

Conversion of a Catechol into a But-2-enolide

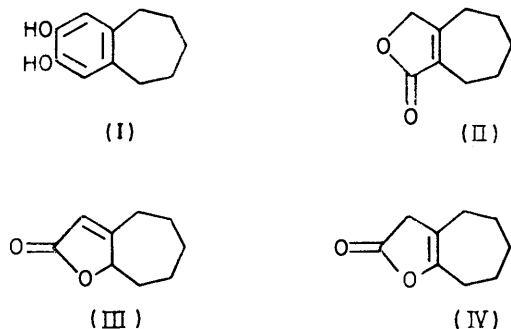
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Reactions of 6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2,3-diol with alkaline oxidising agents gives 2-carboxymethylcycloheptanone, which easily forms the corresponding lactone. An *o*-quinone is demonstrated to be an intermediate. Several other mono- and bi-cyclic *o*-quinones examined do not undergo this type of reaction.

IN 1964¹ it was observed that when the catechol (I) was heated with iodine in nitrobenzene and then left in contact with aqueous sodium hydroxide, an acidic substance was obtained which gave, in moderate yield, a but-2-enolide on treatment with polyphosphoric acid. This butenolide was supposed¹ to have formula (II) and as this transformation of a catechol appeared to be of a novel type, we examined the reaction further.

In the first place, repetition of the original¹ reaction sequence gave variable yields of lactone, the n.m.r. spectrum of which contained a doublet at τ 4.27 (area 1). This suggested that the product had the isomeric structure (III), and this was confirmed by comparison with an authentic sample^{2,†} and by synthesis on a larger scale

† We thank Dr. A. Furst, Hoffmann-La Roche, Basle, for a sample.



by an improved method from the pyrrolidine enamine of cycloheptanone.³

The lactone (III) showed u.v. absorption [λ_{\max} 217 nm ($\log \epsilon$ 4.09)] similar to those of many steroidal but-2-enolides³ and i.r. absorption markedly solvent dependent (ν_{\max} 1760 cm^{-1} in carbon tetrachloride and 1740 cm^{-1} in chloroform) characteristic of similar structures.⁴ In the mass spectrum, the molecular ion ($\text{C}_9\text{H}_{12}\text{O}_2$) was detected along with a prominent $M-\text{CHO}$ peak.⁵ Accordingly the alternative formulation (IV) is ruled out.⁶ The trans-

formation from (I) involves loss of carbon atoms 1 and 2 (or 3 and 4) of the benzene ring and not carbon atoms 2 and 3 as was originally¹ inferred.

Oxidative cleavage of hydroxy-substituted aromatic systems is well known, being induced by enzymic,^{7,8} photochemical,⁹ and mild chemical methods.^{10,11} Although these occasionally give rise to but-2-enolides (*e.g.* refs. 8 and 11) ring carbon atoms are not lost. Loss of one¹² or two¹³ carbon atoms is associated with pyrogallol oxidations. Typical of catechol oxidations in alkaline medium is the appearance of hydroxy-*p*-quinones¹⁴ [*e.g.* (VI) from (V)] but transformations like the conversion of (I) into (III) have not been reported.

We next explored the details of the conversion of the catechol (I) into the butenolide (III). The acidic intermediate was found to be the oxo-acid (VII) obtained during the synthesis (*cf.* ref. 2) of (III). Next it was demonstrated that omission of iodine from the original¹ preparative method had no effect, but that omission of treatment with sodium hydroxide caused the reaction to produce no acidic material. Since it was suspected that an oxidation was taking place, the catechol (I) in benzene was stirred with sodium hydroxide in a stream of air, and the acid (VII) was obtained (60%); but in the absence of air, no reaction took place; omission of sodium hydroxide likewise prevented any reaction. Application of these modified conditions to the methoxyphenol (VIII) had no effect. It seemed possible, therefore, that the *o*-quinone (IX) was involved.

Treatment of the catechol (I) with either active manganese dioxide¹⁵ or 2,3-dichloro-5,6-dicyanobenzoquinone gave red solutions from which a deep red crystalline solid^{16,17} was obtained by keeping the temperature below 25 °C. This appeared to be the *o*-quinone (IX), which could also be obtained from the dimethyl ether of (I) with silver(II) oxide¹⁸ provided that tetrahydrofuran was used as co-solvent. Use of higher temperatures invariably converted (IX) into a dimer to which structure

⁹ T. Matsuura, H. Matsushima, S. Kato, and I. Saito, *Tetrahedron*, 1972, **28**, 5119.

¹⁰ J. A. Elvidge, R. P. Linstead, and P. Sims, *J. Chem. Soc.*, 1951, 3386.

¹¹ J. C. Farrand and D. C. Johnson, *J. Org. Chem.*, 1971, **36**, 3606.

¹² T. W. Campbell, *J. Amer. Chem. Soc.*, 1951, **73**, 4190.

¹³ A. Critchlow, E. Haslam, R. D. Haworth, P. B. Tinker, and N. M. Waldron, *Tetrahedron*, 1967, **23**, 2829.

¹⁴ J. Pilar, I. Buben, and J. Pospisil, *Coll. Czech. Chem. Comm.*, 1970, **35**, 489.

¹⁵ J. S. Belew and C. Tek-Ling, *Chem. and Ind.*, 1967, 1958.

¹⁶ L. Horner and T. Burger, *Annalen*, 1967, **710**, 102.

¹⁷ L. Horner and K. H. Weber, *Chem. Ber.*, 1962, **95**, 1227.

¹⁸ C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, 1972, **94**, 227.

¹ G. R. Proctor, *J. Chem. Soc.*, 1964, 4274.

² P. A. Plattner, A. Furst, and K. J. Jirasek, *Helv. Chim. Acta*, 1946, **29**, 730.

³ I. J. Borowitz, G. J. Williams, L. Gross, and R. Rapp, *J. Org. Chem.*, 1968, **33**, 2013.

⁴ R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Canad. J. Chem.*, 1959, **37**, 2007.

⁵ L. Friedman and F. A. Long, *J. Amer. Chem. Soc.*, 1953, **75**, 2832.

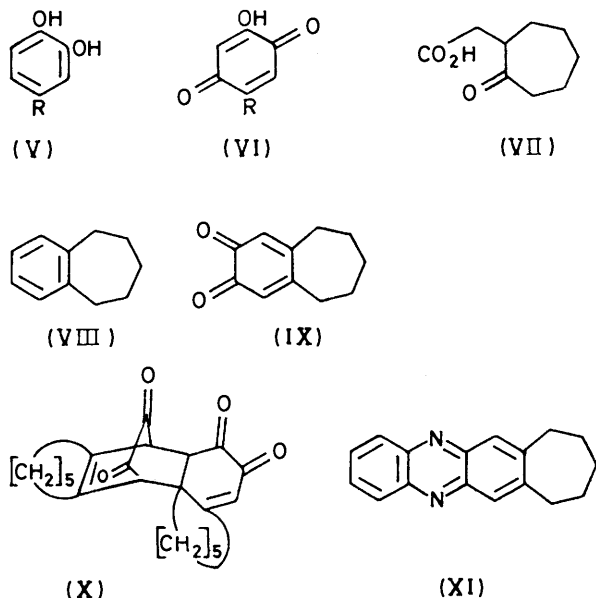
⁶ M. S. Newman and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1945, **67**, 233.

⁷ W. C. Evans, B. S. W. Smith, R. P. Linstead, and J. A. Elvidge, *Nature*, 1951, **168**, 772.

⁸ L. N. Ornston and R. Y. Stanier, *Nature*, 1964, **204**, 1279.

(X) is allocated on spectroscopic grounds (see Experimental section) and by analogy with other dimers of 4,5-dialkyl-*o*-benzoquinones.¹⁹

Next it was shown that the monomeric *o*-quinone (IX) reacted with sodium hydroxide in the absence of air to



give the acid product (VII) and thence the but-2-enolide (III) in 77% overall yield. To establish that the *o*-quinone (IX) was a true intermediate in the reaction of the catechol (I) with air and sodium hydroxide, a trapping experiment was necessary. Thus when the catechol (I) was treated with air and sodium hydroxide in the presence of *o*-phenylenediamine, the product was exclusively the phenazine (XI), obtained separately from the *o*-quinone (IX); none of the acid (VII) was found. Thus the *o*-quinone (IX) is implicated as an intermediate: it seemed that the reaction under study was the consequence of attack on the *o*-quinone (IX) by sodium hydroxide.

There are many precedents for nucleophilic attack on *o*-quinones involving 1,2-, 1,4-, or 1,6-addition of the reagents.¹⁹⁻²² To explain our results we postulate (Scheme) a nucleophilic 1,4-addition of OH⁻ and H⁺ [giving (XIIa)], followed by a retro-aldol ring opening [from (XIIb) to (XIII)], and lastly attack by OH⁻ giving a deacylation [to (XIV)]. There are precedents for each step except (XIII) → (XIV), the enol keten which could well react with sodium hydroxide to give the sodium salt of the acid (VII) or intra-molecularly to give the γ -lactone (III) which would be converted into (VII) by sodium hydroxide.

In an attempt to find out more about this reaction, several catechols and the related *o*-quinones were studied.

¹⁹ L. Horner and K. Strum, *Annalen*, 1955, **597**, 1.

²⁰ H. W. Wanzlick, 'Newer Methods in Preparative Organic Chemistry,' vol. IV, ed. W. Foerst, Verlag Chemie, Weinheim, 1968, p. 139.

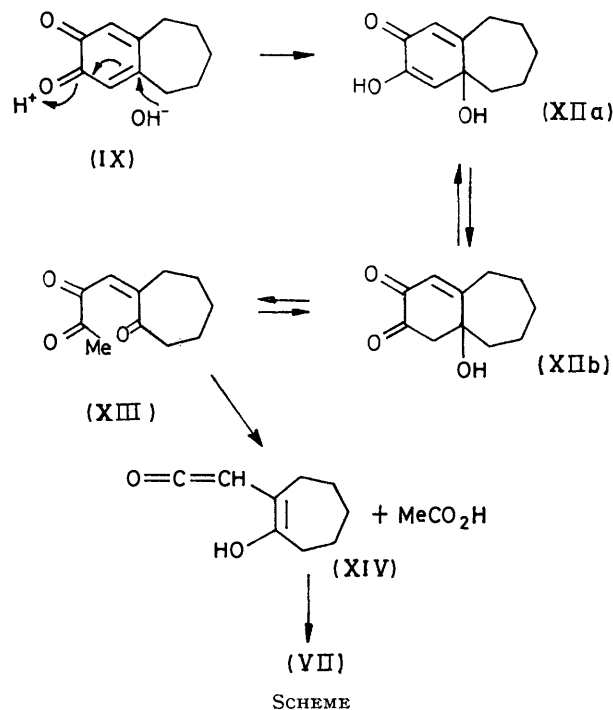
²¹ L. Horner and H. Lang, *Chem. Ber.*, 1956, **89**, 2768.

²² W. M. Horspool, P. I. Smith, and J. M. Tedder, *J. Chem. Soc. (C)*, 1971, 138.

Thus 4-methyl-, 4-(1,1,3,3-tetramethylbutyl)-, 3-methyl-5-*t*-butyl-, 4-isopropyl-5-methyl- and 4,5-dimethyl-*o*-benzoquinone²³ were treated with sodium hydroxide; the products were very complex mixtures.

Next, the bicyclic catechols (XV)–(XVII) (R = H) were studied. In the case of (XV), the corresponding quinone is unstable at ambient temperature;²⁴ the red solution obtained at -78°C which formed a phenazine with *o*-phenylenediamine was treated with sodium hydroxide solution but the products were the catechol (XV) and naphthalene-2,3-diol, presumably produced by disproportionation of the corresponding 1,2-dihydro-naphthalenediol, a process known to occur with 1,2-dihydronaphthalene.²⁵

The *o*-quinone from the catechol (XVI; R = H) reacted with sodium hydroxide to give only intractable tar. Interestingly, treatment of (XVI; R = Me) with silver(II) oxide gave the corresponding dimethoxyindan-1-one, whereas similar treatment of the dimethyl ether of (I) gave the *o*-quinone (IX); thus ring size has a marked effect on the course of these oxidations. The dimethyl ether²⁶ (XVII; R = Me) reacted with silver(II) oxide to give the corresponding *o*-quinone, but although the latter reacted with aqueous sodium hydroxide, many products were formed and none was identified.



Thus the reaction of aqueous sodium hydroxide with the catechol (I) seemed to be the only case where a substantial yield of one acidic product (VII) was obtained.

²³ H. J. Teuber and W. Rau, *Chem. Ber.*, 1953, **86**, 1036.

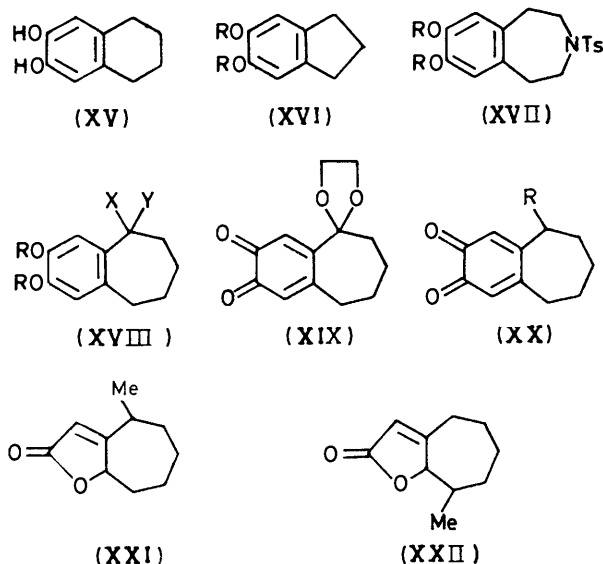
²⁴ W. M. Horspool, P. I. Smith, and J. M. Tedder, *J. Chem. Soc. (C)*, 1971, 1638.

²⁵ W. Wieland, *Ber.*, 1912, **45**, 484.

²⁶ J. Gardent, G. Hazebrucq, and G. Cormier, *Bull. Soc. chim. France*, 1969, 4001.

The catechol (XVIII; R = H, XY = O) did not give an *o*-quinone; the quinone (XIX) gave a multiplicity of products and the quinone (XX; R = Ph) was similar, although in a preliminary experiment on a small scale the results were promising.

Lastly, the quinone (XX; R = Me) was treated with sodium hydroxide and the acidic product was treated with polyphosphoric acid to give a poor yield of lactonic



material (ν_{\max} 1755 cm^{-1}), $\text{C}_{10}\text{H}_{13}\text{O}_2$, apparently a mixture of (XXI) and (XXII) which could not be separated.

EXPERIMENTAL

1-Pyrrolidinocycloheptene.³—Cycloheptanone (20.65 g), pyrrolidine (22.2 g), toluene-*p*-sulphonic acid (0.2 g), and benzene (60 ml) were refluxed for 24 h with a Dean-Stark trap. The usual work-up gave the product (25.5 g; 86.5%), b.p. 62–64° at 0.2 Torr, ν_{\max} (film) 1633 cm^{-1} (C=C).

Ethyl 2-Oxocycloheptylacacetate² [Ethyl Ester of (VII)].—Ethyl bromoacetate (17.3 ml) was added dropwise to the 1-pyrrolidinocycloheptene (25.5 g) in refluxing dry benzene under nitrogen. After being refluxed for 6 h, the mixture was cooled and stirred with water (100 ml) for 1 h at 20 °C and for 0.5 h at 95 °C. The usual work-up gave the product (19.1 g, 63%), b.p. 90–95° at 0.3 Torr (lit.,² 140–145° at 12 Torr), ν_{\max} (film) 1738 (ester) and 1708 (C=O) cm^{-1} , τ 5.94 (2 H, q, *J* 8 Hz, $\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_3$), 6.7–7.9 (5 H, m, $\text{CH}_2\text{CO}_2\text{Et}$, methine, and 3- H_2), 8.0–8.65 (8 H, m, 4-, 5-, 6-, and 7- H_2), and 8.79 (3 H, t, *J* 8 Hz, $\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_3$).

The acid (VII) was obtained as described previously;² τ —1.05br (1 H, exch., CO_2H), 6.8–7.8 (5 H, m, $\text{CH}_2\cdot\text{C}\cdot\text{CH}$ and $\text{CH}_2\cdot\text{CO}_2\text{H}$), and 8.0–8.8 (8 H, m, 4-, 5-, 6-, and 7- H_2). Heating the acid with polyphosphoric acid at 60 °C for 1 h gave the lactone (III), b.p. 85° at 0.15 Torr (89%), m.p. 53.5–54° [from ether–light petroleum (b.p. 40–60°)] (lit.,² 55–56°) (Found: C, 71.35; H, 8.2%; *M*, 152.0836. Calc. for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.05; H, 7.95%; *M*, 152.0837), ν_{\max} .

* We thank Dr. K. Payne, Coalite and Chemical Co., for samples of several catechols.

²⁷ E. Adler and R. Magnusson, *Acta Chem. Scand.*, 1959, **13**, 505.

(CCl_4) 2930, 2858, 1770, and 1637 cm^{-1} , ν_{\max} (CHCl_3) 1740 cm^{-1} , τ 4.27 (1 H, d, *J* 2 Hz, vinyl), 5.05 (1 H, m, methine), 7.38 (2 H, m, allylic CH_2), and 7.5–8.8 (8 H, m, 4 CH_2).

Reaction of 6,7,8,9-Tetrahydro-5H-benzocycloheptene-2,3-diol (I) with Sodium Hydroxide and Air.—The catechol¹ (I) (0.5 g), benzene (70 ml), and aqueous sodium hydroxide (5 ml; 2M) were stirred vigorously during 1 h with air bubbling through. Separation of the aqueous layer, acidification, and extraction with chloroform gave the acid (VII) (0.34 g), which was converted into the lactone (III) (0.24 g) as above.

6,7,8,9-Tetrahydro-3-methoxy-5H-benzocycloheptene-2-ol (VIII).—6,7,8,9-Tetrahydro-2,3-dimethoxy-5H-benzocycloheptene¹ [dimethyl ether of (I)] (1 g) and methylmagnesium iodide (2.42 g) in ether were kept for 3 h under nitrogen in a sealed tube at 140 °C. The usual work-up²⁷ gave the product (0.42 g, 45%), m.p. 109° (lit.,¹ 110°), τ 3.33 (1 H, s, 4-H), 3.42 (1 H, s, 1-H), 4.61br (1 H, s, exch., OH), 6.20 (3 H, s, OMe), 7.33 (4 H, m, benzylic H), and 8.40 (6 H, m, 6-, 7-, and 8-H).

6,7,8,9-Tetrahydro-5H-benzocycloheptene-2,3-quinone¹⁷ (IX).—(a) 6,7,8,9-Tetrahydro-5H-benzocycloheptene-2,3-diol (I) (1.0 g) was stirred for 1 h at –15 °C with active manganese dioxide¹⁵ (2.5 g) and dry methylene chloride (25 ml). The red solution was filtered and evaporated below 25 °C yielding the product as a red solid (0.86 g, 87%), m.p. 110° (lit.,¹⁷ 113–114°), λ_{\max} (EtOH) 213, 271, and 402 nm ($\log \epsilon$ 3.87, 3.57, and 2.97), τ 3.82 (2 H, s, vinyl H), 7.2–7.6 (4 H, m, allylic H), and 8.0–8.4 (6 H, m, 3 CH_2).

(b) 6,7,8,9-Tetrahydro-2,3-dimethoxy-5H-benzocycloheptene¹ [dimethyl ether of (I)] (4.1 g), tetrahydrofuran (160 ml), and silver(II) oxide¹⁸ (10 g) were stirred below 5 °C while nitric acid (20 ml; 6N) was added, followed 3 min later by chloroform (220 ml) and water (50 ml). The usual work-up with evaporation below 25 °C gave the product (3.08 g, 88%) as in (a). The phenazine adduct (XI) prepared from *o*-phenylenediamine in acetic acid had m.p. 180° (lit.,¹⁷ 180°) (Found: *M*, 248.1308. Calc. for $\text{C}_{17}\text{H}_{16}\text{N}_2$: *M*, 248.1313), τ 1.85 (2 H, q, *J* 4 Hz, aryl H), 2.14 (2 H, s, aryl H), 2.3 (2 H, q, *J* 4 Hz, aryl H), 6.8 (4 H, m, benzylic H), and 8.18 (6 H, m, methylene H).

Dimer (X) of the *o*-Quinone (IX).—When solutions of the monomer were evaporated below 50°, the dimer (80%), m.p. 107–109°, was obtained [from light petroleum (b.p. 80–100°)] [Found: C, 75.05; H, 6.8%; *M* (osmometry), 362. $\text{C}_{22}\text{H}_{24}\text{O}_4$ requires C, 75.05; H, 6.9%; *M*, 362], ν_{\max} (Nujol) 1730, 1660, and 1138 cm^{-1} , τ 3.48 (1 H, s, vinyl H), 6.48 (1 H, d, *J* 4 Hz, bridgehead H), 6.72 (1 H, s, bridgehead H), 7.04 (1 H, d, *J* 4 Hz, bridgehead H), and 7.3–8.6 (2 OH, m, methylene H), *m/e* 352, 296, and 176 (relative intensities 13.2, 100, and 36.3).

4-Methyl-*o*-benzoquinone.²⁸—4-Methylcatechol (2 g) and 2,3-dichloro-5,6-dicyanobenzoquinone (3.6 g) were stirred in dry benzene for 20 h; the mixture was filtered to give a red solution. ν_{\max} ²⁸ 1745, 1720, 1690, and 1633 cm^{-1} , which was used without further treatment.

4-(1,1,3,3-Tetramethylbutyl)-*o*-benzoquinone.²⁹—4-(1,1,3,3-Tetramethylbutyl)catechol* (10 g), active manganese dioxide¹⁵ (25 g), and dry methylene chloride (300 ml) were stirred for 20 h. Evaporation of the filtrate below 25 °C gave a red solid (8.08 g, 81%), m.p. 124° (lit.,²⁹ 123°) [from

²⁸ W. Otting and G. Staiger, *Chem. Ber.*, 1955, **88**, 828.

²⁹ H. J. Teuber and G. Staiger, *Chem. Ber.*, 1955, **88**, 802.

light petroleum (b.p. 60—80°)] (Found: *M*, 220.1469. Calc. for $C_{14}H_{20}O_2$: *M*, 220.1463).

3-Methyl-5-*t*-butyl-*o*-benzoquinone.³⁰—Obtained as in the previous case,* the product (86%) had m.p. 54° (lit.,³⁰ 60°) (Found: *M*, 178.0992. Calc. for $C_{11}H_{14}O_2$: *M*, 178.0994).

4-Isopropyl-5-methyl-*o*-benzoquinone.²⁸—Obtained as in the previous case,* the product (90%) had m.p. 70—72° (lit.,²⁸ 71—72°), τ 3.79 (2 H, s, 3- and 6-H), 7.23 (1 H, septet, *J* 8 Hz, methine H), 7.81 (3 H, s, CH_3), and 8.8 [6 H, d, *J* 8 Hz, $CH(CH_3)_2$].

4,5-Dimethyl-*o*-benzoquinone.—Made by the literature²³ method, this had τ 3.8 (2 H, s, vinyl H) and 7.84 (6 H, s, Me).

5,6,7,8-Tetrahydronaphthalene-2,3-diol (XV).—1,2,3,4-Tetrahydro-6,7-dimethoxynaphthalene³¹ (11.45 g), acetic acid (25 ml), and hydrogen bromide-acetic acid (45%; 25 ml) were refluxed for 15 h. The usual work-up gave the product (91%), m.p. 125—128° (lit.,³² 127—128°), τ 3.47 (2 H, s, 1- and 4-H), 5.0br (2 H, s, exch., OH), 7.39 (4 H m, benzylic H), and 8.29 (4 H, m, 6- and 7-H₂).

Phenazine Adduct of 5,6,7,8-Tetrahydronaphthalene-2,3-quinone.—The diol (XV) (100 mg), active manganese dioxide¹⁵ (400 mg), and methylene chloride (10 ml) were stirred at -78 °C for 30 min; the mixture was rapidly filtered and the filtrate was stirred for 1 h at -78 °C with *o*-phenylenediamine (30 mg) and acetic acid (0.2 ml) and poured into water. After washing with aqueous sodium hydroxide, the product (40 mg), m.p. (from methanol) 180—180.5°, was obtained (Found: *M*, 234.1128. $C_{16}H_{14}N_2$ requires *M*, 234.1157), τ 1.85 (2 H, q, *J* 4 Hz, aryl H), 2.13 (2 H, s, aryl H), 2.3 (2 H, q, *J* 4 Hz, aryl H), 6.94 (4 H, m, benzylic H), and 8.11 (4 H, m, methylene H), λ_{max} (C_6H_{12}) 254 and 370 nm (log ϵ 5.06 and 4.13). When the red solution obtained in the first part of this experiment was stirred at -78 °C with sodium hydroxide (1.5 g) and ethanol (25 ml) for 30 min, the product was shown by g.l.c. to consist of a 1:1 mixture of the diol (XV) and naphthalene-2,3-diol (*t_R* 4.4 and 6.6 min, respectively).

5,6-Dimethoxyindan-1-one.—5,6-Dimethoxyindane³³ (XVI; R = Me) (0.32 g) in tetrahydrofuran (18 ml) was treated sequentially with silver(II) oxide³⁴ (0.88 g) and nitric acid (1.8 ml; 6*M*) at -5° with stirring for 3 min. After the usual work-up,¹⁸ a solid (0.34 g, 99%) was obtained, m.p. and mixed m.p. 118—119°.

Ethylene Acetal of 6,7,8,9-Tetrahydro-2,3-dimethoxybenzocyclohepten-5-one.—The ketone (XVIII; R = Me, XY = O) (4.4 g), ethylene glycol (1.24 ml), benzene (200 ml), and toluene-*p*-sulphonic acid (20 mg) were refluxed together for 24 h with use of a water-separator. The product (2.95 g, 56%) had m.p. 84—84.5° (Found: C, 68.65; H, 7.5. $C_{15}H_{20}O_4$ requires C, 68.25; H, 7.55%). Oxidative demethylation with silver(II) oxide as before gave a red oil

(XIX) (95%), ν_{max} (CCl_4) 1 669 cm^{-1} (C=O), τ 3.46 (1 H, s, 4-H), 3.86 (1 H, s, 1-H), 5.9—6.1 (4 H, m, O-CH₂-CH₂-O), 7.0—7.2 (2 H, m, 9-H), and 7.9—8.4 (6 H, m, 6-, 7-, and 8-H).

6,7,8,9-Tetrahydro-2,3-dimethoxy-5-phenyl-5H-benzocyclohepten-5-ol (XVIII; R = Me, X = OH, Y = Ph).—The ketone (XVIII; R = Me, XY = O) (10 g) in dry tetrahydrofuran was added to phenylmagnesium bromide (0.05 mol) in dry tetrahydrofuran. After 2 h at 20 °C, the usual work-up gave the product (13.3 g, 98%), m.p. 120—122° (from light petroleum) (Found: C, 76.7; H, 7.5. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.45%), ν_{max} ($CHCl_3$) 3 580 cm^{-1} (OH).

6,7-Dihydro-2,3-dimethoxy-9-phenyl-5H-benzocycloheptene.—The preceding product (4.6 g) was refluxed for 14 h in benzene with toluene *p*-sulphonic acid (20 mg) to give the product (2.6 g, 60%), m.p. 116° (from light petroleum) (Found: C, 81.5; H, 7.45. $C_{19}H_{20}O_2$ requires C, 81.5; H, 7.2%).

6,7,8,9-Tetrahydro-2,3-dimethoxy-5-phenyl-5H-benzocycloheptene (XVIII; R = Me, X = Ph, Y = H).—The preceding product (4.49 g) was shaken with palladised charcoal (100 mg; 10%) in ethanol (150 ml) under hydrogen; when uptake was complete the product was isolated as usual. Crystallisation from light petroleum (b.p. 60—80°) gave a solid, m.p. 84—85° (3.83 g, 85%) (Found: C, 80.5; H, 7.9. $C_{19}H_{22}O_2$ requires C, 80.9; H, 7.85%). Treatment of this with silver(II) oxide gave the quinone (XX; R = Ph) as a red oil, ν_{max} (CCl_4) 1 715 cm^{-1} (C=O), τ (tetrahydrofuran) 2.6—3.05, 3.8 (1 H, s, 4-H), and 4.38 (1 H, s, 1-H). Reaction with *o*-phenylenediamine in acetic acid at 20 °C gave the corresponding phenazine, m.p. 180° (Found: *M*, 324.1620. $C_{23}H_{20}N_2$ requires *M*, 324.1626). By a similar sequence with methylmagnesium iodide and the ketone (XVIII; R = Me, XY = O) the following were prepared: 6,7-dihydro-2,3-dimethoxy-5-methyl-5H-benzocycloheptene, b.p. 150° at 0.1 Torr (Found: C, 77.15; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.15; H, 8.3%); and 6,7,8,9-tetrahydro-2,3-dimethoxy-5-methyl-5H-benzocycloheptene (XVIII; R = Me, X = Me, Y = H), b.p. 130° at 0.1 Torr (Found: C, 76.0; H, 9.0. $C_{14}H_{20}O_2$ requires C, 76.4; H, 9.15%).

The latter was treated as before with silver(II) oxide and the red quinone obtained was treated with aqueous sodium hydroxide and then polyphosphoric acid to give an oil (15%), b.p. 85—90° at 0.05 Torr (Found: C, 71.7; H, 8.2%; *M*, 166.0983. Calc. for $C_{10}H_{14}O_2$: C, 72.2; H, 8.5%; *M*, 166.0994). G.l.c. showed this to contain two compounds in ratio *ca.* 5:1.

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[5/866 Received, 8th May, 1975]

* See footnote on p. 2487.

³⁰ E. Muller, F. Gunter, and A. Rieker, *Z. Naturforsch.*, 1963, **18b**, 1002.

³¹ R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1932, 1485.

³² T. Momose, H. Oya, Y. Ohkura, and M. Iwaski, *Chem. and Pharm. Bull. (Japan)*, 1954, **2**, 119.

³³ W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 1930, 2510.

³⁴ R. N. Hammer and J. Kleinberg, *Inorg. Synth.*, 1953, **4**, 12.