N.M.R. Spectra and Conformations of 9,10-Dihydroanthracenes

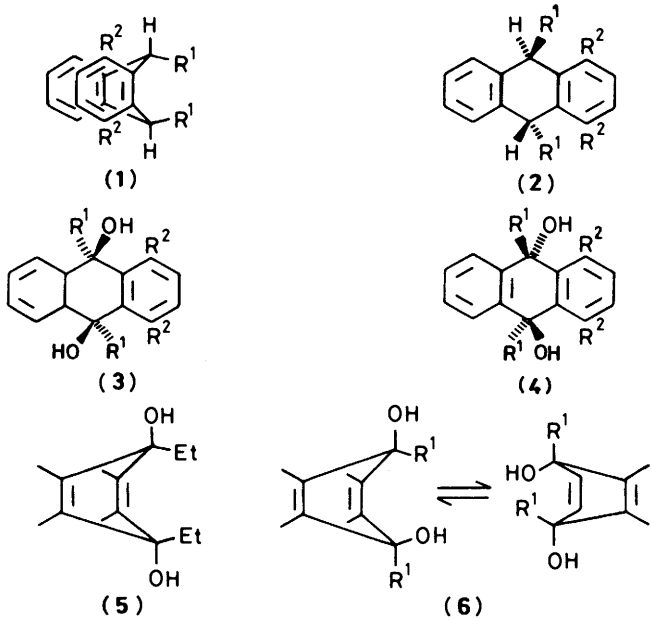
Naseer-ud-din Ahmad, Christopher Cloke, Ian K. Hatton, Norman J. Lewis, and Jake MacMillan*
School of Chemistry, The University, Bristol BS8 1TS

The preparation of a series of substituted 9,10-dihydroanthracenes is described and their proton n.m.r. spectra are discussed. It is suggested that the *trans*-isomers of 9,10-dialkyl-9,10-dihydroanthracenes, substituted in the 9,10- or *peri*-positions adopt a planar ring conformation with the 9,10-dialkyl substituents placed over the ring. It is further suggested that the highfield signal of the β-protons of the 9,10-dialkyl substituents is due partly to the magnetic anisotropy of the aromatic rings, and partly to the magnetic anisotropy of the carbon–carbon bonds from the alkyl groups to the 9-and 10-positions in the central ring.

The extensive, and often contradictory, literature on the conformational analysis of cyclohexa-1,4-dienes has been reviewed by Rabideau.[1] In the case of the 9,10-dihydroanthracenes, n.m.r. evidence indicates that *cis*-9,10-dialkyl derivatives (**1**) exist in solution as boat conformers of the central ring with ψ-axial 9,10-substituents; large substituents, however, appear to cause a flattening of the central ring. The conformations of the *trans*-isomers (**2**) have been less well defined but the symmetry of their ^{1}H n.m.r. spectra indicates that they possess a plane of symmetry at least on the n.m.r. time scale.

The n.m.r. spectra of 9,10-dialkyl-9,10-dihydro-anthracene-9,10-diols are of special interest. In the *trans*-isomers (**4**) the alkyl protons, β- to the ring system, are highly shielded.[2,3] The *trans*-isomers (**4**) are also distinguished from the *cis*-isomers (**3**) by the lower chemical shift of the alkyl protons α- to the ring. In trying to explain the highfield signal of, for example, the methyl protons at δ 0.22 in the *trans*-isomer (**4b**), Cohen *et al.*[3] erroneously concluded that this isomer was the *cis*-9,10-diaxial conformer (**5**), Cocgnacq *et al.*[2] have suggested that the *trans*-isomers (**4**) exist as the rapidly equilibrating boat conformers (**6**) in which the average position of the α- and β-protons of the alkyl substituents are respectively in the deshielding and shielding zones of the aromatic rings. This latter explanation is unsatisfactory on the basis of Johnson–Bovey calculations[4] which, for compound (**4b**), give a maximum shielding of 0.72 p.p.m. for the methyl protons of the axial substituent and a minimum deshielding of 0.01 p.p.m. for the methyl protons of the equatorial substituent. Moreover the *trans*-9,10-dihydroanthracenes (**2**), without the 9,10-dihydroxy substituents, would also be expected to exist in the same equilibrating conformers, but, in the absence of *peri*-substituents (see later) the β-protons of the 9,10-dialkyl substituents in these compounds do not show the exceptionally highfield chemical shifts, shown by the β-protons of the 9,10-dialkyl substituents in the *trans*-isomers (**4**).

This paper describes the preparation of a series of 9,10-dialkyl-9,10-dihydroanthracenes and their 9,10-diols and discusses their ^{1}H n.m.r. spectra in terms of their conformations. The following paper presents *X*-ray diffraction structures for three of these 9,10-dihydroanthracenes.



a; R^1 = Me, R^2 = H
b; R^1 = Et, R^2 = H
c; R^1 = $(CH_2)_2$Me, R^2 = H
d; R^1 = $(CH_2)_2$Ph, R^2 = H
e; R^1 = Pr^i, R^2 = H
f; R^1 = Bu^t, R^2 = H
g; R^1 = Et, R^2 = OMe
h; R^1 = Me, R^2 = OMe

9,10-*Dialkyl*-9,10-*dihydroanthracene*-9,10-*diols*.—The *cis*- and *trans*-isomers, shown in Table 1, were prepared essentially as described by Chodkiewicz *et al.*[5] The *cis*-isomers (**3b,c,d,g,h**) were obtained with unambiguous stereochemistry, by catalytic reduction of the epidioxides (**7b,c,d,g,h**) using 2% palladium on barium carbonate;[6] the alternative method of reduction using lithium aluminium hydride[7,8] was not used because of the risk of isomerisation of the resulting diols (**3**) during acidic work-up (see later). The epidioxides were obtained by photo-oxygenation of the anthracenes (**8b,c,d,g,h**) which were obtained by treating the diols, prepared from anthraquinone and the appropriate alkylmagnesium bromides, with phenylhydrazine and acetic acid.[9] Contrary to a report by Clark,[9] this method did not work for the branched 9,10-di-isopropyl 9,10-diol (**4e**). The product claimed by Clark[9] to be 9,10-di-isopropylanthracene (**8e**) was probably 9-isopropenyl-10-isopropylanthracene (**9**) which was prepared, in the present work, by heating the *trans*-diol (**4e**) with 10M-hydrochloric acid; the analogous alkenylanthracenes (**10**) and (**11**) were likewise obtained from the *trans*-diols (**4c**) and (**4d**). Attempts to prepare 9,10-di-isopropylanthracene (**8e**) by

Table 1. 9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols: chemical shifts (δ)[a] with multiplicity and *J* values (Hz) in parentheses

Compd.	Alkyl substituent protons α	β
(**3b**)	1.75 (q, 7.5)	0.82 (t, 7.5)
(**4b**)	2.15 (q, 7)	0.22 (q, 7.0)
(**3c**)[b]	1.67 (AA'BB', 4.5, 12.2)	1.35 (AA'BB'X_3, 4.5, 12.2, 7.6)
(**4c**)[c]	2.10 (AA'BB', 4.5, 12.2)	0.60 (AA'BB'X_3, 4.5, 12.2, 7.6)
(**3d**)	2.55 (m)	2.06 (m)
(**4d**)	2.50 (m)	1.80 (m)
(**3e**)	1.74 (m)	0.94 (d, 7)
(**4e**)	2.08 (m)	0.50 (d, 7)
(**3g**)	1.77 (dq, 14, 7.5) 2.19 (dq, 14, 7.5)	0.88 (t, 7.5)
(**4g**)	1.89 (dq, 13. 7.5) 2.50 (dq, 13, 7.5)	0.09 (t, 7.5)

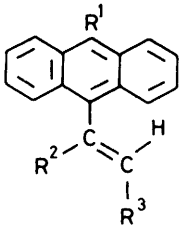
[a] In $CDCl_3$ solution with $SiMe_4$ as internal standard except for compound (**4g**) in CH_2Cl_2 solution with CH_2Cl_2 signal as lock. [b] Me signal at δ 0.75 (t, 7.6). [c] Me signal at δ 0.50 (t, 7.6)

hydrogenation of the 9-isopropenyl-10-isopropylanthracene (**9**) gave *cis*-9,10-dihydro-9,10-di-isopropylanthracene (**1e**). The required 9,10-di-isopropylanthracene (**8e**) was eventually prepared by dehydrogenation of *trans*-9,10-dihydro-9,10-di-isopropylanthracene (**2e**) with 2,3-dichloro-5,6-dicyanobenzoquinone. Contrary to Nogaideli *et al.*[10] *trans*-9,10-dihydro-9,10-di-isopropylanthracene (**2e**) was not dehydrogenated with sulphur but was isomerised to the *cis*-isomer (**1e**).

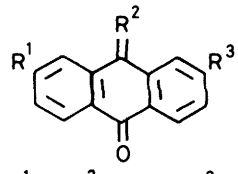
The stereochemistry of the diols, obtained in the Grignard reactions, is of interest. From methylmagnesium bromide and anthraquinone, the *cis*-isomer (**3a**) was obtained in high yield and the *trans*-isomer (**4a**) was not detected (*cf.* ref. 8). From anthraquinone and ethyl, propyl, and β-phenylethyl magnesium bromides the *trans*-isomers (**4b**—**d**) were obtained in low yields and the *cis*-isomers (**3b**—**d**) were not detected. From 1,4-dimethoxyanthraquinone and methylmagnesium bromide the *cis*-diol (**3h**) was obtained in high yield as reported previously by Lepage.[7] Reaction between 1,4-dimethoxyanthraquinone and ethylmagnesium bromide was very slow but, in refluxing anisole, it gave the *cis*- and *trans*-9,10-diols (**3g**) and (**4g**), each in *ca.* 20% yield. The stereochemistry of the 9,10-diols from anthraquinones and Grignard reagents appears therefore to depend upon both *peri*- and 9,10-interactions.

In the reaction of anthraquinone and isopropylmagnesium bromide, the main product was the anthrone (**12**). In attempts to prepare 9,10-dihydro-9,10-di-s-butylanthracene-9,10-diol, the anthrone (**13**) and the olefin (**18**) were isolated and the anthrone (**14**) and the anthraquinone (**15**) were tentatively identified as minor products. Similarly the reaction of anthraquinone and t-butylmagnesium bromide did not give the 9,10-di-t-butyl-9,10-diols (**3f**) or (**4f**); the products were the anthrone (**16**), previously obtained by Cameron and Meckel,[11] and compounds (**17**) and (**19**).

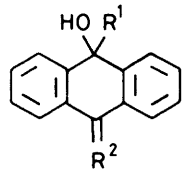
As previously noted by Cocgnacq *et al.*,[2] some of the *trans*-isomers (**4**) were isomerised to the *cis*-isomers (**3**) with acetic acid in chloroform. Thus the *trans*-isomer (**4b**) gave a mixture of the *cis*- and *trans*-isomers (**3b**) and (**4b**) in the ratio 15:1 at room temperature. The trans-diol (**4d**) gave the *cis*-isomer (**3d**) quantitatively at reflux. The *trans*-isomer (**4c**) gave the *cis*-isomer (**3c**) in *ca.* 50% yield at room temperature but, at reflux, gave 9-propyl-10-propylideneanthracene-9-ol (**20**). The *trans*-diol (**4e**) was not isomerised but was partially dehydrated to yield the anthracene (**21**). The *cis*-9,10-dimethyl 9,10-diols (**3a**) and (**3h**) and the *cis*- and *trans*-9,10-diethyl 9,10-diols (**3g**) and



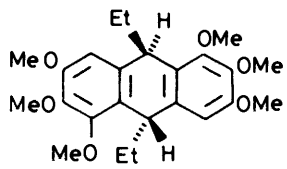
(**9**) R^1 = Pr^i, R^2 = Me, R^3 = H
(**10**) R^1 = CH_2Me, R^2 = H, R^3 = Me
(**11**) R^1 = $(CH_2)_2Ph$, R^2 = H, R^3 = Ph



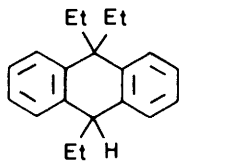
(**12**) R^1 = H, R^2 = OH, Pr^i, R^3 = Pr^i
(**13**) R^1 = H, R^2 = OH, CH(Me)Et, R^3 = CH(Me)Et
(**14**) R^1 = R^3 = CH(Me)Et, R^2 = H, OH
(**15**) R^1 = H, R^2 = O, R^3 = CH(Me)Et
(**16**) R^1 = H, R^2 = OH, Bu^t, R^3 = Bu^t
(**17**) R^1 = H, R^2 = O, R^3 = Bu^t



(**18**) R^1 = CH(Me)Et, R^2 = C(Me)Et
(**19**) R^1 = Bu^t, R^2 = H, OH
(**20**) R^1 = $(CH_2)_2$ Me, R^2 = $CHCH_2Me$
(**21**) R^1 = Pr^i, R^2 = CMe_2



(**22**)



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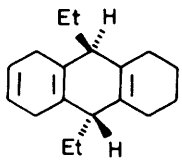

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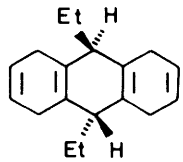

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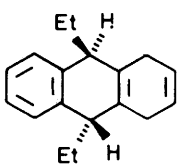

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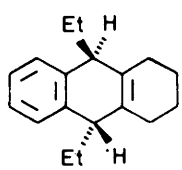


(**27**)

(**4g**) were not isomerised. Because of the instability of some of the *trans*-diols (**4**) to acidic conditions, the Grignard reactions were worked up by acidifying the reaction mixture at 0 °C and then immediately adding aqueous sodium carbonate.

9,10-*Dialkyl*-9,10-*dihydroanthracenes*.—The n.m.r. data for the isomers, prepared in this study, are listed in Table 2. The n.m.r. data for the *cis*-t-butyl compound (**1f**),[12] for di-isoelemicin (**22**),[13] and for 9,9,10-triethyldihydroanthracene (**23**)[14] are taken from the literature.

Harvey and Davis[15] have described the preparation of *cis*-9,10-diethyl-9,10-dihydroanthracene (**1b**) in 95% yield by addition–alkylation of anthracene and assigned its stereochemistry, essentially by ^1H n.m.r. spectroscopy. In our hands,

Table 2. 9,10-Dialkyl-9,10-dihydroanthracenes: chemical shift (δ)[a] with multiplicity and *J* values (Hz) in parentheses

Compd.	Proton signals 9,10	α	β
(1b)	3.77 (t, 7)	1.77 (q, 7)	1.06 (t, 7)
(2b)	3.99 (t, 5.5)	2.08 (dq, 5.5, 7.5)	0.78 (t, 7.5)
(1c)[b]	3.79 (t, 7)	1.58 (m)	1.58 (m)
(2c)[c]	3.95 (t, 6)	2.00 (m)	1.26 (m)
(1e)	3.30 (d, 10)	1.62 (dq, 7, 10)	1.00 (d, 7)
(2e)	3.75 (d, 5.5)	2.30 (dq, 5.5, 7.0)	0.96 (d, 7)
(1f)[12]	3.97 (s)	—	1.04 (s)
(2f)	3.87 (s)	—	1.20 (s)
(1g)	4.00 (dd, 5, 9)	*ca.* 1.48 (m), *ca.* 1.80 (m)	1.00 (t, 7)
(2g)	4.50 (t, 5)	*ca.* 1.68 (m), *ca.* 2.08 (m)	0.10 (t, 7.5)
(22)[13]	4.28 (t, 3.7)	1.70 (m, 3.7, 7.25, 13.5) 2.10 (m, 3.7, 7.25, 13.5)	0.20 (t, 7.25)
(23)[14]	4.00 (t, 6)	1.90 (m), 1.95 (q, 7), 2.07 (q, 7)	0.17 (t, 7), 0.63 (t, 7) 0.77 (t, 7)
(24)	*d*	*d*	0.56 (t, 7)
(25)	*e*	1.68 (dq, 3, 7.5)	0.56 (t, 7.5)
(26)	3.39 (t, *ca.* 3)	1.88 (dq, 3, 7.5, 11.5)	0.44 (t, 7.5)

[a] For $CDCl_3$ solutions with $SiMe_4$ as internal standard except for compound **(22)** ($CHCl_3$ as internal lock) and for compound **(2g)** (CH_2Cl_2 as solvent and internal lock). [b] Methyl signal at δ 0.90 (t, 7). [c] Methyl signal at δ 0.89 (t, 7). [d] Unidentified in other signals at *ca.* 1.25—2.04 (12 H, m), *ca.* 2.40—2.70 (6 H, m), and 5.79 (2 H, s). [e] Unidentified in other signals at *ca.* 2.25—2.90 (10 H, m), 5.79 (4 H, s).

treatment of anthracene with ethyl-lithium, followed by ethyl bromide, consistently gave a mixture (3:1 by n.m.r.) of the *cis*- and *trans*-isomers (**1b**) and (**2b**) from which the *cis*-isomer, m.p. 59—60 °C was isolated. Our results are all the more surprising since Rabideau and Burkholder[16] and Banks *et al.*[17] obtained the *cis*-isomer (**1b**) in high yield by ethylation of 9-ethyl-9,10-dihydroanthracene. Harvey *et al.*[14] have also described the preparation of the *trans*-isomer (**2b**), m.p. 44.5 °C, in quantitative yield by reduction of 9,10-diethylanthracene (**8b**) with lithium in liquid ammonia. In our hands, this reduction under a variety of conditions [presence or absence of iron(III) chloride, ethanol, and oxygen] gave a mixture of products from which the *trans*-isomer (**2b**), m.p. 53.5—56 °C, containing up to 7% of the *cis*-isomer (**1b**), was isolated. On one occasion over-reduction occurred to give the hydroaromatic compounds (**24**), (**25**), (**26**), and possibly (**27**), but this reduction could not be repeated.

Reductive alkylation of anthracene with sodium and propyl bromide or phenethyl bromide gave the *cis*-isomers (**1c**) or (**1d**). With isopropyl bromide, both *cis*- and *trans*-isomers (**1e**) and (**2e**) were formed as previously reported by Zeigler *et al.*[18] Contrary to the results of Redford,[19] but consistent with those of Fu *et al.*[12] and Carruthers and Hall,[20] anthracene, sodium and t-butyl bromide gave the *trans*-isomer (**2f**) and no *cis*-isomer (**1f**).

trans-9,10-Dihydro-9,10-dipropylanthracene (**2c**) and *cis*- and *trans*-9,10-diethyl-9,10-dihydro-1,4-dimethoxyanthracenes (**1g**) and (**2g**) were prepared by reduction of the appropriate anthracenes with lithium in hexamethylphosphoric triamide (HMPT)–tetrahydrofuran (THF). Lapouyade *et al.*[21] have reported that the stereochemical outcome of the reduction of 9,10-diethylanthracene (**8b**) with lithium depends on the HMPT–THF ratio; with an excess of HMPT the *cis*-isomer (**1b**) is formed predominantly and with an excess of THF the *trans*-isomer (**2b**) is the exclusive product. However, in the present work, reduction of 9,10-dipropylanthracene (**8c**) with lithium in various proportions of HMPT and THF gave the *trans*-isomer (**2c**) as the sole product. Also, reduction of 9,10-diethyl-1,4-dimethoxyanthracene (**8g**) in HMPT–THF (1:4) yielded a mixture of the *cis*- and *trans*-9,10-dihydro derivatives (**1g**) and (**2g**). The stereoselectivity, noted by Lapouyade *et al.*[21] for 9,10-diethylanthracene (**8b**) does not therefore seem to be general.

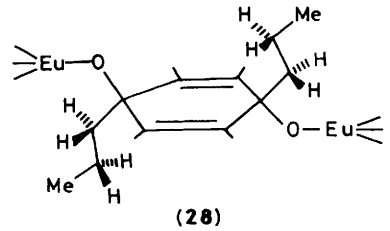
The stereochemistry of the isomeric 9,10-diethyl-9,10-dihydroanthracenes (**1b**) and (**2b**) was established unambiguously by the *X*-ray crystallographic study of the *cis*-isomer (**1b**), described in the following paper. The stereochemistry of the *cis*- and *trans*-isomers (**1e**) and (**2e**) of 9,10-dihydro-9,10-diisopropylanthracene has been established by Zeigler *et al.*[18] and their assignments are supported by the present formation of the *cis*-isomer (**1e**) by catalytic hydrogenation of 9-isopropenyl-10-isopropylanthracene (**9**), and by isomerisation of the *trans*-isomer (**2e**) with sulphur. The stereochemical assignments to the other isomeric pairs were made from their ^1H n.m.r. spectra by analogy with the spectra of the isomeric pairs of established stereochemistry. In particular, as pointed out by Redford,[19] the *peri*-protons showed a greater chemical shift difference from the other aromatic protons in the *trans*-isomers. The 9,10-*trans*-stereochemistry of the hydroaromatic products was assumed from the method of preparation.

Discussion of the N.m.r. Data.—The data in Tables 1 and 2 indicate that the exceptionally highfield signals for alkyl β-protons are characteristic of the *trans*-isomers of 9,10-dialkyl-9,10-dihydroanthracenes which are further substituted in the 9,10 or *peri*-positions. The minimum requirement appears to be one additional substituent in the 9-position [compound (**23**)]. 9,10-Dialkyl substituents alone (even the large t-butyl groups) are not sufficient. These structural requirements suggest that the highfield shifts of the β-protons are a consequence of severe interactions between the 9,10-substituents and the *peri*-positions. From an inspection of molecular models and from the crystal structure of *cis*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol (**3c**), described in the following paper, it can be seen that the *peri*-interactions can be minimised for the *cis*-isomers in a boat conformation of the central ring with the 9,10-substituents in ψ-axial positions (*cf.* Rabideau and Pascal[22]). However, in the case of the *trans*-9,10-dialkyl isomers, further substituted in 9,10 or *peri*-positions, the *peri*-interactions are minimised in a planar conformation with the 9,10-substituents and the *peri*-hydrogens or *peri*-substituents staggered. Molecular models also indicate that non-bonded interactions in a planar conformation of the highly substituted *trans*-isomers can be further minimised when the 9,10-dialkyl substituents are placed over the central ring and there is some n.m.r. evidence that the alkyl substituents in 9,10-dialkyl-9,10-dihydroanthracenes have unique conformations.

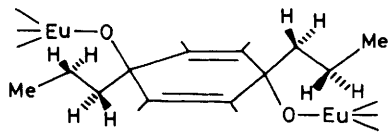
For example, in the *cis*- and *trans-isomers* (**1e**) and (**2e**) of 9,10-dihydro-9,10-di-isopropylanthracene, the *meso*- and isopropylmethine protons show coupling constants of 10 and 5 Hz, respectively. Zeigler *et al.*[18] have therefore suggested that, in the *cis*-isomer (**1e**), the ψ-axial isopropyl groups are rotated to minimise their *trans*-annular interaction, resulting in a dihedral angle of 180° between the *meso*- and isopropylmethine protons; in the *trans*-isomer (**2e**), it was suggested that these protons are eclipsed in a conformation which minimises interactions between the methyl groups and the *peri*-hydrogens. A similar situation obtains for the isomers of 9,10-diethyl-9,10-dihydro-1,4-dimethoxyanthracene; in the *cis*-isomer (**1g**) the *meso*-protons occur as a double doublet (*J* 5 and 9 Hz) and in the *trans*-isomer (**2g**) as a triplet (*J* 5 Hz). There is also clear evidence that the propyl groups in the *cis*- and *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diols (**3c**) and (**4c**) have fixed conformations. In these compounds the methylene protons occur as an AA'BB' system which was analysed[23] from the AA'XX' system, observed in the presence of tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III). The coupling

Table 3. ^{1}H Chemical shift gradients for the 9,10-di-n-propyl 9,10-diol (**4c**) in $CDCl_3$ containing five different concentrations of tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) (negative values denote upfield shifts)

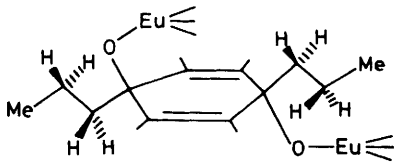
Protons	Observed gradient	Conformation	Calculated gradient (28)	(28)	(28)	(28)	(28)	(29)	(30)
		Eu–O bond length (Å)	3.2	1.5	3.3	5.9	3.9	3.3	3.3
		Eu–O–C angle (°)	120	120	135	120	120	120	120
α-Ar	5.30		6.8	−0.08	3.1	2.9	4.7	6.2	−0.14
β-Ar	1.00		2.4	−0.05	1.0	1.2	1.6	0.1	0.04
α-CH_2	7.11		6.7	1.0	3.2	4.6	6.3	0.53	1.00
β-CH_2	3.89		8.4	−0.71	3.7	2.7	4.6	2.24	−3.04
γ-Me	1.02		1.0	0.01	1.0	1.0	1.0	−1.0	−1.0



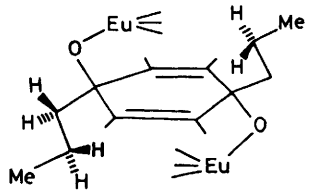
(28)



(29)



(30)



(31)

constants for the *trans*-compound (**4c**) were $J_{ax'}$ 4.5 Hz and J_{ax} 12.2 Hz. Insufficient *cis*-isomer (**3c**) was available for accurate measurements but the *J* values were estimated to be the same.

These *J* values indicate a staggered conformation for the methylene protons of the propyl substituents. Chemical shifts for the *trans*-isomer (**4c**) were measured at five concentrations of the shift reagent and the relative least-squares gradients for the different protons were obtained (Table 3). By reiterative computation[24] the relative gradients for each type of proton were calculated for the conformations (**28**), (**29**), and (**30**) using a series of parameters for the Eu–O bond length and Eu–O–C bond angle. A fourth conformation (**31**) was not considered because of the severe interaction between the europium and the propyl substituent. Since the aromatic proton signals were shifted in sets of four, the europium cannot be associated with a specific oxygen. Shifts were therefore calculated by summation of the fields from the europium on either oxygen. The results of some of the calculations are shown in Table 3. Conformation (**28**) was the only reasonable one. Agreement between the observed and calculated relative gradients was best for a Eu–O bond length of 3.9 Å and a Eu–O–C bond angle of 120°. The long Eu–O bond length is reasonable for a tertiary alcohol.

The conformation (**28**), deduced for the europium(III) complex with *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol (**4c**) has been established for the *trans*-9,10-diol (**4c**) itself in the crystalline state (see following paper). In this conformation, the alkyl β-protons are placed over the planar central ring. It is therefore proposed that the *trans*-9.10-diol (**4c**), and other 9,10-dialkyl-9,10-dihydroanthracenes which are further substituted in the 9,10 or *meso*-positions, are constrained by *meso-peri* interactions into planar conformations in which the 9,10-dialkyl substituents are placed over the central ring. In such conformations, the highfield chemical shift for the β-protons of the 9,10-dialkyl substituents cannot be caused entirely by the magnetic anisotropy of the aromatic rings. For example, Johnson Bovey calculations[4] for such a conformation of the 9,10-diethyl compounds (**2b**) and (**4b**) indicate an aromatic shielding of 0.3—0.35 p.p.m. for the methyl protons. That the magnetic anisotropy of the aromatic rings is only part of the shielding of the alkyl β-protons is supported by the chemical shifts of the methyl protons in the hydroaromatic compounds (**24**), (**25**), and (**26**). It is therefore suggested that the alkyl β-protons are also shielded by the magnetic anisotropy of the eclipsing C–C bonds in the central ring.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra refer to Nujol mulls and u.v. data to ethanol solutions unless otherwise stated. N.m.r. spectra were determined at 100 MHz for $CDCl_3$ solutions with tetramethylsilane as internal standard; exceptionally for compounds with highfield signals, spectra were determined for chloroform or dichloromethane solutions using these solvent signals as internal locks. Mass spectra were obtained using an AEI-GEC MS902 and g.l.c.-mass spectra on LKB9000, Varian MAT CH-7 or AEI MS30 instruments, using silanised glass columns (1.5 m × 4 mm), packed with 2% QF-1 or 3% SE-33 on Gaschrom Q. In analytical t.l.c. (0.3 mm) plates were either viewed directly for Merck Kieselgel HF_{254} or for silica gel G, after spraying with 4% ceric sulphate in 10% aqueous sulphuric acid and heating. For preparative t.l.c., plates of Mallinkrodt SilicAR

TLC-7G, Merck Kieselgel HF_{254}, or Woelm neutral alumina were pre-washed with ethyl acetate. For column chromatography, silica gel MFC (Hopkin and Williams) or Woelm neutral alumina (Grade 1) was used. Recovery means drying with sodium sulphate then evaporation of the filtrate in a rotary evaporator. Light petroleum had b.p. 60—80 °C and ether refers to diethyl ether.

Grignard Reactions.—These reactions were performed in a stream of dry nitrogen gas by adding a solution of the anthraquinone in sodium-dried ether (or anisole) to a cooled ethereal solution of the Grignard reagent (3- to 15-fold excess), prepared in the usual way. The initially vigorous reaction was moderated by cooling in an ice–water mixture. The reaction mixture was boiled for 4 to 11 h, cooled, and poured over an ice–water mixture which was adjusted to pH 7 with 3M-hydrochloric acid then immediately to pH 8 with 1.5M-sodium carbonate. This mixture was extracted with ether and the dried (K_2CO_3) extract was concentrated stepwise until unchanged anthraquinone ceased to be deposited. Further concentration gave a crude product which was worked up as described below for each reaction. Yields were calculated on the anthraquinone consumed.

Photo-oxygenations.—Solutions of the anthracenes in methanol or pyridine were irradiated in a glass tube (4 cm diam.) by a 125 W mercury discharge unit (93% radiation at 365 nm) at a distance of 2—5 cm from the tube. Dried oxygen was bubbled through the solution which was cooled externally by compressed air. Irradiation was continued until the anthracene fluorescence had faded. The reaction solution was then evaporated to dryness to give a crude product, purified as described below for each case.

cis-9,10-*Dimethylanthracene*-9,10-*diol* (**3a**).—From anthraquinone (6.0 g), methyl iodide (15 ml) and magnesium (5.0 g) in refluxing ether for 7 h, the *cis*-9,10-dimethyl 9,10-diol (**3a**) was obtained from ether as needles (4.8 g), m.p. 201—203 °C (lit.,[2] 200 °C); $\lambda_{max.}$ 263.5 nm (ε 713); $\nu_{max.}$($CHCl_3$) 3 577 and 3 350 cm^{-1}; *m/z* 240 (M^+, 0.5%), 225 (100), and 210 (65).

trans-9,10-*Diethyl*-9,10-*dihydroanthracene*-9,10-*diol* (**4b**).—From anthraquinone (4.5 g), ethyl bromide (6 ml), and magnesium (3.32 g) in refluxing ether for 4 h, there was isolated unchanged anthraquinone (200 mg) and the *trans*-9,10-diethyl 9,10-diol (**4b**), needles (1.1 g) m.p. 177—177.5 °C (lit.,[5] 175 °C) (from ethyl acetate–light petroleum); $\lambda_{max.}$ 264 nm (ε 445), $\lambda_{infl.}$ 257 and 273 nm (ε 375 and 316).

9,10-*Diethylanthracene* (**8b**).—*trans*-9,10-Diethyl-9,10-dihydroanthracene-9,10-diol (**4b**) (3.0 g), in acetic acid (26 ml) was added to frozen phenylhydrazine (6 ml) at 0 °C. The mixture was brought rapidly to the boil and kept under reflux for 0.5 h. On concentration, 9,10-diethylanthracene (**8b**) was deposited as yellow plates (1.9 g), m.p. 146—147 °C (lit.,[5] 147 °C); $\lambda_{max.}$(hexane) 252, 260.5, 358, 376, 392, and 397 nm (ε 58 500, 13 200, 4 500, 7 500, 4 800, and 7 800); $\nu_{max.}$ 3 060, 1 620, and 760 cm^{-1}; δ 1.15 (t, *J* 7 Hz, 2 × Me), 3.58 (q, *J* 7 Hz, 2 × CH_2Me), and *ca.* 7.85 (A_2B_2, 8 × ArH).

9,10-*Epidioxy*-9,10-*diethyl*-9,10-*dihydroanthracene* (**7b**).—Prepared from 9,10-diethylanthracene (**8b**) (500 mg) in methanol (40 ml), this compound crystallised from methanol or ethanol as needles (310 mg) m.p. 203—204 °C (lit.,[5] 214 °C) (Found: M^+, 266.128. Calc. for $C_{18}H_{18}O_2$: *M*, 266.130); $\nu_{max.}$ 3 060 and 880 cm^{-1}.

cis-9,10-*Diethyl*-9,10-*dihydroanthracene*-9,10-*diol* (**3b**).—The epidioxide (**7b**) (35 mg) in ethyl acetate (3 ml) was shaken for 3 h at room temperature with 2% palladium on barium carbonate (180 mg) and hydrogen gas. Evaporation of the filtrate gave the *cis*-9,10-diethyl 9,10-diol (**3b**), m.p. 146.8 °C (lit.,[5] 150 °C) (from light petroleum) (Found: C, 80.9; H, 7.6. Calc. for $C_{18}H_{20}O_2$: C, 80.6, H, 7.5%); $\lambda_{max.}$ 260.5 nm (ε 490), $\lambda_{infl.}$ 255, 266, and 270 nm (ε 437, 393, and 286).

Reduction of the epidioxide (**3b**) with lithium aluminium hydride gave a mixture of the *cis*- and *trans*-diols (**3b**) and (**4b**) and hydrogenation with 10% palladium on charcoal yielded the *cis*-isomer (**3b**), 9,10-diethylanthracene (**8b**), starting material and an unidentified compound.

trans-9,10-*Dihydro*-9,10-*dipropylanthracene*-9,10-*diol* (**4c**).—Anthraquinone (9.0 g), propyl bromide (30.75 ml), and magnesium (6.0 g) in refluxing ether for 5 h gave unchanged anthraquinone (1.56 g) and the required 9,10-dipropyl 9,10-diol (**4c**) as needles (4.4 g), m.p. 182 °C (lit.,[5] 179 °C) (from ether) (Found: C, 81.1; H, 8.0. Calc. for $C_{20}H_{24}O_2$: C, 81.1; H, 8.1%); $\lambda_{max.}$ 263.5 nm (ε 423), $\lambda_{infl.}$ 272 nm (ε 296); *m/z* 296 (M^+, 0%), 262 (5), 254 (20), 253 (100), and 211 (27).

The δ-values (in Hz from tetramethylsilane) for $CDCl_3$ solutions of the *trans*-diol (**4c**) (17.6 mg) containing 6.8, 15.7, 24.5, 33.0, and 40.4 mg of tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) were: Me (72, 98, 122, 149.2, and 169.4), β-CH_2 (89.4, 186.2, 280.6, 382.4, and 46.5), α-CH_2 (284, 467.4, 633.8, 827.8, and 967), β-ArH (746.6, 772.8, 797, 824.6, and 844.6), and α-ArH (826.6, 977, 1 093.7, 1 232.7, and 1 342.5).

9,10-*Dipropylanthracene* (**8c**).—The diol (**4c**) (1.0 g) and phenylhydrazine (2.0 ml) were warmed for 0.5 h in acetic acid. On cooling the anthracene (**8c**) was deposited as yellow plates (590 mg), m.p. 140.3—141 °C (lit.,[5] 141 °C) (Found: C, 91.8; H, 8.3. Calc. for C, 91.6; H, 8.5%); $\lambda_{max.}$ 260, 357, 376, and 397 nm (ε 141 500, 5 250, 7 850, and 8 950), $\lambda_{infl.}$ 252 nm (ε 71 600); *m/z* 262 (M^+, 72%), 233 (100), and 191 (83).

9,10-*Epidioxy*-9,10-*dihydro*-9,10-*dipropylanthracene* (**7c**).—Prepared from the anthracene (**8c**) (200 mg) in dry pyridine (50 ml) in a stream of oxygen for 2.5 h, the epidioxide (**7c**) crystallised from methanol as needles (174 mg), m.p. 170—171 °C (lit.,[5] 170 °C); $\lambda_{max.}$ 271 nm (ε 2 940); δ 1.11 (t, *J* 7 Hz, 2 × Me), 1.80 (m, 2 × CH_2CH_2Me), 2.55 (m, 2 × CH_2CH_2-Me), and *ca.* 7.30 (m, 8 × Ar*H*); *m/z* 294 (M^+, 0%), 262 (81), 2 101 (100), and 159 (98).

cis-9,10-*Dihydro*-9,10-*dipropylanthracene*-9,10-*diol* (**3c**).—The epidioxide (**7c**) (50 mg) in ethyl acetate (20 ml) was hydrogenated for 2 h with hydrogen and 2% palladium on barium carbonate (250 mg). The *cis*-9,10-dipropyl 9,10-diol (**3c**) crystallised from light petroleum as prisms (45 mg), m.p. 162—164 °C (lit.,[5] 165 °C) (Found: C, 81.2; H, 8.0. Calc. for $C_{22}H_{24}O_2$: C, 81.0; H, 8.2%); $\lambda_{max.}$ 260 nm (ε 592), $\lambda_{infl.}$ 270 nm (ε 370); *m/z* 296 (M^+, 0%), 278 (3), 262 (96), 235 (46), 231 (40), and 193 (40).

The δ-values (in Hz from tetramethylsilane) for $CDCl_3$ solutions of the *cis*-diol (**3c**) (5.3 mg) to which were added 2.8, 6.3, 8.7, and 11.0 mg of tris(2,2,6,6-tetramethylheptane-4,5-dionato)europium(III) were: Me(78.4, 92, 94.2, and 100), β-CH_2 (137.2, 202.6, 220, and 248.4), α-CH_2 (180, 268, 288.2, and 327), and β-ArH (776.2, 820.6, 857.6, and 884.6).

Hydrogenation of the epidioxide (**7c**) with 10% palladium on charcoal gave a mixture of the *cis*-diol (**3c**) (80%), the *trans*-diol (**4c**) (4%), 9,10-dipropylanthracene (**8c**) (4%), and starting material.

9-trans-*Propenyl*-10-*propylanthracene* (**10**).—The *trans*-diol (**4c**) (300 mg) in acetone (30 ml) and 10M-hydrochloric acid (2.5 ml) were heated on a water-bath for 1 h and then neutralised

with solid potassium carbonate. Recovery gave the propenyl derivative (**10**), as prisms (225 mg), m.p. 116—9 °C (from ethanol) (lit.,[25] 125—126 °C) (Found: C, 92.1; H, 7.6. Calc. for $C_{20}H_{20}$: C, 92.3; H, 7.7%); $\lambda_{max.}$(cyclohexane) 261, 357, 375, and 395 nm (ε 117 000, 4 875, 7 800, and 7 410); $\lambda_{infl.}$ 253 nm (ε 71 500); δ 1.11 (t, *J* 7 Hz, CH_2CH_2*Me*), 1.81 (m, CH_2CH_2Me), 2.07 (dd, *J* 2 and 7 Hz, CH=CH*Me*), 3.50 (m, CH_2CH_2Me), 5.87 (dq, *J* 7 and 16 Hz, CH=C*H*Me), 7.07 (dd, *J* 2 and 16 Hz, –C*H*=CHMe), *ca.* 7.38 (m, 4 × ArH) and *ca.* 8.25 (m, 4 × ArH); *m/z* 260 (M^+, 52%), 231 (75), 217 (55), 216 (37), 215 (52), and 43 (100).

The anthracene (**10**) was also obtained from the *cis*-9,10-dipropyl 9,10-diol (**3c**) under the same conditions but at a slower rate.

9-*Propylidene*-10-*propylanthracen*-10-*ol* (**20**).—A solution of *trans*-9,10-dihydro-9,10-dipropylanthracene-9,10-diol (**4c**) (80 mg) in ethanol-free chloroform (15 ml) and acetic acid (1 ml) was heated under reflux for 8 h and then neutralised with potassium carbonate. Recovery yielded the *propenylanthracene* (**20**) as needles (55 mg), m.p. 134—137 °C (from light petroleum) (Found: M^+, 278.167. $C_{20}H_{22}O$ requires *M*, 278.167); $\lambda_{max.}$ 261 nm (ε 11 715); δ 0.68 and 1.10 (both t, *J* 7 Hz, 2 × Me), *ca.* 1.20 (m, CH_2CH_2Me), 1.64 (m, CH_2Et), 2.56 (q, *J* 7 Hz, $CHCH_2$Me), 6.03 (t, *J* 7 Hz, CHEt), and 7.3—7.80 (m, 8 × Ar*H*).

G.l.c. and t.l.c. of the mother liquors indicated the presence of starting material (6%), the *cis*-9,10-diol (**3c**) (4%), and 9-prop-1-enyl-10-propylanthracene (**10**) (5%).

trans-9,10-*Dihydro*-9,10-*diphenethylanthracene*-9,10-*diol* (**4d**).—The reaction between anthraquinone (15 g), phenethyl bromide (30 ml) and magnesium (10 g) in refluxing ether for 8 h gave anthraquinone (2.0 g) and the *trans*-diol (**4d**), plates (8.25 g), m.p. 223 °C (decomp.) (lit.,[5] 223 °C) (Found: C, 85.9; H, 6.7. Calc. for $C_{30}H_{28}O_2$: C, 85.7; H, 6.7%); $\lambda_{max.}$ 267 nm (ε 3 500); *m/z* 430 (M^+, 0%), 396 (26), 304 (76), 302 (47), 157 (76), and 51 (100).

9,10-*Diphenethylanthracene* (**8d**).—The *trans*-diol (**4d**) and phenylhydrazine (5 ml) were warmed for 0.5 h in acetic acid (20 ml). On cooling, the anthracene (**8d**) was deposited as plates (1.52 g), m.p. 192—194 °C (from acetone) (lit.,[5] 190—191 °C) (Found: C, 92.7; H, 6.65. Calc. for $C_{30}H_{26}$: C, 93.2; H, 6.8%); $\lambda_{max.}$(cyclohexane) 262, 342, 358, 377, and 398 nm (ε 150 540, 3 088, 7 720, 13 896, and 14 050), $\lambda_{infl.}$ 253 nm (ε 81 060); δ *ca.* 3.05 (m, 2 × CH_2Ph), *ca.* 3.85 (m, 2 × CH_2CH_2Ph), *ca.* 7.25 (m, 4 × Ar*H*), and *ca.* 7.88 (m, 4 × ArH); *m/z* 386 (M^+, 14%), 295 (39), and 91 (100).

9,10-*Epidioxy*-9,10-*dihydro*-9,10-*diphenethylanthracene* (**7d**).—The anthracene (**8d**) (200 mg) in pyridine (200 ml) was irradiated in a stream of oxygen for 6 h to give the epidioxide (**7d**) as rhombs (172 mg), m.p. 104—106 °C (from acetone) (lit.,[5] non-crystalline) (Found: C, 85.5; H, 6.2. Calc. for $C_{30}H_{26}O_2$: C, 86.1; H, 6.3%); $\lambda_{max.}$(cyclohexane) 260 nm (ε 1 254), $\lambda_{infl.}$ 267 and 274 nm (ε 902 and 714); δ *ca.* 3.0 (m, 2 × CH_2CH_2Ph) and *ca.* 7.22 (m, 8 × Ar*H*); *m/z* 418 (M^+, 11%), 386 (25), 347 (30), 295 (72), 209 (91), 191 (36), 165 (41), 152 (55), and 105 (100).

cis-9,10-*Dihydro*-9,10-*diphenethylanthracene*-9,10-*diol* (**3d**).—The epidioxide (**7d**) (100 mg) in ethyl acetate (25 ml) was hydrogenated for 4 h over 2% palladium on barium carbonate (300 mg). Recovery gave the *cis*-diol (**3d**) as needles (90 mg), m.p. 193—195 °C (from light petroleum) (lit.,[5] 186 °C); $\lambda_{max.}$ 265 nm (ε 3 150); *m/z* 430 (M^+, 0%), 396 (32), 325 (75), 307 (61), 305 (69), 220 (62), and 101 (100).

9-(trans-2-*Phenylethenyl*)-10-*phenethylanthracene* (**11**).—The *trans*-diol (**4d**) (200 mg) in acetone (50 ml) and 10M-hydrochloric acid (2 ml) were heated for 1 h at 85 °C and then neutralised with potassium carbonate. Recovery gave the *olefin* (**11**), needles (172 mg), m.p. 194—196 °C (from acetone) (Found: C, 93.3; H, 6.5. $C_{30}H_{24}$ requires C, 93.7; H, 6.3%); $\lambda_{max.}$(hexane) 260, 358, 377, and 396 nm (ε 32 640, 1 920, 3 070, and 3 650); δ *ca.* 3.04 (m, CH_2CH_2Ph), *ca.* 3.85 (m, CH_2CH_2Ph), 6.83 and 7.83 (AB, *J* 17 Hz, CH=CH), *ca.* 7.35 (m, 2 × CH_2*Ph* and 4 × ArH), and *ca.* 8.23 (m, 4 × ArH); *m/z* 384 (M^+, 38%), 293 (100), 178 (12), and 215 (43).

trans-9,10-*Dihydro*-9,10-*dipropan*-2-*ylanthracene*-9,10-*diol* (**4e**) *and* 10-*Hydroxy*-3,10-*dipropan*-2-*ylanthracen*-9(10H)-*one* (**12**).—The reaction between anthraquinone (15 g), propanyl bromide (30 ml) and magnesium (15 g) in refluxing ether for 6 h gave anthraquinone (5.2 g) and a crude product which, in hot benzene (200 ml), was washed with warm aqueous sodium dithionite until the aqueous layer was colourless. The residue, recovered from the benzene solution was triturated with light petroleum to give a crystalline mixture (by t.l.c. and g.l.c.) which was separated by p.l.c. on alumina developed with chloroform into: (a) the *trans*-diol (**4e**), R_F 0.75, needles (1.7 g, 12% yield), m.p. 156.5—157 °C (from light petroleum) (Found: C, 81.0; H, 8.0. $C_{20}H_{24}O_2$ requires C, 81.1; H, 8.1%); $\lambda_{max.}$ 261 nm (ε 845); *m/z* 296 (M^+, 0.6%), 278 (3), 262 (14), and 41 (100).

(b) The anthrone (**12**), R_F 0.80, yellow needles (3.57 g, 26% yield) m.p. 110—111 °C (from light petroleum) (lit.,[3] 109—110 °C) (Found: C, 82.6; H, 7.6. Calc. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5%); $\lambda_{max.}$ 238 and 282 nm (ε 7 840 and 20 580); δ 0.61 and 0.63 (each d, *J* 7 Hz, non-equivalent 10-CH*Me*Me), 1.28 (d, *J* 7 Hz, 3-CH*Me*$_2$), 2.08 (q, *J* 7 Hz, 10-C*H*Me$_2$), 2.97 (q, *J* 7 Hz, 2-C*H*Me$_2$), 7.26—7.62 (complex, 2-, 6- and 7-H), 7.67 (d, *J* 2 Hz, 4-H), 7.82 (dd, *J* 2 and 7 Hz, 5-H), 8.05 (d, *J* 8 Hz, 1-H), and 8.10 (dd, *J* 2 and 7.5 Hz, 8-H).

Attempted Preparation of 9,10-*Dipropan*-2-*ylanthracene* (**8e**): *Formation of* 9-*Propen*-2-*yl*-10-*propan*-2-*ylanthracene* (**9**).—(a) The *trans*-diol (**4e**) (20 mg) was unchanged (g.l.c., t.l.c.) after 1 h in refluxing acetic acid (0.4 ml) containing phenylhydrazine (0.1 ml). Acetylphenylhydrazine, m.p. 129 °C, crystallised from the cooled reaction mixture.

(b) The *trans*-diol (**4e**) (40 mg) in ether (20 ml) was heated at 85 °C for 15 min with stannous chloride (40 mg) and 10M-hydrochloric acid (2 ml). Addition of an excess of potassium carbonate and recovery from the filtrate gave the olefin (**9**) as yellow plates (31 mg), m.p. 182 °C (from ethanol) (lit.,[26] 205 °C) (Found: C, 92.2; H, 7.6. Calc. for $C_{20}H_{20}$: C, 92.3; H, 7.7%); $\lambda_{max.}$(hexane) 261, 356, 372, and 394 nm (ε 125 500, 4 650, 7 430, and 8 360); $\lambda_{infl.}$ 254 nm (ε 70 570); δ 1.73 (d, *J* 7 Hz, CH*Me*$_2$), 2.20 (s, =C*Me*), 4.52 (m, *J* 7 Hz, C*H*Me$_2$), 5.05 and 5.67 (both m, C=CH_2), *ca.* 7.36 (m, 2-, 3-, 6-, and 7-H), and 8.28 (m, 1-, 4-, 5-, and 8-H); *m/z* 260 (M^+, 44%), 217 (100), 215 (25), and 202 (21).

The compound (**9**) was also obtained without the stannous chloride.

9,10-*Dihydro*-9-*propan*-2-*yl*-10-*propan*-2-*ylideneanthracen*-9-*ol* (**21**).—The *trans*-diol (**4e**) (40 mg) in chloroform (10 ml) and acetic acid (0.4 ml) was left for 24 h in the dark and then the solution was neutralised with potassium carbonate. Recovery gave the *olefin* (**21**) (28 mg), m.p. 108—110 °C (from light petroleum) (Found: C, 87.2; H, 7.1. $C_{20}H_{22}O$ requires C, 86.3; H, 8.0%); $\lambda_{max.}$ 261.5 nm (ε 12 232); $\nu_{max.}$ ($CHCl_3$), 3 570 cm^{-1} (OH); δ 0.80 (d, *J* 7 Hz, CH*Me*$_2$), 1.85 (s, OH), *ca.* 2.04 (m, =CMe$_2$ and C*H*Me$_2$), and *ca.* 7.40 (m, 8 × Ar*H*); *m/z* 278 (M^+, 4%), 260 (5), and 235 (100).

The anthracene (**9**) which was also detected (*ca.* 5%) by g.l.c.–mass spectrometry of the crude product was formed quantitatively when excess acetic acid was used.

Dehydrogenation of trans-9,10-*Dihydro*-9,10-*dipropan*-2-*ylanthracene* (**2e**).—The dihydroanthracene (**2e**) (264 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (260 mg) in benzene (20 ml) were heated at 80 °C for 5 days in a sealed tube. Recovery from the intensely fluorescent solution and extraction of the residue with light petroleum gave a mixture containing (g.l.c.–mass spectrometry) starting material (30%) *cis*-9,10-dihydro-9,10-dipropan-2-ylanthracene (**1e**) (2%), 9-isopropenyl-10-propan-2-ylanthracene (**9**) (20%) and 9,10-dipropan-2-ylanthracene (**8e**) (65%). Fractional crystallisation from methanol gave 9,10-dipropan-2-ylanthracene (**8e**) containing 10% of the 9-isopropenylanthracene (**9**). The following characterising data for 9,10-dipropan-2-ylanthracene (**8e**) were obtained from this mixture: needles, m.p. 116—118 °C; $\lambda_{max.}$ 261.5, 340, 354, 372, and 393 nm (ε 101 525, 1 924, 4 440, 6 660, and 6 660); $\lambda_{infl.}$ 254 nm (ε 57 640); δ 1.72 (d, *J* 7 Hz, 2 × CH*Me*$_2$), 4.46 (m, 2 × C*H*Me$_2$), and *ca.* 7.88 (m, 8 × Ar*H*); *m*/*z* 254 (*M*$^+$, 42%), 209 (67), 202 (68), 201 (53), 186 (100), 185 (47), 157 (36), and 144 (42).

9,10-*Epidioxy*-9,10-*dipropan*-2-*ylanthracene* (**7e**).—The mixture (100 mg) of 9,10-dipropan-2-ylanthracene (**8e**) and 9-isopropenyl-10-propan-2-ylanthracene (**9**), obtained in the preceding experiment, was irradiated in methanol (60 ml) in a stream of oxygen for 1.5 h. The recovered residue was crystallised from light petroleum to give the *epidioxide* (**7e**), m.p. 118—120 °C (Found: *M*$^+$, 294.162. $C_{20}H_{22}O_2$ requires *M*, 294.162); $\lambda_{max.}$(cyclohexane) 270 nm (ε 1 714); δ 1.47 (d, *J* 7 Hz, 2 × CH*Me*$_2$), 3.07 (m, *J* 7 Hz, C*H*Me$_2$), and 7.23 (m, 8 × ArH); *m*/*z* 294 (*M*$^+$, 1%), 262 (29), 209 (36), 194 (27), 152 (42), and 41 (100).

9,10-*Epidioxy*-9-*isopropenyl*-10-*propan*-2-*ylanthracene*.—The anthracene (**9**) (10 mg) in methanol (10 ml) was photo-oxygenated in the usual way to give the *epidioxide*, needles m.p. 178 °C (from light petroleum) (Found: C, 82.4; H, 7.1. $C_{20}H_{20}O_2$ requires C, 82.3; H, 6.9%); $\lambda_{max.}$ 271 nm (ε 1 371); δ 1.53 (d, *J* 7 Hz, CH*Me*$_2$); 2.10 (s, =C*Me*), 3.10 (s, *J* 7 Hz, C*H*Me$_2$), 5.14 and 5.70 (both m, =CH$_2$), *ca.* 7.17 (m, 2-, 3-, 6-, and 7-H), and *ca.* 7.47 (m, 1-, 4-, 5-, and 8-H); *m*/*z* 292 (*M*$^+$, 4%), 260 (100), 259 (59), 258 (57), 217 (61), 215 (57), 210 (55), and 202 (63).

cis-9,10-*Dihydro*-9-*isopropenyl*-10-*propan*-2-*ylanthracene*-9,10-*diol*.—The above epidioxide (40 mg) in ethyl acetate (20 ml) was hydrogenated for 2 h over 2% palladium on barium carbonate to give the cis-*diol* as needles (35 mg), m.p. 147—149 °C (from light petroleum) (Found: C, 81.3; H, 7.4. $C_{20}H_{22}O_2$ requires C, 81.6; H, 7.5%); $\lambda_{max.}$ 260 nm (ε 1 175); δ 0.79 (d, *J* 7 Hz, CH*Me*$_2$), 1.75 (s, =C*Me*), 1.85 (m, *J* 7 Hz, C*H*Me$_2$), 4.35 and 4.78 (m, =C*H*$_2$), *ca.* 7.25 (m, 2-, 3-, 6-, and 7-H), and 7.67 (m, 1-, 4-, 5-, and 8-H); *m*/*z* 294 (*M*$^+$, 0%), 276 (2), 251 (73), 233 (75), 217 (100), and 215 (54).

cis-9,10-*Dihydro*-9,10-*dipropan*-2-*ylanthracene*-9,10-*diol* (**3e**).—(a) The epidioxide (**7e**) (30 mg) in ethyl acetate (10 ml) was hydrogenated for 2 h over palladium on barium carbonate (100 mg) to give the cis-*diol* (**3e**), needles (23 mg), m.p. 175—176 °C (from light petroleum) (Found: C, 80.8; H, 8.3. $C_{20}H_{24}O_2$ requires C, 81.0; 8.2%); $\lambda_{max.}$ 261 nm (ε 370); *m*/*z* 296 (*M*$^+$, 0%), 262 (3), 253 (82), 211 (94), 210 (100), and 181 (30).

(b) cis-9,10-Dihydro-9-isopropenyl-10-propan-2-yl-anthracene-9,10-diol (40 mg) in ethyl acetate (15 ml) was hydrogenated for 40 h over 10% palladium on charcoal (100 mg) to give the cis-*diol* (**3e**) (34 mg) m.p. 175—176 °C.

Attempted Preparation of 9,10-*Dihydro*-9,10-*dibutan*-2-*ylanthracene*-9,10-*diol*.—From anthraquinone (10 g), butan-2-yl bromide (25 ml), and magnesium (6 g) in refluxing ether for 7 h, anthraquinone (437 mg) was recovered together with a yellow oil which was filtered, in light petroleum, through a column (30 × 2.5 cm) of silica gel. Elution with increasing amounts of ether–light petroleum gave successively: (a) 9-*butan*-2-*yl*-10-*butan*-2-*ylidene*-9,10-*dihydro*-*anthracene*-9-*ol* (**18**) as an intractable oil, even after re-chromatography on silica gel (30 × 2.5 cm) and elution with 2% ether in light petroleum, but homogeneous by t.l.c. and g.l.c. (Found: *M*$^+$, 306.199. $C_{22}H_{26}O$ requires *M*, 306.198); $\lambda_{max.}$ 261 nm (ε 11 016); $\nu_{max.}$(CCl$_4$) 3 590, 3 460 (OH) and 1 634 cm^{-1} (C=O); δ(CH$_2$Cl$_2$) 0.67 and 1.18 (both t, *J* 7 Hz, CH$_2$*Me*), 1.00 (d, *J* 7 Hz, CH*Me*), *ca.* 1.30 (m, C*H*$_2$Me), *ca.* 1.65 [m, C*H*(Me)Et], *ca.* 2.50 [m, =C(Me)C*H*$_2$], 2.06 [s, = C(*Me*)Et] and 7.15—7.70 (m, 8 × Ar*H*); *m*/*z* 306 (*M*$^+$, 2%), 250 (42), 249 (100), and 194 (24).

(b) 3,10-*Dibutan*-2-*yl*-10-*hydroxyanthrone* (**13**) as a yellow oil, homogeneous by t.l.c. and g.l.c. (Found: *M*$^+$, 322.193. $C_{22}H_{26}O_2$ requires *M*, 322.193); $\lambda_{max.}$ 287 nm (ε 15 295); $\nu_{max.}$(CCl$_4$) 3 590, 3 450 (OH), and 1 678 cm^{-1} (CO); δ 0.4—0.8 (2 × CH$_2$*Me* and 1 × CH*Me*), 1.22 (d, *J* 7 Hz, CH*Me*), 1.60 (q, *J* 7 Hz, 2 × C*H*$_2$Me), 2.68 (m, *J* 7 Hz, 2 × C*H*), and 7.2—8.0 (m, 7 × Ar*H*); *m*/*z* 322 (*M*$^+$, 9%), 267 (45), 266 (100), 265 (89), 210 (23), and 209 (26).

Further elution gave small amounts of two compounds, possibly 3,6-dibutan-2-yl-10-hydroxyanthrone, m.p. 110—114 °C; *m*/*z* 322 (3%), 265 (29), and 43 (100); and 2-butan-2-ylanthraquinone; *m*/*z* 264 (31), 235 (100), 207 (25), and 78 (22).

Attempted Preparation of 9,10-*Dihydro*-9,10-*t*-*butylanthracene*-9,10-*diol* (**3f**, **4f**).—From anthraquinone (10 g), t-butyl bromide (20 ml), and magnesium (4 g) in refluxing ether for 11 h, anthraquinone (400 mg) was recovered together with an orange syrup which was dissolved in hot benzene and washed with aqueous sodium dithionite. Recovery from the benzene layer gave a yellow oil which was repeatedly crystallised from light petroleum to give 10-hydroxy-3,10-di-t-butylanthrone (**16**) as needles (37% yield), m.p. 168—170 °C (lit.,[11] 169—170 °C).

The material, recovered from the mother liquors, was chromatographed on a column (30 × 2.5 cm) of silica gel. Elution with 1% acetone in light petroleum gave a mixture of two components (g.l.c.) which were separated by fractional crystallisation from light petroleum to give: (a) 2-t-butylanthraquinone (**17**) as yellow needles (15% yield), m.p. 102.5—103.5 °C (lit.,[11] 102—103 °C) and (b) 9,10-*dihydroxy*-9-*t*-*butylanthracene* (**19**) as needles (2% yield), m.p. 128—133 °C (Found: C, 80.1; H, 7.7. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%); $\lambda_{max.}$ 261 nm (ε 1 005); δ 0.77 (s, C*Me*$_3$), 5.35 (s, 10-H), *ca.* 7.25 (2-, 3-, 6-, and 7-H) and *ca.* 7.65 (1-, 4-, 5-, and 8-H); *m*/*z* 268 (*M*$^+$, 0%), 211 (100), 194 (69), and 155 (37).

cis-9,10-*Dihydro*-1,4-*dimethoxy*-9,10-*dimethylanthracene*-9,10-*diol* (**3h**).—(a) From 1,4-dimethoxyanthraquinone[27] (0.5 g), methyl iodide (2 ml), and magnesium (0.5 g) in refluxing ether for 7 h, the crude product was chromatographed on a column (15 × 1.5 cm) of silica gel. Elution with 1—5% ether in light petroleum gave the *cis*-diol (**3h**) as prisms (0.41 g), m.p. 194—197 °C (from light petroleum) (lit.,[7] 199—200 °C); $\lambda_{max.}$ 289.5 nm (ε 3 000); δ 1.68 (s, 2 × Me), 3.90 (s, 2 × OMe), 5.48 (2 × OH), 6.86 (s, 2-and 3-H), and *ca.* 7.57 (m, 5-, 6-, 7-, and 8-H); *m*/*z* 340 (*M*$^+$, 10%), 325 (42), 310 (35), 307 (100), and 278 (32).

(b) The above diol (10 mg), warmed with phenylhydrazine (0.25 ml) in acetic acid (0.75 ml) for 15 min, gave the 9,10-dimethylanthracene (**8h**) (6 mg), m.p. 76—78 °C (lit.,[7] 78—79 °C) which was photo-oxygenated in methanol (5 ml) for 1 h. The product in ethyl acetate (5 ml) was shaken for 2 h with 2% palladium on barium carbonate (10 mg) to yield the *cis*-diol (**3h**).

cis-*and* trans-9,10-*Diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene*-9,10-*diol* (**3g**) and (**4g**).—1,4-Dimethoxyanthraquinone (2 g) in anisole (100 ml) was added to the Grignard reagent from magnesium (2.5 g) and ethyl bromide (8 ml) in ether (15 ml). The ether was removed by distillation and the reaction mixture was refluxed for 9 h. The recovered orange product was chromatographed on a column (30 × 2.5 cm) of silica gel which was developed with light petroleum–ether (9:1). Elution with this solvent mixture containing 1—10% acetone gave successively: (a) 1,4-dimethoxyanthracene (3%), m.p. 135—136 °C; (b) trans-9,10-*diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene*-9,10-*diol* (**4g**) as needles (21% yield), m.p. 159—162 °C (from light petroleum) (Found: C, 74.0; H, 7.2%; M^+, 328.169. $C_{20}H_{24}O_4$ requires C, 73.2; H, 7.3%; *M*, 328.167); $\lambda_{max.}$ 293 nm (ε 4 290); *m/z* 328 (M^+, 5%), 327 (20), 299 (64), 281 (31), 270 (100), 255 (38), and 240 (88).

(c) cis-9,10-*Diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene*-9,10-*diol* (**3g**) as needles (20% yield), m.p. 140—143 °C (from light petroleum) (Found: C, 72.7; H, 6.9%; M^+, 328.166; $C_{20}H_{24}O_4$ requires C, 73.2; H, 7.3%; M^+, 328.169); $\lambda_{max.}$ 290 nm (ε 3 215); *m/z* 328 (M^+, 1%), 299 (77), 281 (30), 271 (23), 270 (100), and 255 (40).

cis-9,10-*Diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene*-9,10-*diol* (**3g**).—A mixture (350 mg) of *cis*- and *trans*-diols (**3g**) and (**4g**) was heated for 15 min in acetic acid (3 ml) containing phenylhydrazine (1 ml). Elution of the crude product from a column (30 × 2.5 cm) of silica gel with light petroleum gave a yellow, unstable product [δ 1.50 (t, 6 H), 3.80 (m, 4 H), 3.92 (s, 6 H), 6.60 (s, 2 H), and 7.90 (m, 4 H); *m/z* 296 (6%) and 43 (100)] a portion (20 mg) of which was directly photo-oxygenated in methanol (15 ml) for 45 min. The product in ethyl acetate (10 ml) was shaken for 2.5 h with hydrogen and 2% palladium on barium carbonate (20 mg) to give the *cis*-diol (**3g**).

Isomerisation Experiments.—A solution of the 9,10-dialkyl 9,10-diols in ethanol-free chloroform containing 0.5—1.0% acetic acid was kept at room temperature until reaction was complete (g.l.c. and t.l.c. monitoring). The solution was washed with aqueous sodium carbonate and water. The results were:

(a) the *trans*-diol (**4b**) gave a crude product (62 mg) which was purified by t.l.c. on silica gel with dichloromethane to give the *cis*-diol (**3b**) (20 mg), m.p. 146—148 °C. G.l.c. of the total product showed the *cis*:*trans* ratio to be 9:1.

(b) The *cis*-diol (**3b**) gave results identical with (a).

(c) The product from the *trans*-diol (**4c**) (200 mg) was separated by t.l.c. on silica gel with chloroform to give the *cis*-diol (**3c**) (70 mg), m.p. 163—164 °C. G.l.c. of the total product showed the *cis*:*trans* ratio to be 4:3.

(d) The *trans*-diol (**4e**) was dehydrated (see earlier) and the diols (**3a**), (**3g**), (**3h**), and (**4g**) were unchanged.

(e) The *trans*-diol (**4d**) isomerised slowly under these conditions but a solution of it (200 mg) in acetone (50 ml) and glacial acetic acid (1 ml) was refluxed for 10 h to give the *cis*-diol (**3d**) (158 mg), m.p. 190—192.5 °C.

Addition–Ethylation of Anthracene.—Anthracene (90 mg, crystallised from ethanol and thoroughly dried) and ethyllithium (1.06M in benzene; 2 ml) in tetrahydrofuran (3 ml; freshly distilled from lithium aluminium hydride) were stirred at 0 °C in an atomosphere of nitrogen for 45 min. The red colour was discharged by freshly distilled ethyl bromide. Ether was added and the solution was washed with water. Evaporation of the dried organic layer gave an oil (134 mg) which was subjected to p.l.c. with ethyl acetate–light petroleum (5:95). From the band at R_F 0.6, an oily mixture (98 mg) was obtained and shown to be a mixture (3:1) of *cis*- and *trans*-9,10-diethyl-9,10-dihydroanthracene by n.m.r. (see ref. 14 for data). Crystallisation of the product from ethanol gave the *cis*-isomer, m.p. 59—60 °C (lit.,[14] 58—59 °C); *m/z* 236 (M^+, 10%), 207 (100), 191 (8), 189 (6), 179 (51), 178 (91), 176 (10), 165 (3), 152 (8), and 76 (3).

Lithium–Ammonia Reduction of 9,10-*Diethylanthracene* (**8b**).—(a) To a solution of lithium (70 mg) in ammonia (8 ml; redistilled from lithium) at −33 °C was added dry 9,10-diethylanthracene (50 mg) in tetrahydrofuran (8 ml; freshly distilled from lithium aluminium hydride). The reaction mixture was stirred under nitrogen gas at −33 °C. After 45 min iron(III) chloride was added and after a further 45 min ethanol (15 ml) and water (5 ml) were added. The reaction mixture was left overnight and the residue was partitioned between ether and water. Evaporation of the ether gave a gum (50 mg) which was purified by p.l.c. on silica gel–HF with light petroleum–ethyl acetate (95:5). The band at R_f 0.5 gave *trans*-9,10-diethyl-9,10-dihydroanthracene (**2b**) (28 mg), m.p. 53.5—56 °C (from ethanol) (lit.,[15] 44—45 °C) containing *ca.* 7% of the *cis*-isomer by n.m.r.; *m/z* 236 (M^+, 4%), 207 (100), 179 (48), and 178 (86).

When this reduction was repeated without the addition of the iron(III) chloride, a mixture (25 mg) was recovered from p.l.c. at R_F 0.5 and shown to consist of *cis*- and *trans*-9,10-diethyl-9,10-dihydroanthracenes and compound (**26**) in the ratio 22:71:7. Using different proportions of lithium, adding ethanol at the beginning of the reaction, conducting the reaction in the presence of air or at −70 °C, essentially the same results were obtained.

(b) *Preparation of the hydroaromatic compounds* (**24**), (**25**), *and* (**26**). Using the procedure described in (a) but without the nitrogen atmosphere or addition of iron(III) chloride, lithium (0.9 g), ammonia (150 ml) and 9,10-diethylanthracene (1.0 g) gave a crude product which was crystallised from ethanol; it had m.p. 108—112 °C. A portion (180 mg) was fractionated by preparative t.l.c. on silica gel HF with light petroleum to give: (i) trans-9,10-*diethyl*-1,4,5,6,7,8,9,10-*octahydroanthracene* (**24**), R_F 0.7 as needles, m.p. 137—137.5 °C (from ethanol) (Found: C, 89.4; H, 11.4%; M^+, 242.202. $C_{18}H_{26}$ requires C, 89.2; H, 10.8%; *M*, 242.203); *m/z* 242 (M^+, 3%), 213 (100), 185 (34), 171 (21), and 141 (27). (ii) the material from R_F 0.6 was a mixture (3:1) of two compounds by n.m.r. crystallisation from ethanol gave the major component, trans-9,10-*diethyl*-1,4,5,8,9,10-*hexahydroanthracene* (**25**), as needles (75 mg), m.p. 117—118.5 °C (Found: C, 89.8; H, 10.1%; M^+, 240.187. $C_{18}H_{24}$ requires C, 89.9; H, 10.1%; *M*, 240.188); *m/z* 240 (3%), 211 (100), 209 (35), 169 (95), 141 (35), and 55 (28). The minor component contained aromatic protons (δ *ca.* 0.48) and by g.l.c.–mass spectrometry had M^+ 240; it is tentatively assigned structure (**27**). (iii) trans-9,10-*Diethyl*-1,4,9,10-*tetrahydroanthracene* (**26**) R_F 0.5, as needles (81.4 mg), m.p. 101.5—102.5 °C (from ethanol) (Found: C, 90.8; H, 9.7%; M^+, 239.171. $C_{18}H_{22}$ requires C, 90.7; H, 9.3%; M^+, 238.172); *m/z* 238 (10), 209 (100), 181 (44), 179 (32), 178 (37), 167 (31), 71 (25), and 55 (34). This reduction could not be repeated.

cis-9,10-*Dihydro*-9,10-*dipropylanthracene* (**1c**).—Anthracene (15 g) and a dispersion of sodium (6 g) in ether (50 ml) were heated under reflux for 20 h. To the cooled mixture, propyl bromide (20 ml) in sodium-dried ether (20 ml) was added dropwise. After the initial vigorous reaction, the green solution was refluxed for 2 h. Recovery gave a gum which was dissolved in light petroleum. This solution, kept at −5 °C, deposited cis-9,10-*dihydro*-9,10-*dipropylanthracene* (**1c**) which recrystallised from ethanol as needles (60% yield), m.p. 67—68 °C (Found: C, 90.7; H, 9.1. $C_{20}H_{24}$ requires C, 90.7; H, 9.2%); $\lambda_{max.}$(cyclohexane) 270 nm (ε 1 120); $\lambda_{infl.}$ 257 and 263.5 nm (ε 725 and 1 055); *m/z* 264 (M^+, 21%); 222 (75), 221 (100), 191 (51), 179 (78), and 178 (86).

trans-9,10-*Dihydro*-9,10-*dipropylanthracene* (**2c**).—(a) Lithium (*ca.* 0.4 g) was dissolved in hexamethylphosphoramide

(3 ml) and tetrahydrofuran (12 ml) by heating at 60 °C in an atmosphere of nitrogen. After 24 h, the blue solution was cooled to 20 °C and a solution of 9,10-di-n-propylanthracene (88 mg) in hexamethylphosphoramide (2 ml) and tetrahydrofuran (8 ml) was added. The orange solution was stirred at 20 °C for 5 h under nitrogen gas. Water was added dropwise and stirring was continued for 1 h. Extraction with ether and recovery gave trans-9,10-*dihydro*-9,10-*dipropylanthracene* (**2c**) (72 mg), m.p. 58—60 °C (from ethanol) (Found: C, 91.3; H, 8.8. $C_{20}H_{24}$ requires C, 90.9; H, 9.2); $\lambda_{max.}$(cyclohexane) 271 nm (ε 1 530); *m/z* 264 (M^+, 7%), 222 (20), 221 (100), 179 (66), and 178 (54).

(b) When the anthracene (**8c**) (180 mg) was reduced as described in (a) using lithium (*ca.* 0.4 g) and HMPT–THF (7:1) the *trans*-compound (**2c**) was obtained quantitatively.

(c) From the anthracene (**8c**) (70 mg), sodium (0.7 g), HMPT (4.5 ml) and THF (3 ml), the *trans*-isomer was obtained in *ca.* 50% yield.

cis-9,10-*Dihydro*-9,10-*diphenethylanthracene* (**1d**).—Anthracene (10 g) and a dispersion of sodium (4.5 g) in dry ether (40 ml) were heated under reflux for 30 h with stirring and in an atmosphere of nitrogen. Phenethyl bromide (20 ml) in dry ether 20 ml) was added and the reaction was conducted and worked-up as for the dipropyl compound (**1c**) to give cis-9,10-*dihydro*-9,10-*diphenethylanthracene* (**1d**) as an oil (10.2 g), pure by t.l.c. (Found: M^+, 388.218. $C_{30}H_{28}$ requires *M*, 388.219); $\lambda_{max.}$ 271 nm (ε 1 153); *m/z* 388 (2), 180 (54), 179 (77), 178 (100), 177 (31), 176 (49), 152 (44), and 151 (31).

9,10-*Diphenethyl*-1,2,3,4-*tetrahydroanthracene*.—The olefin (**20**) (300 mg) in ethanol (50 ml) was hydrogenated for 40 h over 2% palladium on barium carbonate (300 mg). The filtered reaction mixture was concentrated and cooled to −5 °C to give the tetrahydroanthracene as needles (210 mg), m.p. 158—160 °C (Found: C, 92.6; H, 7.9. $C_{30}H_{30}$ requires C, 92.3; H, 7.7%); $\lambda_{max.}$(cyclohexane) 300 nm (ε 11 700); δ 1.79 (m, CH_2Ph), 2.85 (m, 1-, 2-, 3-, and 4-H), 3.30 (m, $[CH_2]_2Ph$), 7.24 (m, 2 × Ph) and 7.76 (m, 5-, 6-, 7-, and 8-H).

cis- *and* trans-9,10-*Dihydro*-9,10-*dipropan*-2-*ylanthracenes* (**1e**) *and* (**2e**).—(a) Anthracene (15 g) and a dispersion of sodium (5.5 g) in ether (40 ml) were heated under reflux for 50 h with stirring under nitrogen gas. Propan-2-yl bromide (22.5 ml) in ether (22.5 ml) was added dropwise to the cooled solution and the initial reaction was moderated by cooling in an ice–water mixture. The green solution was then refluxed for 2 h. Recovery gave an oil (19.1 g) which deposited anthracene (2.5 g) on cooling. The filtered oil in light petroleum was chromatographed on alumina; elution with the same solvent yielded (i) *trans*-9,10-dihydro-9,10-dipropan-2-ylanthracene (**2e**) as needles (6.7 g), m.p. 75—75.5 °C (from methanol) (lit.,[18] 76—77 °C) (Found: C, 90.7; H, 9.0. Calc. for $C_{20}H_{24}$: C, 90.9; H, 9.2%); $\lambda_{max.}$ 262.5 nm (ε 3 300); *m/z* 264 (M^+, 3%), 221 (45), 179 (100), and 178 (38); (ii) *cis*-9,10-dihydro-9,10-dipropan-2-ylanthracene (**1e**) as rods (0.7 g), m.p. 109—111 °C (from methanol) (lit.,[18] m.p. 109—110 °C) (Found: C, 91.2; H, 9.1. Calc. for $C_{20}H_{24}$: C, 90.9; H, 9.2%); $\lambda_{max.}$ 261.5 nm (ε 2 753); *m/z* 264 (M^+, 4%), 221 (49), 179 (100), and 178 (33).

(b) The olefin (**9**) (20 mg) in ethanol (30 ml) was hydrogenated for 2.5 h over 2% palladium on barium carbonate (100 mg) to give the *cis*-9,10-dihydroanthracene (**1e**) (16 mg).

(c) The *trans*-9,10-dihydroanthracene (**2e**) (40 mg) and sulphur (44 mg) were heated at 220—230 °C for 3 h under nitrogen gas. The sublimate was collected and crystallised from methanol to give the *cis*-9,10-dihydroanthracene (**1e**) (11 mg).

Reductive t-Butylation of Anthracene.—From anthracene (15 g) a dispersion of sodium (6 g) in ether (50 ml) and t-butyl bromide (20 ml) in ether (20 ml), was obtained a gum (6.4 g) which was fractionally crystallised from ether to yield: (a) *trans*-9,10-di-t-butylanthracene (**2f**) as rods, m.p. 176—177 °C (lit.,[20] 176 °C) (Found: C, 90.2; H, 9.5. Calc. for $C_{22}H_{28}$: C, 90.4; H, 9.6%); $\lambda_{max.}$(cyclohexane) 260, 267, and 274 nm (ε 730, 912, and 730); *m/z* 292 (M^+, 0%), 236 (9), 180 (100), and 179 (45). (b) 9-t-Butyl-9,10-dihydroanthracene, needles (34%), m.p. 121.5 °C (from pentane) (lit.,[20] 126 °C) (Found: C, 91.7; H, 8.5. Calc. for $C_{18}H_{20}$: C, 91.5; H, 8.5%); $\lambda_{max.}$ 264 and 271.5 nm (ε 944 and 944); *m/z* 236 (M^+, 0%), 221 (1), 180 (16), 179 (100), and 178 (58).

cis- *and* trans-9,10-*Diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene* (**1g**) *and* (**2g**).—Lithium (*ca.* 0.4 g) was dissolved in HMPT (3 ml) and THF (12 ml) by heating at 70 °C under nitrogen. To the blue solution at 21 °C was added 1,4-dimethoxy-9,10-diethylanthracene (75 mg) in HMPT (2 ml) and THF (8 ml), and the resultant orange solution was stirred for 2 h and 21 °C. An excess of water was added dropwise and the solution was stirred for a further 0—5 h. Extraction with ether and recovery gave a mixture which was separated by preparative g.l.c. on a column (3 m × 9.5 mm) packed with 5% SE-33 on Gaschrom Q (60—80 mesh) into the following two components: (a) trans-9,10-*diethyl*-9,10-*dihydro*-1,4-*dimethoxyanthracene* (**2g**) as an oil (Found: M^+, 296.177. $C_{20}H_{24}O_2$ requires M^+, 296.178); *m/z* 296 (M^+, 11%), 267 (73), 238 (100), and 223 (64); (b) cis-9,10-*Diethyl*-9,10-*dihydroanthracene* (**1g**), as an oil (Found: M^+, 296.177. $C_{20}H_{24}O_2$ requires *M*, 296.178); $\lambda_{max.}$(cyclohexane) 270.5 nm (ε 1 153; *m/z* 296 (M^+, 21%), 267 (73), 238 (100), 223 (73), 184 (48), and 152 (44).

Acknowledgements

N. A. thanks the Central and Punjab Provisional Government, Pakistan, for a Scholarship and leave of absence. C. C., I. K. H., and N. J. L. thank the S.E.R.C. for postgraduate studentships. We also thank Drs. R. J. Goodfellow and M. Murray for the n.m.r. spectra and helpful discussions.

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Received 3 *December* 1984; *Paper* 4/2055