with stirring *endo*-1,2,3,4,6-pentaphenylbicyclo[3.2.0]hept-3-en-2-one (7·0 g).[8] After stirring at room temperature (1 h) the mixture was refluxed (36 h) and then poured into a mixture of hexane (200 ml), water (100 ml), and methanol. The solid was filtered off, the hexane extract evaporated, and combined with it to give crude product (4·0 g) which, after purification, by chromatography on alumina (100 g) and recrystallisation from hexane gave *compound* (4) (3·0 g), m.p. 153—155° (decomp.), $\lambda_{max.}$ 297 nm (ε 14,100), τ 2·6—3·8 (25H, m), 5·90 (1H, s), 5·08 (1H, dd, *J* 10 and 10 Hz), 5·21 (1H, s), 6·68 (1H, dd, *J* 10 and 12 Hz), and 7·07 (1H, dd, *J* 10 and 12 Hz) (Found: C, 94·0; H, 6·4. $C_{38}H_{30}$ requires C, 93·8; H, 6·2%).

exo-7-p-*Chlorophenyl*-3,5-*dimethyl*-4-*methylene*-1,2-*diphenylbicyclo*[3.2.0]*hept*-2-*ene* (5).—Following a similar procedure to the above from *exo*-6-*p*-chlorophenyl-1,3-dimethyl-4,5-diphenylbicyclo[3.2.0]hept-3-en-2-one [8] (3) (1·96 g) there was obtained, after chromatography followed by recrystallisation from ethanol, the pure *material* (0·70 g), m.p. 66—68°, $\lambda_{max.}$ 227 and 252 nm (ε 26,800 and 17,200), τ 2·6—3·6 (14H, m), 5·03 (1H, s), 5·15 (1H, s), 6·14 (1H, dd, *J* 7 and 10 Hz), 7·45 (1H, dd, *J* 10 and 12 Hz), 7·84 (1H, dd, *J* 7 and 12 Hz), 8·21 (3H, s), and 8·75 (3H, s) (Found: C, 84·6; H, 6·5; Cl, 9·1. $C_{28}H_{25}Cl$ requires C, 84·7; H, 6·4; Cl, 8·9%).

endo-7-*Methyl*-6-*phenylbicyclo*[3.2.0]*hept*-2-*en*-6-*ol* (7).—To a solution of phenylmagnesium bromide (0·38 mol) in ether (500 ml) was added, dropwise with stirring, *endo*-7-methylbicyclo[3.2.0]hept-2-en-6-one [12] (26 g) in ether (250 ml) and the mixture was left for 36 h. After the usual work-up (saturated ammonium chloride solution and ice) there was obtained a red oil (40 g) which was purified by chromatography on silica gel (1·8 kg) using pentane–ether (4 : 1) as eluant to give pure *material* (23·5 g). A small sample was distilled, b.p. 92° at 0·1 mmHg, $\lambda_{max.}$ 259 (ε 310), τ (CCl_4) 2·6—3·0 (5H, m), 4·01 (1H, d, *J* 5 Hz with fine splitting), 4·17 (1H, d, *J* 5 Hz, with fine splitting), 6·74 (2H, m), 7·03 (1H, m), 7·26 and 7·60 (each 1H, d, *J* 17 Hz with fine splitting), 8·26br (1H, s), and 9·09 (3H, d) (Found: C, 84·2; H, 7·9. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%).

endo-7-*Methyl*-6-*phenylbicyclo*[3.2.0]*hept*-2-*ene* (8).—To a solution of (7) (19·5 g) in liquid ammonia (350 ml) and ethanol (9·0 g) was added, with stirring under reflux, sodium (4·52 g) in 20 portions and the refluxing continued

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[20] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 797.

[21] R. C. Cookson, J. Hudec, and M. Sharma, *Chem. Comm.*, 1971, 107.

[22] J. S. Swenton, A. R. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 1406; H. E. Zimmerman and A. C. Pratt, *ibid.*, p. 1409; H. E. Zimmerman and G. A. Epling, *ibid.*, p. 1411.

[23] Z. Goldschmidt and A. S. Kende, *Tetrahedron Letters*, 1971, 4625.

[24] R. A. Caldwell and G. W. Sovocool, *J. Amer. Chem. Soc.*, 1968, **90**, 7138.

(30 min). After evaporation of the ammonia, water (200 ml) was added, the mixture extracted with hexane (2 × 200 ml), and the extract evaporated to give the crude product (15·9 g). *G.l.c.* showed it to be almost entirely (>90%) a mixture of epimers (8a and b) in the ratio 5 : 4 and this mixture was used without further purification.

endo-7-*Methyl*-exo-6-*phenylbicyclo*[3.2.0]*hept*-3-*en*-2-*one* (9a).—A solution of the above mixture (14 g) and Methylene Blue (0·4 g) in dimethylformamide (400 ml) was irradiated with an Atlas 13 W fluorescent lamp for 7 days during which time a stream of oxygen was passed through the solution. (Further quantities of dye were added from time to time to replace bleaching losses.) The mixture was then poured onto ice, extracted with ether (3 × 150 ml), the ether layer washed with water (2 × 100 ml), and dried ($MgSO_4$) to give, after removal of solvent, the crude hydroperoxide as a yellow oil. This oil was taken up in pyridine (300 ml) and copper(II) acetate monohydrate (16·1 g) added in one portion with stirring. Over 10 min the solution temperature rose sharply and ice-cooling was applied for 30 min, after which time stirring was continued overnight at room temperature. The mixture was poured onto phosphoric acid (500 ml; 25%) pre-cooled to 0° and extracted with ether (3 × 100 ml), the extract being then washed successively with phosphoric acid, water, and sodium hydrogen carbonate solutions (100 ml each). After removal of the solvent the residue was chromatographed on silica gel (500 g) and eluted with pentane–ether (1 : 1) to give recovered (8) (4·8 g), (9a) (1·7 g), a mixture of (9a and b) (4·0 g), and (9b) (0·6 g). By preparative g.l.c. there was obtained a pure *sample* of (9a) which, after recrystallisation from light petroleum had m.p. 64—65°, $\lambda_{max.}$ 212 and 322 nm (ε 13,900 and 88), ν 1690 cm^{-1}, τ (CCl_4) 2·17 (1H, dd, *J* 3 and 6 Hz), 2·8 (5H, m), 3·73 (1H, d, *J* 6 Hz), 6·63 (1H, m), 6·8—7·5 (3H, m), and 8·89 (3H, d, *J* 6 Hz) (Found: C, 84·8; H, 7·4. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

endo-7-*Methyl*-endo-6-*phenylbicyclo*[3.2.0]*hept*-3-*en*-2-*one* (9b).—By preparative g.l.c. on the crude isomer this was obtained as an oil [containing 2—3% of (9a)], $\lambda_{max.}$ 215 and 321 nm (ε 1400 and 135), ν 1696 cm^{-1}, τ (CCl_4) 2·22 (1H, dd, *J* 3 and 6 Hz), 2·8 (5H, m), 3·60 (1H, dd, *J* 1 and 6 Hz), 5·94 (1H, dd, *J* 9 and 9 Hz), 6·30 (1H, m), 6·5—7·1 (2H, m), and 9·11 (3H, d, *J* 7 Hz) (Found: C, 84·3; H, 7·4%).

endo-6-*Methyl*-4-*methylene*-exo-7-*phenylbicyclo*[3.2.0]*hept*-2-*ene* (11a).—To a solution of the mixed bicyclohexenones (9a and b) (3·5 g) in ether (40 ml) cooled to −78° was added methyl-lithium (29 mmol) in ether followed by ice (20 g). The mixture was allowed to warm to room temperature, the aqueous layer saturated with sodium chloride, and the ether layer separated. Removal of the solvent gave a mixture of the isomeric alcohols (10a and b) in essentially quantitative yield. These were taken up under N_2 in a solution of toluene-*p*-sulphonic acid (110 mg) in dimethylformamide (200 ml), the mixture maintained at 40° for 6 h, then quenched in sodium hydrogen carbonate solution (200 ml of saturated). Using deoxygenated solvents in all subsequent steps the residue, after removal of the ether, was chromatographed on 18 preparative plates (each holding 15 g of silica) which were run in pentane. The u.v. active band (R_F 0·4) was extracted to give a pentane solution of (11a) (0·5 g) containing *ca.* 4% of (11b), which was stored at 0° under nitrogen. Samples of (11a) were isolated as required by evaporation, $\lambda_{max.}$ 243 nm (ε 17,700), τ (CCl_4) 2·85 (5H, m), 3·78br (2H, s), 4·97br (1H, s), 5·32br (1H, s), 6·4—6·8 (2H, m), 7·1—7·5 (2H, m), and 8·94 (3H, d, *J* 6 Hz) (Found: C, 91·9; H, 8·1. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%).

endo-6-*Methyl*-4-*methylene*-endo-7-*phenylbicyclo*[3.2.0]-*hept*-2-*ene* (11b).—The preparative plates from the previous experiment were redeveloped with pentane–ether (1 : 1) and the weakly u.v.-absorbing band at R_F 0·3 was extracted with ether to give (10b) (0·95 g) containing 5% of (10a) but otherwise pure. This was taken up under N_2 in a solution of toluene-*p*-sulphonic acid (0·95 g) in dimethyl sulphoxide (25 ml) and left at 30° for 18 h. The mixture was neutralised with sodium hydrogen carbonate solution (25 ml; saturated) and ice (50 g), then extracted with ether (3 × 30 ml), and the combined extracts were washed with water and dried ($MgSO_4$). After evaporation and preparative chromatography there was obtained the *product* (0·15 g) which was stored under N_2 in pentane, $\lambda_{max.}$ 243 nm (ε 14,900), τ 2·8 (5H, m), 3·73br (2H, s), 5·03br (1H, s), 5·34br (1H, s), 6·07 (1H, dd, *J* 9 and 9 Hz), 6·1—6·6 (2H, m), 6·94 (1H, m), and 9·15 (3H, d, *J* 7 Hz) (Found: C, 91·6; H, 8·2%).

exo-7-*Methylene*-1,2,3,4,5-*pentaphenylbicyclo*[2.2.1]*hept*-2-*ene* (12a).—Following the procedure adopted for the preparation of (4) there was obtained from the reaction of *exo*-pentaphenylbicyclo[2.2.1]hept-2-en-7-one [8] (2·0 g) with a 3·5-fold excess of methylenetriphenylphosphorane, the *product* (1·632), m.p. 136·5—137·5° (from cyclohexane), $\lambda_{max.}$ 267 nm (ε 12,850), τ 2·5—3·7 (25H, m), 4·97 (1H, s), 5·50 (1H, s), 6·23 (1H, dd, *J* 5 and 9 Hz), 6·99 (1H, dd, *J* 9 and 12 Hz), and 7·33 (1H, dd, *J* 5 and 12 Hz) (Found: C, 94·1; H, 6·4. $C_{38}H_{30}$ requires C, 93·8; H, 6·2%).

endo-7-*Methylene*-1,2,3,4,5-*pentaphenylbicyclo*[2.2.1]*hept*-2-*ene* (12b).—This was prepared in a similar fashion from the appropriate ketone (1·0 g) and a 1·5-fold excess of the Wittig reagent. The crude *product* (0·80 g) was recrystallised from cyclohexane–hexane (1 : 10) and had m.p. 205°, $\lambda_{max.}$ 272 nm (ε 12,250), τ 2·3—3·8 (25H, m), 5·59 (1H, dd, *J* 5 and 9 Hz), 5·60 (1H, s), 6·18 (1H, s), 6·92 (1H, dd, *J* 9 and 11 Hz), and 7·45 (1H, dd, *J* 5 and 11 Hz) (Found: C, 93·8; H, 6·2%).

exo- *and* endo-5-p-*Chlorophenyl*-1,4-*dimethyl*-7-*methylene*-2,3-*diphenylbicyclo*[2.2.1]*hept*-2-*ene* (13a *and* b).—These were prepared in a similar manner from the parent ketones.[8] *Compound* (13a) had m.p. 135—137° (decomp.), $\lambda_{max.}$ 232 nm (ε 25,000), τ 2·7—3·1 (14H, m), 5·6 (1H, s), 5·72 (1H, s), 6·87 (1H, dd, *J* 5 and 9 Hz), 7·65 (1H, dd, *J* 5 and 9 Hz), 8·26 (1H, dd, *J* 5 and 12 Hz), 8·69 (3H, s), and 9·17 (3H, s) (Found: C, 85·0; H, 6·4; Cl, 9·2. $C_{28}H_{25}Cl$ requires C, 84·7; H, 6·4; Cl, 8·9%). *Compound* (13b) had m.p. 172° (decomp.), $\lambda_{max.}$ 224 and 269 (ε 44,000 and 9500), τ 2·7—3·8 (14H, m), 5·70 (2H, s), 6·75 (1H, dd, *J* 7 and 9 Hz), 7·8—8·0 (2H, m), 8·59 (3H, s), and 8·75 (3H, s) (Found: C, 84·6; H, 6·4; Cl, 8·6%).

1,4-*Dimethyl*-2,3-*diphenylfulvene*.—To a solution of methylmagnesium iodide [from Mg (1·2 g)] in tetrahydrofuran (50 ml) was added 4-hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-en-1-one (4·5 g) [25] in portions with stirring. The mixture was refluxed for 30 min, the bulk of the solvent removed *in vacuo*, and the residue treated with ammonium chloride (50 g) and ice (100 g). After extraction with ether (4 × 50 ml) the combined extracts were washed with water (100 ml), dried ($MgSO_4$), and the solvent removed. The residue was taken up in dioxan (100 ml) containing sulphuric acid (5 ml),[26] stirred at 40°

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[25] P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Amer. Chem. Soc.*, 1958, **80**, 202.

[26] G. Rio and M. Cherki, *Compt. rend.*, 1964, **259**, 3786.

for 30 min, then poured into water, and extracted with benzene (2 × 50 ml). Evaporation of the benzene extract gave a dark red gum which by p.l.c. and recrystallisation from pentane gave the *product* (0·15 g) as orange needles, $\lambda_{max.}$ 243 and 395 nm (ε 32,200 and 320), τ 2·7—3·1 (10H, m), 4·20 (2H, s), and 7·96 (6H, s) (Found: C, 93·1; H, 7·3. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%).

Photolyses.—General. Irradiations were carried out at 25° under nitrogen using a 125 W medium pressure Hg lamp as light source. The following filter solutions were used: A, potassium carbonate (3·04 g) and potassium dichromate (2·36 g) in water (1 l); B, cupric nitrate trihydrate (430 g) in water (1 l); and C, potassium iodide (1·7 g) in deoxygenated water (1 l) (this solution needed frequent renewal under irradiation).

Product studies. Solutions of (4) (100—200 mg) in benzene, cyclohexane, or pentane or an appropriate mixture (100 ml) were irradiated through Pyrex in an immersion photolysis apparatus. After removal of solvent the nonvolatile photoproducts were separated (t.l.c.) and identified by comparison with authentic samples. Relative amounts were estimated by peak heights in the ^{1}H n.m.r. spectra in C_6D_6 (which gave better separations than $CDCl_3$) using mixtures of known composition as standard. The presence of styrene was shown both by n.m.r. and g.l.c. on the photolysate.

A similar procedure was adopted for (5) with the addition of filter A (3 mm thickness) to remove light λ <313 nm since some of the products were photolabile below this wavelength.

Irradiation of (11a and b) was conducted in quartz u.v. cells (1 cm) containing the substrate (30 mg) in pentane (3 ml). Light was filtered through Vycor and filter C (10 mm thickness). The formation of fulvene was shown by u.v. spectra and the propenylbenzene isomers were estimated by g.l.c. using decane as internal standard.

The photosensitised reaction of (4) was carried out on a ' merry-go-round ' with filter B (18 mm thickness) using Pyrex tubes containing substrate (50 mg) and Michler's ketone (70 mg) in benzene (9 ml). At intervals between 4 and 60 min, tubes were withdrawn, the sensitiser removed by filtration through chromatographic silica gel, and after evaporation of solvent, the residue was examined by ^{1}H n.m.r. spectroscopy as before.

A similar procedure was used for the photosensitised irradiation of (5) using benzophenone as sensitiser and filter B (18 mm). Attempts to photosensitise (11a or b) with either Michler's ketone or benzophenone gave smooth but very slow formation of several products, none of which we were able to identify.

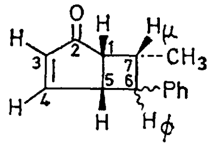
Quantum yields. For compounds (4) and (5) these were determined at 313 nm using light filtered through Pyrex and filter B (2 mm thickness). The photoisomerisation of *trans*-stilbene was used as actinometer since the quantum yield for this reaction at the wavelength employed is accurately known and it is unaffected by light in the visible region of the spectrum. In identical Pyrex tubes (16 mm diameter) were placed either *trans*-stilbene (16 mg) or (4) (12 mg) followed by benzene (9 ml). These were degassed by three freeze–thaw cycles at 5×10^{-4} Torr, sealed, and irradiated simultaneously in a merry-go-round to conversions of <5% The yield of fulvenes from (4) and (5) were measured by u.v. absorbance and the amounts of *cis*- and *trans*-stilbene by g.l.c.

The quantum yield for the sensitised photolysis of (4) was carried in the same apparatus as the direct with the addition of Michler's ketone (50 mg) to each tube. Since the sensitiser absorbs much more strongly than substrate or products at λ >330 nm whereas monochromatic light is unnecessary we employed filter B (18 mm thickness). The photosensitised *trans*- $\longrightarrow$ *cis*-stilbene isomerisation using the same concentration of Michler's ketone was used as actinometer.

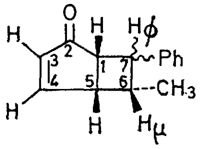
After photolysis the sensitiser was removed by filtration through chromatographic silica gel, the extent of isomerisation of stilbene estimated by g.l.c., and extent of reaction of (4) measured by removing the solvent and measuring the u.v. absorbance of the residue (in 95% EtOH) at 279·5 nm [where (4) and (12a and b) have almost identical ε values (11,200)] and at 297 nm. Results of these estimations were in agreement with those from ^{1}H n.m.r. measurements.

APPENDIX

Since cases are known where photo-oxidation of olefins proceeds without an allylic shift [13] it was first necessary to show that our bicyclohexenones did possess structure (9a and b) and not (18). From chemical shifts with ^{1}H n.m.r. spectra and decoupling experiments protons 3-, 4-, and 5-H and H_μ were readily assigned in both isomers.



(9)



(18)

Addition of Eu(dpm)$_3$ gave a series of shifted spectra in which by far the largest shifts [Δ 3·5 and 3·7 relative to 4-H in (9b and a) respectively] were observed in one of the unassigned four-membered ring protons. This is clearly 1-H which was now sufficiently separated for double irradiation experiments to show that it was coupled to H_μ thus excluding (18). The remaining assignment of the stereochemistry then follows from the fact that in small rings phenyl groups shield *cis*-vicinal protons and methyl groups more than *trans*.[27] In addition, in bicyclo[3.2.0]-hept-2-enes *exo*-protons on the four-membered ring are deshielded relative to the *endo*.[28] Thus the isomer with τ 7·0, 7·24, and 8·89 for H_ϕ, H_μ, and CH_3 group respectively is clearly (9a) while the other isomer with τ for these protons 5·94, 6·73, and 9·11 is (9b).

Using the shift reagent it is possible to obtain additional support for the configuration of (3) [8] if it is assumed that europium adopts a similar location in the complex with (3) as in the corresponding epimer of (9). Here we found $\Delta_6/\Delta_{7\,exo} = 0{\cdot}9 \pm 0{\cdot}01$ while for (9a and b) this ratio was $0{\cdot}90 \pm 0{\cdot}02$ and $0{\cdot}65 \pm 0{\cdot}01$ respectively.

A. J. W. thanks the Salter's Company for a Salter's Studentship and Trinity College for a Research Studentship.

[3/1713 *Received*, 13*th August*, 1973]

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