

Dypnopinacol. Part II.¹ Tautomerism of 4-Methyl-2,4,6-triphenylcyclohexa-2,6-dienyl Phenyl Ketone (Isodypnopinacolone)

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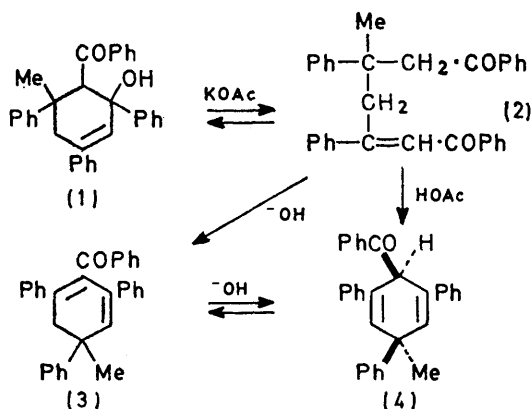
Base-catalysed tautomerisation of 4-methyl-2,4,6-triphenylcyclohexa-2,6-dienyl phenyl ketone (isodypnopinacolone) gives an equilibrium mixture containing 9% of α -homodypnopinacolone. This second ketone is shown to be *t*-4-methyl-2,4,6-triphenylcyclohexa-2,5-dien-*r*-1-yl phenyl ketone.

DYPNOPINACOL (1)¹ undergoes a series of aldol reactions and tautomerisations catalysed by alkali and discovered by Delacre. We have retained the trivial names he employed so as to avoid confusion when referring to his work. Mild base transforms dypnopinacol into α -homodypnopinacol (2) and a stronger base gives isodypnopinacolone (3); the structures of these compounds were discussed in Part I.¹ Delacre² obtained α -homodypnopinacolone by the action of acetic acid on the diketone (2). He demonstrated the conversion of

Fractional crystallisation separated the two isomers. The ¹H n.m.r. spectrum of α -homodypnopinacolone showed the presence of one methyl group, two olefinic protons in identical magnetic environments, and one other aliphatic proton, coupled (*J* 1.5 Hz) with the olefinic protons. When this last proton was replaced by deuterium by treatment with ethan[²H]ol the coupling disappeared. Thus structure (4), without implied stereochemistry, was established. The u.v. spectrum was in accord with a summation of, and no interaction between, acetophenone [λ_{max} 240 nm (ϵ 13,000)] and styrene [λ_{max} 244 nm (ϵ 12,000)] chromophores. There was no evidence from the n.m.r. spectra of crude equilibrium mixtures to indicate the presence of a stereoisomer of (4).

In a series of 4-alkylcyclohexenones the proportion of non-conjugated ketone at equilibrium has been found to vary from 0% for cyclohexenone to 50% for 4-*t*-butylcyclohexenone. Steric effects are thought to be responsible for increasing the stability of the non-conjugated isomer.⁴ The proportion of non-conjugated ketone (4) at equilibrium probably also represents a compromise between the resonance energy and steric strain present in structure (3).

The cyclohexa-1,4-diene ring adopts a boat conformation, and the dimensions of the parent hydrocarbon in the gas phase have been determined from electron diffraction data.⁵ In structure (4) the benzoyl substituent must adopt a pseudoequatorial conformation because the geminal hydrogen atom shows allylic coupling (*J* 1.5 Hz) with the olefinic hydrogen atom. Allylic coupling is usually observed only when the allylic σ -CH bond is in a position of maximum overlap



α -homodypnopinacolone into the isomer (3) by alkali. The conversion of either ketone into an equilibrium mixture by the action of dilute alkali was demonstrated by Terlinck.³ We now present evidence for the structure (4) of α -homodypnopinacolone.

¹H N.m.r. spectra of reaction mixtures confirmed the existence of the equilibrium between α -homodypnopinacolone (9%) and isodypnopinacolone (3) (91%).

¹ Part I, J. Grimshaw and W. B. Jennings, *J. Chem. Soc. (C)*, 1970, 817.

² M. Delacre, *Bull. Acad. roy. belg.*, 1896, [3] 32, 446.

³ E. Terlinck, *Bull. Acad. roy. belg.*, 1904, 1050.

⁴ K. G. Lewis and G. J. Williams, *Tetrahedron Letters*, 1965, 4573.

⁵ H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, 1969, 91, 10; D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2325.

with the olefin π -orbital, that is when the allylic CH is pseudoaxial.⁶

Of the methyl and phenyl groups attached to the second dissymmetric centre, the phenyl group prefers a pseudo-equatorial position. This follows from measurements made on the axial-equatorial conformer ratio of other 4-methyl- and 4-phenyl-cyclohexanol-aluminium chloride complexes where the OAlCl_2 group acts as an equatorial conformation-holding group.⁷ The free energy differences (1.5 and ca. 2.6 kcal mol⁻¹, respectively) between conformers for the two cases are sufficiently far apart to suggest that one stereoisomer of (4), with a pseudoaxial methyl group, will greatly predominate in an equilibrium mixture. Thus the stereochemistry shown (4) can be deduced for α -homodypnopinacolone.

Equilibration in ethan[²H]ol resulted in incorporation of only one atom of deuterium into the recovered isodypnopinacolone (3). This suggests that the cyclohexa-1,3-diene ring adopts one conformation from which one hydrogen atom is preferentially removed on enolisation. The conformation of cyclohexa-1,3-diene in the gas phase has been determined⁵ and the hydrogen atoms attached to C-5 and C-6 have been shown to be distinctly either pseudoaxial or pseudo-equatorial, with *trans*-groups diequatorial, or diaxial. The arguments used in the previous paragraph indicate that phenyl is a conformation-holding group and is pseudo-equatorial. In the ¹H n.m.r. spectrum of [²H₁]isodypnopinacolone (3) the AB quartet due to CH₂ was replaced by a single line with the same τ value as the low-field doublet. This indicates the arrangement *CH₂eqDax* if long-range shielding effects do not invert the usual order where the *Heq* signal appears at lower field than that of *Hax*. Thus in enolisation of compound (3) or its deuterio-derivative it is always the axial C-H or C-D bond which is broken because this has the correct stereochemistry to allow

overlap between the developing carbanion and the π -electron system. In the reverse protonation, or deuteration, of the enol the reagent approaches in an axial direction and *trans* to the adjacent methyl group.

EXPERIMENTAL

For general directions see Part I.¹

4-Methyl-2,4,6-triphenylcyclohexa-2,5-dienyl Phenyl Ketone (α -Homodypnopinacolone) (4).—Isodypnopinacolone (1.0 g) was dissolved in ethanol (30 ml) containing *N*-potassium hydroxide (1.4 ml) and refluxed for 3 h. A sample was removed and diluted with water and the products were isolated with ether. ¹H N.m.r. analysis showed the ratio of isodypnopinacolone (3) to α -homodypnopinacolone (4) to be 10 : 1. The rest of the reaction mixture was allowed to cool, and after 2 h crystals of isodypnopinacolone were collected. The filtrate deposited fluffy needles which were collected after 3 h; addition of water (5 ml) to the filtrate produced a further crop. The last two crops were combined and crystallised from benzene-light petroleum (b.p. 40–60°) to give α -homodypnopinacolone (0.08 g, 8%), m.p. 169–170° (lit.,² 168°), ν_{max} (CHCl₃) 1680 cm⁻¹ (C=O), λ_{max} 214 (ϵ 18,700) and 239 nm (ϵ 17,000), τ (CDCl₃) 8.17 (3H, s, Me), 4.00 (2H, d, olefinic), 4.43 (1H, t) (*J* 1.5 Hz), and 2.3–3.1 (20H, m, aromatic), *m/e* 426 (25%, *M*⁺), 321 (60, *M*⁺ – PhCO), 105 (90, PhCO⁺), 84 (100), and 77 (30).

The experiment was repeated with a solution of potassium in ethan[²H]ol. [²H₁]- α -Homodypnopinacolone had *m/e* 427 (40), 322 (70), and 105 (100). The n.m.r. spectrum (CDCl₃) was unchanged except that the signal at τ 4.43 had disappeared and the signal at τ 4.00 (2H) had collapsed to a singlet. Recovered [²H₁]isodypnopinacolone had τ (CDCl₃) 8.39 (3H, s, Me), 6.77 (1H, s), 3.80 (1H, s, olefinic), and 2.2–3.2 (ca. 20H, m, aromatic). Isodypnopinacolone shows, *inter alia*, τ 7.00 (1H, d) and 6.76 (1H, d) (*J* 16 Hz).¹

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⁶ D. J. Collins, J. J. Hobbs, and S. Sternhell, *Austral. J. Chem.*, 1963, **16**, 1030; S. Sternhell, *Rev. Pure Appl. Chem. (Australia)*, 1964, **14**, 15.

⁷ E. L. Eliel and M. Rerick, *J. Amer. Chem. Soc.*, 1960, **82**, 1367.