Electrophilic Substitution in Naphthalenes: Cyclisation of Naphthylbutanols to Tetrahydrophenanthrene

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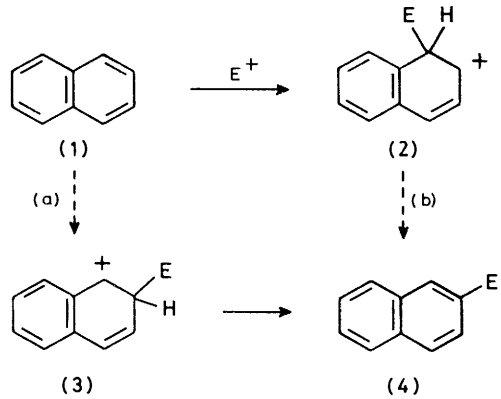
Both 4-(1-naphthyl)butanol and 4-(2-naphthyl)butanol cyclised in refluxing boron trifluoride–ether to give 1,2,3,4-tetrahydrophenanthrene. By use of the corresponding 1,1-dideuteriobutanol derivatives and analysis of the products by 220 MHz ^{1}H n.m.r. spectroscopy it has been demonstrated that the 1-naphthylbutanol cyclises by two distinct pathways, (a) by direct attack (84%) at the 2-position, and (b) by *ipso*-attack (16%) at the 1-position of the naphthalene nucleus, followed by rearrangement. The 2-naphthylbutanol cyclises exclusively by direct substitution at the 1-position. With 4-(4-methoxy-1-naphthyl)-1,1-dideuteriobutanol on the other hand the proportion of *ipso*-substitution rises to 71% as shown by the 360 MHz ^{1}H n.m.r. spectra of the resulting mixture of tetrahydrophenanthrenes.

NAPHTHALENE (1) undergoes electrophilic substitution at both the 1- and 2-positions although the former apparently predominates under conditions of kinetic control, *e.g.* in nitration and halogenation reactions, and in sulphonation reactions below 80°. However, sulphonation of naphthalene at higher temperatures (>160°) gives entirely 2-substitution, whilst acylation under Friedel–Crafts conditions gives both 1- and 2-substituted products depending on the solvent and temperature.[1]

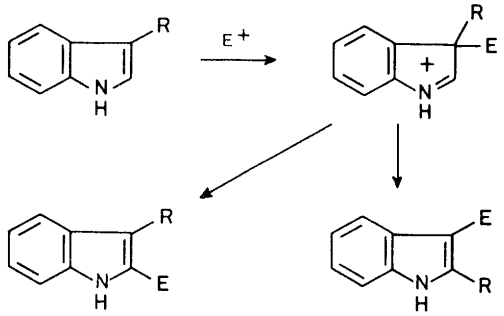
The predominance of 1-substitution under kinetically controlled conditions may be attributed to the lower energy of the transition state leading to the Wheland intermediate (2) compared with that of (3) for 2-substitution. It seemed likely (by analogy with our related studies in the indole field)[2] that electrophilic substitution at the 2-position might occur by two mechanisms, (i) by direct substitution (Scheme 1, path a) and (ii) by rearrangement of an initially formed 1-substituted naphthalene (Scheme 1, path b).



SCHEME 1

With indole itself electrophilic substitution almost invariably occurs at the 3-position[3] but certain 3-substituted indoles will undergo acid-catalysed rearrangement to the corresponding 2-substituted indoles.[4] Moreover 3-alkylindoles also undergo electrophilic substitution at the 3-position (even though this is already substituted); the resulting 3,3-disubstituted indolenines then rearrange with migration of one or other substituent to give the 2,3-disubstituted indoles, by an intra- rather than an inter-molecular process (Scheme 2).[5]

In the naphthalene series evidence has already been obtained[6] by isotopic labelling studies to show that



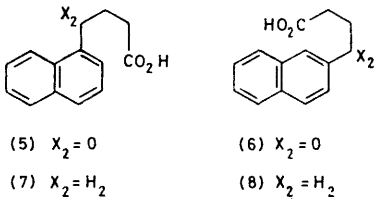
SCHEME 2

sulphonation at the 2-position may occur at least in part by rearrangement of a sulphonic acid group from the 1-position, whilst treatment of 1-alkylnaphthalenes with Friedel–Crafts catalysts leads to the formation of the corresponding 2-alkylnaphthalenes[7] although the intra- or inter-molecularity of the latter process has not been established. It was therefore of considerable interest to investigate the substitution reactions of naphthalene in more detail and accordingly we set out to synthesise appropriate naphthylbutanols and study their cyclisation to tetrahydrophenanthrenes, in an analogous manner to our earlier investigations in the indole series.

The α- and β-naphthyloxobutyric acids (5) and (6) were prepared essentially by established procedures,[8] and the purity of each isomer was checked by h.p.l.c. analysis of the corresponding methyl esters. Clemmensen reduction of each of the oxo-acids then gave the corresponding α- and β-naphthylbutyric acids (7) and (8) respectively;[9]

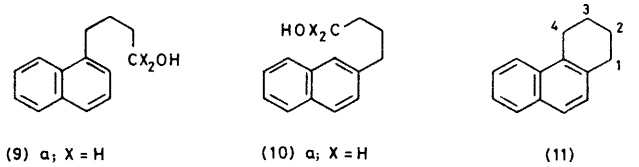
the n.m.r. spectra of these acids confirmed that each was free of the other isomer, the signals due to the methylene protons neighbouring the aromatic nucleus being clearly distinguished. Further reduction of the acid (7) with lithium aluminium hydride then afforded the alcohol [10] (9a) (96%) which cyclised in boiling boron trifluoride–ether to the tetrahydrophenanthrene [8] (11) (82%). The latter, after purification by column chromatography, was converted into its picrate, m.p. 110—111° after recrystallisation; the 1- and 4-methylene proton signals of the picrate were completely resolved in the 220 MHz n.m.r. spectrum, but overlapped in the 90 MHz spectrum.

The pure naphthylbutyric acid (7) was then reduced with lithium aluminium deuteride to the oily dideuterioalcohol (9b) shown by ^{1}H n.m.r. and mass spectroscopy to be fully deuteriated in the CD_2OH group, and the

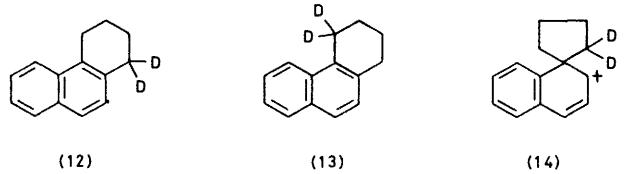


(5) $X_2 = O$ (6) $X_2 = O$

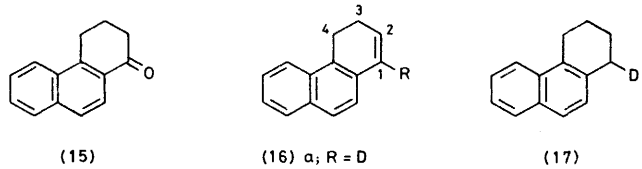
(7) $X_2 = H_2$ (8) $X_2 = H_2$



(9) a; X = H, b; X = D (10) a; X = H, b; X = D (11)



(12) (13) (14)



(15) (16) a; R = D, b; R = H (17)

latter was cyclised in boiling boron trifluoride–ether to give a mixture of deuteriated tetrahydrophenanthrenes (12) and (13). After column chromatography the latter were converted into a mixture of the corresponding picrates, m.p. 109—110° after successive recrystallisations, and analysed by 220 MHz n.m.r. spectroscopy; comparison of the intensities of the signals due to the 1- and 4-methylene protons with those of the 2- and 3-methylene protons showed that the ratio of the two tetrahydrophenanthrenes (12) and (13) formed in the cyclisation was 11 : 1. After allowing for the small secondary isotope effect which would be expected to influence the rearrangement of the intermediate spirocycle (14), the ratio of the two pathways (a) and (b) in the cyclisation (*cf.* Scheme 1) may be calculated as 84 : 16. (The isotope effect, K_H/K_D 1.13, was assumed to be the same as that found experimentally for the analogous rearrangement of the spirocyclic intermediate involved in the cyclisation of indolylbutanol.[11])

The possibility that equilibration of the two deuteriophenanthrenes (12) and (13), had occurred under the conditions of the cyclisation (*cf.* ref. 11) was excluded by the following series of experiments. The acid (7) was cyclised to the ketone [8] (15) and this was reduced with diborane (generated *in situ*) to the tetrahydrophenanthrene (11) (78%) the picrate of which was identical with that of the earlier sample synthesised by cyclisation of the naphthylbutanol (9a). A similar reduction of the cyclic ketone (15) with deuteriodiborane (generated *in situ* from sodium borodeuteride) unexpectedly gave as the only isolable product, the monodeuteriodihydrophenanthrene (16a); the latter showed $\lambda_{max.}$ 308 and 344 nm (weak) in accord with literature data [12] for 1-vinylnaphthalenes. The ^{1}H n.m.r. spectrum showed a broad triplet at τ 3.88 (J 4.5 Hz), consistent with vinylic coupling of the olefinic proton at the 2-position with the 3-CH_2 group, and weak coupling to the deuterium at the 1-position; the 4-CH_2 triplet at τ 6.8 was accompanied by a double triplet (J 9, 4.5 Hz) at τ 7.58 due to the 3-CH_2 group. A minor signal at 3.45 (d, J 10 Hz) indicated the presence of *ca.* 10% of the undeuteriated analogue (16b). The mixture was hydrogenated over palladium–charcoal to give the crude monodeuteriotetrahydrophenanthrene (17) which was then converted into its picrate; ^{1}H n.m.r. analysis of the latter (at 220 MHz) showed that the ratio of proton signals due to the 1- and 4-CH_2 groups was 56 : 100, thus confirming the presence of *ca.* 10% of the non-deuteriated tetrahydrophenanthrene (11). The composition of the mixture was further confirmed by determining the ^{13}C n.m.r. spectrum of the picrate; this showed, in the noise decoupled mode, three singlets due to the 2-, 3- and 4-carbon atoms, and a triplet resulting from C(1)–D coupling in (17), together with a low intensity singlet due to C(1) in the non-deuteriated impurity (11). The reason for the unexpected formation of the olefin (16a) in the deuteriodiborane reduction is not clear, but may be due to undefined minor differences in the reaction conditions; the experiment was not repeated due to shortage of time and purified materials and the monodeuteriotetrahydrophenanthrene (17) in any case sufficed for the remainder of the experiments required.

The picrate of the monodeuteriated material (17) was therefore decomposed with dilute ammonia solution and the hydrocarbon purified by column chromatography before being heated with boron trifluoride–ether under similar conditions to those used in the cyclisation reactions, but for an additional 30 min reaction time. After work-up and conversion to the picrate, the product

was shown both by 220 MHz ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopy to be identical with the starting material (*e.g.* the ratio of the 1- and 4-methylene resonances was still 56 : 100).

Another possible, but unlikely, error in using the ratio of the two recrystallised picrates of (12) and (13) for estimating the proportions formed by each pathway was that selective crystallisation of one or other of the picrates had taken place. Whilst this might be a very small effect for the isomeric deuteriopicrates (12) and (13) a more severe test was to compare the relative solubilities of the picrate of the deuteriated phenanthrene (17) with that of the non-deuteriated analogue (11). Huang-Minlon reduction [13] of the ketone (15) gave the tetrahydrophenanthrene (11) (96%) and the resulting picrate was mixed with that of the monodeuterio-analogue (17) in the ratio 1 : 5.5 by mass; this mixture was analysed quantitatively by 220 MHz ^{1}H n.m.r. spectroscopy. After four recrystallisations, the n.m.r. analysis was repeated but the difference in the relative proportions of the 1- and 4-methylene resonance was $<2\%$. This was well within experimental error, thus showing that differential crystallisation had not occurred to any significant extent.

We next examined the analogous cyclisation of the alcohol (10a). Huang-Minlon reduction of the oxo-acid (6) gave the butyric acid (8) (96%) which was reduced by lithium aluminium hydride to the crystalline alcohol (10a). The latter on treatment with boiling boron trifluoride–ether for 4 h afforded again the tetrahydrophenanthrene (11) (84%), the picrate of which was identical with that prepared originally from the isomeric alcohol (9a). The acid (8), free from its analogue (7), on reduction with lithium aluminium deuteride gave the crystalline dideuterioalcohol (10b) [14] which was shown by ^{1}H n.m.r. and mass spectrometry to be free from the non-deuteriated species (10a). Cyclisation of the dideuterioalcohol (10b) with boron trifluoride–ether, as before, gave crude tetrahydrophenanthrene (13) which was chromatographed, converted into its picrate, and crystallised five times. Examination of this picrate by 220 MHz ^{1}H n.m.r. spectroscopy showed it to contain no detectable triplet resonance at τ 7.0, indicating the complete absence of the isomer (12). This result also confirms the conclusion above that no rearrangement of the isomers (12) and (13) takes place under the conditions of cyclisation of the alcohol.

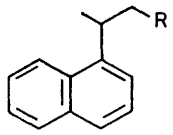
In the above experiments with the 1- and 2-naphthylbutanols we assumed that switch-over of the 4-CH_2 group had occurred exclusively *via* the spirocyclic intermediate (14). Olah, however, has recently shown [7] that alkyl groups can rearrange from the α-position of naphthalene to the thermodynamically more stable β-position in the presence of Lewis acids. In order to rule out this type of pathway, 1-methylnaphthalene [15] was heated with boron trifluoride–ether under the same reaction conditions as those used in the cyclisation of the alcohols (9b) and (10b). The crude reaction product was compared with standard mixtures of 1- and 2-methylnaphthalenes (which can be easily distinguished by ^{1}H n.m.r. spectroscopy) but no 2-methynaphthalene was detected.

We also prepared the 4-(1-naphthyl)pentanol (18f) to test the prediction that cyclisation *via* an intermediate spirocycle (19) would result in preferential migration of the carbon bearing the methyl group (as this would be expected to have a higher migratory aptitude). Thus the acid [16] (18a) was reduced with lithium aluminium hydride to the alcohol (18b) (93%). Conversion into the homologous acid (18e) was achieved through standard procedures *via* the chloride (18c) (81%), and nitrile (18d) (75%).

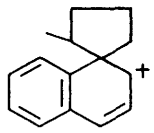
The acid [17] (18e) was reduced in high yield by lithium aluminium hydride to the alcohol (18f), and after purification by p.l.c. the latter was cyclised with refluxing boron trifluoride–ether for 4.5 h. The ratio of the two methyltetrahydrophenanthrenes [18] (20) and (21) was estimated approximately as 3 : 1 by comparing the ratios of the 1- and 4-methine proton resonances relative to those of the aromatic proton signals in the 90 MHz ^{1}H n.m.r. spectra. H.p.l.c. analysis showed that the ratio was 76 : 24, and this was confirmed by dehydrogenation of the mixture with dichlorodicyanoquinone to give the methylphenanthrenes (22) and (23) [19] in the ratio 75 : 25 (as determined by comparison of the ^{1}H n.m.r. signals of the 1- and 4-methyl groups respectively).

It seems likely that the intermediate spirocycle (19) will rearrange regiospecifically to give the 1-methyltetrahydrophenanthrene (21) bcause of the greater migratory aptitude of the secondary carbon atom, and thus the *minimum* proportion of the *ipso*-substitution pathway in the cyclisation of the alcohol (18f) is 25%. The increased proportion of *ipso*-substitution in this case may be a consequence of conformational factors in the cyclisation process favouring electrophilic attack at the α- rather than the β-positions due to steric interactions between the secondary alkyl substituent at the 1-position, and the *peri*-hydrogen atom at the 8-position. The decreased hyperconjugative effect at the 2-position may also contribute.

As mentioned in the introduction cyclisation of indolylbutanol to tetrahydrocarbazole occurs entirely *via* a spirocyclic intermediate (Scheme 2); however, suitably placed methoxy-groups may alter the mechanism and allow direct substitution at the 2-position. Thus, 4-(6-methoxyindol-3-yl)butanol (24) cyclises both by attack at the 2-position (27%) and indirectly by attack at the 3-position (73%) to give 7-methoxytetrahydrocarbazole (25).[20] We, therefore, expected that introduction of a 4-methoxy-group into 1-naphthylbutanol would enhance the extent of *ipso*-substitution (rather than diminish it as in the indole series [20]). Accordingly the acid [21] (26) was reduced with lithium aluminium hydride to the oily alcohol (27a) which was cyclised with boron trifluoride–ether under nitrogen for 2.5 h. After purification by p.l.c. the tetrahydrophenanthrene [22] (28) was converted into its picrate, m.p. 120—121.5°. Unfortunately the 1- and 4-methylene signals of the latter were not completely resolved in the ^{1}H n.m.r. spectrum



(18)

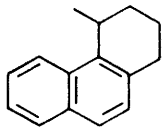


(19)

a; R = CO_2H d; R = CH_2CN

b; R = CH_2OH e; R = CH_2CO_2H

c; R = CH_2Cl f; R = CH_2CH_2OH



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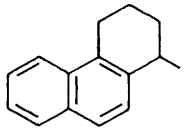

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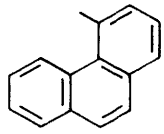

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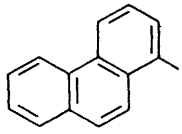

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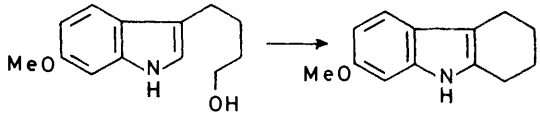
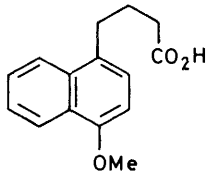


(24) (25)



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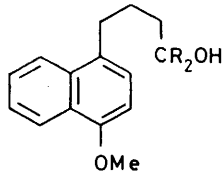
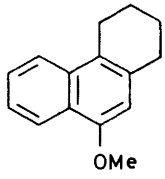


(27) a; R = H b; R = D



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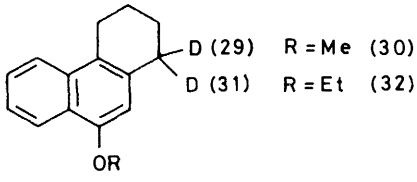
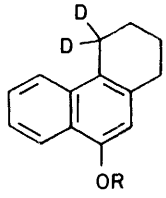
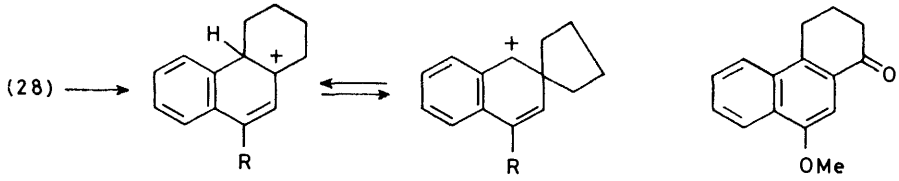






(33) a; R = H
b; R = OMe

(34) a; R = H
b; R = OMe

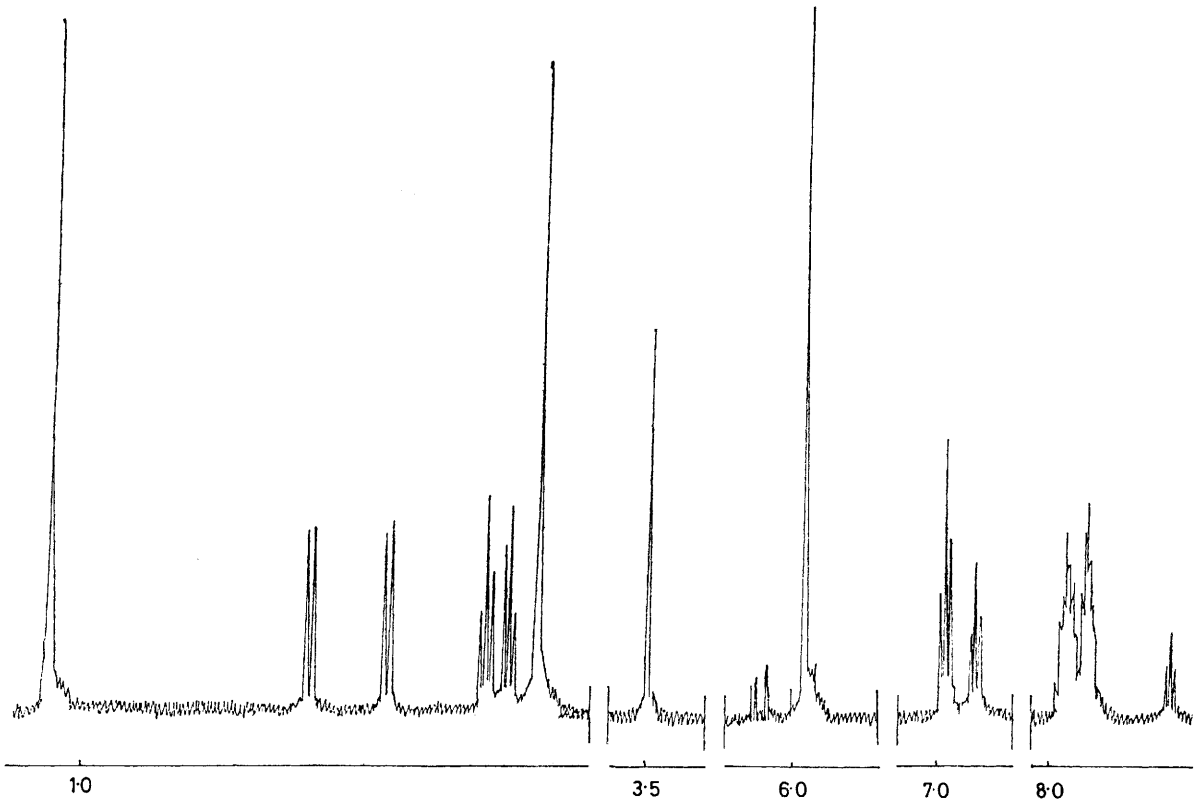
(35)

even at 220 MHz and decoupling of the 2- and 3-methylene groups still did not separate them clearly; calculations indicated, however, that base-line resolution would be expected at 360 MHz.

Reduction of the acid (26) was repeated with lithium aluminium deuteride and gave the dideuterioalcohol (27b) which was identical with the alcohol (27a) in its i.r. and ^{1}H n.m.r. spectra except that the former showed extra bands at 2 280 cm^{-1} (C–D stretch) and showed no signal at τ 6.35. Cyclisation of (27b) as above gave a mixture of the dideuteriotetrahydrophenanthrenes (29) and (30). After purification by p.l.c. the mixture of (29) and (30) showed in its 90 MHz ^{1}H n.m.r. spectrum no loss of deuterium compared with (27b). Spin decoupling as before failed to resolve the 1- and 4-methylene signals completely but indicated that the ratio of (29) to (30) was *ca.* 1.6 : 1. Conversion of this mixture to the picrates and crystallisation (2×) afforded a sample, m.p. 120—122°. This sample gave completely resolved triplets for the 1- and 4-methylene signals of relative intensity 1.6 : 1 in the n.m.r. spectrum measured at 360 MHz (see Figure). This ratio is consistent with cyclisation of the dideuterioalcohol (27b) 23% by the direct pathway (a) and 77% by the indirect pathway (b) (*cf.* Scheme 1).

The 360 MHz spectrum also revealed as the only detectable impurity, a triplet and quartet at τ 8.48 and 5.9 (J 7.5 Hz) respectively. These signals are consistent with *ca.* 10% of the products (31) and (32) of trans-etherification by the boron trifluoride–ether. Their presence does not affect the estimation of the deuterium distribution in the 1- and 4-methylene groups.

As in the case of the tetrahydrophenanthrenes (12) and (13) it was necessary to eliminate the possibility that acid catalysed equilibration of the methoxy-derivatives (29) and (30) had occurred during the cyclisation. Indeed in the presence of hydrofluoric acid derived *via* the water eliminated in the cyclisation of (27b), the equilibration (33b) ⇌ (34b) initiated by protonation at the 1-naphthyl position would be expected to be easier than in the demethoxy series (33a) ⇌ (33b). To test this possibility the ketone [23] (35) was reduced with deuterio-diborane generated *in situ* to the deuteriated tetrahydrophenanthrene (29) (79%). The isomeric purity of the starting ketone was checked chromatographically and by its ^{13}C n.m.r. spectrum. After conversion of (29) into its picrate and recrystallisation the 220 MHz ^{1}H n.m.r. spectrum showed that 10% of the total tetrahydrophenanthrene was undeuteriated at the 1-position. The picrate was reconverted to the tetrahydrophenanthrene (29) which, after purification by p.l.c. was subjected to the original conditions of the cyclisation of the alcohol (27b) but for 3 h. This procedure was also carried out with the addition of 1 mol. equiv. of water at the beginning of the boron trifluoride–ether reflux in order to ensure the presence of hydrofluoric acid. In



360 MHz ^{1}H N.m.r. spectrum of the picrate of the tetrahydrophenanthrenes (30) and (31)

each case, after recovery of the tetrahydrophenanthrene and p.l.c., reconversion to the picrate, and two recrystallisations, the original tetrahydrophenanthrene (29) had rearranged to its isomer (30) by a further 3.5%. Taking this into account, as well as the secondary isotope effect referred to above,[11] the proportions of the indirect and the direct pathways for the cyclisation of the methoxynaphthylbutanol (27) to the methoxytetrahydrophenanthrene (28) may be corrected to 71 and 29%, respectively. The relatively small percentage of *ipso*-substitution in the case of the cyclisation of 4-(1-napthyl)butan-1-ol contrasts with the much larger proportion in the corresponding free radical substitution.[24]

EXPERIMENTAL

M.p.s were determined on a hot stage, and are corrected. Mass spectra were obtained with a Varian CH5-D instrument (a) by electron impact–direct insertion probe at 70 eV and 50 μA or (b) by field desorption at a wire current of 15—20 μA. I.r. spectra were measured on a Unicam SP 200 grating spectrophotometer; u.v. spectra were determined in spectroscopic ethanol on a Unicam SP 800 instrument. N.m.r. spectra were determined on a Perkin-Elmer R32 (90 MHz) spectrometer in $CDCl_3$ unless stated otherwise. Spectra at 220 MHz were carried out by the P.C.M.U. Harwell. T.l.c. was performed on Whatman Silica gel 50F T.L.C.

4-(1-Naphthyl)-4-oxobutyric Acid (5) *and 4-(2-Naphthyl)-4-oxobutyric Acid* (6).—A mixture of naphthalene (40 g) and succinic anhydride (20 g) was slowly added to a well stirred suspension of aluminium trichloride (55 g) in nitrobenzene (140 ml). Stirring was continued for 12 h at 25 °C. The mixture was then cautiously poured onto crushed ice and acidified with dilute hydrochloric acid (250 ml). The crude acid was filtered, washed with water until the washings were neutral, and recrystallised from EtOH (×3) to give 4-(2-naphthyl)-4-oxobutyric acid (6) (10.9 g), m.p. 170—172 °C (lit.,[8] 174 °C), *m/e* 228 (27%, M^+), 210 (3), 156 (12), 155 (100), 128 (7), 127 (54), 126 (7), 101 (3), and 77 (7), $\lambda_{max.}$ 239 (log ε 4.87), 246 (4.93), 273sh (4.24), 282 (4.35), 292 (4.09), 328 (4.88), and 342 nm (4.87), $\nu_{max.}$ (Nujol) 3 200 (CO_2H), 1 700 (CO_2H), 1 680 (ArCO), 860, and 900 cm^{-1}, τ 7.22 (2 H, t, *J* 7 Hz, CH_2CO_2H) and 6.58 (2 H, t, *J* 7 Hz, $ArCOCH_2$).

The organic layer from the filtrate from the above acid (6) was combined with chloroform (50 ml), washed with water, and dried ($MgSO_4$). After filtration, light petroleum (b.p. 60—80 °C) (21) was added and kept for 12 h. The precipitate of crude acid (11.1 g) was recrystallised from methanol to give 4-(1-naphthyl)-4-oxobutyric acid (5) (9.8 g), m.p. 129—131 °C (lit.,[8] 131—132 °C), *m/e* 228 (37%, M^+), 156 (12), 155 (100), 128 (6), 127 (51), 101 (2), and 77 (7), $\lambda_{max.}$ 218 (log ε 4.51), 237 (4.32), 246 (4.25), 272 (3.72), 282 (3.80), 293 (3.83), and 327 nm (3.42), $\nu_{max.}$ (Nujol) 3 550 (CO_2H), 1 680 (ArC=O), 1 700 (CO_2H), 940, and 850 cm^{-1}, τ 7.24 (2 H, t, *J* 7 Hz, CH_2CO_2H), 6.7 (2 H, t, *J* 7 Hz, $ArCOCH_2$), 2.60—2.38 (3 H, m, 5-, 6-, 7-ArH), 2.22—1.96 (3 H, m, 2-, 3-, 4-ArH), 1.42 (1 H, dd, *J* 8,4 Hz, 8-ArH), and 1.1br (1 H, s, CO_2H).

Conversion of the Acids (5) *and* (6) *into their Methyl Esters.*—The keto-acid (30 mg) in AnalaR methanol (5 ml) was treated with concentrated sulphuric acid (1 ml) and kept overnight at 25 °C. The pH was adjusted to 7 and the ester (23 mg) was isolated *via* ether. The purity of each ester was checked by h.p.l.c. on a 3 in × 1/4 in stainless steel column packed with Corasil II (Waters Associates). Elution was with ether–light petroleum (b.p. 40—60 °C) (1 : 9) and detection was at 254 nm on a Cecil Instruments CE 272 spectrophotometer.

Reduction of the Acid (7) *to the Alcohol* (9a).—4-(1-Naphthyl)butyric acid [9] (2 g) in dry tetrahydrofuran (THF) (10 ml) was cautiously added to a solution of lithium aluminium hydride (400 mg) in dry THF under dry nitrogen. The mixture was heated under reflux for 2.5 h before cooling to 25 °C and decomposition with a solution of Rochelle salt. Extraction with ether (3 × 50 ml), washing with saturated sodium carbonate solution (50 ml) and drying ($MgSO_4$) was followed by removal of the solvent under reduced pressure gave the crude alcohol (1.78 g) which on distillation gave pure 4-(1-naphthyl)butan-1-ol (9a), b.p. 142—148 °C at 0.3 mmHg (lit.,[10] 150—155 °C at 0.5 mmHg), *m/e* 200 (85%, M^+), 184 (7), 183 (6), 167 (15), 166 (4), 165 (7), 157 (5), 156 (14), 155 (20), 154 (42), 153 (23), 152 (11), 143 (10), 142 (66), 141 (100), 140 (5), 139 (16), 130 (14), 129 (12), 128 (16), 127 (6), 116 (8), and 115 (53), $\lambda_{max.}$ 218 (log ε 4.65), 224 (4.81), 262sh (4.35), 271 (4.51), 282 (4.52), 293 (4.28), 304 (3.75), 314 (3.57), and 319 nm (3.52), $\nu_{max.}$ (liquid film) 3 450 (OH), 800, and 780 cm^{-1}, τ 8.5br (1 H, s, exchanged with D_2O, CH_2OH), 8.3 (4 H, m, $ArCH_2CH_2CH_2$), 6.95 (2 H, t, *J* 7 Hz, $ArCH_2$), 6.4 (2 H, t, *J* 7 Hz, CH_2OH), and 1.9—2.8 (7 H, m, ArH).

Cyclisation of the Alcohol (9a) *to the Tetrahydrophenanthrene* (11).—The above alcohol (9a) (200 mg) in boron trifluoride–ether (20 ml) was heated at reflux under nitrogen for 4 h. T.l.c. then showed one component corresponding to the tetrahydrophenanthrene (11). The mixture was cooled and poured onto ice (50 g) and the green mixture extracted with ether (3 × 20 ml). After washing with water (5 × 25 ml) and drying ($MgSO_4$) the solvent was removed under reduced pressure to give the crude tetrahydrophenanthrene as a brown oil (156 mg). Purification by p.l.c. [elution with light petroleum (b.p. 40—60 °C)] gave an oil which on treatment with 1.1 moles per mole of picric acid in absolute ethanol gave orange needles of the picrate of the tetrahydrophenanthrene (11), m.p. 103—107 °C. Recrystallisation (×3) afforded the pure picrate, m.p. 110—111 °C (lit.,[8] 111 °C), τ (220 MHz) 8.12 (4 H, m, $ArCH_2CH_2CH_2$), 7.15 (2 H, t, *J* 6 Hz, 1-CH_2), 7.00 (2 H, t, *J* 6 Hz, 4-CH_2), 2.92 (1 H, d, *J* 8 Hz, 10-H), 2.5—2.84 (3 H, m, 6-, 7, 8-H), 2.36 (1 H, d, *J* 8 Hz, 8-H), 2.20 (1 H, d, *J* 8 Hz, 5-H), and 1.12 (2 H, s, ArH of picric acid).

Reduction of the Acid (7) *with Lithium Aluminium Deuteride.*—4-(1-Naphthyl)butyric acid (2.35 g) in dry tetrahydrofuran (15 ml) was cautiously added to a solution of lithium aluminium deuteride (650 mg) in dry THF (40 ml) under dry nitrogen. The mixture was heated under reflux for 2.5 h before cooling to 25 °C and decomposition with Rochelle salt solution. Extraction with ether (3 × 50 ml), washing with saturated sodium carbonate solution (50 ml), and drying ($MgSO_4$) was followed by removal of the solvents under reduced pressure to give the *alcohol* (9b) (1.94 g), *m/e* 204 (2%), 203 (24), 202 (82, M^+), 184 (8), 183 (7), 167 (14), 166 (4), 165 (8), 157 (3), 156 (13), 155 (19), 154 (45), 153 (27), 152 (12), 143 (10), 142 (66), 141 (100), 140 (5), 139 (15), 130 (14), 129 (11), 126 (16), 127 (6), 116 (5), and 115 (51), $\nu_{max.}$ (liquid film) 3 540 (OH), 2 280, 2 180 (C–D), 800, and 780 cm^{-1}, τ 8.6br (1 H, s, exchanged with D_2O, CD_2OH), 8.3 (4 H, m, $ArCH_2CH_2CH_2$), 6.95 (2 H, t, *J* 7

Hz, $ArCH_2$), and 1.9—2.8 (7 H, m, ArH). The *3,5-dinitrobenzoate* had m.p. 130—133 °C (Found: C, 64.6; H, 5.06; N; 7.08. $C_{14}H_{16}{}^2H_2N_2O_6$ requires C, 64.6; H, 5.1; N, 7.2%). The alcohol was chromatographically and spectroscopically pure and was used for the next stage directly.

Cyclisation of the Deuterioalcohol (9b) *to the Deuteriotetrahydrophenanthrenes* (12) *and* (13).—The above alcohol (9b) (1.1 g) in boron trifluoride–ether (80 ml) was heated at reflux under nitrogen for 4 h, when t.l.c. showed the reaction to be complete. The mixture was cooled, poured onto ice (200 g), and then extracted with ether (3 × 50 ml). After washing with water (5 × 50 ml) and drying ($MgSO_4$), the solvent was removed to give the crude hydrocarbons (940 mg). The mixture was isolated by chromatography on grade III alumina (30 g) and eluted with light petroleum (b.p. 40—60 °C) to give an oil (822 mg). Treatment with 1.1 moles per mole of picric acid in absolute ethanol (5 ml) gave the picrates of the hydrocarbons (12) and (13) as orange needles, m.p. 103—107 °C. Recrystallisation (×5) gave a sample, m.p. 109—110 °C, *m/e* 185 (20, $M + 1$), 184 (100 M^+), 183 (15), 182 (4), 181 (4), 180 (5), 179 (4), 169 (9), 168 (8), 167 (15), 160 (9), 165 (4), 156 (39), 155 (17), 154 (20), 153 (10), 152 (5), 143 (13), 142 (9), 141 (6), 92 (8), 91 (8), 90 (9), 89 (4), 84 (10), 83 (12), 77 (14), and 76 (6), τ (220 MHz) 8.12 (4 H, m, $ArCH_2CH_2CH_2$), 7.00 and 7.15 (2 H, two t, each *J* 6 Hz, 1- and 4-CH_2, ratio 11 : 1), 2.92 (1 H, d, *J* 8 Hz, 10-H), 2.50—2.84 (3 H, m, 6-, 7-, 8-H), 2.36 (1 H, d, *J* 8 Hz, 8-H), 2.20 (1 H, d, *J* 8 Hz, 5-H), and 1.12 (2 H, s, ArH of picric acid).

Reduction of the Ketone (15) *to the Tetrahydrophenanthrene* (11).—The above ketone (15) (200 mg) prepared from the acid (7),[8] in dry diglyme (2 ml) containing boron trifluoride–ether (6 ml) was added to a cool (ice-bath) solution of sodium borohydride (100 mg) in dry diglyme (15 ml) with stirring over 10 min. After stirring for 1 h, the solution was heated under reflux for 4 h before cooling and cautious treatment with 2N-hydrochloric acid. Water (50 ml) was added and the mixture extracted with ether (3 × 5 ml). The organic layer was washed with water (3 × 50 ml) and dried before removal of solvent under reduced pressure. The residual crude hydrocarbon (148 mg) was purified by p.l.c. as described above to give 1,2,3,4-tetrahydrophenanthrene (11) as an oil (113 mg). Treatment with picric acid (92 mg) in absolute ethanol (1 ml) deposited the picrate (62 mg), m.p. 108—109 °C, after two recrystallisations. The sample was spectroscopically identical with that from the cyclisation of the alcohol (9a), m.p. 110—111 °C.

Reduction of the Ketone (15) *to the Deuteriodihydrophenanthrene* (16a).—The above ketone (15) (2 g) was dissolved in dry diglyme (20 ml) containing freshly distilled boron trifluoride–ether (60 ml). The green solution was slowly added to a cold solution (ice-bath) of sodium borodeuteride (1 g; 98% ^2H) in dry diglyme (150 ml) with stirring over 10 min. After stirring for 1 h, the solution was heated under reflux for 4 h and then cooled before cautious treatment with 2N-hydrochloric acid. Water (100 ml) was added and the mixture extracted with ether (3 × 50 ml). The organic layer was washed with water (6 × 50 ml) and dried ($MgSO_4$) before removal of solvent under reduced pressure to give the crude dihydrophenanthrene (16a) as an oil (1.80 g), τ 7.58 (2 H, dt, *J* 9, 4.5 Hz, 3-CH_2), 6.80 (2 H, t, *J* 9 Hz, $ArCH_2$), 3.88br (1 H, t, *J* 4.5 Hz, 2-H), 3.45 (1 H, d, *J* 10.0 Hz, ArH), and 1.80—2.76 (6 H, m, ArH), $\lambda_{max.}$ (MeOH) 242 (relative ε 0.44), 250 (0.82), 259 (1.00), 285 (0.08), 296 (0.11), 308 (0.13), 322 (0.10), and 344 nm (0.01).

Reduction of the Deuteriodihydrophenanthrene (16a) *to the Deuteriotetrahydrophenanthrene* (17).—The above hydrocarbon (16a) (1.80 g) was hydrogenated in absolute ethanol (40 ml) over 5% palladised charcoal at atmospheric pressure until the theoretical amount of hydrogen was taken up (220 ml). The solution was filtered through Celite and the ethanol removed under reduced pressure to give an oil (1.75 g). Treatment with picric acid (2.4 g) in absolute ethanol (15 ml) and recrystallisation (×2) gave the picrate of (17) as orange needles, m.p. 108—110 °C, *m/e* 184 (23%), 183 (100, M^+), 182 (30), 181 (4), 180 (3), 179 (7), 178 (4), 169 (2), 168 (11), 167 (12), 166 (15), 165 (9), 155 (40), 154 (34), 153 (16), 152 (8), 142 (16), and 141 (15), τ (220 MHz) 8.12 (4 H, m, $ArCH_2CH_2CH_2$), 7.17br (1.12 H, t, CHD), 7.00 (2 H, t, *J* 6 Hz, 4-CH_2), 2.92 (1 H, d, *J* 8 Hz, 10-H), 2.5—2.84 (3 H, m, 6-, 7-, 8-H), 2.36 (1 H, d, *J* 8 Hz, 9-H), 2.20 (1 H, d, *J* 8 Hz, 5-H), and 1.12 (2 H, s, ArH of picric acid), δ_C (noise decoupled) 22.7 (C-3), 23.0 (C-2), 25.5 (C-4), 29.9 (t, *J* 19 Hz, C-1), and 30.3 p.p.m. [C-1 of (11)] [for the hydrocarbon (11), δ_C 22.8 (C-3), 23.0 (C-2), 25.5 (C-4), and 30.3 (C-1)].

Isomerisation Test for the Deuteriotetrahydrophenanthrene (17).—The above picrate of (17) (1 g) was decomposed with dilute ammonia solution and extracted with ether (3 × 50 ml). The ether extract was washed with more ammonia solution (2 × 50 ml) and water (3 × 50 ml). Drying ($MgSO_4$) followed by removal of the solvent again afforded the hydrocarbon (17). This was further purified by chromatography on Grade III neutral alumina (30 g) and elution with 2% ethyl acetate in light petroleum (b.p. 40—60 °C) gave an oil (470 mg). The oil was refluxed with freshly distilled boron trifluoride–ether (100 ml) under dry nitrogen for 4.5 h. The green solution was cooled, then poured onto ice (150 g), extracted with ether (3 × 25 ml), washed with water (3 × 25 ml), and dried ($MgSO_4$). Removal of the solvent gave a green oil (435 mg). Purification by p.l.c., treatment with picric acid as above regenerated the picrate of (17) (480 mg) which after recrystallisation (×3) gave m.p. 109—110 °C. It showed a 220 MHz ^1H n.m.r. spectrum unchanged from that of the starting material.

Attempted Selective Crystallisation of Tetrahydrophenanthrenes (11) *and* (17).—A mixture of the tetrahydrophenanthrene (11) (100 mg) and the deuteriotetrahydrophenanthrene (17) (550 mg) were mixed by crystallisation from absolute ethanol. The 220 MHz spectrum showed a ratio of 1-CH_2 : 4-CH_2 of 1.0 : 1.62. The sample was recrystallised (×3) to give the picrate (425 mg), m.p. 109—110 °C. The ratio of 1-CH_2 : 4-CH_2 was then 1.0 : 1.67.

Reduction of 4-(2-Naphthyl)butyric Acid (8) *to 4-(2-Naphthyl)butan-1-ol* (10a).—The acid (8)[19] (1.2 g) was dissolved in dry THF (10 ml) and cautiously added to a suspension of lithium aluminium hydride (320 mg) in dry THF (30 ml) under dry nitrogen. The mixture was heated under reflux for 2.5 h before cooling to 25 °C and decomposition with Rochelle salt solution (25 ml). Extraction with ether (3 × 50 ml) was followed by washing with saturated sodium carbonate solution (2 × 25 ml) and saturated sodium chloride solution (20 ml). Drying ($MgSO_4$) and removal of the solvent under reduced pressure gave an oil (1.03 g) which crystallised on standing in the fridge. Recrystallisation from ether–pentane gave the alcohol (10a) (0.92 g), m.p. 37—40 °C (lit.,[14] 37—38 °C), *m/e* 200 (83%, M^+), 199 (2), 184 (7), 183 (5), 167 (14), 166 (3), 165 (9), 157 (5), 156 (12), 155 (21), 154 (44), 153 (22), 152 (10),

143 (10), 142 (66), 141 (100), 139 (17), 130 (14), 129 (12), 128 (16), 126 (7), 116 (4), and 115 (52), $\nu_{max.}$ (liquid film) 3 450 (OH), 860, and 900 cm^{-1}, τ 8.34 (4 H, m, $ArCH_2CH_2CH_2$), 7.80br (1 H, s, exchanged with D_2O, CH_2OH), 7.30 (2 H, t, J 7 Hz, $ArCH_2$), 6.44 (2 H, t, J 7 Hz, CH_2OH), and 2.72—2.14 (7 H, m, ArH).

Cyclisation of the Alcohol (10a) *to the Tetrahydrophenanthrene* (11).—The above alcohol (10a) (400 mg) in boron trufluoride–ether (freshly distilled; 40 ml) was heated to reflux under dry nitrogen for 4 h. The green solution was cooled and then poured onto ice (100 g); extraction with ether (3 × 50 ml) and washing with water (3 × 50 ml) was followed by drying ($MgSO_4$) and removal of the solvent under reduced pressure to give a green oil (305 mg). Purification by p.l.c. as above gave the tetrahydrophenanthrene (11) as a pale yellow oil (265 mg), spectroscopically identical to a sample of (11) prepared above. Treatment with picric acid as before and recrystallisation (×2) gave the picrate of (11) as orange needles, m.p. 109—111 °C (mixed m.p. 109—110 °C with an authentic sample of m.p. 110—111 °C).

Reduction of the Acid (8) *to the Dideuterioalcohol* (10b).—The acid (8) (1.6 g) in dry THF (15 ml) was slowly added to a suspension of lithium aluminium deuteride (700 mg; 99% ^2H) in dry THF (50 ml) under dry nitrogen. The mixture was then heated under reflux for 2.5 h. On cooling the mixture was decomposed with Rochelle salt solution (100 ml) and extracted with ether (3 × 50 ml) and the combined organic layers were washed with saturated sodium carbonate solution (2 × 50 ml) and saturated brine (25 ml) before drying ($MgSO_4$). Work up as before gave the crude alcohol as an oil (1.36 g). Crystallisation from ether–pentane afforded the alcohol (10b) (1.24 g), m.p. 36—38 °C, *m/e* 203 (4%, $M+1$), 202 (25, M^+), 201 (0.4), 187 (0.5), 186 (1), 185 (3), 184 (6), 183 (3), 182 (2), 181 (2), 180 (2), 179 (3), 178 (1), 177 (1), 170 (1), 169 (3), 168 (4), 167 (9), 166 (4), 165 (6), 163 (1), 156 (4), 155 (8), 154 (1), 153 (1), 152 (1), 151 (4), 150 (6), 144 (2), 143 (10), 142 (34), 141 (100%), 139 (12), 131 (2), 130 (6), 129 (7), 128 (10), 127 (6), 126 (4), 125 (3), 124 (1), 116 (6), and 115 (44), $\nu_{max.}$ (liquid film) 3 450 (OH), 2 280, 2 180 (C–D), 860, and 900 cm^{-1}, τ 8.34 (4 H, m, $ArCH_2CH_2CH_2$), 7.94br (1 H, s, exchanged with D_2O, CD_2OH), 7.30 (2 H, t, J 7 Hz, $ArCH_2$), 2.72—2.14 (7 H, m, ArH).

Cyclisation of the Deuterioalcohol (10b) *to the Tetrahydrophenanthrene* (13).—The above alcohol (10b) (1.3 g) in boron trifluoride–ether (freshly distilled; 100 ml) was heated at reflux under dry nitrogen for 4 h. The green solution was cooled and poured onto ice (200 g) and extracted with ether (3 × 50 ml). The ether layer was washed with water (5 × 50 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a green oil (1.12 g). Chromatography on grade III neutral alumina (35 g) and elution with light petroleum (b.p. 40—60 °C) gave the oily tetrahydrophenanthrene (980 mg). Treatment with 1.1 moles per mole of picric acid in absolute ethanol (5 ml) gave the crude picrate, m.p. 104—109 °C. Recrystallisation (×5) gave the pure picrate of (13), m.p. 108—110 °C, *m/e* 229 (3%), 210 (3), 209 (11), 199 (4), 197 (6), 196 (9), 186 (3), 185 (3), 184 (80, M^+), 183 (16), 182 (6), 181 (5), 180 (10), 179 (13), 178 (5), 170 (4), 169 (15), 168 (19), 167 (27), 166 (19), 165 (12), 164 (3), 157 (24), 156 (100), 155 (82), 154 (62), 153 (37), 153 (19), 151 (10), 144 (10), 143 (41), 141 (21), 140 (12), 139 (13), 131 (5), 129 (16), 128 (15), 117 (18), 116 (25), 115 (24), and 114 (10), τ (220 MHz) 8.12 (4 H, m, $ArCH_2CH_2CH_2$), 7.15 (2 H, t, J 6 Hz, 1-CH_2), 2.92 (1 H, d, J 8 Hz, 9-H) 2.80—2.38 (3 H, m, 6-, 7-, 10-H), 2.30 (1 H, dd, J 2.8, Hz, H-8), 2.12 (1 H, dd, J 2, 8 Hz, H-5), and 1.02 (2 H, s, ArH of picric acid). Irradiation of the signal at τ 8.12 caused the triplet at τ 7.15 to collapse to a broad singlet; however no effect was seen in the region at τ 7.0, indicating the absence of any resonance corresponding to the 4-CH_2 signal.

Attempted Isomerisation of 1-*Methylnaphthalene with Boron Trifluoride–Ether*.—The hydrocarbon (150 mg) was dissolved in boron trifluoride–ether (20 ml, freshly distilled and heated at reflux temperature under an atmosphere of dry nitrogen for 4.5 h. The red solution was allowed to cool to room temperature before pouring onto ice (150 g). The mixture was extracted with chloroform (3 × 40 ml) and the organic layer washed with 10% sodium carbonate solution (20 ml) and water (20 ml). This was followed by drying ($MgSO_4$) and removal of the solvent under reduced pressure then gave a brown oil (145 mg). Purification by p.l.c. (elution with hexane) gave an oil (108 mg). Examination by ^1H n.m.r. spectroscopy of both the crude and purified material showed only one singlet (τ 7.34) corresponding to the 1-methyl resonance but not the 2-methyl signal (τ 7.52). Conversion to the picrate in the usual way gave a sample, m.p. 140—142 °C (lit.,[24] 141—142 °C). Careful admixture of known weights of the picrates of 1- and 2-methylnaphthalenes in $CDCl_3$ (0.3 ml) revealed that 1% of 2-methylnaphthalene was easily detectable by n.m.r. spectroscopy in the presence of the 1-methyl isomer.

Preparation of the Acid (18a).—This was prepared as described previously[16] in 87% yield, m.p. 108—109 °C (lit.,[16] 108—110 °C), *m/e* 215 (5.8%), 214 (40.0, M^+), 156 (13), 155 (36), 153 (15), 129 (7.4), 128 (6.8), and 127 (5), $\nu_{max.}$ (Nujol) 2 500 (OH), 1 705 (C=O), 780, and 800 cm^{-1}; τ 8.58 (3 H, d, J 6 Hz, $ArCHCH_3$), 7.36 (2 H, m, $ArCHCH_2CO_2H$), 5.82 (1 H, m, ArCH), 2.7—2.42 (4 H, m, 1-, 3-, 6-, 7-H), 2.34—2.06 (2 H, m, 4-, 5-H), and 1.84 (1 H, dd, J 2,8 Hz, 8-H).

Reduction of the Acid (18a) *to the Alcohol* (18b).—The foregoing acid (2.4 g) in dry THF (20 ml) was added dropwise over 5 min to a suspension of lithium aluminium hydride (700 mg) in dry THF (50 ml). The mixture was heated at reflux for 2 h before cooling to 20 °C. The complex was decomposed with Rochelle salt solution (150 ml) and extracted with ether (3 × 50 ml) and the combined ether extracts were washed with saturated sodium carbonate solution (50 ml) and water (50 ml). The organic layer was then dried ($MgSO_4$) and the solvents removed under reduced pressure to give an oil (2.2 g). Distillation under reduced pressure gave 3-(1-*naphthyl*)*butan*-1-*ol* (18b) (1.89 g), b.p. 120—126 °C at 0.5 mmHg (Found: C, 83.9; H, 8.25. $C_{14}H_{16}O$ requires C, 84.0; H, 8.05%), *m/e* 201 (4%), 200 (M^+, 3), 168 (2), 167 (7), 165 (3), 157 (4), 156 (37), 155 (100), 154 (8), 153 (17), 152 (10), 151 (3), 142 (2), 141 (14), 129 (9), 128 (12), 127 (7), 115 (7), and 77 (3). The picrate had m.p. 72—74 °C, $\lambda_{max.}$ 219sh (log ε 4.42), 224 (4.54), 254 (3.07), 262 (3.30), 272 (3.46), 282 (3.56), 293 (3.43), 304 (2.43), 309 (2.25), and 314 nm (2.21) $\nu_{max.}$ (liquid film) 3 450 (OH), 1 600 (C=C), 800, and 780 cm^{-1}, τ 8.64 (3 H, d, J 6 Hz, $ArCHCH_3$), 8.56br (1 H, s, exchanges with D_2O, CH_2OH), 8.40—7.90 (2 H, m, $ArCHCH_2$), 6.38br (2 H, partially obscured t, J 7 Hz, CH_2OH), 6.30 (1 H, m, $ArCHCH_2$), 2.72—2.50 (4 H, m, 2-, 3-, 6-, 7-H), 2.34 (1 H, dd, J 2,8 Hz, 4-H), 2.16 (1 H, dd, J 2,8 Hz, 5-H), and 1.84 (1 H, dd, J 2,8 Hz, 8-H).

Conversion of the Alcohol (18b) *into the Chloride* (18c).—To

the above alcohol (2.3 g) in dry pyridine (5 ml) was added thionyl chloride (redistilled; 20 ml) over 10 min. The solution was heated at reflux for 2 h and allowed to cool. The excess of thionyl chloride was distilled off under reduced pressure to give a brown residue, which was taken up in chloroform (20 ml). The chloroform solution was washed with 2N-HCl (2 × 30 ml), water (30 ml), saturated sodium carbonate solution (25 ml), and water (25 ml), then dried ($MgSO_4$) and the solvent removed under reduced pressure to give a brown oil (2.26 g). Chromatography on Grade III neutral alumina (45 g) afforded the chloride (18c) as a pale yellow oil when eluted with ethyl acetate–light petroleum (b.p. 40—60 °C) (7 : 13), *m/e* 220 (4%, M^+), 219 (2), 218 (13), 185 (26), 184 (44), 183 (66), 167 (36), 166 (6), 165 (21), 157 (26), 156 (69), 155 (100), 154 (44), 153 (59), 152 (59), 151 (13), 142 (11), 141 (66), 131 (10), 129 (42), 128 (52), 127 (33), 115 (38), 108 (61), 107 (32), and 77 (3), $\lambda_{max.}$ 219sh (log ε 4.57), 226 (4.61), 254 (3.60), 268 (3.73), 279 (3.83), 290 (3.85), 302 (3.77), and 309 nm (3.53), $\nu_{max.}$ (liquid film) 1 505 (CCl), 900, 820, and 775 cm^{-1}, τ 8.66 (3 H, d, *J* 8 Hz, $ArCHCH_3$), 8.16—7.60 (2 H, m, CH_2CH_2Cl), 6.56 (2 H, dt, *J* 7,3 Hz, CH_2CH_2Cl), 6.18 (1 H, m, *J* 8 Hz, $ArCHCH_3$), 2.80 (1 H, d, *J* 8 Hz, H-2), 2.62—2.36 (4 H, m, 3-, 4-, 6-, 7-H), 1.80—1.60 (2 H, m, 5-, 8-H).

Conversion of the Chloride (18c) *into the Nitrile* (18d).—The foregoing chloride (2.14 g) in dimethyl sulphoxide (dry; 3 ml) was added slowly over 15 min to a solution of sodium cyanide (500 mg) in dimethyl sulphoxide (24 ml) at 80 °C. The solution was maintained at 80 °C with stirring for 2.5 h. A precipitate formed and the solution was diluted with water (100 ml) and extracted with ether (4 × 25 ml). The ether solution was washed with water (30 ml) and 2N-HCl (30 ml) to hydrolyse a small amount of isocyanide. Finally washing with water, drying ($MgSO_4$), and removal of the solvent under reduced pressure gave the *nitrile* (18d) as a yellow oil (1.93 g), *m/e* 210 (4%), 209 (23, M^+), 194 (2), 156 (14), 155 (100), 154 (9), 153 (18), and 152 (11), $\lambda_{max.}$ 217 (log ε 4.42), 224 (4.61), 252 (3.13), 262 (3.30), 272 (3.47), 282 (3.55), 289 (3.37), 303 (2.82), and 314 nm (2.57), $\nu_{max.}$ 2 550 (C≡N), 1 260, 800, and 780 cm^{-1}, τ 8.6 (3 H, d, *J* 8 Hz, $ArCHCH_3$), 8.1—7.6 (4 H, m, $ArCHCH_2CH_2C{\equiv}N$), 6.2 (1 H, m, $ArCH\text{-}CH_3$) 2.7—2.2 (5 H, m, 2-, 3-, 4-, 6-, 7-H), 2.08 (1 H, dd, *J* 2,8 Hz, 5-H), 1.84 (1 H, dd, *J* 2,8 Hz, 8-H) (Found: M^+, 209.122 4. $C_{15}H_{15}N$ requires *M*, 209.120 4).

Hydrolysis of the Nitrile (18d) *to the Acid* (18e).—The above nitrile (1.90 g) was dissolved in ethylene glycol monomethyl ether (20 ml) containing a solution of potassium hydroxide (7 g) in water (3 ml). The mixture was refluxed under a stream of nitrogen for 10 h. The solution was then diluted with water (20 ml) and acidified with 6N-HCl. The aqueous layer was extracted with ether (3 × 25 ml) and the ether layer washed with water (3 × 50 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave the acid (18e) as an oil (1.65 g), which crystallised from ethyl ether–light petroleum (b.p. 30—40 °C) to give rosettes of needles, m.p. 76—78 °C (lit.,[17] 78—80 °C), *m/e* 229 (4.7%), 228 (28.3, M^+), 168 (9.1), 167 (6.7), 166 (1.5), 165 (4.2), 156 (13.7), 155 (100), 154 (7), 153 (18), 152 (8.9), 151 (2), 129 (5), 128 (7), 127 (5), 115 (5), and 77 (2), $\nu_{max.}$ 2 500 (OH), 1 700 (C=O), 800, and 780 cm^{-1}, τ 8.65 (3 H, d, *J* 7 Hz, $ArCHCH_3$), 8.1—7.5 (4 H, m, $ArCHCH_2CH_2$), 6.34br (1 H, sextet, *J* 8 Hz, $ArCHCH_3$), 2.70—2.40 (4 H, m, 2-, 3-, 6-, 7-H), 2.30 (1 H, dd, *J* 2, 8 Hz, 4-H), 2.16 (1 H, dd, *J* 2.8 Hz, 5-H), 1.90 (1 H, dd, *J* 2.8 Hz, 8-H), and −0.2br (1 H, s, exchanges with D_2O, CMe_2H).

Reduction of the Acid (18e) [17] *to the Alcohol* (18f).—The above acid (1.25 g) in dry THF (10 ml) was cautiously added to a suspension of $LiAlH_4$ (450 mg) in dry THF (50 ml). After heating under reflux for 3 h the mixture was cooled and decomposed with a saturated solution of Rochelle salt. Ectraction with ether (4 × 25 ml) was followed by washing with saturated sodium carbonate solution and then water (25 ml). Drying ($MgSO_4$) and removal of the solvent under reduced pressure gave the crude alcohol as an oil. P.l.c. with 30% ethyl acetate–light petroleum (b.p. 40—60 °C) (3 : 7) gave the alcohol (18f) as an oil (960 mg), *m/e* 215 (5%), 214 (M^+, 26), 167 (3), 166 (2), 165 (4), 157 (2), 156 (16), 155 (100), 154 (7), 153 (15), 152 (7), 151 (1), 141 (7), 129 (8), 128 (8), 127 (6), 115 (6), 86 (4), and 77 (3), $\lambda_{max.}$ 219 (log ε 4.36), 224 (4.49), 254 (3.01), 263 (3.26), 272 (3.39), 278 (3.46), 289 (3.35), 304 (2.78), 314 (2.48), and 319 (2.31), $\nu_{max.}$ 3 400 (OH), 800, and 780 cm^{-1}, τ 8.64 (3 H, d, *J* 8 Hz, $ArCHCH_3$), 8.56—8.10 (4 H, m, $ArCHCH_2CH_2$), 7.9br (1 H, s, exchanges with D_2O, CH_2OH), 6.42 (2 H, t, *J* 7 Hz, CH_2CH_2OH), 6.62—6.10 (1 H, m, $ArCHCH_2$), 2.64—2.42 (4 H, m, 2-, 3-, 6-, 7-H), 2.32 (1 H, dd, *J* 2,8 Hz, 4-H), 2.16 (1 H, dd, *J* 2,8 Hz, 5-H), 1.84 (1 H, dd, *J* 2,8 Hz, 8-H).

Cyclisation of the Alcohol (18f) *to the Hydrocarbons* (20) *and* (21).—The above alcohol (450 mg) in boron trifluoride–ether (freshly distilled; 20 ml) was heated under reflux in an atmosphere of dry nitrogen for 4.5 h. The green solution was allowed to cool before being poured onto ice (100 g). Extraction with ether (3 × 50 ml) was followed by washing with water (3 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a brown oil (341 mg). This was purified by p.l.c. eluting with hexane to give a mixture of the hydrocarbons (20) and (21) [18] (310 mg) which were immediately chromatographically and spectroscopically examined, *m/e* 196 (100%) (field desorption), τ 8.68 (3 H, d, *J* 8 Hz, 1-CH_3), 8.64 (3 H, d, *J* 8 Hz, 4-CH_3), 8.08 (4 H, m, 2- and 3-CH_2), 7.08 (3 H, m, 1-CH_2 and 1-$CHCH_3$), 6.90 (3 H, m, 4-CH_2), 6.46 (1 H, m, 4-$CHCH_3$), 2.94—2.36 (4 H, m, 6-, 7-, 9-, 10-H), 8.18 (1 H, dd, *J* 2,8 Hz, H-8), 1.92 (1 H, dd, *J* 2,8 Hz). When the resonance at τ 6.46 was irradiated the doublet at τ 8.64 collapsed to a singlet. Similar irradiation of the signal at τ 7.08 caused the doublet at 8.68 to collapse to a singlet. Analysis of the area of the signal at τ 6.46 by tracing and weighing showed the ratio of (20) : (21) to be *ca.* 3 : 1. H.p.l.c. separation was effected on a 25 cm stainless steel column of internal diameter 46 mm packed with Partisil 5, particle size 5. Elution was with hexane, b.p. 60—80 °C and the pump speed was 1 ml min^{-1}. This indicated the ratio of (20) : (21) to be 76 : 24.

Dehydrogenation of the Hydrocarbons (20) *and* (21) *to the Phenanthrenes* (22) *and* (23).—The mixture of tetrahydrophenanthrenes (196 mg) was dissolved in benzene (2 ml) and a solution of dichlorodicyanobenzoquinone (DDQ) (114 mg) in benzene (1 ml) was added and the blue-black solution heated under reflux for 1 h when the solution was a pale orange colour. A further portion of DDQ (114 mg) in benzene (1 ml) was then added. Heating was continued for a further 2 h before the solvent was removed under reduced pressure. P.l.c. (elution with hexane) gave the methylphenanthrenes (22) and (23) (95 mg), *m/e* 193 (16%), 192 (M^+, 100), 191 (59), 190 (15), 189 (33), 188 (3), 187 (4), 182 (5), 181 (31), 180 (2), 179 (8), 178, (23), 177 (3), 176 (5), 167 (4), 166 (8), 165 (25), 164 (3), 163 (4), 155 (3), 154 (2), 153 (5), 152 (7), 151 (4), 150 (2), and 141 (4), $\lambda_{max.}$ 252 (log ε 4.9), 277 (4.2), 284 (4.0), 296 (4.2), 318 (2.50), 325 (2.51),

332 (2.74), 340 (2.6) and 349 nm (2.79), τ 7.30 (1 H, s, 1-CH_3), 6.90 (1 H, s, 4-CH_3), 2.84—2.00 (8 H, m, ArH), 1.46 [1 H, m, 5-H of (23)], and 1.19 [1 H, dd, *J* 22, 8 Hz, 5-H of (22)]. Irradiation of the signal at τ 6.9 caused 14% increase in the signal at τ 1.19. Similar irradiation of the signal at τ 7.30 had little or no effect on the resonances at τ 1.19 and 1.46. The ratio of the methyl resonances 4-CH_3 : 1-CH_3 was found to be 75 : 25 by tracing and weighing of the signals at τ 6.90 and 7.30.

4-(4-*Methoxy*-1-*naphthyl*)*butyric Acid* (26).—This was prepared as previously described [21] in 78% yield, m.p. 129—130 °C, *m/e* 245 (5.5%), 244 (36.5, M^+), 173 (1), 172 (13.5), 171 (100), 170 (0.5), 129 (3), 128 (11), and 127 (3), $\nu_{max.}$ 3 200 (OH), 1 700 (C=O), and 1 095 cm^{-1}, τ 7.95 (2 H, m, $ArCH_2CH_2CH_2$), 7.68 (2 H, t, *J* 8 Hz, $CH_2CH_2CO_2H$), 6.98 (2 H, t, *J* 8 Hz, $ArCH_2$), 6.06 (3 H, s, $ArOCH_3$), 3.28 (1 H, *J* 7 Hz, 3-H), 2.80 (1 H, d, *J* 7 Hz, 2-H), 2.62—2.40 (2 H, m, 6-, 7-H), 2.00 (1 H, dd, *J* 3,8 Hz 5-H), and 1.66 (1 H, dd, *J* 3, 8 Hz, 8-H).

Reduction of the Acid (26) *to the Alcohol* (27a).—The above acid (1.5 g) in dry THF (25 ml) was added dropwise with stirring to a suspension of lithium aluminium hydride (0.5 g) in THF (35 ml). The mixture was heated under reflux temperature for 2.5 h before cooling and decomposition with Rochelle salt solution. Extraction with ether (3 × 50 ml), washing with saturated sodium carbonate solution (20 ml), and drying ($MgSO_4$) was followed by removal of the solvent to give a pale yellow oil (1.37 g). Distillation under reduced pressure gave the alcohol (27a) as an oil (1.16 g), b.p. 141—147 °C at 0.1 mmHg, *m/e* 231 (4.9%), 230 (28, M^+), 229 (17), 228 (0.2), 173 (1), 172 (12.8), 171 (100), 129 (2), 128 (16) 115 (3), and 91 (5), $\lambda_{max.}$ 217 (log ε 4.37), 237 (4.38), 240sh (4.36), 287sh (3.94), 299 (3.76), 311 (3.67), 317sh (3.58), and 324 nm (3.52), $\nu_{max.}$ (liquid film) 3 550 (OH), 1 100, 820, and 770 cm^{-1}, τ 8.32 (5 H, m, $ArCH_2CH_2CH_2CH_2CH$), 7.02 (2 H, t, *J* 8 Hz, $ArCH_2$), 6.38 (2 H, t, *J* 7 Hz, CH_2OH), 6.06 (3 H, s, $ArOCH_3$), 3.30 (1 H, d, *J* 8 Hz, 3-H), 2.80 (1 H, d, *J* 8 Hz, 2-H), 2.60—2.38 (2 H, m, 6-, 7-H), 2.02 (1 H, dd, *J* 3,8 Hz, 5-H), and 1.68 (1 H, dd, *J* 3,8 Hz, 8-H). The *picrate* formed red needles from ethanol, m.p. 82—84 °C (Found: C, 55.0; H, 4.7; N, 9.1. $C_{21}H_{21}N_3O_9$ requires C, 54.9; H, 4.6; N, 9.15%).

Cyclisation of the Alcohol (27a) *to the Hydrocarbon* (28).—The above alcohol (1.25 g) in boron trifluoride–ether (50 ml) was heated under reflux in dry nitrogen for 2.5 h. The mixture was allowed to cool and the green solution extracted with ether (3 × 50 ml). The combined ether extracts were washed with water (25 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure to give a green oil (944 mg). P.l.c. [ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 19)] gave the methoxytetrahydrophenanthrene as a pale yellow oil (878 mg), *m/e* 213 (15%), 212 (100, M^+), 211 (8), 199 (10), 198 (5), 187 (3), 186 (22), 185 (10), 184 (13), 183 (11), 182 (7), 181 (7), 180 (6), 179 (3), 173 (2), 172 (3), 171 (6), 170 (4), 109 (5), 168 (4), 167 (6), 166 (8), 165 (3), 156 (2), 155 (6), 154 (8), 153 (9), 152 (3), 144 (2), 143 (12), 142 (7), 141 (5), 140 (2), 139 (2), 130 (3), 129 (5), 128 (3), 127 (2), 117 (4), 116 (6), and 115 (5), $\lambda_{max.}$ 213 (log ε 4.44), 243 (4.50), 252sh (3.58), 289 (3.70), 301 (3.72), 314 (3.59), and 324 nm (3.49), $\nu_{max.}$ 1 640, 1 620 (C=C), 1 320, 1 285, and 860 cm^{-1}, τ ($CDCl_3$) 8.1 (4 H, m, 2- and 3-CH_2), 7.12 (2 H, overlapping t, *J* 7 Hz, 1-CH_2), 6.98 (2 H, overlapping t, *J* 7 Hz, 4-CH_2), 6.06 (3 H, s, $ArOCH_3$), 3.48 (1 H, s, 10-H 2.62—2.34 (2 H, m, 6-, 7-H), 2.08 (1 H, dd, *J* 2,8 Hz, 8-H), and 1.74 (1 H, dd, *J* 2.8 Hz, 5-H). Irradiation of the resonance at τ 8.1 caused the two overlapping triplets corresponding to the 1- and 4-CH_2 signal to collapse to two broad singlets; however base line resolution was not obtained. The *picrate* deposited from absolute ethanol as dark red needles, m.p. 121—121.5 °C (Found: C, 57.5; H, 4.45; N, 9.65. $C_{21}H_{19}N_3O_8$ requires C, 57.1, H, 4.35; H, 9.5%).

Reduction of the Acid (26) *to the Dideuteriolalcohol* (27b).—The acid (26) (1.5 g) in dry THF (25 ml) was added dropwise with stirring to a suspension of lithium aluminium deuteride (0.5 g; 99% ^2H). The mixture was heated under reflux for 3 h before cooling and decomposition with Rochelle salt solution (25 ml). Extraction with ether (3 × 50 ml), washing with saturated sodium carbonate solution (20 ml), and drying ($MgSO_4$) was followed by removal of the solvent under reduced pressure to give the alcohol (27b) as a pale yellow oil (1.38 g). The compound was chromatographically and spectroscopically pure and was used without further purification as described below, *m/e* 233 (6%), 232 (28, M^+), 231 (1), 229 (3), 186 (1), 185 (2), 184 (3), 173 (2), 172 (14), 171 (100), 170 (1), 169 (3), 141 (5), 140 (2), 139 (3), 131 (5), 129 (4), and 128 (13), $\nu_{max.}$ (liquid film) 3 550 (OH), 2 280, 2 180 (C–D), 1 100, 820, and 770 cm^{-1}; τ 8.32 (4 H, m, $ArCH_2CH_2CH_2$), 7.56br (1 H, s, CH_2OH), 7.00 (2 H, t, *J* 7 Hz, $ArCH_2$), 6.06 (3 H, s, $ArOCH_3$), 3.25 (1 H, d, *J* 8 Hz, 3-H), 2.75 (1 H, d, *J* 8 Hz, 2-H), 2.58—2.30 (2 H, m, 6-, 7-H 7), 2.02 (1 H, dd, *J* 3, 8 Hz, 5-H), and 1.68 (1 H, dd, *J* 3,8 Hz, 8-H).

Cyclisation of the Alcohol (27b) *to the Dideuteriotetrahydrophenanthrenes* (29) *and* (30).—The alcohol (1.1 g) in boron trifluoride–ether (45 ml) was heated under reflux in dry nitrogen for 2.5 h. The mixture was cooled to 20 °C and the green solution extracted with ether (3 × 50 ml). The combined ether extracts were washed with water (2 × 50 ml) and the ether was dried ($MgSO_4$) and then evaporated under reduced pressure to give a brown oil (870 mg). The oil was purified by p.l.c. Elution with ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 19) gave the crude tetrahydrophenanthrenes (29) and (30). Conversion of the mixture into the picrates as previously described, and recrystallisation (×2) gave red needles, m.p. 120—122 °C, τ (360 MHz) 8.1 (4 H, m, 2 and 3-CH_2), 7.02 (2 H, t, *J* 7 Hz, 1-CH_2), 7.16 (2 H, t, *J* 7 Hz, 4 CH_2), 6.06 (3 H, s, $ArOCH_3$), 3.52 (1 H, s, 10-H), 2.64 (1 H, t, *J* 5 Hz, 6-H), 2.57 (1 H, t, *J* 5 Hz, 7-H), 2.16 (1 H, d, *J* 8 Hz, 8-H), 1.87 (1 H, d, *J* 8 Hz, 5-H), and 1.92 (2 H, s, ArH of picric acid). Analysis of the 1- and 4-CH_2 signals by tracing and weighing showed that the ratio of the 4-: 1-CH_2 signals and hence of (29) : (30) was 1.6 : 1.

1-*Oxo*-9-*methoxy*-1,2,3,4-*tetrahydrophenanthrene* (35).—This was prepared as previously described [23] in 84% yield, m.p. 97—98 °C (lit.,[16] 98 °C), *m/e* 227 (16.6%), 226 (100, M^+), 225 (4), 211 (3), 198 (5), 197 (4), 185 (13), 184 (8), 183 (6), 171 (2.5), 170 (27.3), 169 (1.4), 165 (3), 155 (6), 154 (1), 153 (2), 152 (2), 141 (7), 128 (1), 127 (6), and 126 (2), $\lambda_{max.}$ 221 (4.47), 253 (4.5), 261 (4.6), 287 (3.9), 298 (3.9), 312 (3.7), and 354 nm (3.7), τ 7.72 (2 H, q, *J* 7 Hz, $ArCH_2CH_2$), 7.28 (2 H, t, *J* 7 Hz, $CH_2C{=}O$), 6.64 (2 H, t, *J* 7 Hz, $ArCH_2$), 5.98 (3 H, s, $ArOCH_3$), 2.54 (1 H, s, 10-H), 2.46—2.26 (2 H, m, 6-, 7-H), 1.88 (1 H, dd, *J* 3, 8 Hz, 8-H), 1.64 (1 H, dd, *J* 3,8 Hz, 5-H), δ_C (noise decoupled) 22.9 (C-3), 25.0 (C-2), 38.3 (C-4), 55.5 (OCH_3), 99.3 (C-10), 177.7, 124.5, 127.0, 127.7, 128.4, 130.2, 132.4, 135.6, 154.1, and 198.4 p.p.m. (C=O).

Reduction of the Ketone (35) *to the Tetrahydrophenanthrene*

(28).—The above ketone (200 mg) in diglyme (8 ml; dry; freshly distilled) containing $NaBH_4$ (350 mg) was treated with a solution of boron trifluoride–ether (2.95 ml; freshly distilled) in diglyme (6.5 ml) and the mixture stirred at 20 °C for 6 h. The mixture was then poured into water (100 ml) and extracted with ether (3 × 30 ml). The ether extracts were washed with saturated sodium carbonate solution (30 ml) and water (6 × 50 ml) and dried ($MgSO_4$) before removal of the solvent under reduced pressure to give a yellow oil (166 mg). P.l.c. [elution with ethyl acetate–light petroleum (1 : 19)] gave the tetrahydrophenanthrene (28) as an oil (150 mg) whose spectroscopic and chromatographic properties were identical with those of (28) described previously. Conversion to the picrate gave dark red needles, m.p. 120—121 °C. An authentic sample of the picrate of (28), m.p. 120—121.5 °C, gave a mixed m.p. 120—121.5 °C.

Reduction of the Ketone (35) *to the Dideuteriotetrahydrophenanthrene* (29).—The above ketone (1 g) in dry diglyme (40 ml) containing sodium borodeuteride (1.75 g; 98% ^2H) was treated dropwise over 15 min with a solution of boron trifluoride–ether (15 ml; freshly distilled) in diglyme (35 ml) and the mixture stirred for 6 h at 20 °C. The solution was then poured into water (500 ml) and extracted with ether (3 × 50 ml). The combined ether extracts were washed with saturated sodium carbonate solution (100 ml) and water (6 × 100 ml). Drying ($MgSO_4$) and removal of the solvent under reduced pressure gave an oil. Chromatography of this on neutral alumina (35 g; grade III) and elution with ethyl acetate–light petroleum (b.p. 40—60 °C) (1 : 19) gave the hydrocarbon (29) as an oil (750 mg, *m/e* 215 (16.9%), 214 (100, M^+), 213 (48), 212 (8.3), 200 (1.8), 199 (10.5), 198 (5.66), 197 (3), 196 (2), 187 (3), 186 (23), 185 (11), 184 (15), 183 (13), 182 (8), 181 (7), 180 (6), 179 (4), 178 (1), 173 (2), 172 (3), 171 (6), 170 (4), 169 (5), 168 (4), 167 (7), 166 (7), 165 (3), 150 (2), 155 (5), 154 (7), 153 (8), 152 (4), 144 (2), 143 (12), 142 (7), 141 (6), 140 (3), 139 (2), 130 (3), 129 (4), 128 (3), 117 (3), 116 (6), 115 (5), and 107 (4), $\nu_{max.}$ (liquid film) 2 280, 2 180 (C–D), 1 320, 1 285, and 860 cm^{-1}. Treatment as before, with picric acid gave the picrate of (29) which after two recrystallisations afforded red needles (1.34 g), m.p. 120—122 °C, τ (220 MHz) 8.10 (4 H, m, 2- and 3-CH_2), 7.08 (2 H, t, *J* 7 Hz, 4-CH_2), 6.12 (3 H, s, $ArOCH_3$), 3.60 (1 H, s, 10-H), 2.80—2.62 (2 H, m, 6-, 7-H), 2.32 (1 H, d, *J* 8 Hz, 8-H), 2.06 (1 H d, *J* 8 Hz, 5-H), and 1.28 (2 H, s, ArH of picric acid). A small signal at τ 7.16 indicated the presence of 10% of the hydrocarbon (28).

Attempted Isomerixation of the Hydrocarbon (29) *to the Isomer* (30) *with Boron Trifluoride–Ether.*—The above picrate (640 mg) in ether (100 ml) was washed with dilute ammonia solution (3 × 75 ml) and then with water (75 ml) The ether layer was dried (K_2CO_3) and the ether removed under reduced pressure to give an oil. P.l.c. [ethyl acetate–light petroleum (b.p. 40—60 °C) (1 : 19)] gave again the hydrocarbon (29) (316 mg). This was dissolved in boron trifluoride–ether (18 ml; freshly distilled) and heated at reflux temperature under dry nitrogen for 3 h. The green solution was cooled and poured onto ice (200 g) and extracted with ether. The ether solution was filtered and dried ($MgSO_4$) and the solvent removed under reduced pressure to give a green-brown oil. P.l.c. as before gave the recovered hydrocarbon (29) (185 mg). Conversion to its picrate and recrystallisation gave a sample, m.p. 120—121.5 °C. Analysis of the ^1H n.m.r. spectrum at 220 MHz revealed that the small signal at τ 7.16 was now 13.5% of the total of that of the 1- and 4-CH_2 groups.

Attempted Isomerisation of the Hydrocarbon (29) *to the Isomer* (30) *with Boron Trifluride–Ether in the Presence of* 1 *Mole per Mole of Water.*—The picrate of (29) (680 mg) in ether (100 ml) was washed with dilute ammonia solution (3 × 75 ml) followed by water (75 ml). The ether layer was dried (K_2CO_3) and the solvent removed under reduced pressure to give an oil which was purified as previously described to give the hydrocarbon (29) (328 mg). This was dissolved in boron trifluoride–ether (18 ml; freshly distilled) and water (31.1 mg) was added. The mixture was heated at reflux temperature under dry nitrogen for 3 h. Isolation of the hydrocarbon as in the previous experiment gave an oil (165 mg) whose picrate had, after two crystallisations, m.p. 118.5—121.5 °C. The n.m.r. spectrum at 220 MHz revealed that the signal at τ 7.16 was now 14.2% of the total methylene signals. In addition new signals at τ 8.45 (3 H, t, *J* 7.5 Hz, $ArOCH_2CH_3$) and 5.9 (2 H, q, *J* 7.5 Hz, $ArOCH_2CH_3$) were present which were consistent with 21% of the transetherification product (31).

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