

821. *Novel Aromatic Systems. Part I. Some Transformations in the Benzocycloheptenone Series.*

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The chemistry of the dimethoxybenzocycloheptenone (VI; $R = R' = \text{OMe}$) and related compounds has been investigated: difficulty was encountered in attempted dehydrogenations.

DURING the last twenty years, the meaning of the word "aromatic" has been much discussed.¹ It is now recognised that certain unsaturated cyclic structures containing five- and seven-membered rings which are constructed so as to allow gain or loss, respectively, of one electron (leaving 6 electrons associated with the ring), may show some of the chemical and physical properties characteristic of benzene. Among such compounds, the tropones and tropolones [*e.g.*, (I)] have oxygen functions (electron-accepting) directly attached to the seven-membered ring and their properties may be partly explained by representation as extreme polar forms² [*e.g.*, (II)].

As far as we know, the possibility of separating the seven-membered ring and the oxygen function has not been systematically investigated. Accordingly we undertook the synthesis of the hydroxy-ketone (III; $R = \text{H}$) to find whether it resembles the tropolones in any way. The only previous example of a similar kind was reported by Butenandt and his co-workers³ in connection with insect pigments. Thus, the compound formulated as (IVb; $R = \text{H}$) was obtained from the phenoxazinone (IVa) on

¹ (a) Baker and McOmie, *Progr. Org. Chem.*, 1955, **3**, 67; (b) "Non-benzenoid Aromatic Compounds," ed. Ginsburg, Interscience, New York, 1959.

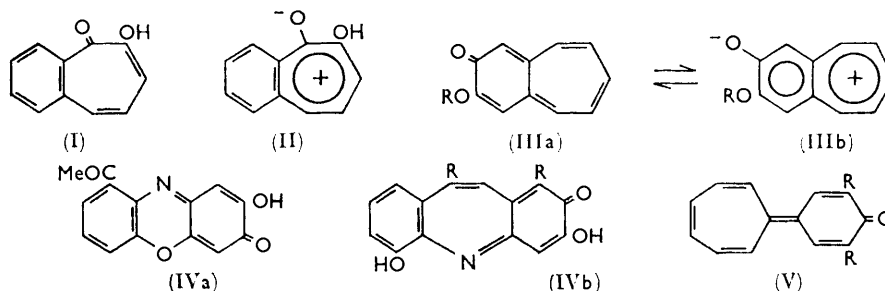
² Pauson, *Chem. Rev.*, 1955, **55**, 9.

³ Butenandt, Biekert, and Neubert, *Annalen*, 1957, **603**, 200.

treatment with alkali, and the compound (IVb; R = Ac) from 2-amino-3-hydroxyacetophenone by aerial oxidation followed by treatment with alkali.

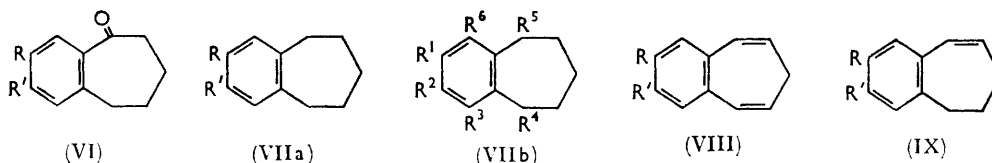
We have also investigated⁴ the related violet pigment (V; R = H) which is the parent of the series that includes the substance (V; R = Me) recently reported by Dutch workers.⁵

It is impossible to construct a model of compound (III) without distortion of the nominal sp^2 bond angles; however it seems that a flat molecule could be constructed



without gross distortion and this would allow delocalisation of electrons which would permit the appearance of "aromatic properties."

Our synthetic work was based on the benzocycloheptenone (VI; R = R' = OMe);⁶ reaction with lithium aluminium hydride in tetrahydrofuran (concentrated solution) gave the benzocycloheptene (VIIa; R = R' = OH) which it was hoped to convert into the benzocycloheptatriene (VIII; R = R' = OH) and thence to the desired product. However, photobromination of the diol (VIIa; R = R' = OH) with 1 mole of *N*-bromosuccinimide caused substitution in the benzene ring and, although with 2 moles of *N*-bromosuccinimide some bromination of the saturated ring occurred,⁷ this approach seemed unpromising. In the case of the acetate (VIIa; R = R' = OAc), one mole of *N*-bromosuccinimide was shown to cause bromination of the seven-membered ring as expected, since dehydrobromination gave the same acetate (IX; R = R' = OAc) as was obtained from the ether (VI; R = R' = OMe) by another route (see below). When the acetate (VIIa; R = R' = OAc) was photobrominated with 2 moles of *N*-bromosuccinimide, the second bromine atom also entered the seven-membered ring since, after hydrolysis and acidification, a bromine-free product [presumably (X)] was obtained in moderate yield. Attempts to dehydrate this product were unsuccessful.



Reduction of the ether (VI; R = R' = OMe) with sodium borohydride presumably gave the expected alcohol, since acidification of the mixture gave the benzocycloheptadiene (IX; R = R' = OMe) but the latter decomposed during attempted demethylation. Catalytic reduction of the diether (IX; R = R' = OMe) gave the cycloheptene (VIIa; R = R' = OMe) which, with aluminium bromide, gave exclusively the monoether (VIIa; R = OH, R' = OMe). If, however, demethylation preceded reduction, the ketones

⁴ Pauson, Proctor, and Rodger, unpublished results.

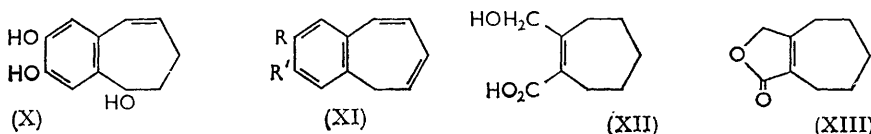
⁵ Bickel, ter Borg, and van Helde, *Rec. Trav. chim.*, 1962, **81**, 599.

⁶ Caunt, Crow, Haworth, and Vodoz, *J.*, 1950, 1631; Bartrop, Johnson, and Meakins, *J.*, 1951, 181.

⁷ Allison and Newbold, *J.*, 1959, 3335.

(VI; R = OH, R' = OH or OMe) were obtained. Borohydride reduction of the dihydroxyketone, followed by acetylation, gave the diacetate (IX; R = R' = OAc). Photobromination of this and hydrolysis of the product by dilute alkali gave a dark, acidic substance, but no diol (XI; R = R' = OH) could be found. Other methods of dehydrobromination were also unsuccessful.

It thus appeared that the diols (XI; R = R' = OH) and (VIII; R = R' = OH) were not readily available by this route, and that (III; R = H) might have to be made by direct dehydrogenation of more saturated substrates. Iodine in nitrobenzene has been successfully employed in the azulene field⁸ but with the diol (VIIa; R = R' = OH) this reagent cleaved the benzene ring, as shown. A hydroxy acid, C₉H₁₄O₃, was obtained in fair yield and from it a lactone, C₉H₁₂O₂. These compounds may be, respectively, (XII) and (XIII): we hope to examine further this interesting conversion from aromatic to alicyclic series. Palladised charcoal at 230° was without effect on the diol (VIIa; R = R' = OH).⁹



The difficulties encountered in this work suggested that more suitable intermediates for compound (III) might be obtained by the condensation of hydroxyphthalaldehydes with acetone derivatives,¹⁰ and this is under investigation.

EXPERIMENTAL

δ-(3,4-Dimethoxyphenyl)valeric Acid.—(a) This was prepared by condensation of veratrole with glutaric anhydride,⁶ followed by reduction. Examination of the neutral material in the first stage gave 1,3-bis-(3,4-dimethoxybenzoyl)propane, m. p. 144—146° (Found: C, 67.8; H, 6.9. C₂₁H₂₄O₆ requires C, 67.75; H, 6.5%). The 2,4-dinitrophenylhydrazone had m. p. 200—202° (Found: C, 59.2; H, 5.2. C₂₇H₂₈N₄O₉ requires C, 58.7; H, 5.1%). The appearance of diketones in reactions of this type has been previously reported.¹¹ It was found expedient to distil the valeric acid *in vacuo* to free it from coloured material.

(b) Veratraldehyde (25 g.), methyl crotonate (30 g.), and t-butyl alcohol (50 ml.) were together added dropwise to a suspension from potassium (11.5 g.) in t-butyl alcohol (250 ml.) with stirring and cooling (~10°) over 3 hr.¹² The mixture was set aside for 24 hr., treated with acetic acid and water, and extracted with chloroform. The extract was distilled *in vacuo* and the residue was refluxed with aqueous alcoholic sodium hydroxide solution. After extraction with benzene, the aqueous layer was acidified to yield a mixture of the two isomeric acids. Extraction with benzene gave *cis,trans*-(3,4-dimethoxyphenyl)penta-2,4-dienoic acid (17 g.) m. p. 148—149° (Found: C, 66.35; H, 6.1. C₁₃H₁₄O₄ requires C, 66.65; H, 6.0%), ν_{\max} . (Nujol) 1695, 1680 cm.⁻¹, λ_{\max} . (EtOH) 206, 241, 334 m μ (ϵ 17,450, 12,450, 28,000). The benzene-insoluble material (3.0 g.) crystallised from ethanol as plates, m. p. 207—208°; presumably of the *trans-trans-isomer* (Found: C, 66.4; H, 6.1%), ν_{\max} . (Nujol) 1680 cm.⁻¹, λ_{\max} . (EtOH) 206, 249, 313 (infl.), 337 m μ (ϵ 12,900, 10,800, 21,000, 31,000). *δ*-(3,4-Dimethoxyphenyl)valeric acid was obtained from the above acids by hydrogenation in ethanol with Raney nickel at 100° and 120 atm. The crude product was boiled with sodium hydroxide since esterification usually took place. The pure product, m. p. 71—74°, had λ_{\max} . (EtOH) 208, 220 (infl.), 280 m μ (ϵ 12,600, 9600, 3660). Progress in the hydrogenation could be conveniently followed by ultra-violet spectroscopy.

4',5'-Dimethoxy-1,2-benzocyclohept-1-en-3-one (VI; R = R' = OMe).—*δ*-Dimethoxyphenylvaleroyl chloride was treated with stannic chloride⁶ and gave, after distillation at 0.1 mm., the

⁸ Treibs, *Annalen*, 1952, **576**, 110.

⁹ Cf. Heilbronner in "Pathways to the Azulenes," ref. 1b.

¹⁰ Cf. Meuche, Strauss, and Heilbronner, *Helv. Chim. Acta*, 1958, **41**, 2220.

¹¹ Garden, Hayes, and Thomson, *J.*, 1956, 3315; Berliner, *Org. Reactions*, 1949, **5**, 247.

¹² We cordially thank Dr. A. Dreiding for supplying this recipe.

ketone, needles, m. p. 70° [from light petroleum (b. p. 60—80°)] (Found: C, 70.0; H, 7.55. Calc for $C_{13}H_{16}O_3$: C, 70.0; H, 7.3%), ν_{\max} . (Nujol) 1675, 1615, 1520 cm^{-1} .

Recovery of the acidic fraction after cyclisation gave α (?)-chloro- δ -(3,4-dimethoxyphenyl)-valeric acid, needles (20%), m. p. 50° [from light petroleum (b. p. 60—80°)] (Found: C, 57.9; H, 6.4; Cl, 12.7. $C_{13}H_{17}ClO_4$ requires C, 57.3; H, 6.3; Cl, 13.0%), ν_{\max} . (Nujol) 3330, 2667, 1712, 1603 cm^{-1} . This acid could not be hydrogenated in the presence of palladised charcoal¹³ and was recovered unchanged after treatment with zinc dust in dilute sodium hydroxide at 100°¹⁴ or with zinc dust in dilute acetic acid at 100°.

4',5'-Dihydroxy-1,2-benzocyclohept-1-en-3-one.—The foregoing dimethoxy-compound (VI; R = R' = OMe) (26 g.), anhydrous aluminium bromide¹⁵ (105 g.), and dry benzene (300 ml.) were refluxed together for 32 hr. and poured into an excess of ice and hydrochloric acid. The suspension was freed from benzene and extracted with (a) chloroform and (b) n-butanol-benzene. The extracts were dried and evaporated leaving the diol, needles (13.59 g.), m. p. 161° (from toluene) (Found: C, 68.4; H, 6.35. $C_{11}H_{12}O_3$ requires C, 68.7; H, 6.3%), ν_{\max} . (Nujol) 3560, 3300, 1650, 1612, 1525 cm^{-1} . The dinitrophenylhydrazone formed prisms, m. p. 244° (from ethanol) (Found: C, 54.55; H, 4.5; N, 15.35. $C_{17}H_{16}N_4O_6$ requires C, 54.85; H, 4.3; N, 15.05%). From the toluene mother-liquor 4'-hydroxy-5'-methoxy-1,2-benzocyclohept-1-en-3-one (VI; R = OH, R' = Me) was obtained (1 g.), m. p. 70° [from light petroleum (b. p. 60—80°)] (Found: C, 70.35; H, 7.1. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.85%) ν_{\max} . (Nujol) 3450 1667 cm^{-1} . The amorphous dinitrophenylhydrazone had m. p. 201° (from ethanol-acetic acid) (Found: C, 55.9; H, 4.85; N, 14.3. $C_{18}H_{18}N_4O_6$ requires C, 55.95; H, 4.7; N, 14.5%).

Sometimes the monomethyl ether (VI; R = OH, R' = OMe) was the major product; the reason is not clear, but a second treatment with aluminium bromide gave the desired product. That the remaining methoxy-group in (VI; R = OH, R' = OMe₃) occupied the 5'-position was deduced from the known¹⁶ resistance of *p*-methoxyacetophenone to demethylation and from the fact that the infrared carbonyl stretching frequency of the monomethyl ether (VI; R = OH, R' = OMe) showed no reduction compared with that of the diether (VI; R = R' = OMe), whereas the frequency of the completely demethylated product (VI; R = R' = OH) was reduced by 17 wave numbers. This is interpreted as being due to the electron-releasing effect of the *para*-hydroxyl group, although increased intermolecular hydrogen-bonding may make a contribution.

4',5'-Dihydroxy-1,2-benzocyclohept-1-ene (VIIa; R = R' = OH).—(a) The dimethoxy-ketone (VI; R = R' = OMe) (71 g.), freshly powdered lithium aluminium hydride (59 g.) and dry tetrahydrofuran (250 ml.) were refluxed for 3 hr., by which time much of the solvent was consumed and an unidentified gas was evolved. Tetrahydrofuran (300 ml.) was added and the mixture refluxed for 7 hr., poured on to ice and hydrochloric acid, and extracted with benzene which was washed with sodium hydroxide (10%). The alkaline solution and washings were acidified, and shaken with chloroform which was dried and evaporated leaving the diol, needles, m. p. 121° [from light petroleum (b. p. 100—120°)] (Found: C, 74.15; H, 8.15. $C_{11}H_{14}O_3$ requires C, 74.15; H, 7.9%), ν_{\max} . (Nujol) 3360, 1612, 1512 cm^{-1} .

The diacetate, obtained by treatment with acetic anhydride in dry pyridine, crystallised from light petroleum (b. p. 60—80°) in clusters of needles, m. p. 126° (Found: C, 69.2; H, 7.1. $C_{15}H_{18}O_4$ requires 68.7; H, 6.9%), ν_{\max} . (Nujol) 1760 cm^{-1} . If ten times the volume of solvent was used, the principal product was 4'-hydroxy-5'-methoxy-1,2-benzocyclohepta-1,3-diene, m. p. 161—162° (subl.) (Found: C, 75.8; H, 7.9. $C_{12}H_{14}O_2$ requires C, 75.75; H, 7.4%), ν_{\max} . (Nujol) 3490, 1612, 1585 cm^{-1} . The identity of the latter was confirmed when it was obtained by reduction of 4'-hydroxy-5'-methoxy-1,2-benzocyclohept-1-en-3-one with sodium borohydride in ethanol, followed by treatment with ethanolic hydrogen chloride. The intermediate 3,4'-dihydroxy-5'-methoxy-1,2-benzocyclohept-1-ene was isolated as a colourless solid, m. p. 99—100° [from light petroleum (b. p. 60—80°)], ν_{\max} . (Nujol) 3455, 1608, 1590 cm^{-1} , but satisfactory analyses could not be obtained. This material readily dehydrated even on thermal treatment which may account for the poor analytical figures.

(b) The dihydroxy-ketone (VI; R = R' = OH) (150 mg.) was subjected to Wolff-Kishner

¹³ Plattner and Roniger, *Helv. Chim. Acta*, 1942, **25**, 590.

¹⁴ Aitken, Badger, and Cook, *J.*, 1950, 331.

¹⁵ Barner, Dreiding, and Schmid, *Chem. and Ind.*, 1958, 1437; Pfeiffer and Loewe, *J. Prakt. chem.*, 1937, [2], **147**, 293.

¹⁶ Ghaswalla and Donnan, *J.*, 1936, 1341.

reduction by the modification of Huang-Minlon¹⁷ and gave the diol (61 mg.), m. p. and mixed m. p. 121°.

4',5'-Diacetoxy-3'-bromo-1,2-benzocyclohept-1-ene (VIIb; R¹ = R² = OAc, R³ = Br, R⁴ = R⁵ = R⁶ = H).—*N*-Bromosuccinimide (7.5 g.), the above diol (VIIa; R = R' = H) (6.4 g.), and dry carbon tetrachloride (200 ml.) were refluxed⁷ for 6 hr. using a 150 w bulb. After cooling, filtration, and removal of solvent, the residue was boiled with sodium hydroxide solution (10%) for 1 hr. The cooled solution was acidified and the product obtained by extraction with chloroform, distillation at 0.1 mm., reaction with acetic anhydride in pyridine, and crystallisation from light petroleum (b. p. 100—120°) as a colourless solid, m. p. 132° (Found: Br, 23.2. C₁₅H₁₇BrO₄ requires Br, 23.4%).

When the diol (9.6 g.) was treated with *N*-bromosuccinimide (20.0 g., 2 moles) as previously and the initial products were refluxed with sodium hydroxide solution, distillation at 160°/0.3 mm. gave 3'-bromo-3(or 7),4',5'-trihydroxy-1,2-benzocyclohept-1-ene (VIIb; R¹ = R² = R⁴(or R⁵) = OH, R³ = Br, R⁶(or R⁴) = R⁶ = H) (3 g.) (Found: C, 48.05; H, 4.8. C₁₁H₁₃BrO₃ requires C, 48.35; H, 4.8%).

The material which failed to distil was treated with acetic anhydride in dry pyridine to give, after distillation at 160°/0.3 mm., 4',5'-diacetoxy-3'(?) ,6'(?)-dibromo-1,2-benzocyclohept-1-ene (VIIb; R¹ = R² = OAc, R³ = R⁶ = Br, R⁴ = R⁵ = H) (Found: C, 42.9; H, 3.8. C₁₅H₁₆Br₂O₄ requires C, 42.9; H, 3.85%).

4',5'-Diacetoxy-3-bromo-1,2-benzocyclohept-1-ene (VIIb; R¹ = R² = OAc, R⁴ = Br, R³ = R⁵ = R⁶ = H).—The diacetate (VIIa; R = R' = OAc) (2.62 g.), *N*-bromosuccinimide (1.8 g., 1 mole), and dry carbon tetrachloride (180 ml.) were refluxed for 6 hr. over a 150 w bulb. After cooling and removal of succinimide (0.98 g.), the solvent was evaporated to leave the *bromo-compound* as a colourless solid (1.05 g.), m. p. 97° [from light petroleum (b. p. 60—80°)] (Found: C, 52.4; H, 5.1; Br, 23.85. C₁₅H₁₇BrO₄ requires C, 52.8; H, 5.0; Br, 23.4%). After 1 month at room temperature, this product became black.

4',5'-Diacetoxy-3,7-dibromo-1,2-benzocyclohept-1-ene (VIIb; R¹ = R² = OAc, R⁴ = R⁵ = Br, R³ = R⁶ = H).—Treatment of the diacetate (VIIa; R = R' = OAc) (1.3 g.) with *N*-bromosuccinimide (1.849 g., 2 mole) in carbon tetrachloride as above gave the *dibromo-compound* as a colourless solid (0.7 g.), m. p. 119° (from light petroleum-ether) (Found: C, 43.3; H, 3.95. C₁₅H₁₆Br₂O₄ requires C, 42.9; H, 3.85%). This material also became black on standing.

4',5'-Dihydroxy-1,2-benzocyclohepta-1,3-diene (IX; R = R' = OH).—The dihydroxy-ketone (VI; R = R' = OH) (1.8 g.) was dissolved in ethanol (50 ml.) and treated with sodium borohydride (3 g.). After 15 hr., the mixture was treated with methanol then dilute hydrochloric acid. Extraction successively with chloroform, benzene, and *n*-butanol gave the *diol* as a buff powder, m. p. 295° (from aqueous alcohol) (Found: C, 74.7; H, 7.2. C₁₁H₁₂O₂ requires C, 75.0; H, 6.9%), ν_{\max} . (Nujol) 3530, 3250, 1618 cm.⁻¹. This diol could not be obtained by reduction of the starting ketone with hydrogen on a platinum oxide catalyst in ethanol nor by demethylation of the 4',5'-dimethoxy-compound with aluminium bromide.

4',5'-Diacetoxy-1,2-benzocyclohepta-1,3-diene (IX; R = R' = OAc).—(a) The phenol from the previous experiment was treated with acetic anhydride in dry pyridine in the usual way and the product, after chromatography on deactivated alumina, crystallised from methanol-light petroleum (b. p. 100—120°) as needles, m. p. 188° (Found: C, 69.45; H, 6.5. C₁₅H₁₆O₄ requires C, 69.25; H, 6.2%).

(b) 4',5'-Diacetoxy-3-bromo-1,2-benzocyclohept-1-ene was refluxed with carbon tetrachloride and triethylamine for 6 hr. The product was acetylated and isolated as before.

4',5'-Dimethoxy-1,2-benzocyclohepta-1,3-diene (IX; R = R' = OMe).—Dimethoxybenzuberone (VI; R = R' = OMe) (14 g.), sodium borohydride (4 g.) and ethanol (300 ml.) were left together overnight and then methanol (25 ml.) was added. After 2 hr. the mixture was poured into dilute hydrochloric acid and extracted with chloroform which was dried and evaporated to leave the product (9.35 g.) as an oil, b. p. 115°/0.2 mm. (Found: C, 75.75; H, 7.9. C₁₃H₁₆O₂ requires C, 76.4; H, 7.9%), ν_{\max} . (Nujol) 1577, 1608 cm.⁻¹.

3,4,5'-Trihydroxy-1,2-benzocyclohepta-1,6-diene (X).—The diacetate (VIIa; R = R' = OAc) (13.0 g.) was brominated with *N*-bromosuccinimide (18.1 g.) as described previously. The crude dibromide was refluxed with 10% aqueous sodium hydroxide (50 ml.) and ethanol (180 ml.) for 10 min., set aside at room temperature for 3 hr., acidified, and left overnight.

¹⁷ Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

After extraction with chloroform and drying and evaporation of the extract, the crude phenol was treated with acetic anhydride (excess) in dry pyridine (100 ml.). After 24 hr., the mixture was poured on to ice and hydrochloric acid, filtered, and dried. Chromatography of the crude product (11.4 g.) on silica gave a brown powder, m. p. 220° (from ethanol), which analyses showed to be inhomogeneous. The crude acetate was hydrolysed by refluxing with aqueous sodium hydroxide (40 ml.; 10%) and ethanol (125 ml.) for 1 hr. Acidification, filtration, and drying gave the crude phenol (6.7 gm.). Chromatography on silica and crystallisation from chloroform then aqueous ethanol gave the *triol* (3.37 g.) as a brown powder, m. p. 210° (Found: C, 69.2; H, 6.1. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%).

This substance resinified when treated with polyphosphoric acid at 100° or with refluxing ethanol containing hydrogen chloride.

4',5'-Dimethoxy-1,2-benzocyclohept-1-ene (VIIa; R = R' = OMe).—*4',5'*-Dimethoxy-1,2-benzocyclohepta-1,3-diene (6.8 g.) in ethanol was hydrogenated at atmospheric temperature and pressure over 2% palladised charcoal (612 ml. absorbed after 24 hr.). The catalyst was filtered off and the solvent evaporated leaving the *product*, which was distilled at 110°/0.05 mm. and crystallised from light petroleum (b. p. 60–80°) at –20° as plates, m. p. 51° (Found: C, 75.4; H, 8.8. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%).

4'-Hydroxy-5'-methoxy-1,2-benzocyclohept-1-ene (VII; R = OH, R' = OMe₃).—(a) The above ether (5.5 g.), anhydrous aluminium bromide (25 g.), and dry benzene (200 ml.) were refluxed for 15 hr. and poured into an excess of dilute hydrochloric acid. The benzene layer and subsequent extracts were repeatedly washed with dilute sodium hydroxide solution from which the phenolic product (3.5 g.) was obtained after acidification and solvent extraction. Crystallisation from light petroleum (b. p. 60–80°) and sublimation *in vacuo* gave the *hydroxy-ether*, m. p. 110° (Found: C, 74.8; H, 8.35. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%), ν_{\max} . (Nujol) 3440, 1618, 1595 cm^{-1} .

(b) *4'-Hydroxy-5'-methoxy-1,2-benzocyclohepta-1,3-diene* (300 mg.) was hydrogenated in ethanol using 5% palladised charcoal. After removal of the solvent, the product (255 mg.) was isolated as in (a).

Action of Iodine and Nitrobenzene on 4'-5'-Dihydroxy-1,2-benzocyclohept-1-ene (VII; R = R' = OH).—The phenol (1.5 g.) was refluxed for 4 hr. with nitrobenzene (70 ml.) and iodine (one large crystal⁸), set aside overnight, and treated with dilute aqueous sodium hydroxide (10% excess) for 3 days at room temperature. The aqueous layer was removed, acidified, and extracted with chloroform which was dried and evaporated. The residue was extracted thrice with boiling light petroleum (b. p. 60–80°). After evaporation, the residual oil (460 mg.) was chromatographed on silica gel and twice distilled to give *2-hydroxymethylcycloheptenecarboxylic acid* (XII), b. p. 115–120°/0.2 mm. (Found: C, 63.75; H, 8.2. $C_9H_{14}O_3$ requires C, 63.5; H, 8.3%), ν_{\max} . (liquid film) 3390, 1712s, 1600 cm^{-1} .

The preceding oil (300 mg.) was heated with polyphosphoric acid for 3 hr. at 95°, diluted with water, and extracted with chloroform to give the product (226 mg.). Two distillations at 120°/0.2 mm. and crystallisation at –20° from light petroleum (b. p. 40–60°) gave colourless *2-hydroxymethylcycloheptenecarboxylic acid lactone* (XIII), m. p. 62° (Found: C, 70.95; H, 8.05%; M, 159. $C_9H_{12}O_2$ requires C, 71.0; H, 7.95%; M, 152), ν_{\max} . (liquid film) 1760 cm^{-1} .

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