Photochemical Reactions. Part IV.[1] Thermal Generation of Photoenols and their Derivatives from Disubstituted 1,2-Dihydrobenzocyclobutenes

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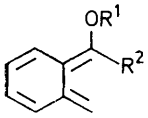
Various disubstituted 1,2-dihydrobenzocyclobutenes bearing at least one oxygen substituent have been prepared and their thermal conversion into substituted *o*-quinonedimethides studied by appropriate trapping reactions. In all cases the oxygen substituent adopts the *E*-configuration. Benzocyclobuten-1(2*H*)-one ethylene acetal and *cis*-1,2-dimethoxy-1,2-dihydrobenzocyclobutene did not open to give a quinone dimethide. Vinylic or phenyl substituents aid the valence isomerisation to the ring opened form. The thermal reactions of the photoenol derived from either 2-methylbenzophenone or 1-phenyl-1,2-dihydrobenzocyclobuten-1-ol have been studied.

On heating, 1,2-dihydrobenzocyclobutenes undergo conrotatory ring opening to the corresponding *o*-quinonedimethides [2] and these species readily participate in cycloaddition reactions of the Diels–Alder type.[3] Such processes are valuable in synthetic work,[4,5] as exemplified by the elegant route to *dl*-chelidonine described by Oppolzer.[6] The observation that 1,2-dihydrobenzocyclobuten-1-ol opens on heating to give the same intermediate dienol (1; $R^1 = R^2 = H$) as obtained by



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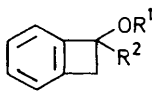

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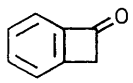

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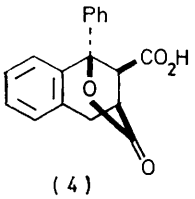

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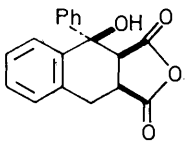

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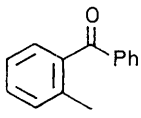

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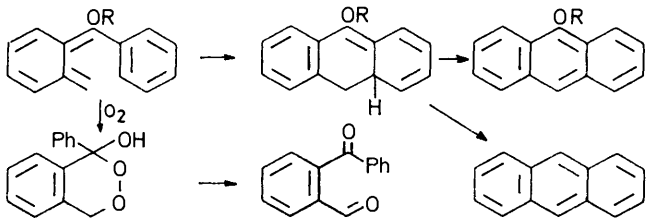
irradiating 2-methylbenzaldehyde [7] should be general, enabling direct access to a variety of photodienols by thermal rather than photochemical means. In this paper some studies directed to this end are described. Some reactions of methoxy- and acetoxy-substituted 1,2-dihydrobenzocyclobutenes are also reported.

The photoenolisation of 2-alkylbenzophenones is well documented.[7] Although flash photolysis studies with 2,4-dimethylbenzophenone indicated the presence of two, isomeric dienols,[7c] assigned as the *E*- and *Z*-isomers, isolation of the trapped derivatives, obtained by cycloaddition with a dienophile, has yielded products from the *E*-isomer [*e.g.* (1; $R^1 = H$, $R^2 = Ph$)] only.[8,9] Thermal generation of the dienol was attempted using the known [10] 1-phenyl-1,2-dihydrobenzocyclobuten-1-ol (2; $R^1 = H$; $R^2 = Ph$), prepared by the addition of phenylmagnesium bromide to benzocyclobuten-1(2*H*)-one (3). Heating the alcohol with maleic anhydride, in refluxing toluene for 4 h afforded the acid lactone (4), previously obtained by Nerdel and Brodowski on heating the initial photochemical adduct (5). In the mother liquors of the reaction product only traces of maleic anhydride and 2-methylbenzophenone (6) could be detected. There was no evidence for the presence of any isomeric adducts related to compound (5). Thus, despite the bulk of the phenyl group only the *E*-dienol (1; $R^1 = H$, $R^2 = Ph$) was formed from the electrocyclic opening of the substituted cyclobutene precursor. When the alcohol (2; $R^1 = H$, $R^2 = Ph$) was heated alone in refluxing toluene, it was smoothly converted into the benzophenone (6). Under these conditions no sign of any anthracene derivatives could be detected (see Scheme 1), demonstrating that a thermal cyclisation of the Elbs-type was not operating at this temperature. This result complements those obtained from the photochemical studies which have indicated that such a cyclisation can occur under the influence of a second quantum of light energy.[11]



Scheme 1

Dienols of the type (1) are known to react with oxygen in the dark [7] and it was anticipated that heating the alcohol (2; $R^1 = H$, $R^2 = Ph$) with oxygen should lead to autoxidation of the dienol. In the event, autoxidation was observed by treating the alcohol with oxygen

[1] Part III, B. J. Arnold, P. G. Sammes, and T. W. Wallace, preceding paper.

[2] (*a*) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, 1962, 15; (*b*) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, 1959, **81**, 4266.

[3] For a recent review on benzocyclobutene chemistry see I. L. Klundt, *Chem. Rev.*, 1970, **70**, 471.

[4] B. J. Arnold, S. M. Mellows, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 1266.

[5] T. Kametani, K. Ogasawara, and T. Takahashi, *Tetrahedron Letters*, 1972, 4847.

[6] W. Oppolzer and K. Keller, *J. Amer. Chem. Soc.*, 1971, **93**, 3836.

[7] (*a*) N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; (*b*) N. D. Heindel, E. W. Sarver, and M. Pfau, *Tetrahedron Letters*, 1968, 3579; (*c*) G. Porter and M. F. Tchir, *J. Chem. Soc.* (*A*), 1971, 3772; (*d*) M. Pfau, E. W. Sarver, and N. D. Heindel, *Bull. Soc. chim. France*, 1973, 183.

[8] F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.

[9] E. Block and R. Stevenson, *J.C.S. Perkin I*, 1973, 308.

[10] L. Horner, P. V. Subramaniam, and K. Eiben, *Annalen*, 1968, **714**, 91.

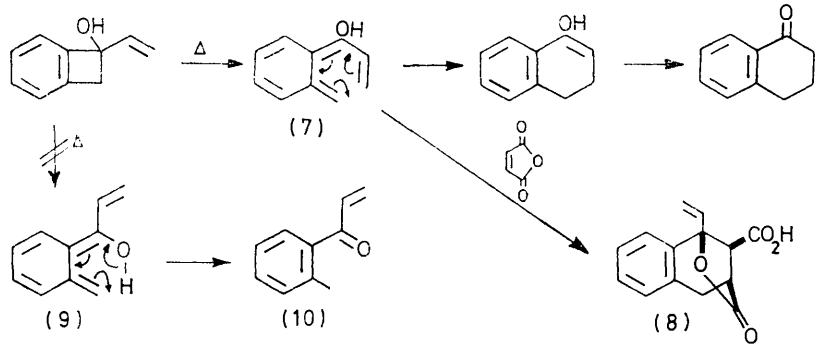
[11] N. D. Heindel, J. Molnar, and M. Pfau, *Chem. Comm.*, 1970, 1393.

in refluxing toluene, in the absence of light. Whilst the product solution gave a positive peroxide test, attempted isolation of peroxide products by p.l.c. was unsuccessful and only 2-benzoylbenzaldehyde could be isolated. The alcohol (2; $R^1 = H$, $R^2 = Ph$) was stable towards oxygen at temperatures below 80°, thus confirming that the oxidation does involve the derived dienol species.

Although no cyclisation of the dienol (1; $R^1 = H$, $R^2 = Ph$) to the dihydro-anthracene system (Scheme 1) was observed in the above reactions they are, in principle, possible and should proceed thermally in a disrotatory mode.[12] Such a process may be precluded with the alcohol by competing, rapid intermolecular proton transfers which lead to the corresponding ketone. In order to block this process the corresponding, known[10] methyl ether (2; $R^1 = Me$, $R^2 = Ph$) was prepared. As expected, this compound was far more stable than the alcohol towards heat, but, after 24 h at 112°, a small quantity of a new compound, identified as 9-methoxyanthracene was isolated. Presumably the thermal cyclisation, carried out in the absence of light, was accompanied by oxidation, or disproportionation to give the anthracene. Heating the ether (2; $R^1 = Me$, $R^2 = Ph$) in the presence of air led to a more complex array of products and these were not investigated further.

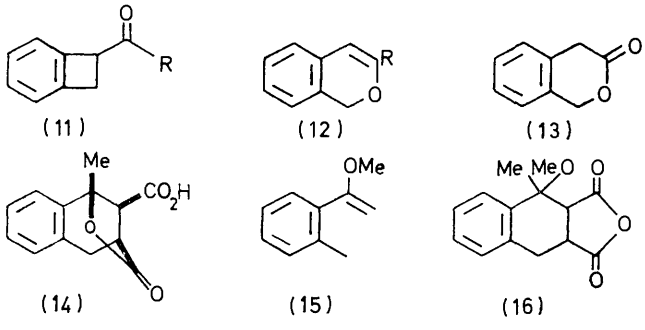
Cyclisation of the hexatriene to cyclohexadiene type, for the phenyl-substituted dienol (1; $R^1 = Me$ or H, $R^2 = Ph$) is inhibited both by the difficulty arising from disturbance of the aromatic character of the phenyl ring and by the subsequent necessity for oxidation or disproportionation of the dihydroanthracene product (Scheme 1). Both these objections were removed by using the vinyl substituted alcohol (2; $R^1 = H$, $R^2 =$ vinyl). This alcohol was very unstable and on heating in refluxing toluene for 30 min it was quantitatively converted into α-tetralone. That this reaction was proceeding *via* the hexatriene intermediate (7) (Scheme 2) could be demonstrated by repeating the reaction in the presence of maleic anhydride. Cycloaddition competed with internal cyclisation to give a mixture of α-tetralone and a single adduct, the lactone acid (8), in the ratio 1 : 2 respectively. In neither case was any 2'-methylacrylophenone formed, thus ruling out formation of the isomeric dienol (9), which would be expected to lead to the acrylophenone (10) by a rapid intramolecular proton shift. A control reaction showed that authentic 2'-methylacrylophenone was unaffected by the thermal conditions of the reaction.

The relative ease of ring opening of the 1-substituted 1,2-dihydrobenzocyclobutenols (2; $R^1 = H$), in the order ($R^2 =$) H < Ph < vinyl illustrates the activation



SCHEME 2

of the process by the unsaturated substituent. Such an effect has been noted previously, particularly for phenyl-substituted benzocyclobutenes.[13] Thus the electronic nature of the substituents, as well as steric effects are important in the electrocyclic ring-opening.[1] Unlike ethereal oxygen atoms, vinyl and other π-bonded substituents have no difficulty in adopting the (*Z*)-configuration in the intermediate species. This appears to be generally true, as borne out by the recent observations that 1-benzoyl-1,2-dihydrobenzocyclobutene (11; R = Ph) is converted into 3-phenylisochromene (12) by heat,[14] and that 1,2-dihydrobenzocyclobutene-1-carboxylic acid forms isochromanone (13).[15]



In an attempt to determine the limits to which the directing influence of the oxygen atom determines the electrocyclic benzocyclobutene to diene process a further

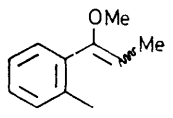
[12] E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Letters*, 1965, 391; E. N. Marvell, G. Caple, and B. Schatz, *ibid.*, p. 385; D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, p. 377.

[13] R. Huisgen and H. Seidl, *Tetrahedron Letters*, 1964, 3381; G. Quinkert, K. Opitz, W. W. Wiersdorf, and M. Finke, *Annalen*, 1966, **693**, 44.

[14] R. Hug, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 10.

[15] R. Watt, Imperial College, unpublished observation.

variety of substituted derivatives were also investigated, Since the methyl group is sterically bigger than a hydroxy-group, 1-methyl-1,2-dihydrobenzocyclobuten-1-ol was prepared, together with the ethyl analogue. As anticipated, heating the methyl derivative (2; R^1 = H, R^2 = Me) in the absence of a dienophile gave 2-methylacetophenone, but less readily than 1,2-dihydrobenzocyclobuten-1-ol itself; 1-ethyl-1,2-dihydrobenzocyclobuten-1-ol (2; R^1 = H, R^2 = Et) reacted even more slowly. With maleic anhydride the methyl derivative gave the lactone (14), but this was accompanied by considerable amounts of 2-methylacetophenone. The latter material can form as a result of intermolecular hydrogen transfer or by either of two possible intramolecular processes involving 1,5-hydrogen shifts, *viz.* hydrogen transfer from the hydroxy-group in a (*Z*)-dienol, or hydrogen transfer from the methyl group in the corresponding, generally preferred, (*E*)-isomer. An indication that the latter process was still the main one operating was obtained by preparing the methyl ether (2; R^1 = Me, R^2 = Me). On heating this in chlorobenzene at 130°, it was smoothly converted into 2-methyl-α-methoxystyrene (15), arising from a 1,5 sigmatropic rearrangement of hydrogen from the (*E*)-diene (1; R^1 = Me, R^2 = Me).[2a,16] In the presence of maleic anhydride complete trapping of the intermediate diene as the adduct anhydride (16) was possible. The ethyl-substituted alcohol (2; R^1 = H, R^2 = Me) was also converted into its methyl ether and this, on heating to 130°, gave a mixture of the *cis*- and *trans*-styrenes (17), which could be readily hydrolysed with dilute acid to give the corresponding propiophenone. The anhydride adduct (16) was found to be a mixture of two isomeric adducts by ^{1}H n.m.r. analysis (ratio 3 : 1). Since 1-methoxy-1,2-dihydrobenzocyclobutene gave only



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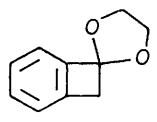

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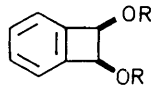

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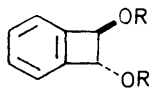

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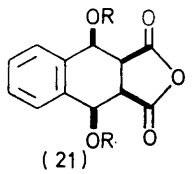

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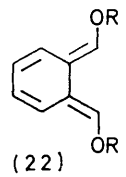


(22)

one adduct with maleic anhydride [1] this loss of stereoselectivity must be associated with the presence of the methyl substituent, which must decrease the original preference for the ' normal ' *endo*-addition process.[17]

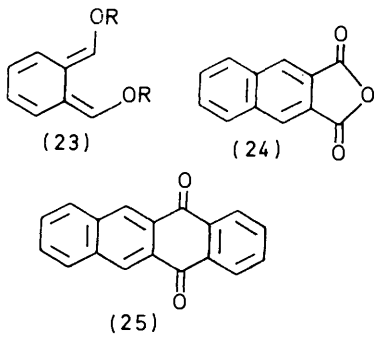
The cyclobutenone (3) could be easily converted into its ethylene acetal (18) by treatment with ethylene glycol and a trace of toluene-*p*-sulphonic acid. For this material, any electrocyclic ring opening must result in one of the ethereal oxygen atoms adopting a (*Z*)-configuration with respect to the adjacent methylene substituent. In the event, attempted trapping of any diene with maleic anhydride completely failed. When the reaction temperature was raised to 140° (refluxing xylene) a slow decomposition of the acetal ensued with liberation of small quantities of the benzocyclobutenone (3) (which is known to open in an electrocyclic manner [18]), but, even with dimethyl butynedioate, no trapped products from the acetal could be detected. A more striking example of the ' forbidden ' nature of the (*Z*)-oxydiene system was provided by a comparison of the two 1,2-disubstituted benzocyclobutenes (19) and (20). The acetoxy-derivatives were prepared by an adaption of the method of Nozaki *et al.*,[19] using 1,2-di-iodo-1,2-dihydrobenzocyclobutene instead of the dibromo-analogue. Treatment of the 1,2-di-iodobenzocyclobutene with silver fluoroborate in methanol afforded the isomeric dimethoxy-derivatives (19; R = Me) and (20; R = Me), which were distinguished by their characteristic n.m.r. spectra, the former, *cis*-isomer showing the methine proton at *ca.* 0·4 p.p.m. downfield compared to the *trans*-isomer. The *trans*-isomer (20; R = Me) was unstable and could not be isolated in an analytically pure state. The instability of the *trans*-isomer is consistent with the observation that the *trans*-diol (20; R = H) is very unstable, even at room temperature, whilst the *cis*-isomer is easily isolated.[19]

Several trapping reactions with the 1,2-disubstituted derivatives were attempted. With maleic anhydride both the *trans*-methoxy- (20; R = Me) and acetoxy- (20; R = Ac) derivatives reacted readily to give good yields of the corresponding adducts (21; R = Me) and (21; R = Ac). Only one isomeric adduct was isolated in each instance, assigned as the all-*cis*-derivatives arising from *endo*-addition to the *o*-quinonedimethide (22). In contrast, no adducts could be obtained from the reactions of either of the *cis*-substituted derivatives (19; R = Me or Ac) with maleic anhydride even at 140°. At this and at higher temperatures general decomposition of the benzocyclobutenes occurred. An attempt to catalyse the reactions of these derivatives with maleic anhydride, using silver fluoroborate, also failed.[20] These results indicate that conrotatory opening of the cyclobutene ring to give *o*-quinonedimethide systems of the type (23) appears to be a disallowed process.

The adduct (21; R = Ac) was unstable to heat. When the trapping reaction was carried out at 140° the product (61% yield) was naphthalene-2,3-dicarboxylic anhydride (24). A similar elimination occurred on treating the diacetate (20; R = Ac) with 1,4-naphthoquinone; the naphthacenequinone (25) was formed in 84% yield.

[16] W. R. Roth and J. König, *Annalen*, 1966, **699**, 24.
[17] *Cf.* D. W. Jones and G. Kneen, *J.C.S. Chem. Comm.*, 1973, 421.
[18] D. R. Arnold, E. Hedaya, V. Y. Merritt, L. A. Karnischky, and M. E. Kent, *Tetrahedron Letters*, 1972, 3917.
[19] H. Nozacki, R. Noyori, and N. Kozaki, *Tetrahedron*, 1964, **20**, 641.
[20] W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 1967, **89**, 4788; F. D. Mango, *Adv. Catalysis*, 1969, **20**, 291.

The above results are consistent with previous work [1,21] and further illustrate the importance of electronic effects on the symmetry-controlled electrocyclic process. Such changes are expected to be general



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for electrocyclic reactions and further implications of these restrictions are under investigation.

EXPERIMENTAL

General experimental details were as described previously.[21] Solvents were dried and distilled before use. Reactions were routinely monitored by heating in a sealed n.m.r. tube in [$^2H_6$]benzene, recording the n.m.r. spectrum at intervals by means of a T60 spectrometer. Preparative thin layer chromatography (p.l.c.) was carried out using Merck silica gel GF_{254}, as 1 mm thick plates. Light petroleum refers to the fraction of boiling range 60—80°.

Benzocyclobuten-1(2H)-one (3).—1,2-Dihydrobenzocyclobuten-1-ol [1] (1 g) and manganese dioxide (dried; 15 g) were heated in refluxing dichloromethane (50 ml) until no alcohol remained (3 h). Filtration and evaporation of the filtrate gave pure ketone (0·9 g, 90%),[22] $\nu_{max.}$ (film) 1775 cm^{-1}, τ 2·44—2·60 (4H, m, aromatic) and 6·00 (2H, s, methylene).

1-Phenyl-1,2-dihydrobenzocyclobuten-1-ol (2; R^1 = H, R^2 = Ph).—This was prepared essentially according to the method of Horner *et al.*[10] To phenylmagnesium bromide [from bromobenzene (0·69 g)] in dry ether (20 ml) at 0° was added a solution of benzocyclobuten-1(2*H*)-one (0·41 g) in ether (15 ml). The suspension was allowed to warm to room temperature over 2·5 h before recooling to 5° and adding a cold saturated NH_4Cl solution. The two layers were separated and the ether layer was dried and purified by p.l.c. ($CHCl_3$). The title alcohol was obtained as a solid (0·47 g, 68%), m.p. 68—69° (lit.,[10] 72—73°), $\nu_{max.}$ 3325 and 1205 cm^{-1}, $\lambda_{max.}$ (EtOH) 216, 247sh, 253sh, 259, 266, and 272 nm. Treatment of a sample of the alcohol with sodium methoxide in methanol afforded 2-methylbenzophenone.[10] Heating the alcohol in toluene at reflux under nitrogen and in the absence of light for 6 h gave complete conversion into 2-methylbenzophenone. T.l.c. gave no indication of any anthracene or anthracenol formation.

Heating the alcohol (40 mg) in toluene (12 ml) whilst passing air through the refluxing solution gave, besides 2-methylbenzophenone, one other principal product. Attempted isolation of this material by p.l.c. gave only mixtures. From its n.m.r. spectrum the new species was assigned as the cyclic peroxide (see Scheme 1), with the methylene group appearing as an AB quartet, J 16 Hz, at τ 4·1—5·1. The solution gave a positive peroxide test. One of the less polar fractions isolated by p.l.c. showed $\nu_{max.}$ 1705 and 1660 cm^{-1}, and the presence of an aromatic aldehyde peak (τ −0·2) in its n.m.r. spectrum, characteristic of 2-benzoylbenzaldehyde.[23]

Methylation of 1-Phenyl-1,2-dihydrobenzocyclobuten-1-ol.—The alcohol (2; R^1 = H, R^2 = Ph) (24 mg) was added in portions to conc. sulphuric acid (1 ml) at 0° whilst stirring. When all the alcohol had dissolved the resulting red solution was treated with methanol (5 ml) with vigorous stirring. The colour of the solution was immediately discharged. The mixture was poured into water (20 ml) and the product extracted with ether. The extracts were washed with water, dried, and evaporated. P.l.c. (1 : 9 acetone–light petroleum) afforded the ether (2; R^1 = Me, R^2 = Ph) (16 mg, 70%) as an oil, $\nu_{max.}$ (CCl_4) 1120 and 1090 cm^{-1}, τ 2·6—2·8 (9H, m, aromatic), 6·2—6·8 (2H, ABq, J 14 Hz), and 6·70 (3H, s, MeO).

Heating the ether (12 mg) in toluene (25 ml) at 110° for 24 h, in the absence of air and light, gave, after p.l.c. ($CHCl_3$), recovered ether (9 mg) and a fluorescent material (1·5 mg), identified as 9-methoxyanthracene by u.v., i.r., and t.l.c. comparison with an authentic sample.[24]

In the presence of air the ether (2; R^1 = Me, R^2 = Ph) gave a more complex mixture of products which were not investigated further.

Trapping of the Phenylcarbinol (2; R^1 = H, R^2 = Ph) *with Maleic Anhydride.*—The alcohol (25 mg) and maleic anhydride (12·5 mg) were heated in refluxing toluene (5 ml) for 4 h. On cooling white crystals were deposited and these were removed by filtration (12 mg); evaporation of the filtrate gave more (25 mg) of the same material but this was recrystallised from toluene before combining with the first crop, yielding a total of 28 mg (75%) of the acid lactone (4), m.p. 180—190° (decomp.) [lit.,[8] 182—184° (decomp.)]. The i.r. spectrum appeared somewhat anomalous (as reported [8]) but, after vigorous drying had $\nu_{max.}$ 3220, 1765, and 1730 cm^{-1}. Traces of occluded toluene were visible in the n.m.r. spectra of non-dried samples. The mother liquors from the crystallisations only contained traces of maleic anhydride and 2-methylbenzophenone. Methylation of the acid with diazomethane afforded an ester which ran as a single compound in a variety of t.l.c. systems.

1-Vinyl-1,2-dihydrobenzocyclobuten-1-ol (2; R^1 = H, R^2 = vinyl).—Vinylmagnesium bromide [from vinyl bromide (1 ml) and magnesium turnings (0·13 g)] in tetrahydrofuran (2 ml) was treated with benzocyclobuten-1(2*H*)-one (0·20 g) in tetrahydrofuran (5 ml) at −5 to 0° and the mixture stirred at this temperature for a further 1·5 h. A saturated solution of NH_4Cl was added at −20°. Ether was added and the mixture allowed to warm to room temperature before separating the two phases, washing the ether extract with water, and back-extracting the aqueous phases with more ether. The combined ether extracts were dried and evaporated under reduced pressure at <25°. P.l.c. on the residue afforded the title compound as an unstable *oil* (170 mg, 70%), $\nu_{max.}$ (film) 3400 cm^{-1}, τ 2·76 (4H, m, aromatic), 3·75 (1H, dd, J 16 and 9 Hz, vinylic H), 4·88 (1H, dd, J 9 and 1·8 Hz, vinylic H), 4·67 (1H, dd,

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J 16 and 1·8 Hz, vinylic H), 6·3—6·9 (2H, ABq, *J* 14 Hz, methylene), and 7·78 (1H, exchanged with D_2O). The alcohol was unstable in air at room temperature and was characterised as its maleic anhydride adduct.

Reactions of the Allylic Alcohol (2; R^1 = H, R^2 = vinyl). —Heating the alcohol (12 mg) in toluene at reflux for 30 min formed one primary product, which gave a pinkish red colour with Brady's reagent. Isolation of the product by p.l.c. gave α-tetralone as an oil, $\nu_{max.}$ (film) 1680 and 1630 cm^{-1}, i.r. and n.m.r. spectra identical with those of an authentic sample. The i.r. and n.m.r. spectra of the crude reaction product, before purification by p.l.c. were also very similar to those of authentic α-tetralone. An authentic sample of 2-methylacrylophenone was prepared, by reaction of vinylmagnesium bromide with 2-methylbenzaldehyde followed by oxidation with manganese dioxide, but none of this could be detected amongst the reaction products. Furthermore, heating the acrylophenone at 110° in toluene for over 1 h caused no change.

The vinyl carbinol (35 mg) and maleic anhydride (24 mg) were heated in deuteriochloroform (1 ml) in a sealed n.m.r. tube at 110° for 30 min. The n.m.r. spectrum showed that a mixture of α-tetralone and the adduct (8) had formed (ratio 1 : 2). Evaporation of the solvent and crystallisation of the residue from light petroleum gave 1,2,3,4-*tetrahydro*-c-1-*hydroxy*-1-*vinylnaphthalene*-r-2,c-3-*dicarboxylic acid* 3,1-*lactone* (8) (30 mg, 50%), $\nu_{max.}$ (Nujol) 3400—2500, 1775, and 1700 cm^{-1}, τ 2·7 (4H, m, aromatic), 3·70 (1H, dd, *J* 16 and 10 Hz), 4·23 (1H, dd, *J* 16 and 2 Hz), 4·40 (1H, dd, *J* 10 and 2 Hz), and 6·7 (4H, m), m.p. 179—184° (from EtOH) (Found: C, 67·6; H, 5·1. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%).

1-*Methyl*-1,2-*dihydrobenzocyclobuten*-1-*ol* (2; R^1 = H, R^2 = Me).—This was prepared according to the method of Horner *et al.*[10] Benzocyclobuten-1(2*H*)-one (0·18 g) in dry ether (10 ml) was added slowly to methylmagnesium iodide [from methyl iodide (308 mg)] in ether (10 ml), maintaining the temperature at −10 to 0°. After 30 min at +5° the mixture was worked up in the usual manner to give the title alcohol (170 mg, 85%), m.p. 79—80° (lit.,[10] 80—81°).

Heating the methyl alcohol in toluene at reflux smoothly converted it into 2-methylacetophenone, identified by comparison with an authentic sample. With maleic anhydride (49 mg) the alcohol (67 mg) reacted slowly (6 days) in refluxing toluene (20 ml) to form a small quantity of 2-methylbenzophenone together with the adduct (14). N.m.r. analysis of the crude product indicated a 1 : 2 ratio of the acetophenone to the adduct. After evaporation, the residue was recrystallised from toluene to give 1,2,3,4-*tetrahydro*-c-1-*hydroxy*-1-*methylnaphthalene*-r-2,c-3-*dicarboxylic acid* 3,1-*lactone* (14) (81 mg, 70%), m.p. 183—184°, $\nu_{max.}$ (Nujol) 3600—2500, 1770, and 1705 cm^{-1}, τ 1·5—2·4br (1H, s, exchanged by D_2O), 2·50—2·95 (4H, m, aromatic), 6·82br (3H, s), 6·92br (1H, s), and 8·15 (3H, s, Me) (Found: C, 67·2; H, 5·3. $C_{13}H_{12}O_4$ requires C, 67·25; H, 5·2%).

Methylation of 1-*Methyl*-1,2-*dihydrobenzocyclobuten*-1-*ol*.—The alcohol (60 mg) was stirred at room temperature in dichloromethane (5 ml) containing an excess of methyl iodide and freshly prepared silver oxide (0·12 g). After 5 h the inorganic solids were filtered off and the filtrate evaporated to give 1-*methoxy*-1-*methyl*-1,2-*dihydrobenzocyclobutene* (2; R^1 = Me, R^2 = Me) (69 mg, 100%), $\nu_{max.}$ (CCl_4) 1200 and 1098 cm^{-1}, τ 2·85 (4H, m), 6·80 (3H, s, MeO), 6·5—7·2 (2H, ABq, *J* 15 Hz), and 8·43 (3H, s, Me) (Found: C, 81·0; H, 7·55. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%).

Heating the ether (60 mg) in CCl_4 (0·5 ml) in a sealed n.m.r. tube at 130° for 30 h eventually gave one major product and some unchanged starting material. The product was unstable to purification by p.l.c. N.m.r. analysis indicated about 75% conversion into product after 30 h reaction. It showed τ 2·7 (aromatic), 5·76 (1H, d, *J* 2 Hz), 5·88 (1H, d, *J* 2 Hz), 6·36 (3H, s, MeO), and 7·70 (3H, s, Me), consistent with its assignment as 2-methyl-α-methoxystyrene (15).

Heating the ether (65 mg) in the presence of maleic anhydride (44 mg) in [$^2H_6$]benzene (0·75 ml) in a sealed n.m.r. tube at 130° for 30 h gave none of the styrene (15), but 1,2,3,4-tetrahydro-1-methoxy-1-methylnaphthalene-2,3-dicarboxylic anhydride (16) (108 mg, 100%), as an oil. This material ran as a single compound on t.l.c. (light petroleum–ethyl acetate–acetic anhydride, 1 : 1 : 0·01), and had $\nu_{max.}$ (film) 1845 and 1770 cm^{-1}, τ (C_6D_6) 3·0 (m), 6·7—7·9 (m), 7·70 (s), 7·90 (s), 8·33 (s), and 8·47 (s). The relative intensities of the peaks at τ 8·47 and 8·33 and at 7·70 and 7·90 were 3 : 1 respectively. It was deduced that the compound was a mixture of two inseparable isomers. The mixture gave a satisfactory microanalysis for the required adduct (Found: C, 68·1; H, 5·6. Calc. for $C_{14}H_{14}O_4$: C, 68·3; H, 5·7%).

Preparation and Reactions of 1-*Ethyl*-1,2-*dihydrobenzocyclobuten*-1-*ol*.—Reaction of benzocyclobuten-1(2*H*)-one with ethylmagnesium bromide in the usual manner gave the ethyl carbinol (2; R^1 = H, R^2 = Et), m.p. 40—41°, $\nu_{max.}$ (Nujol) 3300 cm^{-1}, τ 2·8br (4H, s), 6·81 (2H, ABq, *J* 14 Hz), 7·33 (1H, s, exchanged with D_2O), 8·13 (2H, q, *J* 7 Hz), and 9·0 (3H, t, *J* 7 Hz). Heating the alcohol in toluene at 110° for 7 days slowly gave 2′-methylpropiophenone. In the presence of maleic anhydride an adduct formed, but this was not characterised.

Methylation of a sample of the ethyl carbinol, under the conditions used for the methyl analogue, gave the methyl ether as an oil. Heating this product, as a solution in [$^2H_6$]benzene, at 130°, smoothly afforded a mixture of the two enol ethers (17). The ratio of these was 3 : 2. Attempted purification of these vinylic ethers by p.l.c. resulted in hydrolysis to give the corresponding propiophenone. The propiophenone could also be obtained from the styrene mixture (17) by hydrolysis with dilute hydrochloric acid.

Benzocyclobuten-1(2H)-*one Ethylene Acetal*.—The ketone (0·15 g) in dry benzene (25 ml) containing ethylene glycol (1 ml) and a trace of toluene-*p*-sulphonic acid was heated to reflux in a Dean and Stark separator for 3 h. The mixture was cooled and the organic layer washed with a saturated solution of sodium hydrogen carbonate. After drying, the solvent was removed from the organic phase to give the title acetal as an oil (0·185 g, 95%), $\nu_{max.}$ (film) 1265 cm^{-1}, τ 2·7br (4H, s, aromatic), 5·84 (4H, s, $O{\cdot}CH_2CH_2{\cdot}O$), and 6·43 (2H, s, methylene).

Heating the acetal with maleic anhydride for 2 weeks at 110°, and treatment with an excess of dimethyl butynedioate in toluene at 110° for 30 h both gave no reaction. When the temperature of the latter reaction mixture was increased to 130° no reaction was observed after 24 h. After this time a slow decomposition of the acetal, with formation of benzocyclobuten-1(2*H*)-one, was observed but no adducts from the acetal could be detected. Hydrolysis

of the reaction mixture with dilute acid gave back benzocyclobutenone, but no indication of any adducts.

Preparation of cis- *and* trans-1,2-*Diacetoxy*-1,2-*dihydrobenzocyclobutene*.—*cis*- and *trans*-1,2-Di-iodo-1,2-dihydrobenzocyclobutene was prepared by the method of Jensen and Coleman [25] by refluxing α,α,α′,α′-tetrabromo-*o*-xylene with sodium iodide in ethanol in the dark. The mixture was *ca.* 9 : 1 *trans* : *cis*. Treatment of the mixed di-iodides (5·0 g) with silver acetate (4·7 g) in acetic acid containing 4% v/v water (110 ml) at room temperature for 18 h, followed by filtration and evaporation of the filtrate under reduced pressure, to remove the excess of acetic acid, followed by extraction with benzene, gave *cis*-2-acetoxy-1,2-dihydrobenzocyclobuten-1-ol (2·0 g, 81%), m.p. 114—117° (lit.,[19] 117—118°) Acetylation with acetic anhydride, catalysed by toluene-*p*-sulphonic acid, gave the *cis*-1,2-diacetoxy-1,2-dihydrobenzocyclobutene, b.p. 110—120° at 0·4 mmHg (lit.,[19] 105—110° at 0·4 mmHg). The oil eventually crystallised, m.p. 65—67°.

Treatment of the mixed 1,2-di-iodide (9·0 g) with silver acetate (8·7 g) in refluxing acetic acid (130 ml) containing acetic anhydride (40 ml) for 6 h, followed by filtration, evaporation, and distillation gave *trans*-1,2-diacetoxy-1,2-dihydrobenzocyclobutene (2·8 g, 52%), b.p. 112—115° at 0·8 mmHg (lit.,[19] 99—102° at 0·6 mmHg), m.p. 65—67°.

Trapping Reactions with the 1,2-*Diacetoxybenzocyclobutenes*.—(a) cis-*Isomer*. The ester was heated with maleic anhydride (1·1 equiv.) in [$^2H_6$]benzene, sealed in an n.m.r. tube. No reaction occurred after 90 h at 110°. When the temperature was increased to 140° decomposition of the diacetate occurred with elimination of acetic acid, but no adduct formation could be detected. A similar result was obtained using 1,4-naphthoquinone as the dienophile. The diacetate was stable at 110° for prolonged periods.

(b) trans-*Isomer*. Heating the ester (175 mg) with maleic anhydride (70 mg) at 110° in toluene (25 ml) in the dark for 140 h gave, on cooling, prisms of 1,4-*diacetoxy*-1,2,3,4-*tetrahydronaphthalene*-2,3-*dicarboxylic anhydride* (21; R = Ac) (138 mg, 61%), m.p. 200° then 254—255° (naphthalene-2,3-dicarboxylic anhydride has m.p. 254°), $\nu_{max.}$ (Nujol) 1865, 1790, 1740, and 1240 cm^{-1}, $\lambda_{max.}$ (EtOH) 239, 253, 260, 281, 290sh, 337, and 355 nm (ε 19,700, 17,000, 18,200, 3700, 2350, 1050, and 1420), τ 2·3—2·7 (4H, m, aromatic), 3·65 (2H, m, 2-H, 3-H), 6·10 (2H, m, benzylic), and 7·89 (6H, 2 × Ac) (Found: C, 60·7; H, 4·6. $C_{16}H_{14}O_7$ requires C, 60·4; H, 4·4%).

When the reaction was carried out in xylene instead of toluene the major product was not the diacetate, but naphthalene-2,3-dicarboxylic anhydride (61%), m.p. 254°, identical with an authentic sample.

Heating the *trans*-diacetate (276 mg) with 1,4-naphthoquinone (194 mg) in xylene (15 ml) at reflux for 70 h (reaction subsequently found to be complete well within this time), and cooling afforded crystals of naphthacene-5,12-dione (25) (270 mg, 84%), m.p. 292° (lit.,[26] 294°), $\nu_{max.}$ (Nujol) 1680 cm^{-1}, $\lambda_{max.}$ (dioxan) 282, 293, 310sh, and 388 (ε 33,450, 35,960, 9590, and 5500).

Preparation of cis- *and* trans-1,2-*Dimethoxy*-1,2-*dihydrobenzocyclobutene*.—To a stirred solution of freshly prepared silver fluoroborate (4·0 g) in methanol (20 ml) at room temperature in the dark was added a solution of *cis*- and *trans*-1,2-di-iodo-1,2-dihydrobenzocyclobutene (2·0 g) in methanol (40 ml). After 2·5 h sodium hydrogen carbonate (4·5 g) was added and stirring continued for 3 h before filtering, and evaporation of the filtrate to small bulk. The residue was treated with water (50 ml) and then extracted with dichloromethane to give a crude mixture of the dimethoxy-derivatives (865 mg, 94%) as a pale yellow oil.

An n.m.r. analysis showed the ratio of *cis*- to *trans*-isomers to be 1 : 3 [for the *cis*-isomer: τ 2·7 (aromatic), 4·88 (2H, s, methine protons), and 6·45 (6H, s, 2 × MeO); for the *trans*-isomer: τ 2·7 (aromatic), 5·27 (2H, s, methine protons), and 6·48 (6H, s, 2 × MeO)]. The mixture could not be separated by p.l.c. so it was used directly in trapping reactions. The same mixture of dimethoxy-substituted derivatives was obtained when using pure *cis*- or *trans*-1,2-di-iodo-1,2-dihydrobenzocyclobutene, indicating the existence of a common intermediate during solvolysis.

Trapping Reactions with cis- *and* trans-1,2-*Dimethoxy*-1,2-*dihydrobenzocyclobutene*.—The 1 : 3 mixture of *cis*- and *trans*-ethers (124 mg) was heated with maleic anhydride (70 mg) in [$^2H_6$]benzene (0·5 ml) in a sealed n.m.r. tube at 80°. After 1 h all the *trans*-isomer had reacted whilst the *cis*-isomer remained unchanged. On heating for a longer period at higher temperatures (110°) the *cis*-isomer remained unaffected whilst the initial adduct from the other isomer appeared to decompose with liberation of methanol. The reaction was carried out on a larger scale (using 246 mg of the mixture) in benzene solution. After 3 h the solution was filtered and the filtrate evaporated to give a crystallising oil. Recrystallisation of the solid from chloroform–light petroleum gave 1,4-*dimethoxy*-1,2,3,4-*tetrahydronaphthalene*-2,3-*dicarboxylic anhydride* (21; R = Me) (181 mg, 75% based on starting *trans*-isomer), m.p. 158—159° then 254—255°, $\nu_{max.}$ (Nujol) 1865, 1850, 1785, 1210, 1195, and 1185 cm^{-1}, τ 2·50 (4H, s, aromatic), 5·23 (2H, m, methine protons), 6·32 (2H, m, 2-H and 3-H), 6·73 (6H, s, 2 × MeO) (Found: C, 64·1; H, 5·4. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%).

Attempted Catalysis of Ring-opening of 1,2-*Disubstituted Systems*.—Heating the *cis*-ether (41 mg) in the presence of silver fluoroborate (70 mg) using benzene as solvent gave no sign of the adduct (21; R = Me) after 90 h at 110°. Similarly the *cis*-diacetoxy-derivative (19; R = Ac) also failed to react under comparable conditions. At higher temperatures general decomposition of the derivatives occurred.

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