Tetrahedron, 1965, Vol. 21, pp. 2281 to 2288. Pergamon Press Ltd. Printed in Northern Ireland

THE ELECTROPHILIC SUBSTITUTION OF BENZOCYCLOBUTENE—III

BENZOCYCLOBUTENE-4,5-QUINONE AND SOME RELATED COMPOUNDS

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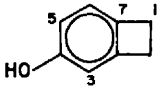
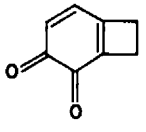
(*Received* 18 *March* 1965)

Abstract—Nitration of 4-acetamidobenzocyclobutene yields 3-(β-acetoxyethyl)-4-nitroacetanilide and 4-acetamido-5-nitrobenzocyclobutene, and thence the 4-amino-5-nitro compound. This last, on diazotization and then reduction, gives 4-nitrobenzocyclobutene, and on diazotization followed by hydrolysis and acetylation, 4-acetamido-5-acetoxybenzocyclobutene. The same acetamidoacetoxy compound is also formed by diazo coupling, reduction and then acetylation of 4-hydroxybenzocyclobutene. Oxidation of 4-hydroxybenzocyclobutene, by nitrosodisulphonate, gives β-hydroxyethyl-1,4-benzoquinone and the remarkably stable benzocyclobutene-4,5-quinone, not benzocyclobutene-3,4-quinone as reported by Horner *et al.* This is shown by the NMR spectrum of the *o*-quinone, and of the corresponding diacetoxy compound, and by conversion of the *o*-quinone, through the corresponding monoxime, to the above 4-acetamido-5-acetoxybenzocyclobutene. The results are analogous to the electrophilic dealkylations and to the high β- relative to α- reactivity characteristic of benzocyclobutene. The stability of the *o*-quinone compares with that of the similarly strained biphenylene-2,3-quinone rather than the corresponding indane compound.

THE relative unreactivity of position 3 in benzocyclobutene towards electrophilic reagents has been interpreted[1,2] as a strain effect. If this is so, then the position 3 of nuclear substituted benzocyclobutenes should likewise be unreactive and result in electrophilic substitution taking place at positions 4 or 5 (deprotonation) and 7 or 8 (dealkylation, as in the parent hydrocarbon[1,2]) depending on the position and nature of the substituent. However, Horner *et al.* report[3] that when 4-hydroxybenzocyclobutene (I) is oxidized by potassium nitrosodisulphonate (Frémy's salt), according to the method of Teuber,[4] the product is benzocyclobutene-3,4-quinone (II). As the



I

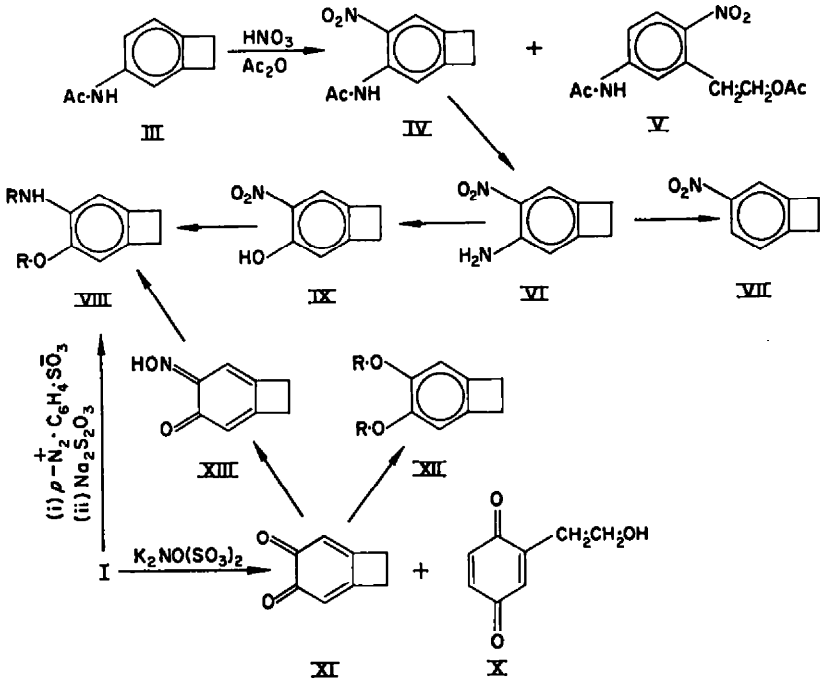


II

orientations of the products obtained in Teuber phenol oxidations are generally similar to those given by other electrophilic reagents,[5] our interpretation of the benzocyclobutene reactions is placed in doubt. We have therefore examined the nitration of

[1] J. B. F. Lloyd and P. A. Ongley, *Tetrahedron* **20**, 2185 (1964).
[2] J. B. F. Lloyd and P. A. Ongley, *Tetrahedron* **21**, 245 (1965).
[3] L. Horner, H. -G. Schmelzer and B. Thompson, *Chem. Ber.* **93**, 1774 (1960).
[4] H.-J. Teuber and G. Jellinek, *Chem. Ber.* **85**, 95 (1952).
[5] H.-J. Teuber and W. Rau, *Chem. Ber.* **86**, 1036 (1953).

4-acetamidobenzocyclobutene, the diazo coupling of the 4-hydroxy compound (I), and the preparation and constitution of Horner's quinone.



Nitration of 4-*acetamidobenzocyclobutene* (III). To facilitate nitration *ortho* to the acetamido group, the reaction is carried out in acetic anhydride.[6] The mixture produced is readily separated by chromatography on silica gel into the bright yellow 4-acetamido-5-nitrobenzocyclobutene (IV) and colourless 3-(β-acetoxyethyl)-4-nitroacetanilide (V), in proportion about 2:1.

The constitution of the substituted benzocyclobutene (IV) is proved by deacylation in methanol, catalysed by methoxide,[7] to the corresponding nitroamine (VI) which on deamination yields the known 4-nitrobenzocyclobutene (VII). Spectroscopic evidence (IR, and UV) is in agreement with this formulation. Thus the nitro group has entered position 5 rather than 3 of the acetamido compound (III).

The structure of the ring opening product (V) follows unambiguously from the spectroscopic evidence (NMR, IR, UV) given in the Experimental section. Since the position taken up by the nitro group must previously have borne a methylene substituent, as indicated by the *para*-oriented acetamido substituent, the reaction can only be formulated as a nitrodealkylation. There is no possibility here that the introduction of a nitro substituent α to the cyclobutene ring has initiated ring opening, as has been suggested[3] in connection with the nitration of the parent hydrocarbon.

Diazo coupling of 4-*hydroxybenzocyclobutene* (I). 4-Hydroxybenzocyclobutene may be prepared by the diazotization and hydrolysis, (4 M H_2SO_4), of the corresponding 4- amino compound.[3] In our hands this method gives rather low yields, which

[6] F. Arnall and T. Lewis, *J. Soc. Chem. Ind.* (*Transactions*) 159 (1929).

[7] P. E. Verkade and P. H. Witjens, *Rec. Trav. Chem.* 62, 201 (1943).

may be due to protolysis of the cyclobutene ring, promoted by an OH substituent and the strong acid used; there are several analogies.[2] In agreement with this, when the reaction is carried out in less strongly acidic media (1·6 M H_3PO_4) excellent yields (about 80%) of the phenol may be obtained.

The phenol couples with diazotized sulphanilic acid to yield a deep red dye which on dithionite reduction yields 4-amino-5-hydroxybenzocyclobutene (VIII, R = H), conveniently characterized as the diacetate (VIII, R = Ac). The structure of the diacetate is established both by spectroscopic and by chemical methods. The NMR and IR spectra show the presence of an intact cyclobutene ring, acetoxy and acetamido substituents, and a 1,2,4,5-tetrasubstituted benzene nucleus. The only exceptional feature here, and in the other nuclear disubstituted benzocyclobutenes that we have examined, is the absence of an IR band at 1200–1210 cm^{-1} which is present in 4-substituted benzocyclobutenes and in the parent hydrocarbon;[1,2] hence this absorption must be associated with the aromatic nucleus and not the cyclobutene ring as we previously suggested. Our chemical proof of structure VIII is the preparation of the same compound from the nitroamine (VI) by diazotization, hydrolysis to the nitrophenol (IX; in 4 M H_2SO_4, the nitro substituent presumably inhibits protolysis of the C_4 ring), reduction, and characterization as the diacetate (VIII, R = Ac) as before.

As the hydroxy-amine (VIII) is the main product of the coupling reaction (about 75%) then the greater reactivity of position 5 relative to 3 in electrotrophilic substitution of the phenol (I) is indicated. The uncharacterized reaction product is highly water soluble and only a small quantity can be separated. This is an amorphous material which oxidizes very rapidly in air; a rather diffuse IR spectrum suggests the presence of hydroxyl and amino groups, and two adjacent aromatic hydrogens. Possibly this material is produced by diazodealkylation of the phenol *para* to the hydroxyl substituent.

Nitrosodisulphonate oxidation of 4-hydroxybenzocyclobutene. This reaction has already been carried out by Horner *et al.*[3] who reported benzocyclobutene-3,4-quinone (II) as the only characterized product, in about 12% yield. We find that the reaction (following Horner's procedure in detail) yields both an *o*- and a *p*-quinone. The *o*-quinone is easily separated from the mixture by virtue of its insolubility in ether at low temperatures. The *p*-quinone is then recovered from the mother liquors and purified by chromatography.

The UV spectrum of the *p*-quinone is closely comparable with that of *p*-toluquinone; NMR and IR data indicate the presence of three quinonoid protons and a β-hydroxyethyl side chain, therefore the compound is β-hydroxyethyl-1,4-benzoquinone (X). The quinone forms a monosemicarbazone of composition in agreement with this formulation. Evidently the compound is a dealkylation product; the quantity isolated corresponds in yield to 35%.

The *o*-quinone is reported by Horner *et al.*[3] as brick red needles that decompose on heating at 140°. Our material, obtained in about 30% yield, is of similar appearance but is stable on heating up to about 158°, when a brown discolouration appears; the compound finally decomposes sharply, and with vigorous deflagration, at 161°. Since the NMR spectrum of the compound shows a two-to-one ratio of methylenic to quinonoid protons, each set appearing as a singlet, then the protons within each set are magnetically equivalent. This precludes the 3,4-quinone (II) as a possible structure

and indicates that the compound should be formulated as benzocyclobutene-4,5-quinone (XI). IR and UV evidence are in agreement with this. As the result is in disagreement with the earlier work[3] we have sought further spectroscopic and chemical proof of structure.

The *o*-quinone takes up one mole of hydrogen over Adam's catalyst to yield the corresponding dihydric phenol (XII, R = H) which forms a diacetate (XII, R = Ac). The NMR spectrum of the diacetate shows the expected benzenoid, methylenic and acetoxy protons, each set as a singlet. This confirms the symmetrical structure (XII) for the diacetate and hence for the *o*-quinone. The IR spectra of both the dihydric phenol and the diacetate support the assigned structures (XII, R = H, R = Ac).

Finally, the *o*-quinone, with hydroxylamine hydrochloride, yields a monoxime (XIII) which by reduction (dithionite) and acetylation is converted to 4-acetamido-5-acetoxybenzocyclobutene (VIII, R = Ac). This constitutes a chemical proof of structure XI for the *o*-quinone.

The evidence advanced by Horner *et al.*[3] for structure II is that the *o*-quinone forms an adduct with 4,5-dimethylpyrogallol. With this reagent *o*-quinones having adjacent unsubstituted positions react to yield benzotropolones.[8] We suggest that in the case of benzocyclobutene-4,5-quinone the formation of a tropolone involves a simultaneous dealkylation, the reaction being facilitated by the lability of the cyclobutene ring.

Benzocyclobutene-4,5-quinone is a remarkably stable compound; for instance, a sample left on the laboratory bench for four months, protected only by a cotton wool plug, is still bright red in colour and has undergone only very slight change in decomposition temperature and IR spectrum; whereas the corresponding indane compound (m.p. 88°, made by nitrosodisulphonate oxidation of 5-hydroxyindane[9]) decomposes perceptibly in 5 hr under such conditions.[9] A solution of the benzocyclobutene quinone in refluxing chloroform is still deep red after 4 hr; however, after a week at room temperature a brown deposit separates from the solution. Possibly the enhanced stability of this compound is due to the rigidity imposed upon it by the deformed bond angles of the cyclobutene ring; the analogy here is with biphenylene-2,3-quinone[10] rather than the corresponding indane quinone.

CONCLUSION

The reactions of the nuclear substituted benzocyclobutenes reported here, leading to products of dealkylation *para* to activating groups, and substitution β to the cyclobutene ring, are as expected from the chemistry of the parent hydrocarbon. In the corresponding reactions of other less strained, nuclear substituted, *o*-dialkyl benzenes, reactivities of activated positions α and β to the alkyl substituents tend to approach one another as strain decreases, and products of either, or both, α and β substitution may be isolated. Examples of this have been reviewed[11,12] in connection with the Mills Nixon effect. We note also the correspondence between the orientation of

[8] L. Horner and W. Dürckheimer, *Z. Naturforsch.* **14b**, 743 (1959).
[9] H. J. Teuber and G. Staiger, *Chem. Ber.* **88**, 802 (1955).
[10] J. M. Blatchly, J. F. W. McOmie and S. D. Thatte, *J. Chem. Soc.* 5090 (1962).
[11] G. M. Badger, *The Structure and Reactions of the Aromatic Compounds* p. 133. Cambridge University Press (1954).
[12] L. D'Albis, *Chim. Mod.* **5**, 209 (1960).

electrophilic substitution on substituted benzocyclobutenes and biphenylenes,[10,13] both series being similarly strained.[2]

EXPERIMENTAL

Mps. are uncorrected. NMR, IR and UV spectra were obtained on Perkin Elmer R10 (60 MC), Infracord-237, and 137-UV instruments respectively.

Nitration of 4-acetamidobenzocyclobutene

A solution of HNO_3 (29 mM) in Ac_2O (5 g) was added during 45 min, to a cooled (0°) stirred suspension of the amide (4·42 g, 27·4 mM) in Ac_2O (35 g); the amide dissolved to give a yellow solution. After standing (15 min) the solution was poured into water (300 ml), the product extracted into $CHCl_3$ (50 ml, × 3), the extracts freed from acid with 5% Na_2CO_3 aq, dried ($MgSO_4$), and the solvent removed. The residue was chromatographed on silica gel (200 g, deactivated by the addition of 5% aq) in $CHCl_3$; these were two well separated fractions.

Crystallization of the first chromatography fraction from light petroleum (b.p. 60–80°) yielded *4-acetamido-5-nitrobenzocyclobutene* (3·11 g, 55%), lemon-yellow needles m.p. 97–98°; IR, in CCl_4, maxima (cm^{-1}) at 3355 m, 1720 s, 1240 s (sec. amide, comparable with *o*-nitroacetanilide), 2940 m (CH_2), 1600 s, 895 m (benzenoid, isolated Ar–H), 1495 s, 1330 s (Ar–NO_2); UV in EtOH, maxima (mμ) at 355 (log ε = 3·15), 281 (3·32), 246 (3·97). (Found: C, 57·97, 57·88; H, 5·13, 4·90; N, 13·72, 13·48. $C_{10}H_{10}N_2O_3$ requires: C, 58·25; H, 4·89; N, 13·59%.) The amide (1·07 g, 5·21 mM) was refluxed in methanolic 0·02-N NaOMe (15 ml). After 1½ hr the solution was cooled, diluted with the aqueous mother liquors from a preliminary experiment, and the product filtered off, washed (aq), and dried, to yield *4-amino-5-nitrobenzocyclobutene* (quantitative), orange, fibrous needles m.p. 110–112°, after recrystallizing from water m.p. 112–113°: IR, KBr disc, maxima (cm^{-1}) at 3460 s, 3330 s, 1630 m (NH_2), 2930m (CH_2), 1590m, 875m (benzenoid, isolated Ar–H), 1500s 1300s (NO_2): UV in EtOH, maxima (mμ) at 417 (log ε = 3·81), 289 (3·74), 261 (3·86), 228 (4·20). (Found: N, 17·40, 17·29; $C_8H_8N_2O_2$ requires: N, 17·06%.)

The second chromatography fraction was highly discoloured, probably due to the presence of oxidation products. Recrystallization from EtOAc yielded colourless *3-(β-acetoxyethyl)-4-nitro-acetanilide* (2·21 g, 30%) leaflets m.p.141·5–142·5°; IR, KBr disc, maxima (cm^{-1}) at 3310 s, 3270 s, 1685 s, 1560 s (sec. amide); 1735 s, 1240 s (acetoxy): 1620 s, 885 m, 845 m (benzenoid, 1,2,4-trisubstituted); 1510 s, 1325 s (Ar–NO_2): NMR, 1 M soln in CF_3CO_2H, N–H as a broadened singlet at 0·86 τ, two *o*-coupled (8 c/s) Ar–H as doublets centred at 1·83 and 2·36 τ and another as a singlet at 2·26 τ, two coupled (6 c/s) methylene groups as triplets at 5·49 and 6·56 τ, and two methyl singlets at 7·50 τ and 7·89 τ: UV in EtOH, maxima (mμ) at 309 (log ε = 3·86) 229 (3·93). (Found: C, 54·58, 54·65; H, 5·56, 5·43; N, 10·34, 10·39. $C_{12}H_{14}N_2O_5$ requires: C, 54·13; H, 5·30; N, 10·52%.)

Deamination of 4-amino-5-nitrobenzocyclobutene

To a cooled (0°) stirred suspension of the nitroamine (200 mg, 1·22 mM) in 4 NHCl aq (4 ml) was slowly added $NaNO_2$ (100 mg, 1·45 mM) in water (1 ml) followed by 30% H_3PO_2 (3 ml). After 1½ hr, at 0°, the mixture was extracted with an equal volume of CH_2Cl_2, and again at hourly intervals up to 4 hr. The combined extracts were dried ($MgSO_4$), concentrated and chromatographed on basic alumina (5 g, activity—I in CH_2Cl_2) to give 4-nitrobenzocyclobutene (156 mg, 86%), m 18–19°, undepressed; IR identical with the known compound.

4-Hydroxybenzocyclobutene

To a cooled (0°), stirred suspension of bis-(4-aminobenzocyclobutene)-sulphate (24 g, 0·071 M) in 1·5 M H_3PO_4 aq (300 ml) was slowly added $NaNO_2$ (11 g, 0·16 M) in water (50 ml) followed by urea (0·5 g) to remove excess HNO_2. The resulting pale-yellow solution was rapidly steam distilled, the distillate (1·5 l) saturated with NaCl, and the phenol, a yellowish solid, filtered off and washed (water); more phenol was extracted from the distillate by Et_2O. The bulked product was chromatographed on silica gel (300 g) in CH_2Cl_2 to yield 4-hydroxybenzocyclobutene (13·4 g, 79%) as colourless needles, m.p. 44–47°. Recrystallization (light petroleum) and vacuum sublimation gave material, m.p. 45·5–47·5°, which still contained a persistent impurity (Found: C, 79·57, 79·63; H, 6·44, 6·49. Calc.

[13] W. Baker, J. F. W. McOmie, D. R. Preston and V. Rogers, *J. Chem. Soc.* 414 (1960).

for C_8H_8O: C, 79·97; H, 6·71%.) IR, KBr disc, maxima (cm^{-1}) at 3500–3050 s, 1235 s, 1200 s, 1160 s, (ArOH); 2920 m, 1450 s (CH_2); 1600 s, 860–850 s (two bands), 815–805 s (two bands), 1,2,4-trisubstituted benzene: NMR (1 M in CCl_4), at 3·18–3·6 τ a multiplet of intensity 1 (hydroxyl and aryl protons), at 7·0 τ a singlet of intensity 1 (benzylic protons): UV in EtOH, a maximum at 283·5 mμ (log $\varepsilon = 3{\cdot}71$).

The product m.p. 44–47° was used in subsequent work.

Diazo coupling of 4-hydroxybenzocyclobutene

A solution of the phenol (0·50 g, 4·2 mM) in 3% NaOH aq (6·75 ml), at 0°, was treated with an aqueous (9 ml) suspension of diazotized sulphanilic acid (4·2 mM) prepared in the usual way, a deep red colouration appeared. To this solution was added sodium dithionite (2·0 g, ca. 10 mM) and the mixture warmed, with stirring, to 45°, when reduction was complete; the solution was now yellow in colour and a flocculent yellow-brown solid had appeared. The mixture was cooled, diluted with water (20 ml, the solid dissolved), extracted with Et_2O (25 ml, × 4) and the combined, dried ($MgSO_4$) extracts taken to dryness to yield *4-amino-5-hydroxybenzocyclobutene* (0·425 g, 75%) as colourless needles which rapidly darkened even in air and especially on heating, m.p. < 144° (dec): IR, KBr disc, Maxima (cm^{-1}) at 3550–2350 s and broad, 1470 s, 1330 s, 1200 s, (phenolic OH); 3380 s, 3310 s, 1600 s and broad, 1310 s ($ArNH_2$); 2920 m, (CH_2); the Ar–H out of plane deformation region was too complex for reliable assignments to be made. The aminophenol was acetylated (pyridine—Ac_2O, 0°, 16 hr), the product separated through $CHCl_3$, chromatographed (silica gel—$CHCl_3$) and recrystallized (EtOH) to yield *4-acetamido-5-acetoxybenzocyclobutene* (0·553 g, 61% overall) as colourless needles, m.p. 159–160°; IR, KBr disc, mixima (cm^{-1}) at 3350 s, 1690 s, 1530 s, 1295 m (amide); 1745 s, 1220 s, (acetoxy); 915 m, 905 m, 885 m, and no others down to 700 (1,2,4,5-tetrasubstituted nucleus): NMR, 0·5 M in $CDCl_3$, 2·2–2·8 τ two protons as a diffuse band with a singlet showing through at 2·36 τ (one N–H, one Ar–H), 3·18 τ a one-proton singlet showing no detectable splitting (Ar–H, no *o*- or *m*- coupling), 6·87 τ a four-proton singlet (two equivalent CH_2's), 7·72 τ and 7·93 τ two three-proton singlets (CH_3COO and CH_3CON respectively): UV in EtOH, maxima (mμ) at 279 (log $\varepsilon = 3{\cdot}29$), 237 (3·68). (Found: C, 65·40, 65·48; N, 6·16, 6·00; N, 6·30, 6·42. $C_{12}H_{13}NO_3$ requires: C, 65·74; H, 5·98; N, 6·39%.)

In another experiment the solid formed during the reduction was centrifuged off, extracted from inorganic material with EtOH, and reprecipitated by the addition of Et_2O. The product (35 mg) was amorphous and rapidly blackened in air; IR, KBr disc, maxima (cm^{-1}) at 3700–2700 s and broad (OH), 1200 s and broad (ArOH), 1035 s (primary OH), 1620 s, 1130 s (NH_2), 1605 s, 830 m (benzenoid, two adjacent Ar–H), the spectrum was not well resolved.

Oxidation of 4-hydroxybenzocyclobutene

(i) The phenol (1·0 g, 8·3 mM) was oxidized by potassium nitrosodisulphonate (6·25 g, 23·3 mM) in 0·038 M KH_2PO_4 aq (430 ml, the solution was at pH ca. 5) following the procedure of Horner *et al.*[8] in detail. The products were extracted into $CHCl_3$ (30 ml, × 8) and the solvent removed under red. press. in a stream of N_2. The solid residue was dissolved in refluxing Et_2O (ca. 250 ml), the solution cooled to −75°, and the resulting crystals filtered off, washed (Et_2O), and dried giving *benzocyclobutene-4,5-quinone* (0·250 g, on unrecovered phenol 28%) as bright red leaflets dec 150–155°. Recrystallization (Et_2O–CH_2Cl_2) gave red needles which were stable on heating up to 158°, thereafter a brown discolouration set in and the crystals decomposed finally with very vigorous deflagration at 161°. (Found: C, 71·47, 71·71; H, 4·74, 4·74. $C_8H_4O_2$ requires: C, 71·63; H, 4·51%.) IR, KBr disc, maxima (cm^{-1}) at 3070 m, 1640 s, 850 s, 840 s (quinonoid, the Ar–H deformation closely comparable with that of indane-5,6-quinone[14] indicating a similar orientation by analogy with benzenoids[14]), 1693 m, 1670 s (*o*-quinonoid C=O[14]), 2950 m, 1440 m (CH_2, "active"): NMR, 1 M in $CDCl_3$, singlets at 3·87 τ and 6·82 τ, intensities 1:2 respectively (equivalent quinonoid and equivalent benzylic protons): UV in EtOH, maxima (mμ) at 528 (log $\varepsilon = 1{\cdot}49$), 384 (3·12), 270 (3·63), in $CHCl_3$ the 528 mμ band was at 548 mμ. The *o*-quinone, in refluxing $CHCl_3$, underwent no decomposition during 4 hr; however after a week at room temp a brown solid had deposited from the solution. The solid quinone on standing 4 months on the laboratory bench underwent little significant change (dec 154–158°; IR—a shoulder at ca. 1300 cm^{-1} had appeared, otherwise no change).

[14] W. Otting and G. Staiger, *Chem. Ber.* **88**, 828 (1955).

The Et_2O mother liquors from which the *o*-quinone had been removed were evaporated to dryness and the residue chromatographed on silica gel (8 g) in $CHCl_3$ yielding unreacted phenol (0·205 g) and *β-hydroxyethyl-1,4-benzoquinone* (0·354 g, 35%), as orange-yellow needles m.p. 38–39°; the colour rapidly darkened on standing: IR, KBr disc, maxima (cm^{-1}) at 3600–3100 s, 1040 s (primary OH), 1680 s (quinonoid C=O), 905 m, 865 m (by analogy with benzenoids, 1,2,4-trisubstituted); in CCl_4 (1% soln) salient features were 3630 m (alcoholic OH), 1662 s (C=O); NMR, 1 M in $CHCl_3$, a three spin system 3·15–3·35 τ (three quinonoid protons), a broad hydroxylic proton triplet (5 c/s separation) at 7·1 τ and two coupled (ca. 6·5 c/s) pairs of methylenic protons at 7·3 τ (triplet) and 6·2 τ (multiplet, coupled to OH and CH_2): UV, maxima (mμ) at 310–305 (log ε = 2·73) in CCl_4, and 247 (4·19) in EtOH (identical with data recorded[15] for *p*-toluquinone). The compound formed a purple brown colour in contact with the skin, a deep red-brown colour with dimethylaniline and rapidly oxidized I^- in acid solution; treatment with aqueous semicarbazide hydrochloride yielded a *monosemicarbazone*, pale-yellow fibres from water m.p. 177–178°, with dec. (Found: N, 19·72, 19·95. $C_9H_{11}N_3O_3$ requires: N, 20·09%.)

(ii) The phenol (1·0 g, 8·3 mM) was oxidized by potassium nitrosodisulphonate (6·0 g, 22·3 mM) in NaOAc aq (pH 8), the experimental procedure being essentially that given by Teuber[9] for the oxidation of 5-hydroxyindane. The products, isolated as before (i), were benzocyclobutene-4,5-quinone (0·332 g, 30%) and the hydroxyethylbenzoquinone (0·428 g, 34%); there was no unreacted phenol in the mixture.

Reduction of benzocyclobutene-4,5-quinone

A solution of the quinone (268 mg, 2·0 mM) in MeOH (30 ml) was hydrogenated over PtO_2 (3 mg) at atm. press. the uptake of H_2 being 2·0 mM. The solution was filtered and the solvent removed under red. press. to leave 4,5-*dihydroxybenzocyclobutene* as a colourless solid m.p. 147–152°: IR, in CH_2Cl_2 maxima (cm^{-1}) at 3550 s, 1130 s (intramolecularly bonded OH), 2920 m (CH_2), 1625 m, 1605 m, 1490 m, 865 m (benzenoid, 1,2,4,5-tetrasubstituted); the solid showed ν_{O-H} at 3420 s, 3280 s. The dihyroxy compound was acetylated in pyridine–AcCl (0°, 40 min), the mixture poured into water and the solid product collected and recrystallized (60–80° petroleum) yielding 4,5-*diacetoxy benzocyclobutene* (321 mg, 73% overall) as colourless needless m.p. 106–107°; IR, in CH_2Cl_2 maxima (cm^{-1}) at 1770 s, 1370 m, 1330 m, 1200 m (acetoxy), 865 m (1,2,4,5-tetrasubstituted nucleus); a fluocarbon mull showed 2950 m (CH_2), 2930 m (CH_2): NMR, 0·5 M in $CDCl_3$, singlets at 3·13 τ, 6·87 τ, 7·78 τ, which, with intensities, correspond to integral multiples of one aryl, two methylene and three acetoxy protons, all protons in each set equivalent. UV in EtOH, maxima (mμ) at 273 (log ε = 3·42) with shoulders at 278 (3·36), 269 (3·40). (Found: C, 65·07, 65·35; H, 5·50, 5·64. $C_{12}H_{12}O_4$ requires: C, 65·44; H, 5·49%.)

4-Acetamido-5-acetoxybenzocyclobutene from 4-amino-5-nitrobenzocyclobutene

The nitroamine (66 mg, 0·40 mM), suspended in 3·5 N H_2SO_4 aq (1 ml) at 0°, was diazotized, the diazonium solution added to refluxing 4 M H_2SO_4 aq (6 ml), containing $CuSO_4 \cdot 5H_2O$ (0·3 g) and the product rapidly steam distilled off. The product (yellow needles) was collected in CH_2Cl_2, the extracts dried ($MgSO_4$), and purified by chromatography on silica gel and vacuum sublimation (50°/0·2 mm) to give 4-*hydroxy-5-nitrobenzocyclobutene* (36 mg, 54%) as a yellow solid m.p. 68–70°: IR, KBr disc, maxima (cm^{-1}) at 3640–3260 s, 3120 m (O—H), 2950 s, 1460 s (CH_2), 1620 m, 1605 s (benzenoid, region below 910 cm^{-1} too complex for useful assignments to be made), 1535 s, 1525 s, 1340 s ($-NO_2$): UV in EtOH, maxima (mμ) at 346 (log ε = 3·29), 282 (3·62), shoulder at 237 (3·48). (Found: N, 8·39; $C_8H_7NO_3$ requires: N, 8·48%.)

The nitrophenol (27 mg, 0·163 mM) and an equivalent quantity of NaOH were dissoved in water (5 ml), treated with dithionite (140 mg, ca. 0·7 mM) and briefly heated to 40° when the yellow solution decolourized. The amino phenol was separated and acetylated as before to give 4-acetamido-5-acetoxybenzocyclobutene (20 mg, 56%), m.p. 159·5–160·5°, undepressed by, and IR identical with, the compound prepared from the diazo coupling of 4-hydroxybenzocyclobutene.

4-Acetamido-5-acetoxybenzocyclobutene from benzocyclobutene-4,5-quinone

A solution of the quinone (64 mg, 0·48 mM) and hydroxylamine hydrochloride (35 mg, 0·50 mM) in 20% NaOH aq (15 ml) was repeatedly extracted with light petroleum (b.p. 30–40°) until the extracts

[15] *Organic Electronic Spectral Data.* Interscience, New York (1960 *et seq.*).

were colourless. After drying (Na_2SO_4) the petroleum was evaporated off leaving *benzocyclobutene-4,5-quinone monoxime* (72 mg, quantitative) as a pale-yellow solid m.p. 149° (dec) which quickly darkened on standing: IR, KBr disc, maxima (cm^{-1}) at 3500–2600 s (O–H), 2930 m (CH_2); 1655 m (C=O); 1630 s, 855 s (analogous to benzenoids bearing an isolated Ar–H), 1515 m, 1005 s (*o*-quinone monoxime[16]); in CCl_4, 3200–2500 vw and broad (intramolecular O–H bond), 1465 s (H-bonded N=O?), characteristic oxime bands were absent. Solutions of the oxime were yellow-green in nonpolar solvents and orange-brown in hydroxylic solvents; a purple complex was formed with Cu^{2+}. Because of its instability the oxime was not purified but reduced directly.

The oxime (28 mg, 0·19 mM) in water (30 ml), was treated with sodium dithionite (70 mg, ca. 0·35 mM) and the product isolated and acetylated as previously described for the diazo coupling product, and the nitrophenol, to yield 4-acetamido-5-acetoxybenzocyclobutene (29 mg, 70%), m.p. 159–160°, undepressed by admixture with the products of the other two preparations; the IR spectra (KBr disc) of the three samples were indistinguishable.

Acknowledgements—We wish to thank Mrs. I. Thirwell for IR and UV spectra, Drs. G. Weiler and F. B. Strauss, Oxford, for microanalyses, Dr. J. Homer for the NMR spectra, and Dr. S. H. Graham, Aberystwyth, and Dr. J. F. W. McOmie, Bristol, for their continued interest. J. B. F. L. is indebted to the College of Advanced Technology, Birmingham, for a Research Fellowship.

[16] D. Hadži, *J. Chem. Soc.* 2725 (1956).