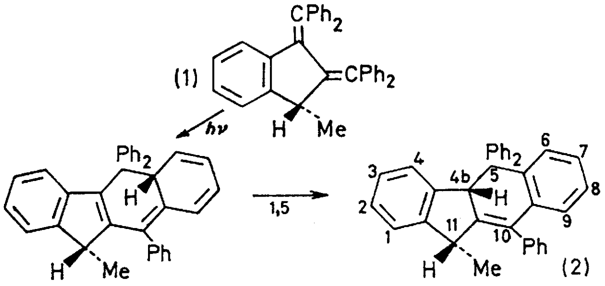
Overcrowded Molecules. Part VI.[1] Photocyclisation of *cis*-9a,10-Dihydro-9-methyl-10,15-diphenyl-9*H*-benzo[5,6]indeno[2,1-*c*] phenanthrene

By **H. G. Heller*** and **K. Salisbury**, Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth

Diphenylketen reacts with (*E*)-2-benzylidene-2,3-dihydro-3-methyl-2,3-dihydrocyclopenta[*c*]phenanthrene-1-one at 180° to yield *cis*-9a,10-dihydro-9-methyl-10,15-diphenyl-9*H*-benz[5,6]indeno[2,1-*c*]phenanthrene having an *anti*-arrangement of methyl and 10-phenyl groups. This overcrowded hydrocarbon undergoes photocyclisation by the less hindered of the two allowed contrarotatory processes to give 5a,6,10b,13e-tetrahydro-5-methyl-6,10b-diphenyl-5*H*-cyclopenta[*def*]naphtho[8,1,2-*pqr*]chrysene having a *cis*-arrangement of 5a-, 6-, and 13e-hydrogens and the methyl group *anti* to both phenyl groups.

1,2-BISDIPHENYLMETHYLENE-3-METHYLINDANE (1) undergoes photochemical electrocyclic ring closure followed by a 1,5-hydrogen shift to yield 4b,5-dihydro-11-methyl-5,5,10-triphenyl-11*H*-benzo[*b*]fluorene (2) having the methyl group *anti* to the 4b-hydrogen, indicating that steric effects determine which of the allowed conrotatory processes occur.[1] A Dreiding model of 1,2-bisdiphenylmethylene-2,3-dihydro-3-methyl-1*H*-cyclopenta[*c*]phenanthrene (7) showed that an analogous photoreaction could not occur for this diene because of the severe steric interactions either between phenyl group D and the phenanthrene nucleus or between phenyl groups B and C, depending on the direction of rotation about the 1-diphenylmethylene group, and that its photorearrangement should be of interest. Unfortunately, diene (7) could not be synthesised in the usual manner by the reaction of diphenylketen with the corresponding ketone (5). Related studies are reported which show that photocyclisation of hydrocarbon (9) occurs in accord with the Woodward–Hoffmann rules[2] by the less hindered of the two allowed controtatory processes, and indicate that it appears immaterial here as in other cases[1,3,4] whether the open-chain valence isomer incorporates the π-electrons of the aromatic system or not.



(*E*)-2-Benzylidene-2,3-dihydro-3-methylcyclopenta[*c*]-phenanthren-1-one (3) reacts with diphenylketen at 180° to yield *cis*-9a,10-dihydro-9-methyl-10,15-diphenyl-9*H*-benzo[5,6]indeno[2,1-*c*]phenanthrene (9) with an *anti*-arrangement of methyl and 10-phenyl groups. Its stereochemistry follows from its n.m.r. spectrum [τ 8·55 (d, $J_{9a,10}$ 7 Hz, Me)] which resembles closely that of hydrocarbon (10) [τ 8·6 (d, $J_{10,10a}$ 8 Hz, Me)] and not that of hydrocarbon (11) [τ 9·2 (d, $J_{10,10a}$ 16 Hz, Me)].[3] A Dreiding model of hydrocarbon (9) shows that the 15-phenyl group overlaps the phenanthrene nucleus on the same side as the 10-phenyl group. The reaction of ketone (3) with diphenylketen is considered to give the thermally unstable β-lactone which eliminates carbon dioxide and either undergoes cyclisation before π-bond formation can occur,[5] or relaxes to diene (8) which, under the reaction conditions, undergoes thermal ring closure followed by a 1,5-hydrogen shift.

Hydrocarbon (9) in light petroleum, on exposure to 366 nm radiation, rearranges to only one of the four possible isomers of 5a,6,10b,13e-tetrahydro-5-methyl-6,10b-diphenyl-5*H*-cyclopenta[def]naphtho[8,1,2-*pqr*]-chrysene (12), m.p. 264—265°. Because of the established stereochemistry of compound (9), hydrocarbon (12) must have a *syn*-arrangement of 5a- and 6-hydrogens and the methyl group *anti* to the 6-phenyl group. Ring closure by disrotatory mode *a* or conrotatory mode *b* would involve severe steric interactions between the 15-phenyl group and the phenanthrene nucleus, and need not be considered further. Ring closure by conrotatory mode *c* or disrotatory mode *d* gives rise to the *cis*- and *trans*-5a,13e-dihydro-isomers (12a) and (12b) respectively. A Dreiding model of isomer (12a) shows that the phenanthrene and benzene rings lie essentially in one plane with the 10- and 11-hydrogens in close proximity and in the deshielding regions of the aromatic rings and that it is therefore to be expected that in this isomer the 10- and 11-hydrogens would appear at low field in the n.m.r. spectrum (*cf.* the n.m.r. spectrum of benzo[*c*]phenanthrene which shows absorptions due to the 1- and 12-hydrogens centred at τ 0·85).[6] A Dreiding model of isomer (12b) shows a strained folded structure with the 10- and 11-hydrogens out of the plane and not in the

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[1] Part V, H. G. Heller and K. Salisbury, *J. Chem. Soc.* (*C*), 1970, 873.

[2] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17; The Conservation of Orbital Symmetry, Academic Press, 1970.

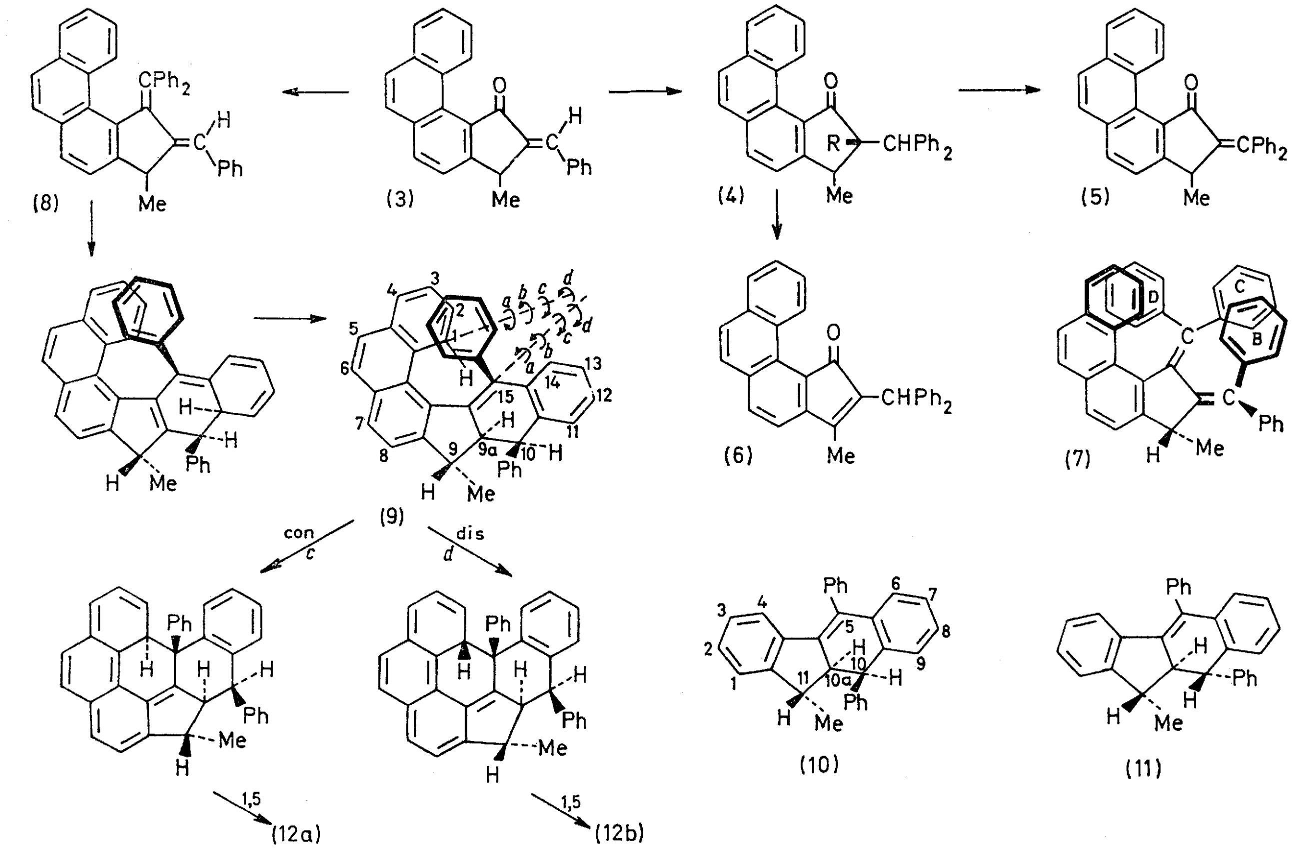
[3] H. G. Heller and K. Salisbury, *J. Chem. Soc.* (*C*), 1970, 399.

[4] G. Quinkert, K. Opitz, W-W. Wiersdorff, and M. Finke, *Annalen*, 1966, **693**, 44; O. L. Chapman and G. L. Eian, *J. Amer. Chem. Soc.*, 1968, **90**, 5329; R. J. Hart, H. G. Heller, and K. Salisbury, *Chem. Comm.*, 1968, 1627.

[5] H. G. Heller and K. Salisbury, *Tetrahedron Letters*, 1968, 2033.

[6] R. H. Martin, N. Defay, and F. Geerts-Evrard, *Tetrahedron*, 1965, **21**, 2421.

deshielding region of the aromatic rings to which they are not attached. The n.m.r. spectrum of hydrocarbon (12) shows marked deshielding of the 10- and 11-hydrogens, which give rise to quartets centred at τ 1·14 and 1·57, indicating that the hydrocarbon is the *cis*-isomer (12a). The high-field aromatic absorptions (τ 3·25—3·85) are assigned to the hydrogens of each *syn*-phenyl group shielded by the adjacent parallel benzene ring {*cf.* aromatic hydrogens of [2,2]paracyclophane (τ 3·64),[7] and the phenyl hydrogens of 1,8-diphenylnaphthalene (τ 3·15) [8]}. The splitting pattern of the methine protons and double resonance studies are consistent with the proposed structure (12a).



2-(3-Phenanthryl)butyric acid,[9] was converted into 2,3-dihydro-3-methyl-1*H*-cyclopenta[*c*]phenanthren-1-one by the action of polyphosphoric acid at 100° [10] and condensed with benzaldehyde in the presence of 10% ethanolic potassium hydroxide to give ketone (3). Reaction of bromide in chloroform with 2-diphenylmethyl-2,3-dihydro-3-methyl-1*H*-cyclopenta[*c*]phenanthren-1-one (4; R = H), prepared by the reaction of phenylmagnesium bromide on ketone (3), gave the 2-bromo-derivative (4; R = Br) which, when boiled with 2,4,6-trimethylpyridine, yielded ketone (5) and 2-diphenylmethyl-3-methyl-1*H*-cyclopenta[*c*]phenanthren-1-one (6), separated by chromatography on alumina.

EXPERIMENTAL

N.m.r. spectra were obtained for solutions in deuteriochloroform, for compounds (4; R = H), (9), and (12a) with a Varian HA-100 (100 MHz) spectrometer, and others with Perkin-Elmer R10 or R12 (60 MHz) spectrometers. U.v. spectra were measured for solutions in chloroform [except for hydrocarbons (9) and (12a) which were studied in n-hexane] with a Unicam SP 500 spectrometer). Chromatography was carried out with Spence type H alumina.

*2,3-Dihydro-3-methyl-*1H*-cyclopenta*[c]*phenanthren-*1*-one.*—2-(3-Phenanthryl)butyric acid [9] (5·0 g.) was stirred (3 h) in polyphosphoric acid (180 g) at 100°.[10] Work-up gave an oily solid (4 g) which was dissolved in light petroleum and kept at 0° for several days. The *dihydro-*3*-methylcyclopentaphenanthren-*1*-one* (2·8 g) crystallised out, m.p. 138—140° (from light petroleum) (Found: C, 86·75; H, 5·85. $C_{18}H_{14}O$ requires C, 86·85; H, 5·75%); $\nu_{max.}$ 1710s cm^{-1} (C=O).

2*-Benzylidene-*2,3*-dihydro-*3*-methylcyclopenta*[c]*phenanthren-*1*-one* (3).—The foregoing ketone (2·0 g) and benzaldehyde (1·0 g) in ethanol (30 ml) was treated with 10% ethanolic potassium hydroxide (3 ml) while the temperature

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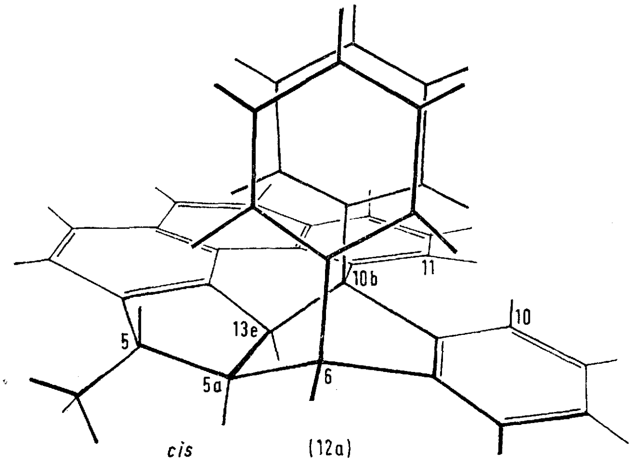
[7] D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, 1963, **85**, 1088.

[8] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, 1963, **28**, 2403.

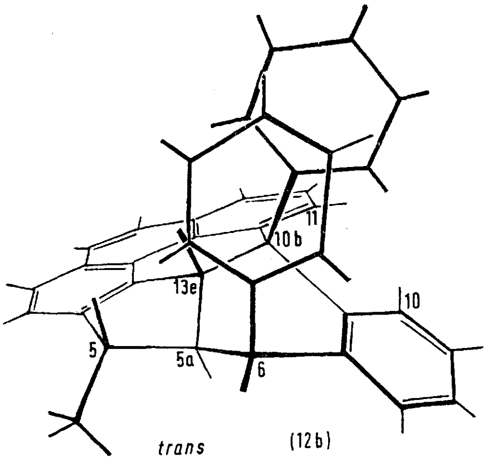
[9] W. E. Bachmann and J. M. Chemerda, *J. Org. Chem.*, 1941, **6**, 36.

[10] B. R. T. Keene and K. Schofield, *J. Chem. Soc.*, 1958, 1080.

of the mixture was maintained at 40° for 30 min. The *benzylidene derivative* (3) (2·4 g) separated from the cooled mixture, m.p. 181° (from acetic acid) (Found: C, 89·85; H, 5·45. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%); $\nu_{max.}$ 1682s cm^{-1} (C=O); τ 0·01 (1H, m, 11-H), 1·88—2·80 (13H, complex m, olefinic and aromatic H), 5·56 (1H, q, *J* 7 Hz, 3-H), and 8·53 (3H, d, *J* 7 Hz, Me).



cis (12a)



trans (12b)

2-*Diphenylmethyl*-2,3-*dihydro*-3-*methylcyclopenta*[c]*phenanthren*-1-*one* (4; R = H).—The benzylidene ketone (3) (3·6 g) in benzene (160 ml) was added to a solution of phenylmagnesium bromide, prepared from bromobenzene (5·0 g) and magnesium (0·8 g) in ether (120 ml), and the mixture was boiled (1 h) and worked-up. The *diphenylmethyl ketone* (4; R = H) (3·5 g) had m.p. 169—170° (from ethanol) (Found: C, 89·65; H, 6·0. $C_{31}H_{24}O$ requires C, 90·2; H, 5·85%); $\nu_{max.}$ 1710s cm^{-1} (C=O); $\lambda_{max.}$ 294 and 319 nm (log ε 4·56 and 3·80); τ 0·90 (1H, d, *J* 8 Hz, 11-H), 1·92—2·284 (17H, complex m, ArH), 5·50 (1H, d, *J* 9 Hz, Ph_2CH), 6·70 (2H, q, *J* 8 Hz, 2- and 3-H, magnetically equivalent), and 8·71 (3H, d, *J* 8 Hz, Me). Irradiation at τ 6·70 caused the Me and the Ph_2CH signals to become singlets.

2-*Bromo*-2-*diphenylmethyl*-2,3-*dihydro*-3-*methylcyclopenta*-[c]*phenanthren*-1-*one* (4; R = Br).—Bromine (0·63 g) in chloroform (15 ml) was added to the diphenylmethyl ketone (4; R = H) (1·5 g) in chloroform (30 ml) at 40°, and the mixture was heated (3 h) at 50°. Removal of the solvent followed by trituration of the resulting oil with ethanol gave the unstable 2-bromo-derivative (4; R = Br) (1·7 g), m.p. 295—296° (decomp.) (from acetic acid); $\nu_{max.}$ 1710s cm^{-1} (C=O); $\lambda_{max.}$ 288 and 330 nm (log ε 4·22 and 3·65); τ 0·74 (1H, m, 11-H), 1·78—3·02 (17H, complex m, ArH), 4·70 (1H, s, Ph_2CH), 5·84 (1H, q, *J* 7 Hz, 3-H), and 8·54 (3H, d, *J* 7 Hz, Me).

2-*Diphenylmethyl*-3-*methyl*-1H-*cyclopenta*[c]*phenanthren*-1-*one* (6) *and* 2-*Diphenylmethylene*-2,3-*dihydro*-3-*methyl*-1H-*cyclopenta*[c]*phenanthren*-1-*one* (5).—A solution of the bromoketone (4; R = Br) (2·0 g) in 2,4,6-trimethylpyridine (12 ml) was boiled (3 h). The cooled mixture was treated with ice and dilute hydrochloric acid and filtered. The residue in benzene was chromatographed on alumina. Elution with light petroleum of the first orange band gave the 2-*diphenylmethyl*-3-*methylcyclopentaphenanthren*-1-*one* (6) (0·8 g, 49%), red crystals, m.p. 152° (from acetic acid) (Found: C, 90·8; H, 5·45. $C_{31}H_{22}O$ requires C, 90·7; H, 5·4%); $\nu_{max.}$ 1695s cm^{-1} (C=O); $\lambda_{max.}$ 304 and 316 nm (log ε 4·33 and 4·38); τ 0·00 (1H, m, 11-H), 2·08—2·80 (17H, complex m, ArH), 4·35 (1H, s, :*CH*·), and 8·15 (3H, s, Me).

The second yellow band gave the 2-*diphenylmethylene*-2,3-*dihydro*-3-*methylcyclopentaphenanthren*-1-*one* (5) (0·6 g, 36%), bright yellow crystals, m.p. 277—279° (from acetic acid) (Found: C, 90·4; H, 5·4. $C_{31}H_{22}O$ requires C, 90·7; H, 5·4%); $\nu_{max.}$ 1680s cm^{-1} (C=O); $\lambda_{max.}$ 289, 340, and 348 nm (log ε 4·35, 4·28, and 4·26); τ 0·45 (1H, m, 11-H), 1·87—2·78 (17H, complex m, ArH), 5·55 (1H, q, *J* 7 Hz, 3-H), and 8·85 (3H, d, *J* 7 Hz, Me).

Reaction of Diphenylketen with Ketones (5) *and* (6).—When ketone (5) or (6) (1 g) was heated (24 h) with diphenylketen (1·2 g) at 205°, no carbon dioxide was evolved and, on work-up, the ketone was recovered in quantitative yield. The only product of these reactions was tetraphenylcyclobutane-1,3-dione, m.p. 249°, identified by mixed m.p. with an authentic sample. The lack of reaction is attributed to the fact that the carbonyl groups of the ketones are sterically hindered.

Reaction of Diphenylketen with the Benzylidene Ketone (3).—An intimate mixture of diphenylketen (1·3 g) and ketone (3) (2·0 g) was heated (5 h) at 180° under nitrogen. The resulting glass was dissolved in benzene and chromatographed on alumina with light petroleum as eluant.

The first band gave 9a,10-*dihydro*-9-*methyl*-10,15-*diphenyl*-9H-*benz*[5,6]*indeno*[2,1-c]*phenanthrene* (9) (1·5 g, 52%), yellow crystals with an intense green fluorescence, m.p. 231—232° (from acetic acid) (Found: C, 93·8; H, 5·9. $C_{38}H_{28}$ requires C, 94·2; H, 5·8%); $\lambda_{max.}$ 245, 303, 318, 360, 375, and 395 nm (log ε 4·63, 4·14, 4·10, 4·10, 4·07, and 4·05); τ 1·32 (1H, q, J_{ortho} 7 Hz, J_{meta} 2 Hz, 1-H), 2·39—3·60 (complex m, ArH), 5·34 (1H, d, $J_{9,10}$ 9·5 Hz, 10-H), 6·18 (1H, q, $J_{9a,10}$ 9·5 Hz, $J_{9,9a}$ 7 Hz, 9a-H), 6·90 (1H, quintet, *J* 7 Hz, 9-H), and 8·55 (3H, d, *J* 7 Hz, Me).* Irradiation at τ 5·34 caused the 9a-H signal to become a doublet (*J* 7 Hz), at τ 6·20, 10-H to become a singlet, at τ 6·90, 9a-H to become a doublet (*J* 7 Hz), and the methyl signal to become a singlet.*

The second band of the column gave unchanged ketone (3) (0·7 g).

Photorearrangement of Hydrocarbon (9).—The hydrocarbon (9) (0·3 g) in light petroleum (600 ml) was exposed (7 days) to 366 nm radiation from a 125 W mercury-vapour lamp. The pale yellow solution turned colourless. Removal of

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* Coupling constants were misquoted as half the actual values in the preliminary communication.[5]

the solvent, followed by chromatography of the residual oil (0·29 g) on alumina with light petroleum as eluant, gave 5a,6,10b,13e-tetrahydro-5-methyl-6,10b-*diphenyl*-5H-*cyclopenta*[def]*naptho*[8,1,2-pqr]*chrysene* (12a), colourless crystals with a blue fluorescence, m.p. 264—265° (from ethanol–benzene) (0·25 g, 85% yield) (Found: C, 94·05; H, 6·2. $C_{38}H_{28}$ requires C, 94·2; H, 5·8%); $\lambda_{max.}$ 268, 276, and 310 nm (log ε 4·34, 4·31, and 3·83); τ 1·14 (1H, q, J_o 8 Hz, J_m 1 Hz, 10- or 11-H), 1·57 (1H, q, J_o 7 Hz, J_m 2 Hz, 10- or 11-H), 2·28—2·90 and 3·25—3·85 (21H, complex m, ArH), 5·02 (1H, d, J 11·6 Hz, 6- or 13e-H), 5·59 (1H, d, J 12·6 Hz, 6- or 13e-H), 6·00 (1H, quintet, J 8 Hz, 5-H), 6·52 (1H, m, 5a-H), and 8·14 (3H, d, J 8 Hz, Me). Irradiation at τ 5·02 caused the 5a-H signal to become a quartet ($J_{5,5a}$ 8 Hz and $J_{5a,6}$ or $J_{5a,13e}$ 12·6 Hz), irradiation at τ 6·52 caused the 6-H and 13e-H signals to become singlets, irradiation at τ 6·00 caused the methyl signal to become a singlet, and irradiation at τ 8·14 caused the 5-H signal to become a doublet (J 8 Hz).*

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