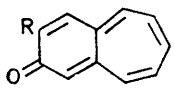
Novel Aromatic Systems. Part XI.[1] Preparation of 1,2-Dihydroxybenzocycloheptenes

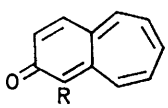
By **Philip D. Carpenter, David J. Humphreys, George R. Proctor,* and Lilias G. Rees,** Department of Pure and Applied Chemistry, The University of Strathclyde, Glasgow G1 1XL

1-Hydroxy- and 1-methoxy-benzocyclohepten-2-one, 2-methoxybenzocyclohepten-1-one, and 5-phenylbenzocyclohepten-2-one have been synthesised: they are only stable in solution. Unsuccessful attempts to prepare 6-methoxyinden-5-ones are recorded.

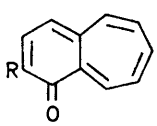
PREVIOUSLY we have described the syntheses and some reactions of benzocyclohepten-2-one (I; R = H)[2] and 3-hydroxy- and 3-methoxy-benzocyclohepten-2-one (I; R = OH or OMe).[1,3] The former was only stable in solution but both the latter were isolable; it was of



(I)



(II)

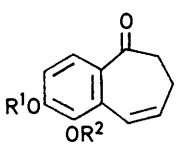


(III)

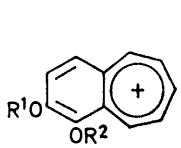
interest to find out whether hydroxy- or methoxy-groups in the 1-position also conferred stability on the benzocyclohepten-2-one system. This paper is concerned with syntheses of compounds (II; R = OH or OMe) and the 2-methoxy-1-ketone (III; R = OMe); all three were only stable in solution.

Our synthetic sequences began with 2,3-dimethoxy- and 2-benzyloxy-3-methoxy-benzaldehyde and proceeded by methods described previously[1-4] (see Experimental section). Cyclisation of 5-(2-hydroxy-3-methoxyphenyl)valeric acid proved troublesome (a lactone was obtained by treatment with polyphosphoric acid) but the 2-acetoxy-compound was successfully cyclised.

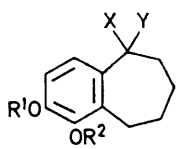
We have commented previously[1] on unexpected difficulties encountered while carrying out hydride reductions of dihydrobenzocycloheptenones: we now report that these difficulties are avoided by use of lithium aluminium hydride (molar quantities) in tetrahydrofuran at −70°. Indeed we have observed that the oxo-group in compounds (IV; R^1 = Me, R^2 = Ac)



(IV)



(V)



(VI)

and (IV; R^1 = Ac, R^2 = Me) is reduced in preference to the acetoxy-group. We have also investigated application of the Bamford–Stevens reaction to the tosylhydrazones of these same ketones but this was less

[1] Part X, D. J. Humphreys and G. R. Proctor, *J.C.S. Perkin I*, 1972, 722.

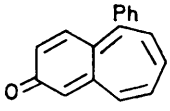
[2] A. M. Khan, G. R. Proctor, and L. Rees, *J. Chem. Soc.* (*C*), 1966, 990.

[3] G. R. Proctor and A. H. Renfrew, *J. Chem. Soc.* (*C*), 1968, 1187.

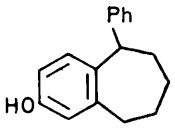
[4] G. R. Proctor, *J. Chem. Soc.*, 1964, 4274.

efficient. The tropylium salts (V; $R^1 = H$, $R^2 = Me$), (V; $R^1 = R^2 = H$), and (V; $R^1 = Me$, $R^2 = H$) were all obtained as unstable solids, unlike those encountered previously,[1-3] and on basification with sodium hydrogen carbonate red solutions of the desired benzocycloheptenones were obtained. Evaporation, however, caused the products to decompose. To establish our claim that the red solutions contained the formulated monomers, freshly prepared samples were hydrogenated catalytically. In this way 1-methoxybenzocycloheptenone (II; R = OMe) gave 6,7,8,9-tetrahydro-1-methoxy-5*H*-benzocycloheptenol (VI; $R^1 = X = Y = H$, $R^2 = Me$) and 2-methoxybenzocycloheptenone (III; R = OMe) gave the 2-methoxy-1-ol (VI; $R^1 = Me$, $R^2 = X = Y = H$). Both products were also synthesised independently.

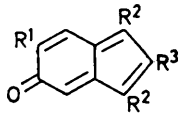
Replacement of hydrogen atoms by phenyl groups in the exocyclic methylene systems of *para*-quinone methides is known to increase stability.[5] Hoping to take advantage of this principle in the present series, we made 5-phenylbenzocycloheptenone (VII) but it too is only stable in solution; reduction gave the tetrahydro-5-phenyl-2-ol (VIII) in fair yield.



(VII)

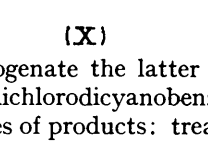


(VIII)

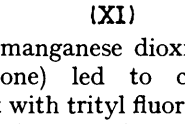


(IX)

It was thought originally[3,4] that the benzocycloheptenones were tropone analogues with potentially a Hückel (10π) ground state. Since our work showed these substances to be much more reactive than expected (*cf.* refs. 1 and 3), we considered the possibility that the corresponding non-Hückel (8π) system (IX) might be of comparable stability. The simplest synthetic approach was from 5,6-dimethoxy-3-phenylindan-1-one (X; $R^1 = R^2 = Me$, $R^3 = H$)[6] *via* the indene (XI) (see Experimental section). Repeated efforts to



(X)



(XI)

dehydrogenate the latter (with manganese dioxide and with dichlorodicyanobenzoquinone) led to complex mixtures of products: treatment with trityl fluoroborate did give an unstable product (apparently $C_{44}H_{34}O_4$) indicating that if the desired compound (IX; $R^1 =$ OMe, $R^2 =$ Ph, $R^3 = H$) had been formed it had reacted with the indene (XI). We tentatively conclude that quinone methides such as (IX) are even more unstable than the benzocycloheptenones. Efforts continue to obtain other 3-substituted benzocycloheptenones.

[5] A. B. Turner, *Quart. Rev.*, 1964, **18**, 347.
[6] F.-H. Marquardt, *Helv. Chim. Acta*, 1965, **48**, 1476

EXPERIMENTAL

5-(2,3-Dimethoxyphenyl)valeric Acid.—2,3-Dimethoxybenzaldehyde was treated with methyl crotonate in the previously described manner.[3,4] The yellow 2,3-dimethoxyphenylpenta-2,4-dienoic acid thus obtained was hydrogenated over 10% palladium–charcoal. The *product* had b.p. 165° at 2 mmHg (Found: C, 65·2; H, 7·85. $C_{13}H_{18}O_4$ requires C, 65·6; H, 7·6%).

6,7,8,9-Tetrahydro-1,2-dimethoxybenzocyclohepten-5-one (VI; $R^1 = R^2 = Me$, XY = O).—5-(2,3-Dimethoxyphenyl)valeric acid (20 g) and polyphosphoric acid (400 g) were stirred together for 40 h at 40°. The neutral product (17 g) had m.p. 40—44° after crystallisation from light petroleum (b.p. 40—60°). Recrystallisation gave a *product* of m.p. 48° (Found: C, 70·9; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·95; H, 7·35%), $\nu_{max.}$ (Nujol) 1666 cm^{-1} (ArCO), τ 2·48 (1H, d, *J* 9 Hz, 4-H), 3·29 (1H, d, *J* 9 Hz, 3-H), 6·12 (3H, s, OMe), 6·23 (3H, s, OMe), 7·0 (3H, t, *J* 6 Hz, 6-H), 7·32 (3H, t, *J* 5 Hz, 9-H), and 8·1—8·35 (4H, m, 7- and 8-H).

6,7,8,9-Tetrahydro-2-hydroxy-1-methoxybenzocyclohepten-5-one (VI; $R^1 = H$, $R^2 = Me$, XY = O).—The preceding ketone (26·0 g), anhydrous aluminium bromide (38·5 g, 1·2 mol. equiv.), and dry benzene (200 ml) were refluxed together for 3 h and poured into ice and hydrochloric acid. After separation, the benzene layer was washed with dilute aqueous sodium hydroxide to remove the phenolic material (16·4 g), which was purified by chromatography on silica gel (eluant chloroform) and by crystallisation from light petroleum (b.p. 60—80°) to give *needles*, m.p. 95° (Found: C, 70·0; H, 7·1. $C_{12}H_{14}O_3$ requires C, 69·95; H, 6·85%).

2-Acetoxy-6,7,8,9-tetrahydro-1-methoxybenzocyclohepten-5-one (VI; $R^1 =$ Ac, $R^2 = Me$, XY = O).—The preceding phenol (8·6 g) was treated with acetic anhydride (in excess) in pyridine for 18 h at 20°; the neutral *product* (10·5 g) was obtained in the usual way and crystallised from benzene–light petroleum (b.p. 60—80°); m.p. 117—118·5° (Found: C, 67·65; H, 6·5. $C_{14}H_{16}O_4$ requires C, 67·8; H, 6·5%), $\nu_{max.}$ (Nujol) 1760 (OAc) and 1663 cm^{-1} (ArCO), τ 2·35 (1H, d, *J* 9 Hz, 4-H), 3·15 (1H, d, *J* 9 Hz, 3-H), 6·17 (3H, s, 1-OMe), 7·1—7·4 (4H, m, 6- and 9-H), 7·67 (3H, s, 2-OAc), and 8·0—8·4 (4H, m, 7- and 8-H).

2-Acetoxy-6,7-dihydro-1-methoxybenzocyclohepten-5-one (IV; $R^1 =$ Ac, $R^2 =$ Me).—The preceding acetate (2·0 g), benzoyl peroxide (10 mg), *N*-bromosuccinimide (1·45 g), and dry carbon tetrachloride (150 ml) were refluxed for 4·5 h by heating over a 150 W lamp. After cooling, the filtrate was washed with aqueous sodium disulphite, dried, and evaporated to leave 2-acetoxy-9-bromo-6,7-dihydro-1-methoxybenzocyclohepten-5-one (2·61 g), m.p. 119—120° (from ether–benzene), τ 2·42 (1H, d, *J* 9 Hz, 4-H), 3·05 (1H, d, *J* 9 Hz, 3-H), 4·2—4·44 (1H, m, 9-H), 6·15 (3H, s, 1-OMe), 6·5—6·9 (2H, m, 8-H), 7·2—8·2 (4H, m, 6- and 7-H), and 7·62 (3H, s, 2-OAc). This material was refluxed for 18 h in benzene (100 ml) containing triethylamine (in excess); filtration, washing with dilute hydrochloric acid, drying, and evaporation gave the *product* (1·9 g), m.p. 117—118° (from ether–benzene) (Found: C, 69·2; H, 6·0. $C_{14}H_{14}O_4$ requires C, 68·7; H, 5·75%), $\nu_{max.}$ (Nujol) 1752 (OAc) and 1652 cm^{-1} (ArCO), τ 2·19 (1H, d, *J* 9 Hz, 4-H), 3·15 (1H, d, *J* 9 Hz, 3-H), 3·45 (1H, d, *J* 11 Hz, 9-H), 3·6—3·9 (1H, m, 8-H), 6·19 (3H, s, 1-OMe), 7·05—7·4 (2H, m, 7-H), 7·4—7·8 (2H, m, 6-H), and 7·68 (3H, s, 2-OAc).

2-Acetoxy-6,7-dihydro-1-methoxybenzocyclohepten-5-one Tosylhydrazone.—The preceding ketone (3·67 g) and tosyl-

hydrazine (2·77 g) were left together for 7 days at 20°. Removal of the solvent left the *product* (0·76 g), m.p. 181—185° (from benzene) (Found: C, 61·15; H, 5·45; N, 6·8. $C_{20}H_{22}N_2O_5S$ requires C, 60·9; H, 5·5; N, 6·75%), $\nu_{max.}$ (film) 3210 (NH) and 1760 cm^{-1} (OAc), τ 1·95 (1H, s, NH), 2·17 (d, *J* 8 Hz, 2H *ortho* to $-SO_2-$), 2·75 (d, *J* 8 Hz, 2H *meta* to $-SO_2-$), 2·79 (1H, d, *J* 9 Hz, 4-H), 3·25 (1H, d, *J* 9 Hz, 3-H), 3·64 (1H, d, *J* 11 Hz, 9-H), 3·8—4·1 (1H, m, 8-H), 6·23 (3H, s, OMe), 7·25—7·5 (2H, m, 6- or 7-H), 7·5—7·9 (2H, m, 7- or 6-H), 7·61 (3H, s, Me), and 7·73 (3H, s, OAc).

Attempted Isolation of 1-*Methoxybenzocyclohepten*-2-*one* (II; R = OMe).—2-Hydroxy-1-methoxybenzocycloheptenium tetrafluoroborate (V; R^1 = H, R^2 = Me) was made first, either (*a*) by reduction of 2-acetoxy-6,7-dihydro-1-methoxybenzocyclohepten-5-one (3·5 g) with lithium aluminium hydride (0·45 g) in dry tetrahydrofuran at −70° followed by treatment of the intermediate (1·0 g) with trityl fluoroborate (3·2 g) in dry dichloromethane, yielding the product (0·6 g) as a violet unstable solid; or (*b*) by treatment of the preceding tosylhydrazone (2·7 g) in ether with n-butyl-lithium (2M; 50 ml) at 40° for 3 h followed by the usual work-up; the unstable intermediate (0·45 g; after chromatography on silica gel) was immediately treated with trityl fluoroborate (1·35 g) giving the salt (0·06 g), indistinguishable from that prepared in (*a*). The tropylium salt (0·21 g) in dichloromethane (10 ml) was stirred with saturated aqueous sodium hydrogen carbonate (25 ml) at 0°. The dried organic layer was passed through a short column of neutral alumina and the red fast-moving band was eluted with chloroform. Evaporation gave a brown powder (0·05 g) from which no red material could be recovered. Immediate catalytic hydrogenation of the freshly prepared red solution yielded 6,7,8,9-*tetrahydro*-1-*methoxy*-5H-*benzocyclohepten*-2-*ol* (VI; R^1 = H, R^2 = Me), b.p. 140° at 0·1 mmHg (Found: C, 74·7; H, 8·3%; M^+, 192·1152. $C_{12}H_{16}O_2$ requires C, 75·05; H, 8·4%; *M*, 192·1150), τ 3·44 (2H, s, 3- and 4-H), 4·2br (1H, s, exch., OH), 6·2 (3H, s, OMe), 7·1—7·4 (4H, m, 5- and 9-H), and 8·1—8·55 (6H, m, 6-, 7-, and 8-H).

6,7,8,9-*Tetrahydro*-1,2-*dihydroxybenzocyclohepten*-5-*one* (VI; R^1 = R^2 = H, XY = O).—6,7,8,9-Tetrahydro-1,2-dimethoxybenzocyclohepten-5-one (VI; R^1 = R^2 = Me, XY = O) (40 g) and anhydrous aluminium bromide (97 g, 2·1 mol. equiv.) were refluxed together for 3 h in dry benzene (800 ml). Work-up as usual [3] gave a grey *solid* (25·5 g), m.p. 175—176° (from ethanol) (Found: C, 68·8; H, 6·65. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·65%), $\nu_{max.}$ 3391, 3195 (OH), and 1641 cm^{-1} (ArCO), τ 1·85br (2H, s, OH), 2·88 (1H, d, *J* 9 Hz, 4-H), 3·34 (1H, d, *J* 9 Hz, 3-H), 6·9—7·1 (2H, m, 9-H), 7·25—7·5 (2H, m, 6H), and 8·1—8·4 (4H, m, 7- and 8-H).

1,2-*Diacetoxy*-6,7,8,9-*tetrahydrobenzocyclohepten*-5-*one* (VI; R^1 = R^2 = Ac, XY = O).—The preceding diol (10·0 g) was treated with acetic anhydride (in excess) in triethylamine for 24 h and poured on ice. The *product* (12·8 g) crystallised from methanol as needles, m.p. 115—116° (Found: C, 64·7; H, 5·95. $C_{15}H_{16}O_5$ requires C, 65·25; H, 5·85%), $\nu_{max.}$ (film) 1775 (OAc) and 1680 cm^{-1} (ArCO), τ 2·39 (1H, d, *J* 9 Hz, 4-H), 2·88 (1H, d, *J* 9 Hz, 3-H), 7·1—7·4 (4H, m, 6- and 9-H), 7·69 (3H, s, OAc), 7·74 (3H, s, OAc), and 8·0—8·3 (4H, m, 7- and 8-H).

1,2-*Diacetoxy*-9-*bromo*-6,7,8,9-*tetrahydrobenzocyclohepten*-5-*one*.—The preceding diacetate (5·0 g), *N*-bromosuccinimide (3·63 g), and benzoyl peroxide (20 mg) were refluxed together for 16 h in dry carbon tetrachloride (180 ml). Work-up as before gave the *product* (5 g), m.p. 130—132° (from benzene) (Found: C, 50·85; H, 4·3. $C_{15}H_{15}BrO_5$ requires C, 50·75; H, 4·25%), $\nu_{max.}$ (Nujol) 1766 (OAc) and 1685 cm^{-1} (ArCO), τ 2·45 (1H, d, *J* 9 Hz, 4-H), 2·76 (1H, d, *J* 9 Hz, 3-H), 4·3 (1H, d, *J* 5 Hz, 9-H), 6·4—6·9 (2H, m, 8-H), 7·2—8·0 (4H, m, 6- and 7-H), 7·62 (3H, s, 1-OAc), and 7·74 (3H, s, 2-OAc).

1,2-*Diacetoxy*-6,7-*dihydrobenzocyclohepten*-5-*one* (IV; R^1 = R^2 = Ac).—The preceding bromide (5 g) was refluxed in triethylamine (in excess) and benzene (100 ml) for 18 h. Work-up gave the *product* (3·1 g), m.p. 129—131° (from ether–benzene) (Found: C, 65·2; H, 5·4. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·15%), τ 2·21 (1H, d, *J* 9 Hz, 4-H), 2·84 (1H, d, *J* 9 Hz, 3-H), 3·46 (1H, d, *J* 11 Hz, 9-H), 3·58—3·8 (1H, m, 8-H), 6·95—7·15 (2H, m, 6-H), 7·4—7·6 (2H, m, 7-H), 7·66 (3H, s, OAc), and 7·71 (3H, s, OAc).

5-(2-*Hydroxy*-3-*methoxyphenyl*)*valeric Acid*.—2-Hydroxy-3-methoxybenzaldehyde (200 g; commercial) was converted into 2-benzyloxy-3-methoxybenzaldehyde (364 g) (*cf.* ref. 7). The latter was treated with methyl crotonate as previously described [3,4] and the 2-benzyloxy-3-methoxyphenylpenta-2,4-dienoic acid thus obtained was hydrogenated (10% palladium–charcoal; ethanol). The *product* (250 g) crystallised from benzene–light petroleum (b.p. 60—80°) in plates, m.p. 83° (Found: C, 64·05; H, 7·3. $C_{12}H_{16}O_4$ requires C, 64·35; H, 7·2%). The O-*benzyl derivative*, obtained by treatment of the hydroxy-acid with benzyl chloride and potassium carbonate in dry methanol followed by hydrolysis with aqueous ethanolic sodium hydroxide, had b.p. 180° at 0·1 mmHg (Found: C, 72·85; H, 7·1. $C_{19}H_{22}O_4$ requires C, 72·65; H, 7·05%). The O-*acetate*, obtained by treatment of the hydroxy-acid with acetic anhydride in pyridine, crystallised from benzene–light petroleum (b.p. 60—80°) and had m.p. 125—128° (Found: C, 63·55; H, 6·95. $C_{14}H_{18}O_5$ requires C, 63·2; H, 6·8%).

Treatment of 5-(2-hydroxy-3-methoxyphenyl)valeric acid (5 g) with thionyl chloride (in excess) followed by anhydrous aluminium chloride (2·25 g) in dry dichloromethane at −20°, and subsequent chromatography (silica gel; benzene) gave the *lactone* as a pale yellow oil (1·25 g), b.p. 140° at 0·2 mmHg (Found: C, 69·75; H, 7·15. $C_{12}H_{14}O_3$ requires C, 69·95; H, 6·85%), $\nu_{max.}$ (film) 1735 cm^{-1} (lactone), τ 2·8—3·3 (3H, m, aryl), 6·2 (3H, s, OMe), 7·3—7·6 (2H, m), 7·65—7·8 (2H, m), and 7·95—8·5 (4H, m). Treatment of the acid with polyphosphoric acid gave the same product (*cf.* ref. 8).

1-*Acetoxy*-6,7,8,9-*tetrahydro*-2-*methoxybenzocyclohepten*-5-*one* (VI; R^1 = Me, R^2 = Ac, XY = O).—5-(2-Acetoxy-3-methoxyphenyl)valeric acid (3·58 g), pyridine (2 drops), and thionyl chloride (in excess) were left together for 18 h. Volatile materials were removed and the residue was treated with tin(IV) chloride (5·5 g) in dichloromethane (250 ml) at −30° for 4 h. Work-up of the neutral fraction gave the *product* (2·85 g), m.p. 117—118° (from benzene) (Found: C, 68·15; H, 6·5. $C_{14}H_{16}O_4$ requires C, 67·8; H, 6·5%), $\nu_{max.}$ (Nujol) 1759 (OAc) and 1667 cm^{-1} (ArCO), τ 2·35 (1H, d, *J* 9 Hz, 4-H), 3·15 (1H, d, *J* 9 Hz, 3-H), 6·16 (3H, s, OMe), 7·0—7·4 (4H, m, 6- and 9-H), 7·68 (3H, s, OAc), and 8·1—8·4 (4H, m, 7- and 8-H).

[7] R. A. Anker, A. H. Cook, and I. M. Heilbron, *J. Chem. Soc.*, 1945, 917.

[8] W. J. Horton and L. L. Pitchforth, *J. Org. Chem.*, 1960, **25**, 131.

1-*Acetoxy*-6,7-*dihydro*-2-*methoxybenzocyclohepten*-5-*one* (IV; R^1 = Me, R^2 = Ac).—The preceding acetate (11·9 g) was treated with *N*-bromosuccinimide (8·5 g) in dry carbon tetrachloride as described for other cases. The crude bromide was refluxed for 2 h with collidine (100 ml). The crude product (10·65 g) was chromatographed on silica gel benzene elution) and recrystallised from benzene–light petroleum (b.p. 60—80°) to give *crystals* (8·1 g), m.p. 118—119° (Found: C, 68·0; H, 5·8. $C_{14}H_{14}O_4$ requires C, 68·35; H, 5·75%), $\nu_{max.}$ (Nujol) 1750 (OAc) and 1660 cm^{-1} (ArCO), τ 2·17 (1H, d, *J* 9 Hz, 4-H), 3·12 (1H, d, *J* 9 Hz, 3-H), 3·41 (1H, d, *J* 11 Hz, 9-H), 3·6—3·85 (1H, m, 8-H), 6·15 (3H, s, OMe), 7·05—7·3 (2H, m, 6-H), 7·4—7·7 (2H, m, 7-H), and 7·66 (3H, s, OAc).

Attempted Isolation of 2-*Methoxybenzocyclohepten*-1-*one* (III; R = OMe).—The preceding compound (3·5 g) and lithium aluminium hydride (0·45 g) were stirred together in dry tetrahydrofuran at −70° for 6 h. Work-up of the phenolic fraction (2·48 g) gave material which was treated with trityl fluoroborate (7·2 g) in dry dichloromethane (50 ml) and kept at −5° for 14 h. The unstable violet fluoroborate (1·05 g) was filtered off; it gave inconsistent analytical figures and showed τ [$(CD_3)_2CO$] 3·0—4·5 (8H, m, OH + ring protons) and 6·2 (3H, s, OMe), $\nu_{max.}$ (Nujol) 3315 (OH) and 1070—1000 cm^{-1} (BF_4^-).

The fluoroborate salt was treated with sodium hydrogen carbonate as previously; a deep red solution was obtained. The product decomposed on attempted isolation, but catalytic hydrogenation (10% palladium–charcoal) of a freshly prepared solution yielded 6,7,8,9-*tetrahydro*-2-*methoxy*-5H-*benzocyclohepten*-1-*ol* (VI; R^1 = Me, R^2 = X = Y = H), which was purified by chromatography (silica gel; benzene) and vacuum sublimation and had m.p. 55—60° (Found: C, 75·4; H, 8·0. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·35%), $\nu_{max.}$ (film) 3515 cm^{-1} (OH). This material was identical with that produced by treatment of 1-acetoxy-6,7,8,9-tetrahydro-2-methoxybenzocyclohepten-5-one with lithium aluminium hydride in tetrahydrofuran at −70°, followed by refluxing the intermediate with toluene-*p*-sulphonyl chloride in triethylamine and catalytic hydrogenation (10% palladium–charcoal) of the resultant oil.

6,7-*Dihydro*-9-*phenyl*-5H-*benzocyclohepten*-3-*ol*.—To the reagent prepared from bromobenzene (11·2 g) and magnesium (1·75 g) in dry ether (100 ml) was added 6,7,8,9-tetrahydro-2-hydroxybenzocyclohepten-5-one [2] (5·0 g) in ether (25 ml) and tetrahydrofuran (25 ml). After 20 h the solution was added to ice and hydrochloric acid and extracted with ether. The intermediate alcohol was refluxed (water separator) in benzene with toluene-*p*-sulphonic acid (30 mg) for 18 h. Evaporation gave the *product* (2·1 g), which was chromatographed on silica gel and crystallised from light petroleum (b.p. 60—80°) as needles (0·76 g), m.p. 109·5—111° (Found: C, 85·25; H, 7·0. $C_{17}H_{16}O$ requires C, 85·5; H, 6·85%), $\nu_{max.}$ (Nujol) 3260 cm^{-1} (OH), τ 2·77 (5H, s, Ph), 3·05—3·5 (3H, m, 1-, 2-, and 4-H), 3·69 (1H, t, *J* 7 Hz, 8-H), 5·02 (1H, s, exch., OH), 7·42 (2H, t, *J* 7 Hz, 7-H), and 7·7—8·2 (4H, m, 5- and 6-H).

Attempt to Isolate 5-*Phenylbenzocyclohepten*-2-*one* (VII).—The preceding phenol (400 mg), 2,3-dichloro-5,6-dicyanobenzoquinone (800 mg), and benzene (20 ml) were stirred together for 16 h and the mixture was poured onto a column of neutral alumina. Elution with chloroform gave a deep red solution [τ 2·4—3·0 (m); the i.r. spectrum showed no OH bands]. Evaporation caused decomcomposition but immediate catalytic (10% palladium–charcoal) hydrogenation yielded 6,7,8,9-tetrahydro-5-phenyl-5*H*-benzocyclohepten-2-ol (VIII) (100 mg), b.p. 145° at 0·05 mmHg (Found: C, 86·1; H, 7·9. Calc. for $C_{17}H_{18}O$: C, 85·8; H, 7·6%), $\nu_{max.}$ (Nujol) 3400 (OH) cm^{-1}, identical with material obtained by hydrogenation of 6,7-dihydro-9-phenyl-5*H*-benzocyclohepten-3-ol.

5,6-*Dihydroxy*-3-*phenylindan*-1-*one* (X; R^1 = R^2 = R^3 = H).—The dimethoxy-ketone [6] (X; R^1 = R^2 = Me, R^3 = H) (10 g) and freshly distilled anhydrous aluminium bromide (44 g) were refluxed together for 3 h in dry benzene (100 ml). After addition of ice, filtration, separation, and evaporation of solvent, the *product* was obtained partly in the residues and partly in the benzene. It crystallised from chloroform as a buff powder (6 g), m.p. 250° (Found: C, 74·5; H, 5·0. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%), $\nu_{max.}$ (KCl) 3400 (OH) and 1640 cm^{-1} (ArCO), τ [$(CD_3)_2SO$] −0·25 and 0·30 (2H, s, OH), 2·4—2·9 (5H, m, aryl), 2·87 (1H, s, 7-H), 3·37 (1H, s, 4-H), 5·48 (1H, dd, 3-H), and 6·6—6·73 (2H, m, 2-H), τ (NaOD) 2·4—2·9 (6H, m, aryl), 3·14 (1H, s, 4-H?), 3·67 (1H, s, 2-H), and 5·7 (1H, s, 3-H). The *diacetate* (obtained with acetic anhydride–pyridine) was chromatographed on silica gel (50% benzene–ether) and crystallised from ethanol; m.p. 122—123° (Found: C, 70·4; H, 5·1. $C_{19}H_{16}O_5$ requires C, 70·4; H, 5·0%).

5-*Hydroxy*-6-*methoxy*-3-*phenylindan*-1-*one* (X; R^2 = R^3 = H, R^1 = Me). The dimethoxy-ketone [6] (X; R^1 = R^2 = Me, R^3 = H) (18 g) and freshly distilled anhydrous aluminium bromide (38 g) were refluxed together for 3 h in dry benzene. Work-up as in the previous experiment with chromatography on neutral deactivated alumina (eluant chloroform) gave a mixture of two monomethyl ethers (13·5 g). Crystallisation from ethanol gave the desired *product*, m.p. 164—165° (Found: C, 75·15; H, 5·75. $C_{16}H_{14}O_3$ requires C, 75·55; H, 5·55%), τ 2·6—2·95 (6H, m, aryl), 3·25 (1H, s, 4-H), 3·56 (1H, s, exch., OH), 5·52 (1H, dd, 3-H), 6·65—7·5 (2H, m, 2-H), and 6·06 (3H, s, OMe). [Repeated chromatography of the material from the crystallisation gave a pale yellow gum presumably, the 6-hydroxy-5-methoxy-isomer; τ 2·55—2·95 (6H, m, aryl), 3·33 (1H, s, 4-H), 4·03 (1H, s, exch., OH), 5·53 (1H, dd, 3-H), 6·65—7·55 (2H, m, 2-H), and 6·13 (3H, s, OMe).] The *acetate*, obtained by treatment of the phenol with acetic anhydride in pyridine, had m.p. 96—97° (from ethanol) (Found: C, 72·8; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

5,6-*Dimethoxy*-1,3-*diphenylindene*.—The dimethoxy-ketone [6] (X; R^1 = R^2 = Me, R^3 = H) (2·68 g) in dry ether (100 ml) was added at 0° to the reagent prepared from magnesium (295 mg) and bromobenzene (1·73 g) in dry ether. The mixture was stirred and refluxed for 1 h and poured into ice and hydrochloric acid. After separation and chromatography on silica gel (eluant benzene), the *product* (1·78 g) crystallised from light petroleum (b.p. 60—80°) as needles, m.p. 107—108° (Found: C, 84·1; H, 6·3. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%), $\nu_{max.}$ (KCl) 1600 cm^{-1} (C=C), τ 2·0—2·8 (11H, m, aryl), 3·0 (1H, s, aryl), 3·37 (1H, d, *J* 2·4 Hz, 6-H), 5·3 (1H, d, *J* 2·4 Hz, 5-H), 6·03 (3H, s, OMe), and 6·11 (3H, s, OMe). This compound decomposed when treated with aluminium bromide or with boron bromide.

5-*Methoxy*-1,3-*diphenylinden*-6-*ol* (XI).—5-Hydroxy-6-methoxy-3-phenylindan-1-one (X; R^2 = R^3 = H, R^1 = Me) (5·55 g) in dry tetrahydrofuran (200 ml) was slowly

added at 0° to the reagent from bromobenzene (34·5 g) and magnesium (6·29 g) in dry tetrahydrofuran (400 ml). The mixture was refluxed for 24 h and poured into ice and dilute sulphuric acid. The product (4·8 g) contained an orange impurity which could not be removed by chromatography. Repeated crystallisation from light petroleum (b.p. 60—80°) gave buff *needles*, m.p. 143—144° (Found: C, 84·1; H, 5·8. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·8%), $\nu_{max.}$ (KCl) 3400 (OH) and 1605 cm^{-1} (C=C), τ 2·3—2·7 (5H, m, aryl), 2·82 (3H, s, aryl), 2·96 (1H, s, aryl), 3·11 (1H, s, aryl), 3·52 (1H, d, *J* 2·4 Hz, 2-H), 5·41 (1H, d, 2·4 Hz, 1-H), 4·42br (1H, s, exch., OH), and 6·14 (3H, s, OMe).

6-*Methoxy*-1,3-*diphenylindan*-5-*ol*.—Hydrogenation of the preceding compound (250 mg) in ethanol (50 ml) over palladised charcoal (10%; 50 mg) gave the *product* [from light petroleum (b.p. 80—100°)] as flakes, m.p. 144—145° (Found: C, 83·5; H, 6·5. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·4%), $\nu_{max.}$ (KCl) 3480 cm^{-1} (OH), τ 2·7 (5H, s, aryl), 2·73 (5H, s, aryl), 3·49 (1H, s, aryl), 3·58 (1H, s, aryl), 4·5br (1H, s, exch., OH), 5·73 (2H, q, 1- and 3-H), and 6·8—8·3 (2H, m, 2-H).

Reaction of 5-*Methoxy*-1,3-*diphenylinden*-6-*ol* (XI) *with Trityl Fluoroborate*.—The indenol (250 mg) and trityl fluoroborate (275 mg) were left for 18 h in dichloromethane (25 ml) in the dark. The deep green solution was chromatographed on silica gel; elution with dichloromethane gave a yellow substance which crystallised from light petroleum (b.p. 60—80°) as a powder (100 mg), m.p. 150° (decomp.) (Found: M^+, 626·25175. Calc. for $C_{44}H_{34}O_4$: *M*, 626·24570).

5,6-*Dimethoxy*-2,3-*diphenylindan*-1-*one* (X; $R^1 = R^2 =$ Me, $R^3 =$ Ph) (cf. *ref.* 6).—Veratrole (14 g), 2-phenylcinnamic acid (23 g; commercial), and polyphosphoric acid (85 g) were stirred and heated at 90° for 12 h. Work-up of the neutral fraction gave the *product* (22·8 g), purified by sublimation *in vacuo* and by recrystallisation from benzene–ethanol; m.p. 176° (carbon analysis consistently 1% low) (Found: M^+, 344·1400. $C_{23}H_{20}O_3$ requires *M*, 344·1412).

5,6-*Dihydroxy*-2,3-*diphenylindan*-1-*one* (X; $R^1 = R^2 =$ H, $R^3 =$ Ph).—The preceding ketone (8 g), anhydrous aluminium bromide (46 g), and dry benzene (100 ml) were refluxed together and the mixture was worked up as usual. The *product* (5·1 g) had m.p. 182—186° (from toluene) (Found: C, 80·0; H, 5·15. $C_{21}H_{16}O_3$ requires C, 79·8; H, 5·1%).

We thank Miss M. Faccenda for technical assistance.

[4/124 *Received*, 23*rd January*, 1974]