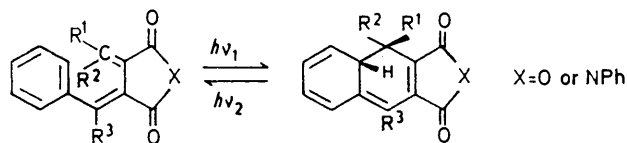


Overcrowded Molecules. Part XII.¹ Thermal and Photochemical Reactions of (2Z,3Z)- and (2Z,3E)-2-Benzylidene-2,3-dihydro-3-mesityl(phenyl)-methylenebenzofuran

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(2Z,3Z)-2-Benzylidene-2,3-dihydro-3-mesityl(phenyl)methylenebenzofuran thermally isomerises to the (2Z,3E)-diene, which undergoes thermal disrotatory ring closure followed by a [1,5] hydrogen shift to yield *cis*-5a,6-dihydro-11-mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan. Irradiation of the (2Z,3Z)-diene causes conversion into the (2Z,3E)-diene and photocyclisation by the conrotatory mode to the *trans*-6,7a-dihydro-intermediate, which undergoes a [1,5] hydrogen shift to give the *trans*-5a,6-dihydrobenzofuran derivative at 80 °C or above, and is oxidised by oxygen.

PHOTOCHROMISM in fulgides and fulgimides² is due to reversible photochemical conrotatory ring closure to give highly coloured 1,8a-dihydronaphthalene intermediates³ (Scheme 1). The failure to observe photochromism in 1,2-bis(arylmethylene)indanes, such as



SCHEME 1

(3c and d),^{1,4} which undergo a similar photochemical electrocyclic reaction at ambient temperatures, could be due to one or a combination of two factors: (i) a low concentration of the photocoloured intermediate (7c or d) at the photostationary state and (ii) a thermal

[1,5] hydrogen shift which is much faster than photocyclisation so that the photocoloured intermediate is removed as it is formed. If the energy of the transition state is constant, an assumption which is not necessarily valid,⁵ then the rate of the thermal [1,5] hydrogen shift should be significantly lowered when the methylene group is replaced by oxygen in the intermediate (7) because the activation energy for the shift will increase as the intermediate (7) is made more stable. The indene and benzofuran units in the intermediates (7d and a) will stabilise these systems by *ca.* 14 and 150 kJ mol⁻¹ respectively.^{6,7} If the rate of the thermal [1,5] hydrogen shift is the critical factor, 2,3-bis(arylmethylene)-2,3-dihydrobenzofurans such as (2a) and (3a) should be photochromic.

The diene (2b), from the reaction of diphenylketen with (*Z*)-2-benzylidenebenzofuran-3(2*H*)-one (1a), is difficult to obtain pure and in good yield because it

¹ Part XI, J. S. Hastings, H. G. Heller, H. Tucker, and K. Smith *J.C.S. Perkin I*, 1975, 1545.

² R. J. Hart and H. G. Heller, *J.C.S. Perkin I*, 1972, 1321.

³ H. G. Heller and M. Szewczyk, *J.C.S. Perkin I*, 1974, 1487.

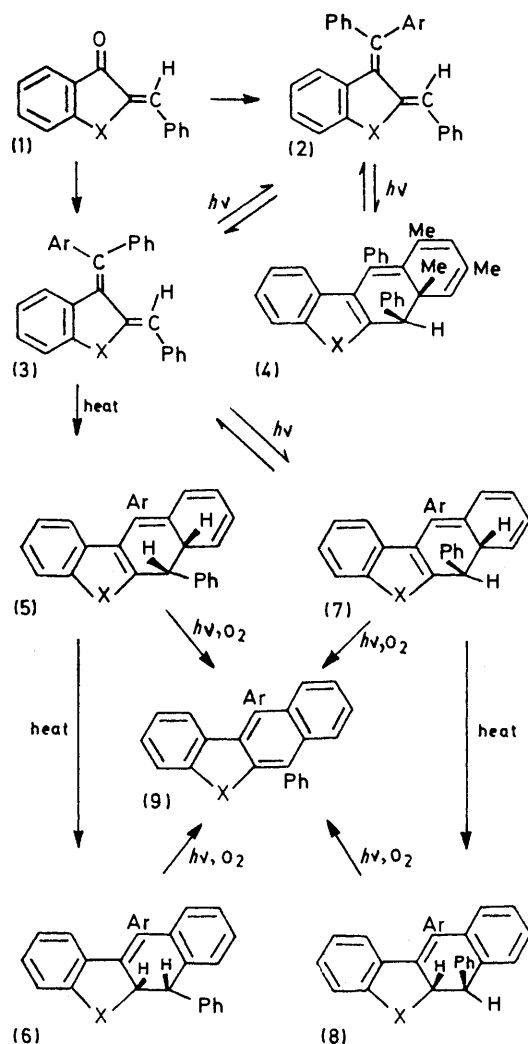
⁴ H. G. Heller and K. Salisbury, *J. Chem. Soc. (C)*, 1970, 399.

⁵ D. Peters, *J. Chem. Soc.*, 1960, 1274.

⁶ G. W. Wheland, 'Resonance in Organic Chemistry,' Wiley, London, 1955, p. 98.

⁷ M. J. S. Dewar, A. J. Hargett, and N. Trinajstić, *J. Amer. Chem. Soc.*, 1969, **91**, 3396.

tends to undergo a 1,4-addition reaction with diphenylketen through its carbonyl double bond to give a vinyl ether.⁸ The less reactive mesityl(phenyl)keten does not react further with the 4:1 mixture of dienes (2a) and (3a) obtained by interaction of mesityl(phenyl)keten



- a; X = O, Ar = 2,4,6-Me₃C₆H₂
 b; X = O, Ar = Ph
 c; X = CH₂, Ar = Ph
 d; X = CH₂, Ar = 2,4,6-Me₃C₆H₂

SCHEME 2

and the ketone (1a) at 56 °C. The stereochemistry of the dienes (2a) and (3a) is assigned on the basis that the mesityl group exerts a greater shielding effect¹ on the olefinic proton in the (2*Z*,3*Z*)-diene (2a) (τ 4.85) than does the phenyl group in the (2*Z*,3*E*)-isomer (3a) (τ 4.65). This assignment is consistent with the observation that interaction of mesityl(phenyl)keten and the ketone (1a) at 140 °C gave the diene (2a) and the *cis*-5a,6-dihydrobenzofuran (6a), and that the diene (2a) is stable at 140 °C but isomerises to the diene (3a) at

180 °C, which at this temperature and presumably at 140 °C also, undergoes disrotatory ring closure and a [1,5] hydrogen shift to give the *cis*-dihydrobenzofuran (6a) ($J_{5a,6}$ 8 Hz).^{4,8} In the reaction of mesityl(phenyl)keten and the ketone (1a) at 140 °C, it is assumed that the *cis*-dihydro-compound (6a) results from rearrangement of the diene (3a).

The 4:1 mixture of the dienes (2a) and (3a) was crystallised once from ethanol and tiny orange needles of the diene (3a) were separated by hand from yellow crystals of the diene (2a) and recrystallised from ethanol (m.p. 166–167°). The diene (3a) could not be isolated by fractional crystallisation or column chromatography. The diene (2a), m.p. 178–179°, was purified by crystallisation from ethanol.

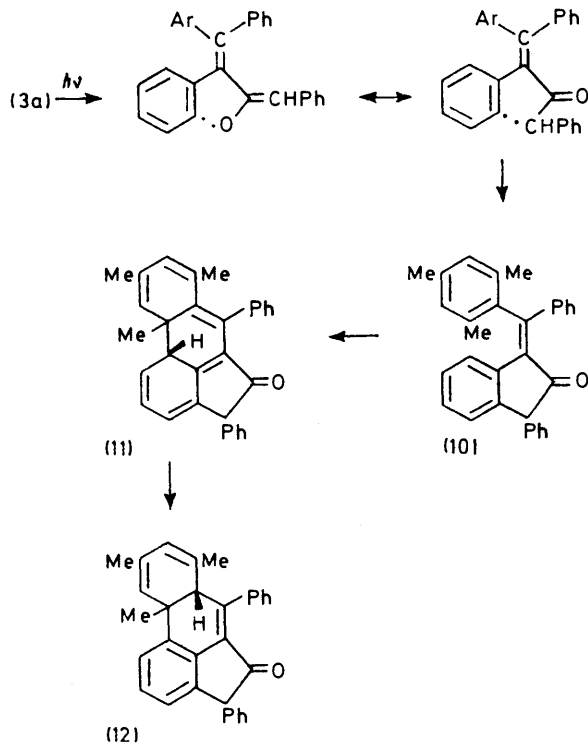
10⁻⁵M-Solutions of the dienes (2a) and (3a) in cyclohexane saturated with oxygen⁹ were irradiated at 366 nm at room temperature and the oxidation was followed by u.v. spectroscopy. The dienes were rapidly oxidised quantitatively to the benzofuran (9a) and the rate of removal of the dienes, monitored by the change in the absorption at the maxima of the long-wavelength bands, followed first-order kinetics and was the same (k 1.33 × 10⁻² min⁻¹) for both dienes. Therefore the rate-determining step is not photochemical isomerisation, (2a) → (3a), which would have changed the stereochemistry of the dienes, but photocyclisation of the diene (3a). Prolonged irradiation of 10⁻⁵M-solutions of the dienes in cyclohexane (17 h) at 20 °C under oxygen-free nitrogen⁴ resulted in no significant change in the u.v. spectra. The solution was saturated with oxygen and irradiated further; it then became colourless within 3 min and showed the characteristic u.v. spectrum of the benzofuran (9a). Irradiation of the diene (2a) in petroleum at 20 °C for 75 h at 366 nm under nitrogen with rigorous exclusion of oxygen caused no detectable change other than formation of a trace of the benzofuran (9a). Neither the diene (3a) nor other isomerisation products could be detected by n.m.r. spectroscopy or t.l.c. On irradiation under similar conditions but in the presence of oxygen, the diene (2a) was quantitatively oxidised to the benzofuran (9a) within 2 h. That photochemical conversion of (2a) into (3a) followed by photochemical conrotatory ring closure to the *trans*-6,7a-dihydrobenzofuran (7a) had taken place was established by irradiating the diene (2a) in cyclohexane under oxygen-free nitrogen at 80 °C, a temperature high enough to promote the thermal suprafacial [1,5] hydrogen shift in the intermediate (7a) but too low to induce electrocyclic ring closure of the diene (3a). No photorearrangement of the diene (2a) took place below 80 °C and no thermal rearrangement occurred below 140 °C. Work-up of mixture from the photoreaction at 80 °C gave a 1:1 mixture of the *trans*-5a,6-dihydrobenzofuran (8a) (J 15 Hz) [cf. (8c)]⁴ and the benzofuran (9a), m.p. 242–243°, which

⁸ J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 1439.

⁹ F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

could not be separated or enriched in one component by fractional crystallisation from a variety of solvents. The composition of the mixture followed from the relative intensities of characteristic methyl absorptions of the two components at τ 7.52 and 7.61. Irradiation of the mixture in cyclohexane in the presence of oxygen gave a quantitative yield of the benzonaphthofuran (9a).

A second crop of crystals, m.p. 217–218°, was obtained from the photoreaction at 80 °C. This product is tentatively assigned the structure (12) from com-



SCHEME 3

bustion analysis and molecular weight determination, an i.r. absorption at 1720 cm^{-1} (C=O), and n.m.r. signals at τ 9.07 (aliphatic Me), 8.20 and 8.50 ($2 \times$ Me), and 5.38 (CH). Treatment of the solution with a drop of hydrochloric acid caused the three methyl absorptions to coalesce to a singlet at τ 8.70 and loss of the absorption at 5.38. A possible mechanism for formation of the photoproduct (12) is light-induced homolytic fission of the furan nucleus¹⁰ in the diene (2a) and radical recombination to give the ketone (10) (reminiscent of the photorearrangement of diaryl ethers¹¹), which undergoes ring closure followed by a [1,5] hydrogen shift.

This study shows that, like 1,2-bis(arylmethylene)-indanes, 2,3-bis(arylmethylene)-2,3-dihydrobenzofurans undergo thermal disrotatory and photochemical con-

rotatory electrocyclic processes in accord with the Woodward–Hoffmann rules.¹² The failure to detect photochromism in the latter system is believed to be due to the equilibrium of the reversible photocyclisation lying heavily on the side of the diene, as is the case for the *cis*-stilbene cyclisation reaction.¹³ The stabilisation of the intermediate (7a) by the benzofuran unit is shown by the temperature (80 °C) required to promote the [1,5] hydrogen shift; for comparison, the intermediate (7d) readily undergoes a hydrogen shift at 20 °C.

EXPERIMENTAL

Molecular weights were determined with an A.E.I. MS902 mass spectrometer. U.v. spectra were measured for solutions in cyclohexane with a Unicam SP 8001A spectrometer and n.m.r. spectra for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring photochemical reactions, when an external standard was used). Chromatography was carried out with Spence type H alumina. Petroleum refers to the fraction of b.p. 60–80°. All solvents were dried and distilled before use. Photoreactions under oxygen-free conditions were carried out as described previously.²

Reaction of Mesityl(phenyl)keten with (Z)-2-Benzylidenebenzofuran-3(2H)-one (1a).—The ketone (1a)¹⁴ (0.75 g) and mesityl(phenyl)keten¹⁵ (0.8 g) were heated (9 h) at 56 °C. The product was chromatographed (benzene). The orange first fraction yielded a *ca.* 4 : 1 mixture of the dienes (2a) and (3a) (0.8 g) after crystallisation from ethanol. Orange needles of (2Z,3E)-2-benzylidene-2,3-dihydro-3-mesityl(phenyl)methylenebenzofuran (3a) were separated by hand and recrystallised from ethanol; yield 3 mg, m.p. 166–167°, λ_{max} 288, 375, and 400 nm ($\log \epsilon$ 4.75, 4.59, and 4.63), τ 2.01–3.30 (16 H, complex m, ArH), 4.65 (1 H, s, :CH·), 7.98 (3 H, s, *p*-Me), and 8.03 (6 H, s, *o*-Me). The composition of the mixture and the n.m.r. spectrum of the diene (3a) followed from a comparison of the n.m.r. spectrum of the mixture with that of pure (2Z,3Z)-2-benzylidene-2,3-dihydro-3-mesityl(phenyl)methylenebenzofuran (2a) (0.50 g), obtained by recrystallisation of the mixture from ethanol as yellow crystals, m.p. 178–179° (Found: C, 90.2; H, 6.35. $\text{C}_{31}\text{H}_{26}\text{O}$ requires C, 89.9; H, 6.3%), λ_{max} 288 and 400 nm ($\log \epsilon$ 4.33 and 4.24), τ 2.4–3.3 (16 H, complex m, ArH), 4.85 (1 H, s, :CH·), 7.60 (3 H, s, *p*-Me), and 7.75 (6 H, s, *o*-Me) [*cf.* (Z)-2-benzylidene-2,3-dihydro-3-diphenylmethylene-5-methylbenzofuran (2b)].⁶

The ketone (1a) (1.1 g) and mesityl(phenyl)keten (1.8 g) were heated (4 h) at 140 °C. The mixture was chromatographed (1 : 10 benzene–petroleum). The first, yellow fraction gave the (Z,Z)-diene (2a) (1.1 g) as yellow crystals, m.p. 178–179° (from propan-2-ol). The second, blue-fluorescent fraction yielded *cis*-5a,6-dihydro-11-mesityl-6-phenylbenzo[b]naphtho[2,3-d]furan (6a) (0.5 g), m.p. 147–148° (from propan-2-ol) (Found: C, 89.9; H, 6.3. $\text{C}_{31}\text{H}_{26}\text{O}$ requires C, 89.9; H, 6.3%), λ_{max} 248, 295, 304, 358, and 375 nm ($\log \epsilon$ 4.41, 4.08, 4.07, 4.41, and 4.38), τ 2.5–3.6 (14 H, complex m, ArH), 3.85 (1 H, d, *J* 7 Hz, 4-H), 4.02 (1 H, d, *J* 8 Hz, 5a-H), 5.22 (1 H, d, *J* 8 Hz, 6-H), and 7.59,

¹⁰ R. Srinivasan, *J. Amer. Chem. Soc.*, 1967, **89**, 4812.

¹¹ N. C. Yang, P. Kumler, and S. S. Yang, *J. Org. Chem.*, 1972, **37**, 4022.

¹² R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

¹³ K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 1967, 662.

¹⁴ J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 2128.

¹⁵ R. C. Fuson, L. J. Armstrong, J. W. Kneisley, and W. J. Shenck, *J. Amer. Chem. Soc.*, 1944, **66**, 1464.

7.86, and 8.07 (9 H, three s, *o*- and *p*-Me) {cf. *cis*-5a,6-dihydro-6,11-diphenylbenzo[*b*]naphtho[2,3-*d*]furan (6b)}.⁶

ca. 10⁻⁴M-Solutions of the dienes (2a) and (3a) and the *cis*-dihydrobenzophenanthofuran (6a) in cyclohexane saturated with oxygen gave, on irradiation at 366 nm, 11-mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan (9a), identified by its characteristic u.v. spectrum.

Thermal and Photochemical Reactions of the (Z,Z)-Diene (2a).—The (Z,Z)-diene (2a) (100 mg), on heating (24 h) at 180 °C under nitrogen, gave *cis*-5a,6-dihydro-11-mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan (6a), m.p. 147–148° (70 mg) (from propan-2-ol).

11-Mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan (9a) was obtained in quantitative yield from the (Z,Z)-diene (2a) (0.2 g) in petroleum (200 ml) saturated with oxygen on irradiation (4 h) at 366 nm; m.p. 238° (from xylene or ethanol) (Found: C, 89.7; H, 5.85. C₃₁H₂₄O requires C, 90.2; H, 5.9%), λ_{max.} 265, 288, 313, 325, 344, and 360 nm (log ε 5.04, 4.30, 4.28, 4.56, 4.19, and 4.22), τ 2.00–3.32 (15 H, complex m, ArH), 7.52 (3 H, s, *p*-Me), and 8.16 (6 H, s, *o*-Me) {cf. 6,11-diphenylbenzo[*b*]naphtho[2,3-*d*]furan (9b)}.⁶ On irradiation (75 h), the (Z,Z)-diene (2a) (0.2 g) in petroleum (200 ml) under nitrogen with rigorous exclusion of oxygen underwent no detectable change. T.l.c. of the material after irradiation showed no rearrangement products and the diene (2a) (0.15 g) was recovered after crystallisation from propan-2-ol.

To ascertain the temperature at which thermal rearrangement of the (Z,Z)-diene (2a) occurred, samples (5 ml) of a 10⁻⁵M-solution of the diene in cyclohexane in ampoules were deaerated by immersion in liquid nitrogen, evacuating the tube, thawing the contents, and repeating the procedure three times. The ampoule was sealed and heated (17 h) at various temperatures. The solution was cooled and the u.v. spectrum determined. No thermal rearrangement occurred at 140 °C or below. No photo-rearrangement occurred below 80 °C on irradiation at 366 nm of the 10⁻⁵M-solution of the (Z,Z)-diene (2a) in cyclohexane with rigorous exclusion of oxygen.

The (Z,Z)-diene (2a) (0.50 g) in boiling cyclohexane (80 ml) was irradiated (48 h) under nitrogen with

rigorous exclusion of oxygen. Solvent was removed and the residue recrystallised from ethanol. The first crop of colourless crystals (0.32 g) consisted of a 1:1 mixture of *trans*-5a,6-dihydro-11-mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan (8a) and 11-mesityl-6-phenylbenzo[*b*]naphtho[2,3-*d*]furan (9a), m.p. 242–243°, which could not be separated or even enriched in one component by recrystallisation from a variety of solvents (Found: M⁺, 414.20 and 412.18. Calc. for C₃₁H₂₆O: M, 414.20. Calc. for C₃₁H₂₄O: M, 412.18), τ 1.98–3.45 (complex m, ArH), 3.75 (1 H, d, J 8 Hz, 10-H shielded by mesityl), 4.29 (1 H, d, J 15 Hz, 5a- or 6-H), 5.54 (1 H, d, J 15 Hz, 5a- or 6-H), and 7.61, 7.74, and 8.10 (9 H, three s, *o*- and *p*-Me). The composition of the mixed crystals follows from the integrals of methyl absorptions of the two components at τ 7.52 and 7.61. The n.m.r. spectrum of the *trans*-dihydrobenzophenanthofuran (8a) was established by a comparison of the n.m.r. spectrum of the mixed crystals with that of the benzophenanthofuran (9a).

A solution of the mixed crystals (m.p. 242–243°; 75 mg) in cyclohexane (80 ml) saturated with oxygen was irradiated for 1 h. Removal of the solvent left the benzophenanthofuran (9a), m.p. 238° (from ethanol), in quantitative yield.

A second crop of yellow crystals gave a ketone [possibly (12)] (85 mg), m.p. 217–218° (from toluene-petroleum) (Found: C, 89.9; H, 6.3%; M⁺, 414.20. Calc. for C₃₁H₂₆O: C, 89.8; H, 6.3%; M, 414.20), ν_{max.} 1720s cm⁻¹ (C=O), τ 2.53–2.73 (10 H, two s, ArH), 2.78–3.16 and 3.9–4.4 (6 H, m, olefinic H), 5.38 (1 H, s, CH), 8.19 (3 H, s, Me), 8.49 (3 H, s, Me), and 9.07 (3 H, s, Me).

On treatment with one drop of 38% hydrochloric acid, the ketone (25 mg) in [²H]chloroform (0.4 ml) rearranged. The n.m.r. spectrum showed τ 2.31–3.24 (15 H, complex m, ArH), 3.71 (1 H, d, J 9 Hz, 7-H shielded by mesityl), and 8.70 (9 H, s, *o*- and *p*-Me).

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