Overcrowded Molecules. Part 15.[1] Some Reactions of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,5-Dibenzylidene-3,4-diphenylcyclopentenones and 2,5-Dibenzylidene-1,3,5-triphenylcyclopenten-1-ols

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Acid-catalysed condensation of 3,4-diphenylcyclopent-2-en-1-one or 3,4-diphenylcyclopent-3-en-1-one with benzaldehyde gives a mixture of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,5-dibenzylidene derivatives, each of which undergoes thermal, acid-catalysed, and photochemical equilibration with its geometrical isomers but not photochemical ring-closure to yield phenanthrene derivatives. These ketones react with phenyl-lithium to give the corresponding 2,5-dibenzylidene-1,3,5-triphenylcyclopenten-1-ols, which undergo acid-catalysed rearrangement to a benzyl diphenyldibenz[*eg*]azulene.

A single compound which showed photopolychromic [2] properties (*i.e.* more than one major reversible colour change on irradiation) would provide an interesting model for studying competing photochemical processes and the basis for a multicoloured reversible image-forming system. The spiropyran derivative (1) [3] undergoes photochemical bond cleavage [process (a)] to give a blue intermediate [*e.g.* (2)]. 1,2-Diphenylcyclopentenes [*e.g.* (3a), (3b)] [4,5] cyclise photochemically [process (b)] to give red 4a,4b-dihydrophenanthrene intermediates [*e.g.* (4a), (4b)]. It therefore seemed possible that spiropyran (7; R¹ = R² = H) [6] or its 1,12-dibromo-3,10-dinitro-derivatives (7; R¹ = NO₂, R² = Br) might undergo one or more of the reactions outlined in Scheme 1. These fluorescent compounds showed neither photochromic nor thermochromic properties on irradiation in different solvents or rigid plastic matrix down to −196 °C or on heating in solution up to 200 °C.[7]

From this study followed an investigation of the stereochemistry of the molecularly overcrowded (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,5-dibenzylidene-3,4-diphenylcyclopentenones (13a), (14a), and (15a) and the course of their photochemical reactions. The condensation of benzaldehyde with indan-1-one and its 3,3-dimethyl derivative (8; R = H or Me) gives only (*E*)-2-benzylideneindan-1-ones (9; R = H or Me).[8] In contrast, benzaldehyde reacts with 3,3-diphenylindan-1-one (8; R = Ph) to yield both (*E*)- and (*Z*)-2-benzylideneindan-1-ones (9; R = Ph) and (10; R = Ph). In the case of

the latter, steric interactions between 3-phenyl substituents and the benzylidene group result in (*E*)- and (*Z*)-isomers having comparable stability.[9]

3,4-Diphenylcyclopent-2-en-1-one   (11; R = H) [10] undergoes acid-catalysed condensation with benzaldehyde [6] to give (*E*)-2-benzylidene-3,4-diphenylcyclopent-3-en-1-one (12) which, in turn, reacts further with benzaldehyde to give a mixture of the (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-dibenzylidene derivatives (13a), (14a), and (15a). 3,4-Diphenylcyclopent-3-en-1-one (3a) [11] condenses with benzaldehyde under similar conditions to give the three dibenzylidene derivatives. Each dibenzylidene derivative undergoes acid-catalysed equilibration [12] with the other two isomers at room temperature or when heated alone as a melt at 200 °C. The ready interconversion is attributed to the comparable stability of the three isomers, resulting from steric interaction between phenyl substituents in the (*E*)-configuration and steric interaction between phenyl and carbonyl groups in the (*Z*)-configuration.

2,2-Dimethyl-3,4-diphenylcyclopent-5-en-1-one   (11; R = Me), from the reaction of benzil with 3-methylbutan-2-one, and described in the literature [13] as 2,2-dimethylcyclopent-3-en-1-one (3c), condenses with benzaldehyde to give the (*Z*)-benzylidene derivative (16; R = Me). The revised structure for the ketone (11; R = Me) follows from its n.m.r. spectrum, which shows a doublet at τ 3.20 due to the olefinic hydrogen allylic coupled (*J* 1.5 Hz) to the methine hydrogen which appears as a doublet at τ 5.61, and methyl singlet

[1] Part 14, P. J. Darcy, R. J. Hart, and H. G. Heller, *J.C.S. Perkin I*, 1978, 571.

[2] B.P. 1,310,812/1964.

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[6] S. Ruhemann and S. I. Levy, *J. Chem. Soc.*, 1913, 551.

[7] C. F. Koelsch, *J. Org. Chem.*, 1951, **16**, 1362.

[8] D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Org. Chem.*, 1964, **29**, 1276.

[9] J. A. Bevan, P. E. Gagnon, and I. D. Rae, *Canad. J. of Research*, 1965, **43**, 2612.

[10] F. R. Japp and G. D. Lander, *J. Chem. Soc.*, 1897, **71**, 123; P. L. Pauson, W. M. Horspool, P. Bladon, S. McVey, and G. D. Broadhead, *J. Chem. Soc. (C)*, 1966, 306.

[11] E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, 1963, **85**, 1788.

[12] D. S. Noyce, W. A. Pryor, and P. A. King, *J. Amer. Chem. Soc.*, 1959, **81**, 5423.

[13] H. Burton, C. W. Shoppee, and C. L. Wilson, *J. Chem. Soc.*, 1933, 720.

absorptions at τ 8.64 and 9.44. A molecular model indicates that the methyl *cis* to the methine hydrogen is deshielded by the carbonyl and will give a signal at lower field than the other methyl which is in the shielding zone of the phenyl group [*cf.* the n.m.r. spectrum of ketone (11; R = H) [10]].

The symmetrical ketone (3c) would be expected to show a singlet absorption for the two methyl groups and also for the methylene group [*cf.* the n.m.r. spectrum of ketone (3a), τ 6.57 (4 H, s, two CH_2) [11]]. The mono- and di-benzylidene-3,4-diphenylcyclopentenone derivatives described above do not show photochromic

(1)   (2)

(3)   (4)   (5)

a; X = CO, R = H
b; X = CH₂, R = H
c; X = CO, R = Me

(6)
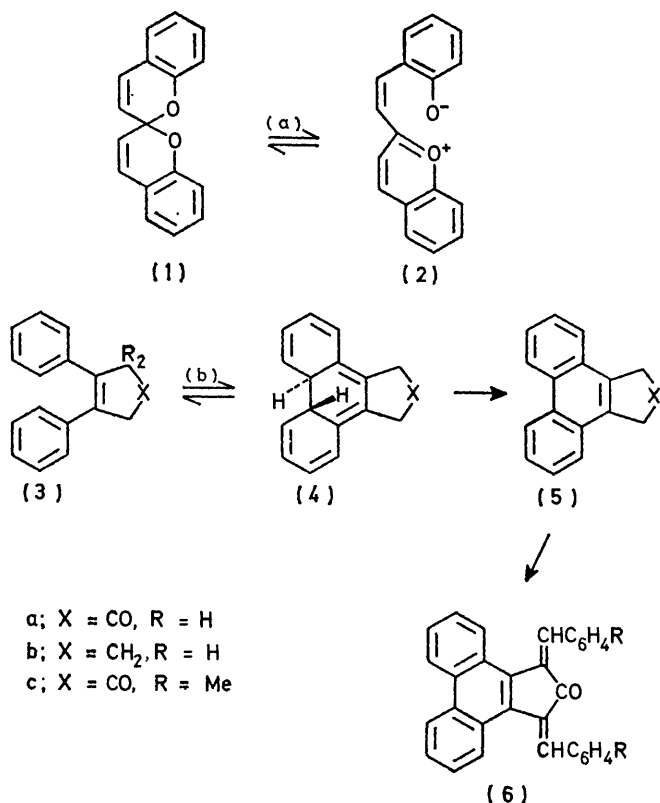
properties and on prolonged irradiation at 366 nm, or with unfiltered u.v. light in benzene alone, or with iodine added as hydrogen abstractor,[14] or benzophenone as triplet sensitizer, gave only a photoequilibrium of geometrical isomers. Irradiation of 3,4-diphenylcyclopent-3-en-1-one (3a) under similar conditions gives 2-oxacyclopenta[*l*]phenanthrene (5a),[4] which undergoes acid-catalysed condensation with benzaldehyde or *p*-methoxybenzaldehyde to yield 1,3-dibenzylidene- and di-*p*-methoxybenzylidene-2-oxacyclopenta[*l*]phenanthrenes (6; R = H or *p*-OMe), which cannot be obtained by photocyclodehydrogenation of 2,5-dibenzylidene- and di-*p*-methoxybenzylidene-3,4-diphenylcyclopentenones.

The stereochemistry of the benzylidene ketones was established by n.m.r. studies. In these derivatives, an olefinic hydrogen *cis* to a carbonyl is deshielded by it and

[14] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

gives a signal at lower field than in the *trans*-arrangement when the olefinic hydrogen is shielded by an aromatic ring.[8,9,15] In this *trans*-arrangement, the *ortho*-hydrogens of a benzylidene group *cis* to the carbonyl are

(7)
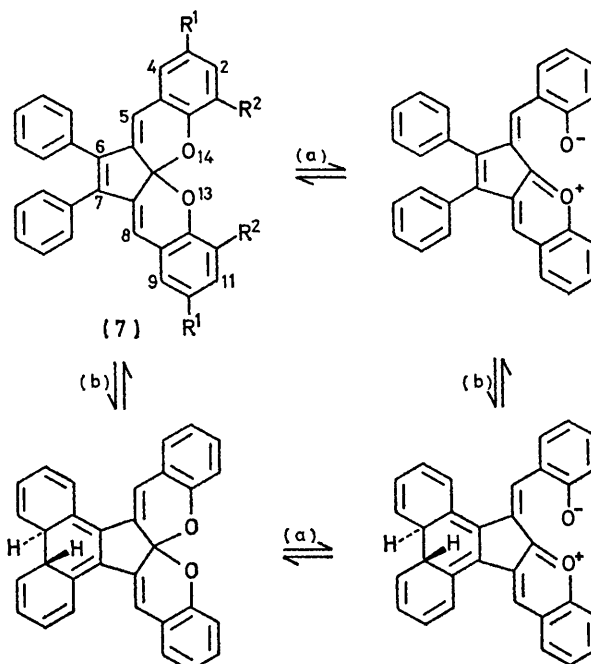
SCHEME 1

deshielded by it and give a characteristic low field multiplet (see Table). The absence of photocyclodehydrogenation reactions in the benzylidene and dibenzylidene ketones cannot be attributed simply to

(8)   (9)   (10)
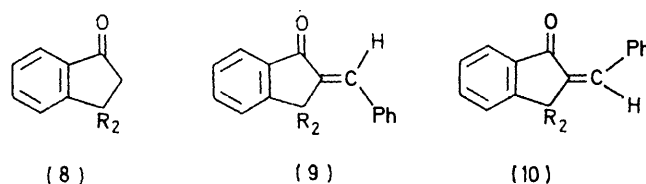
conjugation of the carbonyl group with the benzylidene moiety. The dibenzylidene ketones reacted with phenyl-

N.m.r. (τ values) and u.v. data for 2,5-dibenzylidene-3,4-diphenylcyclopent-3-ene derivatives

Ketones	=CH	*	$\lambda_{max.}$/nm	log ε
(*E,E*)-(13a)	2.28		322, 352	4.56, 4.42
(*E,Z*)-(14a)	2.32, 3.30	1.8—2.2 (2 H)	324, 354	4.54, 4.36
(*Z,Z*)-(15a)	3.25	1.9—2.2 (4 H)	325, 363	4.51, 4.34
Alcohols				
(*E,E*)-(13b)	3.35		342	4.42
(*E,Z*)-(14b)	3.35, 3.52		356	4.50
(*Z,Z*)-(15b)	3.52		348	4.45

* *o*-Hydrogens of (*Z*)-benzylidene group deshielded by carbonyl group.

lithium without isomerisation to give the corresponding 2,5-dibenzylidene-1,3,4-triphenylcyclopent-3-en-1-ols (13b), (14b), and (15b). These alcohols show a strong absorption at 366 nm (see Figure 1) but on irradiation at

[15] H. G. Heller and R. M. Megit, *J.C.S. Perkin I*, 1974, 923.

this wavelength underwent photoequilibration with geometrical isomers only and no photocyclodehydrogenation. It is, therefore, the conjugation of the *cis*-stilbene moiety with the benzylidene groups which, in some way, inhibits photocyclisation, and is not necessarily due to photochemical $E \rightleftharpoons Z$ isomerisation since the spiropyrans (7), in which $E \rightleftharpoons Z$ isomerisation is not possible, are photochemically stable.

The formulae indicate that 2,5-dibenzylidene-1,3,4-triphenylcyclopentenols form resonance-stabilised carbocations. When the alcohols in chloroform were treated with a catalytic amount of trichloroacetic acid, the near colourless solutions changed to deep red and then slowly to dark green. When the reaction mixture was poured into light petroleum, a dark solid separated, which crystallised from benzene and light petroleum as maroon needles (m.p. 203 °C). Chromatography of the green filtrate after work-up, gave green needles of a hydrocarbon, m.p. 176—177 °C, which because of its colour, n.m.r. spectrum, and analysis, is believed to be either 3-benzyl-1,2-diphenyl- or 2-benzyl-1,3-diphenyl-dibenz[*eg*]azulene (19) or (21). The maroon needles are converted into the azulene when boiled in chloroform containing trichloroacetic acid, and from its n.m.r.

a; X = CO
b; X = C(OH)Ph
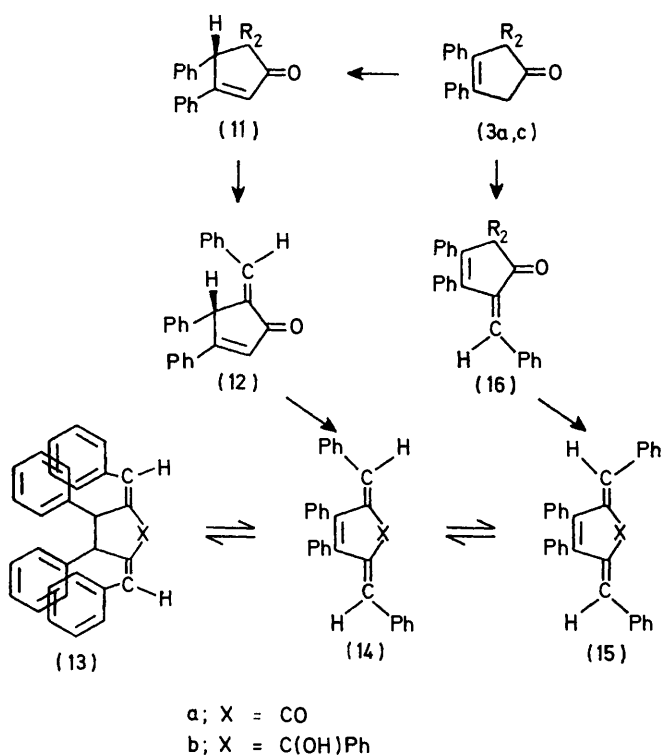
spectrum, mass spectrum, and rearrangement reaction, is assigned either structure (18) or (20).

(*Z,Z*)-2-Benzylidene-5-*p*-methoxybenzylidene-1,3,4-triphenylcyclopentenol (17b; R = Me), from the reaction of (*Z,Z*)-2-benzylidene-5-*p*-methoxybenzylidene-3,4-diphenylcyclopentenone (17a; R = Me) with phenyl-lithium, undergoes an analogous sequence of reactions to yield a maroon hydrocarbon (m.p. 204 °C)

which is converted into a methoxy-derivative of azulene [(19) or (21)], green plates, m.p. 191 °C. Azulene formation follows from an unusual sequence of reactions involving electrophilic attack from the *ortho*-position of a benzylic carbocation on to the *ortho*-position of an
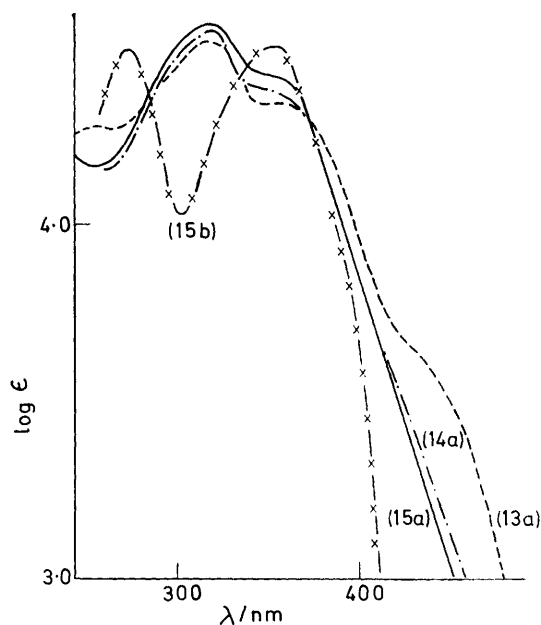

FIGURE 1   U.v. spectra of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,5-dibenzylidene-3,4-diphenylcyclopentenones (13a), (14a), and (15a) and (*Z,Z*)-2,5-dibenzylidene-1,3,4-triphenylcyclopentent-1-ol (15b) in chloroform

adjacent phenyl group, followed by elimination of a proton to give a maroon hydrocarbon which undergoes either an acid-catalysed 1,5- or 1,7-hydrogen shift (Scheme 2). These, the first examples of dibenz[*eg*]-azulenes, do not give blue solutions in organic solvents as do dibenz[*ae*]azulenes [16] (see Figure 2).

EXPERIMENTAL

U.v. spectra were measured for solutions in chloroform with a Unicam SP 1800A spectrometer unless stated otherwise: n.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (SiMe$_4$ as internal standard). Photochemical reactions were carried out in a 1 l Hanovia photoreactor consisting of a medium-pressure mercury discharge lamp contained in a Pyrex glass or quartz thimble and cooling jacket as indicated, immersed in a 1 l flask filled with a solution of the reactant. For photoreactions using 366 nm radiation, an assembly of four 125-W mercury discharge lamps with Woods glass filters (type MBW, Thorn lighting) in a reflecting aluminium housing was employed. Product distributions were determined by n.m.r. studies, *i.e.* by measuring the areas under characteristic peaks of spectra of crude reaction products after removal of solvent. Products were separated by column chromatography on alumina (Spence type H) with light petroleum as eluant.

Spiropyrans were prepared by condensation of 3,4-diphenylcyclopent-2-en-1-one (11; R = H) [9] with 2-

[16] W. Treibs, *Annalen*, 1952, **577**, 201.

hydroxybenzaldehydes (1 : 2 molar proportions) in ethanol saturated with hydrogen chloride. Salicylaldehyde gave 6,7-diphenylcyclopenta[1,2-*b*:1,5-*b'*]bis[1]benzopyran (7; $R^1 = R^2 = H$) [6] as yellow plates (from Me_2SO), m.p. 331 °C, 5-bromo-2-hydroxy-3-nitrobenzaldehyde, and the 1,12-dibromo-3,10-dinitro-derivative (7; $R^1 = NO_2$, $R^2 = Br$) yellow crystals (from chloroform), m.p. 360 °C.

(E)-2-*Benzylidene and* (E,E)-, (E,Z)-, *and* (Z,Z)-2,5-*Dibenzylidene*-3,4-*diphenylcyclopentenones* (12), (13a), (14a), *and* (15a).—(a) 3,4-Diphenylcyclopent-2-enone (11; R = H) [10] (3 g) and benzaldehyde (2.7 g) in acetic acid (150 ml) was cooled to 5 °C and saturated with hydrogen chloride. After 30 h at room temperature the (Z,Z)-isomer (15a) was filtered off and crystallised from toluene, to give orange needles, m.p. 210 °C (Found: C, 91.0; H, 5.7. Calc. for

a; X = CO
b; X = C(OH)Ph
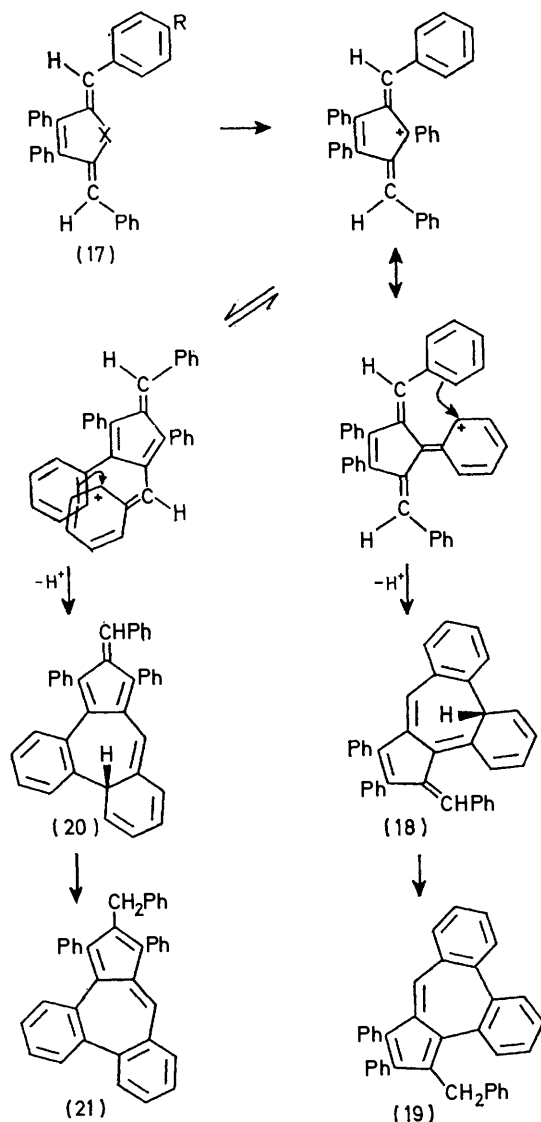
SCHEME 2

$C_{31}H_{22}O$: C, 90.7; H, 5.4%). The filtrate was evaporated to dryness and the residue crystallised from a mixture of toluene and ethanol to give the (E)-*isomer* (12) as yellow

needles, m.p. 185 °C (from ethanol) (Found: C, 89.8; H, 5.75. $C_{24}H_{18}O$ requires C, 89.4; H, 5.75%), $\lambda_{max.}$ 321 nm (log ε 4.39); τ 2.32—3.0 (complex m, ArH), 2.40 (1 H, d, *J* 1.5 Hz, deshielded =CH), 3.08 (1 H, d, *J* 1.5 Hz, =CH), and 4.56 (1 H, t, *J* 1.5 Hz, CH). The filtrate, on slow evaporation, deposited two types of yellow crystals which were separated by hand prior to recrystallisation from ethanol. The (E,Z)-*isomer* (14a) gave small needles, m.p. 181 °C (Found: C,
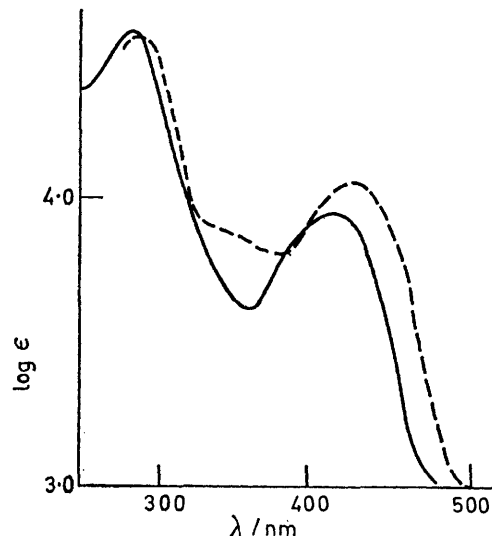

FIGURE 2 U.v. spectra of 3-benzyl-1,2-diphenyl or 2-benzyl-1,3-diphenyldibenz[*eg*]azulene (———) and its methoxy-derivative (— — —) in chloroform

91.0; H, 5.7%) and the (E,E)-*isomer* (13a) formed large needles, m.p. 191—192 °C (Found: C, 90.6; H, 5.4%).

(b) 3,4-Diphenylcyclopent-3-en-1-one (1 g) [11] and benzaldehyde (0.95 g) in acetic acid saturated with hydrogen chloride was left at room temperature (8 days). Work-up gave the (Z,Z)-dibenzylidene isomer (15a) as the major product and a small quantity of (E)-5-benzylidene-3,4-diphenylcyclopent-2-enone (12).

Acid-catalysed Equilibration of the Dibenzylidene Derivatives (13a), (14a), *and* (15a).—The (Z,Z)-isomer (15a) (50 mg) in deuteriochloroform (0.5 ml) saturated with hydrogen chloride gave an equilibrated system within 48 h, containing 14% (Z,Z)-, 78% (E,Z)-, and 8% (E,E)-isomers.

Photochemical Equilibration of Dibenzylidene Derivatives.—(a) The (Z,Z)-isomer (15a) (50 mg) in deuteriochloroform (0.5 ml) gave, after prolonged irradiation at 366 nm, an equilibrated system containing 13% (Z,Z)-, 58% (E,Z)-, and 29% (E,E)-isomers.

(b) The (Z,Z)-isomer (15a) (1 g) in toluene (1 l) containing iodine (30 mg) was irradiated (36 h) in the Hanovia photoreactor (Pyrex glass thimbles). Work-up gave a mixture of geometrical isomers which were separated by column chromatography.

(c) The photoreaction was repeated in benzene (1 l) containing benzophenone (100 mg). Only a mixture of geometrical isomers was obtained.

2-*Oxacyclopenta*[l]*phenanthrene* (5a).—3,4-Diphenyl-cyclopent-3-en-1-one (3 g) in benzene (1 l) was irradiated (12 h) in the Hanovia photoreactor (Pyrex glass thimbles). Work-up gave starting material and ketone (5a) (0.6 g), m.p. 217 °C (lit.,[4] 222.5 °C), τ 1.2—1.5 (2 H, complex m, 4- and 5-H), 2.31, 2.36, and 2.75 (6 H, ArH), and 6.22 (4 H, s,

CH$_2$). Irradiation in benzene at 366 nm gave a 25% yield of ketone (5a) and a 75% recovery of starting material.

(E,Z)-1,3-*Bis*-p-*methoxybenzylidene*-2-*oxacyclopenta*[1]-*phenanthrene* (6; R = *p*-OMe).—The ketone (5a) (2 g) and *p*-methoxybenzaldehyde in ethanol and chloroform (1 : 1) saturated with hydrogen chloride, was set aside at room temperature for 2 weeks. The solution was evaporated to dryness and the residue chromatographed. The main fraction gave the (E,Z)-*Bis*-p-*methoxybenzylidene ketone* (6; R = *p*-OMe) as red cubes, m.p. 209 °C (from toluene) (Found: C, 85.1; H, 5.0. C$_{33}$H$_{24}$O$_3$ requires C, 84.6; H, 5.2%), $\lambda_{max.}$ 259, 279, and 373 nm (log ε 4.57, 4.40, and 4.53); τ 1.2—1.5 (2 H, complex m, 4- and 5-H), 2.00 (2 H, d, *J* 9 Hz, *o*-Hs of Z-*p*-methoxybenzylidene group), 2.16 (1 H, s, =CH *cis* to CO), 2.3—2.95 (complex m, ArH), 3.06 and 3.40 (4 H, d, 9 Hz, *m*-Hs of a *p*-methoxybenzylidene group), and 6.15 and 6.24 (6 H, s, OCH$_3$).

A similar reaction of the ketone (5a) and benzaldehyde gave a mixture of products, presumably 1,3-dibenzylidene derivatives (6; R = H) which could not be separated. The n.m.r. spectrum of the mixture showed the characteristic low-field multiplet at τ 1.2—1.5 assigned to the 4- and 5-Hs of the phenanthrene system.

Photoreaction of (Z,Z)-2,5-*Bis*-p-*methoxybenzylidene*-3,4-*diphenylcyclopentenone.*—The (Z,Z)-bis-p-methoxybenzylidene compound was prepared as described above using 3,4-diphenylcyclopent-2-enone (11; R = H) and *p*-methoxybenzaldehyde in place of benzaldehyde and was obtained as orange needles (from toluene), m.p. 212 °C (Found: C, 84.4; H, 5.6. C$_{33}$H$_{26}$O$_3$ requires C, 84.3; H, 5.6%), τ 3.31 (2 H, s, =CH). Irradiation, as before, gave only a mixture of geometrical isomers and no phenanthrene derivatives (6; R = *p*-OMe).

(Z)-2-*Benzylidene*-5,5-*dimethyl*-3,4-*diphenylcyclopent*-3-*enone* (17; R = Me).—5,5-Dimethyl-3,4-diphenylcyclopent-3-enone (3c) (3.9 g) and benzaldehyde (1.85 g) in ethanol saturated with hydrogen chloride gave, when set aside for 7 days, the (Z)-2-benzylidene ketone (16; R = Me) as pale yellow plates (3.75 g), m.p. 167 °C (from ethanol) (lit.,[13] m.p. 161 °C), τ 2.06 (2 H, m, *o*-Hs of benzylidene group), 2.4—3.0 (complex m, ArH), 3.34 (1 H, s, =CH), and 8.68 (6 H, s, CH$_3$).

Photochemical Isomerisation of the (Z)-2-*Benzylidene Ketone* (17; R = Me).—The (Z)-ketone (17; R = Me) (0.6 g) in toluene was irradiated in a Hanovia reactor (quartz thimble) for 24 h. The crude product, after removal of solvent, showed only (E)- and (Z)-isomers in the ratio 12 : 88. The (E)-*ketone* was separated by recrystallisation from ethanol as yellow crystals, m.p. 138 °C (Found: C, 89.25; H, 6.4. C$_{26}$H$_{22}$O requires C, 89.4; H, 6.3%), τ 2.75—3.05 (m, ArH), 2.50 (1 H, s deshielded =CH), and 8.65 (6 H, s, CH$_3$). The irradiation was repeated in the presence of iodine (40 mg) but no other photoproducts could be detected.

(Z,Z)-2,5-*Dibenzylidene*-1,3,4-*triphenylcyclopent*-3-*en*-1-*ol* (15b).—The (Z,Z)-dibenzylidene ketone (15a) (1 g, 2 mmol) in ether was treated with phenyl-lithium in ether (4 mmol). After being stirred (12 h) at room temperature, the solution was poured onto dilute ammonium chloride solution and the ether layer separated, dried (MgSO$_4$), and solvent removed. The residue was crystallised from ethanol to give the (Z,Z)-*alcohol* (15b) as pale yellow crystals (1.11 g), m.p. 196 °C (Found: C, 90.8; H, 5.7. C$_{37}$H$_{28}$O requires C, 90.95; H, 5.8%).

The (E,Z)-ketone (14a) (0.5 g) gave the (E,Z)-*alcohol*

(14b) (0.51 g), m.p. 181—182 °C (from ethanol) (Found: C, 91.2; H, 5.9%).

The (E,E)-ketone (13a) (0.5 g) gave the (E,E)-*alcohol* (13b) (0.52 g), m.p. 115—116 °C (from ethanol) (Found: C, 91.1; H, 5.9%).

Photoequilibration of (Z,Z)-2,5-*Dibenzylidene*-1,3,4-*triphenylcyclopentenol* (15b).—The (Z,Z)-alcohol (15b) (50 mg) in deuteriochloroform was irradiated at 366 nm for one week until no further change in the n.m.r. spectrum of the solution occurred. The spectrum, though complex, related to a mixture of (Z,Z)-, (E,Z)-, and (E,E)-alcohols and showed no characteristic low-field peaks of the phenanthrene derivative (6; R = H).

Benzyldiphenyldibenz[eg]*azulene* (19) *or* (21).—The (Z,Z)-alcohol (15b) (200 mg) was heated in chloroform (10 ml) containing trichloroacetic acid (3 mg) when the solution turned from near colourless to red, and then to green. The solution was poured into light petroleum (b.p. 60—80 °C) (100 ml) and the dark solid was filtered off and crystallised from benzene and light petroleum, to give fine maroon needles (30 mg) of hydrocarbon (18) or (20), m.p. 203 °C, $\lambda_{max.}$ (toluene) 490 nm (log ε 3.08); τ 2.2—3.4 (complex m, ArH), 3.90 (1 H, m, olefinic H), and 5.17br (1 H, s, methine H). The filtrate was reduced in volume and chromatographed. The green fraction gave the azulene (19) or (21) as dark green needles, m.p. 176 °C (from benzene and light petroleum) (Found: C, 92.8; H, 5.6%; *M*$^+$ 470.5. C$_{37}$H$_{26}$ requires C, 94.5; H, 5.6%; *M* 470.5), $\lambda_{max.}$ 288 and 418 (log ε 4.56 and 3.94); τ 2.7—3.6 (24 H, complex m, ArH) and 6.43 (2 H, s, CH$_2$). The maroon needles when boiled in chloroform containing trichloroacetic acid were converted into the azulene.

Preparation of a Methoxy-derivative of Benzyldiphenyldibenz[eg]*azulene* (19) *or* (21).—(E)-5-Benzylidene-3,4-diphenylcyclopent-2-enone (11; R = H) (0.3 g) and *p*-methoxybenzaldehyde (0.12 g) in ethanol saturated with hydrogen chloride gave (Z)-2-*benzylidene*-(Z)-5-p-*methoxybenzylidene*-3,4-*diphenylcyclopentenone* (0.35 g), orange needles (from ethanol), m.p. 182 °C (Found: C, 87.1; H, 5.7. C$_{32}$H$_{24}$O$_2$ requires C, 87.2; H, 5.4%), $\lambda_{max.}$ 265 and 348 nm (log ε 4.29 and 4.48); τ 1.92 (2 H, d, 9 Hz *o*-Hs of *p*-methoxybenzylidene group deshielded by CO), 2.01 (2 H, m, *o*-Hs of benzylidene group deshielded by CO), 2.4—2.9 (complex m, ArH), 3.10 (2 H, d, *J* 9 Hz, *m*-Hs of *p*-methoxybenzylidene group), and 6.16 (3 H, s, OCH$_3$), and 3.25 and 3.31 (2 H, s, =CH). Work-up of the residues gave (E)-2-*benzylidene*-(Z)-5-p-*methoxybenzylidene*-3,4-*diphenylcyclopentenone*, yellow needles (from toluene and light petroleum), m.p. 168—169 °C (Found: C, 87.4; H, 5.5%), $\lambda_{max.}$ 342 nm (log ε 4.28); τ 1.9 (2 H, d, *J* 9 Hz, *o*-Hs of *p*-methoxybenzylidene group deshielded by CO), 2.41 (1 H, s, =CH of benzylidene group), 2.6—3.3 (complex m, ArH), 3.36 (1 H, s, =CH of *p*-methoxybenzylidene group), and 6.14 (3 H, s, OCH$_3$).

The (Z,Z)-ketone (0.7 g, 1.6 mmol) in ether (80 ml) was treated with phenyl-lithium in ether (3.5 mmol). Work-up gave (Z,Z)-2-*benzylidene*-5-p-*methoxybenzylidene*-1,3,4-*triphenylcyclopent*-3-*en*-1-*ol* (0.6 g), pale yellow cubes (from ethanol), m.p. 208 °C (Found: C, 87.8; H, 6.1. C$_{38}$H$_{30}$O$_2$ requires C, 88.0; H, 5.8%), $\lambda_{max.}$ 290 and 356 nm (log ε 4.32 and 4.43); τ 2.8—3.43 (m, ArH), 3.64 and 3.70 (2 H, s, =CH), and 6.30 (3 H, s, OCH$_3$).

The (Z,Z)-alcohol (200 mg), on treatment with trichloroacetic acid in chloroform, gave maroon crystals (100 mg), m.p. 190—192 °C (from benzene and light petroleum),

$\lambda_{max.}$ (toluene) 287 and 495 nm (log ε 4.43 and 3.15); τ 2.35—3.35 (complex m, ArH), 3.9 (1 H, m, =CHPh), 5.19 (1 H, s, CH), and 6.25 (3 H, s, OCH$_3$) (Found: M^+ 500.213. C$_{38}$H$_{28}$O requires M 500.214). The maroon needles on boiling with trichloroacetic acid in chloroform gave the methoxy-derivative of azulene (19) or (21), dark green plates (from benzene and light petroleum), m.p. 191 °C, $\lambda_{max.}$ 290 and 428 nm (log ε 4.55 and 4.05); τ 2.4—3.7 (complex m, ArH), 6.23 (3 H, s, OCH$_3$), and 6.35 (2 H, s, CH$_2$). The full structure of the maroon crystals or the methoxy-azulene derivative could not be assigned from their 100 MHz n.m.r. spectra.