The Preparation of 2,3,3a,4,5,6-Hexahydro-8-methoxy-1*H*-phenalene

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The previously unknown methoxy substituted benzene derivative 2,3,3a,4,5,6-hexahydro-8-methoxy-1*H*-phenalene (**3a**) has been prepared by two routes. One starts from 6-methoxy-α-tetralone (**4a**) and involves a single 3-carbon extension and cyclization of the alcohol (**7b**); the other starts from 3-(3-methoxyphenyl)propanoic acid (**5a**) and proceeds *via* a 4-carbon extension and a double cyclization of the diol (**10**).

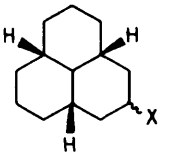
A key intermediate in the preparation of the solvolytic substrates (**1a**)[1,2] *via* alcohols (**1b**) and enone (**2**)[3] is the previously unreported phenalene derivative (**3a**). We now report the preparation of compound (**3a**) by two routes, one starting from 6-methoxy-α-tetralone (**4a**) and involving a single three-carbon annulation, the other starting from 3-(3-methoxyphenyl)propanoic acid (**5a**) *via* a four-carbon extension and a less common bis-annulation.

Results

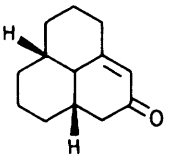
The first step starting from the tetralone (**4a**) is a Stobbe condensation using diethyl succinate and potassium t-butoxide in t-butyl alcohol.[4,5] The condensation product was hydrolysed and decarboxylated under acidic conditions, then worked up to give a major acidic product and a minor neutral one. The acidic product could have been either of the *E* or *Z* exocyclic unsaturated carboxylic acids (**4b**), or the endocyclic isomer (**6a**). The n.m.r. and mass spectroscopic data fit structure (**6a**) better (see Table and the Discussion section). For the present purposes, however, the assignment is not important since the next step involves hydrogenation to give the carboxylic acid (**7a**). Reduction of this in the normal way with lithium aluminium hydride followed by hydrolysis gave the alcohol (**7b**) in 38% yield over the four steps from 6-methoxy-α-tetralone (**4a**). The neutral compound from the Stobbe condensation, hydrolysis, and decarboxylation sequence was anticipated on the basis of earlier findings by Johnson[5] in the related series of reactions of compounds without the methoxy substituent and, although not fully characterized, is ascribed the spiro-lactone structure (**8**) ($\tilde{\nu}$ 1 760 cm^{-1}). The lactone formation corresponds to a 5-*exo-trig* ring closure using Baldwin's nomenclature,[6] and is a favourable process. Lithium aluminium hydride reduction of lactone (**8**) followed by acid hydrolysis and spontaneous dehydration gave the same unsaturated alcohol (**6b**) in 7% yield from (**4a**) as was obtained by lithium aluminium hydride reduction of the unsaturated acid (**6a**). The structural assignment of compound (**6b**) was firmly based upon n.m.r. and mass spectroscopic evidence (see Table and the Discussion section below) and, together with the easy conversion of the lactone (**8**) into the unsaturated acid (**6a**), represents supportive evidence for the structure of lactone (**8**).

Ponaras[7] has reported a Grignard addition reaction to ketone (**4a**) followed by an elimination which gives compound (**6c**) in very high yield. We were unable to obtain comparable results in the reaction of the Grignard reagent generated from 3-bromopropyl tetrahydropyranyl ether (**9a**). We were equally unable to add Wittig reagents to the ketone (**4a**) even using the technique of Adlercreutz and Magnusson[8] specifically designed for easily enolized ketones. We were, however, able to effect addition of the organolithium reagent[9] generated from the bromide (**9a**) and, following hydrolysis, deprotection, and dehydration, obtained the same unsaturated alcohol (**6b**) as was obtained by the two other methods described above.

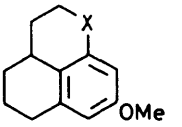
Cyclization of the alcohol (**7b**) was attempted using boron trifluoride in ether and in benzene, formic acid, zinc chloride in acetic anhydride, trifluoroacetic acid in dichloromethane,



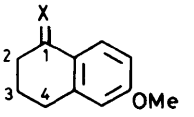
(**1**) **a**; X = OS(O)$_2$C$_6$H$_4$Me-*p*
b; X = OH



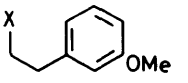
(**2**)



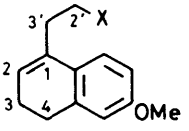
(**3**) a ; X = CH_2
b ; X = CO

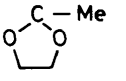


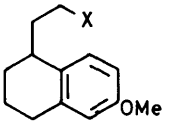
(**4**) a ; X = O
b ; X = $CHCH_2CO_2H$
c ; X = $C(CO_2H)CH_2CO_2H$



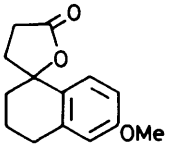
(**5**) a ; X = CO_2H
b ; X = CH_2Br
c ; X = CH_2OH



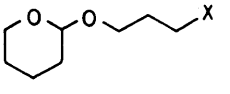
(**6**) a ; X = CO_2H
b ; X = CH_2OH
c ; X = 



(**7**) a ; X = CO_2H
b ; X = CH_2OH



(**8**)



(**9**) a ; X = Br
b ; X = CHO
c ; X = CH_2OH

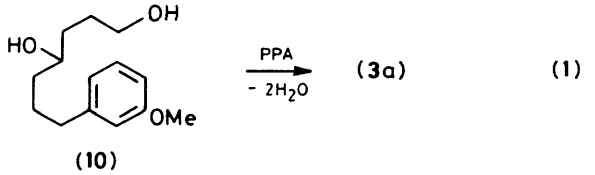
Table. ^{1}H N.m.r. data for compounds (**6a**) and (**6b**)

Compound	Hydrogen (type)*	Chemical shift (δ) (Integration, multiplicity)
(**6a**)	C-3 (allylic)	2.05—2.40 (2 H, m)[a]
	C-4 (benzylic)	2.40—2.95 (6 H, m)
	C-3′ (allylic)	
	C-2′ (α to CO_2H)	
	OMe	3.77 (3 H, s)
	C-2 (vinylic)	5.75 (1 H, t, J ~4.5 Hz)
	aromatic	6.65—6.80, 7.05—7.30 (3 H, m)
	CO_2H	11.0 (1 H, s)
(**6b**)	C(2′ (α to CH_2OH)	1.6—2.0 (2 H, m)[b]
	C-3 (allylic)	2.1—2.4 (2 H, m)[a]
	C-3′ (allylic)	2.50 (2 H, t, J ~8 Hz)[c,d]
	C-4 (benzylic)	2.72 (2 H, t, J ~8 Hz)[c]
	OCH_2	3.68 (2 H, t, J ~8 Hz)[d]
	OMe	3.76 (3 H, s)
	C-2 (vinylic)	5.75 (1 H, t, J ~4.5 Hz)
	aromatic	6.60—6.85, 7.05—7.30 (3 H, m)

* See structure (**6**) for numbering scheme.
[a] Gives triplet (J ~8 Hz) upon decoupling of the vinylic hydrogen (δ 5.75). [b] Gives triplet (J ~8 Hz) upon decoupling of the C-1′ CH_2O signal (δ 3.68). [c] Overlapping signals. [d] Gives a singlet upon decoupling of the C-2′ methylene (δ 1.8).

toluene-*p*-sulphonic acid (PTSA) in benzene and in toluene under reflux, sulphuric acid, and phosphorus pentaoxide in methanesulphonic acid[10] in order to avoid the hazardous method using anhydrous hydrofluoric acid recommended by Johnson,[5] but to no avail. We achieved modest success using polyphosphoric acid in obtaining compound (**3a**) in 53% yield. All attempts to crystallize the phenalene (**3a**) failed. The same cyclization method on carboxylic acid (**7a**) gave the tricyclic ketone (**3b**) which was isolated as a crystalline solid.

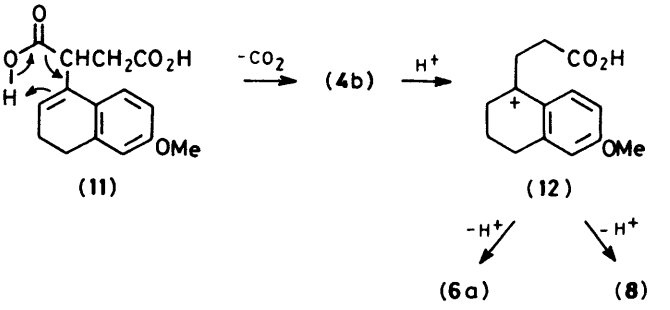
Our other strategy involved a double acid catalysed cyclization as had been used by Nasipuri[11] in the synthesis of some more complex naturally occurring tricyclic analogues. Commercially available 3-(3-methoxyphenyl)propanoic acid (**5a**) was converted into 3-(3-methoxyphenyl)propyl bromide (**5b**) *via* the corresponding alcohol (**5c**) by routine methods.[12] The Grignard reagent from bromide (**5b**) was added to the aldehyde (**9b**) obtained by oxidation[13] of 4-hydroxybutyl tetrahydropyranyl ether (**9c**). Hydrolysis and deprotection of the product by aqueous acid gave the diol (**10**) which, upon being heated with polyphosphoric acid [equation (1)] gave the same aromatic compound (**3a**) as had been obtained by the other route, see above. The spectral data and subsequent conversion of the phenalene (**3a**) into the enone (**2**), whose structure was confirmed by *X*-ray crystallography,[3] support the structural assignment of the methoxy compound.



(10) (1)

Discussion

On the basis of accepted mechanisms,[4,5,14a] hydrolysis of the direct product of the Stobbe condensation will give a compound with an exocyclic double bond from the tetralin to the succinyl residue, *viz.* (**4c**). The decarboxylation, however, is most likely preceded by migration of the double bond to give an intermediate (**11**) which allows a concerted reaction *via* a six-membered transition state (Scheme).[14b,15] This mechanism initially produces the acid (**4b**) with regeneration of the exocyclic double bond. However, the spectroscopic evidence suggests that the isolated unsaturated monocarboxylic acid is (**6a**) and not (**4b**) (Table). In addition to the observed vinylic triplet in the n.m.r. spectrum, acid (**4b**) would have a corresponding doublet at low field due to the allylic methylene alpha to the carboxy group, higher-field multiplets due to the benzylic and allylic methylenes at C-2 and C-4, and, at highest field, the signal due to the homoallylic, homobenzylic methylene at C-3. The observed spectrum is more complicated with neither a low-field doublet nor a high-field signal (δ < 2) due to a homoallylic, homobenzylic C-3 methylene. Instead, the highest field signal is a 2 H multiplet at δ 2.05—2.40 which alone collapses to a triplet (J ~8 Hz) upon decoupling of the vinylic hydrogen at δ 5.75. This can only be due to the C-3 allylic group in structure (**6a**). In the mass spectrum of the unsaturated acid, the base peak (m/z 159.0818) corresponds to $C_{11}H_{11}O$, the unsaturated bicyclic residue obtained upon loss of the $CH_2CH_2CO_2H$ side chain in (**6a**). A similarly intense base peak at m/z 161.0986 ($M^{\cdot+}$ − $CH_2CH_2CO_2H$) is correspondingly observed in the mass spectrum of the carboxylic acid (**7a**) without the double bond. A mechanism for the formation of acid (**6a**) by acid-catalysed isomerization of (**4b**) through a stabilized benzylic carbocation (**12**) also accounts efficiently for the formation of the lactone (**8**) (Scheme).



Scheme.

The unsaturated alcohol (**6b**) was produced both by the methods described above, and by lithium aluminium hydride reduction of the acid (**6a**), and its structure was confirmed independently. Its ^{1}H n.m.r. spectrum (Table) includes a vinylic triplet (δ 5.75, J ~4.5 Hz), irradiation of which affects only the C-3 multiplet (δ 2.1—2.4) converting it into a triplet (J ~8 Hz). Irradiation of the triplet due to the C-1′ CH_2O group (δ 3.68, J ~8 Hz) causes the C-2′ multiplet (δ 1.6—2.0) to collapse to a triplet (J ~8 Hz). Conversely, irradiation at δ 1.8 collapses the C-1′ triplet at δ 3.68 to a singlet; in addition, this decoupling also converts the triplet at δ 2.50 into a singlet (C-3′ methylene), leaving the triplet at δ 2.72 (J ~8 Hz) due to the C-4 benzylic methylene unaffected.

Experimental

Pentane and light petroleum were purified by washing with conc. sulphuric acid followed by fractional distillation from sodium hydroxide pellets; absolute diethyl ether and tetrahydrofuran (THF) were fractionally distilled from calcium hydride. Analytical t.l.c. was with Kieselgel 60 F_{254} (Merck); preparative t.l.c. (p.l.c.) was with Kieselgel GF_{254} (Merck). The following spectrometers were used: Perkin-Elmer 577 (i.r.), Perkin-Elmer R24 (60 MHz ^{1}H n.m.r.), Perkin-Elmer R32 (90 MHz ^{1}H n.m.r), Bruker WP80 (80 MHz ^{1}H n.m.r.), and JEOL D-100 (m.s.).

3-(1,2,3,4-*Tetrahydro*-6-*methoxy*-1-*naphthyl*)*propan*-1-*ol* (**7b**).—(a) *Stobbe reaction.* A solution of ketone (**4a**) (10 g, 0.057

mmol) in diethyl succinate (20 g, 0.115 mol) was added to a stirred solution of potassium t-butoxide in t-butyl alcohol [freshly prepared from potassium (3.0 g, 0.077 mol) and t-butyl alcohol (50 cm^3)] under nitrogen at room temperature during 10 min. The reaction mixture was stirred at room temperature under nitrogen for 10 days before water (350 cm^3) was added. The reaction mixture was extracted several times with ether, then acidified (HCl) and re-extracted with more ether. The combined extracts were evaporated under reduced pressure to leave a dark oil.

(b) *Hydrolysis and decarboxylation.* The above crude product was heated under reflux with acetic acid (100 cm^3), conc. hydrochloric acid (40 cm^3), and water (60 cm^3) for 2.5 h. The reaction mixture was cooled, diluted with more water (300 cm^3), and extracted several times with ether. The combined extract was evaporated under reduced pressure to remove the ether and as much of the acetic acid as possible. The residue was redissolved in ether and the solution was washed with aqueous sodium carbonate. The ether phase was treated with charcoal, dried (Na_2SO_4), filtered, and evaporated to give a neutral product as a pale yellow oil (2.79 g); t.l.c. analysis indicated the presence of a single product, believed to be the lactone (**8**), $\bar{\nu}$(liquid) 2 940, 2 840, 1 760, 1 610, 1 500, 1 280, 1 250, 1 160, 915, and 730 cm^{-1}, which was subsequently reduced with lithium aluminium hydride (see below), plus some unchanged 6-methoxytetralone (**4a**).

The aqueous basic phase was acidified (HCl) and extracted several times with ether. The combined extract containing acidic product was also treated with charcoal, dried (Na_2SO_4), filtered, and evaporated to give crude acid (**6a**) as a dark oil (10.6 g). A sample crystallized and was then recrystallized (from pentane–diethyl ether) to give a pure sample, m.p. 115—116 °C; $\delta(CDCl_3$; 90 MHz) 2.05—2.40 (2 H, m), 2.40—2.95 (6 H, m), 3.77 (3 H, s), 5.75 (1 H, t, $J \sim 4.5$ Hz), 6.65—6.80 and 7.05—7.30 (3 H, m), and 11.0 (1 H, s); $\bar{\nu}$(KBr) 2 500—3 600, 1 695, 1 600, 1 500, 1 305, 1 245, 1 215, 1 040, and 830 cm^{-1} (Found: $M^{\cdot+}$, 232.1097. $C_{14}H_{16}O_3$ requires M, 232.1100); m/z 159.0818 (100%) ($C_{11}H_{11}O$ requires m/z, 159.0810).

(c) *Hydrogenation of compound* (**6a**) *to give compound* (**7a**). The remainder of the crude acid (**6a**) was hydrogenated directly (3.5 atm) in 1:1 ether–THF (100 cm^3) over Pd–charcoal (10%; 1.0 g) for 64 h. Filtration of the solution and evaporation gave crude acid (**7a**) as an oil (10.6 g), a sample of which crystallized and was recrystallized (pentane–diethyl ether) to give the reduced product, m.p. 71—72 °C; $\delta(CDCl_3$, 90 MHz) 1.4—2.3 (6 H, m), 2.42 (2 H, t), 2.5—3.1 (3 H, m), 3.75 (3 H, s), 6.5—6.8 and 6.9—7.3 (3 H, m), and 8.4—9.1 (1 H, br); $\bar{\nu}$(KBr) 2 500—3 500, 1 700, 1 605, 1 500, 1 230, 1 040, and 840 cm^{-1} (Found: $M^{\cdot+}$, 234.1242. $C_{14}H_{18}O_3$ requires M, 234.1256); m/z 161.0986 (100%) ($C_{11}H_{13}O$ requires m/z 161.0967).

(d) *Reduction of acid* (**7a**) *to give the title product* (**7b**). A solution of the remainder of the crude acid (**7a**) in absolute diethyl ether (50 cm^3) was stirred under reflux as lithium aluminium hydride (3.5 g) was cautiously added portionwise. The reaction mixture was stirred at room temperature for 12 h then worked up in the normal way. The product (**7b**) [4.66 g, 0.0212 mol; 38% over the four steps (a)—(d) from (**4a**)] was purified by column chromatography (elution with diethyl ether) and a small sample was distilled (Kugelrohr; 150 °C/0.2 Torr) after all attempts at crystallization had failed, the alcohol (**7b**) had $\delta(CDCl_3)$ 1.4—2.0 (8 H, m), 2.07 (1 H, s), 2.75 (3 H, s), 3.6—3.8 (2 H, m), 3.76 (3 H, s), and 6.55—6.8 and 7.20—7.22 (3 H, m); $\bar{\nu}$(liquid) 3 000—3 600, 2 930, 2 860, 1 605, 1 500, 1 255, and 1 050 cm^{-1} (Found: $M^{\cdot+}$, 220.1462. $C_{14}H_{20}O_2$ requires M, 220.1463).

3-Bromopropyl Tetrahydropyran-2-yl Ether (**9a**).—Dihydropyran (5.1 g, 61 mmol) was added portionwise during 30 min to a stirred solution of 3-bromopropan-1-ol (8.4 g, 61 mmol) and PTSA (*ca.* 20 mg) in diethyl ether (*ca.* 20 cm^3) at 0 °C. The reaction mixture was allowed to come to room temperature overnight and then was washed with aqueous base, dried ($MgSO_4$), filtered, and evaporated. A portion of the residual oil was distilled (Kugelrohr; b.p. 100 °C/15 Torr) to give the title ether, $\delta(CDCl_3)$ 1.3—2.3 (8 H, m), 3.3—4.1 (6 H, m), and 4.6 (1 H, unresolved t).

3-(3,4-*Dihydro*-6-*methoxy*-1-*naphthyl*)*propan*-1-*ol* (**6b**).—(a) *From ketone* (**4a**). A small proportion of a solution of recrystallized ketone (**4a**) (0.25 g, 1.42 mmol) and redistilled bromide (**9a**) (0.36 g, 1.61 mmol) in absolute THF (*ca.* 3 cm^3) was added to lithium (*ca.* 22 mg, 3.2 mmol) under absolute THF (*ca.* 5 cm^3). An extra single drop of the neat bromide (**9a**) was added directly onto the metal which became bright and shiny, and a reaction started. The mixture was then stirred at 0 °C as the rest of the solution of compounds (**4a**) and (**9a**) in THF was added dropwise. After *ca.* 3 h the residual lithium became tarnished and t.l.c. indicated no further change in the composition of the mixture. The excess of lithium was removed, water was added, and the reaction was worked up in the normal way in ether to give a crude product (0.52 g), which was dissolved in THF and the solution was acidified (HCl) and stirred at room temperature for several days. The reaction mixture was worked up in the normal way and the unsaturated alcohol (**6b**) was isolated by p.l.c. and purified by recrystallization (pentane–ether) to afford the title alcohol (70 mg, 22%), m.p. 67—68 °C; $\delta(CDCl_3$; 90 MHz) 1.6—2.0 (2 H, m), 2.1—2.4 (2 H, m), 2.4—2.85 (4 H, overlapping triplets), 3.68 (2 H, t, $J \sim 8$ Hz), 3.76 (3 H, s), 5.75 (1 H, t, $J \sim 4.5$ Hz), and 6.60—6.85 and 7.05—7.30 (3 H, m); $\bar{\nu}$(KBr) 3 100—3 500, 2 930, 2 860, 1 600, 1 300, 1 255, 1 145, 1 080, 1 060, 1 040, 885, and 825 cm^{-1} (Found: $M^{\cdot+}$, 218.1312. $C_{14}H_{18}O_2$ requires M, 218.1307); m/z 174 (100%).

(b) *From lactone* (**8**). The total neutral fraction from the aforementioned Stobbe reaction (2.79 g) was reduced in the normal way with lithium aluminium hydride and worked up following hydrolysis and acidification. After purification by column chromatography (elution with diethyl ether), the product [0.85 g, 7% after the several steps from (**4a**)], was identical with the unsaturated alcohol (**6b**) produced by method (a) above.

Hydrogenation of 3-(3,4-*Dihydro*-6-*methoxy*-1-*naphthyl*)-*propan*-1-*ol* (**6b**).—A solution of compound (**6b**) (1.05 g, 4.8 mmol) in diethyl ether (150 cm^3) was hydrogenated (4 atm) over 10% Pd–charcoal (30 mg) for 24 h. The reaction mixture was filtered and evaporated down to give an oil (0.90 g, 85%), identical by n.m.r. and t.l.c. with the sample of compound (**7b**) obtained *via* the Stobbe reaction (see above).

4-(*Tetrahydropyran*-2-*yloxy*)*butanal* (**9b**).—(a) Dihydropyran (21 g, 0.25 mol) was added dropwise to a stirred solution of PTSA (*ca.* 50 mg) and butane-1,4-diol (22.5 g, 0.25 mol) in diethyl ether (50 cm^3). After 15 h, the reaction mixture was extracted with aqueous sodium carbonate, dried ($MgSO_4$), filtered, and evaporated down. The residual oil (36.8 g) was chromatographed on silica gel (290 g), the elution being with 1:1 (v/v) ether–light petroleum and monitoring by t.l.c. Combination of appropriate fractions and evaporation of the solvent yielded the mono-protected compound (**9c**) (16.8 g, 39%), pure by t.l.c.; $\bar{\nu}$(liquid) 3 100—3 600, 2 930, and 2 860 cm^{-1}; $\delta(CCl_4)$ 1.3—2.0 (10 H, m), 3.1—3.8 (6 H, m), and 4.5 (1 H, br).

(b) A solution of compound (**9c**) (1.8 g, 10.3 mmol) in dichloromethane (redistilled; 15 cm^3) was added to a stirred ice-cold slurry of pyridinium chlorochromate [13] (4.5 g, 20.9 mmol)

and sodium acetate (0.34 g, 4.1 mmol) in dichloromethane (15 cm^3) under argon. The reaction mixture deposited a dark tar-like material, and after about 30 min it was allowed to warm up to room temperature. After a further 1 h, the reaction mixture was diluted with ether (100 cm^3) and the supernatant liquid was decanted off. The residue was washed with several portions of ether, and the combined solution was percolated through a short column of Florisil (10 g) and evaporated down to give the alcohol (**9b**) as an oil pure by t.l.c. (1.65 g, 92%), $\tilde{\nu}$(liquid) 2 930, 2 860, 2 700, and 1 720 cm^{-1}; $\delta(CDCl_3)$ 1.3—2.1 (8 H, m), 2.4—2.7 (2 H, m), 3.1—3.9 (4 H, m), 4.6 (1 H, br), and 9.8 (1 H, unresolved t).

1-(3-*Bromopropyl*)-3-*methoxybenzene* (**5b**).—(a) A solution of the commercially available acid (**5a**) (25.0 g, 0.139 mol) in anhydrous THF (60 cm^3) was cautiously added dropwise to a stirred slurry of lithium aluminium hydride (6.0 g, 0.16 mol) in anhydrous THF (10 cm^3) at such a rate as to maintain a brisk reflux (*ca.* 40 min). The reaction mixture was then heated under reflux for *ca.* 15 h, cooled, then worked up in the normal way to give the alcohol (**5c**) as an oil (22.1 g, 96%) uncontaminated (t.l.c.) with the starting material; $\tilde{\nu}$(liquid) 3 100—3 600, 2 940, 2 860, 1 600, 1 580, 1 475, 1 450, 1 260, 1 150, 1 055, 1 040, 775, and 695 cm^{-1}.

(b) A solution of triphenylphosphine (70.8 g, 0.27 mmol) in ether (300 cm^3) was added to a stirred solution of compound (**5c**) (22.2 g, 0.134 mol) and tetrabromomethane (89.5 g, 0.27 mol) in ether (200 cm^3) during 30 min.[12] The reaction mixture began to boil gently under reflux and deposited a sticky white material which became granular after *ca.* 1 h. The reaction mixture was stirred for a further 2 h, then was allowed to cool and settle for *ca.* 15 h. It was then filtered (water-pump) through Celite and the residue was well washed with more ether. The combined ether phase was evaporated down to leave an oil (82.6 g), which was chromatographed on alumina (350 g), the elution being with 10% chloroform in hexane. Monitoring (t.l.c.) allowed combination of fractions to give a solution containing a single product. This solution was evaporated down to leave the title bromide (**5b**) as an oil, which was distilled (90—97 °C/0.1 Torr) (23.5 g, 77%), $\delta(CDCl_3)$ 1.8—2.3 (2 H, m), 2.5—2.8 (2 H, m), 3.3 (2 H, t, *J* 6.2 Hz), 3.70 (3 H, s), and 6.5—7.2 (4 H, m); $\tilde{\nu}$(liquid) 3 000, 2 940, 2 840, 1 600, 1 580, 1 490, 1 450, 1 260, 1 155, 1 050, 780, and 695 cm^{-1}.

7-(3-*Methoxyphenyl*)*heptane*-1,4-*diol* (**10**).—(a) A solution of the freshly distilled aldehyde (**9b**) (0.25 g, 1.45 mmol) in ether was added to a stirred solution of the Grignard reagent, prepared in the normal way from compound (**5b**) (0.50 g, 2.18 mmol) and magnesium turnings (0.06 g, 2.5 mmol) in ether, under argon. After a vigorous reaction, t.l.c. indicated the absence of starting aldehyde (**9b**), whereupon the reaction mixture was worked up in the normal way to yield 7-(3-methoxyphenyl)-4-hydroxyheptyl tetrahydropyranyl ether, which was isolated by p.l.c. (0.23 g, 49%); $\delta(CCl_4)$ 1.1—1.9 (14 H, m), 2.3—2.7 (2 H, m), 3.1—3.8 (5 H, m), 3.7 (3 H, s), 4.5 (1 H, m), and 6.4—6.7 and 6.8—7.2 (4 H, m); $\tilde{\nu}$(liquid) 3 100—3 600, 2 940, 2 860, 1 600, 1 580, 1 450, 1 260, 1 150, and 1 030 cm^{-1}. In another reaction on the same scale, the Grignard reagent was added to the aldehyde with no evident improvement in yield.

(b) Several drops of 6M-hydrochloric acid were added to a vigorously stirred solution of 7-(3-methoxyphenyl)-4-hydroxyheptyl tetrahydropyranyl ether (0.400 g, 1.24 mmol) in chloroform (5 cm^3) and the reaction was monitored by t.l.c. After 2 h, sufficient anhydrous sodium carbonate was added to neutralize the acid and dry the solution, which was then filtered and evaporated. The title product was isolated by p.l.c. (100 mg; 34%); $\delta(CCl_4)$ 1.1—1.9 (8 H, m), 2.3—2.7 (2 H, m), 3.3—3.7 (3 H, m), 3.70 (3 H, s), 4.1—4.6 (2 H, m), and 6.4—6.7 and 6.9—7.2 (4 H, m); $\tilde{\nu}$(liquid) 3 100—3 600, 2 930, 2 850, 1 600, 1 580, 1 480, 1 450, 1 260, 1 150, 1 050, and 750 cm^{-1} (Found: $M^{\cdot+}$, 238.1547. $C_{14}H_{22}O_3$ requires *M*, 238.1569); *m/z* 134 (100%).

2,3,3a,4,5,6-*Hexahydro*-8-*methoxy*-1H-*phenalene* (**3a**).—(a) *Cyclization of* 3-(1,2,3,4-*tetrahydro*-6-*methoxy*-1-*naphthyl*)-*propan*-1-*ol* (**7b**). The saturated alcohol (**7b**) (1.17 g, 5.31 mmol) was heated in polyphosphoric acid (82—85% P_2O_5; 61 g) at 80 °C for 30 min with occasional stirring of the mixture. The reaction mixture was cooled, diluted with ice–water, and extracted three times with ether. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, dried ($CaCl_2$), filtered, and evaporated down to give a residue which was distilled (Kugelrohr; 140 °C/0.05 Torr) to afford the title compound (0.57 g, 53%); $\delta(CDCl_3$; 90 MHz) 1.6—2.1 (8 H, m), 2.6—2.9 (5 H, m), 3.74 (3 H, s), and 6.47 (2 H, s); $\tilde{\nu}$(liquid) 3 000, 2 930, 2 850, 1 600, 1 480, 1 150, 1 050, and 850 cm^{-1} (Found: $M^{\cdot+}$, 202.1347. $C_{14}H_{18}O$ requires *M*, 202.1357); *m/z* 174.1053 (100%) ($C_{12}H_{14}O$ requires *m/z* 174.1045).

(b) *Double cyclization of* 7-(3-*methoxyphenyl*)*heptane*-1,4-*diol* (**10**). The diol (**10**) (90 mg) was added to polyphosphoric acid (*ca.* 8 g) and the mixture was heated to 90 °C for 40 min and occasionally stirred. The reaction mixture was cooled and diluted with water and the product was isolated in the normal way with chloroform. The product was identical (i.r., n.m.r., t.l.c.) with that obtained by cyclization of compound (**7b**), see above.

Cyclization of 3-(1,2,3,4-*Tetrahydro*-6-*methoxy*-1-*naphthyl*]-*propanoic Acid* (**7a**).—Compound (**7a**) (0.92 g) in polyphosphoric acid (*ca.* 70 g) was heated to 105 °C for 20 min; the mixture was then cooled and diluted with water. A crude neutral product was isolated as an oil (0.49 g) in the normal way and purified by distillation (Kugelrohr; 160 °C/0.05 Torr) followed by recrystallization (from pentane–ether to afford the ketone (**3b**), m.p. 69—70 °C; $\delta(CCl_4)$ 1.2—2.3 (6 H, m), 2.5—2.95 (5 H, m), 3.76 (3 H, s), and 6.83 and 7.37 (2 H, ABq, *J* 3 Hz); $\tilde{\nu}$(KBr) 2 920, 2 860, 1 670, 1 595, 1 470, 1 310, 1 290, and 1 040 cm^{-1}; $\lambda_{max.}$(EtOH) 329 (log ε 4.53) and 263 nm (4.93) [Found: $M^{\cdot+}$, 216.1155 (100%). $C_{14}H_{16}O_2$ requires *M*, 216.1151].

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References

1 H. Maskill, *Nature* (*London*), 1981, **294**, 606.
2 C. J. Coles and H. Maskill, *J. Chem. Soc., Chem. Commun.*, 1983, 367; C. J. Coles, MSc Thesis, University of Stirling, 1985.
3 P. Murray-Rust and J. Murray-Rust, *Acta Crystallogr., Sect. B*, 1979, **35**, 193.
4 W. S. Johnson and G. H. Daub, *Org. React.*, 1951, **6**, 1.
5 W. S. Johnson, H. C. E. Johnson, and J. W. Petersen, *J. Am. Chem. Soc.*, 1945, **67**, 1360.
6 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
7 A. A. Ponaras, *Tetrahedron Lett.*, 1976, 3105.
8 P. Adlercreutz and G. Magnusson, *Acta Chem. Scand., Ser. B*, 1980, **34**, 647.
9 P. E. Eaton, R. H. Mueller, G. R. Carlson, D. A. Cullison, G. F. Cooper, T.-C. Chou, and E.-P. Krebs, *J. Am. Chem. Soc.*, 1977, **99**, 2751.
10 P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4071.
11 D. Nasipuri and G. Pyne, *J. Chem. Soc.*, 1963, 4720; D. Nasipuri, G. Pyne, D. N. Roy, R. Bhattacharya, and P. Dutt, *ibid.*, 1964, 2146.
12 J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, 1968, **46**, 86.
13 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.
14 J. March, 'Advanced Organic Chemistry,' Wiley, New York, 3rd edn., 1985, (*a*) p. 835, (*b*) p. 562.
15 D. B. Bigley and M. J. Clarke, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1.

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