# Photorearrangement of 2,3,3a,7a-Tetrahydro-4,5,6,7-tetraphenylindene

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Irradiation of the title compound (1) gives 1,2,8,9-tetraphenylbicyclo[5.2.0]nona-2,8-diene (5) rather than a cyclopentene (2) or (3) as previously suggested.

DURING work on tetraphenylcyclobutadiene [1] we noted that the tetraphenylindene (1) gave a single photoisomer, which was formulated as a cyclopentene [(2) or (3)]

(1)   (2)   (3)

(4)
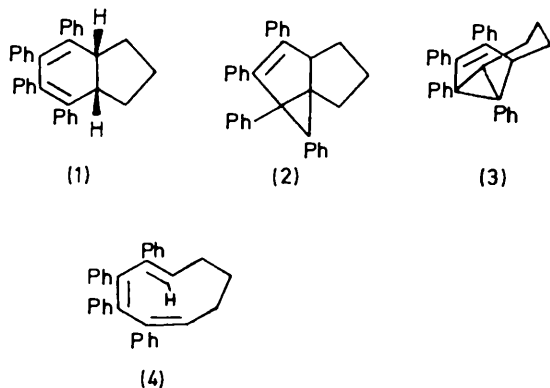
since its u.v. spectrum [$\lambda_{max.}$ (EtOH) 278 nm (ϵ 12,700)] was similar to that of tetraphenylcyclopentene.[2] It was

suggested that structure (3) was derived by initial ring-opening of (1) to a cyclononatriene (4) followed by $\pi^4{}_s + \pi^2{}_a$ addition (photo-Diels–Alder reaction [3]). Although this sequence has since been found to have general validity [4] we subjected photo-(1) to the more probing spectral scrutiny now possible.

The 90 MHz n.m.r. spectrum of the isomer showed an unsymmetrical triplet (1H, J ~8 Hz) at δ 5·85, a double doublet (1H, J 3·25 and 12 Hz) at 3·01, and complex multiplets (4H) and (2H) centred at 2·1 and 1·55 respectively. A double-resonance experiment indicated that the signal at δ 5·85 is due to an olefinic, rather than a shielded aromatic proton, and the structures (2) and (3) are thus eliminated. This was confirmed by hydroxylation of photo-(1) (OsO_4–pyridine) to a diol which lacked the olefinic resonance but showed a broad triplet at δ 4·45 (CHOH). These observations suggested that photo-(1) was derived by closure of a cyclononatriene, e.g. (4) which involved only two of the double bonds present. Other structures for photo-(1) are

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[2] N. O. V. Sonntag, S. Linder, E. J. Becker, and P. E. Spoerri, J. Amer. Chem. Soc., 1953, 75, 2283.
[3] A. Padwa and S. Clough, J. Amer. Chem. Soc., 1970, 92, 5803.
[4] W. G. Dauben, R. G. Williams, and R. D. McKelvey, J. Amer. Chem. Soc., 1973, 95, 3932, and references cited therein.

therefore the cyclobutene (5) and bicyclobutane (6).* The diol derived from (5) would have structure (7). This is consistent with the chemical shift of the cyclobutene proton H-7 [δ 3·01 in (5) and 3·7 in (7)], and with

(5)

(6)

(7)

(8)
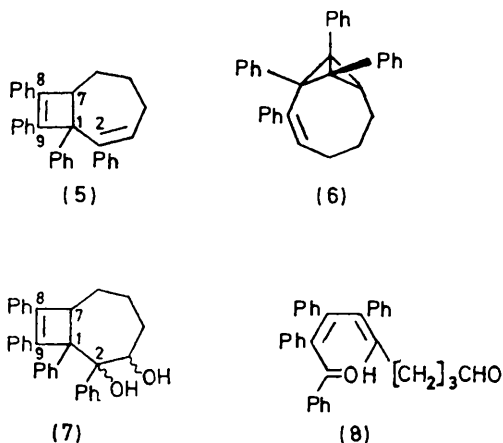
lead tetra-acetate cleavage of the diol to a labile keto-aldehyde (8; or a stereoisomer); polysubstituted cyclobutenes open readily to dienes.[5] However, the diol absorbs at shorter wavelength [$\lambda_{max.}$ (EtOH) 267 nm (ε 13,530)] than known 1,2-diphenylcyclobutenes ($\lambda_{max.}$ 285—303 nm).[6] Whilst conjugation of the C-9 phenyl group with the C(8)–C(9) double bond in (5) and (7) could be inhibited by steric interference with the C-2 phenyl group the observed $\lambda_{max.}$ is at first sight in better agreement with the bicyclobutane formulation (6); 1,3-diphenylbicyclobutanes generally have $\lambda_{max.}$ ~270 nm.[7] However, this absorption, which may depend on overlap of the phenyl π-systems with the central bond of the bicyclobutane (of 96% p-character [8]), is absent in the presence of exo-substituents which presumably inhibit proper orientation of the phenyl groups.† Thus (9; R = H) has $\lambda_{max.}$ 281 nm (ε 13,800) [10] but (9; R = Ph)


(9)

(10)
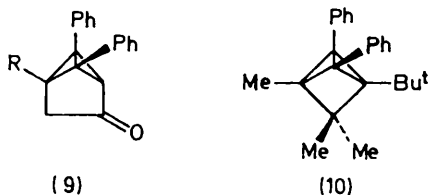
shows only a shoulder at 243 nm (ε 16,982).[11] Since (9; R = Ph) should be the better model for the chromophore in the diol derived from (6) structure (5) must be

* If the splittings of the olefinic (H-3) proton resonance (J 12 and 3·5 Hz) are due to the adjacent CH_2 protons, these cannot then be equivalent. The 4-CH_2 protons in (5) are not equivalent even if the conformation of the cycloheptene ring is inverting rapidly, whereas they are equivalent in (6) unless the cyclooctane ring is inverting slowly: this is suggested by examination of a model, which indicates a large barrier to inversion in (6).

† In this respect the homotetrahedrane (10) [$\lambda_{max.}$ 272 nm (ε 4467)] [9] is exceptional, perhaps because inclusion of the CMe_2 bridge moves the exo-substituents downwards away from the vicinity of the phenyl groups. Conjugation would be lost when the phenyl groups and the central bond of the bicyclobutane are coplanar. The methyl groups on the bridge might inhibit such a conformation thus ensuring conjugation.

preferred for photo-(1). Structure (5) is also suggested by the failure of photo-(1) to react with trifluoroacetic acid under ambient conditions. A firm decision in favour of structure (5) was made on the basis of the proton decoupled [13]C n.m.r. spectrum of photo-(1). The three methylene carbons appear at δ 19·97, 24·99, and 28·84 (relative to internal Me_4Si), the cyclobutene C-7 resonates at 56·61, and the cyclobutene C-1 as a less intense signal at 62·28. The other (sp^2) carbons appear below δ 126. Since structure (6) would be expected to show resonance for seven carbons in the upper field region it is clearly untenable. In the analogous bicyclobutane (11) the carbons of the bicyclobutane skeleton resonate at the δ values shown.[12]

In boiling xylene (5) is converted into the trans-tetrahydroindene (12) which has u.v. absorption very

(11)

(12)
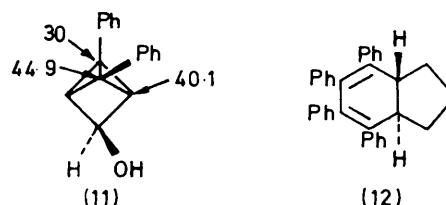
similar to that of (1). This transformation presumably [13] involves conrotatory opening to the cyclononatriene (4) which undergoes disrotatory closure to (12). The diol (7) is unchanged on similar heating. Conceptually, the simplest route from (1) to (5) involves photo-induced conrotatory opening to (4) followed by thermal closure to the cyclobutene. Comparable thermal ring closure of cis-trans-cyclo-octa-1,3-diene has been noted.[14] These arguments favour a cis-ring fusion for (5), but we do not consider that a trans-stereochemistry is ruled out.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform measured either with a Varian A60 or a Bruker spectrometer at 90 MHz (^{1}H spectra) and 22·63 MHz (^{13}C spectrum). Mass spectra were obtained with an A.E.I. MS 902 instrument. Petroleum refers to light petroleum

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[6] A. T. Blomquist and E. A. LaLancette, J. Org. Chem., 1964, 29, 2331; A. T. Blomquist and Y. C. Meinwald, J. Amer. Chem. Soc., 1957, 79, 5317; 1959, 81, 667; H. H. Freedman, and M. Frantz, ibid., 1962, 84, 4165; R. M. Dodson and A. G. Zielske, J. Org. Chem., 1967, 32, 28.

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[13] Cf. P. Radlick and W. Fenical, Tetrahedron Letters, 1967, 4901; K. M. Schumate and G. J. Fonken, J. Amer. Chem. Soc., 1965, 87, 3996; 1966, 88, 1073; E. Vogel, W. Grimme, and E. Dunne, Tetrahedron Letters, 1965, 391.

[14] R. S. H. Liu, J. Amer. Chem. Soc., 1967, 89, 112.

(b.p. 60—80°) and chromatography on silica to short-column chromatography over Kieselgel G (Merck).[15]

1,2,8,9-*Tetraphenylbicyclo*[5.2.0]*nona*-2,8-*diene* (5).— 2,3,3a,7a-Tetrahydro-4,5,6,7-tetraphenylindene (1) was irradiated, and the photo-product was isolated, as previously described.[1] The product formed rods (from ethanol), m.p. 124—125° [Found: C, 93·4; H, 6·7%; M (Osmometer), 400; M^+, 424·218. Calc. for $C_{33}H_{28}$: C, 93·35; H, 6·65%; M^+, 424·219], δ_H (90 MHz) 1·55 (2H, m), 2·1 (4H, m), 3·01 (1H, dd, J 3·25 and 12 Hz), 5·85 (1H, t, J 8 Hz), 6·55 (2H, m), 6·83 (8H, m), 7·33 (8H, m), and 7·83 (2H, m), δ_C (22·63 MHz) 19·97, 24·99, and 28·84 [C(4)—C(6)], 56·61 [C(7)], 62·28 [C(1)], 126·61—128·72 (aromatic carbons), and 134·51, 136·53, 142·19, 142·97, 143·23, 144·14, and 144·33 [olefinic C(2), C(3), C(8), C(9), and substituted aromatic carbons].

Thermolysis of Compound (5).—The photo-product (5) (70 mg) was heated in boiling xylene (4 ml) in a nitrogen atmosphere (8·5 h). Progress of the reaction was monitored by u.v. spectroscopy and the u.v. spectrum of the product changed little after 5 h heating. The n.m.r. spectrum of the crude product obtained by evaporation of xylene under reduced pressure was that of trans-2,3,3a,7a-*tetrahydro*-4,5,6,7-*tetraphenylindene* (isolated below) and indicated the absence of the corresponding *cis*-isomer. The product crystallised from ethanol (30 mg), m.p. 162—164° (Found: C, 93·05; H, 6·5%), $\lambda_{max.}$ 322 nm (ε 12,660), δ 7·04 (10H), 6·76 (10H), 3·0 (2H, m), and 2·0—1·0 (6H, m).

Hydroxylation of Compound (5).—The photo-product (5) (167 mg), osmium tetraoxide (100 mg), and pyridine (1·5 ml) were stirred (4 days). The product was stirred with sodium disulphite (209 mg), water (3·2 g), and pyridine (2·1 ml) (1 h). The product was extracted into methylene chloride, and the extract was washed with water, dried (MgSO₄),

and evaporated to dryness; the residue was chromatographed on silica. Elution with benzene–ether (9 : 1) gave first a non-polar fraction which was discarded, and then 1,2,8,9-*tetraphenylbicyclo*[5.2.0]*non*-8-*ene*-2,3-*diol* (7) (66 mg) as a noncrystallisable foam (Found: M^+, 458·225; $M^+ - H_2O$, 440·214. $C_{33}H_{30}O_2$ requires M, 458·224; $M - H_2O$, 440·213), $\nu_{max.}$ 3460 and 3600 cm⁻¹, $\lambda_{max.}$ 267 nm (ε 13,530), δ (CDCl₃–D₂O) 2·0br (3H, m), 2·30br (3H, m), 3·7br (1H, dd, J 9 and 6 Hz), 4·45br (1H, t, $J \sim 5$ Hz), and 6·6—7·5 (20H, m). In the absence of D₂O the hydroxy-protons appeared at δ 1·48 and 3·04, and the signal at δ 4·4 was a broad singlet. The yield of diol dropped to 25% when the reaction time was extended to 32 days.

Cleavage of the Diol (7) *with Lead Tetra-acetate*.—The diol (7) (130 mg) in methylene chloride (4 ml) was treated with lead tetra-acetate (130 mg) (15 min). The solution was washed with water, dried (MgSO₄), and evaporated at room temperature under reduced pressure. 9-*Oxo*-6,7,8,9-*tetraphenylnona*-5,7-*dienal* (8) crystallised when freshly prepared but on attempted recrystallisation or on standing at room temperature it was partly converted into a second substance as indicated by n.m.r. spectroscopy and t.l.c. in benzene. Freshly prepared crystalline samples were used for the measurement of spectra (Found: M^+, 456. $C_{33}H_{30}O_2$ requires M, 456). The base peak in the mass spectrum corresponds to $M - [CH_2]_3CHO$ (tetraphenylpyrylium cation?), $\nu_{max.}$ 1655, 1715, and 2700 cm⁻¹, δ 1·17 (2H, quint, J 7 Hz), 1·88 (4H, 4 br lines, $J \sim 7$ Hz), 5·72 (1H, t, J 7·5 Hz), 6·8—7·4 (18H, m, aromatic), 7·9 (2H, m, aromatic), and 9·4 (1H, t, $J \sim 1$ Hz).

[15] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.