

Photoreactions of 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one

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Irradiation of the title compound (3; R = Ph) gives mainly 3a,7a-dihydro-3,4,5,7a-tetraphenylinden-1-one (4) together with the 3,4,7,7a-tetraphenyl isomer (6) and the di- π -methane rearrangement product 1,3,8,9-tetra-phenyltricyclo[4.3.0.0^{2,9}]nona-3,7-dien-5-one (5).

In extension of work on inden-2-ones (1)¹ we considered preparation of unbridged [9]annulenes, *e.g.* (2), by photochemical ring-opening of dihydroindenones (3).² As an initial test of the feasibility of such a route we studied the photochemistry of the readily available³ derivative (3; R = Ph). No evidence for a reaction of the type (3) \rightarrow (2) was obtained. Irradiation of (3; R = Ph) gave one major and two minor photoisomers. The major product, m.p. 188–190°, is probably the unidentified compound similarly obtained by Houk and Northington.⁴ This compound, identified as the dihydroindenone (4), was accompanied by the cyclopropane (5) and the dihydroindenone (6). The constitution (4) is based on the following evidence. Like (3; R = Ph), the isomer (4) showed carbonyl absorption (1706 cm⁻¹) indicative of a cyclopentenone. In the n.m.r. spectrum of (4) the H_b signal appears as a doublet (J_{ab} 2 Hz) at τ 5.37, and one olefinic proton gives a doublet (J_{cd} 10 Hz) at τ 4.15. Resonances for the other olefinic protons are obscured by overlap with aromatic resonance at τ 3.6. The presence of a conjugated diene system in (4) follows from rapid reaction with phenyltriazoline-dione⁵ to give the adduct (7) in which J_{cd} has, as expected, been reduced (to 6.5 Hz). Allylic coupling is no longer observed in the adduct. Reduction of (4) with lithium aluminium hydride gives an alcohol (8) which shows allylic (J_{ab} 1.8 Hz), vicinal (J_{ae} *ca.* 2.2 Hz), and homoallylic coupling (J_{be} *ca.* 2.2 Hz) which supports the positioning of the carbonyl group and the protons H_a and H_b in (4). Hydroxylation of (4) (OsO₄ in pyridine) gave two stereoisomeric diols (9), the n.m.r. spectra of which (J_{cd} *ca.* 3 Hz) substantiate the presence of a di-

substituted double bond in (4). Moreover, in one of the diols (9) homoallylic coupling (J_{bc} *ca.* 2 Hz) serves to locate the double bond in (4) with respect to H_b.

With methanolic hydrogen chloride (4) gives the conjugated isomer (10), ν_{\max} 1693 cm⁻¹, λ_{\max} 365 nm, J_{ab} 17, J_{ac} 6.5, J_{bc} 3 Hz. The similar system (11)⁶ prepared for comparison shows ν_{\max} 1643 and 1676 cm⁻¹, λ_{\max} 390 nm, and geminal coupling of 16 Hz.

The structure of the di- π -methane rearrangement product (5) is consistent with the observed spectroscopic properties (Experimental section). The n.m.r. spectrum shows resonance for H_b at τ 6.18 in agreement with the shift (τ 6.2) reported⁷ for the similar cyclopropane proton in (12). On heating (5) is cleanly converted into (4). This transformation can be interpreted in several ways including a vinylcyclopropane rearrangement to (13) followed by a carbonyl migration (13; arrows) for which there is good precedent.⁸

The photoproduct (6) has spectroscopic properties in accord with the proposed structure. In particular J_{cd} is reduced (to 6.5 Hz) in comparison with the related coupling in (4) and the long-wavelength u.v. band (335 nm) is similar in position and appearance to that shown by the model compound (14) (λ_{\max} 342 nm). The latter was prepared by reaction of *N*-phenylmaleimide with 2,5-diphenylthiophen 1,1-dioxide. As for (6), the n.m.r. spectrum of (14) showed no allylic coupling in the six-carbon ring.

The photoproducts (4)–(6) may arise from a common diradical intermediate (15); radical pairing gives the di- π -methane product (5), whilst 1,2- and 1,4-acyl shifts lead to (4) and (6), respectively. The diradical (15) may be formed by the normal collapse of an initial di- π -methane intermediate (16) to the more stable diradical.⁹

¹ J. M. Holland D. W. Jones, *J. Chem. Soc. (C)*, 1971, 608.

² *Cf.* the preparation of [10]annulenes: E. E. van Tamelen and R. H. Greeley, *Chem. Comm.*, 1971, 601; S. Masamune, K. Hojo, K. Hoso, G. Bigam, and D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4966.

³ C. F. H. Allen and E. W. Spanagel, *J. Amer. Chem. Soc.*, 1933, **55**, 3773.

⁴ K. N. Houk and D. J. Northington, *Tetrahedron Letters*, 1972, 303.

⁵ R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. (C)*, 1967, 1905.

⁶ C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, 1955, **20**, 315.

⁷ N. G. Dauben and J. H. Smith, *J. Org. Chem.*, 1967, **32**, 3244.

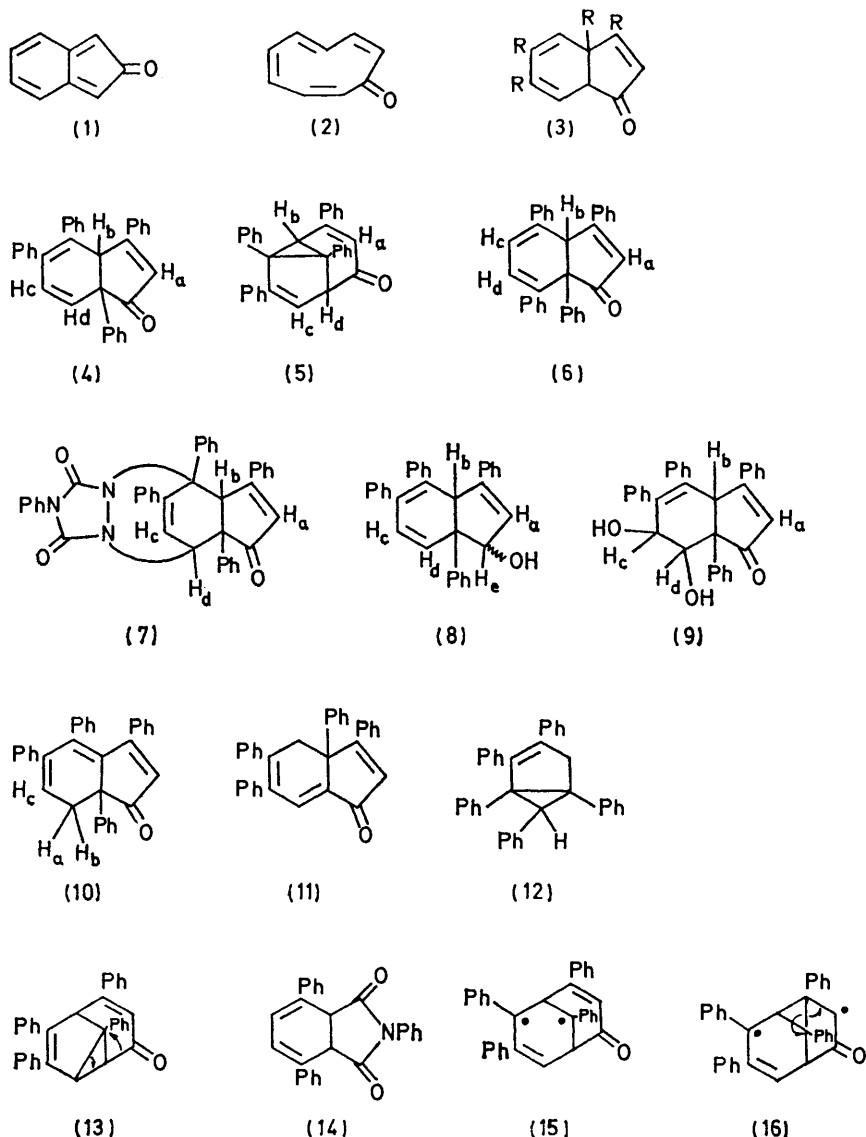
⁸ H. Monti and M. Bertrand, *Tetrahedron Letters*, 1969, 1235; E. Bagglioni, K. Schaffner, and O. Jeger, *Chem. Comm.*, 1969, 1103; M. J. Jorgensen, and A. F. Thacker, *ibid.*, p. 1030.

⁹ H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 1409, 6259, 6269; H. E. Zimmerman and A. A. Baum, *ibid.*, 1971, **93**, 3646.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified, i.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60 spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light

(13H, m), and 2.62 (5H, s). The mother liquor left after removal of the above crystalline solid was evaporated to dryness and chromatographed on silica. Elution with benzene-petroleum (95:5) gave 3a,7a-dihydro-3,4,7,7a-tetraphenylinden-1-one (6) (90 mg), m.p. 155–157° (from ethanol) (Found: C, 90.60; H, 5.65%), ν_{\max} 1702 cm^{-1} , τ 5.46 (1H, d, J 2 Hz), 3.7 (1H, d, J 2 Hz), 3.52 (1H, d,



petroleum (b.p. 60–80°) and chromatography on silica to short-column chromatography over Kieselgel G (Merck).¹⁰

Irradiation of 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one (3; R = Ph).—The title compound (1.7 g) in degassed acetonitrile (100 ml) was irradiated (7.5 h) in a nitrogen-flushed quartz flask placed 2 cm above an Engelhard-Hanovia medium pressure U.V.S. 200 W lamp. The crude product on concentration to small bulk gave 3a,7a-dihydro-3,4,5,7a-tetraphenylinden-1-one (4) (900 mg), m.p. 188–190° (from chloroform-ethanol) (Found: C, 90.65; H, 5.7. $\text{C}_{33}\text{H}_{24}\text{O}$ requires C, 90.8; H, 5.5%), ν_{\max} 1706 cm^{-1} , τ 5.37 (1H, d, J 2 Hz), 4.15 (1H, d, J 10 Hz), 3.65 (4H, m), 3.15

J 7 Hz), 3.34 (1H, d, J 7 Hz), 3.2–2.5 (20H). Further elution of the column gave first a mixture of compounds (3; R = Ph) and (4) (250 mg), then a mixture of (3; R = Ph) and (5) (320 mg). The second mixture was dissolved in benzene and a benzene solution of phenyltriazaolinedione was added dropwise until the red colour just persisted. The product was chromatographed on silica (elution with benzene) to give 1,3,8,9-tetraphenyltricyclo-[4.3.0.0^{2,9}]nona-3,7-dien-5-one (5) (138 mg), m.p. 205–207° (from benzene-petroleum) (Found: C, 90.65; H, 5.65%), ν_{\max} 1664 cm^{-1} , τ 6.18 (1H, s), 6.05 (1H, d, J 2.2 Hz), 3.94

¹⁰ B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

(1H, d, J 2.2 Hz), 3.32 (1H, s), 3.15—2.1 (20H, m). Irradiation of (3; R = Ph) (500 mg) as described above (6 h) gave compounds (4) (270 mg) and (5) (30 mg). The absence of starting material allowed clean separation of the photoproducts by crystallisation and chromatography on silica in benzene-petroleum (95 : 5) as before.

Reactions of 3a,7a-Dihydro-3,4,5,7a-tetraphenylinden-1-one (4).—(a) *With methanolic hydrogen chloride*. The title compound (50 mg) was dissolved in methanol (4 ml). The solution was saturated with dry hydrogen chloride, set aside for 10 min, and evaporated to dryness; the residue was taken up in methanol and the solution evaporated to small bulk. 7,7a-Dihydro-3,4,5,7a-tetraphenylinden-1-one (10) (30 mg) crystallised, m.p. 168—169° (from methanol) (Found: C, 90.65; H, 5.7%), ν_{\max} 1693 cm^{-1} , τ 7.35 (1H, dd, J 17 and 3 Hz), 6.76 (1H, dd, J 17 and 6.5 Hz), 3.95 (1H, dd, J 6.5 and 3 Hz), 3.8 (1H, s), 3.5—2.1 (20H, m).

(b) *With lithium aluminium hydride*. The title compound (100 mg), lithium aluminium hydride (100 mg), and anhydrous ether (10 ml) were boiled under reflux (4 h). Water (2 drops) was added and the mixture was boiled for 2 h. The solution was filtered, dried (MgSO_4), and evaporated, and the residue was crystallised from benzene-petroleum to give 3a,7a-dihydro-3,4,5,7a-tetraphenylinden-1-ol (8) (60 mg), m.p. 175—177° (Found: C, 90.5; H, 5.9. $\text{C}_{33}\text{H}_{26}\text{O}$ requires C, 90.4; H, 6.0%), ν_{\max} 3380 cm^{-1} , τ (CDCl_3 - D_2O) 5.52 (1H, t, J 2.2 Hz), 4.52 (1H, d, J 1.8 Hz), 4.13 (1H, dd, J 2.2 and 1.8 Hz), 3.7—2.2 (22H, complex m, aromatic and olefinic). In the absence of D_2O the hydroxy-resonance appeared at τ 7.96, and the signal at 4.52 was a broad singlet.

(c) *With 4-phenyl-1,2,4-triazoline-3,5-dione*. The photoproduct (80 mg) and dienophile (35 mg) in benzene (5 ml) were set aside for 1 h. Evaporation of solvent and crystallisation from ethanol gave the adduct (7) (90 mg), m.p. 235—239° (decomp.) (Found: C, 80.35; H, 4.85; N, 7.15. $\text{C}_{41}\text{H}_{29}\text{N}_3\text{O}_3$ requires C, 80.5; H, 4.7; N, 6.9%), ν_{\max} 1708, 1720, and 1773 cm^{-1} , τ 5.51 (1H, s, $W_{\frac{1}{2}}$ 1.5 Hz), 4.08 (1H, d, J 6.5 Hz), 3.51 (1H, d, J 6.5 Hz), 3.44 (1H, s), and 3.4—2.2 (25H, m, aromatic).

In the same way the alcohol (8) gave a dihydro-derivative of the adduct (7), m.p. 235—239° (decomp.) (from ethanol) (Found: C, 80.3; H, 5.25; N, 6.55. $\text{C}_{41}\text{H}_{31}\text{N}_3\text{O}_3$ requires C, 80.3; H, 5.1; N, 6.85%), ν_{\max} 1710, 1763, and 3520 cm^{-1} , τ (CDCl_3 - D_2O) 5.7br (1H, s, $W_{\frac{1}{2}}$ 2 Hz), 5.52 (1H, d, J 2.8 Hz), 4.18 (1H, d, J 6 Hz), 4.06 (1H, dd, J 2.8 and 1 Hz), and 3.6—3.0 and 2.9—2.3 (26H, complex multiplets). In the absence of D_2O the hydroxy-resonance appeared at τ 7.9 and the signal at 5.32 was broad.

(d) *With osmium tetroxide*. The photoproduct (4) (197 mg), osmium tetroxide (115 mg), and pyridine (1.5 ml) were stirred for 7 days. A mixture of sodium disulphite (275 mg), water (4.2 g), and pyridine (2.8 ml) was added and stirring was continued (1 h). The product was extracted into methylene chloride, and the extract was washed with

water, dried (MgSO_4), and evaporated to dryness; the residue was chromatographed on silica. Elution with ether-benzene (30 : 70) gave first starting material (4) (30 mg). Continued elution gave one stereoisomer of 3a,6,7,7a-tetrahydro-6,7-dihydroxy-3,4,5,7a-tetraphenylinden-1-one (9) (60 mg), which crystallised from petroleum containing a little chloroform as a chloroform solvate, m.p. 145—149° (Found: M^+ , 470.187. $\text{C}_{33}\text{H}_{26}\text{O}_3$ requires M , 470.188), ν_{\max} (film) 1666 and 3410 cm^{-1} , τ (CDCl_3 - D_2O) 5.5 (1H, d, J 2.5 Hz), 5.33 (1H, d, J 2.5 Hz), 5.28 (1H, d, J 1.5 Hz), 3.54 (1H, d, J 1.5 Hz), 3.5—2.2 (20H, complex m). In the absence of D_2O one hydroxy-proton resonance appeared at τ 7.1br (s) and the other as a sharp doublet (J 8 Hz) at 4.42; the resonance at τ 5.5 was then broad. Continued elution gave a second stereoisomer of (9) (40 mg) which crystallised from petroleum with the aid of chloroform as a solvate, m.p. 118—121° (Found: M^+ , 470.187), ν_{\max} 1689 and 3420 cm^{-1} , τ [$(\text{CD}_3)_2\text{CO}$ - D_2O] 5.21br (1H, dd, J 3 and 2 Hz), 5.08 (1H, d, J 3 Hz), 4.85br (1H, dd, J 2 and 1 Hz), 3.7 (1H, d, J 1 Hz), and 3.3—2.1 (20H, complex m). In the absence of D_2O signals at τ 6.7 (1H, d, J 7.5 Hz) and 6.19 (1H, d, J 5 Hz) due to hydroxy-protons were observed and the signals at 5.21 and 5.08 were complex multiplets.

Pyrolysis of 1,3,8,9-Tetraphenyltricyclo[4.3.0.0^{2,9}]nona-3,7-dien-5-one (5).—The title compound (10 mg) was heated at 200° (15 min) and the cooled product was crystallised from ethanol to give compound (4) (6 mg), identical (mixed m.p. and i.r. spectrum) with material previously prepared.

3a,7a-Dihydro-3,4,7,7a-tetraphenylinden-1-one (6) with 4-Phenyl-1,2,4-triazoline-3,5-dione.—The dihydroindenone (6) (40 mg) in benzene (4 ml) reacted slowly with the dienophile added in portions over 2 h at 0°. Evaporation and crystallisation of the product from ethanol gave an adduct (60 mg), m.p. 225—226° (decomp.) (Found: C, 80.5; H, 4.85; N, 6.55. $\text{C}_{41}\text{H}_{29}\text{N}_3\text{O}_3$ requires C, 80.5; H, 4.7; N, 6.9%), ν_{\max} 1690, 1720, and 1775 cm^{-1} , τ 5.21br (1H, s, $W_{\frac{1}{2}}$ 2 Hz), 3.77 (1H, d, J < 1 Hz), and 3.4—2.2 (27H, complex m).

Reaction of 2,5-Diphenylthiophen 1,1-Dioxide with N-Phenylmaleimide.—The diene (268 mg)¹¹ and dienophile (173 mg) in xylene (15 ml) were boiled under reflux (18 h). The cooled product was filtered to remove an insoluble crystalline solid (120 mg); the mother liquor was evaporated and the residue passed in benzene-ether (95 : 5) down a silica column. The evaporated eluate gave the adduct (14) (180 mg), m.p. 212—214° (from chloroform-ethanol) (Found: C, 82.85; H, 5.0; N, 3.55. $\text{C}_{26}\text{H}_{19}\text{NO}_2$ requires C, 82.7; H, 5.1; N, 3.7%), ν_{\max} 1710 and 1777 cm^{-1} , τ 5.46 (2H, s, $W_{\frac{1}{2}}$ ca. 1 Hz), 3.47 (2H, s, $W_{\frac{1}{2}}$ ca. 1 Hz), and 3.0—2.2 (15H, complex m).

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¹¹ J. L. Melles and H. J. Backer, *Rec. Trav. chim.*, 1953, **72**, 314.