Aust. J. Chem., 1995, **48**, 1707–1725

Synthesis of Helical Molecules Based on 5,6,6a,7,8,12b-Hexahydrobenzo[*c*]-phenanthrene-5,8-dione

Julie Cheung,[A] *Leslie D. Field,*[A] *Francesca Regaglia*[A] *and Sever Sternhell*[A,B]

[A] Department of Organic Chemistry, University of Sydney, N.S.W. 2006.
[B] Author to whom correspondence should be addressed.

Abstract

Synthetic routes based on Newman's[1–7] synthesis of a number of polycyclic aromatic hydrocarbons were modified and developed to give a convenient preparation (Scheme 1) of 11 helical molecules formally based on hexalindione (1). In contrast to Newman's work,[1–7] we determined the stereochemistry at C6a–C12b in (1a–k) and, in some cases, were able to control it. We also investigated the competitive formation of six- and seven-membered rings in the reaction yielding the hexacyclic derivatives (1d, e). In addition, we report an unusual fragmentation (Scheme 2) leading to the unexpected by-product 4-methoxyacetophenone (16) in the synthesis of (1h).

Introduction

While large polymeric helical molecules, such as DNA and segments of proteins, are common, non-polymeric organic molecules which adopt helical structures are relatively rare. Limited examples of these small helical molecules include helicenes,[8] hindered biaryls[9] and 4,5-disubstituted dihydrophenanthrenes.[10] In these molecules, a strain is produced by the overcrowding of non-bonded atoms or groups and this strain is relieved by bond bending and bond stretching. Helical structures are thus generated in these molecules by distortions in the geometry.

Small helical molecules are of interest for two reasons. Firstly, helical molecules are inherently chiral due to their twisted skeletons and therefore can either be right- or left-handed in orientation. These molecules can racemize (i.e., interconvert between the right- and left-handed helix) by inversion and the kinetic studies of such processes were expected to provide an extension to the variety of processes

[1] Newman, M. S., and Wolf, M., *J. Am. Chem. Soc.*, 1952, **74**, 3225.
[2] Newman, M. S., and Wise, R. M., *J. Am. Chem. Soc.*, 1956, **78**, 450.
[3] Newman, M. S., and Lednicer, D., *J. Am. Chem. Soc.*, 1956, **78**, 4765.
[4] Newman, M. S., and Phillips, D. R., *J. Am. Chem. Soc.*, 1959, **81**, 3667.
[5] Newman, M. S., and Boden, H., *J. Org. Chem.*, 1961, **26**, 1759.
[6] Newman, M. S., Mentzer, R. G., and Slomp, G., *J. Am. Chem. Soc.*, 1963, **85**, 4018.
[7] Newman, M. S., and Blum, J., *J. Am. Chem. Soc.*, 1964, **86**, 503.
[8] Laarhoven, W. H., and Prinsen, W. J. C., *Top. Curr. Chem.*, 1984, **125**, 63, and references therein.
[9] Bott, G., Field, L. D., and Sternhell, S., *J. Am. Chem. Soc.*, 1980, **102**, 5618.
[10] Cosmo, R., and Sternhell, S., *Aust. J. Chem.*, 1987, **40**, 35, 1107; Cosmo, R., Hambley, T. W., and Sternhell, S., *J. Org. Chem.*, 1987, **52**, 3119.

Manuscript received 21 February 1995 0004-9425/95/101707$10.00

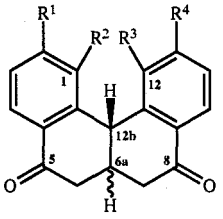
already examined[9–12] in the quantitative studies of the relationship between the molecular deformation and inversion barriers in well defined molecular frameworks.

Secondly, as a result of their chirality, these helical molecules must exhibit chiroptic properties when resolved. The pure enantiomers could be useful as chiral auxiliaries for chiral inductions, as cosupports for chromatography or as shift reagents for n.m.r. spectroscopy. In addition, they may act as orienting agents in liquid-crystalline phases,[13] possibly providing materials for electrooptical display devices, or in larger biological systems such as cell membranes.

This work describes the synthesis of a number of small helical molecules (1a–k) (Table 1) based on the 5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione skeleton (1) which will be referred to as hexalindione derivatives. These diones were designed to be amenable to a large range of chemical modifications for the purposes of inversion and chiroptic studies. In particular, the energy penalty associated with the inversion process of these molecules was expected to be the direct consequence of the non-bonded interaction of the groups at C 1 and C 12, and thus the inversion rates of these molecules could be controlled by modifications at these two positions. In addition, modifications at the carbonyl groups (C 5 and C 8) would permit systematic variation for chiroptic studies by, e.g., altering the length of attachments at C 5 and C 8.

Table 1. Derivatives of 5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1) synthesized by the sequence described in Scheme 1

Compound	Stereochemistry at C 6a–C 12b	Substituents R^1	R^2	R^3	R^4	Overall yield (%)
(1a)	*trans*	H	H	H	H	15
(1b)	*cis*	H	H	H	H	2
(1c)	*trans*	benzo		H	H	8
(1d)	*trans*	benzo		benzo		9
(1e)	*cis*	benzo		benzo		2
(1f)	*trans*	H	Me	Me	H	18
(1g)	*cis*	H	Me	Me	H	2
(1h)	*trans*	H	OMe	OMe	H	4
(1i)	*trans*	H	Me	H	H	24
(1j)	*trans*	H	OMe	H	H	14
(1k)	*cis*	H	OMe	H	H	6



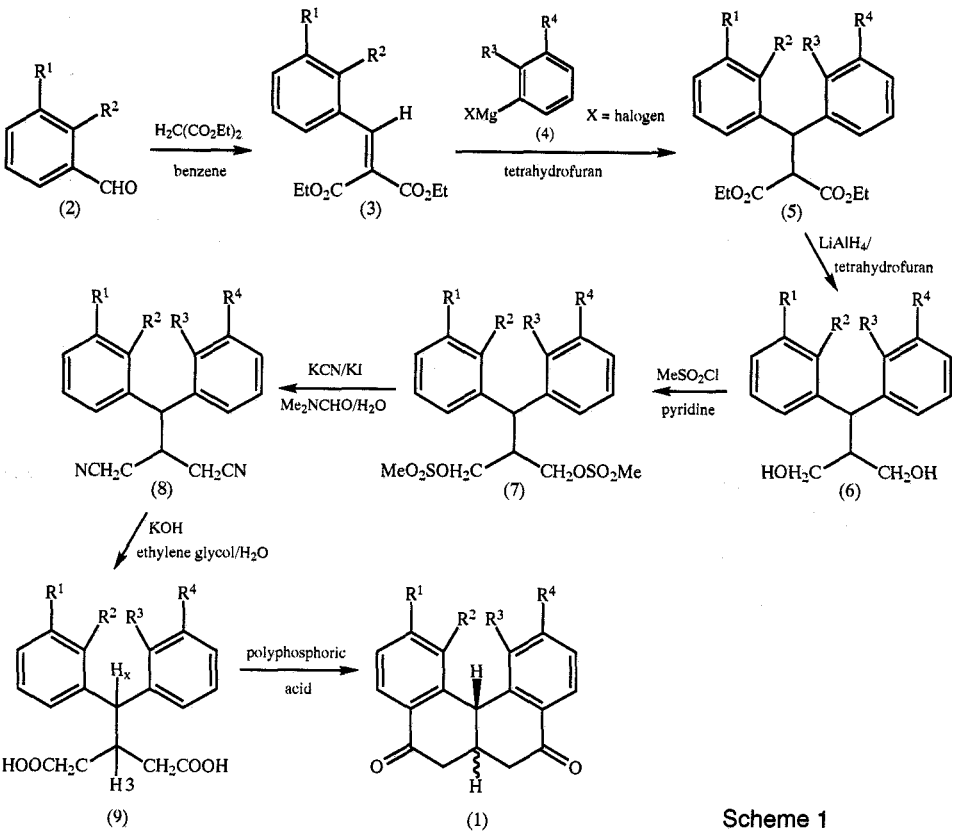
(1)

Preparation of Compounds

Having established the family of hexalindiones (1) as the synthetic targets, we chose a modified method of Newman *et al.*[1–7] as the basis of the general synthetic sequence (Scheme 1). Newman[1,3,5,7] has reported the synthesis of a number of the series: a mixture of (1a,b), a mixture of (1f,g), (1i), and a mixture of (1j,k), but most of the intermediates were not fully characterized. He also did not consider in detail the nature of the stereochemistry at the C 6a–C 12b junction.

[11] Newsom, I. A., Ph.D. Thesis, The University of Sydney, 1983.
[12] Crossley, M. J., Field, L. D., Forster, A. J., Harding, M. M., and Sternhell, S., *J. Am. Chem. Soc.*, 1987, **109**, 341.
[13] Solladié, G., and Zimmermann, R. G., *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 348.

In the present work, a number of helical compounds of this kind were prepared (Table 1) by varying the nature of the aromatic aldehyde (2) used as the starting material and the Grignard reagent (4) used in the second step in Scheme 1. The target molecules, as well as all the important intermediates, were fully characterized (see Experimental).



Scheme 1

Newman[3] assumed that the diones formed were totally of the *trans* form, derived from ring fusions of the less strained rotamer (9α) of the preceding glutaric acids (Fig. 1). However, we found that in some cases [diones (1c,i)] only the *trans* isomers were formed, and in the remaining diones both *cis* and *trans* isomers were present. The presence of the two isomeric products could be rationalized on the following grounds.

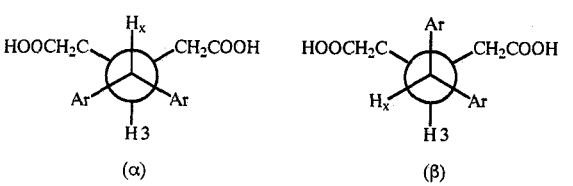


Fig. 1. The two possible rotamers (α) and (β) of the glutaric acids (9).

The stereochemistry of the diones was determined by the ring closure of the glutaric acids, and there are two possible rotamers of the glutaric acids (9)

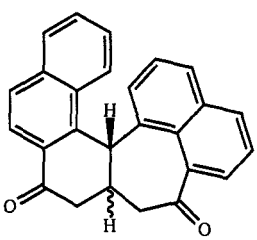
(Fig. 1) which may undergo ring closure. At room temperature, the glutaric acids (9) exist predominantly in the form of rotamer (α) because the coupling constants $^3J(H_x,H3)$ in the ^1H n.m.r. spectra have the values of approximately 12 Hz, corresponding to the conformation in which the two protons are *anti* with respect to one another. The predominant cyclization products, the *trans* form, were thus obtained as a result of the cyclization proceeding via the more stable rotamer (α). The rotamer (β) would cyclize to give the corresponding *cis* dione.

Table 2. Ratio and combined yields of *trans*-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1a) and *cis*-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1b) obtained from the glutaric acid (9; $R^1 = R^2 = R^3 = R^4 = H$) at various reaction temperatures

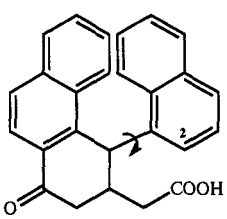
Temp. (°C)	Time (min)	Ratio of *trans* (1a) to *cis* (1b)	Combined yield (%)	Temp. (°C)	Time (min)	Ratio of *trans* (1a) to *cis* (1b)	Combined yield (%)
180	5	1·5:1	34	95	60	7·2:1	80
165	10	1·7:1	40	85	90	8·3:1	63
120	40	6·4:1	90	65	300	9·5:1	58

In the synthesis of diones (1a,b), the cyclization process was further investigated by carrying out the reaction at various temperatures. It was found that the cyclization step was kinetically controlled. As the reaction conditions became more severe, the proportion of *cis* dione (1b) formed increased (Table 2). The reaction time was increased as the reaction temperature was lowered in order for the reaction to reach completion. The ratios of the two isomers were determined by g.l.c. Since the ring closure was irreversible, the distribution of the products obtained was presumably determined by the equilibrium that exists between rotamers (9α; Ar = phenyl) and (9β; Ar = phenyl). At lower temperatures (65–70°), the equilibrium favoured the more stable rotamer (9α; Ar = phenyl) producing predominantly the *trans* dione (1a). As the temperature was increased, the proportion of the less stable rotamer (9β; Ar = phenyl) began to increase, generating an increasing proportion of the *cis* dione (1b).

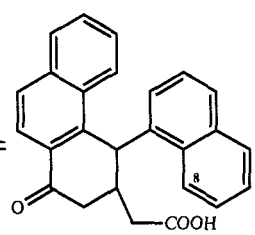
In the case where R^1–R^2 = benzo, R^3–R^4 = benzo, an additional product, the dione (10), was also formed. The diones (1d,e) and (10) were presumably derived from the (unobserved) intermediate rotamers (11) which can cyclize either at C 2 or C 8.



(10)



(11a)

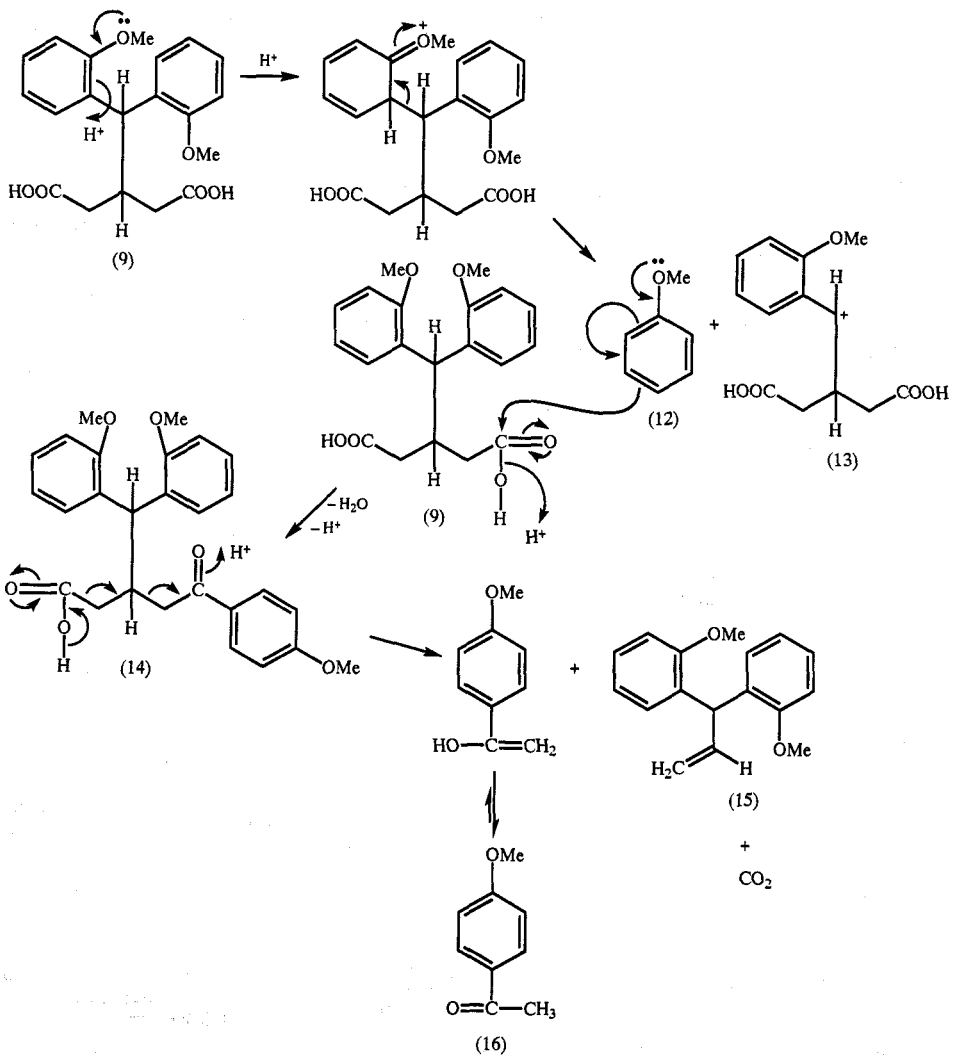


(11b)

Although C 8 would be expected to be the more reactive site due to steric and electronic factors, the formation of a seven-membered ring is presumably not as favourable as the formation of a six-membered ring, and thus only a small proportion of dione (10) was obtained.

Dione (10) was the only product obtained by Newman[3] when he carried out the cyclization of glutaric acid (9; R^1–R^2 = benzo, R^3–R^4 = benzo), in two steps using hydrogen fluoride followed by aluminium chloride. However, the stereochemistry of the obtained product was not determined. In the present work, the cyclization of glutaric acid (9; R^1–R^2 = benzo, R^3–R^4 = benzo) in the presence of polyphosphoric acid gave dione (10) in both *trans* and *cis* forms, as well as diones (1d,e).

The cyclization of the glutaric acid (9; $R^1 = R^4 = H$, $R^2 = R^3 = OMe$) gave two major products: dione (1h) and 4-methoxyacetophenone (16) in similar proportion. A possible mechanism for the generation of compound (16) is shown in Scheme 2. In the presence of polyphosphoric acid, the glutaric acid (9; $R^1 = R^4 = H$, $R^2 = R^3 = OMe$) undergoes a two-step rearrangement to generate anisole (12). An acid-catalysed electrophilic substitution of anisole (12) by the carbonyl group



Scheme 2

of the glutaric acid (9) occurs predominantly in the *para* position producing the intermediate (14). Further rearrangement of this intermediate (14) in the presence of excess acid leads to the eventual formation of 4-methoxyacetophenone (16). The postulated by-product (15) is presumably consumed by the polyphosphoric acid.

The reaction was repeated under the same condition but with the addition of a four times molar excess of anisole (12). On the basis of the ^{1}H n.m.r. spectrum of the crude product, the reaction proceeded to give the same major products (1h) and (16) in 50% total yield, as well as at least 10 other minor products containing methoxy groups as seen by the numerous methoxy signals around δ 3. Attempts to isolate the intermediates (14) and (15) failed. The ^{1}H n.m.r. spectrum and the g.l.c. of the crude product also showed that there was an increased amount of 4-methoxyacetophenone (16) (Table 3). This indicated that anisole was indeed formed during the cyclization step of the glutaric acid (9) which led to the formation of (16), and is therefore consistent with the mechanism proposed in Scheme 2. The formation of this by-product (16) is kinetically controlled; as the temperature of the reaction was lowered (120°), the proportion of this compound decreased (Table 3).

Table 3. The ratios and combined yields of dione (1h) and 4-methoxyacetophenone (16) at various reaction conditions

Reaction condition	Ratio of (1h) to (16)	Yield (%)
Polyphosphoric acid, 120°	2·6:1	26
Polyphosphoric acid, 140°	1·4:1	67
Polyphosphoric acid+anisole, 140°	0·3:1	50

Thus a large variety of helical molecules of this kind can be generated by the described synthetic route. Provided that the cyclization step is carried out at a moderate temperature and that the steric interaction of the groups at the bay positions (C 1 and C 12) is relatively large, the *trans*-isomers of the diones (1) can be generated essentially free from the *cis*-isomers.

Experimental

General Procedures

Melting points were determined on a Reichert Micro Melting Point Apparatus and are uncorrected.

The basic ^{1}H n.m.r. data in this section were acquired on Bruker WM 400 (400 MHz), Bruker AMX 400 (400 MHz), Bruker AC 200F (200 MHz) and Varian EM 390 (90 MHz) spectrometers as dilute solutions in $CDCl_3$. Each signal is recorded in terms of chemical shifts (in ppm) from internal $SiMe_4$, multiplicity, coupling constant in Hz, and assignment. The proton noise decoupled ^{13}C n.m.r. data were acquired on a Bruker AC 200F (50 MHz) spectrometer. Each signal is described in terms of chemical shift in ppm downfield from $SiMe_4$, and assignment.

Infrared spectra were recorded on a Digilab FTS 20/80 Fourier-transform spectrometer, a Perkin–Elmer 710B spectrophotometer or a Perkin Elmer 1600 FTIR spectrometer. Ultraviolet spectra were recorded on a Hitachi 150-20 spectrophotometer.

Mass spectra were obtained on an AEI MS 902 (modified) mass spectrometer at 70 eV. Peaks are described in terms of mass/charge ratio (m/z) and intensity (%) relative to the base peak.

Microanalyses were performed by the Commonwealth Microanalytical Service, Melbourne, or the Microanalytical Unit, University of New South Wales.

trans-5,6,6a,7,8,12b-Hexahydrobenzo[_c_]phenanthrene-5,8-dione (1a)

Diethyl Benzylidenemalonate (3a)

A mixture of benzaldehyde (2a) (26 g, 0·25 mol), diethyl malonate (44·24 g), benzoic acid (1·65 g), piperidine (2·21 ml) and benzene (50 ml) was heated at reflux for 23 h by using a water condenser fitted with a Dean–Stark apparatus. After 5·4 ml of water (120% of theoretical quantity) had been collected, benzene (50 ml) was added and the organic layer was washed with hydrochloric acid (3 M), water and saturated sodium hydrogen carbonate solution, then dried over anhydrous calcium chloride, and filtered. Evaporation of the solvent under reduced pressure yielded the crude material as a dark orange oil which was distilled to give diethyl benzylidenemalonate (3a) (65·14 g, 95%) as a clear oil, b.p. 125–130°/0.4 mmHg (lit.[14] 140–142°/4 mmHg). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 1·29, t, J 7·0 Hz, 3H, CH_3; 1·34, t, J 7·0 Hz, 3H, CH_3; 4·31, q, J 7·0 Hz, 2H, CH_2; 4·33, q, J 7·0 Hz, 2H, CH_2; 7·35–7·47, m, 5H, 5×ArH; 7·75, s, 1H, olefinic H.

Diethyl Benzhydrylmalonate (5a)

A solution of phenylmagnesium iodide (4a) in ether was prepared by the addition of iodobenzene (8 g) to a suspension of magnesium turnings (1 g) in dry ether (50 ml) over 1 h at such a rate as to maintain a gentle reflux. A crystal of iodine was added to initiate the reaction. After cooling to room temperature, a solution of diethyl benzylidenemalonate (3a) (6·07 g, 26 mmol) in dry ether (50 ml) was added and the resultant solution was heated at reflux for 4 h under nitrogen. The ether solvent was then replaced with benzene, and the reflux was continued overnight. The mixture was quenched by the dropwise addition of saturated ammonium chloride solution. The organic layer was washed with brine, then dried over anhydrous magnesium sulfate, and filtered. The solvent was removed from the filtrate under reduced pressure. The crude product was distilled to give diethyl benzhydrylmalonate (5a) (5·59 g, 70%), b.p. 150–155°/0·5 mmHg (lit.[7] 172–178°/1 mmHg), which solidified on standing. Recrystallization from cyclohexane gave colourless needles, m.p. 59–60° (lit.[4] 60–62°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 1·01, t, J 7·0 Hz, 6H, 2×CH_3; 3·99, q, J 7·0 Hz, 4H, 2×CH_2; 4·32, d, J 12·0 Hz, 1H, CH; 4·75, d, J 12·0 Hz, 1H, Ar_2CH; 7·14–7·30, m, 10H, 10×ArH.

2-Benzhydrylpropane-1,3-diol (6a)

A solution of diethyl benzhydrylmalonate (5a) (6 g, 18 mmol) in dry ether (20 ml) was added dropwise to a stirred slurry of lithium aluminium hydride (1 g) in dry ether (50 ml) at 0°. The mixture was heated at reflux for 3 h under nitrogen and cooled. Hydrochloric acid (10 M) was added slowly to decompose the excess lithium aluminium hydride. The ether layer was washed with hydrochloric acid (3 M) and brine, then dried over anhydrous magnesium sulfate, and filtered. The solvent was removed from the filtrate under reduced pressure to give 2-benzhydrylpropane-1,3-diol (6a) (4·26 g, 96%). Recrystallization from ethanol gave colourless needles, m.p. 60–62° (lit.[7] 62–64°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·56–2·63, m, 1H, H2; 3·61, dd, J 10·9, 6·4 Hz, 2H, H1_a and H3_a; 3·78, dd, J 10·9, 3·1 Hz, 2H, H1_b and H3_b; 3·96, d, J 11·9 Hz, 1H, Ar_2CH; 7·10–7·40, m, 10H, 10×ArH.

2-Benzhydrylpropane-1,3-diol Bismethanesulfonate (7a)

Methanesulfonyl chloride (3·34 g) was added dropwise to a solution of 2-benzhydrylpropane-1,3-diol (6a) (2·92 g, 12 mmol) in dry pyridine (50 ml) maintained at 0°. The solution was stirred for 4 h at 0° and poured into cold water. The mixture was extracted with ethyl acetate; the combined ethyl acetate extracts were washed with hydrochloric acid (3 M) and brine, then dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under reduced pressure to give 2-benzhydrylpropane-1,3-diol bismethanesulfonate (7a) (1·96 g, 81%).

[14] Allen, C. F. H., and Spangler, F. W., *Org. Synth.*, 1955, Collect. Vol. 3, 377.

Recrystallization from ethanol yielded colourless needles, m.p. 130–132° (lit.[7] 132–133°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·90, s, 6H, 2×SCH_3; 3·02–3·10, m, 1H, H2; 3·97, d, J 12·0 Hz, 1H, Ar_2CH; 4·08, dd, J 10·0, 6·5 Hz, 2H, H1_a and H3_a; 4·32, dd, J 10·0, 3·2 Hz, 2H, H1_b and H3_b; 7·20–7·35, m, 10H, 10×ArH.

β-Benzhydrylglutaronitrile (8a)

A solution of potassium cyanide (1·11 g) and potassium iodide (0·04 g) in water (12 ml) was added to a solution of 2-benzhydrylpropane-1,3-diol bismethanesulfonate (7a) (1·29 g, 3·24 mmol) in dimethylformamide (25 ml), and the mixture was stirred at 90° for 4·5 h. The mixture was cooled to 60°, poured onto ice, and stirred vigorously. The mixture was extracted with ether; the combined ether extracts were washed with hydrochloric acid (3 M) and brine, then dried over anhydrous magnesium sulfate, and filtered. The solvent was removed from the filtrate under reduced pressure to yield crude β-benzhydrylglutaronitrile (8a) as a tan solid (0·69 g, 82%) which was recrystallized from benzene/light petroleum, m.p. 130–132° (lit.[7] 135·0–135·5°). ν_{max} (chloroform): 3020w, 2251s (CN), 1496m, 1453m, 1427w cm^{-1}. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·42, dd, J 17·5, 7·5 Hz, 2H, Hα_a and Hα'_a; 2·67, dd, J 17·5, 3·5 Hz, 2H, Hα_b and Hα'_b; 2·92–3·00, m, 1H, Hβ; 3·86, d, J 11·5 Hz, 1H, Ar_2CH; 7·24–7·38, m, 10H, 10×ArH.

β-Benzhydrylglutaric Acid (9a)

A solution of β-benzhydrylglutaronitrile (8a) (2·0 g, 7·69 mmol) and potassium hydroxide (6·59 g) in a mixture of water (1 ml) and ethylene glycol (40 ml) was heated at reflux with vigorous stirring for 5 h. The mixture was cooled and diluted with water (50 ml). The mixture was extracted with a 1:1 benzene/ether mixture. The aqueous layer was acidified and extracted with ether. The combined organic extracts were washed with brine, then dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent from the filtrate under reduced pressure yielded β-benzhydrylglutaric acid (9a) (0·69 g, 82%) as a light tan solid which was recrystallized from acetone/benzene, m.p. 175–177° (lit.[7] 176–177°). ν_{max} (chloroform): 3065br (OH), 3015w, 1717s (C=O), 1494m, 1452m, 1293w cm^{-1}. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·15, dd, J 15·0, 10·5 Hz, 2H, Hα_a and Hα'_a; 2·49, dd, J 15·0, 2·2 Hz, 2H, Hα_b and Hα'_b; 3·35–3·45, m, 1H, Hβ; 3·67, d, J 11·0 Hz, 1H, Ar_2CH; 7·15–7·38, m, 10H, 10×ArH.

trans-*5,6,6a,7,8,12b-Hexahydrobenzo[c]phenanthrene-5,8-dione (1a)*

β-Benzhydrylglutaric acid (9a) (1·0 g, 3·36 mmol) was stirred into polyphosphoric acid (20·0 g) held at 65–70°. After 4 h, the colour had changed from pale yellow to dark brown. The hot mixture was poured onto ice (40 g), and stirred until no further change in appearance occurred. The mixture was extracted with ether; the combined ether extracts were washed with saturated sodium bicarbonate solution and brine, then dried over anhydrous magnesium sulfate, and filtered. The removal of the organic solvent from the filtrate under reduced pressure yielded a light brown oil (0·49 g, 58%) which was shown by ^{1}H n.m.r. to be a 9:1 mixture of *trans*-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1a) and *cis*-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1b). The crude oil was purified by preparative normal phase h.p.l.c. [Whatman Partisil-10 column; eluent: ethyl acetate (10%) and triethylamine (0·04%) in light petroleum]. The first major component, trans-*5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1a) (47 mg, 54%), was recrystallized from methanol to give white needles, m.p. 230–232° (Found: C, 82·6; H, 5·3. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%). ν_{max} (chloroform): 3026w, 3020w, 1687s (C=O), 1600m, 1315m, 1284m, 1265w, 1255w cm^{-1}. λ_{max} (chloroform): 250·4 (log ϵ 4·36), 291·1 nm (3·61). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·75–2·88, m, 5H, H6α, H6β, H6a, H7β and H7α; 4·50, d, J 11·0 Hz, 1H, H12b; 7·50, ddd, J 8·0, 8·0, 0·9 Hz, 2H, H3 and H10; 7·65, dd, J 8·0, 0·9 Hz, 2H, H1 and H12; 7·68, ddd, J 8·0, 8·0, 0·9 Hz, 2H, H2 and H11; 8·01, dd, J 8·0, 0·9 Hz, 2H, H4 and H9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 37·2, C6a; 44·8, C6 and C7; 45·2, C12b; 127·0, 127·5, 128·1 and 133·0, C1, C2, C3, C4, C9, C10, C11 and C12; 134·2 and 141·4, C4a, C8a, C12a and C12c; 196·9, C5 and C8. Mass spectrum: m/z 262 (M, 42%), 220 (100), 194 (70), 165 (36), 82 (38), 69 (17), 44 (62).

The second major component, cis-*5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1b) (5·3 mg, 6%), was obtained as pale yellow solid which was recrystallized from methanol to give yellow needles, m.p. 155–158° (Found: C, 82·4; H, 5·1. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%). ν_{max} (chloroform): 3056w, 1684s (C=O), 1600m, 1479w, 1301w, 1290m, 1255w cm^{-1}. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·65, br s, 2H, H 6α and H 7α; 2·86, br s, 2H, H 6β and H 7β; 3·20–3·23, m, 1H, H 6a; 4·50, d, J 4·1 Hz, 1H, H 12b; 7·23, br s, 2H, H 1 and H 12; 7·41, dd, J 7·5, 7·5 Hz, 2H, H 3 and H 10; 7·54, br s, 2H, H 2 and H 11; 8·04, dd, J 7·5, 1·3 Hz, 2H, H 4 and H 9. Mass spectrum: m/z 262 (M, 85%), 220 (56), 194 (100), 165 (40), 118 (19), 83 (30), 41 (41), 28 (54).

trans-1,2,2a,3,4,10c-Hexahydrodibenzo[c,g]phenanthrene-1,4-dione (1c)

Diethyl 1-Naphthylmethylenemalonate (3b)

A solution of 1-naphthaldehyde (2b) (250 g, 1·61 mol) in dry benzene (250 ml) was treated in a similar manner as (2a) to yield a dark brown oil. Distillation of the crude oil afforded diethyl 1-naphthylmethylenemalonate (3b) (350 g, 65%), b.p. 140–150°/0·15 mmHg (lit.[3] 203–205°/2 mmHg). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 1·05, t, J 7·0 Hz, 3H, CH_3; 1·35, t, J 7·0 Hz, 3H, CH_3; 4·15, dq, J 10·0, 7·0 Hz, 2H, CH_2; 4·35, dq, J 10·0, 7·0 Hz, 2H, CH_2; 7·15–8·03, m, 7H, 7×ArH; 8·47, s, 1H, olefinic H.

Diethyl 1-Naphthyl(phenyl)methylmalonate (5b)

(A) *From diethyl benzylidenemalonate (3a) and 1-naphthylmagnesium iodide (4b).* A solution in dry ether (20 ml) of 1-naphthylmagnesium iodide (4b), freshly prepared from 1-iodonaphthalene (1 g) and magnesium turnings (0·2 g), was added slowly to a stirred solution of diethyl benzylidenemalonate (3a) (1 g, 3·89 mmol) in dry ether (20 ml). The mixture was treated in a similar manner as for the synthesis of (5a) to yield diethyl 1-naphthyl(phenyl)methylmalonate (5b) (1·26 g, 79%) as a yellow solid which was used in the next step without further purification. A sample recrystallized from ethanol had m.p. 98–99° (lit.[15] 99·5–101·5°). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 0·86, t, J 7·0 Hz, 3H, CH_3; 1·04, t, J 7·0 Hz, 3H, CH_3; 3·90, q, J 7·0 Hz, 2H, CH_2; 3·92, q, J 7·0 Hz, 2H, CH_2; 4·48, d, J 12·1 Hz, 1H, CH; 5·64, d, J 12·1 Hz, 1H, Ar_2CH; 6·88–8·36, m, 12H, 12×ArH.

(B) *From phenylmagnesium iodide (4a) and diethyl 1-naphthylmethylenemalonate (3b).* A solution of phenylmagnesium iodide (4a), freshly prepared from a suspension of iodobenzene (1 g) and magnesium turnings (0·2 g) in dry ether (20 ml), was added slowly to a solution of diethyl 1-naphthylmethylenemalonate (3b) (1·26 g, 4·22 mmol) in dry ether (20 ml). The reaction was carried in a similar manner as above to yield diethyl 1-naphthyl(phenyl)methylmalonate (5b) (0·29 g, 18%) as a yellow oil which solidified on standing, m.p. 99–101° (lit.[15] 99·5–101·5°). The ^1H n.m.r. spectra of the major products from reactions (A) and (B) were identical.

2-[1-Naphthyl(phenyl)methyl]propane-1,3-diol (6b)

Diethyl 1-naphthyl(phenyl)methylmalonate (5b) (0·5 g, 1·4 mmol) in dry ether (20 ml) was treated in a similar manner as (5a) to yield 2-[1-naphthyl(phenyl)methyl]propane-1,3-diol (6b) (0·4 g, 95%) which was recrystallized from ethanol to give colourless crystals, m.p. 113–116°. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·73–2·80, m, 1H, H 2; 3·70 and 3·71, dd and dd, J 10·9, 6·2 Hz, 2H, H 1_a and H 3_a; 3·84 and 3·87, dd and dd, J 10·9, 3·0 Hz, 2H, H 1_b and H 3_b; 4·94, d, J 12·0 Hz, 1H, Ar_2CH; 7·01–8·32, m, 12H, 12×ArH.

2-[1-Naphthyl(phenyl)methyl]propane-1,3-diol Bismethanesulfonate (7b)

2-[1-Naphthyl(phenyl)methyl]propane-1,3-diol (6b) (0·15 g, 0·51 mmol) was treated in a similar manner as (6a) to give 2-[1-naphthyl(phenyl)methyl]propane-1,3-diol bismethanesulfonate (7b) (0·14 g, 62%) as an orange solid. Recrystallization from ethanol gave white needles, m.p. 138–140°. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·66, s, 3H, SCH_3; 2·98, s, 3H, SCH_3; 3·21–3·29, m, 1H, H 2; 4·09 and 4·12, dd, and dd, J 12·2, 6·5 Hz, 2H, H 1_a and H 3_a; 4·40 and 4·43,

[15] Newman, M. S., and Flanagan, H. R., *J. Org. Chem.*, 1958, **23**, 796.

dd and dd, *J* 12·2, 3·1 Hz, 2H, H1$_b$ and H3$_b$; 4·88, d, *J* 12·0 Hz, 1H, Ar_2CH; 7·16–8·25, m, 12H, 12×ArH.

β-[1-Naphthyl(phenyl)methyl]glutaronitrile (8b)

2-[1-Naphthyl(phenyl)methyl]propane-1,3-diol bismethanesulfonate (7b) (0·5 g, 1·1 mmol) was treated in a similar manner as (7a) to yield β-[1-naphthyl(phenyl)methyl]glutaronitrile (8b) (0·22 g, 65%). A sample recrystallized from ethanol had m.p. 51–54°. ν_{max} (chloroform): 3020w, 2250m (CN), 1730w, 1599m, 1494m, 1454m, 1427s, 1249m, 1031m cm^{-1}. λ_{max} (chloroform): 284·4 (log ε 3·85), 225·6 nm (4·78). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·49 and 2·52, dd and dd, *J* 12·4, 6·7 Hz, 2H, H1α_a and Hα'_a; 2·73 and 2·77, dd and dd, *J* 12·4, 3·2 Hz, 2H, Hα_b and Hα'_b; 3·52–3·60, m, 1H, Hβ; 4·81, d, *J* 12·0 Hz, 1H, Ar_2CH; 7·19–8·25, m, 12H, 12×ArH.

β-[1-Naphthyl(phenyl)methyl]glutaric Acid (9b)

β-[1-Naphthyl(phenyl)methyl]glutaronitrile (8b) (0·1 g, 0·3 mmol) was treated in a similar manner as (8a) to yield β-[1-naphthyl(phenyl)methyl]glutaric acid (9b) (79 mg, 70%). Recrystallization from benzene/light petroleum gave white needles, m.p. 60–63°. ν_{max} (chloroform): 3060br (OH), 1718s (C=O), 1450w, 1415m, 1293m, 971m cm^{-1}. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·23 and 2·26, dd and dd, *J* 13·0, 9·2 Hz, 2H, Hα_a and Hα'_a; 2·53 and 2·58, dd and dd, *J* 13·0, 1·2 Hz, 2H, Hα_b and Hα'_b; 3·11–3·19, m, 1H, Hβ; 4·58, d, *J* 12·0 Hz, 1H, Ar_2CH; 7·10–8·18, m, 12H, 12×ArH.

trans-*1,2,2a,3,4,10c-Hexahydrodibenzo[c,g]phenanthrene-1,4-dione (1c)*

β-[1-Naphthyl(phenyl)methyl]glutaric acid (9b) (1·0 g, 2·87 mmol) was stirred into polyphosphoric acid (20 g) which was held at 120° for 1 h. The reaction was worked up in a similar manner as (9a) to yield trans-*1,2,2a,3,4,10c-hexahydrodibenzo[c,g]phenanthrene-1,4-dione* (1c) (0·5 g, 56%) which was recrystallized from methanol, m.p. 89–90° (Found: C, 84·6; H, 5·0. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·2%). ν_{max} (chloroform): 3020w, 1687s (C=O), 1599m, 1462w, 1454w, 1313m, 1282m cm^{-1}. λ_{max} (chloroform) 254·3 (log ε 3·09), 289·4 (2·45), 335·4 nm (1·82). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·56–3·05, m, 5H, H2a, CH_2 (C3) and CH_2 (C2); 4·91, d, *J* 11·0 Hz, 1H, H10c; 6·51, dd, *J* 7·8, 1·5 Hz, 1H, H11; 7·20, ddd, *J* 7·8, 7·8, 1·5 Hz, 1H, H12; 7·34, ddd, *J* 7·8, 7·8, 1·5 Hz, 1H, H13; 7·44, ddd, *J* 8·6, 8·6, 1·6 Hz, 1H, H8; 7·64, ddd, *J* 8·6, 8·6, 1·6 Hz, 1H, H9; 7·77, dd, *J* 8·6, 1·6 Hz, 1H, H7; 7·96, d, *J* 8·6 Hz, 1H, H6; 7·94–7·99, m, 2H, H10 and H14; 8·08, d, *J* 8·6 Hz, 1H, H5. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 36·6, C2a; 42·3 and 45·5, C3 and C2; 44·2, C10c; 122·9, 125·7, 126·2, 126·3, 126·7, 127·1, 127·7, 128·3, 128·7 and 132·4, C10, C9, C8, C7, C6, C5, C14, C13, C12 and C11; 131·8, 132·3, 133·8, 135·7, 138·7 and 144·7, C6a, C4a, C14a, C10d, C10b and C10c; 197·0 and 197·9, C4 and C1. Mass spectrum: *m/z* 312 (M, 18%), 270 (13), 244 (12), 105 (24), 91 (48), 85 (14), 77 (22), 55 (33), 44 (100).

trans-3,4,4a,5,6,12c-Hexahydrohexahelicene-3,6-dione (1d)

Diethyl Di-1-naphthylmethylmalonate (5c)

A solution of 1-naphthylmagnesium iodide (4b) in ether was prepared from 1-iodonaphthalene (7·5 g, 35 mmol) and magnesium turnings (12·15 g) in dry ether (50 ml). After cooling to 0°, a solution of diethyl 1-naphthylmethylenemalonate (3b) (155 g, 0·515 mol) in dry benzene (150 ml) was added slowly and the resultant solution was treated in a similar manner as (4a) to yield diethyl di-1-naphthylmethylmalonate (5c) (215 g, 98%). A sample was recrystallized from ethanol to give white crystals, m.p. 109–110° (lit.[3] 109–113°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 0·78, t, *J* 7·1 Hz, 6H, 2×CH_3; 3·70, q, *J* 7·0 Hz, 4H, 2×CH_2; 4·50, d, *J* 11·8 Hz, 1H, CH; 6·49, d, *J* 11·8 Hz, 1H, Ar_2CH; 7·28–8·35, m, 14H, 14×ArH.

2-(Di-1-naphthylmethyl)propane-1,3-diol (6c)

Diethyl di-1-naphthylmethylmalonate (5c) (0·85 g, 2 mmol) in dry ether (10 ml) was treated in a similar manner as (5a) to yield 2-(di-1-naphthylmethyl)propane-1,3-diol (6c) (0·63 g,

92%). Recrystallization from benzene gave white fibrous crystals, m.p. 77–80° (lit.[3] 75°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·19, br, 2H, 2×OH; 2·82–2·90, m, 1H, H2; 3·75, dd, J 10·5, 6·5 Hz, 2H, H1$_a$ and H3$_a$; 4·39, dd, J 11·3, 3·3 Hz, 2H, H1$_b$ and H3$_b$; 5·72, d, J 10·0 Hz, 1H, Ar_2CH; 7·28–8·35, m, 14H, 14×ArH.

2-(Di-1-naphthylmethyl)propane-1,3-diol Bismethanesulfonate (7c)

2-(Di-1-naphthylmethyl)propane-1,3-diol (6c) (5 g, 14·6 mmol) was treated in a similar manner as (6a) to give 2-(di-1-naphthylmethyl)propane-1,3-diol bismethanesulfonate (7c) (5·9 g, 81%). Recrystallization from benzene gave white fibrous crystals, m.p. 146–151° (lit.[3] 145–150°). ^{1}H n.m.r. [400 MHz, $CDCl_3/(CD_3)_2SO$]: δ 2·68, s, 6H, 2×SCH_3; 3·31–3·37, m, 1H, H2; 4·13, dd, J 10·0, 6·3 Hz, 2H, H1$_a$ and H3$_a$; 4·39, dd, J 10·0, 3·3 Hz, 2H, H1$_b$ and H3$_b$; 5·74, d, J 11·5 Hz, 1H, Ar_2CH; 7·28–8·35, m, 14H, 14×ArH.

β-(Di-1-naphthylmethyl)glutaronitrile (8c)

2-(Di-1-naphthylmethyl)propane-1,3-diol bismethanesulfonate (7c) (5·9 g, 11·8 mmol) was treated in a similar manner as (7a) to yield β-(di-1-naphthylmethyl)glutaronitrile (8c) (3·2 g, 75%) as a light tan foam which was spectroscopically pure. ν_{max} (chloroform): 3064m, 3052m, 3014m, 2251s cm^{-1} (CN). λ_{max} (ethanol): 217·6 (log ϵ 5·06), 284·8 nm (4·79). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·64, dd, J 17·2, 4·4 Hz, 2H, Hα_b and Hα'_b; 2·70, dd, J 17·2, 7·0 Hz, 2H, Hα_a and Hα'_a; 3·21–3·27, m, 1H, Hβ; 5·75, d, J 12·5 Hz, 1H, Ar_2CH; 7·28–8·35, m, 14H, 14×ArH. Mass spectrum: m/z 360 (M, 40%), 267 (100), 252 (58), 239 (16), 133 (45), 43 (11).

β-(Di-1-naphthylmethyl)glutaric Acid (9c)

β-(Di-1-naphthylmethyl)glutaronitrile (8c) (1·54 g, 4·3 mmol) was treated in a similar manner as (8a) to yield β-(di-1-naphthylmethyl)glutaric acid (9c) (1·67 g, 98%). Recrystallization from benzene/light petroleum gave white needles, m.p. 227–230° (lit.[3] 224–225°). ^{1}H n.m.r. [400 MHz, $CDCl_3/(CD_3)_2SO$]: δ 2·46, dd, J 16·7, 3·8 Hz, 2H, Hα_b and Hα'_b; 2·67, dd, J 16·7, 7·6 Hz, 2H, Hα_a and Hα'_a; 3·39–3·47, m, 1H, Hβ; 6·15, d, J 10·8 Hz, 1H, Ar_2CH; 7·28–8·35, m, 14H, 14×ArH.

trans-*3,4,4a,5,6,12c-Hexahydrohexahelicene-3,6-dione (1d)*

β-(Di-1-naphthylmethyl)glutaric acid (9c) (0·54 g, 1·4 mmol) was treated in a similar manner as (9b) to yield a red crude material (0·15 g, 28%). Analytical g.l.c. showed that it contained four major components. The resultant material was dissolved in dichloromethane, and purified by preparative normal phase h.p.l.c. [Whatmann Partisil-10 column; eluent: ethyl acetate (15%) in light petroleum]. The first major fraction was shown by ^{1}H n.m.r. to be cis-*7,8,8a,9,10,16b-hexahydronaphtho[1′,8′:3,4,5]cyclohepta[1,2-c]phenanthrene-7,10-dione* (10a) (13 mg, 2·5%). A sample was recrystallised from benzene/light petroleum, m.p. 122–125° (Found: M^+, 362·1300. $C_{26}H_{18}O_2$ requires M^+, 362·1307). λ_{max} (chloroform): 255·2 (log ϵ 4·62), 288·8 nm (4·13). ^{1}H n.m.r. (600 MHz, $CDCl_3$): δ 2·69, dd, J 10·8, 10·8 Hz, 1H, H9β; 2·79, dd, J 16·8, 4·0 Hz, 1H, H8β; 2·87, dd, J 16·8, 13·6 Hz, 1H, H8α; 2·96, dd, J 10·8, 7·6 Hz, 1H, H9α; 3·48–3·55, m, 1H, H8a; 5·50, d, J 5·0 Hz, 1H, H16b; 6·69, dd, J 8·7, 1·2 Hz, 1H, H16; 7·08, dd, J 8·8, 1·0 Hz, 1H, H1; 7·16, ddd, J 8·8, 8·8, 1·0 Hz, 1H, H3; 7·21, dd, J 8·1, 8·1 Hz, 1H, H15; 7·47, ddd, J 8·1, 8·1, 1·3 Hz, 1H, H2; 7·64, dd, J 8·0, 8·0 Hz, 1H, H12; 7·80, dd, J 8·1, 1·2 Hz, 1H, H14; 7·85, dd, J 8·8, 1·3 Hz, 1H, H4; 7·92, d, J 8·8 Hz, 1H, H5; 7·98, dd, J 8·0, 1·4 Hz, 1H, H11; 8·05, dd, J 8·0, 1·4 Hz, 1H, H13; 8·27, d, J 8·8 Hz, 1H, H6. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 38·6, C8a; 43·6, C16b; 40·0 and 48·5, C8 and C9; 122·4, 125·4, 125·5, 126·5, 127·1, 127·3, 128·4, 128·4, 128·7, 128·8, 129·5 and 132·8, C1, C2, C3, C4, C5, C6, C11, C12, C13, C14, C15 and C16; 130·6, 130·8, 131·6, 134·0, 135·0, 136·4, 138·2 and 142·7, C4a, C6a, C10a, C13a, C13b, C16a, C16c and C16d; 197·0 and 203·0, C7 and C10.

The second major fraction, trans-*7,8,8a,9,10,16b-hexahydronaphtho[1′,8′:3,4,5]cyclohepta[1,2-c]phenanthrene-7,10-dione* (10b), was obtained as a pale solid (34 mg, 4·5%). A sample recrystallized from methanol had m.p. 207–209° (Found: C, 86·2; H, 4·9. $C_{26}H_{18}O_2$

requires C, 86·2; H, 5·0%). ν_{max} (chloroform): 2952m, 1682s (C=O), 1336w, 1313w, 1277w cm^{-1}. λ_{max} (chloroform): 253·6 ($\log\epsilon$ 4·93), 291·0 nm (4·10). ^1H n.m.r. [400 MHz, $CDCl_3/(CD_3)_2CO$]: δ 2·85, dd, J 9·6, 9·6 Hz, 2H, H 9α and H 9β; 2·99, dd, J 14·8, 6·7 Hz, 1H, H 8α; 3·06–3·22, m, 1H. H 8a; 3·44, dd, J 14·8, 9·2 Hz, 1H, H 8β; 5·28, d, J 9·3 Hz, 1H, H 16b; 6·27, dd, J 7·3, 1·3 Hz, 1H, H 16; 7·14, dd, J 7·3, 7·3 Hz, 1H, H 15; 7·13–7·20, m, 2H, H 1 and H 2; 7·52, dd, J 8·1, 8·0 Hz, 1H, H 3; 7·70, dd, J 8·2, 7·2 Hz, 1H, H 12; 7·84, dd, J 7·3, 1·3 Hz, 1H, H 14; 7·92, dd, J 7·2, 1·6 Hz, 1H, H 11; 7·98, dd, J 8·0, 1·2 Hz, 1H, H 4; 7·97 and 8·03, AB quartet, J 8·9 Hz, 2H, H 5 and H 6; 8·16, dd, J 8·2, 1·6 Hz, 1H, H 13. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 37·3, C 8a; 46·2, C 16b; 45·0 and 52·3, C 8 and C 9; 122·0, 125·5, 126·2, 126·4, 126·5, 126·6, 127·7, 128·0, 128·5, 128·6, 128·8 and 133·0, C 1, C 2, C 3, C 4, C 5, C 6, C 11, C 12, C 13, C 14, C 15 and C 16; 129·6, 131·3, 132·7, 134·1, 136·4, 138·1, 140·7 and 142·5, C 4a, C 6a, C 10a, C 13a, C 13b, C 16a, C 16b and C 16d; 198·1 and 204·2, C 7 and C 10. Mass spectrum: m/z 362 (M, 100%), 343 (13), 319 (35), 303 (17), 289 (16), 265 (28), 155 (22), 146 (10), 132 (30), 32 (13), 28 (81).

The third major fraction consisted of the desired trans-*3,4,4a,5,6,12c-hexahydrohexahelicene-3,6-dione* (1d) (88 mg, 17%). A sample recrystallized from methanol had m.p. 270–273° (Found: C, 86·2; H, 4·9. $C_{26}H_{18}O_2$ requires C, 86·2; H, 5·0%). ν_{max} (chloroform): 3062m, 3029br, 1686s (C=O), 1367m, 1338m, 1317w, 1256m, 822w cm^{-1}. λ_{max} (chloroform): 249·1 ($\log\epsilon$ 4·69), 295·7 (4·06), 346·1 nm (3·68). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·77, dd, J 14·0, 14·0 Hz, 1H, H 5β; 2·86, dd, J 18·9, 11·5 Hz, 1H, H 4β; 2·90, dd, J 14·0, 3·9 Hz, 1H, H 5α; 3·17, dd, J 18·9, 4·9 Hz, 1H, H 4α; 3·13–3·24, m, 1H, H 4a; 5·29, d, J 10·3 Hz, 1H, H 12c; 6·24, dd, J 8·3, 0·8 Hz, 1H, H 13; 6·55, ddd, J 8·3, 6·8, 1·5 Hz, 1H, H 14; 7·04, ddd, J 8·6, 6·6, 1·1 Hz, 1H, H 11; 7·20, ddd, J 8·3, 6·8, 0·8 Hz, 1H, H 15; 7·30, dd, J 8·6, 1·1 Hz, 1H, H 12; 7·43, ddd, J 8·6, 6·6, 1·1 Hz, 1H, H 10; 7·70, dd, J 8·3, 1·5 Hz, 1H, H 16; 7·81, and 8·02, AB quartet, J 8·3 Hz, 2H, H 2 and H 1; 7·87, dd, J 8·6, 1·1 Hz, 1H, H 9; 7·98 and 8·18, AB quartet, J 8·3 Hz, 2H, H 8 and H 7. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 35·6, C 4a; 43·0 and 46·7, C 5 and C 4; 45·8, C 12c; 122·5, 122·7, 125·1, 125·8, 125·8, 126·7, 127·5, 128·2, 128·3, 128·5, 128·6, 128·7, C 12, C 11, C 10, C 9, C 8, C 7, C 2, C 1, C 16, C 15, C 14 and C 13; 131·6, 132·5, 132·5, 133·2, 135·5, 136·3, 140·1 and 144·7, C 8a, C 6a, C 2a, C 16a, C 12e, C 12d, C 12b and C 12a; 197·5 and 197·9, C 6 and C 3. Mass spectrum: m/z 362 (M, 22%), 320 (25), 293 (14), 278 (30), 262 (42), 220 (93), 194 (87), 165 (70), 155 (50), 141 (44), 127 (52), 105 (57), 83 (37), 71 (70), 63 (34), 55 (98), 41 (100), 28 (92).

The final major fraction contained cis-*3,4,4a,5,6,12c-hexahydrohexahelicene-3,6-dione* (1e) (21 mg, 4%). A sample recrystallized from benzene/light petroleum had m.p. 114–116° (Found: M^+, 362·1304. $C_{26}H_{18}O_2$ requires M^+, 362·1307). ν_{max} (chloroform): 3064m, 3030br, 1677s (C=O), 1461m, 1352m, 1278m, 1233m, 823m cm^{-1}. λ_{max} (chloroform): 207·2 ($\log\epsilon$ 4·70), 246·4 (4·84), 289·2 (4·30), 349·6 nm (3·81). ^1H n.m.r. (400 MHz, $CDCl_3$, 210 K): δ 2·57, dd, J 18·0, 4·5 Hz, 1H, H 5β; 2·72, dd, J 18·0, 12·6 Hz, 1H, H 5α; 2·81, dd, J 18·0, 0·1 Hz, 1H, H 4α; 3·08–3·16, m, 1H, H 4a; 3·20, J 18·0, 6·0 Hz, 1H, H 4β; 5·71, d, J 3·1 Hz, 1H, H 12c; 6·58, dd, J 8·0, 8·0 Hz, 1H, H 14; 6·72, d, J 8·0 Hz, 1H, H 13; 7·23, dd, J 8·0, 8·0 Hz, 1H, H 15; 7·60, dd, J 8·0, 8·0 Hz, 1H, H 11; 7·69, dd, J 8·0, 8·0 Hz, 1H, H 10; 7·70, d, J 8·0 Hz, 1H, H 16; 7·70, dd, J 8·3, 1·5 Hz, 1H, H 16; 7·86, AB quartet, J 8·0 Hz, 2H, H 2 and H 1; 8·02, d, J 8·0 Hz, 1H, H 9; 8·06, AB quartet, J 8·0 Hz, 2H, H 8 and H 7; 8·30, d, J 8·0 Hz, 1H, H 12. ^{13}C n.m.r. (50 MHz, $CDCl_3$, 215 K): δ 37·5, C 4a; 39·2, C 12c; 39·3 and 42·6, C 5 and C 4; 122·8, 123·2, 125·0, 126·1, 126·7, 127·7, 128·0, 128·9, 128·9, 129·1, 129·2 and 129·4, C 12, C 11, C 10, C 9, C 8, C 7, C 2, C 1, C 16, C 15, C 14 and C 13; 130·2, 131·7, 131·8, 131·9, 135·5, 137·2, 139·7 and 146·6, C 8a, C 6a, C 2a, C 16a, C 12e, C 12d, C 12b and C 12a; 197·0 and 198·8, C 6 and C 3.

trans-1,12-Dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1f)

Diethyl (2-Methylbenzylidene)malonate (3d)

2-Tolualdehyde (2d) (20 g, 0·17 mol) was treated in a similar manner as (2a) to give a crude oil. Distillation of the crude material afforded diethyl (2-methylbenzylidene)malonate (3d) as a clear oil (38·8 g, 89%), b.p. 159–165°/1·5 mmHg (lit.[1] 128°/0·6 mmHg). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 1·15, t, J 7·0 Hz, 3H, CH_3; 1·33, t, J 7·0 Hz, 3H, CH_3; 2·36, s, 3H, $ArCH_3$; 4·21, q, J 7·0 Hz, 2H, CH_2; 4·31, q, J 7·0 Hz, 2H, CH_2; 7·10–7·36, m, 4H, 4×ArH; 7·97, s, 1H, olefinic H.

Diethyl (2,2′-Dimethylbenzhydryl)malonate (5d)

The Grignard reagent (4d), prepared from 2-bromotoluene (6 g, 35 mmol) and magnesium turnings (1 g) in dry tetrahydrofuran (40 ml), was cooled to 0°. A solution of diethyl (2-methylbenzylidene)malonate (3d) (6 g, 24 mmol) in dry tetrahydrofuran (10 ml) was added to the Grignard reagent (4d), and the mixture was treated in a similar manner as (3a) to yield a crude oil. Distillation of the crude material afforded diethyl (2,2′-dimethylbenzhydryl)malonate (5d) as a yellow viscous oil (6·87 g, 84%), b.p. 228–234°/1·0 mmHg (lit.[5] 175–190°/0·7–0·8 mmHg), which solidified on standing. A sample with m.p. 53–55° (lit.[1] 52·8–53·8°) was obtained by recrystallization from benzene/light petroleum. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 0·97, t, J 7·0 Hz, 6H, 2×CH_3; 2·40, s, 6H, 2×ArCH_3; 3·96, q, J 7·0 Hz, 4H, 2×CH_2; 4·35, d, J 10·0 Hz, 1H, CH; 5·21, d, J 10·0 Hz, 1H, Ar_2CH; 7·05–7·34, m, 8H, 8×ArH.

2-(2,2′-Dimethylbenzhydryl)propane-1,3-diol (6d)

Diethyl (2,2′-dimethylbenzhydryl)malonate (5d) (2 g, 5·65 mmol) was treated in a similar manner as (5a) to yield 2-(2,2′-dimethylbenzhydryl)propane-1,3-diol (6d) (1·23 g, 81%). A sample recrystallized from benzene/light petroleum gave shiny colourless needles, m.p. 80–82° (lit.[1] 79·4–80·4°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·35, s, 6H, 2×ArCH_3; 2·54–2·62, m, 1H, H2; 3·60–3·74, m, 4H, 2×CH_2; 4·35, d, J 11·2 Hz, 1H, Ar_2CH; 7·03–7·36, m, 8H, 8×ArH.

2-(2,2′-Dimethylbenzhydryl)propane-1,3-diol Bismethanesulfonate (7d)

2-(2,2′-Dimethylbenzhydryl)propane-1,3-diol (6d) (2·2 g, 8·2 mmol) was treated in a similar manner as (6a) to yield 2-(2,2′-dimethylbenzhydryl)propane-1,3-diol bismethanesulfonate (7d) (2·54 g, 73%) as an orange solid. A sample recrystallized from ethanol had m.p. 197–198° (lit.[1] 197·5–198·5°). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·42, s, 6H, 2×ArCH_3; 2·91, s, 6H, 2×SCH_3; 2·99–3·13, m, 1H, H2; 4·04, dd, J 9·9, 6·3 Hz, 2H, H1$_a$ and H3$_a$; 4·28, dd, J 9·9, 3·4 Hz, 2H, H1$_b$ and H3$_b$; 4·48, d, J 11·8 Hz, 1H, Ar_2CH; 7·11–7·40, m, 8H, 8×ArH.

β-(2,2′-Dimethylbenzhydryl)glutaronitrile (8d)

2-(2,2′-Dimethylbenzhydryl)propane-1,3-diol bismethanesulfonate (7d) (2·22 g, 5·2 mmol) was treated in a similar manner as (7a) to give a crude residue of β-(2,2′-dimethylbenzhydryl)glutaronitrile (8d) (1·2 g, 79%). ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·43, s, 6H, 2×ArCH_3; 2·87–3·04, m, 4H, 2×CH_2; 2·88–3·02, m, 1H, Hβ; 4·46, d, J 11·2 Hz, 1H, Ar_2CH; 7·12–7·35, m, 8H, 8×ArH.

β-(2,2′-Dimethylbenzhydryl)glutaric Acid (9d)

β-(2,2′-Dimethylbenzhydryl)glutaronitrile (8d) (1·2 g, 9·2 mmol) was treated in a similar manner as (8a) to yield the crude β-(2,2′-dimethylbenzhydryl)glutaric acid (9d) (1·3 g, 96%) as a light tan solid which was recrystallized from benzene/light petroleum, m.p. 206–209° (lit.[1] 205·6–206·8°). ν_{max} (chloroform): 3037m, 1714s (C=O), 1456w, 1077w, 1028w cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·36, s, 6H, 2×ArCH_3; 2·53, dd, J 11·9, 7·7 Hz, 2H, Hα_a and Hα'_a; 2·52, dd, J 11·9, 3·0 Hz, 2H, Hα_b and Hα'_b; 3·17–3·24, m, 1H, H3; 4·07, d, J 11·4 Hz, 1H, Ar_2CH; 6·99–7·41, m, 8H, 8×ArH.

trans-*1,12-Dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1f)*

β-(2,2′-Dimethylbenzhydryl)glutaric acid (9d) (100 mg, 0·3 mmol) was treated in a similar manner as (9b) to yield trans-*1,12-dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1f) (64 mg, 73%) as a pale yellow solid. An analytical sample was recrystallized from methanol, m.p. 230–232° (Found: C, 82·9; H, 6·4. $C_{20}H_{18}O_2$ requires C, 82·8; H, 6·2%). ν_{max} (chloroform): 3080w, 1679s (C=O), 1587w, 1460w, 1307w, 1268w cm^{-1}. λ_{max} (chloroform): 253·8 (log ϵ 4·10), 299·7 nm (3·57). ^{1}H n.m.r. (600 MHz, $CDCl_3$): δ 1·50, s, 3H, 12-CH_3; 2·13, s, 3H, 1-CH_3; 2·56, dd, J 14·0, 13·8 Hz, 1H, H6β; 2·64, dd, J 18·4, 10·9 Hz, 1H, H7β; 2·68, dd, J 14·0, 3·9 Hz, 1H, H6α; 2·73–2·85, m, 1H, H6a; 2·96, dd, J 18·4, 4·4 Hz, 1H, H7α; 4·30, d, J 10·8 Hz, 1H, H12b; 7·19, dd, J 7·4, 1·1 Hz, 1H, H11; 7·27, dd, J 7·4, 7·4 Hz, 1H, H10; 7·41, dd, J 7·4, 7·4 Hz, 1H, H3; 7·45, dd, J 7·4, 1·7 Hz,

1H, H2; 7·74, dd, *J* 7·4, 1·1 Hz, 1H, H9; 7·85, dd, *J* 7·4, 1·7 Hz, 1H, H4. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 22·8 and 23·8, 1-CH_3 and 12-CH_3; 38·8, C6a; 46·3 and 49·2, C6 and C7; 49·3, C12b; 128·2, 128·8, 129·8, 130·8, 138·5 and 140·2, C4, C9, C10, C3, C2 and C11; 136·8, 137·6, 139·3, 142·5, 142·9 and 145·7, C1, C4a, C8a, C12, C12a and C12c; 201·3 and 202·1, C5 and C8. Mass spectrum: *m/z* 290 (M, 75%), 248 (100), 233 (47), 222 (100), 178 (32), 130 (38), 89 (29), 41 (38), 28 (56).

cis-1,12-Dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1g)

β-(2,2′-Dimethylbenzhydryl)glutaric acid (9d) (100 mg, 0·3 mmol) was stirred into polyphosphoric acid (10 g) which was held at 180°. The mixture was stirred at 180° for 10 min and worked up in the same manner as for the preparation of the *trans* dione (1f) to yield a light brown oil (75 mg, 86%). Analytical g.l.c. showed that the oil was a 12:1 mixture of *trans*-1,12-dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1f) and *cis*-1,12-dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1g). Purification by preparative normal phase h.p.l.c. (Whatman Partisil-10 column; eluent: ethyl acetate (12%) and triethylamine (0·04%) in light petroleum) gave the major product, *trans*-1,12-dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1f), as a white solid (64 mg, 73%), and the minor component, cis-*1,12-dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1g) (5·3 mg, 6%), as a pale yellow solid which was recrystallized from ethanol, m.p. 155–156°C (Found: C, 83·0; H, 6·5. $C_{20}H_{18}O_2$ requires C, 82·8; H, 6·2%). ν_{max} (chloroform): 3005w, 1675s (C=O), 1585w, 1459w, 1089w cm^{-1}. λ_{max} (chloroform): 258·1 ($\log\epsilon$ 4·21), 300·2 nm (3·54). ^{1}H n.m.r. (600 MHz, $CDCl_3$): δ 1·43, s, 3H, 12-CH_3; 2·52, s, 3H, 1-CH_3; 2·56, dd, *J* 17·1, 1·6 Hz, 1H, H6β; 2·57, dd, *J* 17·1, 11·0 Hz, 1H, H6α; 2·74, dd, *J* 18·8, 0·1 Hz, 1H, H7α; 2·94–3·02, m, 1H, H6a; 3·05, dd, *J* 18·8, 5·6 Hz, 1H, H7β; 4·70, d, *J* 3·2 Hz, 1H, H12b; 7·18, d, *J* 7·5 Hz, 1H, H2; 7·23, dd, *J* 7·5, 7·5 Hz, 1H, H3; 7·37, dd, *J* 7·5, 7·5 Hz, 1H, H10; 7·44, d, *J* 7·5 Hz, 1H, H11; 7·87, d, *J* 7·5 Hz, 1H, H4; 7·99, d, *J* 7·5 Hz, 1H, H9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 20·2 and 20·7, 1-CH_3 and 12-CH_3; 35·9, C6a; 39·5 and 42·9, C6 and C7; 40·2, C12b; 126·1, 126·4, 127·3, 127·8, 135·3 and 139·2, C2, C3, C4, C9, C10 and C11; 133·2, 134·4, 136·9, 137·7, 138·3 and 145·8, C1, C4a, C8a, C12, C12a and C12c; 201·3 and 202·1, C5 and C8. Mass spectrum: *m/z* 290 (M, 56%), 275 (58), 257 (18), 222 (100), 178 (45), 165 (14), 119 (28), 89 (20), 63 (14), 41 (43).

trans-1,12-Dimethoxy-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1h)

Diethyl (2-Methoxybenzylidene)malonate (3e)

2-Methoxybenzaldehyde (2e) (20 g, 0·15 mol) was treated in a similar manner as (2a) to yield a crude oil. Distillation of the crude material afforded diethyl (2-methoxybenzylidene)malonate (3e) (33·02 g, 81%) as a pale yellow oil, b.p. 148–151°/1·55 mmHg. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 1·23, t, *J* 7·2 Hz, 3H, CH_3; 1·33, t, *J* 7·2 Hz, 3H, CH_3; 3·86, s, 3H, OCH_3; 4·27, dq, *J* 10·0, 7·2 Hz, 2H, CH_2; 4·31, dq, *J* 10·0, 7·2 Hz, 2H, CH_2; 6·90, d, 7·6 Hz, 1H, ArH3; 6·92, dd, *J* 7·6, 7·6 Hz, 1H, ArH4; 7·37, dd, *J* 8·0, 8·0 Hz, 1H, ArH5; 7·39, d, *J* 8·0 Hz, 1H, ArH6; 8·09, s, 1H, olefinic H.

Diethyl (2,2′-Dimethoxybenzhydryl)malonate (5e)

The Grignard reagent (4e), prepared from 2-iodoanisole (10 g) and magnesium turnings (2 g) in dry tetrahydrofuran (50 ml), was added to a stirred solution of diethyl (2-methoxybenzylidene)malonate (3e) (6·0 g, 21·5 mmol) and cuprous bromide (2·0 g) in dry tetrahydrofuran (50 ml). The mixture was treated in a similar manner as (3a) to yield diethyl (2,2′-dimethoxybenzhydryl)malonate (5e) (6·42 g, 85%) as a yellow solid which was used for the next step without further purification. A sample recrystallized from cyclohexane had m.p. 81–83°. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 0·99, t, *J* 6·0 Hz, 6H, 2×CH_2CH_3; 3·78, s, 6H, 2×OCH_3; 3·97, q, *J* 6·0 Hz, 4H, 2×CH_2; 4·79, d, *J* 12·0 Hz, 1H, Ar_2CH; 5·30, d, *J* 12·0 Hz, 1H, CH; 6·78, dd, *J* 8·2, 0·9 Hz, 2H, ArH3 and ArH3′; 6·84, ddd, *J* 8·2, 8·2, 0·9 Hz, 2H, ArH5 and ArH5′; 7·12, ddd, *J* 8·2, 8·2, 1·6 Hz, 2H, ArH4 and ArH4′; 7·40, dd, *J* 8·2, 1·6 Hz, 2H, ArH6 and ArH6′.

2-(2,2′-Dimethoxybenzhydryl)propane-1,3-diol (6e)

Diethyl (2,2′-dimethoxybenzhydryl)malonate (5e) (6·42 g, 19·5 mml) was treated in a similar manner as (5a) to yield 2-(2,2′-dimethoxybenzhydryl)propane-1,3-diol (6e) (4·44 g, 84·5%). Recrystallization of the crude material from ethanol gave white needles, m.p. 126–129°. ν_{max} (chloroform): 3495br (OH), 2940m, 2893m, 1599m, 1490s, 1464m, 1289m, 1224m, 1185w, 1037m, 960w cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·40–2·56, m, 1H, H2; 3·70–3·78, m, 4H, 2×CH_2; 3·82, s, 6H, 2×OCH_3; 5·00, d, J 12·0 Hz, 1H, Ar_2CH; 6·85, dd, J 7·4, 1·2 Hz, 2H, ArH3′ and ArH3″; 6·91, ddd, J 7·4, 7·4, 1·2 Hz, 2H, ArH5′ and ArH5″; 7·15, ddd, J 7·4, 7·4, 2·0 Hz, 2H, ArH4′ and ArH4″; 7·32, dd, J 7·4, 2·0 Hz, 2H, ArH6′ and ArH6″.

2-(2,2′-Dimethoxybenzhydryl)propane-1,3-diol Bismethanesulfonate (7e)

2-(2,2′-Dimethoxybenzhydryl)propane-1,3-diol (6e) (4·44 g, 17 mmol) was treated in a similar manner as (6a) to yield 2-(2,2′-dimethoxybenzhydryl)propane-1,3-diol bismethanesulfonate (7e) (6·1 g, 87·3%) as a light orange solid. A sample was recrystallized from ethanol, m.p. 96–99°. ν_{max} (chloroform): 3037w, 1730m, 1585w, 1491m, 1360s (S=O), 1241s, 1240s, 1175s (S=O), 1038m, 972m cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·05, s, 3H, SCH_3; 2·85, s, 3H, SCH_3; 3·82, s, 6H, 2×OCH_3; 3·81–3·97, m, 1H, H2; 4·09, dd, J 10·0, 6·4 Hz, 2H, H1_a and H3_a; 4·29, dd, J 10·0, 3·2 Hz, 1H, H1_b and H3_b; 4·71, d, J 12·0 Hz, 1H, Ar_2CH; 6·82, dd, J 8·2, 0·9 Hz, 2H, ArH3′ and ArH3″; 6·92, ddd, J 8·2, 8·2, 0·9 Hz, 2H, ArH5′ and ArH5″; 7·17, ddd, J 8·2, 1·7 Hz, 2H, ArH4 and ArH4″; 7·42, dd, J 8·2, 1·7 Hz, 2H, ArH6′ and ArH6″.

β-(2,2′-Dimethoxybenzhydryl)glutaronitrile (8e)

2-(2,2′-Dimethoxybenzhydryl)propane-1,3-diol bismethanesulfonate (7e) (6·1 g, 14 mmol) was treated in a similar manner as (7a) to yield β-(2,2′-dimethoxybenzhydryl)glutaronitrile (8e) (3·19 g, 79%) which was recrystallized from benzene/cyclohexane, m.p. 101–102°. ν_{max} (chloroform): 3072w, 2942m, 2813m, 2249m (CN), 1601m, 1578m, 1484s, 1460m, 1278w, 1249s, 1119m, 1049m, 1020m cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·43, dd, J 10·2, 7·6 Hz, 2H, Hα_a and Hα'_a; 2·63, dd, J 10·2, 3·8 Hz, 2H, Hα_b and Hα'_b; 3·23–3·39, m, 1H, Hβ; 3·82, s, 6H, 2×OCH_3; 4·69, d, J 12·0 Hz, 1H, Ar_2CH; 6·84, dd, J 8·4, 0·8 Hz, 2H, ArH3′ and ArH3″; 6·90, ddd, J 8·4, 8·4, 0·8 Hz, 2H, ArH5′ and ArH5″; 7·19, ddd, J 8·4, 8·4, 1·7 Hz, 2H, ArH4′ and ArH4″; 7·37, dd, J 8·4, 1·7 Hz, 2H, ArH6′ and ArH6″.

β-(2,2′-Dimethoxybenzhydryl)glutaric Acid (9e)

β-(2,2′-Dimethoxybenzhydryl)glutaronitrile (8e) (3·4 g, 12 mmol) was treated in a similar manner as (8a) to yield β-(2,2′-dimethoxybenzhydryl)glutaric acid (9e) (3·01 g, 70%) as a light tan solid. A sample recrystallized from benzene/light petroleum had m.p. 197–198°. ν_{max} (chloroform): 3063br (OH), 2937w, 2688w, 1716s (C=O), 1599w, 1491m, 1463m, 1438m, 1419w, 1295w, 1246m, 1117w, 1034m, 899w cm^{-1}. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 2·38 and 2·47, dd and dd, J 11·0, 8·0 Hz, 1H, Hα_a and Hα'_a; 2·50, dd, J 11·0, 1·5 Hz, 2H, Hα_b and Hα'_b; 3·02–3·18, m, 1H, Hβ; 3·98, s, 6H, 2×OCH_3; 4·36, d, J 12·1 Hz, 1H, Ar_2CH; 6·82, dd, J 8·2, 1·0 Hz, 1H, ArH3′; 6·93, ddd, J 7·4, 7·4, 1·0 Hz, 1H, ArH5′; 7·12–7·40, m, 6H, 6×ArH.

trans-*1,12-Dimethoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1h)*

β-(2,2′-Dimethoxybenzhydryl)glutaric acid (9e) (100 mg, 0·3 mmol) was treated in a similar manner as (9b) to yield a dark brown oil. Purification by preparative normal phase h.p.l.c. [Whatman Partisil-10 column; eluent: ethyl acetate (12%) and triethylamine (0·4%) in light petroleum] gave the first major component as a clear yellow oil (45 mg, 10%), which was shown by ^{1}H n.m.r. and mass spectrometry to be 4-methoxyacetophenone (16). A sample recrystallized from ethanol had identical m.p. (35–36°)[16] and ^{1}H n.m.r. parameters to that of an authentic Aldrich sample.

[16] Reychler, A., *Bull. Soc. Chim.*, 1915, **17**, 514.

The second major component trans-*1,12-dimethoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1h), was obtained as a white solid (14·5 mg, 15%) which was recrystallized from methanol, m.p. 209° (Found: C, 74·4; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). ν_{max} (chloroform): 3011w, 2939w, 1685s (C=O), 1596w, 1489m, 1310m, 1264s, 1181w, 908w cm^{-1}. λ_{max} (chloroform): 319·9 ($\log\epsilon$ 3·75), 255·7 (4·12), 239·3 nm (4·10). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·55, dd, J 13·8, 13·8 Hz, 1H, H 6β; 2·59, dd, J 18·4, 11·3 Hz, 1H, H 7β; 2·64, dd, J 13·8, 4·0 Hz, 1H, H 6α; 2·70–2·81, m, 1H, H 6a; 2·93, dd, J 18·4, 4·5 Hz, 1H, H 7α; 3·32, s, 3H, 12-OCH_3; 3·74, s, 3H, 1-OCH_3; 4·28, d, J 10·7 Hz, 1H, H 12b; 6·98, dd, J 7·9, 1·0 Hz, 1H, H 11; 7·05, dd, J 7·9, 1·0 Hz, 1H, H 2; 7·30, dd, J 7·9, 7·9 Hz, 1H, H 10; 7·39, dd, J 7·9, 7·9 Hz, 1H, H 3; 7·46, dd, J 7·9, 1·0 Hz, 1H, H 4; 7·50, dd, J 7·9, 1·0 Hz, 1H, H 9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 35·9, C 6a; 40·9, C 12b; 43·4 and 46·2, C 6 and C 7; 55·5 and 55·8, 1-OCH_3 and 12-OCH_3; 112·8, 117·3, 117·5, 119·8, 127·5 and 127·8, C 2, C 3, C 4, C 9, C 10 and C 11; 131·6, 133·7, 133·9 and 136·7, C 4a, C 8a, C 12a and C 12c; 157·4 and 160·9, C 1 and C 12; 197·4 and 197·6, C 5 and C 8. Mass spectrum: m/z 322 (M, 100%), 307 (11), 280 (64), 253 (30), 239 (10), 165 (18), 152 (11), 146 (21), 126 (17), 41 (10).

trans-1-Methyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1i)

Diethyl (2-Methylbenzhydryl)malonate (5f)

A solution of 2-tolylmagnesium iodide (4f) in tetrahydrofuran was prepared by the dropwise addition of 2-iodotoluene (6 g, 38 mmol) to a stirring suspension of magnesium turnings (1 g) in dry tetrahydrofuran (50 ml). After cooling the Grignard reagent (4f) to 0°, a solution of diethyl benzylidenemalonate (3a) (5·7 g, 23 mmol) in dry tetrahydrofuran (5 ml) was added, and the resultant solution treated in a similar manner as for the synthesis of (5a) to yield crude diethyl (2-methylbenzhydryl)malonate (5f) which was purified by distillation to give a clear yellow oil (5·3 g, 64%), b.p. 180–185°/1·0 mmHg (lit.[5] 182–186°/0·9–1·2 mmHg). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 0·99, t, J 7·0 Hz, 3H, CH_3; 1·00, t, J 7·0 Hz, 3H, CH_3; 2·38, s, 3H, $ArCH_3$; 3·98, q, J 7·0 Hz, 2H, CH_2; 4·00, q, J 7·0 Hz, 2H, CH_2; 4·33, d, J 12·1 Hz, 1H, CH; 4·97, d, J 12·1 Hz, 1H, Ar_2CH; 7·07–7·39, m, 9H, 9×ArH.

2-(2-Methylbenzhydryl)propane-1,3-diol (6f)

Diethyl (2-methylbenzhydryl)malonate (5f) (5·3 g, 15 mmol) was treated in a similar manner as (5a) to yield 2-(2-methylbenzhydryl)propane-1,3-diol (6f) (3·8 g, 97%). A sample was recrystallized from carbon tetrachloride to give white needles, m.p. 105–107° (lit.[5] 105·8–106·8°). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·37, s, 3H, CH_3; 2·55–2·68, m, 1H, H 2; 3·62 and 3·66, dd and dd, J 12·0, 6·0 Hz, 2H, H 1_a and H 3_a; 3·80 and 3·81, dd and dd, J 12·0, 3·0 Hz, 2H, H 1_b and H 3_b; 4·29, d, J 12·0 Hz, 1H, Ar_2CH; 7·10–7·50, m, 9H, 9×ArH.

2-(2-Methylbenzhydryl)propane-1,3-diol Bismethanesulfonate (7f)

2-(2-Methylbenzhydryl)propane-1,3-diol (6f) (4 g, 16 mmol) was treated in a similar manner as (6a) to give 2-(2-methylbenzhydryl)propane-1,3-diol bismethanesulfonate (7f) (6·1 g, 99%). Recrystallization from ethanol gave white needles, m.p. 130–131° (lit.[5] 132–134°). ^1H n.m.r. (200 MHz), ($CDCl_3$): δ 2·36, s, 3H, $ArCH_3$; 2·89, s, 3H, SCH_3; 2·95, s, 3H, SCH_3; 2·98–3·40, m, 1H, H 2; 4·05 and 4·10, dd and dd, J 12·0, 6·0 Hz, 2H, H 1_a and H 3_a; 4·20, d, J 12·0 Hz, 1H, Ar_2CH; 4·30 and 4·35, dd and dd, J 12·0, 3·0 Hz, 2H, H 1_b and H 3_b; 7·10–7·50, m, 9H, 9×ArH.

β-(2-Methylbenzhydryl)glutaronitrile (8f)

2-(2-Methylbenzhydryl)propane-1,3-diol bismethanesulfonate (7f) (6·1 g, 15 mmol) was treated in a similar manner as (7a) to yield β-(2-methylbenzhydryl)glutaronitrile (8f) (3·25 g, 80%), which was recrystallized from ethanol, m.p. 108–109°. ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·39, s, 3H, CH_3; 2·37 and 2·44, dd and dd, J 17·2, 7·6 Hz, 2H, H α_a and H α'_a; 2·61 and 2·74, dd and dd, J 17·2, 3·3 Hz, 2H, H α_b and H α'_b; 2·89–3·05, m, 1H, H β; 4·13, d, J 12·0 Hz, 1H, Ar_2CH; 7·15–7·42, m, 9H, 9×ArH.

β-(2-Methylbenzhydryl)glutaric Acid (9f)

β-(2-Methylbenzhydryl)glutaronitrile (8f) (3·3 g, 12 mmol) was treated in a similar manner as (8a) to yield β-(2-methylbenzhydryl)glutaric acid (9f) (3·3 g, 75%). Recrystallization from chloroform gave white needles, m.p. 202–204° (lit.[5] 201–204°). ν_{max} (chloroform): 3010br (OH), 1683s (C=O), 1214m, 1041w, 929w cm^{-1}. ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·32, s, 3H, CH_3; 2·16 and 2·17, dd and dd, *J* 14·7, 9·2 Hz, 2H, Hα_a and Hα'_a; 2·45 and 2·52, dd and dd, *J* 14·7, 2·7 Hz, 2H, Hα_b and Hα'_b; 3·35–3·51, m, 1H, Hβ; 3·90, d, *J* 11·0 Hz, 1H, Ar_2CH; 7·20–7·50, m, 9H, 9×ArH.

trans-*1-Methyl-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1i)*

β-(2-Methylbenzhydryl)glutaric acid (9f) (100 mg, 0·3 mmol) was treated in a similar manner as (9b) to yield *trans*-1-methyl-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1i) (60 mg, 68%). A sample recrystallized from methanol had m.p. 180–183° (lit.[5] 180–182°). ν_{max} (chloroform): 3025w, 1711s (C=O), 1488m, 1297w, 1236m, 1105w, 1026w cm^{-1}. λ_{max} (chloroform): 284·8 (log ε 2·16), 251·6 nm (2·72). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·13, s, 3H, CH_3; 2·50–2·91, m, 5H, H6a, H6α, H6β, H7α and H7β; 4·28, d, *J* 10·0 Hz, 1H, H12b; 6·86, dd, *J* 7·6, 1·8 Hz, 1H, H12; 7·35, ddd, *J* 7·6, 7·6, 1·8 Hz, 1H, H10; 7·39, ddd, *J* 7·6, 7·6, 1·8 Hz, 1H, H11; 7·40, dd, *J* 7·6, 7·6 Hz, 1H, H3; 7·51, dd, *J* 7·6, 1·4 Hz, 1H, H2; 7·85, dd, *J* 7·6, 1·4 Hz, 1H, H4; 7·89, dd, *J* 7·6, 1·8 Hz, 1H, H9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 24·7, CH_3; 40·0 and 48·1, C6 and C7; 45·7, C6a; 48·5, C12b; 127·7, 128·5, 130·5, 130·7, 131·0, 136·1 and 139·0, C2, C3, C4, C9, C10, C11 and C12; 136·8, 137·8, 141·0, 141·8 and 146·8, C1, C4a, C8a, C12a and C12c; 209·0 and 212·0, C5 and C8. Mass spectrum: *m/z* 290 (M, 65%), 234 (94), 208 (100), 165 (19), 116 (28), 89 (33), 41 (50).

trans-1-Methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1j)

Diethyl (2-Methoxybenzhydryl)malonate (5g)

The Grignard reagent, prepared from 2-bromoanisole (4g) (6 g) and magnesium turnings (1 g) in dry tetrahydrofuran (50 ml), was added to a stirred solution of diethyl benzylidenemalonate (3a) (6·4 g, 23 mmol) and cuprous bromide (2·0 g) in dry tetrahydrofuran (50 ml). The mixture was treated in a similar manner as for the synthesis of (5a) to yield diethyl (2-methoxybenzhydryl)malonate (5g) (6·78 g, 88%) as a yellow solid which was used in the next step without further purification. A sample recrystallized from cyclohexane had m.p. 78–80° (lit.[7] 81·5–82·0°). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 0·98, t, *J* 7·0 Hz, 3H, CH_3; 0·99, t, *J* 7·0 Hz, 3H, CH_3; 3·77, s, 3H, OCH_3; 3·98, q, *J* 7·0 Hz, 4H, CH_2; 4·47, d, *J* 12·4 Hz, 1H, Ar_2CH; 5·11, d, *J* 12·4 Hz, 1H, CH; 6·78, dd, *J* 7·9, 1·0 Hz, 1H, ArH3; 6·87, ddd, *J* 7·9, 7·9, 1·0 Hz, 1H, ArH5; 7·10–7·35, m, 7H, 7×ArH.

2-(2-Methoxybenzhydryl)propane-1,3-diol (6g)

Diethyl (2-methoxybenzhydryl)malonate (5g) (6·78 g, 19 mmol) was treated in a similar manner as (5a) to yield 2-(2-methoxybenzhydryl)propane-1,3-diol (6g) (5·13 g, 99%). Recrystallization from ethanol gave white needles, m.p. 69–72° (lit.[7] 70–72°). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·51–2·60, m, 1H, H2; 3·61–3·78, m, 4H, 2×CH_2; 3·84, s, 3H, OCH_3; 4·56, d, *J* 12·0 Hz, 1H, Ar_2CH; 6·85, dd, *J* 8·0, 1·0 Hz, 1H, ArH3; 6·91, ddd, *J* 8·0, 8·0, 1·0 Hz, 1H, ArH5; 7·10–7·39, m, 7H, 7×ArH.

2-(2-Methoxybenzhydryl)propane-1,3-diol Bismethanesulfonate (7g)

2-(2-Methoxybenzhydryl)propane-1,3-diol (6g) (5·13 g, 19 mmol) was treated in a similar manner as (6a) to yield 2-(2-methoxybenzhydryl)propane-1,3-diol bismethanesulfonate (7g) (5·0 g, 62%) as a light orange solid. A sample recrystallized from ethanol had m.p. 123–125°. ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·87, s, 3H, SCH_3; 2·88, s, 3H, SCH_3; 3·20–3·37, m, 1H, H2; 3·82, s, 3H, OCH_3; 4·06 and 4·12, dd and dd, *J* 10·5, 6·5 Hz, 2H, H1_a and H3_a; 4·31 and 4·32, dd and dd, *J* 10·5, 3·0 Hz, 2H, H1_b and H3_b; 4·42, d, *J* 12·3 Hz, 1H, Ar_2CH; 6·83, dd, *J* 8·5, 1·0 Hz, 1H, ArH3; 6·94, ddd, *J* 8·5, 8·5, 1·0 Hz, 1H, ArH5; 7·15–7·39, m, 7H, 7×ArH.

β-(2-Methoxybenzhydryl)glutaronitrile (8g)

2-(2-Methoxybenzhydryl)propane-1,3-diol bismethanesulfonate (7g) (5·0 g, 12 mmol) was treated in a similar manner as (7a) to yield β-(2-methoxybenzhydryl)glutaronitrile (8g) (3·1 g, 92%) which was recrystallized from benzene/cyclohexane, m.p. 99–100° (lit.[7] 100–101°). ν_{max} (chloroform): 3015w, 2353m (CN), 1671m, 1491m, 1456m, 1241s, 1113w, 1026m, 701m cm^{-1}. ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·38 and 2·47, dd and dd, *J* 10·5, 7·5 Hz, 2H, Hα_a and Hα'_a; 2·67 and 2·47, dd and dd, *J* 10·5, 3·0 Hz, 2H, Hα_b and Hα'_b; 3·00–3·17, m, 1H, Hβ; 3·98, s, 3H, OCH_3; 4·36, d, *J* 12·1 Hz, 1H, Ar_2CH; 6·53, dd, *J* 7·5, 1·0 Hz, 1H, ArH3; 6·95, ddd, *J* 7·5, 7·5, 1·0 Hz, 1H, ArH5; 7·14–7·35, m, 7H, 7×ArH.

β-(2-Methoxybenzhydryl)glutaric Acid (9g)

β-(2-Methoxybenzhydryl)glutaronitrile (8g) (3·1 g, 11 mmol) was treated in a similar manner as (8a) to yield β-(2-methoxybenzhydryl)glutaric acid (9g) (2·01 g, 55%) as a light tan foam. A sample was recrystallized from chloroform, m.p. 138–140° (lit.[7] 164·0–164·5°). ^1H n.m.r. (200 MHz, $CDCl_3$): δ 2·38 and 2·47, dd and dd, *J* 11·0, 8·0 Hz, 2H, Hα_a and Hα'_a; 2·50, dd, *J* 11·0, 1·5 Hz, 2H, Hα_b and Hα'_b; 3·00–3·17, m, 1H, Hβ; 3·98, s, 3H, OCH_3; 4·36, d, *J* 12·1 Hz, 1H, Ar_2CH; 6·82, dd, *J* 8·2, 1·0 Hz, 1H, ArH3; 6·93, ddd, *J* 7·4, 7·4, 1·0 Hz, 1H, ArH5; 7·12–7·40, m, 7H, 7×ArH.

trans-*1-Methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1j)*

β-(2-Methoxybenzhydryl)glutaric acid (9g) (190 mg, 0·3 mmol) was treated in a similar manner as (9b) to yield a light tan foam (233 mg, 80·4%). ^1H n.m.r. showed that the crude material was a 2 : 1 mixture of *trans*-1-methoxy-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene-5,8-dione (1j) and *cis*-1-methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione (1k). Purification by preparative normal phase h.p.l.c. [Whatman Partisil-10; eluent: ethyl acetate (12%) and triethyl-amine (0·4%) in light petroleum] gave the first major component, trans-*1-methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1j), as a white solid (86 mg, 52%) which was recrystallized from benzene/light petroleum, m.p. 209–212° (Found: C, 78·4; H, 5·6. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%). ν_{max} (chloroform): 3013w, 2956w, 1682s (C=O), 1597m, 1578w, 1308m, 1280m, 1643w, 1019w cm^{-1}. λ_{max} (chloroform): 306·0 (log ε 2·54), 258·2 (2·47), 252·4 nm (3·07). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·53–2·94, m, 5H, H6α, H6β, H7α, H7β and H6a; 3·95, s, 3H, OCH_3; 4·94, d, *J* 11·2 Hz, 1H, H12b; 6·73, dd, *J* 7·6, 1·5 Hz, 1H, H12; 7·27, dd, *J* 8·1, 1·5 Hz, 1H, H2; 7·37, ddd, *J* 7·6, 7·6, 1·5 Hz, 1H, H10; 7·39, ddd, *J* 7·6, 7·6, 1·5 Hz, 1H, H11; 7·42, dd, *J* 8·1, 8·1 Hz, 1H, H3; 7·75, dd, *J* 8·1, 1·5 Hz, 1H, H4; 8·15, dd, *J* 7·6, 1·5 Hz, 1H, H9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 36·8, C6a; 43·0, C12b; 43·1 and 45·7, C6 and C7; 55·2, OCH_3; 115·1, 119·4, 125·2, 126·8, 127·5, 128·6 and 132·4, C2, C3, C4, C9, C10, C11 and C12; 128·3, 133·7, 135·6 and 144·6, C4a, C8a, C12a and C12c; 157·8, C1; 197·1 and 197·7, C5 and C8. Mass spectrum: *m/z* 292 (M, 100%), 250 (83), 235 (16), 224 (57), 219 (17), 209 (25), 202 (13), 189 (16), 178 (13), 165 (55), 152 (43), 146 (17), 126 (10), 115 (13), 89 (10), 83 (10), 76 (29), 63 (18), 51 (13), 44 (43), 32 (100).

The second component, *cis-1-methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene-5,8-dione* (1k), was obtained as a white solid (40 mg, 24%) which was recrystallized from benzene/light petroleum to give colourless crystals, m.p. 202–205° (Found: C, 78·1; H, 5·6. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%). λ_{max} (chloroform): 303·6 (log ε 2·25), 252·4 nm (2·84). ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·50–3·03, m, 5H, H6α, H6β, H7α, H7β and H6a; 3·93, s, 3H, OCH_3; 4·91, d, *J* 3·1 Hz, 1H, H12b; 6·71, dd, *J* 7·5. 1·0 Hz, 1H, H12; 7·23, dd, *J* 7·5, 1·0 Hz, 1H, H2; 7·31, ddd, *J* 7·5, 7·5, 1·0 Hz, 1H, H10; 7·38, ddd, *J* 7·5, 7·5, 1·0 Hz, 1H, H11; 7·44, dd, *J* 7·5, 7·5 Hz, 1H, H3; 7·71, dd, *J* 7·5, 1·0 Hz, 1H, H4; 8·08, dd, *J* 7·5, 1·0 Hz, 1H, H9. ^{13}C n.m.r. (50 MHz, $CDCl_3$): δ 35·0, C6a; 36·1, C12b; 39·5 and 43·8, C6 and C7; 56·0, OCH_3; 115·1, 120·0, 126·9, 127·2, 128·6, 129·3 and 134·2, C2, C3, C4, C9, C10, C11 and C12; 132·3, 132·8, 133·8 and 140·6, C4a, C8a, C12a and C12c; 157·1, C1; 196·1 and 196·8, C5 and C8. Mass spectrum: *m/z* 292 (M, 100%), 250 (64), 235 (11), 224 (34), 218 (11), 209 (14), 165 (31), 152 (24), 118 (10), 76 (17), 44 (26), 32 (100).

Acknowledgments

The authors express thanks to the Australia Research Council, and to the Cooperative Research Centre for Molecular Engineering and Technology for financial support.