Novel Aromatic Systems. Part X.[1] Some Aspects of the Chemistry of 2,3-Dihydroxybenzocycloheptenes

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Some reactions of 3-methoxybenzocyclohepten-2-one are described and its n.m.r. spectrum is discussed. Hydride reductions of various derivatives of 2,3-dihydroxybenzocycloheptenones have been carried out and the products identified. A convenient synthesis of 5-aryl-3-methoxybenzocyclohepten-2-ones is reported.

In Part V [2] we discussed the synthesis of the first isolable members of a new type of aromatic system (I; R^1 = OH or OMe, R^2 = H), which we discuss further here.

Initially,[3] tropone was regarded as an aromatic compound. Latterly, however, critical appraisal of dipole moment [4] and n.m.r. data [5] and measurement of the *X*-ray parameters for 2-chlorotropone [6] have conclusively shown that we [3] were in error in regarding structure (II) as an important contributor to the ground state of tropone. Tropolone, however, is by most criteria aromatic. In the present series, 3-hydroxybenzocyclohepten-2-one (I; R^1 = OH, R^2 = H) is comparable with tropolone and might be expected to undergo electrophilic substitution. Unfortunately we find that the dominant tendency for proton addition [2] frustrates observation of other reactions: thus, addition of bromine to the benzocycloheptenone (I; R^1 = OH, R^2 = H) gives a mixture of tropylium salts, presumably the unsubstituted tropylium bromide (III; R = OH, X = Br) and the monobrominated compound. On increasing the basicity, several red substances were isolated, but since the hydroxy-derivatives [*e.g.* (I; R^1 = OH, R^2 = H)], unlike the methoxy-analogues (I; R^1 = OMe, R^2 = H), cannot be chromatographed, it was not possible to purify them. Although the methoxy-derivative (I; R^1 = OMe, R^2 = H) is not the best substrate for a chemical test of aromaticity, its comparative ease of handling encouraged us to examine it further. Treatment of (I; R^1 = OMe, R^2 = H) with tetranitromethane in chloroform yielded a red salt, which we regard as the corresponding tropylium nitrite, since treatment of it with sodium hydrogen carbonate regenerated the starting material. Compound (I; R^1 = OMe, R^2 = H) decomposed on treatment with acetic anhydride, but reacted with bromide to yield a yellow bromotropylium salt, which, on making the solution basic, gave a dark red product, whose n.m.r. spectrum indicated that it was probably a 5-bromo-derivative. This formulation is preferred over the alternative 1- (IV) or 4-bromo-compounds since the two 1H singlets (1- and 4-H) discernible in the original spectrum of (I; R^1 = OMe, R^2 = H) are still present (one is overlaid by a multiplet). One of these singlets is significantly deshielded (τ 2·52), as would be expected if a bromine atom was located in a neighbouring position. The n.m.r. spectrum does not eliminate the 9-bromo-isomer, although there seems no mechanistic reason for its production. Thus a substitution has been achieved by addition–elimination; substitution of the 5-position can also be brought about by nucleophilic reagents.[2]

The deshielding of protons as a result of a diamagnetic ring current is diagnostic of aromaticity, and while the quantitative application [7] of this effect has been criticised,[8] it is a most useful probe, provided that relevant reference compounds are available. Previously,[2] we decided, arbitrarily, that since the protons of the methoxy-compound (I; R^1 = OMe, R^2 = H) had chemical shift values between τ 2·0 and 3·1 (in the aromatic region), the molecule sustained a diamagnetic ring current. This argument is weakened by the appreciation that protons in αβ-unsaturated aliphatic and alicyclic carbonyl compounds are frequently found in the region τ 1·5—3·5. We have therefore attempted to synthesise relevant reference compounds [*e.g.* (V) and (VI); R = H and Ph].

Our synthesis [2,9] involved the reduction of several dihydrobenzocycloheptenones (VII) in variable yields. Reinvestigation of the reduction with lithium aluminium hydride of the acetoxy-ketone (VII; R^1 = R^2 = OAc) showed that the product was a mixture containing both the desired alcohol (VIII; R^1 = R^2 = R^3 = OH) [since it gave the known [2] tropylium salt (III; R = OH, X = BF_4) on treatment with trityl fluoroborate] and an inseparable mixture of two products (after acetylation) (VIII; R^1 = R^2 = OAc, R^3 = H) and (X; R^1 = R^2 = OAc, R^3 = R^4 = X = H)]. We examined the tetrahydrobenzocycloheptenones (IX) next; in almost every case complications arose.

The most unexpected results were obtained from the reduction of the dihydroxy-ketone (IX; R^1 = R^2 = OH, X = H) with borohydride and from the reduction of the diacetoxy-ketone (IX; R^1 = R^2 = OAc, X = H) with both the borohydride and lithium aluminium

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[4] D. J. Bertelli and T. G. Andrews, *Tetrahedron Letters*, 1967, **45**, 4467; *J. Amer. Chem. Soc.*, 1969, **91**, 5280.
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[8] R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Comm.*, 1965, 43.
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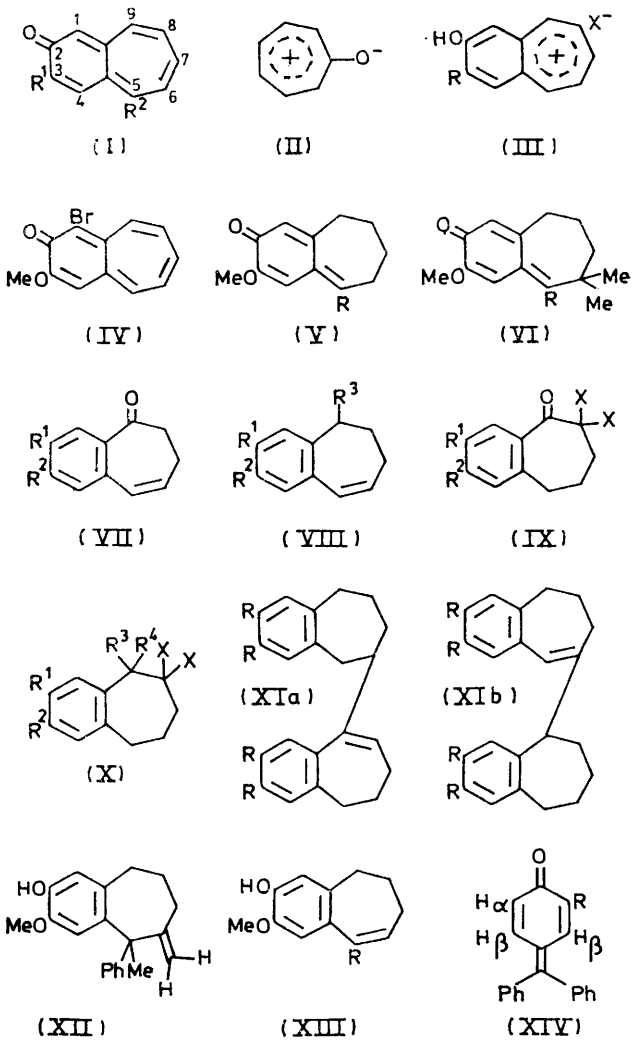
hydride: the main product (after acetylation) was dimeric ($C_{30}H_{32}O_8$). With lithium aluminium hydride less reproducible results were achieved; as well as the



dimer, we usually also isolated the tetrahydro-acetate (X; $R^1 = R^2 = OAc$, $R^3 = R^4 = X = H$) and on one occasion, instead of the dimer, we found the triacetate (X; $R^1 = R^2 = R^3 = OAc$, $R^4 = X = H$). We regard the dimeric tetra-acetate as (XIa; R = OAc) or (XIb; R = OAc) on mechanistic grounds (formed *via* an aldol-type condensation). The n.m.r. spectrum does not distinguish between the two, for although the olefinic proton signal appears as a broad singlet [favouring structure (XIb)], we cannot estimate with certainty the magnitude of splitting expected in (XIa). A symmetrical C(5)–C(5) dimer, which could have arisen *via* a pinacol-type reduction, seems unlikely since there is only one double bond in the product. We now recognise that the phenolic product which we previously [3] regarded as (VIII; $R^1 = R^2 = OH$, $R^3 = H$) must be reformulated as (XIa or b; R = OH).

Reductions of various other tetrahydrobenzocycloheptenones (IX; X = H, R^1 and R^2 = OMe, OH, or OAc) gave mixtures (see Experimental section) but certain trends are apparent. For example, when sodium borohydride in dry methanol is used, the methyl ether of the expected alcohol is obtained, and in one reduction of (X; $R^1 = OH$, $R^2 = R^3 = OMe$, $R^4 = X = H$) it was the main product. The alcohols are readily dehydrated and can only be isolated if the mixture is not acidified. When lithium aluminium hydride or sodium dihydrobis-(2-methoxyethoxy)aluminate (S.D.A.) is used, one of the products is always the fully reduced benzocycloheptene (X; $R^3 = R^4 = X = H$).

The benzocycloheptenone (IX; $R^1 = OMe$, $R^2 = OH$, X = Me), prepared by conventional procedures from the hydroxy-methoxy-ketone (IX; $R^1 = OMe$, $R^2 = OH$, X = H), could be reduced to the corresponding alcohol with either lithium aluminium hydride or S.D.A. Treatment of the same ketone with phenylmagnesium bromide was apparently successful, but if the mixture was acidified, the main product was an olefin (XII) produced by a Wagner–Meerwein rearrangement.

We had hoped that dehydrogenation of (X; $R^1 = OMe$, $R^2 = OH$, $R^3 = p\text{-}MeO\cdot C_6H_4$, $R^4 = X = H$) with dichlorodicyanoquinone (DDQ) might have given a quinone methide (V; $R = p\text{-}MeO\cdot C_6H_4$), a suitable model compound for n.m.r. spectroscopy, but the only compound isolated was the olefin (XIII; $R = p\text{-}MeO\cdot C_6H_4$). The latter compound reacted further with DDQ to give the substituted benzocyclohepten-2-one (I; $R^1 = OMe$, $R^2 = p\text{-}MeO\cdot C_6H_4$); probably this dehydrogenation is facilitated by the extra stabilisation of the intermediate carbonium ions, since neither of the compounds (XIII; R = H) or (X; $R^1 = OMe$, $R^2 = OH$, $R^3 = R^4 = X = H$) gave compound (I; $R^1 = OMe$, $R^2 = H$) with DDQ. This constitutes a convenient synthesis of 5-aryl-3-methoxybenzocyclohepten-2-ones.

Since our efforts to synthesise model compounds (V) and (VI) were unsuccessful, we used simpler quinone methide molecules for comparison. The n.m.r. spectra of the methides (XIV; R = H and OMe) [10] contain olefinic signals for H_α at τ 3·75 and 3·52, respectively; compared with these the 1- and 4-H signals of (I; $R^1 = OMe$, $R^2 = H$) are deshielded by at least 0·5 p.p.m. Moreover, the proton adjacent to the methoxy-group in (XIV; R = OMe) has a signal at τ 3·52 (J 1 Hz, H_β), which is shielded by more than 0·5 p.p.m. compared with the equivalent proton (H_β) in (XIV; R = H). The apparent absence of such an upfield shift in compound (I; $R^1 = OMe$, $R^2 = H$) is striking. It is now necessary to study further derivatives of the parent system (I; $R^1 = R^2 = H$) and to estimate the π-bond order (*cf.* ref. 11) for both these and the quinone methides (XIV) before classifying these compounds as aromatic or otherwise.

[10] P. Carpenter, unpublished results.
[11] Z. Yoshida, S. Yoneda, and M. Hazama, *Chem. Comm.*, 1971, 716.

EXPERIMENTAL

Bromination of 3-Hydroxybenzocyclohepten-2-one (I; R^1 = OH, R^2 = H).—The title compound (135 mg) in carbon tetrachloride–chloroform (40 ml; 1 : 1 v/v) was treated dropwise with bromine (125 mg) in chloroform (3 ml). The precipitate (135 mg) was washed with carbon tetrachloride and chloroform and dried (Found: C, 43·3; H, 2·85; Br, 39·1%). A solution of this material in methanol–chloroform was shaken with aqueous sodium hydrogen carbonate solution (2·5%); the organic layer yielded a deep red material, which gave several coloured spots on t.l.c. (alumina).

Reactions of 3-Methoxybenzocyclohepten-2-one (I; R^1 = OMe, R^2 = H).—(a) *With tetranitromethane.* To the title compound (186 mg) in chloroform–carbon tetrachloride (20 ml; 1 : 1 v/v) at 0° was added tetranitromethane (200 mg) in carbon tetrachloride (10 ml). After 30 min, the solvent was evaporated (at less than 40°) and the residue chromatographed on neutral, deactivated alumina. Elution with chloroform gave a red powder [M^+, 233·07011 (rel. intensity 0·0044) and *m/e* 186·06794 (1·0). $C_{12}H_{11}O_2^+NO_2^-$ requires 233·06880 and 186·06807].* When this material was shaken with sodium hydrogen carbonate solution, the title compound could be extracted with chloroform.

(b) *With bromine.*—The title compound (250 mg) in chloroform (10 ml) and carbon tetrachloride (80 ml) was treated dropwise with bromine (215 mg) in carbon tetrachloride (7 ml). The dull yellow precipitate was collected, washed, and dried (450 mg) ($M^+ - 1$, 265·97716, 263·97824. $C_{12}H_{10}BrO_2$ requires $M - 1$, 265·97667, 263·97864).* This salt in methanol (20 ml) and chloroform (150 ml) was shaken with aqueous sodium hydrogen carbonate solution (2·5%); the deep red organic layer was separated, washed with water, dried, and evaporated to leave the product (320 mg), an intensely red powder, m.p. 135° (from benzene) (Found: C, 54·15; H, 3·8%; M^+, 265·97849, 263·97902. $C_{12}H_9BrO_2$ requires C, 54·35; H, 3·4%; M^+, 265·97667, 263·97864), τ 1·3—1·6 (1H, m), 2·0—2·25 (1H, m), 2·4—2·8 (2H, m), 2·52 (1H, s), 2·9 (1H, s), and 5·95 (3H, s, OMe).

Reduction of 2,3-Diacetoxy-6,7-dihydro-5H-benzocycloheptene-5-one [2] (VII; R^1 = R^2 = OAc).—(a) *With lithium aluminium hydride.* The title compound (2·38 g) in dry tetrahydrofuran (50 ml) was added during 30 min under nitrogen to lithium aluminium hydride (2·5 g) in dry tetrahydrofuran (75 ml), and after a further 30 min the mixture was heated under reflux for 1 h. After addition of water and dilute hydrochloric acid, the product was extracted in the usual way and acetylated with acetic anhydride (excess)–pyridine. After the usual work-up, the acetates (2·0 g) were repeatedly chromatographed both on columns of silica and on preparative plates; the main fraction (730 mg) consisted of an inseparable mixture of 2,3-diacetoxy-6,7-dihydro-5*H*-benzocycloheptene (VIII; R^1 = R^2 = OAc, R^3 = H) (*M*, 260·10451. $C_{15}H_{16}O_4$ requires *M*, 260·10485), τ 3·38—3·71 and 3·9—4·25 (m, CH:CH) and 2,3-diacetoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene [3] (*M*, 262·12069. Calc. for $C_{15}H_{18}O_4$: *M*, 262·12050).

(b) *With sodium borohydride.* The title compound (2·0 g) in methanol (75 ml) was treated with sodium borohydride (1·0 g) in small portions at 20° and stirred for 3 h. After addition of water and dilute hydrochloric acid, the product was extracted with chloroform and acetylated (acetic anhydride–pyridine). T.l.c. showed that there were several compounds of low R_F present, along with a little of the mixture of acetates described in the previous paragraph.

Reduction of 2,3-Dihydroxy-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one [3] (IX; R^1 = R^2 = OH, X = H).—Sodium borohydride (1·5 g) was added in portions to the title compound (3·4 g) in methanol at 20°. After 2 h, water and dilute hydrochloric acid were added and the dimer (XIa or b; R = OAc) was extracted with chloroform, and treated with acetic anhydride (excess)–pyridine. The acetate [3] (1·94 g) crystallised from ethanol in plates, m.p. 186—187° (Found: C, 69·0; H, 6·1%; *M*, 520·21037. Calc. for $C_{30}H_{32}O_8$: C, 69·2; H, 6·2%; *M*, 520·20970), $\nu_{max.}$ (KCl) 1770 cm^{-1} (OAc), τ 3·0—3·1 (4H, m, aryl), 3·75br (1H, s, vinyl), 6·4—6·55 (1H, m, CH), 7·05—7·4 (4H, m, benzylic), 7·22 (12H, s, OAc), and 7·6—8·8 (10H, m).

Reduction of 2,3-Diacetoxy-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one [2] (IX; R^1 = R^2 = OAc, X = H).—(a) *With sodium borohydride.* Sodium borohydride (0·4 g) was added in portions to the acetoxy-ketone (1·0 g) in dry methanol (50 ml) with stirring at 20°. After 2 h, the usual work-up gave a gum which was treated with acetic anhydride in pyridine. The resulting acetate (950 mg) crystallised from ethanol to give plates, m.p. 186—187° (350 mg), identical with the foregoing dimer.

(b) *With lithium aluminium hydride.* The acetoxy-ketone (5·18 g) in dry tetrahydrofuran (100 ml) was added dropwise during 30 min to lithium aluminium hydride (5·6 g) stirred in dry tetrahydrofuran (150 ml) under nitrogen. After heating under reflux for 1 h, the mixture was treated with ice, dilute hydrochloric acid, and chloroform. The product from the chloroform extracts was acetylated with acetic anhydride (excess) in pyridine and the crude acetate was chromatographed on silica gel. Benzene eluted 2,3-diacetoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (X; R^1 = R^2 = OAc, R^3 = R^4 = X = H) (1·46 g), m.p. 116—117° (lit.,[3] 126°) (identical with the product of acetylation of 6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2,3-diol,[3] τ 3·05 (2H, s, 1- and 4-H), 7·15—7·4 (4H, m, 5- and 9-H), 7·73 (6H, s, OAc), and 8·05—8·5 (6H, m, CH_2). Ether eluted 2,3,5-*triacetoxy-6,7,8,9-tetrahydro-5H-benzocycloheptene* (X; R^1 = R^2 = R^3 = OAc, R^4 = X = H) (2·94 g), m.p. 74·5° (Found: C, 63·8; H, 6·4. $C_{17}H_{20}O_6$ requires C, 63·7; H, 6·3%), $\nu_{max.}$ (KCl) 1765 and 1735 (OAc) cm^{-1}, τ 2·79 (1H, s, 1- or 4-H), 2·99 (1H, s, 4- or 1-H), 4·05 (1H, t, *J* 5 Hz, 9-H), 7·05—7·45 (2H, m, 5-H), 7·7 (6H, s, OAc), 7·86 (3H, s, OAc), and 8·0—8·6 (6H, m, CH_2). In another experiment under apparently similar conditions, chromatography gave 2,3-diacetoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (0·93 g) and the dimeric acetate (3·76 g) described in the previous section.

Reduction of 6,7,8,9-Tetrahydro-2-hydroxy-3-methoxy-5H-benzocyclohepten-5-one [2] (IX; R^1 = OMe, R^2 = OH, X = H).—A solution of sodium dihydrobis-(2-methoxyethoxy)-aluminate (S.D.A.) in benzene (70%, 5 ml) was diluted with dry benzene (25 ml) and added slowly to a stirred solution of the ketone (1·0 g) in dry benzene (75 ml) at 20°. After 2 h, water and dilute hydrochloric acid were added and the product (860 mg) was extracted with chloroform and crystallised from light petroleum (b.p. 60—80°) as needles, m.p. 95—97°. This appeared on t.l.c. to be a

* We find that hydroxyphenyltropylium salts commonly show a molecular ion at $M - 1$ rather than *M*.

ıethgle substance but n.m.r. spectroscopy and elemental analyses indicated it was a mixture (*ca.* 1 : 1) of 6,7-dihydro-2-methoxy-5*H*-benzocyclohepten-3-ol [τ 3·67 (dt, *J* 12 Hz, *J* 2 Hz) and 4·18 (dt, *J* 12 Hz, *J* 5 Hz)] and 6,7,8,9-tetrahydro-3-methoxy-5*H*-benzocyclohepten-2-ol [3] (X; R^1 = OH, R^2 = OMe, R^3 = R^4 = X = H) [Found: C, 74·85; H, 7·85%; *M* (osmometry), 189; *M* (mass spectroscopy), 192·11515 (rel. inten. 1·0), 190·09953 (0·84). Calc. for $C_{12}H_{16}O_2$: C, 74·95; H, 8·4%; *M*, 192·11502. Calc. for $C_{12}H_{14}O_2$: C, 75·75; H, 7·9%; *M*, 190·09937]. Acetylation of this mixture with acetic anhydride–pyridine gave, after the usual work-up, 3-*acetoxy*-6,7-*dihydro*-2-*methoxy*-5H-*benzocycloheptene* (VIII; R^1 = OAc, R^2 = OMe, R^3 = H), m.p. 97—98° [from light petroleum (b.p. 60—80°)] (Found: C, 72·5; H, 6·9%; *M*, 232·10924. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%; *M*, 232·10994), $\nu_{max.}$ (KCl) 1760 (OAc) and 1610 (C=C) cm^{-1}, τ 3·18 and 3·21 (2H, s, 1- and 4-H), 3·61 (1H, dt, *J* 12 Hz, *J* 1·9 Hz), 4·08 (1H, dt, *J* 12 Hz, *J* 4·4 Hz), 6·2 (3H, s, OMe), 7·19—7·3 (2H, m, CH_2), 7·5—7·7 (2H, m, CH_2), 7·7 (3H, s, OAc), and 7·94—8·2 (2H, m, CH_2).

Reduction of 2-*Acetoxy*-6,7,8,9-*tetrahydro*-3-*methoxy*-5H-*benzocyclohepten*-5-*one* (IX; R^1 = OMe, R^2 = OAc, X = H).—(a) *With sodium borohydride.* Sodium borohydride (2 g) was added in portions to a stirred solution of the ketone (5·0 g) in dry methanol at 20°. After 3 h, the usual work-up gave a brown oil (5·3 g) which was acetylated as before. Chromatography of the product on silica gel with benzene as eluant gave 3-acetoxy-6,7-dihydro-2-methoxy-5*H*-benzocycloheptene (1·16 g), m.p. 97—98°, as in previous paragraph, and (chloroform elution) an oil (3·74 g) considered to be 2-acetoxy-6,7,8,9-tetrahydro-3,5-dimethoxybenzocycloheptene (X; R^1 = R^3 = OMe, R^2 = OAc, R^4 = X = H), $\nu_{max.}$ (film) 1765 and 1745sh cm^{-1} (OAc), τ 2·9—3·3 (2H, m, 1- and 4-H), 5·7—5·85 (1H, m, 5-H), 6·2 (3H, s), 6·65 (3H, s), 7·1—7·5 (1H, m,) 7·72 (3H, s), and 7·9—8·65 (6H, m).

(b) *With lithium aluminium hydride.* The ketone (4·93 g) was treated with lithium aluminium hydride (5·04 g) in dry tetrahydrofuran (100 ml). In the usual way the product (2·9 g) was obtained from light petroleum (b.p. 60—80°) as a solid, m.p. 95—97°, as before, and shown to be a mixture (*ca.* 1 : 2) of 6,7,8,9-tetrahydro-3-methoxy-5*H*-benzocyclohepten-2-ol and 6,7-dihydro-2-methoxy-5*H*-benzocyclohepten-3-ol.

Reduction of 6,7,8,9-*Tetrahydro*-3-*hydroxy*-2-*methoxybenzocyclohepten*-5-*one* (IX; R^1 = OH, R^2 = OMe, X = H).—Sodium borohydride (2 g) was added in portions to the ketone (5·0 g) in dry methanol during 2 h at 20°. The usual procedure gave 6,7,8,9-*tetrahydro*-3,9-*dimethoxy*-5H-*benzocyclohepten*-2-*ol* (X; R^1 = OH, R^2 = R^3 = OMe, R^4 = X = H), flakes, m.p. 146—147° (Found: C, 70·2; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2%), τ 3·08 and 3·33 (2H, s. 1- and 4-H), 4·44 (1H, s, exchangeable, OH), 5·78 (1H, m, 5-H), 6·13 (3H, s, OMe), 6·69 (3H, s, OMe), 6·9—7·6 (2H, m, CH_2), and 7·7—8·6 (6H, m, CH_2). The *acetate* was obtained from light petroleum (b.p. 40—60°) as needles, m.p. 79—80° (Found: C, 68·1; H, 7·6. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%), $\nu_{max.}$ (KCl) 1755 cm^{-1} (OAc), τ 3·07 and 3·30 (2H, s, 1- and 4-H), 5·82 (1H, t, 5-H), 6·22 (3H, s, OMe), 6·72 (3H, s, OMe), 6·9—7·6 (2H, m, CH_2), 7·73 (3H, s, OAc), and 8·0—8·5 (6H, m, CH_2).

Reduction with lithium aluminium hydride gave several inseparable products.

6,7-*Dihydro*-2-*methoxy*-9-(p-*methoxyphenyl*)-5H-*benzocyclohepten*-3-*ol* (XIII; R = *p*-MeO·C_6H_4).—To a Grignard solution from *p*-bromoanisole (92·1 g), magnesium (13·1 g), and dry tetrahydrofuran (500 ml), was added 2-acetoxy-6,7,8,9-tetrahydro-3-methoxy-5*H*-benzocyclohepten-5-one (12·4 g) dropwise at 0°. After heating under reflux for 2 h, the mixture was added to ice and dilute sulphuric acid and worked up as before. Chromatography on silica gel gave (benzene elution) the *product* (XIII; R = *p*-MeO·C_6H_4) (9·56 g), m.p. 148—149° [from light petroleum (b.p. 60—80°)] (Found: C, 77·0; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\nu_{max.}$ (KCl) 3380 cm^{-1} (OH), τ 2·65 and 3·07 (4H, dd, aryl), 3·06 and 3·38 (2H, s, 1- and 4-H), 3·6 (1H, t, 8-H), 4·3 (1H, s, exchangeable, OH), 6·12 (3H, s, OMe), 6·23 (3H, s, OMe), and 7·2—8·2 (6H, m, CH_2).

6,7,8,9-*Tetrahydro*-3-*methoxy*-5-(p-*methoxyphenyl*)-5H-*benzocyclohepten*-2-*ol* (X; R^1 = OMe, R^2 = OH, R^3 = *p*-MeO·C_6H_4, R^4 = X = H).—The foregoing compound (1·0 g) was hydrogenated in ethanol over palladised charcoal (100 mg; 10%). In the usual way the *product* (900 mg) was obtained as needles, m.p. 86—87° [from light petroleum (b.p. 60—80°)] (Found: C, 76·3; H, 7·4. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%), τ 2·64 and 3·66 (2H, s, 1- and 4-H), 2·8—3·2 (4H, m, aryl), 4·48 (1H, s, exchangeable, OH), 5·78 (1H, m, 5-H), 6·13 and 6·31 (6H, s, 2 × OMe), 7·1—7·4 (2H, m, 9-H), and 7·7—8·6 (6H, m, CH_2).

3-*Methoxy*-5-(p-*methoxyphenyl*)*benzocyclohepten*-2-*one* (I; R^1 = OMe, R^2 = *p*-MeO·C_6H_4).—6,7-Dihydro-2-methoxy-5-(*p*-methoxyphenyl)-5*H*-benzocyclohepten-3-ol (790 mg) in dry benzene (40 ml) was added to 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (1·15 g) in dry benzene (40 ml) at 20°. The mixture was left in the dark for 20 h and then chromatographed in chloroform on neutral deactivated alumina to give a dark red powder (320 mg), m.p. 250° (decomp.) (from benzene–hexane), which gave unsatisfactory analyses (C *ca.* 1% low) (Found: *M*, 292·10981. $C_{19}H_{16}O_3$ requires *M*, 292·10994), τ 2·5—3·4 (10H, m, aryl), 6·1 (3H, s, OMe), and 6·33 (3H, s, OMe).

2-*Benzyloxy*-6,7,8,9-*tetrahydro*-3-*methoxy*-5H-*benzocyclohepten*-5-*one* (IX; R^1 = OMe, R^2 = $PhCH_2$·O, X = H).—6,7,8,9-Tetrahydro-2-hydroxy-3-methoxy-5*H*-benzocyclohepten-5-one (4·13 g), anhydrous potassium carbonate (1·8 g), benzyl chloride (2·7 g), and dry methanol (40 ml) were heated under reflux for 5 h and filtered hot. The *benzyl ether* (4·17 g) separated on cooling and was recrystallised from methanol to give needles, m.p. 91—92° (Found: C, 77·1; H, 6·8. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\nu_{max.}$ (KCl) 1650 cm^{-1} (C=O).

2-*Benzyloxy*-6,7,8,9-*tetrahydro*-3-*methoxy*-6,6-*dimethyl*-5H-*benzocyclohepten*-5-*one* (IX; R^1 = OMe, R^2 = $PhCH_2$·O, X = Me).—The ketone previously described (2·96 g) in t-butyl alcohol (30 ml) was added to a solution of potassium (3·9 g) in t-butyl alcohol (100 ml). After heating under reflux for 2 h, methyl iodide (2·5 ml) in t-butyl alcohol (20 ml) was added and the heating was continued for 2 h. Methyl iodide (10 ml) was then added and the mixture was further heated under reflux for 6 h. The product was obtained in the usual way and purified by chromatography on silica gel to give a gum (3·5 g), $\nu_{max.}$ (film) 2920 (C–H) and 1670 (C=O) cm^{-1}, τ 2·44—2·69 (5H, m, aryl), 3·04 and 3·3 (2H, s, 1- and 4-H), 4·81 (2H, s, $PhCH_2$·O), 6·10 (3H, s, OMe), 7·2—7·4 (2H, t, 9-H), 8·0—8·45 (4H, m, CH_2), and 8·81 (6H, s, Me).

6,7,8,9-*Tetrahydro*-2-*hydroxy*-3-*methoxy*-6,6-*dimethyl*-5H-*benzocyclohepten*-5-*one* (IX; R^1 = OMe, R^2 = OH, X =

Me).—The preceding benzyloxyketone (1·29 g) was hydrogenated in ethanol (100 ml) over palladised charcoal (150 mg; 10%) to give the *product* (920 mg), which crystallised from light petroleum (b.p. 60—80°) as needles, m.p. 107—108° (Found: C, 71·5; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%), $\nu_{max.}$ (KCl) 3220br (OH) and 1650 (C=O) cm^{-1}, τ 3·05 and 3·27 (2H, s, 1- and 4-H), 4·03 (1H, s, exchangeable, OH), 6·11 (3H, s, OMe), 7·18—7·36 (2H, t, CH_2), 7·96—8·43 (4H, m, CH_2), and 8·8 (6H, s, Me).

6,7,8,9-*Tetrahydro*-3-*methoxy*-6,6-*dimethyl*-5H-*benzocycloheptene*-2,5-*diol* (X; R^1 = OMe, R^2 = R^3 = OH, R^4 = H, X = Me).—S.D.A. in benzene (2 ml, 70%) diluted with dry benzene (25 ml) was added dropwise with stirring to the foregoing phenolic ketone (370 mg) in dry benzene (25 ml). After heating under reflux for 2 h, the mixture was poured into water and the pH adjusted to 7. Extraction in the usual way gave the *product* (330 mg) as small crystals, m.p. 94—95° (from light petroleum) (Found: C, 70·8; H, 8·85. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%), $\nu_{max.}$ (KCl) 3450, 3380, 3220 (OH), 2940, and 2850 (C–H) cm^{-1}, τ 3·17 and 3·30 (2H, s, 1- and 4-H), 4·37 (1H, s, exchangeable 2-OH), 5·66 (1H, s, 5-H), 6·15 (3H, s, OMe), 6·9—7·25 (1H, m, CH_2), 7·35—7·7 (1H, m, CH_2), 7·9—8·25 (4H, m, CH_2), 8·04 (1H, s, exchangeable, 5-OH), 9·06 (3H, s, Me), and 9·17 (3H, s, Me). Treatment of this material with either polyphosphoric acid at 40° or with dicyclohexylcarbodi-imide in dichloromethane under reflux produced many products.

6,7,8,9-*Tetrahydro*-3-*methoxy*-6,6-*dimethyl*-5-*phenyl*-5H-*benzocycloheptene*-2,5-*diol* (X; R^1 = OMe, R^2 = R^3 = OH, R^4 = Ph, X = Me) (with Mrs. L. Rees).—The foregoing ketone (2·3 g) in dry ether (100 ml) was added dropwise to the Grignard reagent from magnesium (2·7 g) and bromobenzene (15·6 g) in dry ether (250 ml) with stirring. After 1 h at 20°, the mixture was added to saturated ammonium chloride solution (excess) and worked up as usual. T.l.c. showed the presence of several products including the desired material ($\nu_{max.}$ 3540 cm^{-1}) which was the major product; however, it could not be obtained pure and was used without further purification. Treatment of [illegible]*phenyl*-[illegible] chro[illegible] material with dilute mineral acid at 25°, polyphosphoric acid at 50°, dicyclohexylcarbodi-imide at 100°, or triphenylphosphine in carbon tetrachloride at 25°, caused total conversion into 6,7,8,9-*tetrahydro*-3-*methoxy*-5-*methyl*-6-*methylene*-5-*phenyl*-5H-*benzocyclohepten*-2-*ol* (XII), which was purified by chromatography and had b.p. 150° at 0·15 mmHg [Found: *M* (mass spectroscopy), 294·1633. $C_{20}H_{22}O_2$ requires *M*, 294·1620. Carbon analyses were consistently 1% low], τ 2·65—3·0 (5H, m, 5-Ph), 3·33 (1H, s, 1- or 4-H), 3·52 (1H, s, 1- or 4-H), 4·8br (1H, exchangeable OH), 4·9br (1H, s, :CH_2), 5·57br (1H, s, :CH_2), 6·38 (3H, s, OMe), 7·3 (2H, t, 1-H), 7·77 (2H, t, 7-H), 8·24 (3H, s, Me), and 8·65—9·1 (2H, m, 8-H).

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