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

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On heating, 1,2-dihydrobenzocyclobuten-1-ol and its derivatives undergo an electrocyclic, conrotatory ring opening to form the corresponding o-quinonedimethide species in which the oxygen substituent always adopts the (E)-configuration. The dimethide species can be trapped with a variety of dienophiles, including maleic anhydride and quinones. These trapping experiments prove that the o-quinonedimethide species produced thermally are identical with the photoenols formed during the irradiation of o-alkylaromatic ketones. The rate of ring opening of substituted benzocyclobutenols depends on the electronic nature of the substituents as well as their size.

IT has been proposed that photolysis of 2-methylbenz-aldehyde (1) can lead to the dienol (2) and that transient formation of the cyclobutenol (3; R = H) can be involved in this process.[1] In order to provide evidence for this scheme it was necessary to demonstrate that heating benzocyclobutenol does lead to the same (E)-dienol (2) before final collapse to the aldehyde (1). It is known that heating benzocyclobutenols converts them

[1] Part II, B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, preceding paper.

into the corresponding carbonyl compounds,[2] Furthermore, the reaction can be catalysed by base.[3] For

(1)   (2)   (3)

(4)   (5)   (6)

(7)
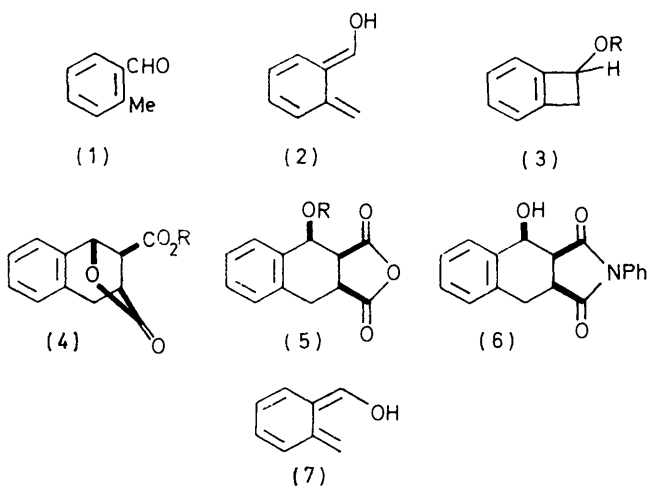
benzocyclobutenol the conversion into 2-methylbenzaldehyde was virtually complete after heating it at 110° for 5 h. The thermal reaction was not due to a base catalysed process (e.g. at the walls of the reaction vessel) since it was reproducible and unaffected by using apparatus which had been carefully washed with acid prior to use.

The intermediate formation of the (E)-dienol (2) was demonstrated by heating the alcohol in the presence of 1 equiv. of maleic anhydride. Disappearance of the alcohol at 110° proceeded at the same rate as in the absence of the dienophile but only traces of 2-methylbenzaldehyde were produced, the principal product being the adduct (4; R = H), characterised as its methyl ester (4; R = Me). The acid was previously obtained by heating the initial photochemical adduct (5; R = H), obtained from the irradiation of 2-methylbenzaldehyde (1) in the presence of maleic anhydride.[1] An examination of the residues from the reaction mixture showed that a small amount of the anhydride (5; R = H) was present. In subsequent reactions heating was carried out for a slightly longer period in order to effect a complete conversion of the hydroxy-anhydride into the lactone (4; R = H). Use of a slight excess of the dienophile completely inhibited the formation of the trace amounts of the aldehyde (1) observed in the reaction mixture. When N-phenylmaleimide was used as the dienophile, the expected adduct (6) formed, which did not readily undergo subsequent transannular cyclisation. Dimethyl butynedioate was also added to the alcohol (see Experimental section).

Based on previous stereochemical assignments[1] these results imply that the benzocyclobutenol preferentially opens to produce the (E)-dienol (2) via a selective, conrotatory process.[4] No adduct corresponding to

trapping of the (Z)-dienol (7) could be detected. Ring opening occurred at a relatively low temperature, the parent benzocyclobutene not undergoing detectable rearrangement until temperatures of 150° or more.[5] In order to estimate the activation energy for ring opening of the benzocyclobutenol a sample was resolved and the dextrorotatory form isolated. This separation was achieved by prior formation of the hydrogen phthalate ester (3; R = hydrogen phthaloyl) from the alcohol and phthalic anhydride in pyridine. Resolution of the acid as its brucine salt afforded the optically active ester from which the optically active alcohol (3; R = H), $[\alpha]_D^{28}$ +60°, was released by reduction with lithium aluminium hydride. Heating the active alcohol at 110° smoothly gave 2-methylbenzaldehyde (1). The rate of decrease of its optical activity was the same as the increase in the concentration of aldehyde, indicating that proton transfer processes (step 2, Scheme) were faster than the rate of racemisation (step 3). Since it had already been shown that the rate of trapping with, for example, maleic anhydride, was dependent on the ring opening stage (step 1) it may be concluded that the

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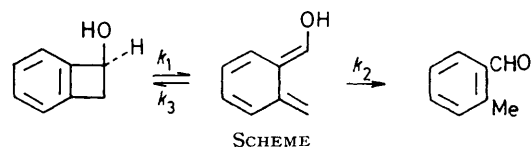
rates of the relative processes are in the order $k_2 > k_3 > k_1$, provided that the energy of the intermediate dienol lies above that of the ground state benzocyclobutenol. Although the dienol (2) has been detected from spectroscopic studies at low temperatures[6] no absorption due to this species could be detected in the u.v. spectrum of the alcohol (3; R = H), which justifies the latter assumption.

Because of the failure to observe any racemisation of the starting alcohol in the above experiments, a sample of the optically active methyl ether (3; R = Me) was prepared by methylation of the optically active alcohol with methyl iodide in the presence of silver oxide. The ether had $[\alpha]_D^{25}$ +38°. Although little general decomposition occurred in the temperature range 80—130°, racemisation was observed at temperatures above 80°. From these experiments an estimate for the free energy of activation for the opening of the cyclobutene ring of 31 kcal mol^{-1} was obtained. The recovery of racemic starting material from these experiments is the first firm evidence for the reversibility of the process, benzocyclobutene to o-quinonedimethide, in the oxygen substituted

[2] Y. Kitaura and T. Matsuura, Tetrahedron, 1971, 27, 1597.
[3] M. P. Cava and K. Muth, J. Amer. Chem. Soc., 1960, 82, 652; L. Horner, P. V. Subramanian, and K. Eiben, Annalen, 1968, 714, 91.

[4] For opening of cyclobutenes, see E. Vogel, Annalen, 1958, 615, 14; R. E. K. Winter, Tetrahedron Letters, 1965, 1207; E. Gil-Av and T. Shabtei, J. Org. Chem., 1964, 29, 757; H. M. Frey, Trans. Faraday Soc., 1962, 58, 957; R. Criegee, D. Seebach, R. E. K. Winter, B. Börretzen, and H. A. Brune, Chem. Ber., 1965, 98, 2339. For opening of benzocyclobutenes, see F. R. Jensen and W. E. Coleman, J. Amer. Chem. Soc., 1958, 80, 6149; G. Quinckert, W.-W. Wiersdorff, M. Finke, K. Opitz, and F.-G. von der Haar, Chem. Ber., 1968, 101, 2302.
[5] F. R. Jensen, W. E. Coleman, and A. J. Berlin, Tetrahedron Letters, 1962, 15.
[6] G. Wettermark, Photochem. Photobiol., 1965, 4, 621.

series (cf. step 3, Scheme). Recently Oppolzer has obtained similar results for a series of nitrogen substituted analogues.[7] In the presence of maleic anhydride the (+)-1-methoxybenzocyclobutene disappeared at a rate identical to the rate of adduct formation. Since the adduct (5; R = Me) was racemic, trapping of a planar intermediate is established. Thus, the chirality of the starting benzocyclobutenyl species does not influence the subsequent course of the reaction. A similar result (viz. racemic adduct) was obtained by trapping the optically active alcohol (3; R = H), which demonstrates that hydrogen bonding between the reactants before ring opening is not important. The adduct from the methyl ether [viz. (5; R = Me)] was, however, formed stereoselectively and, from an analysis of its ¹H n.m.r. spectrum it was again assigned as the all cis-isomer depicted.

In contrast to the relatively rapid rate of reaction observed in the opening of the alcohol (3; R = H) and its corresponding methyl ether, the reaction of the acetate (3; R = Ac) with maleic anhydride was much slower, reaction taking 4 h at 180°. A comparison of the rates of trapping of the substituted cyclobutenes indicates the trend OMe > OH ≫ OAc and hence the presence of a powerful inductive effect exerted by the substituents. Since the rates of reaction are limited by the rate of electrocyclic opening of the cyclobutene ring, cycloaddition being a much faster process, the substituents are primarily affecting the electrocyclic process. Although the effect of heteroatom substituents on the rates of electrocyclic processes have been noted previously,[5,8] little account of their importance has been made. Most of the previous work on the cyclobutene to butadiene reaction relates to substitution by alkyl[9] or phenyl[10] groups.

An immediate consequence of the appropriate substitution of substrates undergoing electrocyclic reactions is to help control synthetic reactions. Since the alcohol opens to form the reactive dienol under very mild conditions, compared to the parent benzocyclobutene, cycloaddition reactions can be carried out with a wide range of dienophiles. For example, the alcohol (3; R = H) reacts with naphthoquinone in refluxing benzene to give good yields of the tetracyclic naphthacene (8) directly and stereoselectively (yield 75%). This adduct was unstable to acid and base and was readily dehydrated at temperatures above 100°. The product from heating the adduct (8) was not the expected product (9), since this is known to disproportionate to form the naphthacenequinone (10) and the corresponding benzanthrone (11).[11] Careful dehydration of the adduct (8), using a trace of toluene-p-sulphonic acid in toluene, followed by oxidation with manganese dioxide

in benzene at room temperature led to the quinone (10) directly and cleanly. Oxidation of the initial adduct (8) with manganese dioxide yielded a mixture of the naphthacenequinone (10) and the expected 5-hydroxy-naphthacenequinone. 1,2-Dihydrobenzocyclobuten-1-ol also reacted with 2,3-diacetoxynaphthoquinone to give the expected adduct (12), but in this case the yield was much reduced (18%), presumably because of the steric hindrance about the dienophilic bond.

An interesting result was obtained with 2-phenyl-5-oxonaphthofuran (13). In refluxing toluene, the benzo-cyclobutenol (3; R = H) reacted smoothly with this dienophile to give two isomeric adducts (established from microanalytical and mass spectral data). Assuming the active intermediate is the (E)-dienol (2), four possible stereoisomers are predicted for the adducts, those resulting from exo or endo and head or tail addition. Oxidation of either isomer with manganese dioxide in benzene afforded the same mixture of the inseparable compounds (14) and (15). Assuming a cis-orientation about positions 6a and 12a, the adducts must therefore be isomeric about position 7. The i.r. and ¹H n.m.r. spectra (see Experimental section) allowed specific assignments to be made to the two adducts. The less polar isomer showed intramolecular hydrogen bonding and this can only exist in the all-cis isomer (16), whilst the more polar material must be the trans-cis adduct (17) in which intramolecular hydrogen bonding between the hydroxy and adjacent carbonyl group is not possible. Since both adducts have the same substitution pattern they must arise by exo- and endo-addition to the dienol (2).

(8) (9) (10) (11) (12)
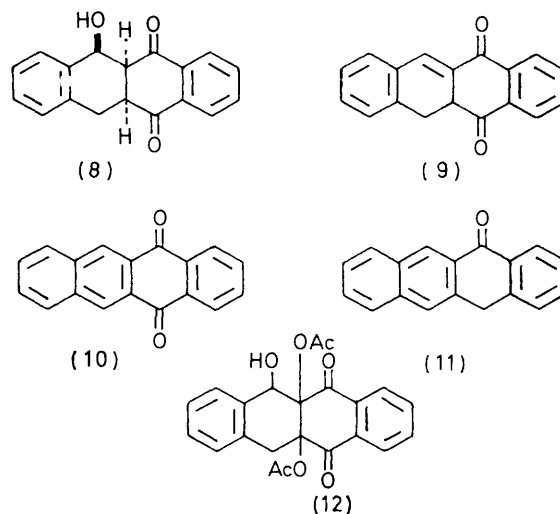
Exo-addition is encouraged by the presence of the phenyl substituent at position 2 of the naphthofuran (13)[12] which can adopt a conformation orthogonal to the plane of the rest of the molecule. The approach to

[7] W. Oppolzer, J. Amer. Chem. Soc., 1971, 93, 3834.

[8] R. Gompper, E. Kutter, and H. Kast, Angew. Chem. Internat. Edn., 1967, 6, 171; U. Svanholm and V. D. Parker, J.C.S. Chem. Comm., 1972, 645; G. F. Emerson, L. Watts, and R. Pettit, J. Amer. Chem. Soc., 1965, 87, 131.

[9] H. M. Frey, J. Metcalfe, and B. M. Pope, Trans. Faraday Soc., 1971, 67, 750 and references therein; see also ref. 4.

[10] G. Quinkert, K. Opitz, W.-W. Wiersdorff, and M. Finke, Annalen, 1966, 693, 44; J. I. Brauman and W. C. Archie, jun., Tetrahedron, 1971, 27, 1275; see also ref. 4.

[11] L. F. Fieser, J. Amer. Chem. Soc., 1931, 53, 2329.

[12] D. H. R. Barton, B. Halpern, Q. N. Porter, and D. J. Collins, J. Chem. Soc. (C), 1971, 2166.

the dienol in the preferred *endo*-direction is thus in-hibited, resulting in competition with the abnormal *exo*-addition mode.[13]

(13)   (14)

(15)   (16)

(17)
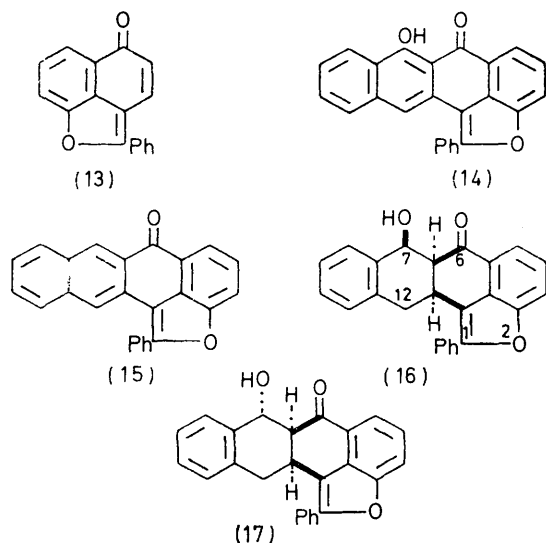
Non-stereoselective addition to the dienol (2) was also observed with acrylonitrile. Although the reaction between acrylonitrile and the benzocyclobutenol (3; R = H) proceeded efficiently at 110° to give an oil (>95%), which was homogeneous to multiple elution t.l.c., and which analysed correctly, its ¹H n.m.r. spectrum showed complex signals which indicated the presence of a mixture of isomers. These could be

(18)   (19)   (20)
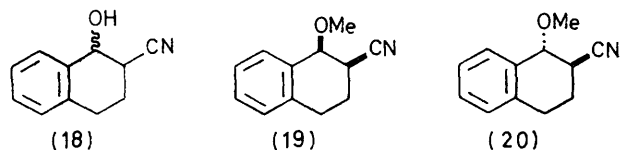
separated after methylation with methyl iodide, using silver oxide in dry dichloromethane. The two isomers (19) and (20) (ratio 7 : 3 respectively) were not separately epimerised by further exposure to the methylating conditions, indicating that the initial adduct (18) was a mixture of the two epimeric alcohols. A similar mixture of the methyl ethers (19) and (20) was obtained by direct reaction of the cyclobutenyl ether (3; R = Me) with acrylonitrile (product ratio 7 : 3 respectively). Considerable precedent exists for the lower selectivity of addition by acrylonitrile, compared, for example, to maleic anhydride, since less secondary orbital over-lapping is possible.[14]

Heating a sample of the major adduct (19) in toluene eventually produced 3,4-dihydro-2-cyanonaphthalene (20) but no epimerisation into the minor isomer occurred under these conditions.

In summary, photodienols of the type (2), which were formerly only obtained by irradiation of the correspond-ing *o*-alkylaromatic ketone, can now be conveniently prepared by heating 1,2-dihydrobenzocyclobuten-1-ols, thus greatly extending the synthetic utility of these reactive intermediates. Some reactions of disubstituted benzocyclobutenes and their derivatives are discussed in the following paper.

EXPERIMENTAL

General experimental details were as described previ-ously.[1] Solvents were dried and distilled before use. 1,2-Dihydrobenzocyclobuten-1-yl acetate was prepared according to the method of Wasserman and Solodar,[15] using the method of Logullo *et al*,[16] to prepare benzyne. Hydrolysis of the acetate to give the alcohol (3; R = H) was achieved by methanolysis using Amberlite IR-120(H) ion exchange resin in the acid form as catalyst. The alcohol had m.p. 58—59° (lit.,[3] 58—59°). Maleic anhydride was sublimed before use.

Reaction of the Alcohol (3; R = H) *with Maleic Anhydride.* —The alcohol (0·062 g) and maleic anhydride (0·051 g) in toluene (20 ml) were heated at reflux (110—111°) for 5·5 h when no alcohol remained. Evaporation of the solvent to *ca.* 10 ml afforded a crystalline solid (0·09 g, 82%), m.p. 130—160°, which was a mixture of the hydroxy-anhydride (5; R = H) and the acid lactone (4; R = H). In a similar run reflux was continued for 18 h and evaporation afforded the pure acid lactone directly (0·093 g, 84%), m.p. 163—165° (lit.,[17] 160—164°).

Methylation of a sample of the acid with diazomethane gave the methyl ester (4; R = Me), m.p. 91—92° (lit.,[1] 91—92°).

Reaction of the Alcohol (3; R = H) *with Dimethyl Butyne-dioate.*—The alcohol (0·062 g) and the acetylenic ester (0·079 g) were heated together in toluene (20 ml) for 4·5 h. The unstable product was dehydrated by further heating in toluene (10 ml) containing a trace of toluene-*p*-sulphonic acid for 2 h to give dimethyl naphthalene-2,3-dicarboxylate (0·080 g, 63%), m.p. 45—48°, identical with an authentic sample.

Reaction of the Alcohol (3; R = H) *with 1,4-Naphtho-quinone.*—The alcohol (0·062 g) and 1,4-naphthoquinone (0·083 g) were dissolved in benzene (20 ml) and heated at reflux for 89 h in the dark. Evaporation to small bulk and recrystallisation of the product from benzene gave 6-*hydroxy*-5a,6,11,11a-*tetrahydronaphthacene*-5,12-*quinone* (8) (0·089 g, 65%), m.p. 285° (subl.). The mother liquor showed, by t.l.c., more of the adduct together with a small amount of the starting naphthoquinone. The adduct had ν_{max} 3500, 1690, and 1595 cm⁻¹, τ 1·7—2·9 (8H, m, aromatic), 5·0 (1H, m), 5·65 (1H, d, exchanged with D_2O), and 6·2—7·4 (4H, m, saturated CH). A detailed 100 MHz examin-ation showed H-6 to be present as a double doublet, *J* 6·5, and 3·0 Hz. The larger coupling constant was to the alcohol proton; the smaller was to H-5a, centred at τ 7·0, and is consistent with a *cis*-configuration about these centres if the hydroxy-group adopts a *pseudo*-equatorial conformation; rings B and c exist as half-chair con-

[13] D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.

[14] H. Krieger, *Suomi Kemst.*, 1962, **35B**, 4 (*Chem. Abs.*, 1962, **57**, 11,041i); Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, 1970, **92**, 6548.

[15] H. H. Wasserman and J. Solodar, *J. Amer. Chem. Soc.*, 1965, **87**, 4002.

[16] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.

[17] S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.

formers; M^+ 278 (weak) and 260 (Found: C, 77·5; H, 5·2. $C_{18}H_{14}O_3$ requires C, 77·5; H, 5·0%).

Reactions of the Quinone Adduct (8).—The adduct (30 mg) in benzene (15 ml) was stirred at room temperature with freshly dried MnO_2 for 15 min. The reagent was removed by filtration and the residual liquors evaporated to give orange needles, m.p. 294°. T.l.c. showed the product to be a mixture of two very closely running compounds. The mass spectrum showed M^+ 274 and 258, corresponding to a mixture of compounds (10) and 5-hydroxynaphthacene-6,11-quinone. The mixture (26 mg) had $v_{max.}$ 1680 and 1620 cm⁻¹, and a weak, broad bonded OH absorption.

Dehydration of the adduct (8) (20 mg) using toluene-*p*-sulphonic acid in benzene at reflux for 15 min, followed by oxidation with manganese dioxide at room temperature and filtration and evaporation, gave, from nitrobenzene, pale yellow crystals of naphthacene-5,12-quinone (10) (12 mg), m.p. 288° (lit.,[11] 285°), $v_{max.}$ (Nujol) 1680 cm⁻¹, $\lambda_{max.}$ (dioxan) 282, 293, 310, and 390 nm (ε 34,000, 35,000, 9800, and 5000). The compound gave a violet colour with conc. H_2SO_4, which was discharged by dilution with water, precipitating yellow crystals.

Reaction of the Alcohol (3; R = H) *with the Naphthofuran* (13).—The alcohol (0·122 g) and the furan (0·254 g) in toluene (40 ml) were heated at reflux for 7 h in the dark. The mixture was evaporated to dryness and the products isolated by p.l.c. to give two products. The less polar material was 7β-*hydroxy*-6α,7,12,12aα-*tetrahydro*-1-*phenyl-naphthaceno*[1,12-bc]*furan*-6-*one* (16) (0·121 g, 33%), m.p. 165—182° (decomp.) (from benzene–light petroleum) as off-white, fluorescent needles, $v_{max.}$ 3525, 3250, and 1670 cm⁻¹, $\lambda_{max.}$ 274, 293, 304, and 356 nm (ε 20,130, 13,470, 10,700, and 13,070), changed to $\lambda_{max.}$ 245, 303, 335, and 396 and then 254, 313, 336, and 420 with a drop of base, τ 2·0—3·2 (8H, m, aromatic), 4·92 (1H, dd, J 11 and 5 Hz, larger J collapses with D_2O, H-7), 5·37 (1H, d, J 11 Hz, exchanged with D_2O, OH), 5·7—6·0 (1H, m, from decoupling experiments this had J 5, 5·5, and 11 Hz, H-6a), 6·30 (1H, m, H-12a), 6·6—7·35 (2H, AB part of an ABX system, J_{gem} 18 Hz, 12-H_2), *m/e* 366 (M^+), 349, 348, 347, 331, 319, 318, 289, 248, and 247 (Found: C, 81·7; H, 5·0. $C_{25}H_{18}O_3$ requires C, 82·0; H, 4·9%). The more polar product was the 7α-*hydroxy-isomer* (17) (0·164 g, 45%), m.p. 159—170° (decomp.) (from acetonitrile), $v_{max.}$ (Nujol) 3460 and 1680 cm⁻¹, $\lambda_{max.}$ 274, 293, 305, and 352 nm (ε 21,960, 14,950, 12,200, and 14,950), changed with base as for its isomer (16), τ 2·0—3·2 (12H, m, aromatic), 4·40 (1H, s), 5·45—5·82 (1H, m, J 5, 5·5, and 11 Hz, H-12a), 6·50 (1H, m, J ca. 5 Hz), 6·66—7·45 (2H, AB part of an ABX system, J_{gem} 18 Hz, also J 5·5 and 11 Hz, 12-H_2), and 7·88br (1H, s, exchanged with D_2O, OH), *m/e* 366 (M^+), 349, 348, 347, 346, 319, 318, 289, 248, and 247 (Found: C, 81·8; H, 5·1. $C_{25}H_{18}O_3$ requires C, 82·0; H, 4·9%).

Oxidation of either of the adducts (16) or (17), using MnO_2 in benzene at room temperature, gave the same mixture of products, M^+ 362 and 346, corresponding to a mixture of the naphthacene derivatives (14) and (15).

When the adducts (16) and (17) were separately dehydrated using 2N-NaOH (6 drops) in ethanol (50 ml) at room temperature (40 mg scale), both gave a yellow crystalline precipitate of 1-phenylnaphthaceno[1,12-bc]-furan-6-one (15) (>90%), m.p. 245° (lit.,[18] 245°), identical with an authentic sample.

[18] E. Aufderhaar, J. E. Baldwin, D. H. R. Barton, D. J. Faulkner, and M. Slaytor, *J. Chem. Soc.* (C), 1971, 2175.

Reaction of the Alcohol (3; R = H) *with* 2,3-*Diacetoxy-*1,4-*naphthoquinone.*—The alcohol (0·136 g) and the quinone (0·295 g) were heated together in toluene (25 ml) at reflux for 22 h. On cooling, crystals of the adduct were obtained and washed with a little solvent to give 5a,11a-*diacetoxy*-6-*hydroxy*-5a,6,11,11a-*tetrahydronaphthacene*-5,12-*quinone* (76 mg, 18%), m.p. 175—177°, $v_{max.}$ (Nujol) 3550—3350br,w, 1750, 1730, 1720, and 1705 cm⁻¹, $\lambda_{max.}$ 226, 255, and 301 nm (ε 15,500, 4250, and 1060), *m/e* 394 (M^+), 292, 274, 263, 258, 247, 246, 202, and 191, τ 1·80—2·97 (8H, m, aromatic), 3·99 (1H, s, H-6), 5·49 (1H, s, exchanged with D_2O), 5·88 and 6·70 (each 1H, d, J 16 Hz, 11-H_2), and 7·87 and 8·10 (2 × Ac) (Found: C, 67·0; H, 4·7. $C_{22}H_{18}O_7$ requires C, 67·0; H, 4·6%).

Reaction of the Alcohol (3; R = H) *with* N-*Phenyl-maleimide.*—The alcohol (0·125 g) and N-phenylmaleimide (0·178 g) were heated in toluene (40 ml) at reflux for 5 h. Evaporation of the solvent and recrystallisation of the residue from ethanol gave N-*phenyl*-1β-*hydroxy*-1,2α,3α,4-*tetrahydronaphthalene*-2,3-*dicarboximide* (6) (0·248 mg, 83%), m.p. 163—165°, $v_{max.}$ (Nujol) 3450, 1760, and 1700 cm⁻¹, τ 4·8—5·1br (1H, s, C*H*OH), 6·25 (1H, d, J 10 Hz, exchanged by D_2O, OH), and 6·4—7·2 (4H, m) (Found: C, 73·8; H, 4·8. $C_{18}H_{15}NO_3$ requires C, 73·75; H, 5·1%).

Resolution of the Alcohol (3; R = H).—The alcohol (0·50 g) in dry pyridine (5 ml) was treated with phthalic anhydride (0·62 g) at room temperature for 18 h. The mixture was poured into an excess of dilute HCl and the solution was extracted with dichloromethane to give the ester *acid phthalate* (0·81 g, 72%), m.p. 112—113°, $v_{max.}$ (Nujol) 3500—2500, 1725, and 1690 cm⁻¹ (Found: C, 71·8; H, 4·6. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The reaction was repeated on a larger scale in 88% yield. The ester (4·0 g) and brucine (5·9 g) were dissolved in hot ethanol, and the solution was filtered and slowly cooled, to give needles of the salt (4·0 g, 41%), m.p. 121—127° after two recrystallisations from EtOH. The salt was stirred at room temperature with an excess of dilute HCl, and the free acid ester extracted into dichloromethane. Evaporation of the extract gave the acid ester, $[\alpha]_D^{22}$ +8° (c 3·5, $CHCl_3$), as an oil which crystallised (1·64 g). A portion of the ester (1·6 g) was reduced with lithium aluminium hydride (1·2 g) in dry ether (150 ml) under N_2 at room temperature. Addition of saturated NH_4Cl solution, followed by extraction into ether, afforded the optically active alcohol (0·56 g, 75%), m.p. 45—52°, $[\alpha]_D^{28}$ +60°. The ¹H n.m.r. spectrum and t.l.c. properties of this material were identical with that of the racemic alcohol.

Treatment of the Optically Active Alcohol (3; R = H).— Thermal reactions of the alcohol were carried out in sealed tubes. Reactions were followed by ¹H n.m.r. spectroscopy. The rate of disappearance of the alcohol was also followed by changes in optical rotation with time, readings being taken on aliquot portions which were rapidly cooled to room temperature. The half-life for the disappearance of the alcohol, and for the formation of 2-methylbenzaldehyde, at 112° was 92 min. The rate of disappearance was unaffected by the presence of maleic anhydride. (These reactions were carried out on 0·5% w/v solutions.) Since considerable error was present in estimates of the aldehyde concentration, accurate rate studies were not possible.

Methylation of the Alcohol (3; R = H).—A solution of the alcohol (0·99 g) in chloroform (50 ml) with methyl iodide (4·0 g) and freshly prepared silver oxide (2·0 g) was stirred

at room temperature for 16 h. After filtering and evapor-ation the methyl ether was obtained as a pale yellow oil (1·1 g, 100%). A sample was microdistilled at 20—21° and 0·25 mmHg, to give pure 1,2-*dihydro*-1-*methoxybenzocyclo-butene* (3; R = Me), as an oil, $\nu_{max.}$ (film) 1210 cm^{-1}, τ 2·73br (4H, s, aromatic), 5·02 (1H, dd, *J* 2 and 4 Hz, 1-H), 6·75 and 7·0 (2H, AB part of an ABX system, J_{gem} 15 Hz, also *J* 4 and 2 Hz respectively), and 6·53 (3H, s, MeO) (Found: C, 80·2; H, 7·6. $C_9H_{10}O$ requires C, 80·55; H, 7·5%).

In a similar manner a sample of the optically active alcohol was methylated to give the optically active ether, $[\alpha]_D^{25}$ +38° (*c* 2·0, benzene).

Trapping Reactions on the Ether (3; R = Me).—The ether (0·13 g) and maleic anhydride (0·096 g) in toluene (40 ml) were heated at reflux for 6 h. Evaporation of the solvent left c-1-*methoxy*-1,2,3,4-*tetrahydronaphthalene*-r-2,c-3-*dicarboxylic anhydride* (5; R = Me) (0·23 g, 100%), as an oil which crystallised, m.p. 134—135° (from EtOH), $\nu_{max.}$ (Nujol) 1860 and 1780 cm^{-1}, τ 2·63br (4H, s, aromatic), 5·24 (1H, distorted d, *J* 3 Hz), 6·5—6·87 (4H, m), and 6·87 (3H, s, MeO), τ (C$_6$D$_6$) 2·2—2·8 (4H, m), 5·15 (1H, d, *J* 3 Hz, -CHO-), 6·2—7·1 (4H, m), and 6·84 (3H, s). The n.m.r. pattern was almost identical with that observed for the anhydride produced by trapping of 1,2-dihydrobenzo-cyclobuten-1-ol with maleic anhydride, after exchange of the hydroxy-proton with D_2O. (Dreiding models show two possible conformations of the perhydro-ring. In the conformation with the methoxy-substituent in the pseudo-equatorial position, the torsion angle between H-1 and H-2 was *ca.* 50°.) (Found: 67·1; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·25; H, 5·2%).

When the reaction was repeated, using optically active ether, the product was formed at the same rate and was identical with the racemic product described above. The rate of disappearance of the ether was the same as the rate at which the adduct formed, *i.e.* trapping was faster than the process leading to racemisation. At 112° the half-life for trapping was 72 min.

Thermolyses of the Methyl Ether (3; R = Me).—Samples of (+)-1-methoxy-1,2-dihydrobenzocyclobutene (2% w/v) in dry [$^2H_6$]benzene were heated in sealed tubes at 82, 112, and 130°, the reaction being monitored by readings of the rotation at intervals. That no general decomposition occurred was shown by examining the ^1H n.m.r. spectrum of the samples during and after reaction. First order kinetics were observed over several half-lives in the case of the two higher temperatures, and to one half-life (*ca.* 35 h) for the lower temperature. Calculated rates for the racemisation were k^{82} 5·55 × 10^{-6}, k^{112} 1·63 × 10^{-4}, and k^{130} 1·14 × 10^{-3} s^{-1} from which the activation energy for the overall process of 31 Kcal mol^{-1} was obtained.

Reaction of the Acetate (3; R = Ac) *with Maleic An-hydride.*—The acetate [15] (0·175 g) and maleic anhydride

(0·102 g) were heated together at 180° for 4 h. Evapor-ation under reduced pressure left an oil which crystallised to give c-1-*acetoxy*-1,2,3,4-*tetrahydronaphthalene*-r-2,c-3-*di-carboxylic anhydride* (5; R = Ac) (0·11 g), m.p. 128—131° (from EtOH), $\nu_{max.}$ 1840, 1745, and 1725 cm^{-1}, τ 2·5—2·9 (4H, m, aromatic), 3·91 (1H, m, C*H*OAc), 6·35—6·90 (4H, m), and 8·03 (3H, s, Ac), τ (C$_6$D$_6$) 2·65—3·34 (4H, m, aromatic), 4·10 (1H, d, *J* 4·3 Hz, C*H*OAc), 6·9—7·6 (4H, m), and 8·60 (3H, s, Ac) (Found: C, 64·4; H, 4·6. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%).

When the trapping reaction was carried out at 112° using toluene as solvent, it was found, by ^1H n.m.r. analysis, that trapping had occurred to *ca.* 10% completion after 48 h, giving a half-life for the reaction of over 250 h.

Reactions with Acrylonitrile.—Heating the alcohol (3; R = H) (64 mg) with acrylonitrile (four-fold excess) in toluene (20 ml) for 6 h gave, after evaporation, the crude adducts (18) (0·099 g, 100%) as a yellow oil. This mixture could not be separated by t.l.c. using several solvent systems. A purified (t.l.c.) sample of the epimeric mixture had $\nu_{max.}$ (film) 3450 and 2275 cm^{-1}. Its n.m.r. spectrum showed the expected resonances, but as multiplets, con-sistent with the presence of a mixture of epimers. When the ether (3; R = Me) (0·134 g) was heated with acrylo-nitrile (three-fold excess) in toluene (40 ml) overnight a mixture of two adducts formed. These were separated by p.l.c. The less polar material, isolated as an oil (0·067 g) has been tentatively assigned as r-2-*cyano*-c-1-*methoxy*-1,2,3,4-*tetrahydronaphthalene* (19). (Assignment made on the basis that the major isomer would be expected to arise from *endo*-addition of acrylonitrile to the *E*-dienol ether.) It had $\nu_{max.}$ (CCl$_4$) 2270, 1105, and 1090 cm^{-1}, τ 2·75br (4H, s, aromatic), 5·53 (1H, d, *J* 5 Hz, H-1), 6·50 (3H, s, MeO), 6·6—7·2 (3H, m), and 7·4—8·3 (2H, m) (Found: C, 75·7; H, 6·75; N, 7·3. $C_{12}H_{13}NO$ requires C, 77·0; H, 6·95; N, 7·5%).

The more polar isomer was isolated as a solid (0·029 g). After recrystallisation from light petroleum this was tentatively assigned as r-2-*cyano*-t-1-*methoxy*-1,2,3,4-*tetra-hydronaphthalene* (20), m.p. 76—77°, $\nu_{max.}$ (CCl$_4$) 2270 and 1105 cm^{-1}, τ 2·75 (4H, m, aromatic), 5·76 (1H, d, *J* 4 Hz, H-1), 6·44 (3H, s, MeO), 6·7—7·25 (3H, m), and 7·7—8·0 (2H, m) (Found: C, 76·7; H, 6·8; N, 7·3. $C_{12}H_{13}NO$ requires C, 77·0; H, 6·95; N, 7·5%).

Methylation of a sample of the epimeric alcohol mixture (18), using methyl iodide–silver oxide in dichloromethane at room temperature for 48 h, gave two methyl ethers, identified by direct spectral comparison, as the ethers (19) and (20), ratio 7 : 3 respectively.