Dypnopinacol. Part IV.[1] Tautomerism of α- and β-Photodypnopinacolones (6-*exo*- and 6-*endo*-Methyl-1,3,6-triphenylbicyclo[3,1,0]hex-2-en-2-yl Phenyl Ketone)

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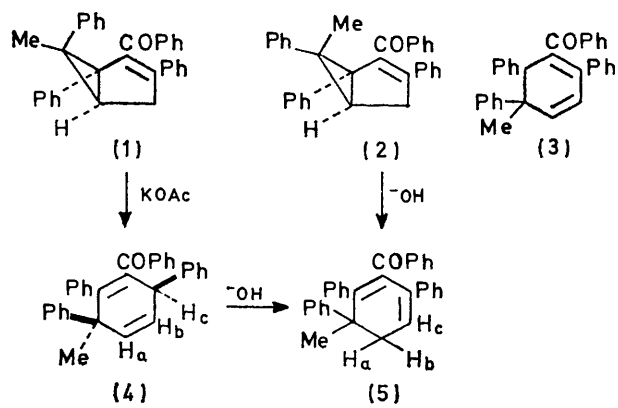
α- and β-Photodypnopinacolones (6-*exo*- and 6-*endo*-methyl-1,3,6-triphenylbicyclo[3,1,0]hex-2-en-2-yl phenyl ketone) are isomerised by bases to give 3-methyl-2,3,6-triphenylcyclohexa-1,5-dienyl phenyl ketone (δ-photodypnopinacolone). Mild base converts the α-isomer into *r*-3-methyl-2,3,*t*-6-triphenylcyclohexa-1,4-dienyl phenyl ketone (γ-photodypnopinacolone), which is converted by stronger base into the δ-isomer.

We have previously[1] shown α- and β-photodypnopinacolone to have structures (1) and (2), respectively. By the action of a weak base,[2] α-photodypnopinacolone is converted into an isomer, γ-photodypnopinacolone. The ^{1}H n.m.r. spectrum of the γ-isomer indicated the presence of a methyl group and three other aliphatic protons, two of which are olefinic. When the isomerisation was carried out in ethan[^{2}H]ol one atom of deuterium was incorporated into the γ-isomer in place of the non-olefinic aliphatic proton. This greatly simplified the n.m.r. spectrum. The olefinic protons appear strongly coupled (J 10 Hz) indicating them to be vicinal

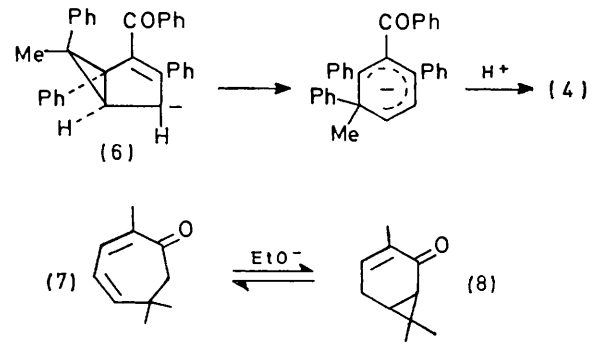


and *cis*, and the isolated aliphatic proton is coupled to both olefinic protons. This suggests the arrangement $CH_a{=}CH_b{\cdot}CH_c$, with H_c replaceable by deuterium. The n.m.r. spectrum is complicated because J_{ab} approximates to the separation between the H_a and H_b signals.

The rearrangement to γ-photodypnopinacolone appears to involve rupture of the cyclopropane ring as there is no strong band in the i.r. spectrum of the γ-isomer in the region 1000—1030 cm^{-1}.[3] Structures (3) and (4) appear likely; the u.v. spectrum ($\lambda_{max.}$ 248 and 259 nm) and the n.m.r. data best fit the latter (4). Structure (3) is not acceptable as it would be expected to show less spin–spin coupling between the aliphatic protons and a u.v. absorption like that of 1,3,5-triphenylcyclohexa-1,3-diene ($\lambda_{max.}$ 254 and 317 nm)[4] or at even longer wavelengths owing to the extra carbonyl conjugation.

The conversion of α-photodypnopinacolone into the γ-isomer is now seen as a 6π-electrocyclic reaction initiated by the enol-stabilised carbanion (6).[5] Reprotonation, after the bond rearrangement, takes place at a point of high electron density and probably from the least hindered side, flanked by a methyl group, to yield structure (4). The boat conformation of cyclohexa-1,4-dienes was discussed in Part II.[6] The structure (4), which allows both phenyl groups attached to sp^3-hybridised carbon atoms to adopt a pseudoequatorial conformation, will be more stable than the stereoisomer where one of these phenyl groups must be pseudoaxial, so we conclude that the stereochemistry of γ-photodypnopinacolone is as given (4).

The conditions which lead to the transformation (1) ⟶ (4) must be carefully controlled otherwise δ-photodypnopinacolone is obtained. In agreement with Delacre, we find that rearrangement of β-photodypnopinacolone in alkali leads directly to the δ-isomer, so we



are unable to check a possibility that the stereochemistry of the conversion (1) ⟶ (4) is influenced by the cyclopropane ring stereochemistry.

Related examples of bond rearrangement in enolate

[1] Part III, C. W. Alexander and J. Grimshaw, preceding paper.
[2] M. Delacre, *Bull. Soc. chim. France*, 1925, [4] **87**, 440; M. Delacre, *Bull. Acad. roy. belg.*, 1896, [3] **32**, 95.
[3] J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482.
[4] G. F. Woods, J. C. Oppelt, and R. B. Isaacson, *J. Amer. Soc.*, 1960, **82**, 5232.
[5] R. B. Woodward and R. Hofmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.
[6] Part II, C. W. Alexander and J. Grimshaw, *J.C.S. Perkin I*, 1972, 1372.

ions are known. A related 6π-system is involved in the reactions of eucarvone (7) to form derivatives of bicyclo[4,1,0]heptene (8).[7] An equilibrium exists between compounds (7) and (8) and the structure of the product, whether a derivative of (7) or of (8), from reactions of eucarvone with a particular reagent depends upon the reagent and conditions used.

Isomerisation of α-, β-, or γ-photodypnopinacolones by alkali yields δ-photodypnopinacolone.[2] This isomer has a long-wavelength u.v. absorption ($\lambda_{max.}$ 250 and 347 nm) indicating a highly conjugated chromophore. The n.m.r. spectrum shows a methyl group and three other aliphatic protons, two at high field and one at low field indicating the system $CH_aH_b{\cdot}CH_c{=}C$. The H_a and H_b resonances appear as a complex group of lines because J_{ab} approximates to the separation between the H_a and H_b signals. One atom of deuterium was incorporated into this isomer, in place of H_a, when the rearrangement was carried out in ethan[^{2}H]ol. This caused a simplification of the ^{1}H n.m.r. spectrum so that J_{ac} and J_{bc} could be estimated (as 6 and 3·5 Hz). The spectral data are best accommodated by structure (5) for δ-photodypnopinacolone. This isomer is the most stable and conjugated product from the action of alkali on the γ-isomer.

EXPERIMENTAL

For general directions see Part III.[1]

γ-Photodypnopinacolone (r-3-*Methyl*-2,3,t-6-*triphenylcyclohexa*-1,4-*dienyl Phenyl Ketone*) (4).—α-Photodypnopinacolone [1] (1·0 g) was suspended in refluxing ethanol (50 ml) and N-potassium hydroxide (0·9 ml) was added. After 6 h under reflux the solution was neutralised with N-sulphuric acid, filtered, and set aside for 8 days. The crystalline deposit (0·63 g) was recrystallised from benzene (2 ml) to give γ-photodypnopinacolone as rhombs, m.p. 169—170° (lit.,[2] m.p. 169°), $\nu_{max.}$ ($CHCl_3$) 1660 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 248 (ε 11,300) and 259 nm (ε 10,800), τ ($CDCl_3$) 8·54 (3H, s, Me), 4·22 (1H, complex, H_a), 4·26 (1H, complex, H_b), 5·10 (1H, q, H_c), and 2·4—3·8 (m, 20H, aromatic), J_{ab} 10, J_{ac} 2·5, J_{bc} 1 Hz, *m/e* 426 (45%, M^+), 411 (30, M^+ — Me), 329 (12), 105 (100, $PhCO^+$), 91 (12), and 77 (42, Ph^+).

The experiment was repeated in ethan[^{2}H]ol with N-potassium deuterioxide and N-deuterium chloride in deuterium oxide. A [$^2H_1$]-γ-photodypnopinacolone was isolated, *m/e* 427 (50%, M^+), 412 (30, M^+ — Me), and 105 (100), τ ($CDCl_3$) as before except the signal at τ 5·10 had disappeared, and $J_{ac} = J_{bc} = 0$; signals at τ 4·22 and 4·26 collapsed to an AB quartet.

δ-Photodypnopinacolone (3-*Methyl*-2,3,6-*triphenylcyclohexa*-1,5-*dienyl Phenyl Ketone*) (5).—(a) α-Photodypnopinacolone (1·0 g) was refluxed for 2 h with a solution of potassium hydroxide (1·0 g) in ethanol (20 ml). The solution was filtered hot, cooled, and set aside for 6 h. The crystalline product crystallised from ethanol as needles (0·49 g, 48%) of δ-photodypnopinacolone, m.p. 139—140° (lit.,[2] 140°), $\nu_{max.}$ 1678 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 250 (ε 30,100) and 347 nm (ε 8000), τ (C_6D_6) 8·62 (3H, s, Me), 4·20 (1H, complex, H_c), 7·37 (2H, complex, H_a + H_b), and 2·1—3·3 (m, aromatic), J_{ac} 6, J_{bc} 3·5 Hz, *m/e* 426 (53%, M^+), 411 (5, $M^+ - CH_3$), 321 (16, M^+ — PhCO), 229 (21), 228 (19), 215 (21), 115 (22), 105 (100, $PhCO^+$), and 77 (45, Ph^+).

The experiment was repeated with a solution of potassium in ethan[^{2}H]ol to give [$^2H_1$]-δ-photodypnopinacolone, *m/e* 427 (50, M^+) and 105 (100, $PhCO^+$), τ (C_6H_6) as before except τ 4·20 (1H, d, H_c) and 7·16 (1H, d, H_b), J_{bc} 3·5 Hz.

(b) β-Photodypnopinacolone [1] (0·06 g) was treated with potassium hydroxide in ethanol as in (a) to give δ-photodypnopinacolone (0·020 g, 33%), m.p. 139—140°.

We thank the Ministry of Education, N. Ireland, for a studentship (to C. W. A.).

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[7] *E.g.*, E. J. Corey, H. J. Burke, and W. A. Remers, *J. Amer. Chem. Soc.*, 1955, **77**, 4941; 1956, **78**, 180.