

Preparation and Dimerisation of 2-Phenylinden-1-one

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The preparation of 2-phenylindenone and its conversion into truxone-type photodimers (the tetrahydrocyclobuta-di-indenediones (6) and (7) and a Diels–Alder-type dimer {the tetrahydrobenz[*a*]indeno[2.1-*c*]fluorene-5,10-dione (5)} are described.

THE red diketone (1), which has been the subject of an X-ray structural determination,¹ is obtained in place of the expected 2-phenylinden-1-one (2) in the cyclisation of 2-phenylcinnamoyl chloride,¹ in the pyrolysis or base-induced dehydrobromination of 2-bromo-2-phenylindan-1-one, and from oxidation of 1-bromo-2-phenylindene with dimethyl sulphoxide.² 2-Phenylinden-1-one (2), hitherto known only as its oxime prepared directly from 2-phenylindene,³ could not be obtained by an otherwise flexible synthesis of indenones.⁴

Reduction of the indane-1,3-dione, a route used to prepare indenone,⁵ has now been adapted for the preparation of 2-phenylinden-1-one. Reduction of 2-phenylindane-1,3-dione with zinc and acetic acid gave two stereoisomeric hydroxy-ketones (3) and (4), from which the former (3) was isolated. Repetition of an earlier hydrogenation of 2-phenylindane-1,3-dione,⁶ yielded the isomer (4). The hydroxy-ketones (3) and (4) are readily dehydrated to 2-phenylinden-1-one by boiling briefly in dilute methanolic hydrochloric acid, but when high concentrations of hydroxy-ketones are used the dimer (5) is the main product. Dehydration in acid of the hydroxy-ketones (3) and (4) contrasts with the behaviour of indenone itself, which adds water or other solvents in the presence of acid.⁵

2-Phenylinden-1-one is an orange crystalline ketone that yields colourless, less soluble products during recrystallisation; however a boiling dilute solution in carbon tetrachloride is stable for 24 h in the absence of light. In daylight colourless crystals are deposited, and we have isolated three of the four possible truxone-type photodimers [(6) and (7) with either *syn*- or *anti*-configuration about the central ring].

Conversion of 2-phenylinden-1-one into the dimer (5) takes place readily in acidic solutions: in trifluoroacetic acid, the dimer (5) is the only product and the dimerisation is complete within 15 min at room temperature. It was identified from its reactions and its spectra. It is dehydrogenated to the diketone (1) by selenium dioxide, it has three non-aromatic protons, one exchangeable in alkali, and it is acidic enough to give reversibly an orange salt (8) even with ammonia (this can be used for locating it on thin-layer plates). Its u.v. spectrum shows a large shift in alkali, almost identical with that exhibited by 2-

¹ A. L. Bednowitz, W. C. Hamilton, R. Brown, L. G. Donaruma, P. L. Southwick, R. Kropf, and R. A. Stanfield, *J. Amer. Chem. Soc.*, 1968, **90**, 291.

² S. Wawzonek, G. R. Hansen, and A. R. Zigman, *Chem. Comm.*, 1969, 6.

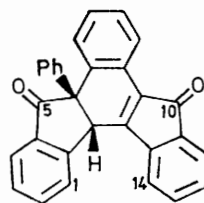
³ E. Bergmann and W. Schreiber, *Ber.*, 1933, **66**, 44.

⁴ M. B. Floyd and G. R. Allen, *J. Org. Chem.*, 1970, **35**, 2647.

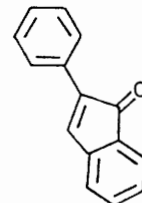
⁵ P. H. Lacy and D. C. C. Smith, *J. Chem. Soc. (C)*, 1971, 41.

⁶ T. T. Dumpis and G. Vanags, *Doklady Akad. Nauk S.S.S.R.*, 1962, **142**, 92.

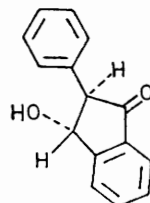
phenylindan-1-one except that the absorption of the latter does not have a shoulder in the visible region;



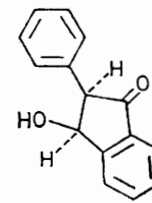
(1)



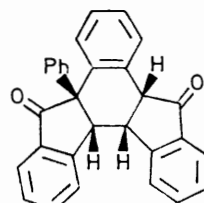
(2)



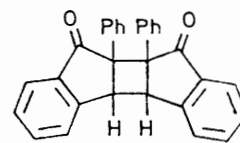
(3)



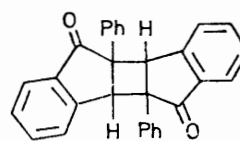
(4)



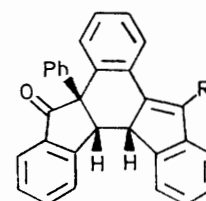
(5)



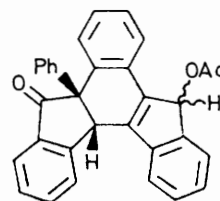
(6)



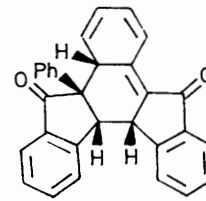
(7)

(8) R = O⁻ M⁺

(9) R = OAc



(10)



(11)

benzyl phenyl ketone gives a similar anion spectrum but only in more concentrated alkali. Acetate-catalysed acetylation of the dimer (5) leads to the acetate (10), but

in the presence of sufficient acetic acid the reaction stops at the enol acetate stage (9), presumably because in a sufficiently protic medium, acetate anion is not basic enough to promote the prototropic rearrangement (9) \rightleftharpoons (10).

The stereochemistry of the dimer (5) throws light on the mechanism of dimerisation of 2-phenylinden-1-one in acidic solutions. The dimer (5) and its enol acetate (9) presumably have the same *cis*-5a,14c-configuration as the diketone (1).¹ The dimer (5) and its enol acetate (9) both have a distinctive one-proton n.m.r. signal, at τ 4.9 and 3.9, respectively, and spin decoupling identifies these as due to aromatic protons, since each shows vicinal coupling with protons resonating in the aromatic region, at τ 3.0 and 2.6, respectively. Protons close to and axial to an aromatic ring are shielded by it, and models reveal this to be so for a proton at position 1 or 14 depending on which way the molecule is twisted, provided that the 5a,14c and 9b,14b ring junctions are in a *syn*-relationship, as shown in the formulae (5) and (9).

The *cis, syn, cis*-configuration thus derived for the dimer (5) shows that the dimerisation of 2-phenylinden-1-one is not only stereospecific, as are most Diels-Alder reactions, but that it also obeys Alder's *endo* rule.⁷ This is consistent with a concerted cycloaddition mechanism, and the presumed initial product of addition, between 2-phenylinden-1-one acting as a diene and its conjugate acid acting as a dienophile, is the species (11), which can isomerise into the dimer (5) *via* the enol or the enolate (8) without disturbing the *syn*-configuration of the central ring.

EXPERIMENTAL

trans-3-Hydroxy-2-phenylindan-1-one (3).—2-Phenylindane-1,3-dione (from benzylidenephthalide,⁸ by isomerisation with sodium methoxide⁹) (2 g) and acetic acid (50 ml) were warmed to give a clear solution, then stirred at 40° as zinc powder (5 g) was added. The temperature rose to 50° and the reaction then subsided. The mixture was stirred for 0.5 h, then filtered, and the solids were washed with acetic acid. Filtrate and washings were combined, concentrated *in vacuo* below 50°, and diluted with ethyl acetate. The solution was washed with aqueous sodium hydrogen carbonate, dried (MgSO₄), and concentrated. Redissolution in carbon tetrachloride followed by concentration (twice) afforded a pale yellow glass (2.2 g). N.m.r. spectroscopy showed this to consist of the epimeric hydroxyketones (3) and (4). Chromatography on silica gave 2-phenylindenone (2) (0.05 g) (eluted with benzene) and *trans*-3-hydroxy-2-phenylindan-1-one (3) (1.73 g) [eluted with ethyl acetate-benzene (1 : 9)] as yellowish crystals, m.p. 85–87° (Found: C, 80.1; H, 5.5. C₁₅H₁₂O₂ requires C, 80.3; H, 5.4%); ν_{\max} (CHCl₃) 3600, 3450, 1720, and 1610 cm⁻¹; λ_{\max} (MeOH) 244, 283, 290, and 315sh nm (log ϵ 4.02, 3.29, 3.29, and 2.65); τ (CDCl₃) 2.3–3.1 (9H, m), 4.9br (1H, sharpening after D₂O exchange to d, *J* 4 Hz), 6.1br (1H, s, exchange-

able in D₂O), and 6.5 (1H, d, *J* 4 Hz); *m/e* 224 (*M*⁺, 98%) and 178 (100%).

cis-3-Hydroxy-2-phenylindan-1-one (4).—2-Phenylindane-1,3-dione (1.12 g) in ethyl acetate was hydrogenated over palladium-charcoal at atmospheric pressure for 1.5 h; the orange colour of the dione was discharged in half this time, and uptake of hydrogen reached 255 ml. Removal of the solid and concentration gave colourless prisms (from carbon tetrachloride) (201 mg) (m.p. 115–120°; *cf.* ref. 6); τ (CDCl₃) 2.1–3.0 (9H, m), 4.5br (1H, sharpening after D₂O exchange to d, *J* 7 Hz), 5.9 (1H, d, *J* 7 Hz), and 8.1br (1H, s, exchangeable in D₂O).

The doublets (*J* 4 and 7 Hz) in the spectra of compounds (3) and (4) are attributed to these isomers respectively by analogy with *J*_{trans} and *J*_{cis} of indanone (respectively 3.49 and 8.65 Hz).¹⁰

2-Phenylinden-1-one (2).—3-Hydroxy-2-phenylindan-1-one (100 mg) in boiling methanol (10 ml) was treated with concentrated hydrochloric acid (0.5 ml) and boiled under reflux for 20 min. The solution was then concentrated *in vacuo* and extracted with ethyl acetate. The extract was washed with sodium hydrogen carbonate solution, dried (Na₂SO₄), and concentrated to an orange oil. This was chromatographed on a short column of silica gel (benzene as eluant) to give 2-phenylinden-1-one as orange prisms (62 mg), m.p. 75–76°. Recrystallisation from petroleum (b.p. 60–80°) resulted in losses due to formation of insoluble substances, but gave a *product* of m.p. 81–83° (Found: C, 87.1; H, 4.6. C₁₅H₁₀O requires C, 87.4; H, 4.8%); ν_{\max} (CHCl₃) 1715 and 1605 cm⁻¹; λ_{\max} (MeOH) 261, 275sh, 300sh, and 430 nm (log ϵ 4.51, 4.32, 3.24, and 3.24); τ (CDCl₃) 2.2–3.1 (m); *m/e* 206 (100%), 178 (31), 176 (21), and 152 (11), *m*^{*} 153.5 (206 \rightarrow 178), and 129.5 (178 \rightarrow 152). Carried out on a larger scale, this dehydration gave proportionately less 2-phenylindenone.

5a,9b,14b,14c-Tetrahydro-5a-phenylbenz[a]indeno[2,1-c]-fluorene-5,10-dione (5).—(a) 2-Phenylinden-1-one (395 mg) in trifluoroacetic acid (20 ml) gave a clear deep red solution whose colour faded. After 15 min, t.l.c. and n.m.r. spectroscopy showed that only compound (5) was present. Concentrated *in vacuo* and recrystallisation from benzene-chloroform gave colourless prisms, m.p. 272–282°, decomposing to an orange melt (Found: C, 87.1; H, 4.8. C₃₀H₂₀O₂ requires C, 87.3; H, 4.9%); ν_{\max} (CS₂) 1730 and 1720 cm⁻¹; λ_{\max} (EtOH) 245, 299, 319, and 355sh nm (log ϵ 4.38, 4.02, 4.09, and 3.58); λ_{\max} (ethanolic 0.1N-KOH) 246, 293sh, 362, and 450sh nm (log ϵ 4.30, 4.02, 4.24, and 3.56); τ (CDCl₃) 2.0–3.1 (16H, m), 4.9 (1H, d, *J* 7 Hz, collapsing to s on irradiation at τ 2.96), and 5.7–6.1 (3H, m, collapsing to 2H, s at τ 5.9 with NaOD in D₂O); *m/e* 412 (*M*⁺, 100%), 394 (25), 307 (12), 294 (12), and 206 (12); *m*^{*} 376.8 (412 \rightarrow 394), 239 (394 \rightarrow 307), and 210 (412 \rightarrow 294).

(b) 3-Hydroxy-2-phenylindan-1-one (6.4 g) in methanol (60 ml) and concentrated hydrochloric acid (3 ml) was boiled under reflux; solid separated and after 20 min this was collected, washed with methanol, and dried (3.3 g). Two recrystallisations from benzene-chloroform gave the dimer (5) (1.4 g).

Photodimers from 2-Phenylinden-1-one.—2-Phenylinden-1-one (398 mg) in ethanol-free chloroform (2 ml) was exposed to full daylight in a narrow tube for 1 week, during which time large colourless crystals were deposited. These were col-

⁷ H. Wollweber in 'Methoden der Organischen Chemie (Houben-Weill)', Thieme Verlag, Stuttgart, 1970, p. 789.

⁸ R. Weiss, *Org. Synth.*, 1933, 13, 10.

⁹ F. Nathanson, *Ber.*, 1893, 26, 2576.

¹⁰ S. Forsen, B. Gestblom, R. A. Hoffman, and S. Rodmar, *J. Mol. Spectroscopy*, 1966, 21, 372.

lected, washed with carbon tetrachloride, and dried (197 mg). The filtrate was concentrated to a fluffed glass. Both products were separated into their constituents by preparative t.l.c. on silica, developed with benzene. The crystals contained only the truxones A and B (see Table); the filtrate, as well as yielding more of these, contained the truxone C, some 2-phenylinden-1-one, some of the red diketone (1), and an unidentified compound, $C_{30}H_{18}O_3$, m.p. 328—330° (6% yield). Truxones A—C all had similar mass spectra: m/e 412 (M^+ , 0.5%) and 206 (100%).

Photodimers (tetrahydrodiphenylcyclobutadienediones) from 2-phenylinden-1-one

Truxone	R_F (C_6H_6)	M.p. (°C)	$\nu_{max.}$ ($CHCl_3$) cm^{-1}	τ ($CDCl_3$) (2H s)	Found * %C	%H	Yield %
A	0.48	339—340	1705	5.25	87.4	4.9	40
B	0.24	317—320	1705	5.37	87.5	4.9	25
C	0.15	230—232	1715	5.14	87.7	4.9	12

* $C_{30}H_{20}O_2$ requires C, 87.3; H, 4.9%.

Dehydrogenation of the Dimer (5).—The dimer (5) (99 mg) and selenium dioxide (54 mg) were boiled under reflux for 3 h in benzene (20 ml) and 2-methylpropan-2-ol (20 ml), the colour gradually becoming deep orange. Removal of the solvents *in vacuo* left a crystalline residue that was resolved on a preparative silica thin-layer plate (20 × 20 × 0.2 cm) developed with chloroform. The orange zone of R_F 0.5 yielded a red solid, still smelling of selenium (105 mg). This was triturated with acetone and drained giving 5a,14c-dihydro-5a-phenylbenz[a]indeno[2,1-c]fluorene-5,10-dione (1) (69 mg) as red prisms, m.p. and mixed m.p.¹ 264—266°, $\nu_{max.}$ (CS_2) 1718 cm^{-1} ; τ ($CDCl_3$) 1.6 (1H, q), 1.9—3.1 (16H, m), and 5.3 (1H, s); m/e 410 (100%).

Alkali Shifts in Absorption Spectra.—(a) 2-Phenylindan-1-one: ¹¹ $\lambda_{max.}$ (EtOH) 245, 286sh, 294, and 325sh nm (log ϵ 4.07, 3.40, 3.43, and 2.86); $\lambda_{max.}$ (ethanolic 0.1N-KOH) 359 nm (log ϵ 4.13); τ (CD_3OD) 2.0—3.0 (9H, m), 5.9—7.0 (3H, m); τ (NaOD in CD_3OD) 2.0 (2H, d, J 7 Hz), 2.3—3.1 (7H, m), and 6.6 (2H, s).

(b) Benzyl phenyl ketone: ¹² $\lambda_{max.}$ (EtOH) 243, 280sh, and 325sh nm (log ϵ 4.13, 3.18, and 2.81); $\lambda_{max.}$ (ethanolic 27% KOH) 347 nm (log ϵ 3.99).

10-Acetoxy-10,14c-dihydro-5a-phenylbenz[a]indeno[2,1-c]-

fluorene-5(5aH)-one(10).—The dimer (5) (111 mg) and potassium acetate (50 mg) were boiled under reflux for 1 h in acetic anhydride (10 ml). The mixture was diluted with ethyl acetate, washed with water, then concentrated *in vacuo* to a glass that was resolved on a preparative silica thin-layer plate (20 × 20 × 0.2 cm) developed twice with benzene. The zone fluorescing yellow in near u.v. light (R_F 0.3) yielded a glass (127 mg) that was recrystallised from acetone-hexane giving compound (10) (63 mg), probably a mixture of 10-epimers, as small cream needles, m.p. 187—249° (Found: C, 84.3; H, 5.0. $C_{32}H_{22}O_3$ requires C, 84.6; H, 4.9%); $\nu_{max.}$ (CS_2) 1742, 1720, and 1232 cm^{-1} ; $\lambda_{max.}$ 243, 250sh, 294sh, 313sh, 326sh, 335, and 354sh nm (log ϵ 4.47, 4.40, 3.95, 4.07, 4.13, 4.15, and 3.96); τ ($CDCl_3$) 2.0—3.2 (18H, m), 5.3 (1H, s), and 7.8 (3H, s); m/e 454 (M^+ , 79%), 412 (26), 411 (79), 410 (37), 394 (63), 393 (100), and 289 (53), m^* 373.8 (454 → 412) and 342 (454 → 394).

10-Acetoxy-14b,14c-dihydro-5a-phenylbenz[a]indeno[2,1-c]-fluorene-5(5aH)-one (9).—The dimer (5) (140 mg) and acetic anhydride (20 ml) were boiled under reflux while aqueous 10% sodium acetate (0.5 ml) was added dropwise, then boiled for 0.5 h. The mixture was diluted with ethyl acetate, washed with water, then concentrated *in vacuo* to a glass that was chromatographed on a preparative silica thin-layer plate (20 × 20 × 0.2 cm) developed four times with benzene. The zone fluorescing blue in near-u.v. light (R_F 0.2) yielded crystals (99 mg) which afforded colourless prisms (65 mg), m.p. 285—286° (from carbon tetrachloride) (recrystallised again from benzene for analysis) (Found: C, 84.5; H, 4.9. $C_{32}H_{22}O_3$ requires C, 84.3; H, 4.9%); $\nu_{max.}$ (CS_2) 1777, 1718, and 1192 cm^{-1} ; $\lambda_{max.}$ (EtOH) 241, 256sh, 290, 301, 313, and 352sh nm (log ϵ 4.37, 4.29, 4.23, 4.25, 4.27, and 3.65); τ ($CDCl_2$) 2.1—3.0 (16H, m), 3.9br (1H, dd, collapsing to s on irradiation at τ 2.6), 5.75 (1H, d, J 5 Hz), 5.9 (1H, d, J 5 Hz), and 7.7 (3H, s); m/e 454 (M^+ , 16%), 412 (100), and 394 (55), m^* 373.8 (454 → 412).

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¹¹ P. C. Jocelyn, *J. Chem. Soc.*, 1954, 1640.

¹² C. F. H. Allen and W. E. Barker, *Org. Synth.*, 1932, 12, 16.