

The Irradiation of 2-Methylbenzophenone in the Presence of Dienophiles

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The u.v. irradiation of 2-methylbenzophenone in the presence of the dienophiles, dimethyl acetylenedicarboxylate, tetracyanoethylene, dimethyl maleate, dimethyl fumarate, 4-hydroxybut-2-enoic acid lactone, and crotonaldehyde has been examined and the constitutions of the phenyltetralin products elucidated.

SINCE the initial report by Yang that some *o*-alkylbenzophenones underwent photochemical enolization on u.v. irradiation,¹ considerable effort has been expended on the details of energy and geometric changes involved in the process and the nature of the transient intermediates. Notable contributions have been made,²⁻⁵ and techniques as diverse as flash spectroscopy, product trapping by dienophiles, deuterium exchange, and identification of oxidation products have been used. Evidence now points to the formation of both geometric isomeric enols, in the most general case, (1*Z*) and (1*E*) from 2-methylbenzophenone (1), with the less stable (1*Z*) having a shorter life-time in aprotic solvents due to rapid internal reketonization, and the more stable (1*E*) being the form trapped by dienophiles.^{6,7}

¹ (a) N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; (b) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Amer. Chem. Soc.*, 1963, **85**, 2671.

² J. N. Pitts, jun., H. W. Johnson, jun., and T. Kuwana, *J. Phys. Chem.*, 1962, **66**, 2456.

³ (a) G. Porter and M. R. Topp, *Proc. Roy. Soc.*, 1970, *A*, **315**, 163; (b) G. Porter and M. F. Tchir, *Chem. Comm.*, 1970, 1372; (c) A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2051.

Our interest in this reaction lay in the potential application, as yet little exploited, in synthesis. The conversion of 2-methylbenzophenone (1), by u.v. irradiation in the presence of dimethyl acetylenedicarboxylate to the adduct (2)¹ prompted the expectation that judicious choice of appropriate benzophenones and dienophiles would provide attractive syntheses of lignans. A novel and convenient entry, for example, might be provided to three common naturally occurring lignan types, the aryltetralins of which at least two

⁴ (a) W. A. Henderson, jun., and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5424; (b) E. F. Ullman and K. R. Huffman, *Tetrahedron Letters*, 1965, 1863; (c) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417; (d) E. F. Ullman, *Accounts Chem. Res.*, 1968, **1**, 353; (e) K. R. Huffman, M. Loy, W. A. Henderson, jun., and E. F. Ullman, *J. Org. Chem.*, 1968, **33**, 3469; (f) K. R. Huffman, M. Loy, W. A. Henderson, jun., and E. F. Ullman, *Tetrahedron Letters*, 1967, 931.

⁵ (a) M. Pfau, N. D. Heindel, and T. F. Lemke, *Compt. rend.*, 1965, **261**, C, 1017; (b) N. D. Heindel, E. W. Sarver, and M. A. Pfau, *Tetrahedron Letters*, 1968, 3579; (c) M. Pfau, E. W. Sarver, and N. D. Heindel, *Compt. rend.*, 1969, **268**, C, 1167; (d) N. D. Heindel, J. Molnar, and M. Pfau, *Chem. Comm.*, 1970, 1373.

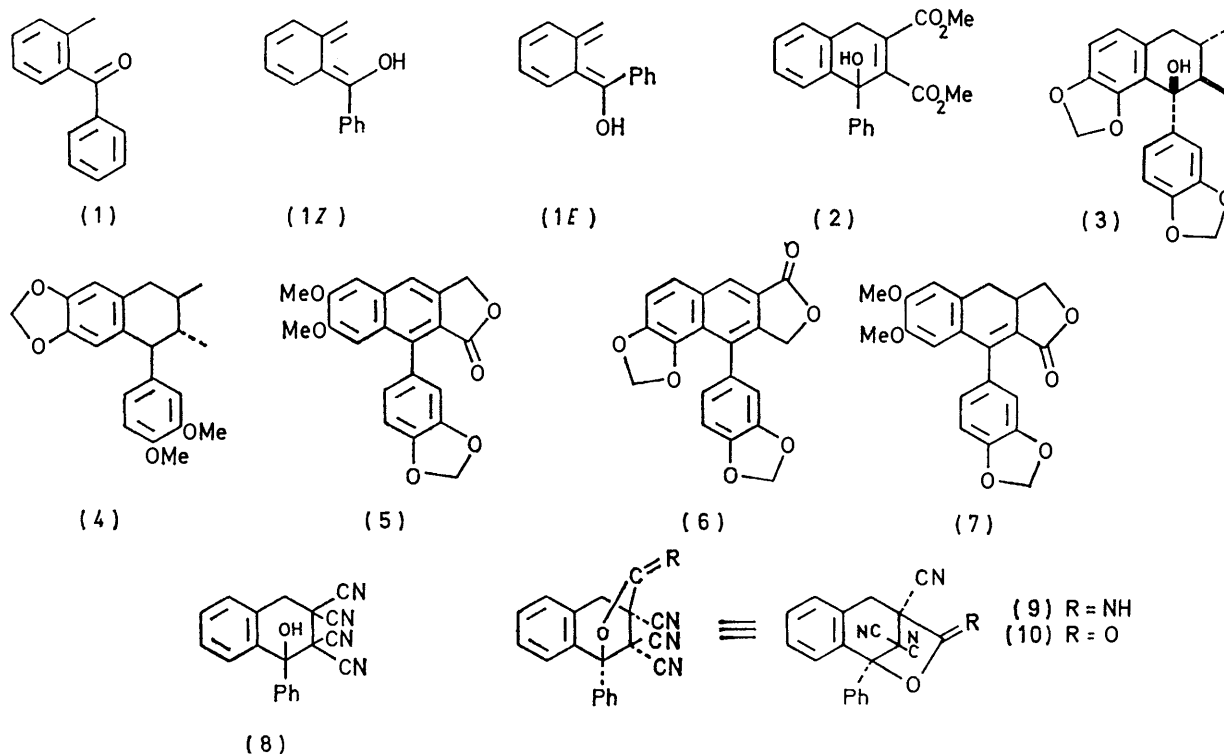
⁶ F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.

⁷ S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.

dozen members are known [*e.g.* hydroxytobain (3)⁸ and galcatin (4)⁹], the aryl-naphthalenes [at least thirteen members known, *e.g.* justicidin B (5)^{10,11} and helioxanthin (6)¹²] and the aryl-dihydronaphthalenes [*e.g.* collinusin (7)¹¹].

We have examined the photoirradiation of 2-methylbenzophenone (1) in the presence of the dienophiles (*a*)

tion of the reaction mixture, had a molecular weight (mass spectrum) and empirical analysis for a 1 : 1 adduct; since it absorbs, however, in the i.r. region at 3322 (NH) and 1721 (C=N) cm^{-1} , we consider that the adduct should be formulated as the cyclic imide (9). In another experiment in which the product was purified by silica gel chromatography, there was obtained in



dimethyl acetylenedicarboxylate, (*b*) tetracyanoethylene, (*c*) dimethyl maleate, (*d*) dimethyl fumarate, (*e*) 4-hydroxybut-2-enoic acid lactone, and (*f*) crotonaldehyde, with a view to finding convenient experimental conditions and establishing the stereochemistry of the addition process. A study⁶ of the irradiation of (1) with maleic anhydride, maleic acid, and fumaric acid complements this work.

The product we obtained in 53% yield by irradiation of compound (1) with dimethyl acetylenedicarboxylate had constants in excellent agreement with those reported¹ and the n.m.r. and mass spectra fully supported the suggested structure (2).

We chose next to examine the reaction with tetracyanoethylene, since no problem of configurational assignment would exist with the expected adduct (8). The product, obtained in 22% yield by direct crystalliza-

tion of the reaction mixture, had a molecular weight (mass spectrum) and empirical analysis for a 1 : 1 adduct; since it absorbs, however, in the i.r. region at 3322 (NH) and 1721 (C=N) cm^{-1} , we consider that the adduct should be formulated as the cyclic imide (9). In another experiment in which the product was purified by silica gel chromatography, there was obtained in

addition to (9) a product $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_2$ whose i.r. spectrum lacks OH or NH absorption, but displays a carbonyl band at 1805 cm^{-1} . We consider this product to be the corresponding lactone (10), formed from (9) by partial hydrolysis.

¹⁰ (a) K. Munakata, S. Marumo, K. Ohta, and Y.-L. Chen, *Tetrahedron Letters*, 1967, 3821; (b) K. Ohta, Y.-L. Chen, S. Marumo, and K. Munakata, *Agric. Biol. Chem.*, 1969, **33**, 610; (c) M. Okigawa, T. Maeda, and N. Kawano, *Tetrahedron*, 1970, **26**, 4301.

¹¹ (a) T. R. Govindachari, S. S. Sathe, N. Viswanathan, B. R. Pai, and M. Srinivasan, *Tetrahedron*, 1969, **25**, 2815; (b) E. Block and R. Stevenson, *Chem. and Ind.*, 1970, 894.

¹² (a) R. S. Burden, L. Crombie, and D. A. Whiting, *J. Chem. Soc. (C)*, 1969, 693; (b) T. L. Holmes and R. Stevenson, *Tetrahedron Letters*, 1970, 199; *J. Chem. Soc. (C)*, 1971, 2091.

⁸ (a) T. Gilchrist, R. Hodges, and A. L. Porte, *J. Chem. Soc.*, 1962, 1780; (b) R. Wallace, A. L. Porte, and R. Hodges, *ibid.*, 1963, 1665; (c) F. Kohen, I. Maclean, and R. Stevenson, *J. Chem. Soc. (C)*, 1966, 1775; (d) T. B. H. McMurry and H. K. Kennedy-Skipton, *Tetrahedron Letters*, 1966, 975.

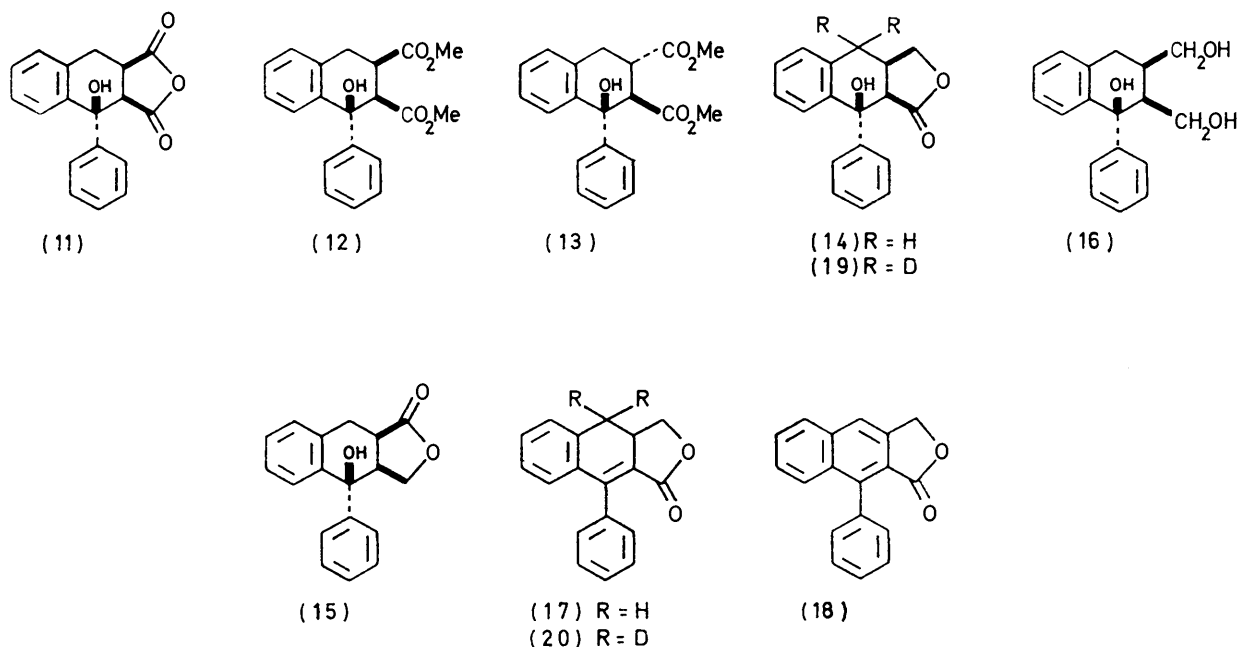
⁹ (a) G. K. Hughes and E. Ritchie, *Austral. J. Chem.*, 1954, **7**, 104; (b) A. W. Schrecker and J. L. Hartwell, *J. Amer. Chem. Soc.*, 1955, **77**, 432; (c) S. M. Adjangba and D. Billet, *Bull. Soc. chim. France*, 1962, 1970.

reaction of compound (1) with fumaric acid, followed by diazomethane treatment. It has been assigned the *trans*-diester structure ⁶ (13).

Our interest ^{11,12} in developing new routes to phenyltetralin lactones led us to examine the irradiation of the ketone (1) with 4-hydroxybut-2-enoic acid lactone, previously reported to be a rather unreactive dienophile.^{13,14} We have found that this lactone, for which convenient preparative procedures now exist,^{15,16} under the standard irradiation conditions in benzene solution yielded an adduct in 7% yield. When conducted in refluxing benzene solution, the yield was increased to 50%, supporting our belief that the cycloaddition is a thermal

characterized by dehydrogenation to the phenyltetralin lactone (18).

The lactone (17) has a highly characteristic spectrum which has been computer analysed.¹⁸ The five non-benzenoid protons give an absorption pattern of at least 18 lines, the six most downfield of which appear as two pseudo-triplets centred at δ 4.02 and 4.72. These have been ascribed to the lactone protons, the triplet appearance being a consequence of the surprising similarity of the vicinal, *cis*- and *trans*-coupling constants (all *ca.* 9 Hz). We sought to confirm this assignment by synthesis of the corresponding lactone with deuterium at the C-4 benzylic positions. The 4,4-dideuterio-*cis*- γ -lactone (19)



process involving the ground state enol. The mass spectrum and elemental analysis indicated that the product was a 1 : 1 adduct and the presence of a hydroxy-group and γ -lactone function was apparent from the i.r. spectrum. Reduction with lithium aluminium hydride yielded a triol (16) identical with that produced by similar reduction of the anhydride (11). The adduct accordingly could be formulated as either (14) or (15). A distinction in favour of structure (14) was possible from various features of the n.m.r. spectrum. In (14), for example, 2-H would be expected to give a simple doublet, whereas this would not be the case with either 2- or 3-H in (15). In fact, a doublet at δ 3.67 (J 9.5 Hz), attributable to 2-H in (14) is found. Chemical support was obtained by dehydration of (14) in excellent yield by treatment with hydrochloric acid in methanol to yield the known, conjugated γ -lactone (17)¹⁷ which was further

was accordingly obtained by irradiation of trideuterio-methylbenzophenone with 4-hydroxybutenoic acid lactone and exhibited, apart from the absence of benzylic absorption, a ¹H n.m.r. spectrum identical to that of compound (14). Dehydration of compound (19), as before, yielded the dideuterio, conjugated lactone (20), in the considerably simplified spectrum of which the two pseudo-triplets at δ 4.02 and 4.71 remained, as anticipated.

Irradiation of the ketone (1) with *trans*-crotonaldehyde gave a 1 : 1 adduct, isolated in 27% yield by direct crystallization, and formulated as (21) by comparison with the established configurations of the adducts (13) and (14). The i.r. spectrum indicated the presence of hydroxy and aldehyde functions. An indication that the aldehyde function was at C-2 came from consideration of the u.v. spectra of the products obtained by treatment with 2,4-dinitrophenylhydrazine; in addition to the

¹³ J. J. Leavitt, Ph.D. Dissertation, Harvard University, 1942.

¹⁴ H. L. Holmes, *Org. Reactions*, 1948, **4**, 72.

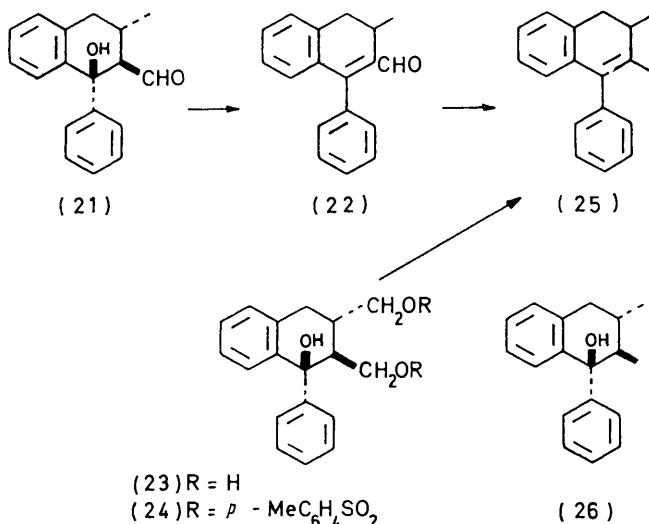
¹⁵ R. Palm, H. Ohse, and H. Cherdron, *Angew. Chem. Internat. Edn.*, 1966, **5**, 994.

¹⁶ C. C. Price and J. M. Judge, *Org. Syntheses*, 1965, **45**, 22.

¹⁷ L. H. Klemm, D. Hsu Lee, K. W. Gopinath, and C. E. Klopfenstein, *J. Org. Chem.*, 1966, **31**, 2376.

¹⁸ C. E. Klopfenstein, Ph.D. Dissertation, University of Oregon, 1966.

expected derivative (M^+ , 446; orange; λ 360 nm) there was obtained a dehydration product (M^+ , 428; red; λ 408 nm) indicative of diarylethylene carbonyl conjugation. We found that the aldehyde (21) could be readily dehydrated in 95% yield by heating under reflux with florisil and the product has spectroscopic characteristics (conjugated carbonyl in i.r., singlet aldehyde and doublet methyl group signals in ^1H n.m.r.) fully consistent with structure (22).



One unsuccessful attempt to obtain unequivocal proof of the configuration assigned to compound (21) was based on the hope of obtaining the common product (26) from both the *trans*-diester (13) and the aldehyde adduct. For this purpose, compound (13) was reduced with lithium aluminium hydride to yield the triol (23). An attempt to convert this to the phenyldimethyltetralin (26) by lithium aluminium hydride reductive cleavage of the derived bistoluene-*p*-sulphonate (24) was frustrated by accompanying dehydration to yield instead 1-phenyl-2,3-dimethyl-3,4-dihydronaphthalene (25), also obtained on Huang-Minlon reduction of the conjugated aldehyde (22).

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian A-60A spectrometer with deuteriochloroform as solvent (unless otherwise specified) and tetramethylsilane as internal standard; chemical shifts are given in δ values. U.v. spectra were determined using a Cary 14 spectrophotometer, and i.r. spectra as KBr discs using a Perkin-Elmer 137 spectrophotometer. Mass spectra were recorded on a A.E.I. MS-12 spectrometer (only the molecular ion and parent peak ion percentages are reported).

Analytical t.l.c. was conducted using 0.25 mm thick layers of silica gel GF₂₅₄ (Merck) with product visualization by (a) u.v. fluorescence, (b) iodine vapour adsorption or, (c) spraying with 3.5% molybdato-phosphoric acid. Preparative t.l.c. was conducted using 1.00 or 1.75 mm thick layers of silica gel PF₂₅₄₊₃₆₆ (Merck) with elution of products by stirring with a hot solvent for ca. 30 min. or continuous extraction from a Soxhlet extractor.

A Hanovia 8A-1 high-pressure quartz lamp inserted in a Pyrex insert immersion well and equipped with a cooling jacket was used in irradiation experiments. The solution to be irradiated was deoxygenated by prior vigorous bubbling of nitrogen gas through it for 30 min, then maintaining a mild stream of nitrogen during the entire irradiation time. Heating, when required, was accomplished by reducing the cooling water rate of flow.

Dimethyl 1-Hydroxy-1-phenyl-1,4-dihydronaphthalene-2,3-dicarboxylate (2).—A solution of 2-methylbenzophenone (1.96 g) and dimethyl acetylenedicarboxylate (2.84 g) in benzene (185 ml) was irradiated for 20 h. Evaporation of the solvent gave a residual yellow oil (4.12 g) which solidified on standing. One crystallization from benzene-cyclohexane and one from ether-light petroleum gave the adduct (2) as prisms (1.77 g, 53%), m.p. 111.5–112.5° (lit.,¹ m.p. 112°); ν_{max} 3460 (OH) and 1740 and 1717 cm^{-1} (CO); ν_{max} (CHCl₃) 1719 cm^{-1} ; δ 3.55 (s, 2-CO₂Me), 3.74 (s, 3-CO₂Me), 3.80 (s, 4-H₂), 4.23 (s, OH), and 7.08–7.47 (9H, m, ArH); m/e 338 (M^+ , 23), 290 ($M - \text{H}_2\text{O} - \text{OMe}$, 100).

Irradiation of 2-Methylbenzophenone with Tetracyanoethylene.—A solution of 2-methylbenzophenone (1.96 g) and tetracyanoethylene (1.28 g) in ethyl acetate (180 ml) was irradiated for 23.5 h during which the colour changed from pale yellow to green to brown-red. Removal of the solvent gave a viscous red oil, which on trituration with ether yielded a beige solid (950 mg). Crystallization from chloroform-ether gave *r*-5,12,12-tricyano-4-imino-3-oxa-*c*-2-phenyltricyclo[5.4.0.1^{2,5}]dodeca-1(7),8,10-triene (9) as beige crystals (702 mg), m.p. 194–199° (darkens at 170°). Analytical t.l.c. with 10% ethyl acetate-chloroform gave one spot (R_F 0.58) (Found: C, 74.3; H, 3.6; N, 17.0. C₂₀H₁₂N₄O requires C, 74.05; H, 3.75; N, 17.3%); ν_{max} 3322 (NH) and 1721 cm^{-1} (C=N); δ 3.98br (4-H₂), 6.80–8.00 (9H, m, ArH), 8.13br (NH, exchanged with D₂O); m/e 324 (M^+ , 45) and 196 (C₁₄H₁₂O⁺, 100; 'retro-Diels-Alder' fragment).

In a similar experiment in which the product mixture was purified by column chromatography on silica gel, in addition to the same imidate, m.p. 193–197°, there was obtained by elution with ether-light petroleum the corresponding lactone (10), needles, m.p. 197.5–198°. Analytical t.l.c. with 10% ethyl acetate-chloroform gave one spot (R_F 0.73) (Found: C, 73.6; H, 3.4; N, 12.9. C₂₀H₁₁N₃O₂ requires C, 73.85; H, 3.4; N, 12.9%); ν_{max} 1805 cm^{-1} (lactone); δ 4.07br (4-H₂) and 7.03–8.12 (9H, m, ArH); m/e 325 (M^+ , 42) and 195 (C₁₄H₁₁O⁺, 100; 'retro-Diels-Alder' - H fragment).

Dimethyl r-1-Hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-c,3-c-dicarboxylate (12).—A solution of 2-methylbenzophenone (3.92 g) and dimethyl maleate (2.88 g) in benzene (120 ml) was irradiated for 17 h. Evaporation of the solvent gave a residual mixture of crystals and viscous yellow oil. Crystallization from cyclohexane yielded crystals (2.20 g, 35%) which on one further recrystallization from methanol gave the *cis*-dimethyl ester (12), plates, m.p. 137–138° (lit.,⁶ m.p. 137–138°) (Found: C, 70.4; H, 6.05. Calc. for C₂₀H₂₀O₅: C, 70.55; H, 5.9%); ν_{max} 3460 (OH) and 1748 and 1716 cm^{-1} (CO); δ 2.81–3.32 (m, 3-H and 4-H₂), 3.63(s) and 3.65(s) (2 × CO₂Me), 3.73 (half d, 2-*t*-H, other half d under methyl ester resonance), 6.57br (OH, exchanged by D₂O), and 7.02–7.57 (9H, m, ArH); m/e 340 (M^+ , 4) and 195 ('retro-Diels-Alder' - H fragment, 100).

Dimethyl r-1-Hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-c,3-t-dicarboxylate (13).—A solution of 2-methylbenzophenone (3.92 g) and dimethyl fumarate (2.88 g) in benzene was irradiated (18–24 h), the solvent removed, and the residue crystallized from ether–light petroleum to yield the *trans*-dimethyl ester (13), large prisms (3.63 g, 58%), m.p. 124–124.5° (lit.,⁶ 122.5–123°) (Found: C, 70.7; H, 5.85. Calc. for C₂₀H₂₀O₅: C, 70.55; H, 5.9%; ν_{\max} 3534 (OH) and 1724 cm⁻¹ (CO); δ 3.13–3.88 (11 lines, 2-*t*-H, 3-*c*-H, and 4-H₂), 3.41 (s, CO₂Me), 3.73 (s, CO₂Me), 4.22 (OH, exchanged by D₂O), and 6.73–7.47 (9H, m, ArH); *m/e* 340 (M⁺, 11) and 195 ('retro-Diels–Alder' – H fragment, 100).

r-1-Hydroxy-3-c-hydroxymethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-c-carboxylic Acid γ -Lactone (14).—A solution of 2-methylbenzophenone (2.37 g) and 4-hydroxybut-2-enoic acid lactone (1.01 g) in benzene was irradiated under reflux for 24 h, the solvent was removed, and the residual yellow gum (2.94 g) triturated with ether–light petroleum to give a solid which crystallized from methylene chloride–light petroleum to give the *cis*- γ -lactone (14), needles (1.66 g), m.p. 144–145° (Found: C, 77.7; H, 5.85. C₁₈H₁₆O₃ requires C, 77.1; H, 5.75%); ν_{\max} 3472 (OH) and 1751 cm⁻¹ (γ -lactone); δ 2.50–2.62 (m, 4-H₂), 2.78–3.21 (m, 3-*t*-H), 3.67 (d, 2-*t*-H, *J* 9.5 Hz), 4.01 (dd, *c*-H of lactone CH₂, *J* 9.5, and 2.0 Hz), 4.48 (dd, 4-*t*-H of lactone CH₂, *J* 9.5 and 7.25 Hz), 5.47 (s, OH), and 7.10–7.92 (9H, ArH); *m/e* 280 (M⁺, 11) and 195 ('retro-Diels–Alder' – H fragment). When the reaction was conducted at room temperature, the yield of lactone (14) was 7%.

3-Hydroxymethyl-1-phenyl-3,4-dihydronaphthalene-2-carboxylic Acid Lactone (17).—Conc. hydrochloric acid (2 drops) was added to a solution of the *cis*- γ -lactone (14) (96 mg) in methanol (10 ml) and the mixture was heated under reflux for 15 min. The solid (90 mg) which separated on cooling as needles was the conjugated lactone (17), m.p. 197.5–198.5° (lit.,¹⁷ m.p. 194.5–195.5°) (Found: C, 82.35; H, 5.4. Calc. for C₁₈H₁₄O₂: C, 82.4; H, 5.4%); ν_{\max} 1748 (conjugated γ -lactone); n.m.r. spectrum complex, in agreement with previous descriptions;^{17,18} *m/e* 262 (M⁺, 56) and 203 (100).

3-Hydroxymethyl-1-phenyl-naphthalene-2-carboxylic Acid Lactone (18).—This was obtained by *N*-bromosuccinimide dehydrogenation of (17) as previously described,¹⁷ m.p. 186–187.5° (lit.,¹⁷ m.p. 185–187°); ν_{\max} 1761 cm⁻¹ (phthalide); δ 5.39 (d, lactone CH₂, *J* 1.2 Hz); *m/e* 260 (M⁺, 96) and 231 (M – CHO⁺, 100).

r-1-Hydroxy-2-c,3-c-bishydroxymethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (16).—(a) Lithium aluminium hydride (404 mg) was added to a solution of the *cis*- γ -lactone (14) in tetrahydrofuran (35 ml), the mixture was heated under reflux for 36 h, and the product worked-up in the usual way. Crystallization from ethyl acetate–light petroleum gave the triol (16), needles, m.p. 132–136° (Found: C, 76.05; H, 7.15. C₁₈H₂₀O₃ requires C, 76.05; H, 7.1%); ν_{\max} 3333 cm⁻¹ (OH); δ [(CD₃)₂SO] 1.92–2.50 (m, 3-*t*-H), 2.85 (dd, 4-H₂, *J* 7.5 and 2.0 Hz), 3.37–3.82 (m, 2-*t*-H and 4 × CH₂OH), 4.62 (t, primary OH, *J* 5 Hz), 4.84 (t, primary OH, *J* 5 Hz), 6.10 (s, tertiary OH), and 7.17–7.31 (9H, m, ArH); *m/e* 284 (M⁺, 1.5) and 195 (100). Analytical t.l.c. with 10% ethyl acetate–chloroform showed one spot (*R_F* 0.26).

(b) Similar reduction of the *cis*-anhydride (11) [m.p. 146–148 and 195–200° (lit.,⁶ m.p. 150°)] (419 mg) yielded the same triol (261 mg), m.p. and mixed m.p. 132–136°.

4,4-Dideuterio-r-1-hydroxy-3-c-hydroxymethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-c-carboxylic Acid γ -Lactone (19).—A solution of 2-trideuteriomethylbenzophenone^{4c,6} (226 mg) and 4-hydroxybut-2-enoic acid lactone (180 mg) in benzene (10 ml) was degassed by the freeze–thaw method, and irradiated with refluxing under nitrogen. Evaporation of solvent and crystallization from ether–light petroleum yielded the 4,4-dideuterio-*cis*- γ -lactone (19), needles, m.p. 142–143°, ν_{\max} 3497 (OH) and 1754 cm⁻¹ (lactone); δ 2.80–3.30 (m, 3-*t*-H), 3.70 (d, 2-*t*-H, *J* 9.5 Hz), 4.03 (dd, *c*-H of lactone CH₂, *J* 9.5 and 2.0 Hz), 4.50 (dd, *t*-H of lactone CH₂, *J* 9.5 and 7.25 Hz), 5.47 (s, OH), and 7.12–7.95 (9H, ArH); *m/e* 282 (M⁺, 12) and 197 (100).

4,4-Dideuterio-3-hydroxymethyl-1-phenyl-3,4-dihydronaphthalene-2-carboxylic Acid Lactone (20).—A solution of the 4,4-dideuterio-*cis*- γ -lactone (19) (32 mg) in methanol (5 ml) containing conc. hydrochloric acid (1 drop) was heated under reflux for 3 h, concentrated to half volume, and the solid which separated on cooling was collected and washed with cold methanol. This yielded the 4,4-dideuterio-conjugated lactone (20), m.p. 195–197°, ν_{\max} 1748 cm⁻¹ (conjugated γ -lactone); δ 3.22–3.63 (m, 3-H), 4.02 (t) and 4.71 (t) (*J* 9 Hz for both, lactone CH₂), and 6.83–7.50 (9H, m, ArH); *m/e* 264 (M⁺, 36) and 204 (100).

r-1-Hydroxy-3-t-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-c-carbaldehyde (21).—A solution of 2-methylbenzophenone (3.92 g) and freshly distilled *trans*-crotonaldehyde (1.60 g) in benzene (130 ml) was irradiated for 23 h. The solid (5.44 g) obtained on evaporation of the solvent crystallized from ether–light petroleum to give the aldehyde (21), prisms (1.30 g), m.p. 156–157° (Found: C, 80.95; H, 6.6. C₁₈H₁₈O₂ requires C, 81.15; H, 6.8%); ν_{\max} 3610 (OH) and 1712 cm⁻¹ (aldehyde); δ 1.12 (m, distorted or overlapping d, Me), 2.60–3.23 (m, OH, 4-H₂, 2- and 3-H), 6.83–7.57 (9H, ArH), and 9.96 (d, CHO, *J* 3.5 Hz); *m/e* 266 (M⁺, 1.6) and 195 (100).

Action of 2,4-Dinitrophenylhydrazine on Aldehyde (21).—A mixture of the hydroxy-aldehyde (189 mg) and 2,4-dinitrophenylhydrazine (161 mg) in acetic acid (10 ml) was boiled for 5 min, cooled, diluted with water, and the precipitate (206 mg) was collected. Preparative t.l.c. (silica gel PF; 1 mm; 10% ethyl acetate–chloroform) yielded a yellow solid (196 mg) and an orange solid (10 mg). Crystallization of the yellow solid from aqueous ethanol yielded the 2,4-dinitrophenylhydrazone of the parent hydroxy-aldehyde, orange needles, m.p. 210.5–212° (darkens at 200°), λ_{\max} (CHCl₃) 360 nm (log ϵ 4.35); *m/e* 446 (M⁺). Crystallization of the orange solid from aqueous ethanol yielded the 2,4-dinitrophenylhydrazone of the dehydrated aldehyde, red plates, m.p. 193.5–194°, λ_{\max} (CHCl₃) 408 nm (log ϵ 4.21); *m/e* 428 (M⁺).

3-Methyl-1-phenyl-3,4-dihydronaphthalene-2-carbaldehyde (22).—Florisol (2 g; Fisher; 100–200 mesh) was added to a solution of the hydroxy-aldehyde (21) (200 mg) in benzene (40 ml), the mixture was heated under reflux for 12 h, filtered, and washed with ethyl acetate (200 ml). Evaporation of the combined filtrate and washings gave a residual solid (184 mg) which on one crystallization from ether–light petroleum gave the conjugated aldehyde (22), prisms (176 mg, 95%), m.p. 115–116° (Found: C, 87.35; H, 6.75. C₁₈H₁₆O requires C, 87.05; H, 6.5%); ν_{\max} 1656 cm⁻¹ (conjugated aldehyde); δ 1.02 (d, 3-Me, *J* 7 Hz), 2.52–2.97 (m, 3-H), 3.22 (q, benzylic, *J* 13 and 6.5 Hz), 3.28 (q, benzylic, *J* 13 and 6.0 Hz), 7.65 (9H, m, ArH), and 9.67 (s, CHO); *m/e* 248 (M⁺, 100).

r-1-Hydroxy-2-*c*,3-*t*-bishydroxymethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (23).—A solution of the 2-methylbenzophenone-dimethyl fumarate adduct (13) (1.43 g) in tetrahydrofuran (60 ml) was added slowly to a stirred mixture of lithium aluminium hydride (1.61 g) in tetrahydrofuran (50 ml) at 0°. The product was worked-up in the usual way, and purified by preparative t.l.c. on silica gel PF (1.75 mm) with 10% ethyl acetate-chloroform. Recrystallization of the product (589 mg) from benzene-ethanol gave the triol (23), m.p. 160–166° (Found: C, 76.15; H, 6.95. C₁₈H₂₀O₃ requires C, 76.05; H, 7.1%); ν_{\max} 3356 cm⁻¹ (OH); δ [(CD₃)₂SO] 1.83–2.48 (m, 3-*c*-H), 3.02br (d, 4-H₂, *J* ca. 8 Hz), 3.40–3.90 (2-*t*-H and 2 × CH₂OH), 4.63 (t, primary OH, *J* 5.5 Hz), 4.75 (t, primary OH, *J* 5.5 Hz), 5.80 (s, tertiary OH), and 6.73–7.65 (9H, m, ArH); *m/e* 284 (M⁺, <1) and 77 (C₆H₅⁺, 100).

2,3-Dimethyl-1-phenyl-3,4-dihydronaphthalene (25).—(a) A solution of the triol (23) (176 mg) and toluene-*p*-sulphonyl chloride (842 mg) in pyridine (10 ml) was set aside at 0° for 72 h, ice was added, and the mixture extracted with chloroform. The extract was washed successively with water, cold 2*N*-hydrochloric acid, water, 5% sodium hydrogen carbonate solution, and water, dried (Na₂SO₄), and evaporated to yield the crude triol bistoluene-*p*-sulphonate (24), solid (290 mg), ν_{\max} 3590 (OH), 1360, 1190 and 1178 (S=O) and 552 cm⁻¹ (sulphonate ester); δ 2.45 (s, 2 × ArMe), 2.25–3.20 (5H, m), 3.88–4.45 (4H, m), 6.70–7.92 (17H, m, ArH). A solution of this product (271 mg)

and lithium aluminium hydride (50 mg) in tetrahydrofuran was heated under reflux for 16 h, then worked-up in the usual way by chloroform extraction to yield a gum (228 mg). T.l.c. on silica gel PF (1.0 mm), with 10% ethyl acetate-chloroform gave 2,3-dimethyl-1-phenyl-3,4-dihydronaphthalene as an oil (*R*_F 0.51) which, as reported,¹⁹ dissolves in conc. sulphuric acid with formation of a bright yellow colour; δ 1.04 (d, 3-Me, *J* 7 Hz), 1.70 (s, 2-Me), 2.02–2.55 (m, 3-H), 2.58 (dd, 4-H, *J* 15 and 3 Hz), 3.19 (4-H, *J* 15 and 6.5 Hz), and 6.42–7.50 (9H, ArH).

(b) A mixture of the conjugated aldehyde (22) (118 mg), potassium hydroxide (87 mg), and 85% hydrazine hydrate (93 mg), in triethanolamine (17 ml) was heated at 195° for 4 h, then acidified with conc. hydrochloric acid, and diluted with water to 200 ml. It was continuously extracted with ether for 16 h, the extract was dried (Na₂SO₄), and evaporated. Purification of the product by t.l.c. (silica gel PF; 1.0 mm) using chloroform gave the hydrocarbon as an oil (68 mg, 61%) with i.r. (OH and CO absent) and n.m.r. spectrum identical with that obtained in (a).

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¹⁹ A. Müller and K. Kösmendy, *J. Org. Chem.*, 1953, **18**, 1237.