SYNTHESIS AND STEREOCHEMISTRY OF SOME 9,10-DIHYDROANTHRACENES

by

Leslie Hewitt, B.A.

A thesis submitted to the
University of Keele in
partial fulfilment of the
requirements for the Degree
of Doctor of Philosophy.

Department of Chemistry,
University of Keele.

July, 1968.

SUMMARY

The geometry of the 9,10-dihydroanthracene system is discussed, leading to an explanation of the relevance of conformational analysis for 9,10-dihydroanthracene derivatives. Synthetic routes to 9,10-dialkyl-9,10-dihydroanthracene-9,10-diols are reviewed, indicating any assignments of configuration or conformation which have been made for such diols. Products derived by dehydration of these diols are then discussed.

The products isolated from the Grignard reactions of ethylmagnesium bromide, _n_-propylmagnesium bromide, _t_-butylmagnesium bromide, isopropylmagnesium chloride, and neopentylmagnesium chloride with anthraquinone are described. In the main, these products are diols of the above type, or substituted anthrones formed by a 1,2-addition of Grignard reagent to one of the carbonyl groups of anthraquinone, or substituted anthrones formed by a 1,6-addition of Grignard reagent to anthraquinone. Detailed conformational analysis of the diethyl and di-_n_-propyl diols is made, and an unsuccessful attempt to elucidate the complete structure of the 1,6-addition products is described.

The dehydration of the diethyl and dimethyl diols with acetyl chloride is shown to give 9,10-substituted anthracene derivatives.

ACKNOWLEDGMENTS

I would like to thank Professor H. D. Springall and the University of Keele for the provision of laboratory facilities, and the Science Research Council for financial support.

I am indebted to Professor I. T. Millar for his guidance and encouragement during the work, and to Dr. D. Cohen for helpful discussions.

I would also like to thank Mrs. J. A. Morrough for the typing of this thesis and Mr. P. J. Deighton for assistance with the diagrams.

All the work reported in this thesis was carried out by the Author under the supervision of Professor I. T. Millar.

L. Hewitt

CONTENTS

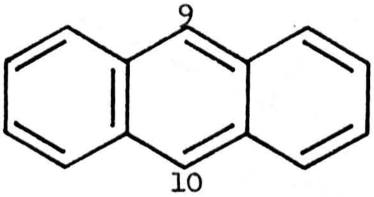
LIST OF FIGURES

LIST OF FIGURES (Contd.)

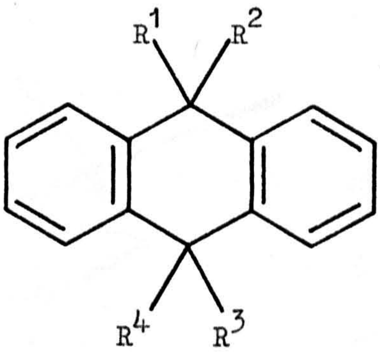
INTRODUCTION

Geometry of the 9,10-Dihydroanthracene System

The planarity of the anthracene molecule (I) has been established by detailed X-ray examination[1] of single anthracene crystals.



(I)



(II)

When the carbon atoms in the 9,10-positions of anthracene become saturated, they assume the normal tetrahedral configuration, and the system is then referred to as the 9,10-dihydroanthracene system (II). From a Dreiding model of the 9,10-dihydroanthracene system, it is seen that the molecule may be regarded as being in a pseudo boat form, i.e. it has a non-planar middle ring in a boat conformation (Fig. 1).

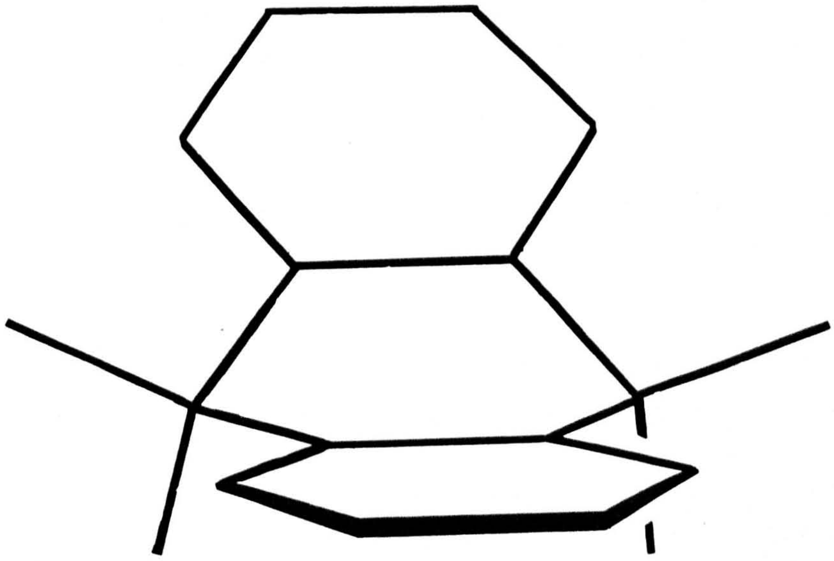


Fig. 1

Diagrammatic representation of the 9,10-dihydroanthracene system

X-ray analysis[2] (1954) has confirmed this pseudo boat form for 9,10-dihydroanthracene (II; $R^1 = R^2 = R^3 = R^4 = H$), showing that the three rings in 9,10-dihydroanthracene are not planar, and that the molecule is bent about the line joining the carbon atoms 9 and 10, so that the two halves of the molecule are inclined to each other at an angle of approximately 145° (Fig. 2).

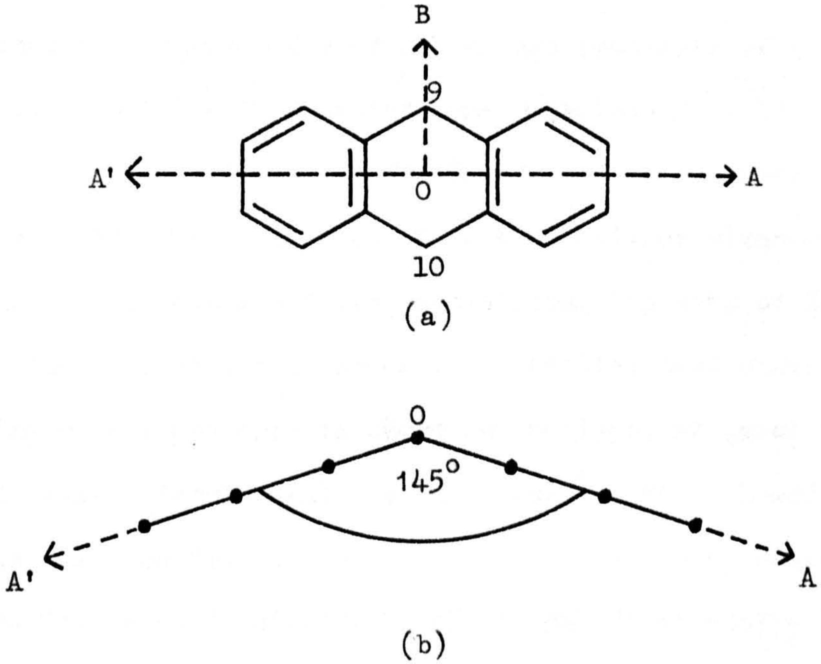


Fig. 2

(a) Diagram of the 9,10-dihydroanthracene molecule. O is the mid-point of the line joining atoms 9 and 10. OB passes through atom 9.

(b) The shape of the molecule as seen in projection on the plane perpendicular to OB.

The measured dipole moment of 0.4 D in benzene shows that the 9,10-dihydroanthracene molecule is also folded in solution.[3]

Herbstein[4] (1959) from his calculation of molecular strain energy for 9,10-dihydroanthracene, arrived at an approximate value of 150° for the angle of folding of the molecule (the dihedral angle[4]).

Experimental evidence[5] (1964) of the non-planarity of the central ring of 9,10-dihydroanthracene derivatives, has come from potentiometric measurements of ionisation constants of a series of 10-substituted-9,10-dihydroanthracene-9-carboxylic acids (II, page 1; $R^1=R^4=H$; $R^2=CO_2H$; $R^3=CO_2H$, H, CH_2OH, etc.). In contrast with the data, outlined so far, in support of a non-planar structure for 9,10-dihydroanthracene and its derivatives, two sets of X-ray results for 9,10-dihydroanthracene derivatives have shown virtual planarity of the molecule in these derivatives, at least in the crystal phase. Ferrier and his co-workers[6] (1960) showed by X-ray analysis that the dimethyl-9,10-dihydroanthracene-9,10-dicarboxylate molecule (II, page 1; $R^1=R^4=H$, $R^2=R^3=CO_2Me$) is virtually planar, and Yannoni and co-workers[7] (1965) have shown, also by X-ray analysis, that the 9,9,10,10-tetrachloro-9,10-dihydroanthracene molecule (II, page 1; $R^1=R^2=R^3=R^4=Cl$) is essentially planar.

Configuration and Conformation in the 9,10-Dihydroanthracene System

An interesting consequence of the folding of the 9,10-dihydroanthracene molecule is that two types of geometrically distinct carbon-hydrogen bonds in the meso-position can be distinguished, two being orientated almost at right angles to the line joining the 9- and 10-positions, designated pseudoaxial (a'), and two along the 9,10-axis, designated pseudoequatorial (e')[8] (Fig. 3).

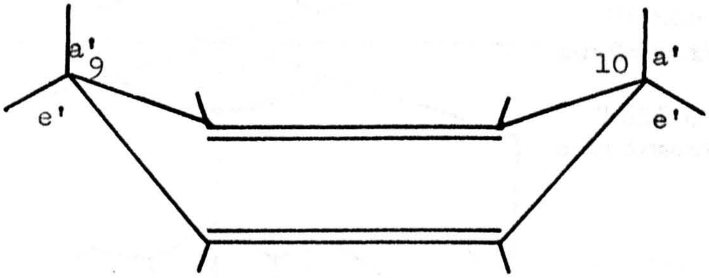


Fig. 3 (partial structure)

It is convenient to use the terms "pseudoaxial" and "pseudoequatorial" in this case, because the middle ring of the 9,10-dihydroanthracene system may be regarded as a substituted-1,4-cyclohexadiene, and the geometrical arrangement of the bonds at the "ends" of a 1,4-cyclohexadiene boat may be related to the orientations of the bonds of cyclohexane chairs[9] and cyclohexane "half chairs".[10] A Dreiding model of 9,10-dihydroanthracene shows that the molecule folds easily about the 9,10-axis, so that the original "folded" conformation is converted into a "reverse folded" conformation, with the strained planar conformation intermediate between these two "folded" conformations (Fig. 4).[8]

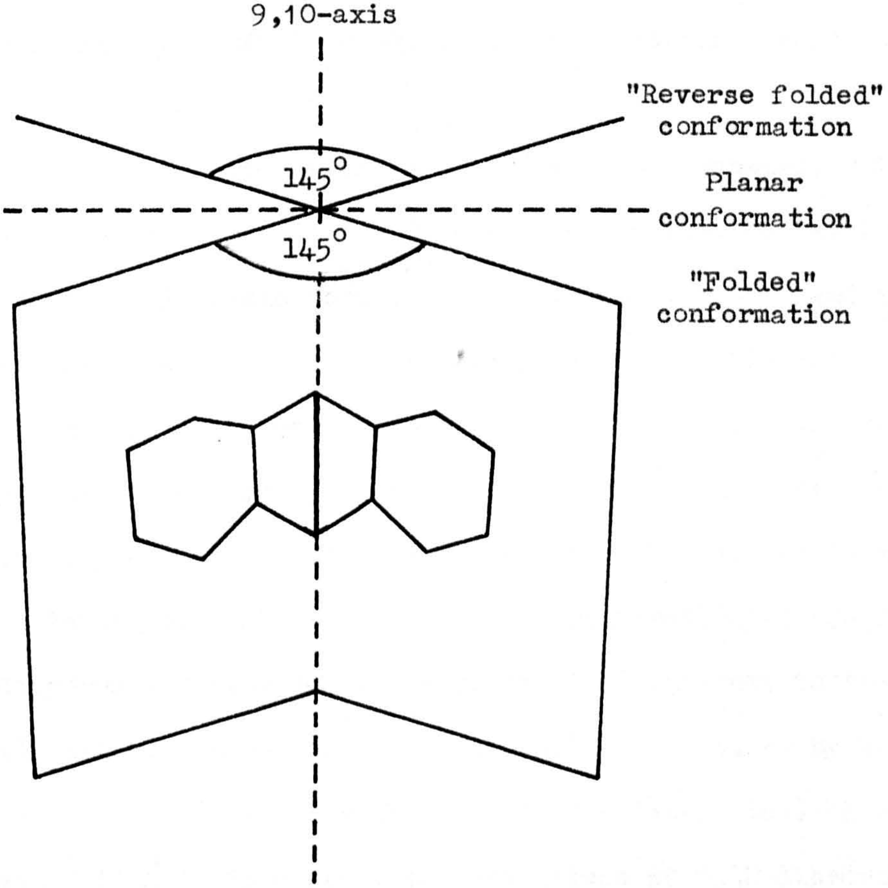


Fig. 4

Interconversion of a' and e' bonds occurs when the molecule is "reverse folded". The strained planar conformation constitutes only a small energy barrier to the "folding" of the molecule, and a value of 0.8 kcal./mole has been calculated[4] for this potential barrier in 9,10-dihydroanthracene (II, page 1; $R^1=R^2=R^3=R^4=H$). Although the energy of the two folded conformations of 9,10-dihydroanthracene will be the same, the energy of the "folded" and "reverse folded" conformations will not be equal when two dissimilar groups are present at one or both meso positions.[8]

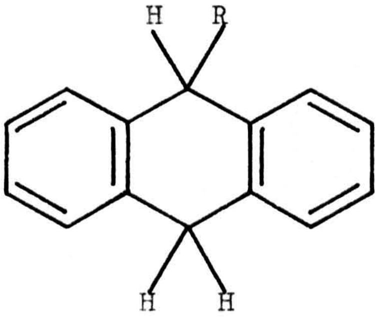
Thus 9,10-disubstituted-9,10-dihydroanthracenes, with identical substituents in the 9- and 10-positions, can empirically exist in three isomeric forms; two cis forms, (a', a') and (e', e'), and one trans (a', e'). If the energy barrier to "folding" of the molecule is small enough to allow the molecule to vibrate rapidly through the planar configuration, or if the molecule assumes a planar structure, the distinction between the two cis forms would vanish.

Having now outlined briefly the conformational problem of 9,10-dihydroanthracene derivatives, it is of interest to trace the gradual acknowledgement of this conformational problem by workers dealing with 9,10-dihydroanthracene derivatives. Schlenk and Bergmann[11] (1928), in a study of derivatives of 9,10-dihydroanthracene, stated that they had obtained more forms than seemed then to be required by stereochemical theory, and explained the extra forms as being due to "folding" of the molecule. Meerwein and Migge[12] (1929) accounted for some of Schlenk and Bergmann's "extra" isomers by showing that in fact they were mixtures. The general conformational problem of

9,10-dihydroanthracene derivatives was first stated explicitly by Campbell and her co-workers[3] (1938), and later fully considered by Beckett and Mulley[8] (1955). The latter workers went on to explain the observed differences in the reactions and reactivities of certain cis- and trans-disubstituted 9,10-dihydroanthracenes, in terms of the preferred conformations of the isomers. Similar generalisations, relating reactivity of meso-substituted 9,10-dihydroanthracenes with conformational differences, were made later (1963) by Beckett and Walker.[13]

At the time of writing, very few conformational assignments have been made for 9,10-dihydroanthracene derivatives, and the examples that can be found are all from recent years. The major part of the stereochemical work on 9,10-dihydroanthracene derivatives is concerned only with configurational, i.e. cis, trans assignments, and in some instances these assignments are made either without proof or with tenuous proof; in other instances rigorous proof for the assignments is given (e.g., see ref. 14, and see and compare refs. 15, 16 and 17). Before reviewing the specific area of this large topic which was selected for study, and before presenting the results obtained, brief mention should be made of the conformational assignments that have been made in other work on 9,10-dihydroanthracene derivatives.

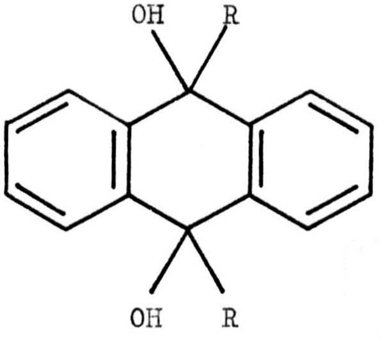
Carruthers and Hall[18] (1966) reported the isolation of 9-<u>t</u>-butyl-9,10-dihydroanthracene (III; R = $C(CH_3)_3$), and gave evidence to show that the t-butyl group was in the pseudoequatorial (e') conformation.



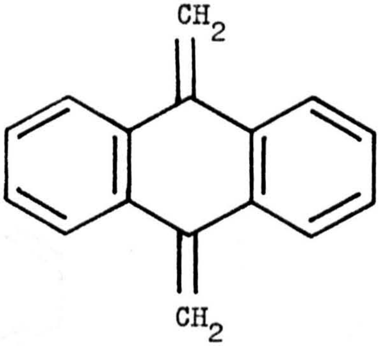
(III)

Part of this evidence was the non-equivalence of the two benzylic protons in the 10-position, as shown by the p.m.r. spectrum of this compound. The two benzylic protons appear as an AB quartet in the p.m.r. spectrum, indicating that the molecule exists in a preferred conformation. Similar examples, which likewise show an AB system for the two benzylic protons, have been reported for 9-triphenylsilyl-9,10-dihydroanthracene[19] (III; R = $Si(Ph)_3$), 9-n-butyl-9,10-dihydroanthracene[20,21] (III; R = $(CH_2)_3CH_3$), 9-methyl-9,10-dihydroanthracene[21] (III; R = CH_3), and 9-ethyl-9,10-dihydroanthracene[22] (III; R = CH_2CH_3). Moreover, Nicholls and Szwarc[22] (1966) concluded that the ethyl group in 9-ethyl-9,10-dihydroanthracene (III; R = CH_2CH_3) was in a pseudoequatorial (e') conformation.

9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols (IV)



(IV)

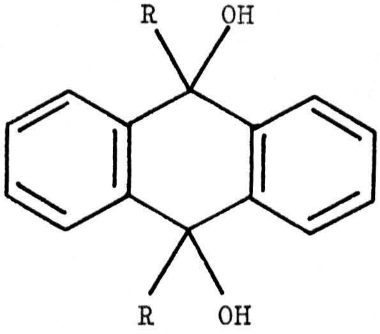


(V)

9,10-Dimethylanthracene-9,10-diol (IV; R = CH_3) has been used previously in this Department, in the generation of the reactive intermediate, 9,10-anthraquinodimethane (V).[23,24] Because of the stereochemical interest of 9,10-dihydroanthracene derivatives, as already outlined, it was decided to undertake a stereochemical study of compounds in this series (IV). Moreover, during the course of the work, it was found[25,26] that compounds in this series (IV), lend themselves to stereochemical study by means of infrared and p.m.r. spectroscopy. A thorough study of the reactions used in the syntheses or attempted syntheses of compounds in this series (IV) has also proved of interest, as have some of the products formed by the dehydration of compounds in this series.

Synthesis of 9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols

The compounds in this series are represented by the general formula (VI).

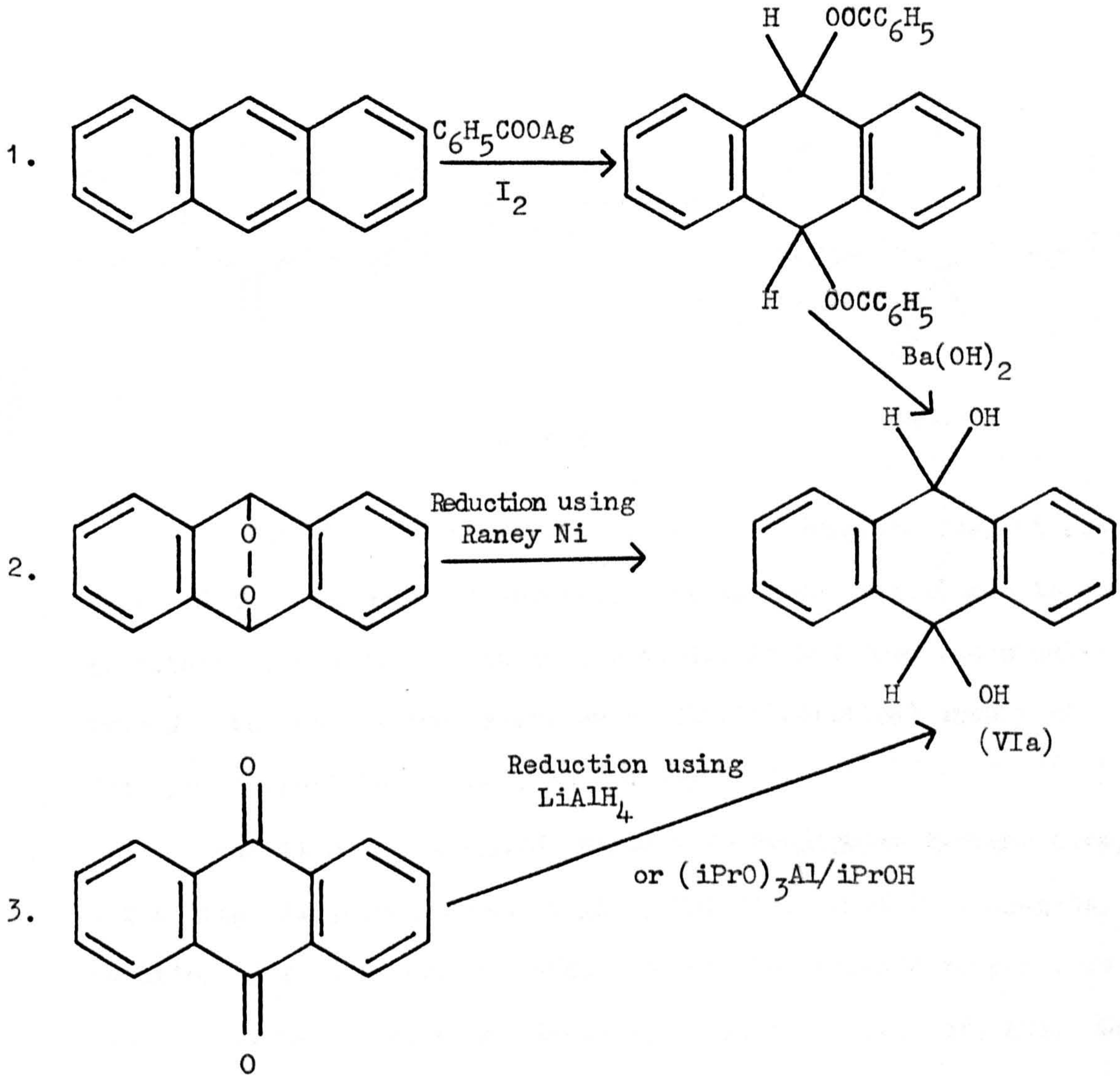


a. R = H

b. R = Alkyl

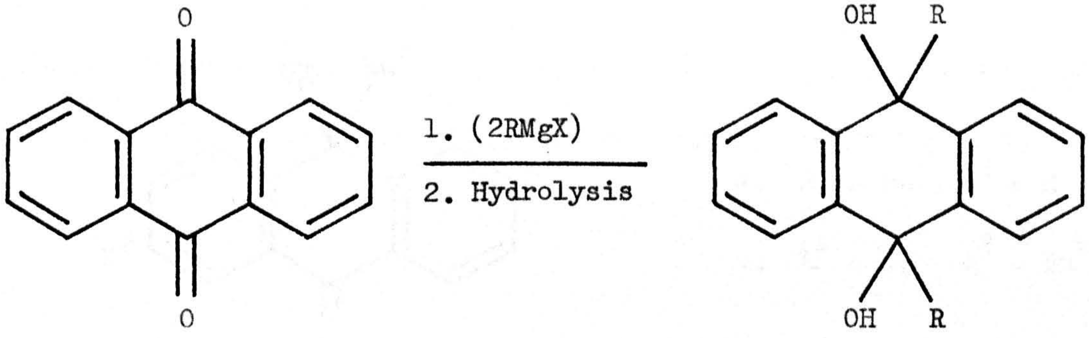
(VI)

9,10-Dihydroanthracene-9,10-diol (VIa); This compound was first made by Prévost,[27] by treating anthracene with silver benzoate and iodine and hydrolysis of the resulting dibenzoate (Scheme I; equation 1). Later, Dufraisse and Houpillart[28] synthesised this diol (VIa) by catalytic reduction of anthracene photoöxide (Scheme I; equation 2). More recently, VIa has been obtained by reducing 9,10-anthraquinone with either lithium aluminium hydride[29] or aluminium isopropoxide[30] (Scheme I; equation 3).



Scheme I

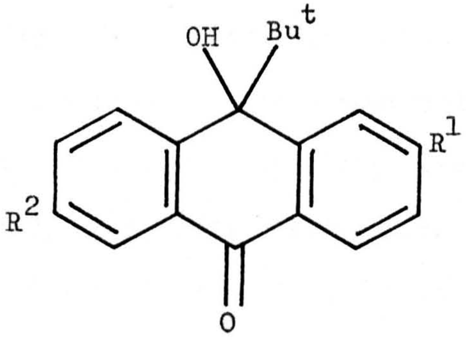
9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols (VIb); Most of the syntheses reported for compounds in this series (VIb), have involved a double 1,2-addition of the appropriate Grignard reagent to 9,10-anthraquinone.[31-38, 25,26] (Scheme II).



Scheme II (VIb)

Although theoretically two moles of Grignard reagent are required for each mole of anthraquinone in these reactions, in order to obtain reasonable yields of the diols, it has been the usual practice to use a large excess over this theoretical amount of Grignard reagent (e.g. refs. 33 and 39).

Reactions of Grignard reagents to conjugated systems have, for a long time, been known to give products formed by conjugate addition (i.e. 1,4- and 1,6-addition) of the Grignard reagent, as well as products formed by simple 1,2-addition (e.g. ref. 40). Only one example of such conjugate addition of a Grignard reagent to anthraquinone has been reported, and this was recently (1967) by Cameron and Meckel,[41] who isolated a compound of structure (VIIa) or (VIIb), from the reaction of t-butylmagnesium chloride on anthraquinone.

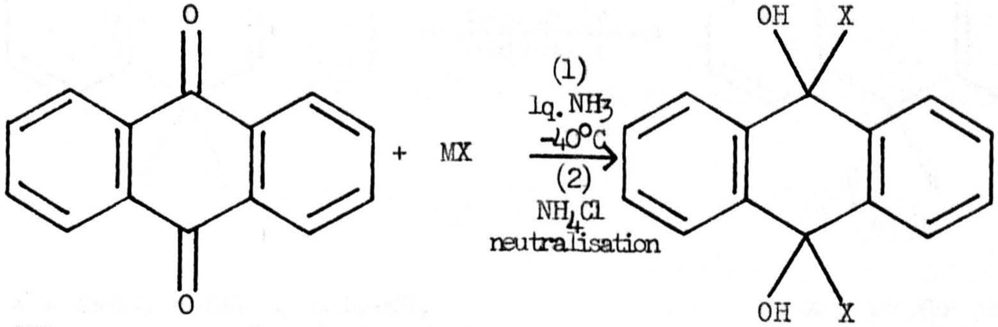


a. $R^1 = Bu^t$, $R^2 = H$

b. $R^1 = H$, $R^2 = Bu^t$

(VII)

Other organometallic reagents, akin to Grignard reagents, have been used more recently in the synthesis of the diols in the series (VIb). Propyl lithium reagent has been used[42] in the synthesis of 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol (VIb, page 11; R = nPr), by its reaction with anthraquinone. An indirect route to the diols has been by the use of α- and β-unsaturated organometallic reagents and their ready reaction with anthraquinone (Scheme III).

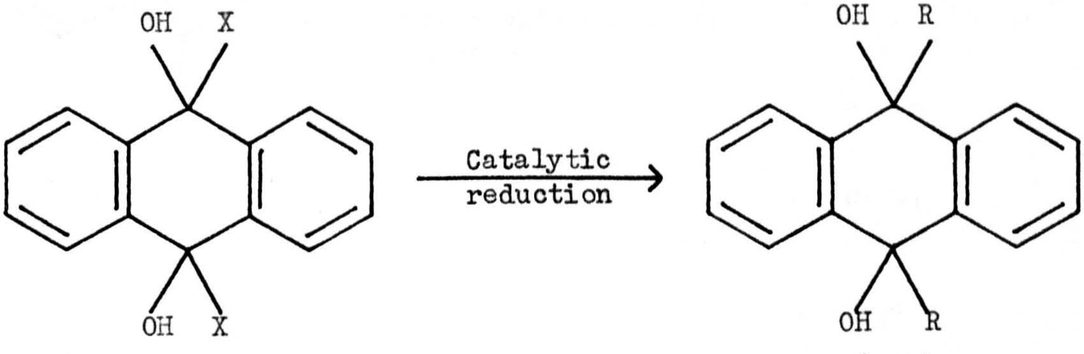


X = C≡CH,
C≡CCH_3,
H_2CC≡CH,
or H_2CHC=CH_2.

MX = an α- or β- unsaturated organometallic reagent.

Scheme III

Rio[43] first demonstrated this type of reaction on anthraquinone (referred to variously as alkynylation, ethynylation, propynylation, propargylation and allylation reactions) by his reaction of the sodium or lithium salt of phenyl acetylide on anthraquinone. Since then, several reactions of this type have been reported,[42, 44-50] using a variety of metallic derivatives of the appropriate unsaturated compounds, as indicated in Scheme III (the use of derivatives of lithium,[44(b), 44(c)] sodium[42, 44(a), 45,50] potassium,[42,50] magnesium[42,49] aluminium,[42,46,48,49] and zinc[47] have all been recorded). The conversion of the α- and β-unsaturated diols thus formed (Scheme III) into the fully saturated analogues in the series (VIb, page 11), has been effected by catalytic reduction using hydrogen, and palladium/charcoal,[44(a)] palladium chloride on calcium carbonate,[50] or platinum oxide[49,50] catalysts in alcoholic solvents (Scheme IV).



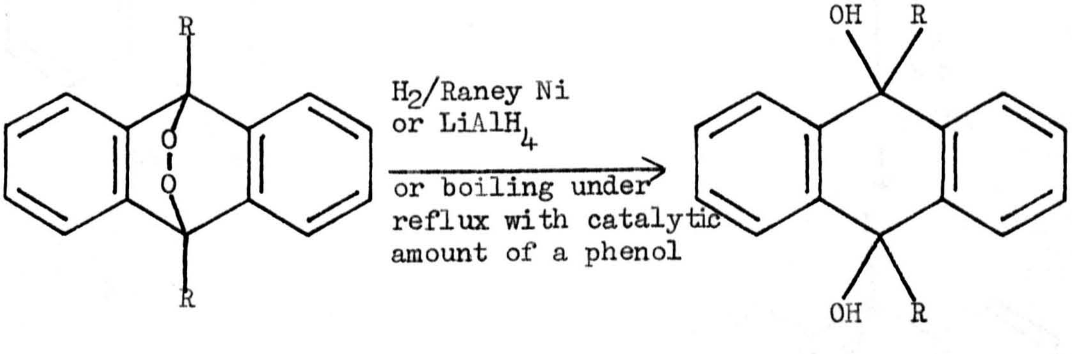
(VIb)

X = $C\equiv CH$, $C\equiv CCH_3$, $H_2CC\equiv CH$, or $H_2CHC=CH_2$.

R = CH_2CH_3 or $(CH_2)_2CH_3$

Scheme IV

A final synthetic method that has been used in the preparation ofdiols in the series represented by VIb, is identical to the method, described previously, for synthesising 9,10-dihydroanthracene-9,10-diol (VIa, page 11) by catalytic reduction of anthracene photoöxide.[28] By an obvious extension of this method, 9,10-dialkyl-9,10-dihydroanthracene-9,10-diols (VIb, page 11) have been made by reducing catalytically,[51] or more commonly, with lithium aluminium hydride,[42,50,52,53] the photoöxides of 9,10-dialkylanthracenes (Scheme V).

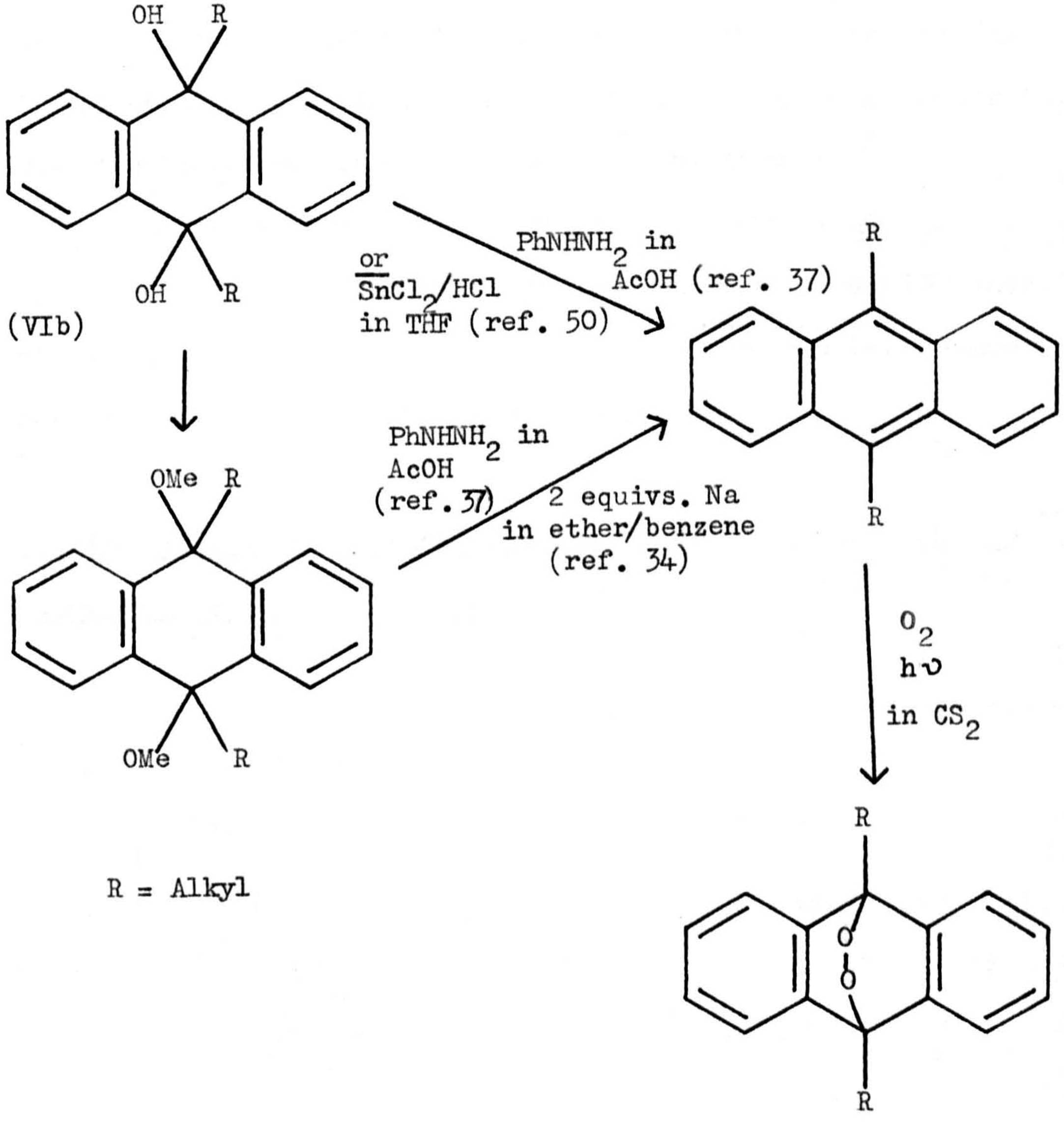


(VI b)

R = Alkyl

Scheme V

As a synthetic method, the above has one major drawback, in that, as illustrated in Scheme VI, the photoöxides are prepared from 9,10-dialkylanthracenes, which in turn are best made from the corresponding diols, or their dimethyl ethers, of the type VIb (e.g. refs 34 and 37).

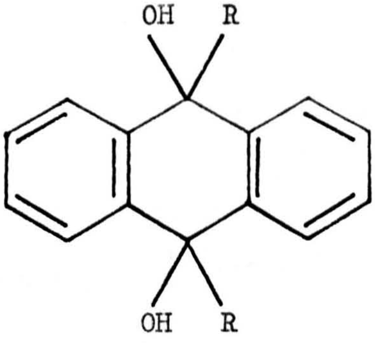


Scheme VI

However, diols of the type VIb have been synthesised[51,52,53] by this method (Scheme V), other synthetic routes to 9,10-dialkylanthracenes having been found, not involving the appropriate diol itself as starting material. Also, the circular route from diol, to photoöxide, to diol, has, as will be seen, important implications when the stereochemistry of the diols is considered.[42,50]

Of the methods outlined above, for synthesising diols of the type VIb, the Grignard reaction method (Scheme II, page 13) normally gives by far the lowest yields of desired products (e.g. compare ref. 32, p. 1969 with ref. 50, p. 1195).

Configurational and Conformational Assignments for 9,10-*Dialkyl*-9,10-*dihydroanthracene*-9,10-*diols* (VIa, VIb)

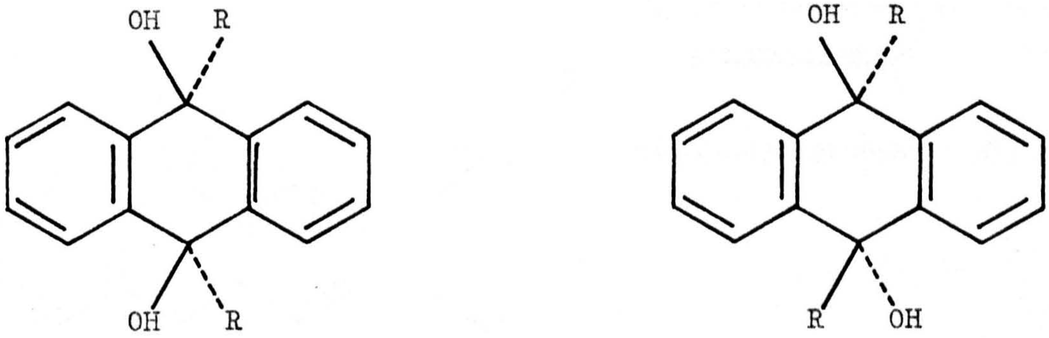


(VI)

a. R = H

b. R = Alkyl

The configurational (i.e. cis, trans) and conformational (i.e. pseudoaxial a', pseudoequatorial e') features of substituted 9,10-dihydroanthracenes of the above type (VI), have been outlined earlier (page 4). Relatively few stereochemical assignments, either of configuration or conformation, have been made for this class of compounds (VI), and most of the assignments made have been solely configurational,[53,54,38,42] (Fig. 5).

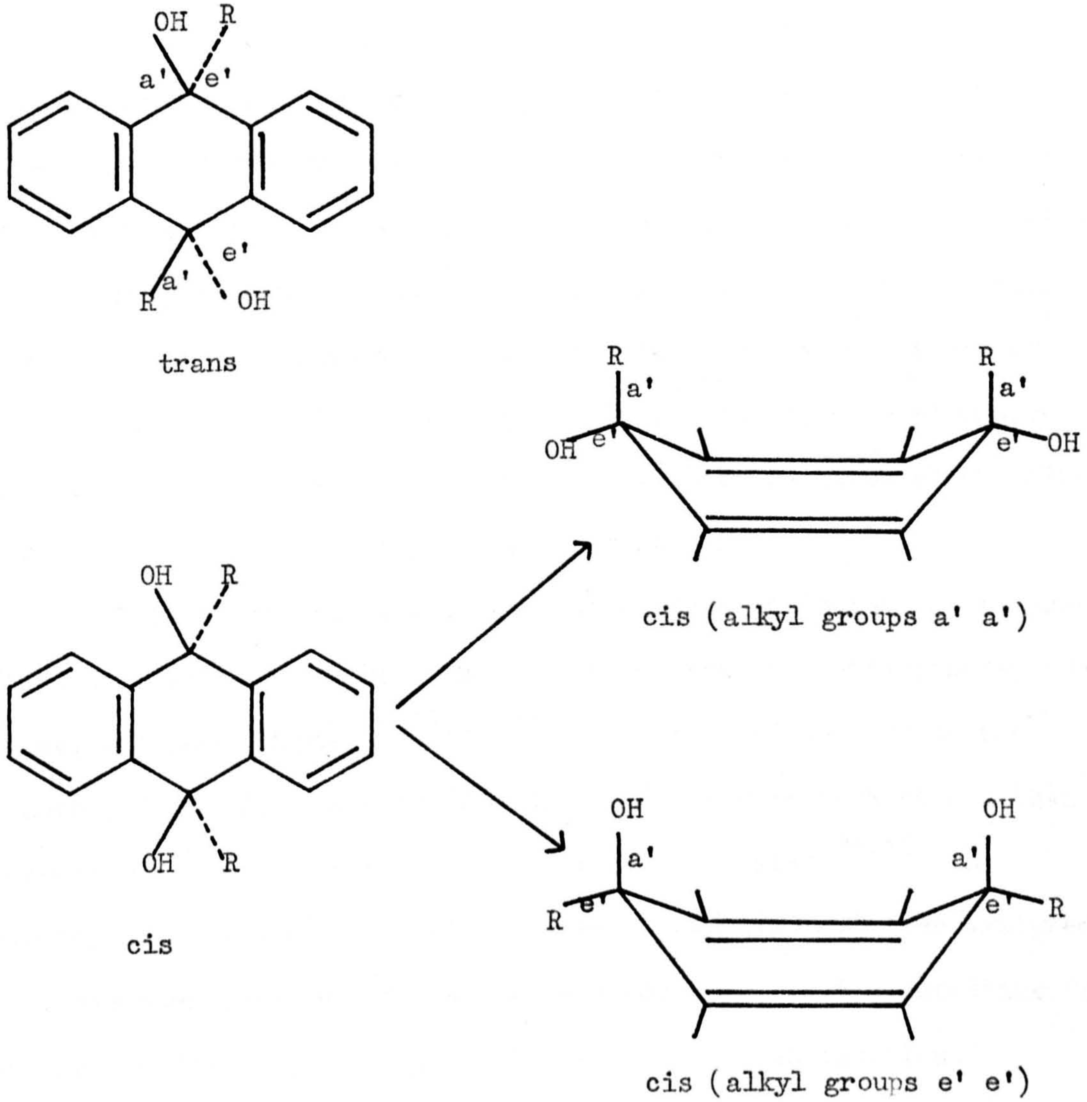


cis

trans

Fig. 5. Configuration

More recently, assignments of conformation and configuration (Fig. 6) have been reported.[25,26,50,55]



a' = pseudoaxial

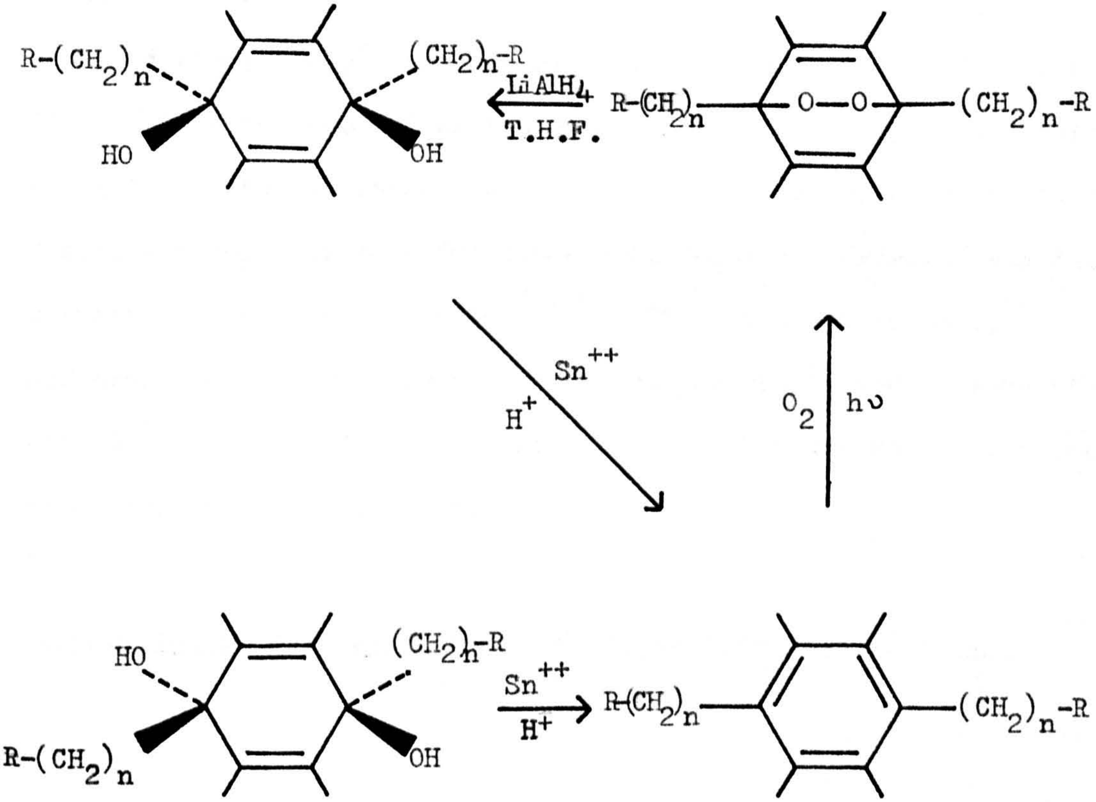
e' = pseudoequatorial

Fig. 6. Configuration and conformation (some partial structures)

Dufraisse and his co-workers,[54] and in particular, Lepage,[53] have reported the isolation of cis-9,10-dihydroanthracene-9,10-diol (VIa, page 18) from the catalytic reduction of anthracene photoöxide,[28] and its reduction using lithium aluminium hydride. The assignment of a cis configuration was made on the basis of its mode of formation. They reported this same cis isomer isolated from the reactions of anthraquinone with aluminium isopropoxide,[30] and lithium aluminium hydride.[29] (See Scheme I, page 12). This last reaction also yielded a second isomer, which they assigned trans.

This approach, of giving a cis assignment to the isomer prepared from, or identical to the isomer prepared from the corresponding photoöxide, has been adopted[38,51,52,53] in the case of isomers of the dimethyl diol (VIb, page 18; $R = CH_3$). A trans assignment has then accordingly been given to any other isomer isolated.[38,53] The dimethyl diol isomer prepared from the photoöxide, and thus assigned cis, has been reported[52,53] as being dimorphous, each crystalline form having a different, and sharp melting point.[53] An identical observation has been made[53] for the isomer, assigned cis in the way described, isolated from the Grignard reaction of methylmagnesium iodide on anthraquinone.

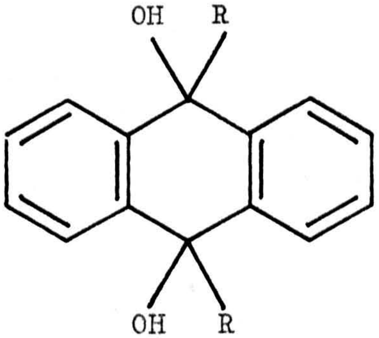
This method of determining the configuration of diols of type VIb, has been elegantly formalised by Chodkiewicz and his co-workers,[42] who adopted the cyclic procedure as in Scheme VII.



Scheme VII - partial structures

Thus, they were able to characterise cis and trans isomers of the diethyl and di-n-propyl diols (VIb, page 18; R = CH_2CH_3 and $(CH_2)_2CH_3$ respectively). They did not, at that time, take conformational considerations into account. We in this Department were the first to report[25,26] conformational assignments for diols of this type, and have isolated two cis isomers (a'a' and e'e'; see Fig. 6) of the diethyl diol,[25] and one cis isomer (a'a') of the di-n-propyl diol,[26] from the product of the reaction of the appropriate Grignard reagent on anthraquinone. Our conformational assignments are based on p.m.r. and infrared data for these compounds. Chodkiewicz and his co-workers have since reported[55,50] different infrared data,[50] different interpretations of the p.m.r. spectra,[55] and consequently conflicting conformational assignments for what are ostensibly the same compounds (see Discussion).

<u>Dehydration of</u> 9,10-<u>Dialkyl</u>-9,10-<u>dihydroanthracene</u>-9,10-<u>diols</u>

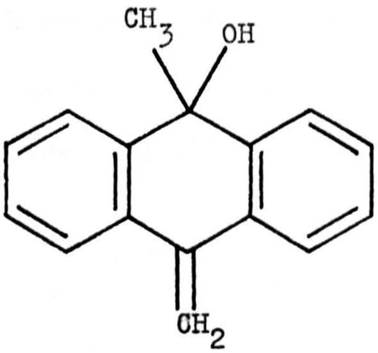


R = Alkyl

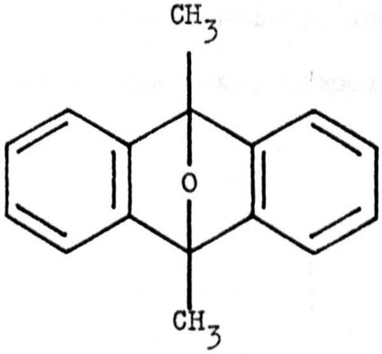
(VIb)

It has long been known that diols of the type VIb are particularly susceptible to dehydration, and by-products formed in this way have often been encountered after reaction of alkylmagnesium halides with anthraquinone (see, e.g., ref. 32). Guyot and Staehling[31] maintained that dehydration takes place in the presence of excess of the Grignard reagent, but this observation has not been made by later workers.[34,39,35,37] Dehydration is most easily effected by acids,[35] and to avoid it, the Grignard complexes are best decomposed with aqueous ammonium chloride (e.g.s. refs. 39, 35).

Guyot and Staehling[31] found that when 9,10-dimethyl-9,10--dihydroanthracene-9,10-diol (VIb; R = CH_3) is boiled with acetic acid, a yellow substance corresponding to a mono-dehydration product is formed, which they suggested had the structure VIII or IX.

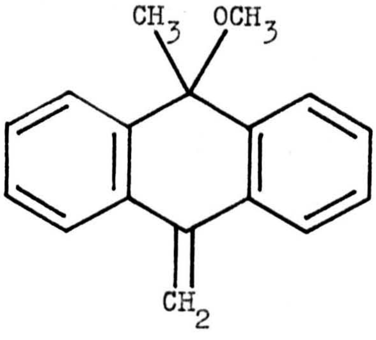


(VIII)



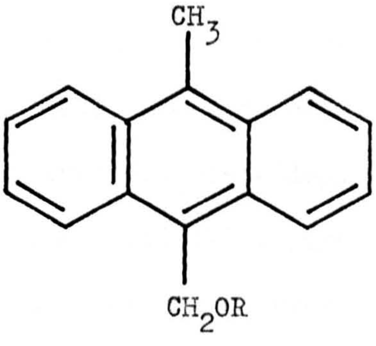
(IX)

The same workers also isolated[31] a compound, to which they assigned structure X, by the action of heat on the dimethyl ether of the same diol (VIb; R = Me).



(X)

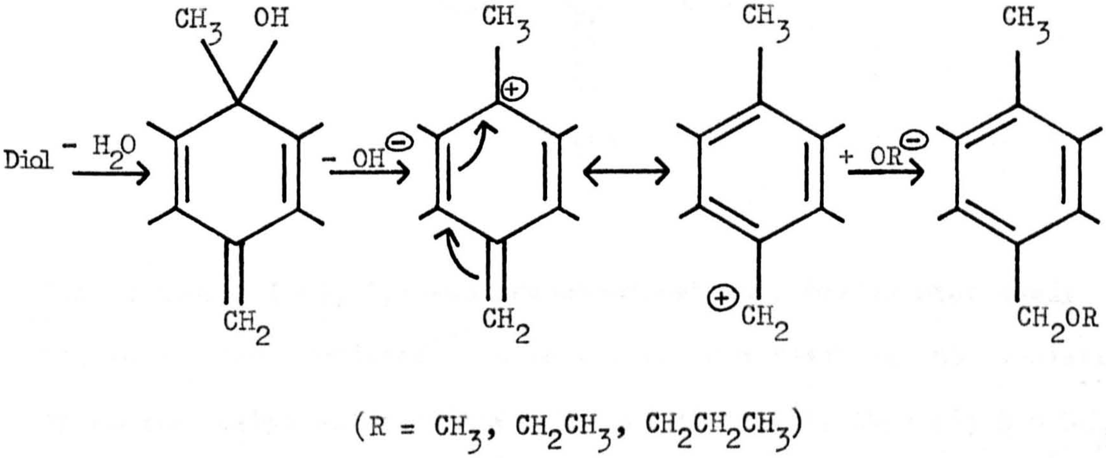
Badger and Pearce[35] have since claimed that none of the above structures (VIII, IX, X) is in accord with the properties of either of the two compounds, and went on to establish that when a boiling alcoholic solution of the dimethyl diol (VIb; R = CH_3) is treated with acid, the dehydration is accompanied by 1,5-anionotropic rearrangement and alkylation by the alcohol used as solvent. Thus they isolated and fully characterised (by independent synthesis in one case) compounds of the type XI.



(XI)

R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$

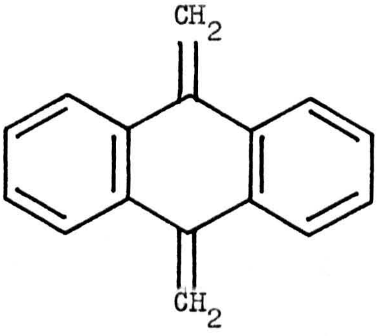
They used both mineral acid and picric acid to effect this conversion (the latter forming the picrate of XI in each case, from which the parent compounds (XI) could easily be generated). Their proposed mechanism for this type of reaction is illustrated in Scheme VIII.



Scheme VIII - partial structures

1,5-Anionotropic shifts of the above type have been reported in the anthracene series by other workers (e.g., see ref. 56), and examples in the benzanthracene and dibenzanthracene series have been reported (e.g. see ref. 57).

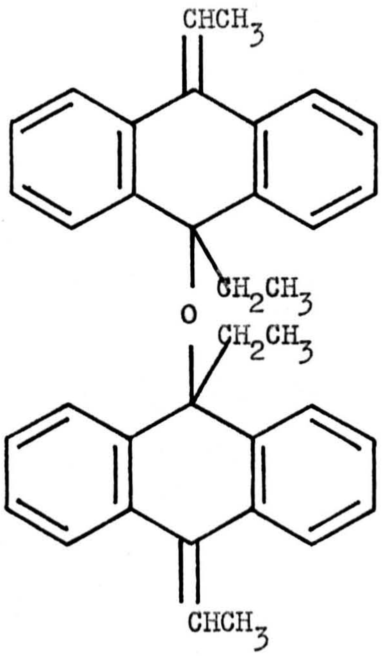
Guyot and Staehling,[31] by the action of acetic anhydride on the dimethyl diol (VIb, page 23; R = CH_3) also isolated, but did not fully characterise, a compound which they claimed was formed by a double dehydration of the dimethyl diol (VIb, page 23 ; R = CH_3), and thus suggested structure V for it.



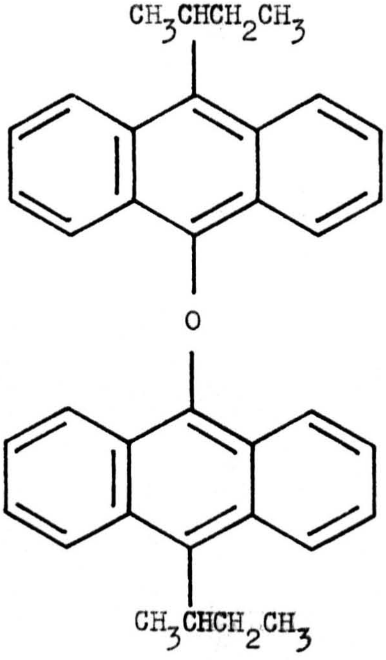
(V)

This compound (V), 9,10-anthraquinodimethane, has as previously mentioned been reported[24] to be formed as a reactive intermediate, by thermal dehydration of the dimethyl diol (VIb, page 23; R = CH_3).

Clarke and Carleton[32] isolated two compounds, which they tentatively assigned the 'bimolecular' structures XII and XIII, by dehydration of the diethyl diol (VIb, page 23; R = CH_2CH_3) with dilute mineral acid. They obtained the same two compounds by reaction of ethylmagnesium bromide and anthraquinone, during synthesis of the diethyl diol (which was also isolated).

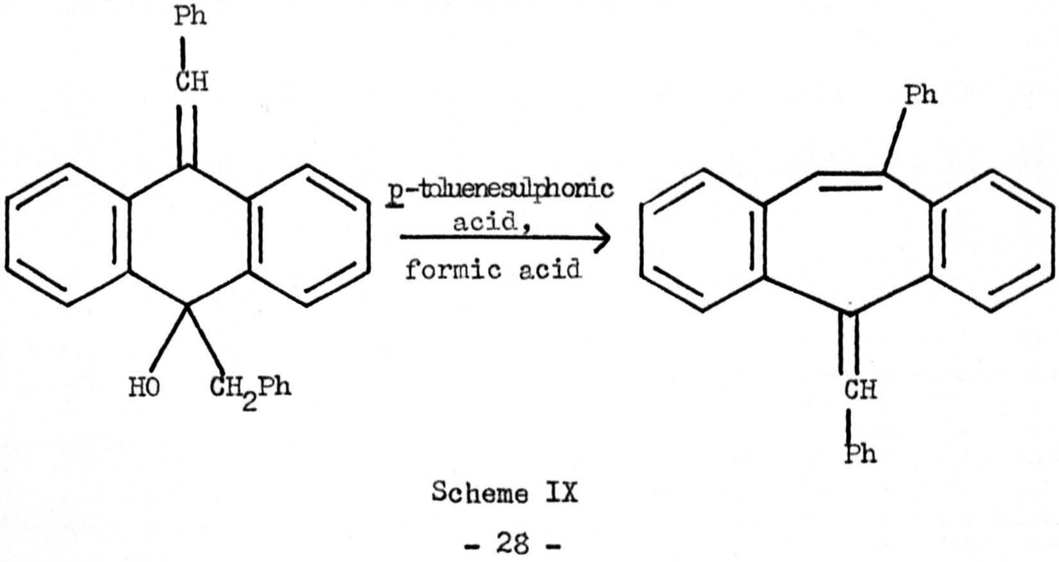


(XII)



(XIII)

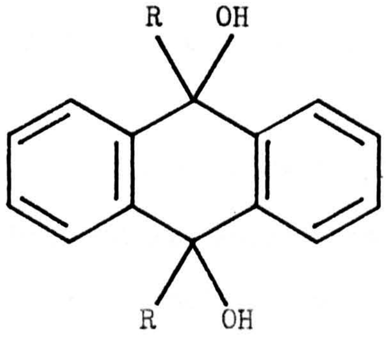
In conclusion it is worth noting that other reactions, involving the dehydration of hydroxy-derivatives of 9,10-dihydroanthracene, have been reported (e.g. refs. 56(g), 58, 59), and in these cases, rearrangement resulting in ring enlargement of the middle ring occurs, resulting in the formation of a 2,3,6,7-dibenzocyclohepta-2,4,6-triene system, e.g. Scheme IX (ref. 58).



Scheme IX

EXPERIMENTAL DISCUSSION

As stated in the Introduction, the initial object of the work undertaken was to synthesise compounds in the series VI, and in the light of the stereochemical interest of 9,10-dihydroanthracene derivatives, outlined earlier, to see if absolute stereochemical assignments (configuration, and conformation) could be made for these compounds.



R = Alkyl

(VI)

We have found[25,26] that the compounds we have isolated in this series (VI), lend themselves to detailed stereochemical analysis, by means of proton magnetic resonance and infrared spectroscopy. The synthetic method exclusively adopted in our attempts to isolate diols of this type, has been the method of Grignard addition of a large excess of the appropriate alkylmagnesium halide to anthraquinone (see Scheme II, page 13). The reactions carried out have involved the use of ethyl, n-propyl, t-butyl, iso-propyl, and neopentyl halide. The results obtained can be conveniently discussed in sections, under the types of products isolated from these reactions. A short section at the end deals with some dehydration products which have been isolated, derived from diols of type VI.

A. 9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols (VI)

Of the Grignard reactions carried out, only those involving the use of ethyl bromide, and n-propyl bromide, gave diols of this type.

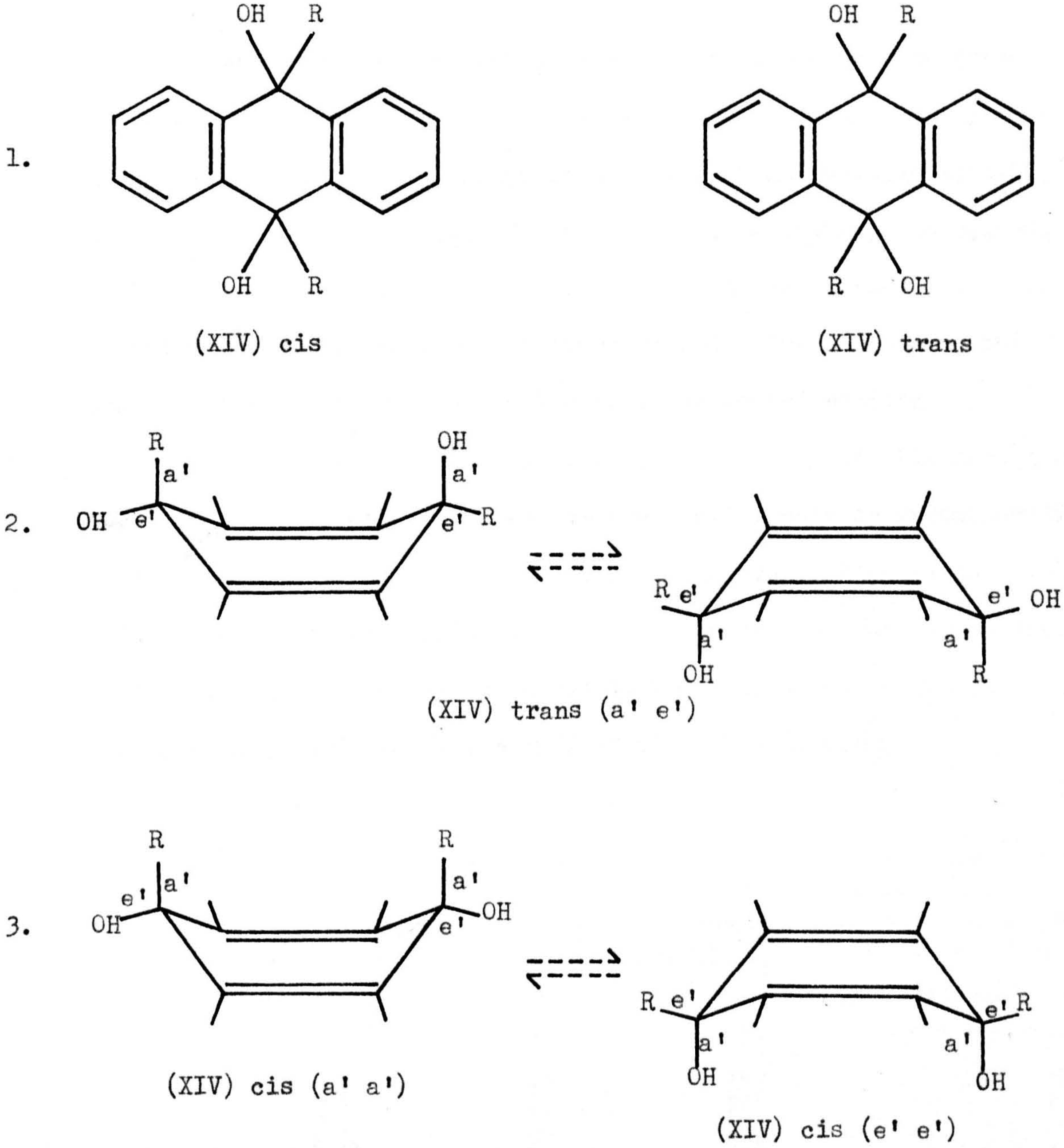
By way of recapitulation, Scheme X summarises the stereochemical possibilities for these diols.

With reference to Scheme X, the following points should be made:

(1) If the molecule is planar, only configurational (cis, trans) assignments are applicable (Scheme X, 1).

(2) If the molecule vibrates rapidly through the planar configuration, again only configurational assignments are applicable (Scheme X, 2 and 3 with equilibrium arrows).

(3) If, in all cases, the molecule is rigid, and in a pseudo boat conformation, two conformationally distinct cis isomers are possible (Scheme X, 3, without equilibrium arrows). In these circumstances, only one conformationally distinct trans isomer is possible (Scheme X, 2, without equilibrium arrows). The point should be made that equilibration, conformational preference, and planarity of the molecule, may separately occur in different isomers of the same compound, e.g. trans isomer may equilibrate, and the cis isomers exhibit conformational rigidity, etc.



a. R = CH_2CH_3 ; b. R = $CH_2CH_2CH_3$

a' = pseudoaxial (where used, refer to alkyl groups)

e' = pseudoequatorial

Scheme X (2. and 3. partial structures)

The major readily isolable and identifiable product from the reaction of ethylmagnesium bromide and anthraquinone (ethylmagnesium iodide and anthraquinone failed to give a crystalline, identifiable product) is cis (a' a')-9,10-diethyl-9,10-dihydroanthracene-9,10-diol (XIV a, cis (a' a'), page 31).[25] In the reactions carried out, this isomer was produced in yields between 20-40%. The conformational assignment follows from the following experimental evidence:

(1) The proton magnetic resonance spectrum of this isomer of the diethyl diol (Fig. 7) shows the two ethyl groups as magnetically equivalent, with the methyl triplet at an unusually high field (9.80τ), and the methylene quadruplet at 7.80τ (compare with the p.m.r. spectra[60] of ethanol and n-propanol; ethanol: 6.30τ (CH_2), 8.78τ (CH_3); <u>n</u>-propanol: 6.40τ (α-CH_2), 8.40τ (β-CH_2), 9.10τ (CH_3)).

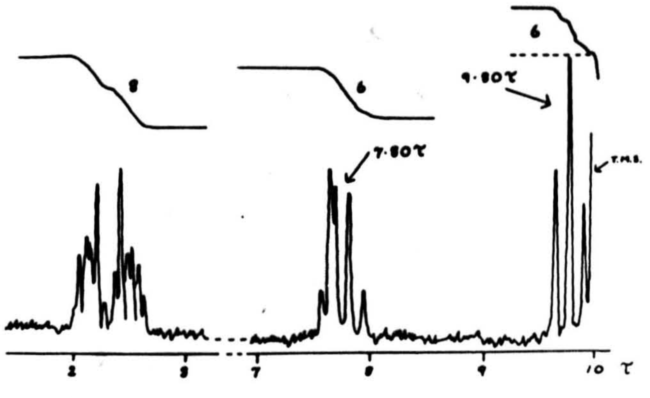
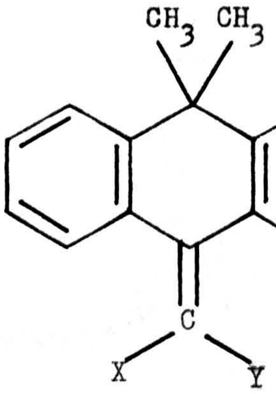


Fig. 7

P.m.r. spectrum, in $CDCl_3$, of the isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

Inspection of a Dreiding molecular model of this compound (see Fig. 1, page 2) indicates that if the molecule is in a pseudo boat conformation, which the model shows to be its normal valence conformation; the appreciable up-field shift of the methyl protons in the p.m.r. spectrum can be explained qualitatively, by assuming that the ring-current effect[61] from the two benzene nuclei shields the methyl protons, thus causing an anisotropic up-field shift in the p.m.r. resonance of these protons. It has been suggested[62] previously (1964) that the ring-current effect in derivatives of 9,10-dihydroanthracene of the type XV, may be the predominant or almost exclusive factor responsible for the difference in chemical shift of the two methyl groups, of between 16-28 c.p.s. (at 60 Mc) observed in the p.m.r. spectra of these derivatives.



X = Br

Y = Br, C_6H_5, CO_2H, CO_2CH_3

(XV)

Smith and Shoulders[63] have also reported similar observations attributable to such a ring-current effect in their work on 9,10-dihydroanthracene derivatives, and other workers[18,64] have implied that some of their observations in this system might be accounted for by the ring-current effect. The up-field shift of the methyl protons of the diethyl diol isomer, which we observe in the p.m.r. spectrum of this compound (Fig. 7) illustrates, without doubt, the importance of the ring-current effect in this system, and it is reasonable to conclude that in this isomer, the molecule is in a 'folded' conformation. By adding a drop of tetranitromethane to the p.m.r. sample of this diol, a deep-red π-complex is formed, and the anisotropic effect of the aromatic ring current is modified sufficiently to cause the methyl protons to resonate at the more 'normal' value of 9.10τ (Fig. 8).[26] The methylene protons resonate at 8.15τ under these conditions.

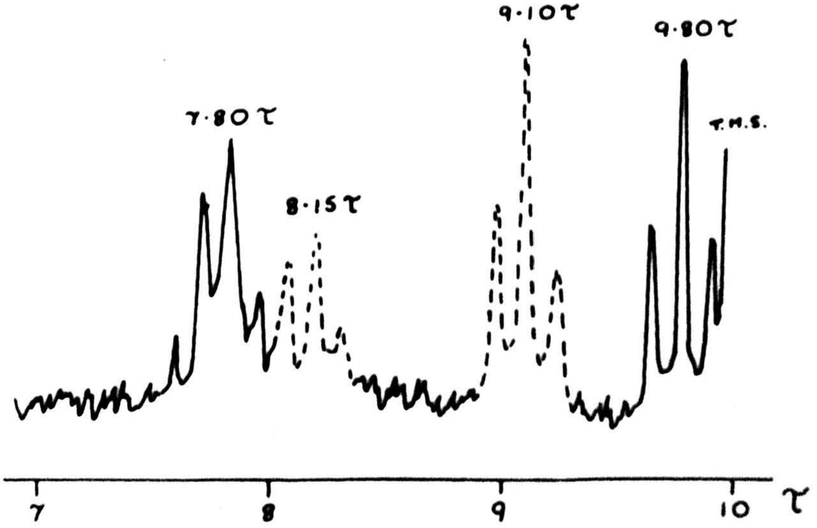


Fig. 8

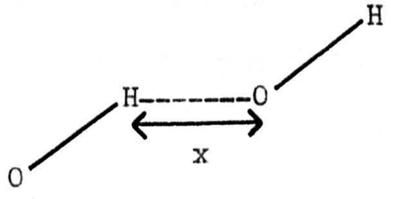
----- Peaks which appear on addition of tetranitromethane

The use of π-complex formation to modify the anisotropic effect in the p.m.r. spectrum of the isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

It is clear that this displacement is due to a modification of the ring anisotropic effect since, for example, the p.m.r. spectrum of the alkyl group in n-propylbenzene is virtually unaltered on formation of a π -complex with tetranitromethane; only small shifts (less than 0.04τ) are observed in such cases, in which the alkyl group does not lie above the ring in the shielding region.[26]

Without further evidence, however, it is not possible to say whether the molecule in this isomer is equilibrating, or in a rigid conformation (Scheme X, page 31).

(2) If the hydroxyl groups in the 9 and 10 positions of this diethyl diol are cis, and pseudoaxial, measurements from a Dreiding model give an approximate value of 2.4Å for the H----O separation (Fig. 9).

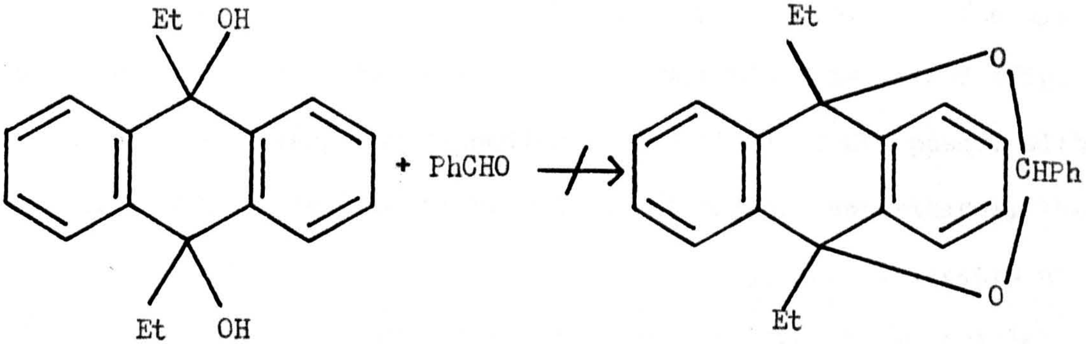


Hydroxyls a' a', x ≈ 2.4 Å

Hydroxyls e' e', x ≈ 5.6 Å

Fig. 9

If the hydroxyls are cis, and pseudoequatorial, this distance is approximately 5.6 Å. The maximum distance over which intramolecular hydrogen bonding can occur, has been given[65(a)] as approximately 3.4 Å; so the detection of intramolecular hydrogen bonding in this molecule is a crucial factor in distinguishing between the two possible cis conformations, if the molecule is rigid. If intramolecular hydrogen bonding occurs in this isomer of the diethyl diol in question, and the infrared spectrum does in fact show a bonded hydroxyl peak at 3470 $cm.^{-1}$, modification of this hydrogen bonding by chelation or protonation might affect the p.m.r. spectrum of the diol. Thus, p.m.r. spectra of the diol, with small quantities of urea, ethylene glycol dimethyl ether, and trifluoroacetic acid (TFA), separately in the p.m.r. samples, were recorded. The p.m.r. spectrum of the diol in deuterated methanol (CH_3OD) was also recorded. No significant changes in the p.m.r. spectrum were observed in all these cases, other than the appearance of new peaks, caused by the dehydration of the diol in the TFA sample. An unsuccessful attempt was made to obtain a crystalline condensation product of the diol with benzaldehyde (by Scheme XI).

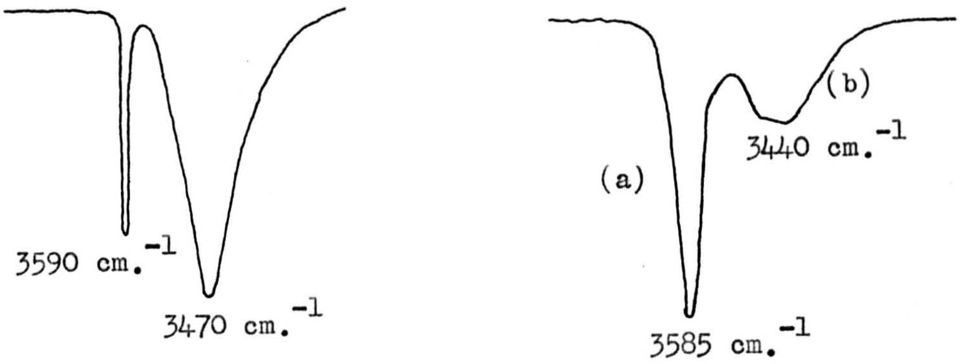


Scheme XI

This condensation would be expected to be possible only if the hydroxyl groups in the molecule were pseudoaxial. As no product of this type was isolated from the reaction, no definite conclusions in this respect can be made.

The only sure way of establishing the character of a bonded hydroxyl band in the infrared spectrum, consists in determining the dependence of the molar extinction coefficient of the band on concentration. For intramolecular hydrogen-bonded bands, extrapolation of the molar extinction coefficient to zero concentration, does not give a curve passing through the origin.[65(b)] Measurements of this kind were made therefore,[25] for the two hydroxyl peaks in the infrared spectrum of this isomer, for concentrations of 0.03-0.11 M/l. The results, shown in Fig. 10, give no conclusive evidence for the presence of intramolecular hydrogen bonding. The possibility remains, however, that an intramolecular hydrogen-bonded peak nevertheless exists under the intermolecular hydrogen-bonded peak in the infrared spectrum.

(3) The proton magnetic resonance spectrum of this diethyl diol isomer changes strikingly[25] as the temperature is raised (Fig. 11). Thus at 65°C new peaks corresponding to the ethyl group appear, with the methyl triplet centred at 9.20 τ . At higher temperatures, the methyl triplet at 9.80 τ diminishes in intensity, and disappears at 102°C, but at these temperatures, although the lower field triplet remains, the spectrum is complicated by the formation of dehydration products. This change was not reversed on lowering the temperature. Though not so clearly seen, a similar change does appear to occur



Nujol

Ethanol-free chloroform sol$\underline{^{n}}$.

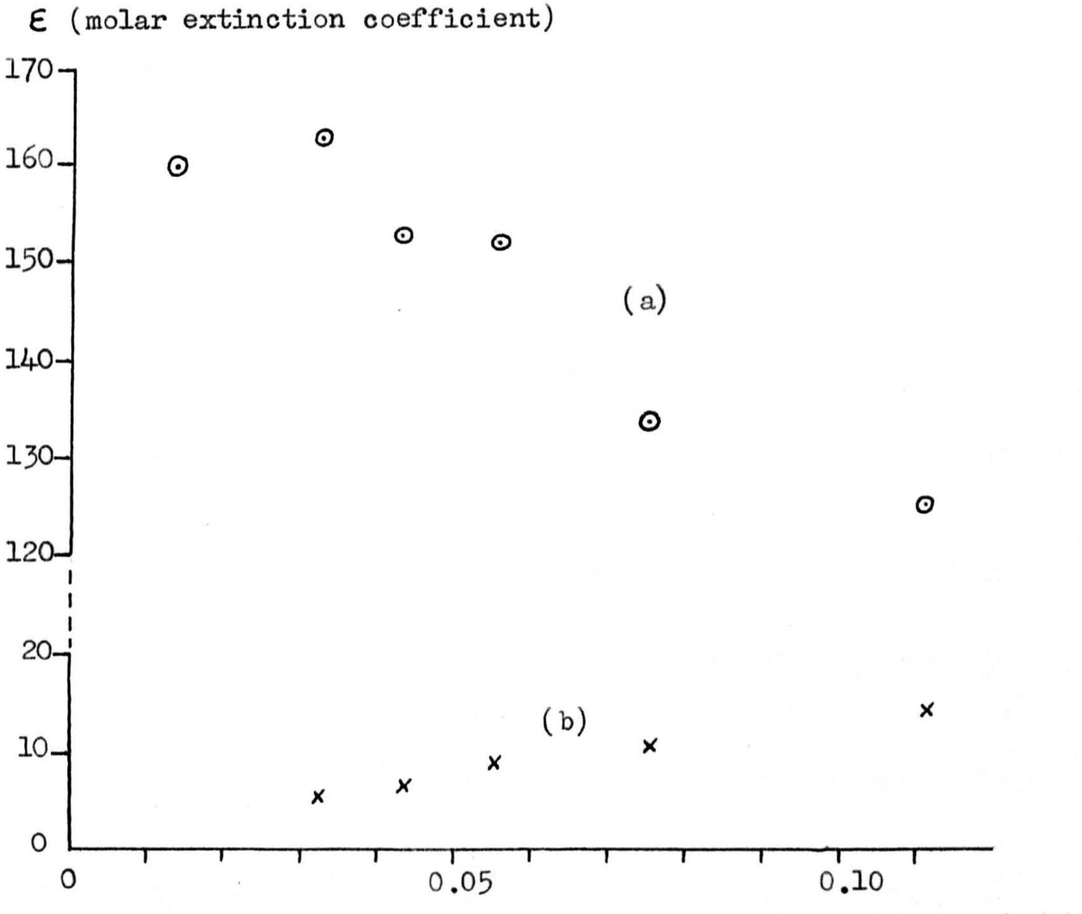


Fig. 10

Infrared dilution curves for the hydroxyl bands in the isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

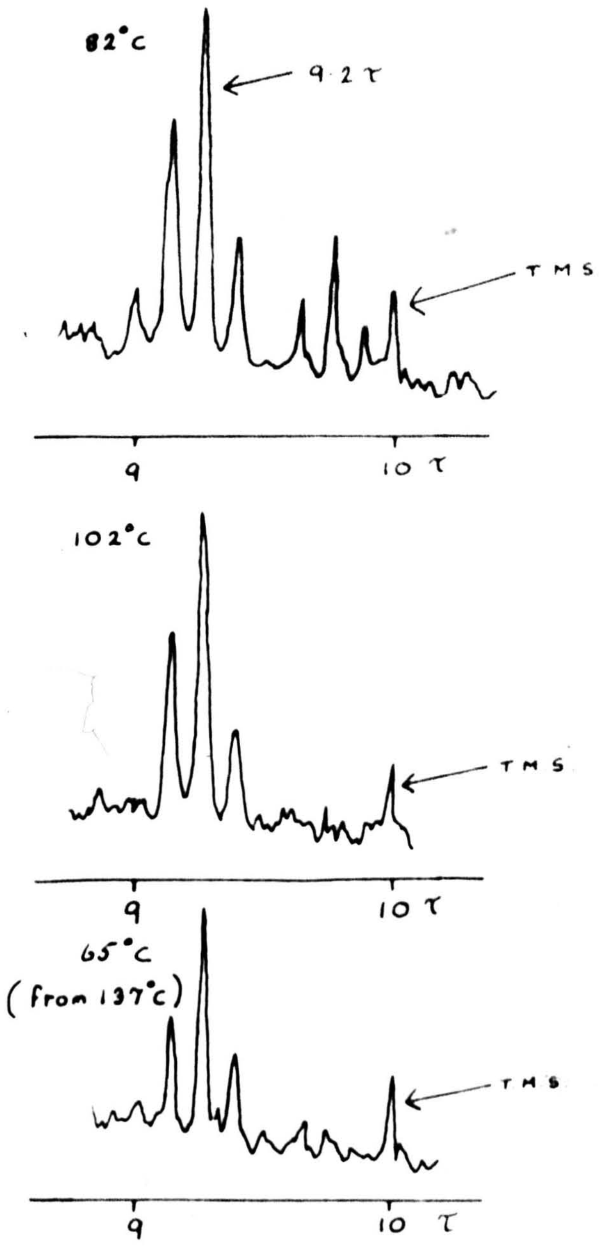
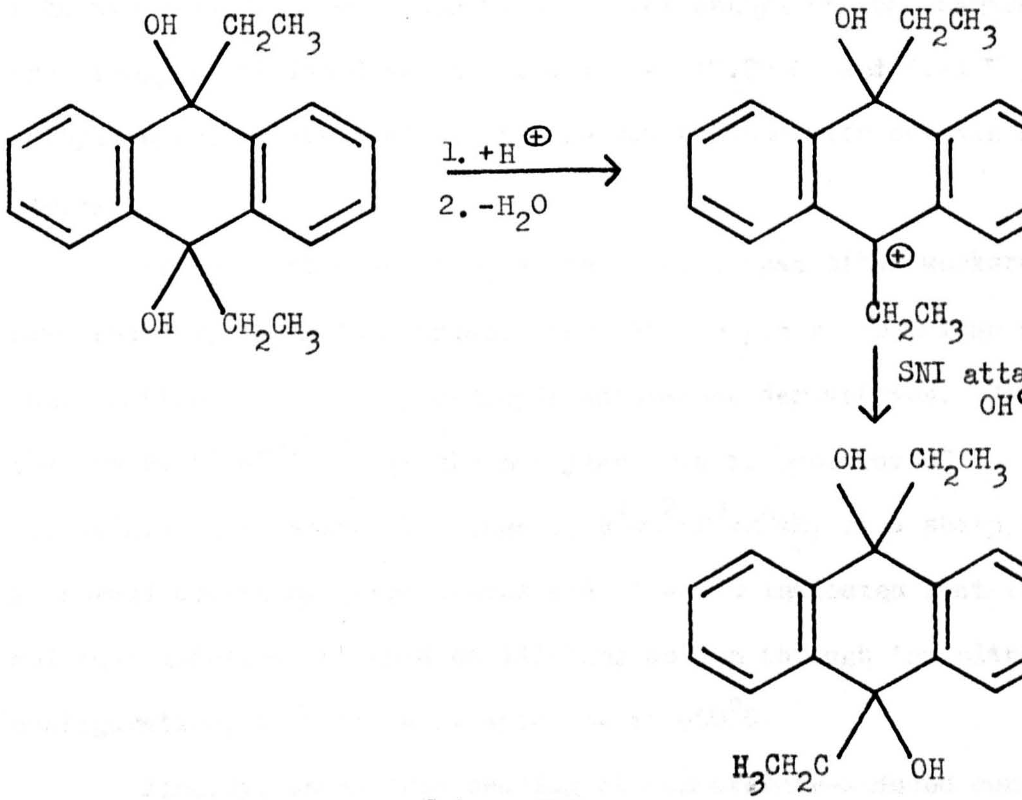


Fig. 11

P.m.r. spectra (9.00-10.00 τ region) as the temperature is increased, of the isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

for the methylene quadruplet, with the new quadruplet now centred at 8.21 τ when the temperature is raised. This result is significant, as it can be concluded from it that the molecule, under these conditions, is "flipping" from a "folded" to a "reverse-folded" conformation (see Fig. 4, page 6), and the 9- and 10-substituents change accordingly from being cis in one conformation, to cis in the other conformation (see Scheme X, 3, page 31). By heating the sample as above, a conformational change involving a carbonium ion intermediate as shown in Scheme XII is avoided, so the above observations cannot be attributed to any conformational change involving conversion from a cis to a trans conformation, or vice versa.



Scheme XII

The irreversibility of these changes rule out any rationalisation of these observations involving a change from a rigid to an equilibrating molecule, or vice versa. Thus, by logical elimination of the conformational possibilities in this way, the conclusion that the observed changes result from a cis to cis conformational change of the molecule, is the only possible explanation accounting for these observations. Though this conclusion is complete as it stands, it is intended in the future to record the p.m.r. spectra and study the changes, if any, of the isolated diethyl diol isomer at temperatures below 33.4°C.

Thus from this result, one is able to fix the p.m.r. chemical shifts for the ethyl groups in both cis conformations of this compound (the two values ($9.80\,\tau$ and $9.20\,\tau$) for methyl proton chemical shift are firmly established and the two values ($7.80\,\tau$ and $8.21\,\tau$) for the methylene proton chemical shift, are established with certain reservations).

It is worth commenting at this point that other workers[62,63,18,22] have recently found the variable temperature p.m.r. technique useful in conformational work on 9,10-dihydroanthracene derivatives. For example, the observation[63,22] that the methylene p.m.r. spectrum of 9,10-dihydroanthracene (II, page 1; $R^1=R^2=R^3=R^4=H$) is a sharp singlet at normal operating temperatures and at -60°C indicates that this molecule undergoes a rapid oscillating motion through the planar configuration, at temperatures as low as -60°C.

Finally, under this heading of temperature-induced conformational changes in the diethyl diol, it is worth noting that the difficulties and observations encountered in determining the melting point of the isolated diethyl diol isomer (which by the criteria of t.l.c. analysis was a single isomer) may be attributed in part to such conformational changes on heating. Dehydration of the diol as the temperature is raised, however, would also account in part for these observations.

(4) Proton magnetic resonance spectra of the diethyl diol isomer isolated, were recorded at intervals after the addition of a drop of 0.1% acetic acid to the p.m.r. sample. The results are shown in Fig. 12.

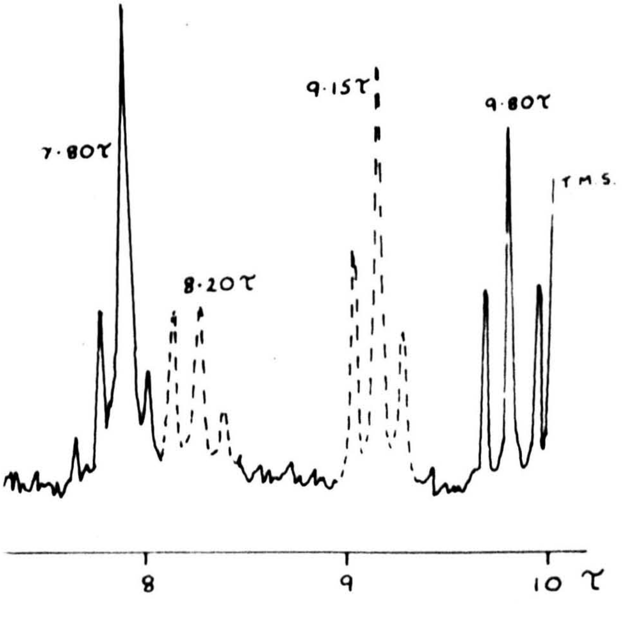


Fig. 12

----- Peaks which appear on addition of acid

P.m.r. spectrum of the isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol (readily isolable from the product of the Grignard reaction), in $CDCl_3$ containing a drop of 0.1% acetic acid.

These spectra also showed[25] the gradual appearance of a lower field methyl triplet at 9.15 τ , and a lower field quadruplet at 8.20 τ . This process is also accompanied by dehydration reactions of the diol, when higher concentrations of acid are used. Under these conditions of weak acidity, conditions which would not cause the molecule to "flip", the conformational change observed is most likely to be one involving a carbonium ion intermediate, as illustrated in Scheme XII (page 40). This result supports some of the interpretations given to the variable temperature p.m.r. spectra, as the conformational changes observed here, are from a cis conformation (given the p.m.r., variable temperature results) to the other cis conformation, with the ethyl group p.m.r. resonances at 9.15 τ and 8.20 τ (compare the values of 9.20 τ and 8.21 τ obtained from the variable temperature p.m.r). The trans conformation would presumably be an intermediate in this change (Scheme XII, page 40) but as the original p.m.r. ethyl group resonances eventually diminish to nearly zero intensity, some complete conversion to the second cis isomer occurs.

This conversion under the influence of dilute acid was used to secure the second cis isomer of the diethyl diol. A sample of the cis isomer, isolated from the Grignard reaction, was suspended in 0.1% acetic acid, or 2% hydrochloric acid, for thirteen or four days respectively. Column chromatography of the resulting material separated the two cis isomers of the diethyl diol. No trans isomer was isolated. The pure second cis isomer shows, not surprisingly, p.m.r. resonances at 9.15 τ (triplet) and 8.16 τ (quadruplet), corresponding to the two magnetically equivalent ethyl groups in the molecule. Addition of a drop of tetranitromethane to the p.m.r. sample produces a deep-red π -complex, but no observable change in the p.m.r. spectrum occurs, indicating the absence of any ring-current anisotropic effect in this isomer. The infrared spectrum of this isomer shows three hydroxyl bands (Nujol, and in carbon tetrachloride), the graphs (Fig. 13) of the molar extinction coefficients of which, plotted as a function of the concentration in carbon tetrachloride (0.007-0.030 M/l), indicate that the hydroxyl band at 3551 cm.$^{-1}$ is an intramolecular hydrogen-bonded hydroxyl band (see page 37).

The occurrence of intramolecular hydrogen bonding in this isomer suggests that the hydroxyl groups in the molecule must be both in pseudoaxial positions (see pages 31 and 35). The two ethyl groups would thus be pseudoequatorial. This compound is therefore, cis(e' e')-9,10-diethyl-9,10-dihydroanthracene-9,10-diol (XIV a, cis (e' e'), page 31).[25] It follows from the reasoning outlined previously, that the diethyl diol isomer, readily isolable from the Grignard reaction, has a cis configuration, with both ethyl groups in the pseudoaxial conformation (XIV a, cis (a' a'), page 31).[25]

(5) A comparison of the conformational assignments now made for the two isomers of the diethyl diol isolated, and their respective p.m.r. spectra, reveals that the stereochemical conclusions made, imply a greater shielding effect of the ring-current on the methyl protons when an ethyl group is pseudoaxial in this compound than when an ethyl group is pseudoequatorial. In order to confirm the validity of this

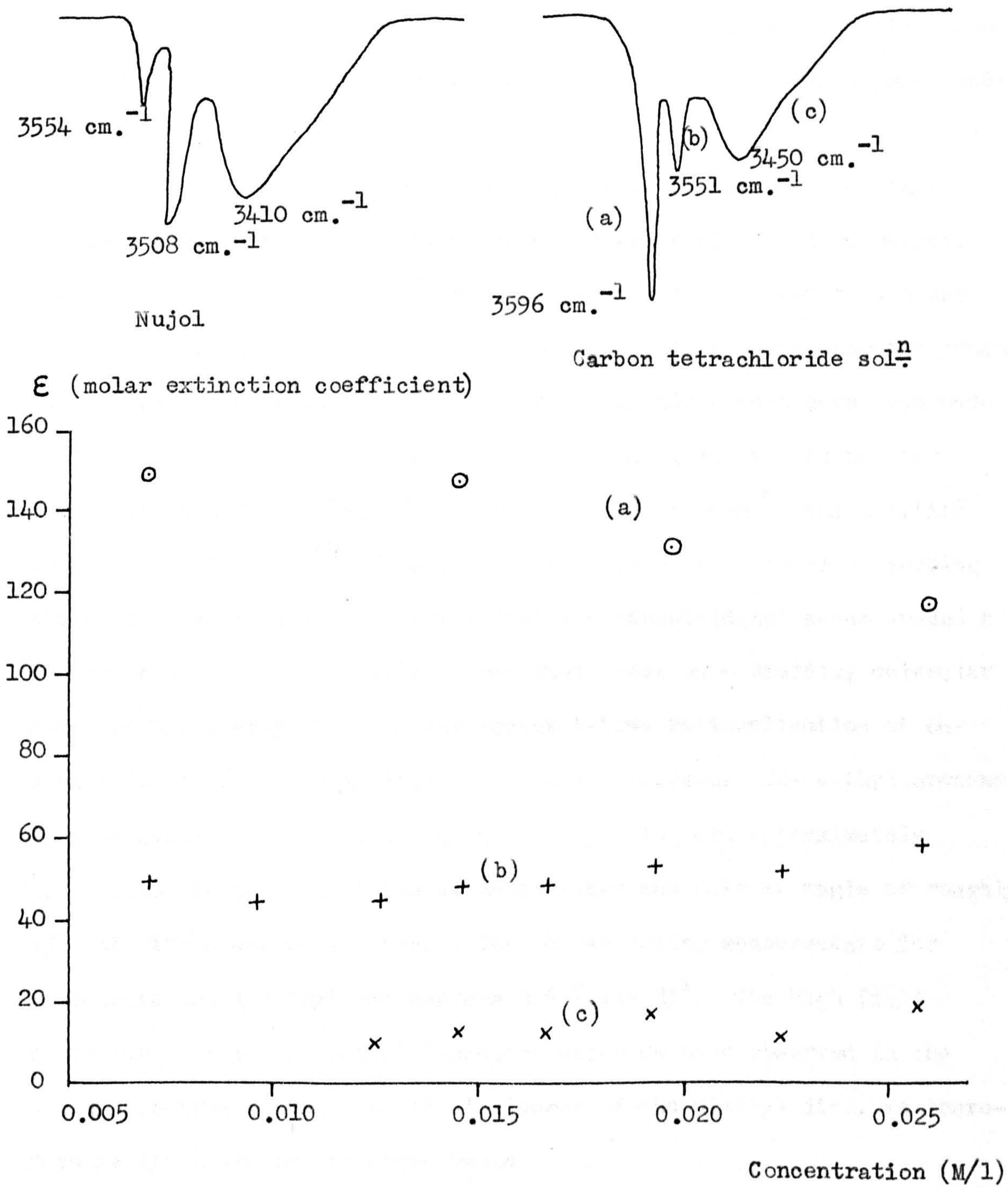


Fig. 13

Infrared dilution curves for the hydroxyl bands in the second isomer of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol isolated.

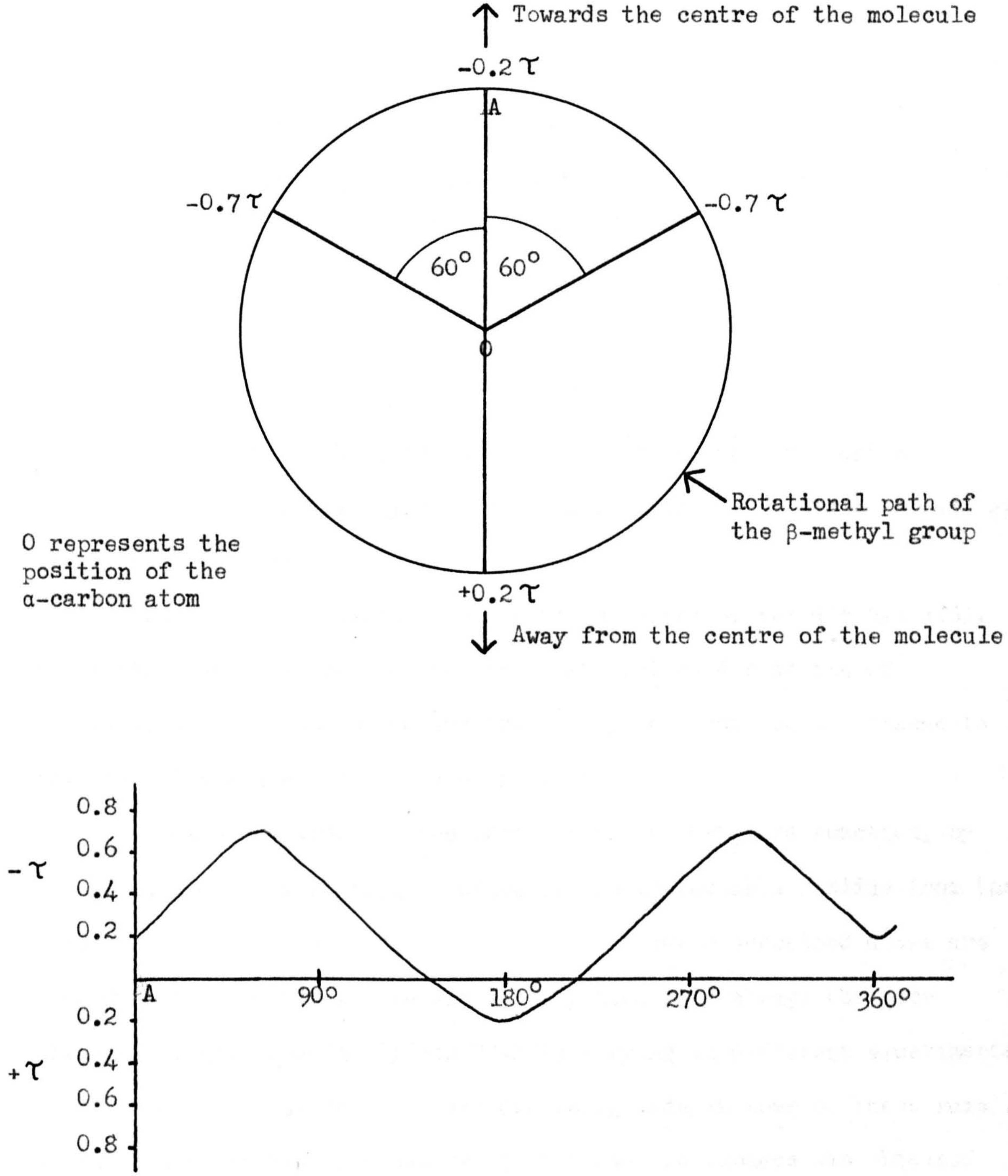
implication, and to rationalise the magnitude of the shielding effect observed for axial β-protons, at least semi-quantitatively, it is necessary to consider, briefly, calculations of the magnitude of this effect, made on a basis of theory.

The concept of a local magnetic field, generated by a ring current arising from the interaction of an externally applied magnetic field and a system of π electrons, was originally invoked to account for the low-field proton magnetic resonance absorption of aromatic protons. Theoretical calculations of the magnitude of this effect have been made on the basis of a model due to Pauling,[66] and explicitly stated for the p.m.r. problem by Pople[67] and Waugh and Fessenden,[68] and modified by Johnson and Bovey.[69] From the predictions of this model concerning the spatial arrangement of "shielding" and "deshielding" zones around a benzene ring, and from simple measurements made on a Dreiding molecular model of the diethyl diol, a semi-quantitative rationalisation of our observations and conformational assignments emerges. The methyl protons of a pseudoaxial ethyl group in the diethyl diol are approximately 3.2 Å from the centres of the aromatic rings and make an angle of roughly 55° with the plane of the ring. The corresponding measurements for pseudoequatorial methyl protons are 3.6 Å and 35°. The high field resonance of the pseudoaxial β-protons which we have observed in the p.m.r. spectrum of the cis (a' a') isomer of the diethyl diol, is therefore rationalised on the above basis.

More quantitatively, values of approximately 0.6 τ (shielding) and 0.1 τ (deshielding) are obtained for the anisotropic shifts of pseudoaxial β-protons and pseudoequatorial β-protons respectively, in the diethyl diol, from molecular model measurements as above and reading off the values of the anisotropic shifts corresponding to these measurements in tables,[70] which have been compiled on the basis of Johnson and Bovey's[69] theoretical calculations. Because of the major difficulty encountered in making acceptable measurements from a model, caused by the free rotation of the β-methyl group around the α-carbon atom, a series of values for the anisotropic shift of the pseudoaxial β-protons was obtained as above, but at specific angular positions of the β-methyl group in this rotational motion. These values are plotted in Fig. 14 The graph indicates a mean shielding value of approximately 0.5-0.6 τ for the axial β-protons.

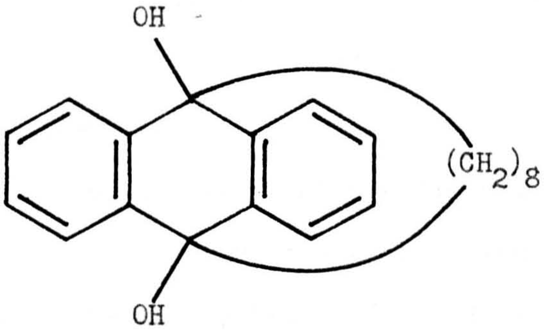
It is reasonable to conclude that although the values obtained must be regarded as only approximate (because of the crudity of the measurements from which they are derived) the order of magnitude of these values is comparable with the magnitude of the effect we have observed, and so provides support for our conformational assignments for the two isomeric cis diethyl diols.

Unsuccessful attempts were made to isolate a compound of structure XVI, by use of a Grignard reaction using 1,8-dibromoöctane, magnesium, and anthraquinone.



Negative τ values: shielding
Positive τ values: deshielding

Fig. 14



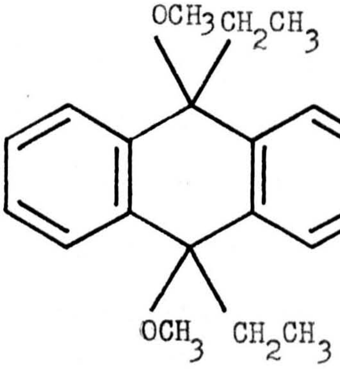
(XVI)

It was hoped that, in the light of the anisotropic effect already observed in this system, the p.m.r. pattern for the methylene groups would be of interest.

An attempt to synthesise the trans isomer of the diethyl diol, by raising the reaction temperature of the Grignard reaction of anthraquinone and ethylmagnesium bromide by the addition of benzene to the solvent mixture, also proved unsuccessful.

A detailed study of the products of the Grignard reaction, by use of column chromatography applied to the intractable residue from the organic layer, has shown that both the cis isomers described above are formed in the reaction. The cis (a' a') isomer is always the more abundant isomer isolated (yield 20-40%; varying in different experiments, slight modifications in the procedure being made in some of these runs). In all the experiments, a mixture of the two cis isomers was obtained (0.5-12.0% yield). Only when the hydrolysis stage of the reaction was carried out using aqueous ammonium chloride did column chromatography of the intractable residue from the organic layer yield crystalline products, one of these being the cis (e' e') isomer (5% yield). A large quantity (17 - 30%) of unchanged anthraquinone was always isolated from the reaction product.

The dimethyl ether (XVII) of the diethyl diol, synthesised by treating the cis (a' a') isomer of the diol with methanol in which a trace of hydrogen chloride had been dissolved, showed through the low intensity peaks at 9.20 τ (triplet), 8.15 τ (quadruplet), and 7.28 τ (singlet) in the p.m.r. spectrum, that it (i.e. XVII) is formed in more than one isomeric form in this reaction.



(XVII)

The cis (a' a') isomer of the dimethyl ether is the main isomer formed, but the formation of another isomeric form (or other isomeric forms) is interesting insofaras Beckett and Lingard,[38] in their work on the etherification of two isomers of 9,10-dimethyl-9,10-dihydroanthracene-9,10-diol (VI, page 29; R = CH_3) (which they assigned as cis and trans isomers) concluded that both these isomers gave the same dimethyl ether.

They rationalised this conclusion by postulating that intermediate carbonium-ion formation would permit the sterically more favoured dimethyl ether to be formed from either diol. A similar result to Beckett and Lingard's was apparently obtained by Pinazzi[71] on etherification of cis- and trans-9,10-diphenyl-9,10-dihydroanthracene-9,10-diol.

The results obtained to date on the products (diols) from the reaction of n-propylmagnesium bromide and anthraquinone, though not as comprehensive as the results described previously for the diethyl diols, seem to indicate a close similarity to the results on the diethyl diols. Fig. 15(a) shows the p.m.r. spectrum, recorded on a 60 Mc/sec. instrument, of the readily isolable major isomer of 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol (VI, page 29, R = $CH_2CH_2CH_3$) from the Grignard reaction (in the reactions carried out, this isomer was produced in yields of up to 33%). This spectrum (Fig. 15(a)) shows a large singlet superimposed on a multiplet at 9.40 τ corresponding to the four β-methylene and six γ-methyl protons. The similarity in chemical shift of the β-methylene and γ-methyl protons observed in this spectrum is attributed to the aromatic anisotropic effect, which shields the β-methylene protons, causing them to resonate at an unusually high field. We have seen previously that when an alkyl group is in the pseudoaxial position in this class of compounds, p.m.r. peaks due to protons attached to the β-carbon atom are shifted about 0.6 τ up field. Thus, by analogy in this way to our previous results, it is concluded that this isomer of the di-n-propyl diol is the cis (a' a') isomer (XIVb, cis (a' a'), page 31).[26] The p.m.r. spectrum of this isomer

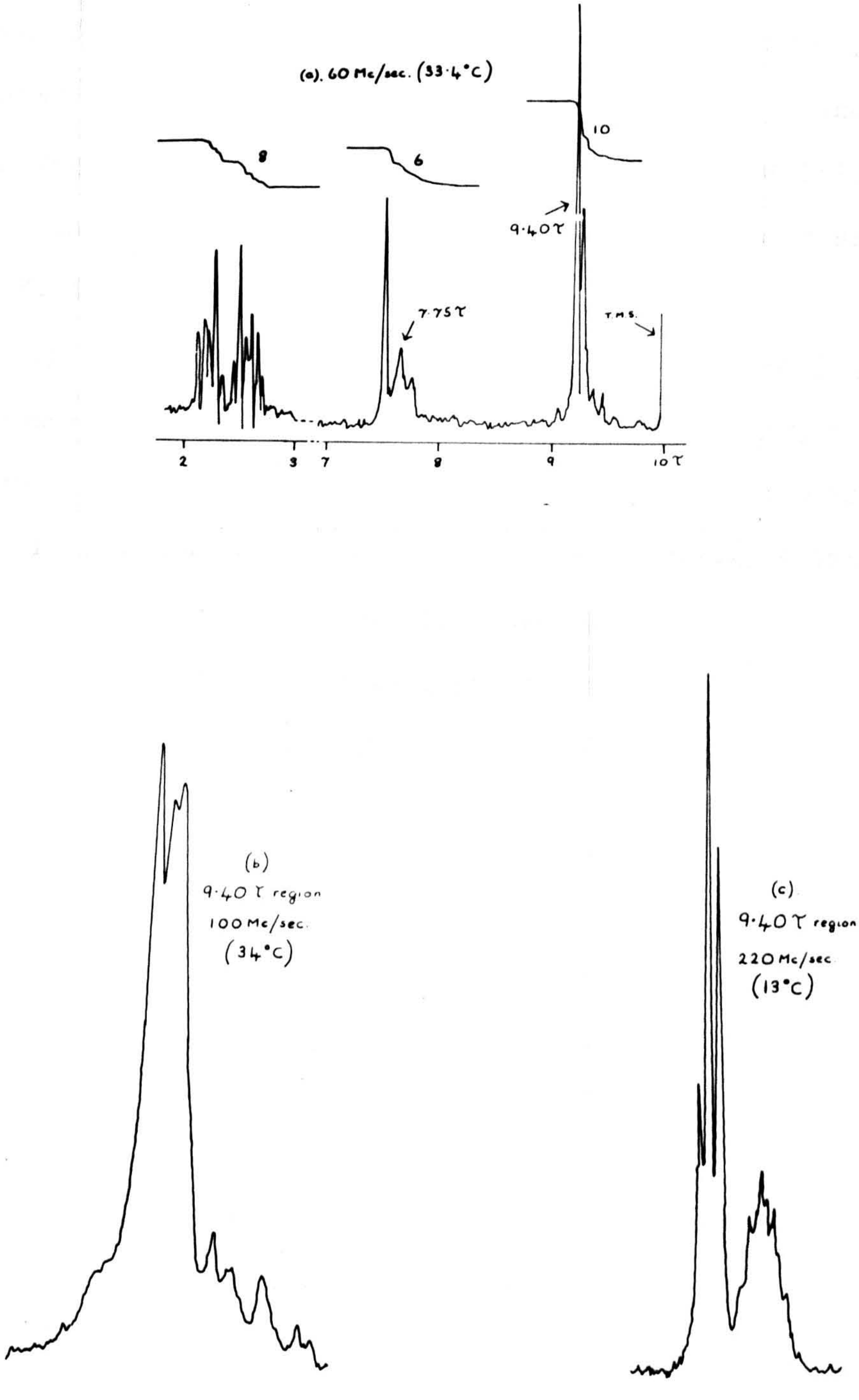


Fig. 15

P.m.r. spectra (in $CDCl_3$) of the isomer of 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction. (a) At 60 Mc/sec. (33.4°C). (b) 9.40τ region at 100 Mc/sec. (34°C). (c) 9.40τ region at 220 Mc/sec. (13°C).

recorded on a 220 Mc/sec instrument shows the usual β-methylene and γ-methyl coupling for an n-propyl group, for the resonances in the 9.40 τ region (Fig. 15(c)) of the p.m.r. spectrum of this isomer, and also shows the β-methylene protons which resonate at slightly higher field than the γ-methyl protons.

By adding a drop of tetranitromethane (or a small quantity of tetracyanoethylene) to the p.m.r. sample of this isomer, a deep-red π-complex is formed, and the anisotropic effect of the aromatic ring current is modified sufficiently to induce the normal splitting pattern associated with an n-propyl group. Thus the p.m.r. spectrum (at 60 Mc/sec) of the π-complex shows a methyl triplet at 9.20 τ , and a complex multiplet between 8.10-9.00 τ (Fig. 16).[26]

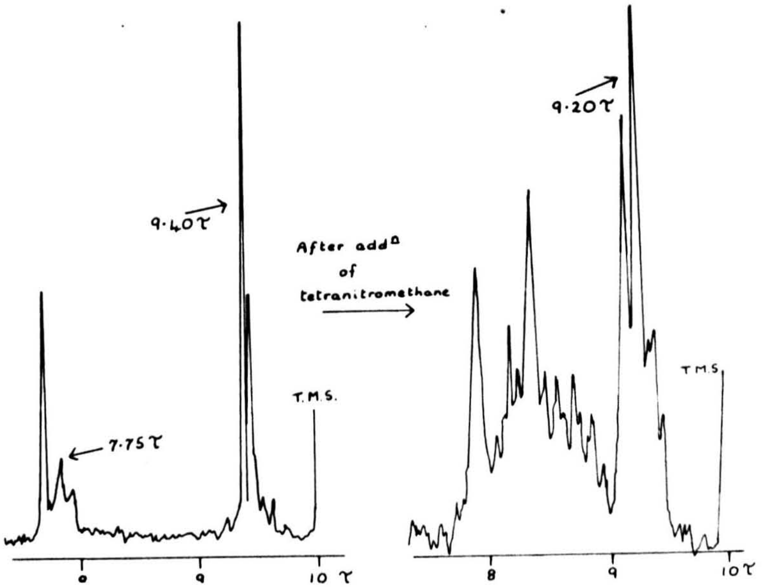
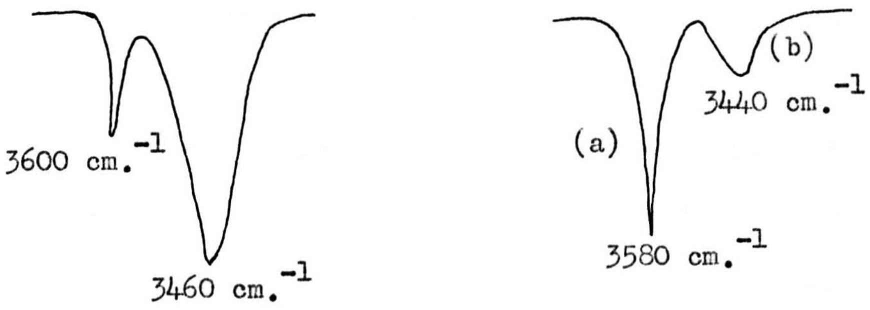


Fig. 16

The use of π-complex formation to modify the anisotropic effect in the p.m.r. spectrum of the isomer of 9,10-di-*n*-propyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

The infrared spectrum of this isomer of the *n*-propyl diol shows two hydroxyl bands (in Nujol, and ethanol-free chloroform). The graphs (Fig. 17) of the molar extinction coefficients of these, plotted as a function of the concentration in ethanol-free chloroform (0.034-0.06 M/l), give no conclusive evidence of intramolecular hydrogen bonding (see pages 35-37).



Nujol

Ethanol-free chloroform sol$^{\underline{n}}$.

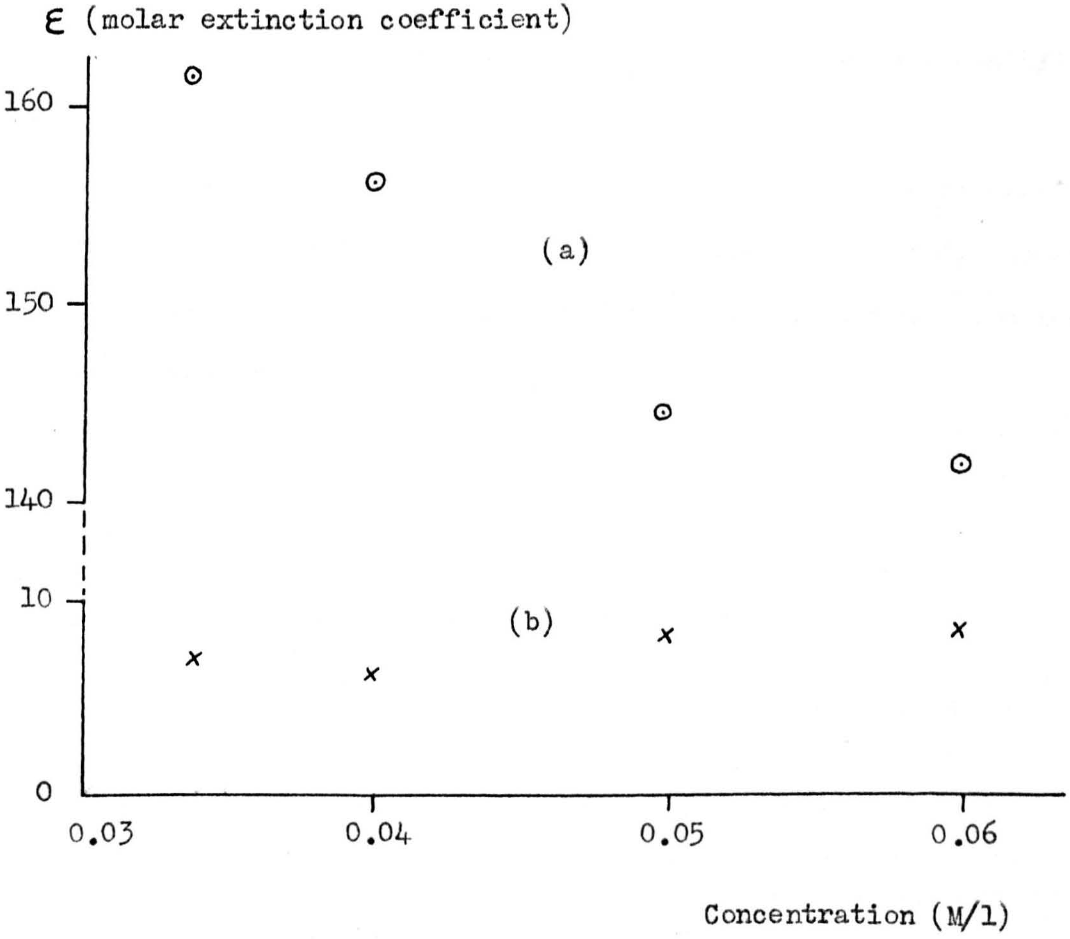


Fig. 17

Infrared dilution curves for the hydroxyl bands in the isomer of 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol, readily isolable from the product of the Grignard reaction.

Variable-temperature p.m.r. work on this isomer is in progress at the time of writing. Though the results from this work are not sufficiently complete to merit inclusion in this thesis, it is worth commenting that readings taken as the temperature of the p.m.r. sample is increased do indicate a cis (a' a') to cis (e' e') conformational change in the sample, similar to the change observed for the cis (a' a') diethyl diol. The difficulties and observations encountered in determining the melting point of the isolated di-n-propyl isomer (which by the criteria of t.l.c. analysis was a single isomer) may be attributed in part to such conformational changes as in the cis (a' a') diethyl diol case.

The p.m.r. spectra of this di-n-propyl diol isomer, recorded at intervals after the addition of a drop of 0.1% acetic acid, showed the gradual appearance of a methyl triplet at 9.23 τ, and a complex multiplet between 8.17-9.00 τ (Fig. 18).

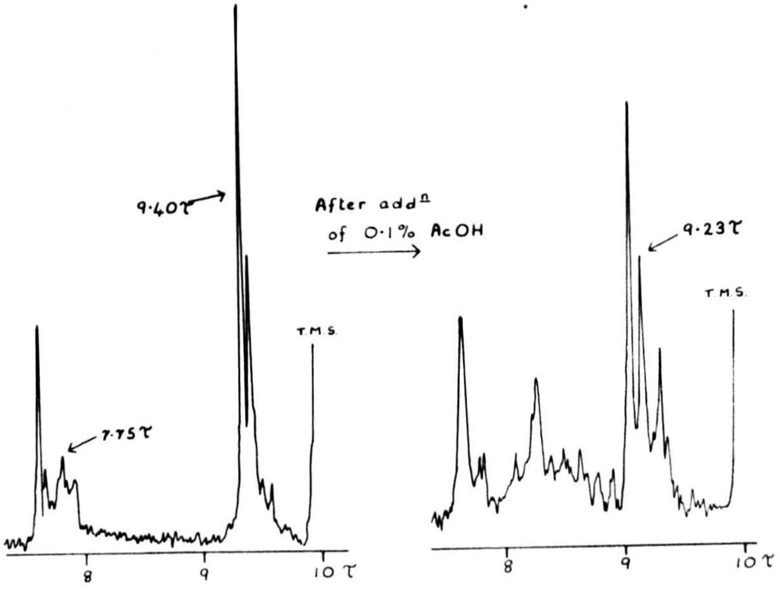


Fig. 18

P.m.r. spectrum of the isomer of 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol (readily isolable from the product of the Grignard reaction), in $CDCl_3$ containing a drop of 0.1% acetic acid.

As with the similar observation for the cis (a' a') isomer of the diethyl diol, the change observed here is most likely to be a conformational change involving a carbonium ion intermediate (see Scheme XII, page 40).

A preliminary, more detailed study of the products of the reaction of n-propylmagnesium bromide and anthraquinone, using column chromatography of the intractable residue from the organic layer, indicates that both the cis isomers of the di-n-propyl diol are formed in the reaction. As was found in the diethyl diol work, the cis (a' a') isomer of the di-n-propyl diol, described above, is the more abundant isomer isolated (yields of 18.5 and 33% obtained in two different experiments). Column chromatography of the intractable residue from the organic layer gave a crude sample of the cis (e' e') isomer of the di-n-propyl diol (XIVb, cis (e' e'), page 31) in 8.4% yield. The p.m.r. spectrum of this second isomer, as yet not fully purified, shows resonances at 9.24 τ (triplet) 8.00-8.80 τ (triplet superimposed on a complex multiplet), and 2.00-2.62 τ (symmetrical, complex multiplet). The infrared spectrum shows three hydroxyl peaks. A large quantity (15.0 and 18.5%) of unchanged anthraquinone was isolated in both runs of the Grignard reaction.

The conformational assignments described above, which have been reported by us in preliminary communications,[25,26] are in conflict with assignments made by Chodkiewicz and her co-workers.[42,55,50,49] That we are discussing the same isomers of the diethyl and di-n-propyl diols is apparent from the correspondence of physical properties (melting points and spectral data) found by us and by them. Our results[25,26] were the first conformational assignments reported for diols of this type. An earlier communication[42] by Chodkiewicz et al. tended to assume that the molecules in question were equilibrating rapidly (see Scheme X, page 31), and thus they made only configurational assignments for the diethyl and di-n-propyl diols. That equilibration of this kind is not always the case for derivatives of 9,10-dihydroanthracene is now clear[18,19,20,21,22] (see pages 8 and 9). Chodkiewicz and co-workers' configurational assignments[42] were based on the not unreasonable assumption that diols of the type in question, prepared by reductively opening 9,10-dialkylanthracene photoöxides (see Scheme V, page 16) had a cis configuration. Thus by means of the cyclic route: diol → photoöxide → diol, described earlier (see pages 21 and 22), they assigned trans configurations to the two isomers of the diethyl and di-n-propyl diols which we have assigned cis (a' a'). The isomers of these diols which we have ascribed cis (e' e'), have also been given cis assignments by Chodkiewicz et al.[42] on the basis of the reasoning above and in later reports[55,50,49] the same workers gave cis (a' a') conformational assignments to these cis isomers. They based the latter conclusions on their observation that no intramolecular hydrogen bonding was detectable in either of these cis isomers,[50] a result in direct conflict to what we have observed[25] (see pages 44, 45, and 58). They did observe intramolecular hydrogen bonding, however, in the corresponding unsaturated cis diols, by the reduction of which (see Scheme IV, page 15) they obtained the saturated cis diols, in which they didn't observe intramolecular hydrogen bonding.

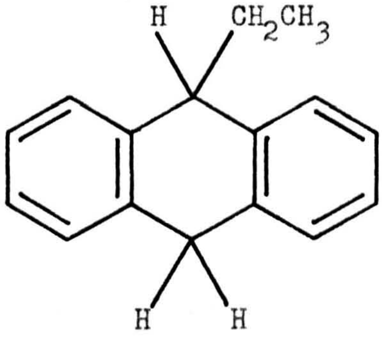
Chodkiewicz and co-workers have rationalised the p.m.r. data on these isomers, by concluding[55] that their trans isomers of the diethyl and di-n-propyl diols (corresponding to our cis (a' a') **isomers**) are equilibrating rapidly through the planar conformation, and the equivalence of the two ethyl and n-propyl groups in the spectra, is caused by an averaging effect of the p.m.r. resonances, caused by this equilibration of the molecules. If this were the case, one would have to postulate a very much greater shielding effect for the β-carbon atom protons than is calculated, albeit approximately, by the Johnson and Bovey method[69,70] (see pages 44, 46-48), since the alkyl groups would be in a pseudoaxial (shielding) region for only 50% of the time. The absence of high field shift of the protons attached to the β-carbon atoms in the isomers of the diethyl and di-n-propyl diols, which they have assigned cis (a' a') and which correspond to the isomers we have assigned cis (e' e'), is explained by Chodkiewicz by asserting that because of pseudoaxial interactions, the alkyl groups have a tendency to be oriented towards the exterior of the molecule and thus away from the shielding region which, as we have seen, causes a marked up-field shift for axial β-protons.

The main points of the conflict now having been outlined, in conclusion the following additional points may be noted:

(1) If it is accepted that diols of this type prepared by reductive opening of 9,10-dialkylanthracene photoöxides are cis, it is not unreasonable to expect such cis isomers to be cis (e' e') i.e. with the hydroxyl groups a' a' . This assumption would be compatible with our conformational assignments for the cis (e' e') isomers. However, it should also be noted that it has been reported[53] that reduction of 9,10-dimethoxyanthracene photoöxide gives rise to a mixture of cis and trans isomers of the corresponding diol.

(2) The conformational changes we have observed (see pages 37, 39-42, and 56) by running p.m.r. spectra of certain isomers of these diols at elevated temperatures, provide as yet undisputed evidence in favour of our conformational assignments for these diols.

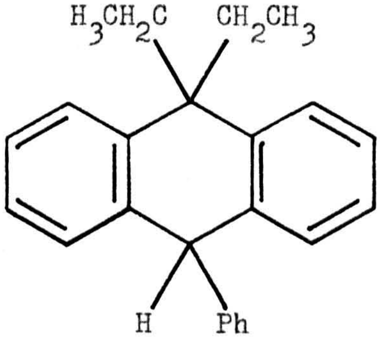
(3) Two sets of observations reported recently[22,21,64] lend support to our conformational assignments. Firstly, Nicholls and Szwarc[22,21] reported the isolation of 10-ethyl-9,10-dihydroanthracene (XVIII), in which they conclude that the ethyl group is pseudoequatorial.



(XVIII)

They report p.m.r. resonances of 9.18τ (methyl) and 8.38τ (methylene) for the ethyl group in this compound. As pointed out[21] by these workers, these chemical shift values agree with the values (9.15τ and 8.16τ) which we have observed for pseudoequatorial ethyl groups in the cis (e' e') isomer of the diethyl diol. Nicholls and Szwarc's conformational conclusion is based on the assumption that the pseudoaxial hydrogens in XVIII absorb at a higher field in the p.m.r. spectrum than the pseudoequatorial hydrogen, in agreement with the theoretical deductions of Johnson and Bovey.[69]

Secondly, Koptyug and his co-workers[64] have recently reported p.m.r. data for 10,10-diethyl-9-phenyl-9,10-dihydroanthracene (XIX).



(XIX)

They report values of 7.88 τ, and 8.11 τ for the resonances of the methylene groups, and 9.40 τ, and 9.67 τ for the resonances of the methyl groups in this compound. A Dreiding model of this compound indicates that, for steric reasons, the phenyl group in the 9-position of this compound is likely to be pseudoequatorial, and that if it were pseudoaxial, it should exert a considerable shielding effect on the β-protons of the pseudoaxial ethyl group. Such a shielding effect should also be noticeable in the p.m.r. spectrum if the molecule were equilibrating through the planar conformation. Thus given these assumptions of a rigid molecule and a pseudoequatorial phenyl group in the 9-position, the reported ethyl group resonances are compatible with the values we have observed for pseudoaxial and pseudoequatorial ethyl groups in the diethyl diol isomers we have described.

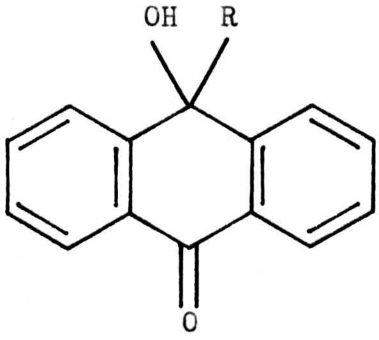
B. Products Other than 9,10-*Dialkyl*-9,10-*dihydroanthracene*-9,10-*diols* (VI, page 29), Isolated from the Products of the Grignard Reactions of Alkylmagnesium Halides and Anthraquinone.

As indicated previously, of the Grignard reactions of the above type carried out, only those involving the use of ethylmagnesium bromide and *n*-propylmagnesium bromide gave diols of the type VI (page 29). Clark [37] reported that the reaction of isopropylmagnesium chloride and anthraquinone gives a 5% yield of 9,10-di-isopropyl-9,10-dihydroanthracene-9,10-diol (VI, page 29; R = $CH(CH_3)_2$). We have not been able to isolate any of this diol from the reaction, using the same procedure as Clark. Nogaideli and co-workers[72] have reported a result similar to ours in this respect. The products we have isolated from this reaction are discussed below. It was hoped that by using halides with 'bulky' alkyl groups (*t*-butyl, isopropyl, and neopentyl), a diol with a trans configuration might be isolated; as noted earlier (under A), the diethyl and di-*n*-propyl diols isolated have had cis configurations. No such trans diols having been isolated using organomagnesium reagents, an unsuccessful attempt was made to prepare *t*-butyl lithium by the method of Petrov and co-workers,[73] in the hope of procuring a trans diol by the reaction of this organolithium reagent with anthraquinone.

No identifiable product other than unchanged anthraquinone (45%)

was isolated from the reaction of isopropylmagnesium bromide and anthraquinone. A large amount of unchanged anthraquinone (up to 60%) was isolated from the products of all the Grignard reactions investigated.

(1) Substituted anthrones of type XX have been isolated using column chromatography from the products of the Grignard reactions of ethylmagnesium bromide (4% yield), n-propylmagnesium bromide (20% yield), and neopentylmagnesium chloride (18.3% yield) with anthraquinone.



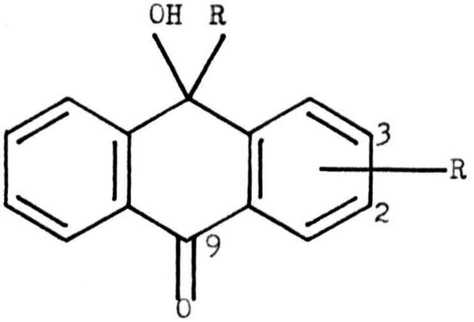
(XX)

R = CH_2CH_3, $CH_2CH_2CH_3$, or $CH_2C(CH_3)_3$

At the time of writing, an analytically pure sample of 10-hydroxy-10-n-propyl-9-anthrone (XX; R = $CH_2CH_2CH_3$) has not been obtained. These products (XX) are formed by the 1,2-addition of the Grignard reagent to one of the carbonyl groups of anthraquinone, and they are presumably intermediates in the formation of diols of type VI (page 29) in the cases where R = CH_2CH_3 or $CH_2CH_2CH_3$. Modification of the anisotropic effect observable in the p.m.r. spectra of these compounds, using tetranitromethane (see page 34), was not possible as no formation of π-complexes with this reagent occurred with these compounds.

(2) Substituted anthrones of type XXI have been isolated

from the products of the Grignard reactions of t-butylmagnesium bromide (up to 27% yield), isopropylmagnesium chloride (27% yield), and neopentylmagnesium chloride (22.5% yield) with anthraquinone. The structure XXI was deduced from spectral data for these compounds. The p.m.r. spectra of fractions obtained from the column chromatography of the intractable residues from the organic layers of the ethylmagnesium bromide and n-propylmagnesium bromide reactions, indicate that compounds of type XXI are formed in small yields (less than 6.5%) in these cases.



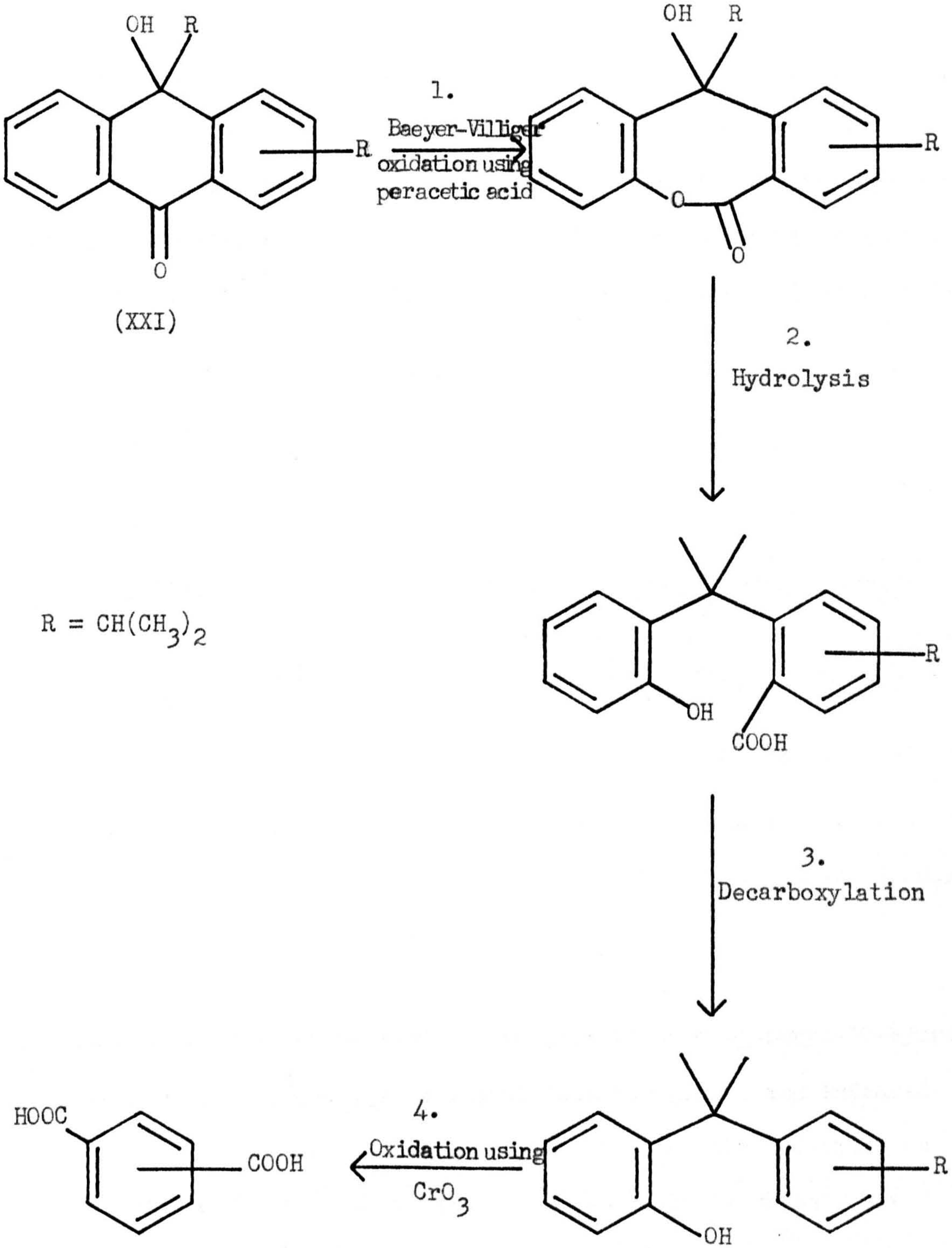
(XXI)

R = CH_2CH_3, $CH_2CH_2CH_3$,
$C(CH_3)_3$, $CH(CH_3)_2$,
or $CH_2C(CH_3)_3$

Unsuccessful attempts were made to isolate in a pure form the compound of this type (XXI), in which R = CH_2CH_3, using extensive column chromatography and preparative t.l.c. on the fraction obtained from the chromatography of the intractable residue from the ethylmagnesium bromide reaction. Thus at the time of writing, compounds of the type XXI in which R = CH_2CH_3 or $CH_2CH_2CH_3$ have not been isolated in pure form. During the course of this work, Cameron and Meckel[41] reported the isolation of a compound of type XXI (R = $C(CH_3)_3$) in 25% yield from the reaction of t-butylmagnesium chloride and anthraquinone (see Introduction, page 13). As these workers[41] pointed out, formation of di-adducts of this type (XXI) presumably involves nucleophilic 1,6-addition of the Grignard reagent, an addition process without previous direct analogy in the anthraquinone series. In their preliminary report,[41] Cameron and Meckel were not able to state whether the alkyl group (t-butyl in their case) attached to the aromatic nucleus was in a 3- or a 2-position. We have attempted to clarify this point by carrying out the reaction sequence as shown in Scheme XIII, starting with 3 (or 2), 10-di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$).

Scheme XIII indicates one of the several possible courses this reaction sequence might follow, but it was hoped that provided part of the reaction followed the course outlined in Scheme XIII, the isolation and identification of the phthalic acid isomer produced, would enable us to unambiguously assign a complete structure to compounds of type XXI. A small quantity of solid acidic material was isolated at the end of this reaction sequence and this was esterified with diazomethane. V.p.c. analysis of this esterified material, however, did not show the presence of one of the dimethyl esters of the three phthalic acid isomers, so this structural problem remains unresolved.

The use of π-complex formation of compounds of this type (XXI) with tetranitromethane, to modify any possible anisotropic effects observable in the p.m.r. spectra of these compounds, was not possible



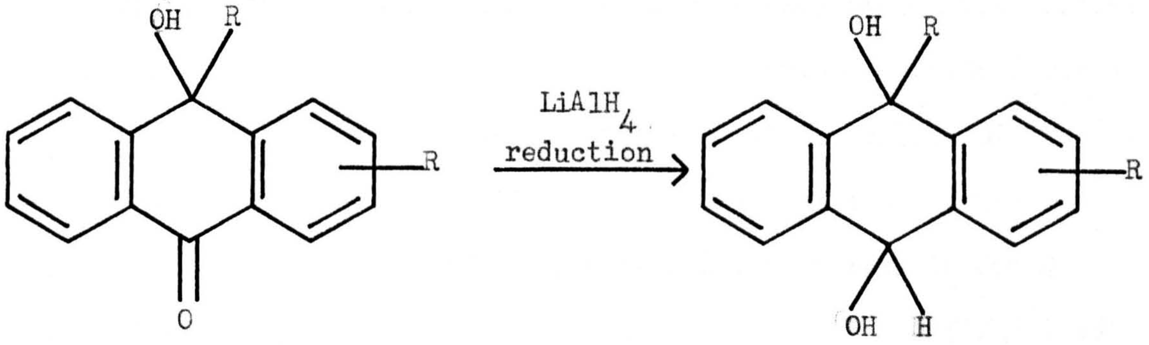
(XXI)

R = $CH(CH_3)_2$

(one of the possible products)

Scheme XIII

as these substituted anthrones did not form such π-complexes. Unsuccessful attempts were made to prepare carbonyl derivatives (hydrazones, semicarbazones, and oximes) of these substituted anthrones. However, reduction of the carbonyl group in these substituted anthrones using lithium aluminium hydride was found to be possible (Scheme XIV).



XXI

XXII

R = $C(CH_3)_3$ or $CH(CH_3)_2$

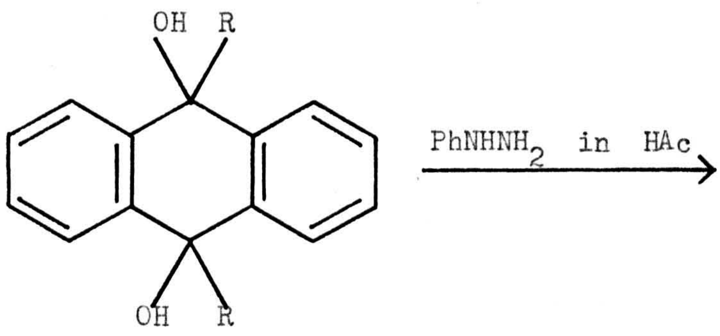
Scheme XIV

When this reduction was carried out on 3(or 2),10-di-t-butyl-10-hydroxy-9-anthrone (XXI; R = $C(CH_3)_3$), evidence from the p.m.r. and infrared spectra of the reaction product, did indicate that the reduction as shown in Scheme XIV had taken place to an appreciable extent, but attempted purification of the product using column chromatography gave only intractable material. The reduction of 3(or 2),10-di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$) gave pure

3(or 2),10-di-isopropyl-9,10-dihydroanthracene-9,10-diol (XXII; R = $CH(CH_3)_2$). The appearance of two peaks at 4.37τ and 4.53τ in the p.m.r. spectrum of this compound (XXII; R = $CH(CH_3)_2$) assigned to the benzylic proton, indicates that a mixture of cis and trans isomers is produced in the reaction (two peaks appear because of the different chemical shifts of pseudoaxial and pseudoequatorial benzylic protons in this compound). The single resonance position (9.26τ d., 8.00τ sept.) observed for the isopropyl group in the 10-position, indicates that this group is pseudoequatorial in both isomers (see page 46). T.l.c. analysis of this product did not show any separation of these isomers.

As mentioned earlier, Clark[37] reported the isolation of the di-isopropyl diol (VI, R = $CH(CH_3)_2$) in 5% yield from a Grignard reaction, identical with the reaction from which we have isolated 3(or 2),10-di-isopropyl-10-hydroxy-9-anthrone (XXI, R = $CH(CH_3)_2$) as the main product (27% yield). Clark treated the diol he isolated with phenylhydrazine in acetic acid,[37] and obtained 9,10-di-isopropylanthracene in 29% yield (Scheme XV).

We have repeated this reaction (Scheme XV) on the product (XXI, R = $CH(CH_3)_2$) from the Grignard reaction, and found that the only isolable product from the reaction was 1-acetyl-2-phenylhydrazine.



(VI)

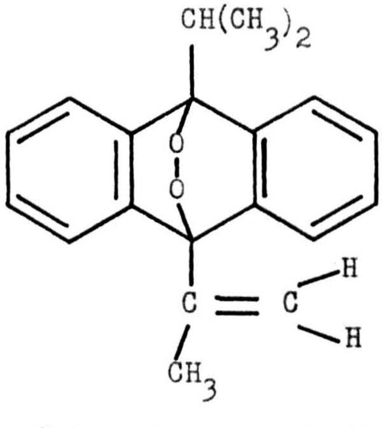
$R = CH(CH_3)_2$

Scheme XV

Before leaving this section, it is worth commenting on the observed non-equivalence of the 10-isopropyl methyl protons in the p.m.r. spectrum of XXI ($R = CH(CH_3)_2$). A chemical shift difference of 1.5 c.p.s. (at 60 Mc/sec) is observed for the two sets of methyl protons of the isopropyl group in this compound. There is currently much interest[74,75,76,77,78,79] in the magnetic non-equivalence of protons in methylene and isopropyl methyl groups in certain geometrical situations, and it seems reasonable, from the information available in the literature (e.g. ref. 78) to conclude that the non-equivalence we have observed, is due to a combination of steric hindrance to free rotation of the two methyl groups and the anisotropic effect of the aromatic ring current.

(3) Column chromatography of the intractable residues from the organic layers of the t-butylmagnesium bromide and neopentylmagnesium chloride reactions, both gave highly coloured, intractable fractions (3.3 g. and 1.3 g. respectively). In both instances, these fractions came off the column on elution with solvents of low polarity, and although these fractions were not identified, it is probable that they were hydrocarbons.

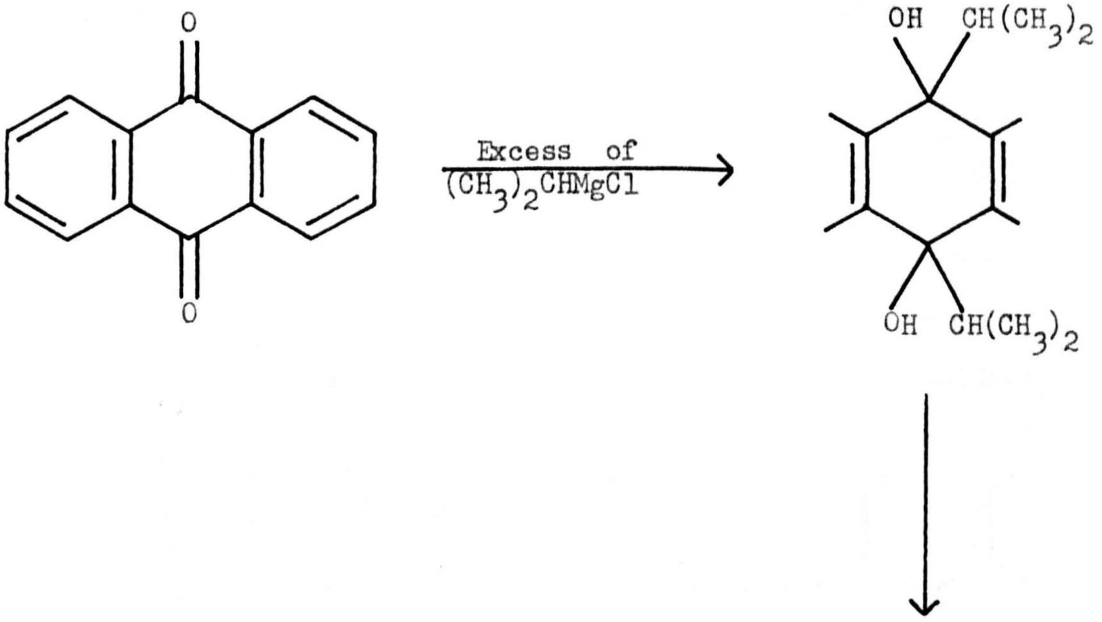
Column chromatography of the intractable residue from the organic layer of the isopropylmagnesium chloride Grignard reaction, gave a product which has tentatively been assigned structure XXIII.



XXIII

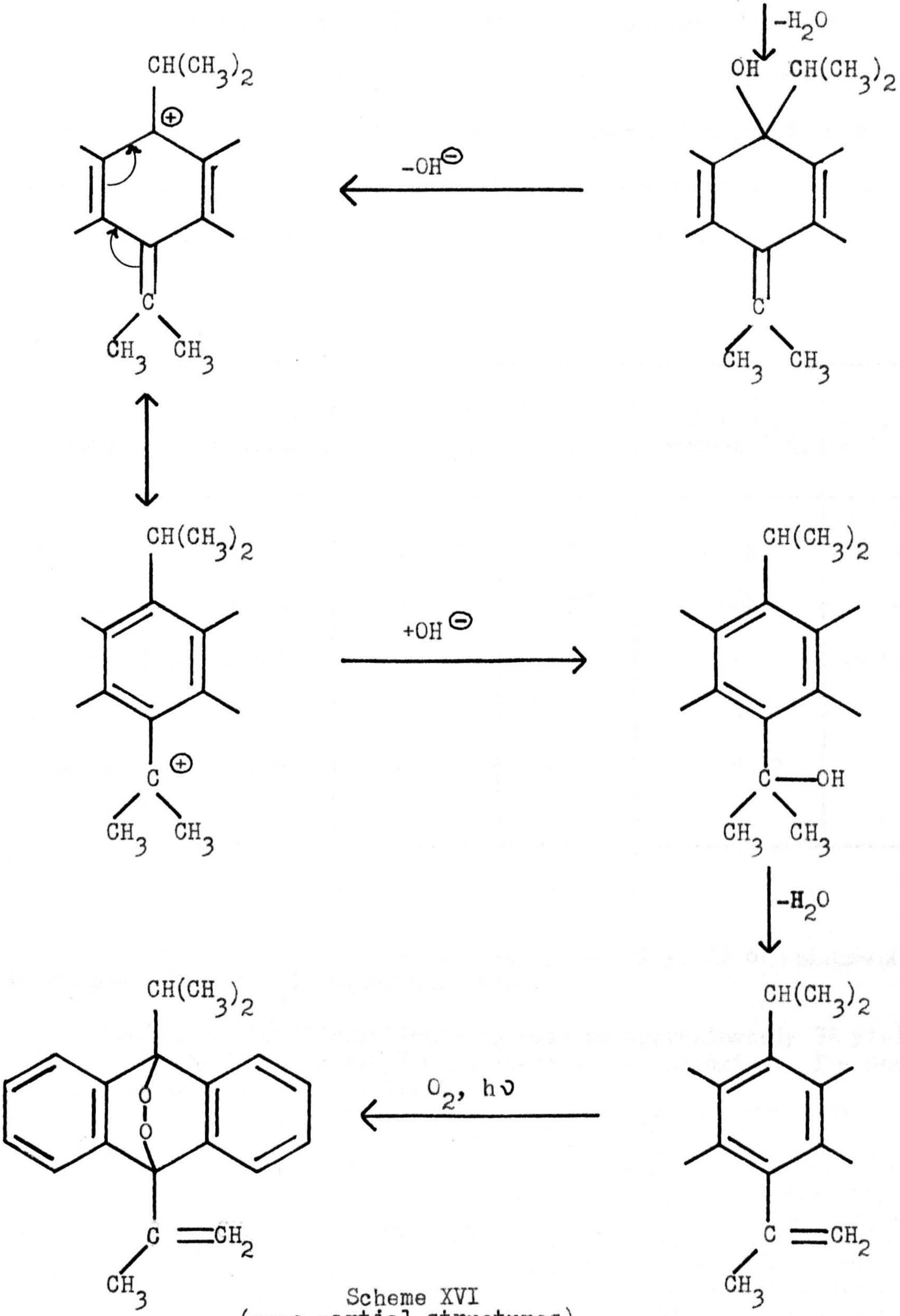
The assignment of a photoöxide structure to this compound is based on analytical data which indicates the presence of two oxygen atoms in the molecule. No hydroxyl or carbonyl bands appear in the infrared spectrum of this compound. However, on testing a sample of this compound for the liberation of iodine from acidified potassium iodide, no such liberation of iodine was observed. A positive result for this test might be expected for a photoöxide. The presence of an olefinic double bond was indicated by the decolourisation of bromine in carbon tetrachloride, and the presence of a methylvinyl $(CH_3\overset{|}{C}{=}CH_2)$ group is consistent with the p.m.r. spectrum of this compound (XXIII). The latter shows the two methene protons of the methylvinyl group as being non-equivalent, because of their different spatial positions, and allylic coupling between the methyl group and the cis and trans methene protons. A possible mechanism for the formation of XXIII in the Grignard reaction, is shown in Scheme XVI.

A good analysis of compound XXIII, consistent with the tentative structure assigned to it, has not been obtained.



Scheme XVI

Scheme XVI (Contd.)



XXIII

Scheme XVI
(some partial structures)

In conclusion, the table in Fig. 19 summarises the products we have isolated from the Grignard reactions of alkylmagnesium halides and anthraquinone. The reactions with ethylmagnesium iodide and isopropylmagnesium bromide are not included in the table, as only unchanged anthraquinone was isolated from these reactions.

Alkyl Halide	% Unchanged Anthraquinone	% Diol (VI)		% Mono-1,2-adduct (XX)	% 1,6-di-adduct (XXI)
		cis (a'a')	cis (e'e')		
EtMgBr	up to 30%	up to 40%	5%	4%	< 6.5%[†]
n-PrMgBr	up to 18.5%	up to 33%	8.4%[†]	20%[†]	< 6.5%[†]
t-BuMgBr	up to 54%	-	-	-	up to 27%
iso-PrMgCl	60%	-	-	-	27%
neopentyl MgCl	23%	-	-	18.3%	22.5%

The 'EtMgBr' reaction also gave up to 12% yield of a mixture of cis (a'a') and cis (e'e') isomers of the diethyl diol.

The 'iso-PrMgCl' reaction also gave an approximately 3% yield of 9-isopropyl-10-(1'-methylvinyl)anthracene 9,10-photoöxide. The structure of this compound is not confirmed.

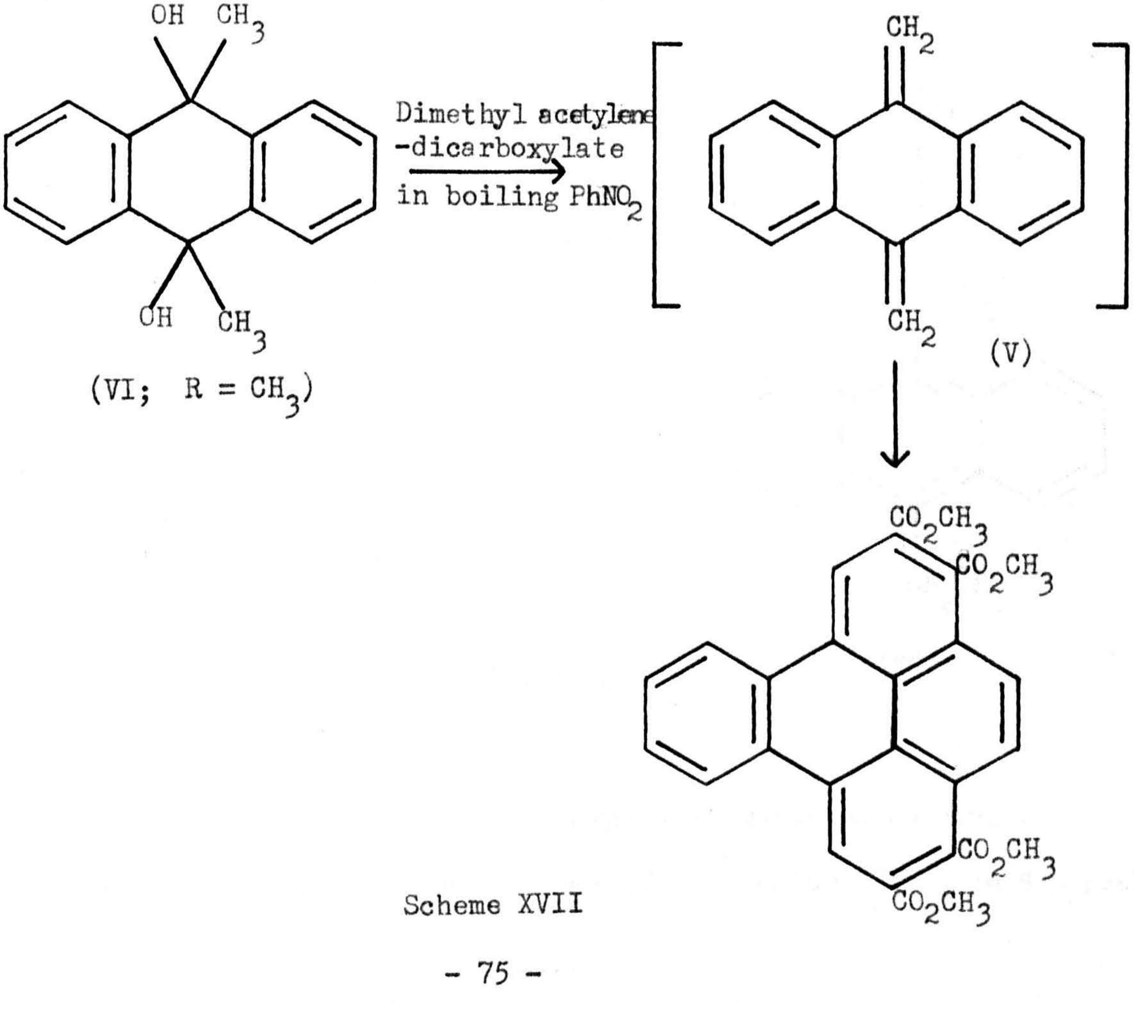
[†] Not isolated in pure form.

Fig. 19

Products Formed by the Dehydration of 9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols (VI, page 29).

Compounds corresponding to the two compounds isolated by Clarke and Carleton,[32] and assigned the 'bimolecular' structures XII and XIII (see pages 27-28) by these workers, have not been isolated from the product of the ethylmagnesium bromide and anthraquinone Grignard reaction described above.

A 1:2-Diels-Alder adduct, analogous to the product isolated[24] from the reaction of the dimethyl diol (VI; R = CH_3) with dimethyl acetylenedicarboxylate in boiling nitrobenzene (Scheme XVII), was not isolated from a similar reaction using the diethyl diol.

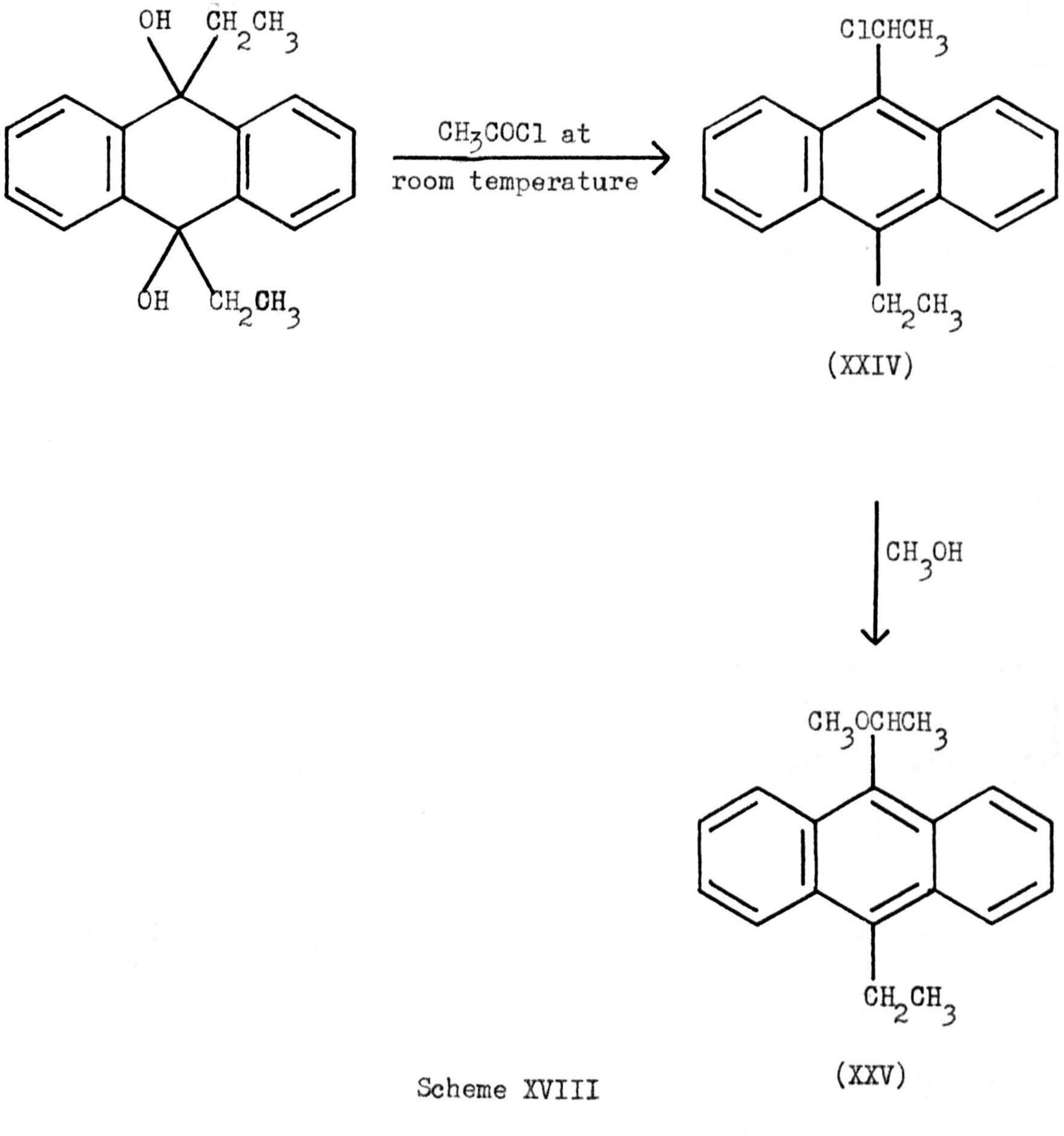


(VI; R = CH_3)

(V)

Scheme XVII

The diethyl diol, however, was found to react quantitatively with acetyl chloride, giving 10-(1'-chloroethyl)-9-ethylanthracene (XXIV) (Scheme XVIII).



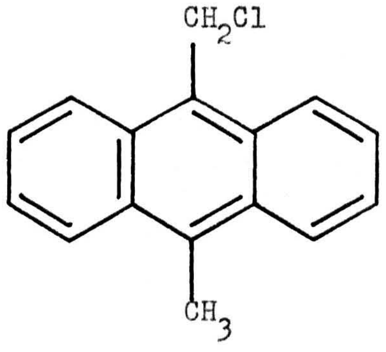
(XXIV)

(XXV)

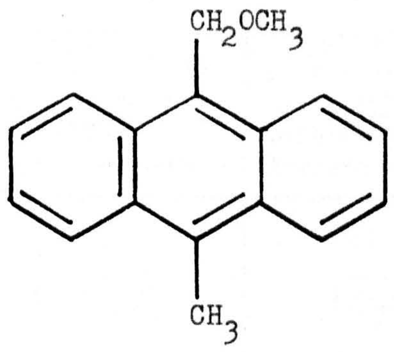
Scheme XVIII

The chloro-compound (XXIV) reacts with methanol to give 9-ethyl-10-(1'-methoxyethyl)anthracene (XXV) (Scheme XVIII) in 81% yield.

Clarke and Carleton[32] also isolated, but did not identify compound XXV by a similar reaction sequence. The methoxy-compound (XXV) was also isolated in 74% yield by the addition of a few drops of methanol saturated with hydrogen chloride, to a hot concentrated solution of the diethyl diol in methanol. The use of acetyl chloride to prepare the 10-chloromethyl derivative (XXVI) of 9-methylanthracene from the dimethyl diol (VI; R = CH_3), by a reaction similar to the one shown in Scheme XVIII, has been used by Hauptmann and co-workers.[80] We have repeated this reaction on the dimethyl diol and isolated XXVI (100% yield), reaction of which with methanol gives 10-methoxymethyl-9-methylanthracene (XXVII)



(XXVI)



(XXVII)

(compare Scheme XVIII) in 40% yield. The methoxy-compound (XXVII) was also isolated by treating the ether-insoluble fraction from the Grignard reaction of methylmagnesium iodide and anthraquinone with 10% acetic acid solution. Guyot and Staehling[31] first prepared XXVII by the action of heat on the dimethyl ether of the dimethyl diol, and later Badger and Pearce[35] isolated it by treating a boiling methanolic solution of the dimethyl diol with acid (mineral acid or picric acid, the latter giving the picrate of XXVII). Using this latter method,[35] we have been able to isolate the methoxy-compound (XXV) derived from the diethyl diol (see above); when picric acid was used, however, the picrate of XXV was not formed, though an impure sample of XXV was isolated from the reaction product.

The fully aromatic structures of compounds XXIV and XXV have been assigned by comparison of their ultraviolet spectral data with the ultraviolet spectral data reported for 9,10-dimethylanthracene[81] and 10-ethoxymethyl-9-methylanthracene[35] (Fig. 20).

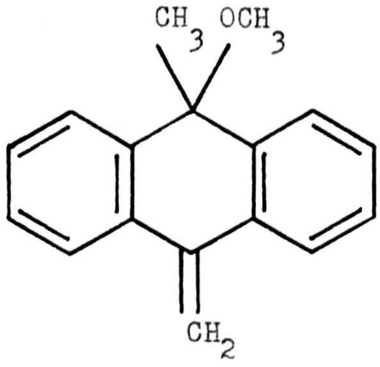
9,10-Dimethyl-anthracene (ref. 81) Solvent: heptane	10-Ethoxymethyl--9-methylanthracene (ref. 35) Solvent: alcohol	10-(1'-Chloroethyl)--9-ethylanthracene (XXIV) Solvent: hexane	9-Ethyl-10-(1'-methoxyethyl)-anthracene (XXV) Solvent: hexane
252 (4.91)	252 (4.93)	253 (4.81)	253 (4.94)
260 (5.27)	259 (5.24)	260.5 (5.03)	259.5 (5.19)
	310 (2.69)		
325 (3.00)	325 (3.08)		323 (3.04)
341 (3.41)	339 (3.48)	340.5 (3.39)	338 (3.49)
358 (3.76)	355 (3.80)	358 (3.73)	354 (3.84)
377 (3.99)	374 (4.01)	373 (3.91)	373 (4.06)
393 (3.78)	387 (3.71)		
399 (4.00)	395 (3.98)	397 (3.89)	394 (4.06)

U.v. data for 9,10-dimethylanthracene, 10-ethoxymethyl-9-methylanthracene, and compounds XXIV and XXV: mμ ($\log_{10} \varepsilon$).

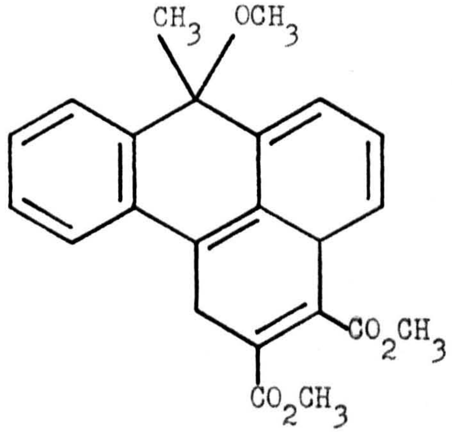
Fig. 20

The mechanism postulated by Badger and Pearce[35] for the formation of 10-methoxymethyl-9-methylanthracene (XXVII) (see Scheme VIII, page 26) can equally be applied to the formation of compounds XXIV and XXV in the above reactions.

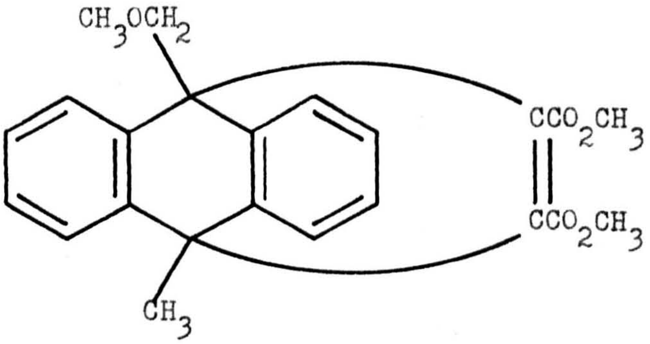
Finally, it should be pointed out that Hankinson[82] treated 10-methoxymethyl-9-methylanthracene (XXVII) with dimethyl acetylenedicarboxylate in boiling acetic anhydride, and in the belief at that time that compound XXVII had the structure 9-methyl-9-methoxy-10-methylene-9,10-dihydroanthracene (X) he postulated a structure (XXVIII) for the product isolated from this reaction.



(X)



(XXVIII)



(XXIX)

The spectral data he records[83] for the product (XXVIII), however, is consistent with a structure XXIX for this compound. The latter compound (XXIX) would be the expected product of this reaction if the original methoxy-compound has a structure XXVII.

EXPERIMENTAL

Preliminary Notes

Melting points were determined on a Kofler block and are uncorrected.

Infrared (i.r.) absorption spectra were measured with Perkin-Elmer Infracord and 257 grating spectrophotometers, and with a Unicam S.P. 200 G spectrophotometer.

Ultraviolet (u.v.) absorption spectra were measured with Unicam S.P. 700 and 800 spectrophotometers.

Proton magnetic resonance (p.m.r.) spectra, unless stated otherwise, were recorded on a Perkin-Elmer R10, 60 Mc/sec instrument, with tetramethylsilane as internal standard ($10.0\,\tau$). Unless indicated otherwise, spectra were recorded at the normal sample operating temperature of 33.4°C.

Microanalyses were carried out by Mr. J. F. Boulton in the Department of Chemistry, University of Keele, and by Drs. G. Weiler and F. B. Strauss of Oxford.

Compounds are colourless unless otherwise described.

Diethyl ether for use in Grignard reactions was first dried over anhydrous calcium chloride, followed by boiling under reflux over sodium and redistillation. Ether dried in this way was stored over sodium, this being replaced periodically until its metallic appearance persisted. Light petroleum, benzene and diethyl ether for use in chromatography were dried over sodium.

The Grignard Reaction of Ethylmagnesium Halide and Anthraquinone

1. Using ethyl iodide

Anthraquinone (25 g., 0.12 mole) in dry benzene (250 ml.) was added in portions to ethylmagnesium iodide (from magnesium (24.5 g., 1.01 mole) and ethyl iodide (81 ml., 1.0 mole; dried over $CaCl_2$ and redistilled)) in dry ether (850 ml.), and the mixture was heated under reflux for four hours. Some of the ether (approximately 400 ml.) was distilled from the reaction product, and crushed ice (500 g.) and ammonium chloride (100 g.) were added to the cooled reaction product. The suspended solid in the reaction product was removed by filtration, and heated with 10% acetic acid. The infrared spectrum of this residual solid showed it to be unchanged anthraquinone. The organic liquors were dried (Na_2SO_4) and on evaporation of the solvents, yielded a red oil. Column chromatography of a sample (2.0 g.) of this oil, using Woelm alumina (activity 1), failed to give any solid material from the oil.

2. Using ethyl bromide

(a) The procedure of Clarke and Carleton[32] was followed, using ethyl bromide dried over Na_2SO_4 and redistilled.

The ether-insoluble solid from the reaction product was heated in 2N hydrochloric acid. The infrared spectrum of this solid showed it to be mainly unchanged anthraquinone.

The ether-soluble fraction of the reaction product gave, on evaporation of the ether, more unchanged anthraquinone, and 15 g. of 9,10-diethyl-9,10-dihydroanthracene-9,10-diol (XIVa, cis (a' a')). Yield, 40%. It formed needles from benzene m.p. 176-7°C (lit.[32,34,44(a),50] m.p. 172°C, 169-171°C, 170°C, 176°C). Small signs of change (dehydration, or partial melting, etc.) were observed at temperatures below 176°C, even after repeated recrystallisation of the diol.

Found: C, 80.7; H, 7.5%

Calc. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5%

ν_{max}(Nujol): 3590, 3470 (O-H stretching; free and H-bonded OH), 1042, 1005, 980, 961, 930, 890, 775, 770 (C-H out-of-plane bending; four adjacent aromatic protons, 745 $cm.^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ ($\log_{10} \varepsilon$): 216 (4.20), 259 (2.71), 268 shoulder (2.56).

P.m.r. in $CDCl_3$ (see Fig. 7, page 32): 9.80 τ tr. (6H; J = 7 c.p.s.), 7.80 τ q. (6H; J = 7 c.p.s.: integration shows 4H on adding a drop of D_2O), 2.10-2.75 τ symmetrical, complex multiplet (8H).

On adding a drop of tetranitromethane to the p.m.r. sample, a deep-red complex is formed (in solution) and new peaks appear at 9.10 τ tr. and 8.15 τ q. whilst the original peaks at 9.80 τ and 7.80 τ gradually disappear (see Fig. 8, page 34).

When all the ether had been evaporated from the ether-soluble fraction of the reaction product, a red, intractable material remained. Column chromatography, using Woelm alumina (activity 1), of a sample (2.0 g.) of this intractable material, failed to give solid material.

The dimethyl ether of the diol was made by adding a drop of methanol, in which a trace of hydrogen chloride had been dissolved, to a warm solution of the diol (0.5 g., 0.002 mole) in a minimum quantity of methanol: 0.43 g. of 9,10-diethyl-9,10-dimethoxy-9,10-dihydroanthracene (XVII) was precipitated (78% yield). Recrystallised from methanol; m.p. 178-180°C (lit.[32,34] m.p; 178°C, 179-180.5°C).

Found: C, 81.2; H, 8.0%

Calc. for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2%

ν_{max}(Nujol): 1310, 1092, 1068, 935, 889, 772, 768 (C-H out-of-plane bending; four adjacent aromatic protons), 738 $cm.^{-1}$

P.m.r. in $CDCl_3$: 9.72τ tr. (6H; J = 7 c.p.s.), 7.85τ q. (4H; J = 7 c.p.s.), 7.10τ s. (6H), 2.45τ complex multiplet (8H). The appearance of peaks of very low intensity in the 9.20τ , 8.15τ , and 7.28τ regions, indicates the presence of a small quantity of other isomer(s).

(b) Stereochemistry of the diethyl diol: A sample of this diol, when applied to a t.l.c. plate prepared using Kieselgel PF_{254}, and developed with a benzene/ether mixture (2:1), showed a single spot on visualisation with u.v. light or iodine.

(1) Addition of small samples of urea and ethylene glycol dimethyl ether, separately, to p.m.r. samples of the diol, produced no observable change in the peaks assigned to the diol in the p.m.r. spectrum. The p.m.r. spectrum of the diol in deuterated methanol[84] (CH_3OD), was identical with the spectrum of the diol in deuterochloroform,

apart from an additional methyl singlet in the former spectrum, ascribed to the solvent. A drop of trifluoroacetic acid, added to a p.m.r. sample of the diol, produced a red colour and gave a very complex spectrum, presumably because of dehydration of the diol due to the acid.

(2) The diethyl diol (1.0 g., 0.004 mole) and benzaldehyde (0.4 ml., 0.004 mole) were boiled under reflux until the diol was in solution. A crystal of *p*-toluenesulphonic acid was added, and the whole boiled under reflux for $\frac{1}{2}$ hr. (see ref. 85 for method). The organic solvents were evaporated, leaving a yellow intractable material. Column chromatography of a sample (0.6 g.) of this reaction product, using Woelm alumina (activity 1), failed to separate any crystalline or identifiable material.

(3) Measurements of the molar extinction coefficients for the diethyl diol infrared hydroxyl peaks at 3585 cm.$^{-1}$ and 3440 cm.$^{-1}$, in ethanol-free chloroform,[86] were made in the concentration range of 0.03-0.11 M/l (see Fig. 10, page 38).

(4) Proton magnetic resonance spectra of the diethyl diol in deuterochloroform were recorded in the temperature range 33-137°C[†] (see Fig. 11, page 39).

(5) Proton magnetic resonance spectra of the diethyl diol in deuterochloroform (containing a drop of 0.1% acetic acid) were recorded at intervals after the addition of the acetic acid (see Fig. 12, page 42).

[†] I am grateful to Perkin-Elmer, Beaconsfield, for the initial recording of these spectra.

(c) (1). The Grignard reaction of ethylmagnesium bromide and anthraquinone was repeated, using the same procedure as before,[32] except that in this reaction, 60 mls. of dry benzene was added to the reaction mixture. Unchanged anthraquinone (9 g., 30%) was recovered from the reaction product, and 9,10-diethyl-9,10-dihydroanthracene-9,10-diol (7.5 g., 20%) was isolated. A small quantity (0.2 g., 0.5% yield) of a 'mixed isomers' sample of the diethyl diol was also isolated from the reaction product. Recrystallised from benzene; m.p. 155-7°C.

Found: C, 80.15; H, 7.6% (Calc. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5%) P.m.r. in $CDCl_3$: 9.80τ tr., 9.15τ tr., 8.20τ q., 7.80τ q. (total integration of all these corresponding to 12H), 2.1-2.75τ symmetrical complex multiplet (8H). The relative integrated intensities of the two ethyl group resonances changed on repeated recrystallisation.

An intractable residue (10 g.) remained after evaporation of all the solvent from the organic layer of the reaction product. Column chromatography of a 5.0 g. sample of this residue, using silicic acid impregnated with silver nitrate[87] as column packing, separated a small amount (0.1 g.) of solid material from the intractable residue. Unsuccessful attempts were made to purify this by vacuum sublimation, but the substance was not identified.

(2) The Grignard reaction, repeated using the same procedure[32] (without the benzene), yielded unchanged anthraquinone (9.0 g., 30%), the diethyl diol (9.4 g., 24% yield) (single isomer), and the diethyl diol (2.3 g., 6% yield) (mixed isomers).

(3) The reaction, repeated as before[32] (without the benzene), except that hydrolysis of the Grignard complex was effected by the slow addition of the reaction product to iced ammonium chloride solution, rather than by the slow addition of iced, aqueous hydrochloric acid to the reaction product, yielded unchanged anthraquinone (4.0 g., 13%), the diethyl diol (13.1 g., 35%) (single isomer), the diethyl diol (4.7 g., 12% yield) (mixed isomers), and a red, intractable residue (8.4 g.). This residue was chromatographed on an alumina column (Woelm alumina, activity 1; 500 g. alumina in a 50 x 4 cm. column). Light was excluded from the column. Elution with 1:3/light petroleum (60/80°C):benzene, gave 1.1 g. anthraquinone (5.1 g. total from reaction, 17%). Elution with 4:1/benzene:ether, gave 2.6 g. of a mixture of compounds (p.m.r. in $CDCl_3$: 9.80 τ tr., 9.65 τ tr., 8.65 τ tr., 7.90 τ q., 7.18 τ q., 1.50-2.70 τ complex multiplet). Elution with 1:2/benzene:ether, gave 10-ethyl-10-hydroxy-9-anthrone (1.3 g., 4% yield) (XX; R = CH_2CH_3). It formed clusters of needles from light petroleum (60/80°C); m.p. 106-108°C (lit.[88,89,55] m.p. 107°C, 108°C).

Found: C, 80.8; H, 5.8%

Calc. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9%

ν_{max}(Nujol) 3500 (O-H stretching), 1660 (C=O), 1602, 1590, 1355, 1322, 1310, 1013, 935, 760, 685 $cm.^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ ($\log_{10}\varepsilon$): 216 (4.13), 270 (4.20).

P.m.r. ($CDCl_3$): 9.64 τ tr. (3H; J = 7 c.p.s.), 7.94 τ q. (2H; J = 7 c.p.s. 7.18 τ s. (1H; peak disappears on adding drop of D_2O), 1.60-2.60 τ complex multiplet (8H). There was no colour produced on addition of a drop of tetranitromethane, and no noticeable change in resonance positions of peaks in the spectrum.

Column chromatography of the intractable residue from reaction (contd.): elution with 2:1/ether:ethyl acetate, gave a second pure isomer of 9,10-*diethyl*-9,10-*dihydroanthracene*-9,10-*diol* (XIVa, cis (e' e')) (1.9 g., 5% yield). Recrystallised from light petroleum (60/80°C); m.p. 135-144°C (lit.[42,55,50] m.p. 150°C).

Found: C, 80.6; H, 7.3% (Calc. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5%)

ν_{max}(Nujol): 3554, 3508, 3410 (O-H stretching; free and H-bonded OH), 1185, 1142, 1080, 1050, 975, 962, 917, 890, 777, 755 (C-H out-of-plane bending; four adjacent aromatic protons) cm.$^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ($\log_{10}\varepsilon$): 211 (4.31), 259 (3.00), 268 shoulder (2.70).

P.m.r. ($CDCl_3$): 9.15τ tr. (6H; J = 7 c.p.s.), 8.16τ q. (6H, J = 7 c.p.s.: integration shows 4H on adding a drop of D_2O), 2.10-2.80τ symmetrical complex multiplet (8H).

On adding a drop of tetranitromethane to the p.m.r. sample, a deep-red complex was formed (in solution), no new peaks appeared, nor was there any observable change in the resonance positions of the peaks already present.

Measurements of the molar extinction coefficients for the infrared hydroxyl peaks of this isomer of the diethyl diol, at 3596 cm.$^{-1}$, 3551 cm.$^{-1}$, and 3450 cm.$^{-1}$ in carbon tetrachloride, were made in the concentration range of 0.007-0.030 M/l(see Fig. 13, page 45).

This second isomer of the diethyl diol was also isolated by suspending a sample of the first isomer isolated in 0.1% acetic acid for 13 days, or in 2% hydrochloric acid for 4 days. Column chromatography (Woelm alumina, activity 1) of the resulting material gave pure samples of the two isomers of the diethyl diol, already described.

T.l.c. analysis, using Kieselgel PF_{254}, of the mixed isomers sample isolated from the original Grignard reaction product, indicated that it was a mixture of the two isomers already described.

T.l.c. analysis, using Kieselgel PF_{254}, of the fraction isolated from the column by elution with 4:1/benzene:ether, indicated that this sample contained three components; the diethyl diol (first isomer); 10-ethyl-10-hydroxy-9-anthrone; and a third, unidentified component. A good separation of these three components was not obtained with t.l.c. Further column chromatography of this fraction using alumina (Woelm alumina, activity 1), and Florisil (100-200 mesh) column packings, failed to give effective separation of these three components. Isolation of the pure components of this mixture was not obtained using preparative t.l.c. (20 x 20 cm. plates; Kieselgel PF_{254} 1 mm. thick; repeated elution with benzene).

The Grignard Reaction of 1,8-Dibromoöctane, Magnesium and Anthraquinone: Attempted Synthesis of 9,10-Octano-anthracene-9,10-diol (XVI).

The tetrahydrofuran (T.H.F.) used in the reaction was first dried over sodium hydroxide, and 85% of the T.H.F. distilled from the sodium hydroxide under nitrogen. This was then boiled under reflux over sodium for 1 hr. and redistilled under nitrogen, from the sodium. Lithium aluminium hydride (1 g./litre of T.H.F.) was added to the distillate, which was stored, under nitrogen, in the dark. The T.H.F. was distilled from this, under nitrogen, into the reaction vessel as required.

The toluene used in the reaction was boiled under reflux over sodium for 3 hr., redistilled from the sodium, and stored over sodium wire.

The 1,8-dibromoöctane used in the reaction was shaken twice with water, and then dried over anhydrous calcium chloride. It was finally fractionated, using a large fractionation column packed with Fenske helices.

The Grignard reagent (from 5.4 g. magnesium (0.22 mole) and 20 ml. (30 g.) of 1,8-dibromoöctane (0.11 mole) in T.H.F. (150 ml.)) was added in portions, over 6 hr. to anthraquinone (20.5 g., 0.1 mole) in T.H.F. (125 ml.), and toluene (125 ml.). The reaction was carried out under nitrogen. When the addition was complete, the mixture was boiled under reflux for 17 hr. The cooled product was then added, in portions, to ammonium chloride (75 g.) and crushed ice (500 g.). The infrared spectrum of the insoluble solid in the reaction product (4.0 g.) showed it to be unchanged anthraquinone. The organic layer from the reaction product was dried (Na_2SO_4) and on evaporation of the solvents from this layer, more anthraquinone was deposited (1.0 g.; 5.0 g. total anthraquinone recovered, 25%). A wine-coloured intractable residue (20.5 g.) remained when all the solvents had been evaporated. All attempts to isolate any identifiable crystalline solid other than small quantities of anthraquinone, from this residue, proved unsuccessful (trituration with solvents, column chromatography using Woelm alumina, activity 1, and vacuum sublimation were all tried).

The Grignard Reaction of n-Propylmagnesium Bromide and Anthraquinone

1. The n-propyl bromide used in the reaction was first dried (Na_2SO_4) and redistilled.

Anthraquinone (30 g., 0.14 mole) suspended in ether (72 ml.) was added, in portions, to n-propylmagnesium bromide (from magnesium (20.1 g., 0.83 mole) and n-propyl bromide (76 ml., 0.83 mole)) in ether (700 ml.), and the mixture was heated under reflux for 7 hr. Dilute hydrochloric acid (from 154 ml. of concentrated hydrochloric acid (d = 1.18), diluted with water/crushed ice) was then added slowly to the cooled reaction product, in order to hydrolyse the Grignard complex. The ether-insoluble solid from the reaction product was suspended in warm 10% acetic acid (500 ml.) for a few minutes. The infrared spectrum of this solid (4.5 g.) showed it to be mainly unchanged anthraquinone (15% of total used in the reaction). The ether layer from the reaction was dried (Na_2SO_4), and allowed to evaporate slowly at room temperature. More anthraquinone (1.0 g., 3.5%) separated first from the ether layer

(5.5 g. total anthraquinone recovered; 18.5%), and was removed by filtration, and then 9,10-di-n-propyl-9,10-dihydroanthracene-9,10-diol (XIVb, cis (a' a')) was precipitated (8.0 g., 18%).

It formed needles from benzene; m.p. 180°C (lit.[33,42,55,50,49] 171-172°C, 179°C). It showed definite signs of change (dehydration, or partial melting, etc.) from approximately 160°C, even after repeated recrystallisation of the diol.

Found: C, 80.9; H, 7.9%

Calc. for $C_{20}H_{24}O_2$: C, 81.0, H, 8.2%

ν_{max}(Nujol): 3600, 3460 (O-H stretching; free and H-bonded OH), 1045, 1019, 1000, 985, 965, 921, 900, 780, 755 (C-H out-of-plane bending; four adjacent aromatic protons) $cm.^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ ($\log_{10}\varepsilon$): 212.5 (4.28), 262 (2.78), 271 shoulder (2.62).

P.m.r. in $CDCl_3$ (see Fig. 15 , page 52): 9.40 τ singlet superimposed on a multiplet (10H), 7.75 τ tr., subsplit (4H, J = 7 c.p.s.), 7.55 τ s. (2H: peak disappears on addition of drop of D_2O), 2.10-2.65 τ symmetrical complex multiplet (8H).

Proton magnetic resonance spectra of the di-n-propyl diol in deuterochloroform, were recorded on 100 and 220 megacycle instruments at 34°C and 13°C respectively[†] (see Fig. 15 , page 52).

[†] I am grateful to Mr. R. Warren, of the Department of Chemistry, University of Manchester, for recording these spectra, the 220 Mc/sec. spectra being recorded by him at the I.C.I. Petrochemicals and Polymer Laboratories, Runcorn.

On adding a drop of tetranitromethane to the p.m.r. sample, a deep-red complex is formed (in solution), and peaks appear in the 60 Mc/s spectrum at $9.20\,\tau$ tr. and $8.10\text{-}9.00\,\tau$ (complex multiplet), the original peaks at $9.40\,\tau$ and $7.75\,\tau$ gradually disappearing (see Fig. 16 , page 54). A similar result was observed when a small quantity of tetracyanoethylene was added to the p.m.r. sample.

When all the ether had been removed from the organic layer of the Grignard reaction product, a red intractable residue remained.

2(a) Measurements of the molar extinction coefficients for the di-n-propyl diol infrared hydroxyl peaks at 3580 cm.$^{-1}$ and 3440 cm.$^{-1}$ in ethanol-free chloroform,[86] were made over the concentration range 0.034-0.06 M/l (see Fig. 17 , page 55).

(b) Proton magnetic resonance spectra of the di-n-propyl diol in deuterochloroform, containing a drop of 0.1%acetic acid were recorded at intervals after the addition of the acetic acid (see Fig. 18 page 57).

(c) A sample of this diol, on t.l.c. analysis using Kieselgel PF$_{254}$, showed only one spot on iodine visualisation, after elution with 4:1/benzene:ether.

3. The reaction of n-propylmagnesium bromide with anthraquinone was repeated under identical conditions, except that hydrolysis of the Grignard complex was effected by adding the cooled reaction product, in portions, to ammonium chloride (90 g.) in water and crushed ice. Unchanged anthraquinone (3.5 g., 12%) was recovered from the reaction, along with the di-n-propyl diol (12.5 g., 29%) and 21.0 g. of a red

intractable residue. A sample of this residue (10.5 g.) was chromatographed on an alumina column (Woelm alumina, activity 1; 500 g. alumina in 50 x 4 cm. column). Light was excluded from the column. Elution with benzene gave 0.5g anthraquinone (4.5 g., 15% recovered from reaction as a whole, allowance being made for the fact that only half the residue was chromatographed). Elution with 1:1/benzene:ether gave 0.8 g. of the di-*n*-propyl diol already described (14.1 g.; 33% yield for complete reaction). Elution with 1:4/benzene:ether, gave 1.4 g. of a solid, the p.m.r. spectrum of which, in deuterochloroform, shows peaks at 9.40τ (singlet superimposed on a multiplet), 9.00τ (triplet), 7.40 - 8.50τ (complex multiplet), 7.22τ (triplet), and 1.45-2.70τ (complex multiplet). Elution with 3:1/ether:ethyl acetate, gave 3.7 g. of crude 10-*hydroxy*-10-*n*-*propyl*-9-*anthrone* (XX; R = $CH_2CH_2CH_3$) (7.4 g., 20% yield for complete reaction). The p.m.r. spectrum of this fraction shows resonances at 9.38τ (singlet superimposed on a multiplet), 8.01τ (triplet), 7.03τ (singlet), and 1.50-2.60τ (complex multiplet). Elution with 1:2/ether:ethyl acetate, gave 1.8 g. (3.6 g.; 8.4% yield for complete reaction) of crude, second isomer of 9,10-*di*-*n*-*propyl*-9,10-*dihydroanthracene*-9,10-*diol* (XIVb, cis (e' e')).

The p.m.r. spectrum of this isomer shows resonances at 9.24τ (triplet), 8.00-8.80τ (triplet superimposed on a complex multiplet), and 2.00-2.62τ (symmetrical, complex multiplet). The infrared spectrum of this isomer shows O-H stretching peaks at 3555 cm.$^{-1}$, 3505 cm.$^{-1}$, and 3320 cm.$^{-1}$.

The Grignard Reaction of t-Butylmagnesium Bromide and Anthraquinone

1. The procedure adopted was identical with the procedure used in the reaction of n-propylmagnesium bromide and anthraquinone (see page 92) using half the molar quantities of reactants in this case i.e. anthraquinone (15 g., 0.07 mole), magnesium (10 g., 0.42 mole), and t-butyl bromide (47 ml., 0.42 mole), and hydrolysis using ice-cold aqueous hydrochloric acid (from 77 ml. of concentrated acid (d = 1.18)).

Unchanged anthraquinone (8.1 g., 54%) was recovered from the reaction product, and a red intractable residue remained on complete evaporation of solvent from the ether layer of the reaction product. Trituration of this residue with light petroleum (60/80°C) gave a crude sample of 3(or 2),10-di-t-butyl-10-hydroxy-9-anthrone (XXI; R = $C(CH_3)_3$) (1.7 g.).

2. The reaction was repeated using twice the molar quantities of reactants used in (1). The t-butyl bromide was dried (Na_2SO_4) and redistilled. Unchanged anthraquinone (15.5 g., 52%) and a red intractable residue (21.5 g.) were recovered from the reaction product. Trituration of the residue with light petroleum (60/80°C) gave crude 3(or 2),10-di-t-butyl-10-hydroxy-9-anthrone (7.8 g.) as before. Recrystallisation of this solid (from benzene) failed to remove the impurities. A sample of this solid (1.5 g.) was chromatographed on an alumina column (Woelm alumina, activity 1; 110 g. alumina in 30 x 2½ cm. column). Elution with light petroleum (60/80°C):benzene (1:2) gave pure 3(or 2),10-di-t-butyl-10-hydroxy-9-anthrone (1.0 g.; total yield 11%).

Recrystallised from light petroluem (60/80°C); m.p. 172-173°C.

Found: C, 81.6; H, 8.1%

$C_{22}H_{26}O_2$ requires : C, 81.95; H, 8.1%

ν_{max}(Nujol): 3455 (O-H stretching), 1652 (C=O), 1601, 1317, 1258, 1196, 1114, 1095, 1055, 1013, 940, 909, 881, 852, 756, 744, 705, 699 $cm.^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ ($\log_{10}\varepsilon$): 213.5 (4.27), 239 shoulder (3.91), 286.5 (4.18).

P.m.r. ($CDCl_3$): 9.22τ s. (9H), 8.62τ s. (9H), 7.60τ s. (1H: peak disappears on addition of a drop of D_2O), 1.75-2.70τ complex multiplet (7H). There was no colour produced or any noticeable change in the p.m.r. spectrum on addition of a drop of tetranitromethane to the sample. The p.m.r. spectrum was unaltered when recorded at a sample temperature of 200°C.[†]

Calculated M.W. (cryoscopically determined in CH_2Cl_2) 317;[‡] theoretical value 322.

This compound did not form a hydrazone derivative with Brady's reagent. An attempt to form the methyl ether of this compound was unsuccessful.

[†] I am grateful to Perkin-Elmer Ltd., Beaconsfield, for recording this spectrum.

[‡] This molecular weight was determined in the University Chemical Laboratory, Cambridge.

The above compound was the only isolable and identifiable product from the chromatographic column. A larger sample (6.5 g.) of the crude material, chromatographed on a larger column (32 x 4 cm. column, packed with 350 g. activity 1 Woelm alumina) gave 4.5 g. of the pure compound on elution with light petroleum (60/80°C):benzene (1:1).

3. The Grignard reaction was repeated as in (2) except that the hydrolysis stage of the reaction was carried out by adding the cooled reaction product, in portions, to ice-cold ammonium chloride solution. Unchanged anthraquinone (9.6 g., 32%), crude 3(or 2),10-di-t-butyl-10-hydroxy-9-anthrone (4.2 g.) (XXI; R = $C(CH_3)_3$), and a red intractable residue (26.3 g.) were recovered from the reaction product. A sample (7.9 g.) of the intractable residue was chromatograhed on an alumina column (Woelm alumina, activity 1; 515 g. alumina in 50 x 4 cm. column). Light was excluded from the column. Elution with benzene gave a highly coloured, intractable and unidentifiable fraction (1.0 g.; 3.3 g. total weight). Elution with benzene:ether (1:1) gave XXI (R = $C(CH_3)_3$), already described (2.9 g.; approximately 27% total yield). No other product was isolated from the column.

<u>Lithium Aluminium Hydride Reduction of</u> 3(or 2), 10-<u>Di</u>-<u>t</u>-<u>butyl</u>-10-<u>hydroxy</u>-9-<u>anthrone</u> (XXI; R = $C(CH_3)_3$).

The ether used in the reaction was dried ($CaCl_2$), boiled over sodium and redistilled.

3(or 2),10-Di-t-butyl-10-hydroxy-9-anthrone (0.9 g., 0.003 mole) in ether (60 ml.) was added in portions to $LiAlH_4$ (0.5 g., 0.013 mole) in ether (150 ml.). When addition was complete, the reaction mixture was boiled under reflux for 3 days. Hydrolysis of the reaction product and decomposition of excess $LiAlH_4$ was effected by adding 'wet' ether in portions, to the cooled reaction product. The ether layer was dried (Na_2SO_4) and all the ether evaporated, leaving a solid residue (0.8 g.). The i.r. spectrum (Nujol) of this residue showed two hydroxyl peaks (3550 cm.$^{-1}$, and 3330 cm.$^{-1}$), and a very small carbonyl peak (1670 cm.$^{-1}$). The p.m.r. spectrum contained singlets at 9.18τ (low intensity), 9.07τ and 8.62τ and two broad, low intensity peaks at 4.30τ and 4.48τ. Column chromatography (activity 1 Woelm alumina; 21 g. alumina in 18 x 1½ cm. column; light excluded from the column) of this residue, gave only intractable fractions, which were not identified.

The Grignard Reaction of Isopropylmagnesium Halide and Anthraquinone

1. Using isopropyl bromide

The isopropyl bromide used in the reaction was dried (Na_2SO_4) and redistilled.

Anthraquinone (30 g., 0.14 mole) suspended in ether (72 ml.) was added to isopropylmagnesium bromide (from magnesium (20.1 g., 0.83 mole) and isopropyl bromide (77.5 ml., 0.83 mole)) in ether (700 ml.). The procedure for the reaction was as in the previous Grignard reactions;

the hydrolysis was effected using ice-cold dilute hydrochloric acid (from 154 ml. of concentrated hydrochloric acid (d = 1.18)). Unchanged anthraquinone (13.5 g., 45%) was recovered from the reaction product, and on evaporation of all the solvent from the organic layer an intractable residue (22.5 g.) remained. This residue in benzene (500 ml.) was shaken with sodium bisulphite solution[90] (2 x 500 ml.), water (2 x 500 ml.), and dried (Na_2SO_4). Evaporation of the benzene yielded an intractable residue. No solid material was isolated from this residue on trituration with solvents (light petroleum (60/80°C), benzene, carbon tetrachloride, and acetone). The i.r. spectrum of this residue (CCl_4 solution) showed no hydroxyl absorption.

2. <u>Using isopropyl chloride</u>

The isopropyl chloride used in the reaction was dried (Na_2SO_4) and redistilled.

Anthraquinone (52 g., 0.25 mole) in ether (150 ml.) was added to isopropylmagnesium chloride (from magnesium (24 g., 1.0 mole) and isopropyl chloride (91.3 ml., 1.0 mole)) in ether (450 ml.). The procedure adopted in the reaction was due to Clark[37] (aqueous ammonium chloride hydrolysis). Unchanged anthraquinone (25.4 g., 49%) was recovered from the reaction product and a red intractable residue (40 g.) remained when all the solvent had been removed from the organic layer of the reaction product. The i.r. spectrum (CCl_4 solution) of this residue showed strong hydroxyl absorption. This residue in hot benzene (600 ml.) was shaken with sodium dithionite solution (5 x 250 ml.), with water (2 x 500 ml.), and then dried (Na_2SO_4). Evaporation of the benzene, yielded a dark-red intractable residue (35 g.). Trituration of this residue with light petroleum (40/60°C) gave 3(or 2),10-di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$) (16.5 g., 22.5% yield). It formed clusters of needles from light petroleum (60/80°C); m.p. 109-111°C.

Found: C, 81.5; H, 7.5%

$C_{20}H_{22}O_2$ requires: C, 81.6; H, 7.5%

ν_{max}(Nujol): 3410 (O-H stretching), 1652 (C=O), 1609, 1587, 1325, 1292, 1270, 1179, 1061, 1040, 963, 937, 912, 868, 851, 762, 751, 700 $cm.^{-1}$.

$\lambda_{max}^{95\%\ EtOH}$ $m\mu$ ($\log_{10} \epsilon$): 210.5 (4.37), 237.5 shoulder (3.89), 283 (4.23).

P.m.r. ($CDCl_3$): 9.35τ d. (two doublets superimposed with 1.5 c.p.s. separation at 60 Mc/sec; 6H, J = 7 c.p.s.), 8.66τ d. (6H, J = 7 c.p.s.), 7.87τ sept. (1H, J = 7 c.p.s.), 6.94τ sept. (J = 7 c.p.s.) and s. superimposed (2H; singlet disappears on addition of a drop of D_2O and integration then 1H), 1.68-2.70τ complex multiplet (7H). No colour or noticeable change in the p.m.r. spectrum was produced by the addition of a drop of tetranitromethane to the p.m.r. sample.

T.l.c. analysis of this compound using Kieselgel PF_{254} and elution with benzene:ether (4:1), showed one spot on iodine visualisation.

Unsuccessful attempts were made to make hydrazone, semicarbazone, and oxime derivatives of this compound (XXI; R = $CH(CH_3)_2$). It did not condense with Girard 'T' reagent.

The solvent from the mother liquors of the trituration was removed, leaving an intractable residue (15.5 g.). A sample (7.8 g.)

of this residue was chromatographed on an alumina column (Woelm alumina, activity 1; 510 g. of alumina in 48 x 4 cm. column). Light was excluded from the column. Elution with light petroleum (60/80°C):benzene (1:2), gave a cream-coloured solid (0.9 g.; 1.8 g. for whole reaction). T.l.c. analysis of this solid using Kieselgel PF_{254}, indicated that it contained two components. Recrystallisation (from ether) or further column chromatography (24 g. activity 1 Woelm alumina in 18.5 x 1.5 cm. column; light was excluded from the column) failed to separate the two components. One of the components of this mixture was isolated using preparative t.l.c. (20 x 20 cm. plates, Kieselgel PF_{254} 1 mm. thick, elution with benzene).

The i.r. (Nujol) spectrum of the original mixture showed no hydroxyl or carbonyl peaks. The p.m.r. spectrum (in $CDCl_3$) of this mixture showed peaks at 8.42 τ (doublet), 8.20 τ (doublet), 7.80 τ (singlet with fine splitting), 7.70 τ (singlet with fine splitting), 6.78 τ (septuplet), 5.30 τ (septuplet), 4.70 τ (broad, low intensity doublet with fine splitting), 4.10 τ (broad, low intensity singlet with fine splitting), 2.19-2.70 τ (complex multiplet), 1.20-1.80 τ (low intensity complex multiplet). The mixture showed fluorescence in solution, which seemed to disappear gradually on standing. The pure component isolated from this mixture (approximately 50% of the mixture) using preparative t.l.c., did not show fluorescence in solution. It decolourised a solution of bromine in carbon tetrachloride. It did not appear to liberate iodine from acidified potassium iodide solution. It formed needles from ether or chloroform/light petroleum (60/80°C);

m.p. 180-181°C.

Found: (1) C, 81.3; H, 6.8% (2) C, 81.0; H, 6.6%

(3) C, 80.2; H, 7.0%

($C_{20}H_{20}O_2$ requires: C, 82.15; H, 6.9%)

ν_{max}(Nujol): 1215, 1165, 1109, 1030, 1010, 910, 890, 770 $cm.^{-1}$

Approximate M.W. (determined using vapour pressure osmometry[†]): 300. $\lambda_{max}^{cyclohexane}$ mμ ($\log_{10} \varepsilon$), using M.W. 300: 219.5 (4.35).

P.m.r. ($CDCl_3$): 8.40 τ d. (6H, J = 7 c.p.s.), 7.80 τ s. (3H; fine splitting, J ≈ 0.5 c.p.s.), 6.77 τ sept. (1H, J = 7 c.p.s.), 4.67 τ s. (1H; fine splitting, J < 0.5 c.p.s.), 4.10 τ s. (1H; fine splitting, J ≈ 0.5 c.p.s.), 2.19-2.70 τ symmetrical complex multiplet (8H).

Initial chromatographic column (contd.): elution with benzene:ether (4:1) gave another sample (0.6 g.) of the single compound described above (approximately 2.1 g. total yield). Elution with benzene:ether (1:1) gave unchanged anthraquinone (3.0 g.; 31.4 g., 60% total yield). Elution with benzene:ether (1:4) gave 3(or 2),10-di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$) (1.8 g.; 20.1 g., 27% total yield).

3(or 2),10-Di-isopropyl-10-hydroxy-9-anthrone (1.0 g., 0.003 mole) in acetic acid (6 ml.) was treated with phenylhydrazine (2.5 ml.) and heated rapidly; then boiled under reflux for $\frac{1}{4}$ hr.[37] The only solid isolated from the reaction was 1-acetyl-2-phenylhydrazine (it formed needles from benzene, m.p. 129-230°C (lit.[91] 128.5°C)). The identity of this compound was established by m.p., analysis, and spectral data.

[†] Determination by R. Pattison in the Department of Chemistry, University of Keele.

Lithium Aluminium Hydride Reduction of 3(or 2),10-Di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$).

The ether used in the reaction was dried ($CaCl_2$), boiled over sodium and redistilled.

3(or 2),10-Di-isopropyl-10-hydroxy-9-anthrone (2.0 g., 0.007 mole) in ether (100 ml.) was added in portions to $LiAlH_4$ (0.560 g., 0.014 mole) in ether (300 ml.). The reaction was carried out under nitrogen. When the addition was complete, the reaction mixture was boiled under reflux for 3 days. Hydrolysis of the reaction product and decomposition of excess $LiAlH_4$ was effected by the slow addition of 'wet' ether to the cooled reaction product. The ether layer was dried (Na_2SO_4) and all the ether evaporated, leaving a colourless intractable residue. This residue was dissolved in a minimum quantity of ether, and on addition of light petroleum to this solution, 3(or 2),10-di-isopropyl-9,10-dihydroanthracene-9,10-diol (XXII; R = $CH(CH_3)_2$) was precipitated (0.7 g., 35%). Recrystallised from benzene; m.p. 107-111°C (decomp.).

Found: C, 81.6; H, 8.1%

$C_{20}H_{24}O_2$ requires: C, 81.0; H, 8.2%

ν_{max}(Nujol): 3360 (O-H stretching), 1190, 1178, 1145, 1035, 1010, 810, 752 (C-H out-of-plane bending; four adjacent aromatic protons) $cm.^{-1}$.

$\lambda_{max}^{95\%\ EtOH}$ $m\mu$ ($\log_{10}\epsilon$): 216.5 (4.18), 264.5 (2.77), 273 (2.63).

P.m.r. ($CDCl_3$): 9.26 τ d. (6H, J = 7 c.p.s.), 8.67 τ d. (6H, J = 7 c.p.s.), 8.00 τ sept. superimposed on broad OH peak (latter disappears on addition of drop of D_2O, and integration goes from 3H to 1H. Septuplet then remains, J = 7 c.p.s.), 6.95 τ sept. (1H, J = 7 c.p.s.), 4.37 τ and 4.53 τ, low intensity peaks (1H), 2.00-2.68 τ complex multiplet (7H). T.l.c. analysis of this compound using Kieselgel PF_{254} and elution with benzene:ether (2:1) showed one spot on iodine visualisation.

The Grignard Reaction of Neopentylmagnesium Chloride and Anthraquinone

The neopentyl chloride (purchased from K and K Laboratories, Plainview, N.Y.) used in the reaction was dried (Na_2SO_4) and redistilled using a large fractionation column, packed with Fenske helices. It was 'v.p.c. pure' after distillation. The ethylene dibromide used in the reaction was dried (Na_2SO_4) and redistilled. The neopentylmagnesium chloride was prepared by the method of Rossi and co-workers.[92]

A mixture of magnesium (21.6 g., 0.9 mole), neopentyl chloride (51 ml., 0.42 mole), and ether (150 ml.) was stirred under dry nitrogen and a solution of ethylene dibromide (36 ml., 0.42 mole) in ether (250 ml.) was added over a period of 6½ hr. No heat was required to maintain a steady reaction. On completion of the addition, the entire mixture was boiled with stirring for an additional 1¾ hr. Anthraquinone (15 g., 0.07 mole) in ether (75 ml.) was then added over a period of ½ hr. to the reaction mixture at room temperature, and when the addition was completed, the entire mixture was boiled under reflux for 12½ hr., under dry nitrogen. After this time, the reaction product was cooled (ice), and hydrolysed by gradual addition of it to iced, aqueous ammonium chloride (50 g.). The procedure for the work-up of the hydrolysed reaction product was identical to the procedure adopted in the Grignard reactions described previously. Unchanged anthraquinone (1.0 g., 6.7%) was recovered from the reaction product, and a red intractable residue (19.0 g.) remained on removal of all the solvents from the ether layer of the reaction product. The i.r. spectrum (CCl_4 solution) of this residue showed hydroxyl absorption. On trituration of this residue with methanol, more unchanged anthraquinone (0.9 g.; 1.9 g., 13% total recovered) was recovered. The mother liquors from this trituration were evaporated to dryness and an intractable residue remained. Trituration of this with light petroleum (40/60°C gave 3(or 2), 10-di-neopentyl-10-hydroxy-9-anthrone (XXI; R = $CH_2C(CH_3)_3$), (2.2 g., 8.7% yield).

It formed needles from benzene/light petroleum (60/80°C); m.p. 172-173°C.

Found: C, 82.6; H, 8.7%

$C_{24}H_{30}O_2$ requires: C, 82.2; H, 8.6%

ν_{max}(Nujol): 3412 (O-H stretching), 1645 (C=O), 1605, 1580, 1325, 1280, 1268, 1235, 1200, 1178, 1155, 1020, 1000, 935, 913, 908, 847, 804, 770, 700 $cm.^{-1}$

$\lambda_{max}^{95\%\ EtOH}$ mμ ($\log_{10} \varepsilon$): 213 (4.35), 240 shoulder (3.91), 286.5 (4.26).

P.m.r. ($CDCl_3$): 9.70 τ s. (9H), 9.02 τ s. (9H), 7.76 τ s. (2H), 7.35 τ s. (2H) 7.23 τ s. (IH: peak disappears on addition of a drop of D_2O), 1.61-2.77 τ complex multiplet (7H).

No colour or observable change in the p.m.r. spectrum was produced on addition of a drop of tetranitromethane to the p.m.r. sample.

A sample of the compound (XXI; R = $CH_2C(CH_3)_3$), on t.l.c. analysis using Kieselgel PF_{254}, showed only one spot on u.v. visualisation, after elution with benzene:ether (4:1).

This compound did not form a hydrazone derivative with Brady's reagent.

The mother liquors from the above trituration were evaporated to dryness, and an intractable residue remained (16.0 g.). A sample (6.0 g.) of this residue was chromatographed on an alumina column (Woelm alumina, activity 1; 535 g. alumina in 50 x 4 cm. column). Light was excluded from the column. Elution with light petroleum (60/80°C):benzene (1:3) gave a coloured, intractable and unidentifiable fraction (0.5 g.; 1.3 g. for whole of the residue). Elution with benzene:ether (4:1) gave unchanged anthraquinone (0.6 g.; 1.6 g. for whole of the residue; 3.5 g., 23% total yield). Elution with benzene:ether (1:2) gave XXI (R = $CH_2C(CH_3)_3$), already described (1.3 g.; 3.5 g. for whole of the residue; 5.7 g., 22.5% total yield). Elution with ether:ethyl acetate (4:1) gave 10-*hydroxy*-10-*neopentyl*-9-*anthrone* (XX; R = $CH_2C(CH_3)_3$) (1.4 g.; 3.7 g., 18.3% total yield).

Recrystallised from benzene/light petroleum (60/80°C); m.p. 157-159°C.

Found: C, 81.5; H, 7.0%

$C_{19}H_{20}O_2$ requires: C, 81.4; H, 7.2%

ν_{max}(Nujol): 3450 (O-H stretching), 1652 (C=O), 1602, 1584, 1327, 1269, 1177, 1150, 1019, 996, 938, 887, 775, 698, 658 $cm.^{-1}$.

$\lambda_{max}^{95\% \ EtOH}$ mμ ($\log_{10} \varepsilon$): 216.5 (4.21), 237 shoulder (3.81), 275.5 (4.17).

P.m.r. ($CDCl_3$): 9.74 τ s. (9H), 7.72 τ s. (2H), 6.85 τ s. (1H; peak disappears on addition of drop of D_2O), 1.64-2.60 τ complex multiplet (8H).

No colour or observable change in the p.m.r. spectrum was produced on addition of a drop of tetranitromethane to the p.m.r. sample.

A sample of this compound (XX; R = $CH_2C(CH_3)_3$), on t.l.c. analysis using Kieselgel PF_{254}, showed only one spot on u.v. or iodine visualisation, after elution with benzene:ether (4:1).

Attempted Elucidation of the Complete Structure of the Products (XXI) Formed by Conjugate (1,6) Addition of Alkylmagnesium Halides to Anthraquinone (see Scheme XIII, page 67)

Stage 1.

The procedure used by Doering and Speers[93] for the oxidation of benzophenone using peracetic acid, was adopted in this reaction.

A mixture of 3(or 2),10-di-isopropyl-10-hydroxy-9-anthrone (XXI; R = $CH(CH_3)_2$) (1.0 g., 0.003 mole), glacial acetic acid (20 ml.), and concentrated sulphuric acid (3.5 ml.), was added in portions to ice-cold 36/40% peracetic acid[⁄] (4 ml.), over a period of $\frac{3}{4}$ Hr. The dark-coloured solution produced, which was fluorescent, gradually became a lighter colour and the fluorescence disappeared slowly after the addition to the peracetic acid and stirring the reaction mixture at room temperature. The reaction mixture was stirred at room temperature for

---

[⁄] I am grateful to Laporte Industries, Ltd., General Chemicals Division, Luton, for providing the 36/40% peracetic acid, free of charge.

3 days, after which time the reaction mixture was yellow coloured and showed no fluorescence. Any excess peracetic acid was then decomposed with freshly prepared ferrous sulphate solution, and the reaction product was neutralised (aqueous NaOH) and extracted with ether (3 x 100 ml.). The ether solution was dried (Na_2SO_4) and evaporated to dryness, leaving a yellow intractable residue (0.8 g.).

Stage 2

The intractable residue (0.8 g.) from stage 1 was hydrolysed by boiling under reflux for 3½ hr. with an approximately N solution of potassium hydroxide in methanol (50 ml.). The hydrolysis was carried out under nitrogen. The red solution produced was cooled and acidified (2N aqu. HCl). On acidification, the solution went yellow. It was then extracted with chloroform (3 x 150 ml.) and the chloroform solution from the extraction was dried (Na_2SO_4) and evaporated to dryness, leaving a dark-yellow, intractable residue (0.7 g.).

Stage 3

The residue (0.7 g.) from stage 2, redistilled quinoline (30 ml.), and copper bronze (1.0 g.) were refluxed together under nitrogen, for 3¾ Hr. After this time, the reaction product was cooled and the copper powder removed by filtration. Extraction of the resulting filtrate with 5% aqueous sodium hydroxide, proved unsuccessful. The quinoline solution, with added ether (100 ml.) was therefore extracted with 2N hydrochloric acid (3 x 100 ml.) to remove quinoline. The resulting ether solution was dried (Na_2SO_4) and evaporated to dryness, leaving an intractable residue (0.8 g.).

Stage 4

Chromium trioxide (3 g.), dissolved in a minimum quantity of water and then glacial acetic acid (15 ml.) added, was mixed with the residue (0.8 g.) from stage 3 in glacial acetic acid (10 ml.). The mixture was boiled under reflux for 2 hr. and cooled. The resulting solution was dark-green. A green solid was precipitated on dilution of this solution with a large volume of water. A sample (0.13 g.) of this precipitate was collected by filtration and prolonged drying on a water pump. This was warmed with aqueous ammonium hydroxide (15 ml.) and the insoluble portion of the solid removed by filtration. A pink solid was precipitated from the filtrate on acidification (2NHCl), and was collected by filtration: m.p. 285-295°C. The i.r. spectrum (Nujol) of this solid showed an acid hydroxyl peak, and carbonyl peaks at 1695 $cm.^{-1}$ and 1678 $cm.^{-1}$.

Esterification of this solid was carried out using diazomethane.

A sample of isophthalic acid was prepared by oxidation of m-xylene using potassium permanganate.

Dimethyl isophthalate and dimethyl terephthalate were prepared by the esterification with diazomethane of isophthalic and terephthalic acids respectively.

V.p.c. analysis

This was done using a Pye Model 64 gas chromatograph, fitted with a 9 ft. column, packed with 5% diethylene glycol succinate polymer. This stationary phase resolved a mixture of the dimethyl esters of the three phthalic acids, whereas a 4 ft. column packed with 10% silicone SE-30 did not. A flame ionisation detector was used.

V.p.c. analysis of the reaction product from stage 4, after esterification, did not indicate the presence of any of the dimethyl esters of the three phthalic acids in the sample.

The Reaction of 9,10-Dialkyl-9,10-dihydroanthracene-9,10-diols with Acetyl Chloride

1. 9,10-Diethyl-9,10-dihydroanthracene-9,10-diol (cis a' a') (0.5 g., 0.002 mole) was allowed to stand in redistilled acetyl chloride (8 ml., 0.11 mole) for 10 min. at room temperature. The diol dissolved in the acetyl chloride, giving a red coloured solution. Heat was produced during the reaction. The acetyl chloride was evaporated at room temperature, and a dark-yellow, crystalline solid (0.5 g.) remained, which was 10-(1'-chloroethyl)-9-ethylanthracene (XXIV) (99% yield). Recrystallised from light petroleum; m.p. (after four recrystallisations) 112-114°C.

Found: C, 80.7; H, 6.4; Cl, 12.5%

$C_{18}H_{17}Cl$ requires: C, 80.5; H, 6.3; Cl, 13.2%

ν_{max}(Nujol): 1620, 1266, 1245, 1220, 1185, 1105, 1064, 1027, 1006, 953, 929, 766 (C-H out-of-plane bending; four adjacent aromatic protons), 745, 669, 649 cm.$^{-1}$.

λ_{max}^{Hexane} mμ ($\log_{10} \varepsilon$): 253 shoulder (4.81), 260.5 (5.03), 340.5 (3.39), 358 (3.73), 373 (3.91), 397 (3.89).

P.m.r. (CCl_4): 8.57τ tr. (3H; J = 7 c.p.s.), 7.80τ d (3H; J = 7 c.p.s.), 6.42τ q. (2H; J = 7 c.p.s.), 3.40τ q. (1H; J = 7 c.p.s.), 2.47-2.80τ complex multiplet (4H), 1.35-1.95τ complex multiplet (4H).

Found: M.W. = 250[†] (vapour pressure osmometry), 281[††] (cryoscopic)
Calc. for $C_{18}H_{17}Cl$: M.W. = 268.5.

This compound (XXIV) gave positive results in Lassaigne and Beilstein tests for the presence of chlorine.

When 10-(1'-chloroethyl)-9-ethylanthracene (XXIV) (0.5 g., 0.002 mole) was boiled in methanol (55 ml.) for 15 min. (the solution was fluorescent) and the volume of methanol reduced to about half, 9-*ethyl-10-(1'-methoxyethyl)anthracene (XXV)* (0.4 g., 81%) was deposited. Recrystallisation from methanol gave pale-yellow plates, m.p. 136-138°C.

Found: C, 86.3; H, 7.8%
$C_{19}H_{20}O$ requires: C, 86.3; H, 7.6%

ν_{max}(Nujol): 1619, 1229, 1203, 1185, 1109 (C-O stretching in non-cyclic ether), 1065, 1040, 960, 929, 845, 764 (C-H out-of-plane bending; four adjacent aromatic protons), 657 cm.$^{-1}$.

λ_{max}^{Hexane} mμ ($\log_{10}\varepsilon$): 253 shoulder (4.94), 259.5 (5.19), 323 shoulder (3.04), 338 (3.49), 354 (3.84), 373 (4.06), 394 (4.06).

P.m.r. (CCl_4): 8.52τ tr. (3H; J = 7 c.p.s.), 8.16τ d. (3H; J = 7 c.p.s.), 6.86τ s. (3H), 6.34τ q. (2H; J = 7 c.p.s.), 4.07τ q. (1H; J = 7 c.p.s.), 2.48-2.65τ complex multiplet (4H), 1.55-1.80τ complex multiplet (2H), 1.12-1.35τ complex multiplet (2H).

[†] Determined by Miss V. Roe, Chemistry Department, University of Keele.
[††] Determined in the University Chemical Laboratory, Cambridge.

The same compound (XXV) was also isolated (74% yield) by the addition of a few drops of methanol, saturated with hydrogen chloride, to a hot concentrated solution of the diethyl diol (cis a' a') in methanol.

When 10-(1'-chloroethyl)-9-ethylanthracene (XXIV) was boiled in ethanol, no isolable product was obtained. An intractable residue remained on complete evaporation of the ethanol.

2. 9,10-Di-n-propyl-9,10-dihydroanthracene-9,10-diol (cis a' a') (0.5 g., 0.002 mole) was allowed to stand in redistilled acetyl chloride (8 ml., 0.11 mole) for 10 min. at room temperature. A yellow solution was obtained which yielded an intractable residue on evaporation of the acetyl chloride. No solid was isolated from this residue.

3. Cis-9,10-dimethyl-9,10-dihydroanthracene-9,10-diol was isolated by the method of Beckett and Lingard.[38] When this diol (0.5 g., 0.002 mole) was treated with acetyl chloride (8 ml., 0.11 mole) as in the previous reactions (1. and 2.), 10-chloromethyl-9-methylanthracene (XXVI) (0.5 g., 100%) was isolated. It formed yellow needles from benzene m.p. 190°C (decomp.) (lit.[35,94] m.p. 192°C (decomp.), 180-90°C (decomp.)). ν_{max}(Nujol): 1621, 1275, 1249, 1185, 1065, 957, 846, 809, 790, 769, 759 (C-H out-of-plane bending; four adjacent aromatic protons), 685, 671 cm.$^{-1}$ P.m.r. ($CDCl_3$): 6.88τ s (3H), 4.35τ s (2H), 2.20-2.50τ complex multiplet (4H), 1.40-1.70τ complex multiplet (4H).

Recrystallisation of this compound (XXVI) in methanol, gave 10-methoxymethyl-9-methylanthracene (XXVII) (40% yield). It formed needles from methanol m.p. 108.5°C (lit.[35] m.p. 108-109°C).

Found: C, 86.5; H, 6.8%

Calc. for $C_{17}H_{16}O$: C, 86.4; H, 6.8%

ν_{max}(Nujol): 1622, 1194, 1185, 1095 (C-O stretching in non-cyclic ethers), 948, 935, 790, 772, 747, 740 (C-H out-of-plane bending; four adjacent aromatic protons), 682, 650 $cm.^{-1}$.

P.m.r. ($CDCl_3$): 6.89 τ s. (3H), 6.44 τ s. (3H), 4.51 τ s. (2H), 2.15-2.50 τ complex multiplet (4H), 1.30-1.65 τ complex multiplet (4H).

This compound (XXVII) was also isolated from the ether-insoluble fraction from the Grignard reaction of methylmagnesium iodide and anthraquine,[38] by standing this fraction in 10% aqueous acetic acid for several hours and recrystallisation of the resultant solid in methanol.

The Reaction of the Diethyl and Di-n-propyl Diols with Picric Acid in Alcoholic Solvent

The procedure adopted was identical to that used by Badger and Pearce[35] for the dimethyl diol. A solution of the diethyl diol (cis a' a') (1.12 g., 0.004 mole) and picric acid (2.0 g., 0.009 mole) in alcohol (methanol, ethanol or n-propanol; 100 ml.) was boiled under reflux for 2 hr. A similar reaction was carried out with the di-n-propyl diol (cis a' a') (0.62 g., 0.002 mole) and picric acid (1.0 g., 0.005 mole) in methanol (50 ml.). The mixture in each case was concentrated and cooled. No picrates were isolated from the reaction products. A mixture (1.9 g.) of 9-ethyl-10-(1'-methoxyethyl)anthracene (XXV) (main component), picric acid, and the dimethyl ether(s) of the diethyl diol were isolated from the reaction of the diethyl diol in methanol. The components of this mixture were identified from its i.r. and p.m.r. spectra. Analysis of this mixture showed that the picrate of XXV had not been formed in the reaction. Picric acid was the only product recovered from the reactions of the diethyl diol in ethanol and n-propanol (0.4 g., and 1.2 g. respectively). The dimethyl ether(s) (0.3 g.) of the di-n-propyl diol was the only product isolated from the reaction of this diol in methanol. The identity of this product was established from its i.r. and p.m.r. spectra.

REFERENCES

1. J. M. Robertson, Proc.Roy.Soc., 1933(A) 140, 79; A. McL. Mathieson, J. M. Robertson, and V. C. Sinclair, Acta Cryst., 1950, 3, 245; F. R. Ahmed and D.W.J. Cruikshank, Ibid., 1952, 5, 852.

2. W. G. Ferrier and J. Iball, Chem. and Ind., 1954, 1296.

3. I.G.M. Campbell, C. G. Le Fèvre, R.J.W. Le Fèvre, and E. E. Turner, J.Chem.Soc., 1938, 404.

4. F. H. Herbstein, J.Chem.Soc., 1959, 2292.

5. P. Courtot, P. Derible, and Le Hung Danh, Bull.Soc.chim.France, 1964, 10, 2602.

6. R. P. Ferrier, J. Iball, and K.J.H. Mackay, Acta Cryst., 1960, 13, 277.

7. N. F. Yannoni, A. P. Krukonis, and J. Silverman, Science, 1965, 148, 231; N. F. Yannoni and J. Silverman, Acta Cryst., 1966, 21, 390.

8. A. H. Beckett and B. A. Mulley, Chem. and Ind., 1955, 146; J.Chem.Soc., 1955, 4159.

9. D.H.R. Barton, O. Hassel, K. S. Pitzer, and V. Prelog, Nature, 1953, 172, 1096; Science, 1954, 119, 49.

10. D.H.R. Barton, R. C. Cookson, W. Klyne, and C. W. Shoppee, Chem. and Ind., 1954, 21.

11. W. Schlenk and E. Bergmann, *Annalen*, 1928, *463*, 98.

12. H. Meerwein and A. Migge, *Ber*., 1929, *62B*, 1046.

13. A. H. Beckett and J. Walker, *Tetrahedron*, 1963, *19*, 545.

14. J. Mathieu, *Ann.Chim.(France)*, 1945, *20*, 215.

15. G. M. Badger, M. L. Jones, and R. S. Pearce, *J.Chem.Soc*., 1950, 1700.

16. A. H. Beckett and R. G. Lingard, *J.Chem.Soc*., 1959, 2409.

17. L. M. Jackman and J. W. Lown, *J.Chem.Soc*., 1962, 3776.

18. W. Carruthers and G. E. Hall, *J.Chem.Soc*., 1966(B), 861.

19. H. Gilman and O. L. Marrs, *J.Org.Chem*., 1962, *27*, 1879.

20. H.J.S. Winkler, R. Bollinger, and H. Winkler, *J.Org.Chem*., 1967, *32*, 1700.

21. D. Nicholls and M. Szwarc, *Proc.Roy.Soc*., 1967(A), *301*, 231.

22. D. Nicholls and M. Szwarc, *J.Amer.Chem.Soc*., 1966, *88*, 5757.

23. I. T. Millar and K. V. Wilson, *Proc.Chem.Soc*., 1963, 217.

24. I. T. Millar and K. E. Richards, *J.Chem.Soc*., 1967(C), 855.

25. D. Cohen, L. Hewitt, and I. T. Millar, *Chem. and Ind*., 1966, 1532.

26. C.R.M. Butt, D. Cohen, L. Hewitt, and I.T. Millar, *Chem.Comm*., 1967, 309.

27. M. C. Prévost, *Compt.rend*., 1935, *200*, 408.

28. C. Dufraisse and J. Houpillart, Compt.rend., 1937, 205, 740.

29. E. Boyland and D. Manson, J.Chem.Soc., 1951, 1837.

30. S. Coffey and V. Boyd, J.Chem.Soc., 1954, 2468.

31. A. Guyot and Ch. Staehling, Bull.Soc.chim.France, 1905, (3)33, 1144.

32. L. Clarke and P. W. Carleton, J.Amer.Chem.Soc., 1911, 33, 1966.

33. J. W. Cook, E. C. Dodds, and W. Lawson, Proc.Roy.Soc., 1936(B), 121, 133.

34. W. E. Bachmann and J. M. Chemerda, J.Org.Chem., 1939, 4, 583.

35. G. M. Badger and R. S. Pearce, J.Chem.Soc., 1950, 2314.

36. A.L.J. Beckwith and W. A. Waters, J.Chem.Soc., 1956, 1108.

37. K. J. Clark, J.Chem.Soc., 1956, 1511.

38. A. H. Beckett and R. G. Lingard, J.Chem.Soc., 1961, 588.

39. J. W. Cook, E. C. Dodds, C. L. Hewett, and W. Lawson, Proc.Roy.Soc., 1934(B), 114, 272 (see also ref. 33).

40. H. M. Crawford, J.Amer.Chem.Soc., 1941, 63, 1070.

41. D. W. Cameron and W. Meckel, Chem.Comm., 1967, 623.

42. W. Chodkiewicz, P. Cadiot, and A. Willemart, Compt.rend., 1961, 253, 954.

43. G. Rio, Ann.Chim.(France), 1954, 9, 182.

44. (a) W. Ried and H-J. Schmidt, Chem.Ber., 1957, 90, 2553.
    (b) W. Ried and A. Urschel, Chem.Ber., 1958, 91, 2459.
    (c) W. Ried and G. Dankert, Chem.Ber., 1959, 92, 1223.

45. W. Chodkiewicz and Paul Cadiot, Compt. rend., 1958, 247, 2383.

46. R. Skowronski and W. Chodkiewicz, Compt.rend., 1960, 251, 547.

47. M. Gaudemar, Bull.Soc.chim.France, 1962, 974.

48. L. Miginiac-Groizeleau, Ann.Chim.(France), 1961, 6, 1071.

49. J-C. Cognacq, R. Skowronski, W. Chodkiewicz, and P. Cadiot, Bull.Soc.chim.France, 1967, 880.

50. J-C. Cognacq, G. Guillerm, W. Chodkiewicz, and P. Cadiot, Bull.Soc.chim.France, 1967, 1190.

51. P. F. Southern, and W. A. Waters, J.Chem.Soc., 1960, 4340.

52. Y. Lepage, Compt.rend., 1959, 248, 1193.

53. Y. Lepage, Ann.Chim.(France), 1959, (13)4, 1137.

54. C. Dufraisse, G. Rio, and Y. Lepage, Compt.rend., 1958, 247, 1928.

55. J-C. Cognacq, M-P. Simonnin, W. Chodkiewicz, and P. Cadiot, Compt.rend., 1967(C) 264, 915.

56. (a) E. De B. Barnett and M. A. Matthews, Ber., 1926, 59B, 1429.
    (b) P. L. Julian and W. Cole, J.Amer.Chem.Soc., 1935, 57, 1607.
    (c) R. B. Sandin, R. Kitchen, and L. F. Fieser, J.Amer.Chem.Soc., 1943, 65, 2018.

56. (d) P. L. Julian, W. Cole, G. Diemer, and J. G. Schafer, *J.Amer.Chem.Soc.*, 1949, *71*, 2058.

(e) J. Jadot and J. Roussel, *Bull.Soc.roy.Sci.Liège*, 1954, *23* 363.

(f) P. Tardieu, *Compt.rend.*, 1959, *248*, 2885.

(g) P. Tardieu, *Ann.Chim.(France)*, 1961, *6*, 1445.

(h) A.L.J. Beckwith, W. B. Renfrow, A. Renfrow, and J. K. Teubner, *Tetrahedron Letters*, 1968, 3463.

57. (a) R. B. Sandin and L. F. Fieser, *J.Amer.Chem.Soc.*, 1940, *62*, 3098.

(b) G. M. Badger, F. Goulden, and F. Ll. Warren, *J.Chem.Soc.*, 1941, 18.

(c) G. M. Badger and R. S. Pearce, *J.Chem.Soc.*, 1950, 2311.

58. E. D. Bergmann, M. Rabinovitz, and S. Glily, *Tetrahedron, Suppl. 8, Part 1*, 1966, 141.

59. K. G. Flynn and G. Bergson, *Arkiv Kemi*, 1967, *27*, 393.

60. "N.m.r. Spectra Catalog," Varian Associates, 1962 and 1963, combined Vols. 1 and 2, spectrum 14 (ethanol) and spectrum 43 (*n*-propanol).

61. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, London, 1959, p. 180-183.

62. D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Canad.J.Chem.*, 1964, *42*, 565.

63. W. B. Smith and B. A. Shoulders, J.Phys.Chem., 1965, 69, 2022.

64. V. A. Koptyug, V. A. Bushmelev, and T. N. Gerasimova, Zhur. obshchei Khim., 1967, 37, 140 (see J.Gen.Chem.(U.S.S.R.), 1967, 37, 127).

65. (a) R. A. Raphael, E. C. Taylor, and H. Wynberg (Editors), "Advances in Organic Chemistry. Methods and Results", Interscience Publishers, a division of John Wiley and Sons, London, 1965, Vol. 5, Chp. 5; M. Tichý, "The Determination of Intramolecular Hydrogen Bonding by Infrared Spectroscopy and its Applications in Stereochemistry", p. 116.

(b) See ref. 65(a), p. 121.

66. L. Pauling, J.Chem.Phys., 1936, 4, 673.

67. J. A. Pople, J.Chem.Phys., 1956, 24, 1111.

68. J. S. Waugh and R. W. Fessenden, J.Amer.Chem.Soc., 1957, 79, 846.

69. C. E. Johnson, Jr., and F. A. Bovey, J.Chem.Phys., 1958, 29, 1012.

70. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press Ltd., London, First Edition, 1965, Vol. 1, Appendix B, p. 595, "Table of Predicted Values of Shielding Contributions from Ring Currents in Aromatic Hydrocarbons".

71. C. Pinazzi, Compt.rend., 1946, 223, 1150.

72. A. I. Nogaideli, N. N. Skhirtladze, and N. I. Tabashidze, Soobshch.Akad.Nauk Gruz.SSR, 1966, 42, 595. (see Chem.Abs., 1966, 65, 16918 e).

73. A. Petrov, E. Sokolowa, and Gao-Chin-Lan, Bull.Soc.chim.France, 1958, 178.

74. N. S. Bowman, D. E. Rice, and B. R. Switzer, J.Amer.Chem.Soc., 1965, 87, 4477.

75. (a) B. Halpern, J. W. Westley, and B. Weinstein, Chem.Comm., 1967, 160.

(b) J. W. Westley and B. Weinstein, Chem.Comm., 1967, 1232.

76. M. L. Martin and G. J. Martin, Bull.Soc.chim.France, 1966, 2117.

77. M. Kajtár and L. Radics, Chem.Comm., 1967, 784.

78. T. S. Sorensen, Canad.J.Chem., 1967, 45, 1585.

79. W. McFarlane, Chem.Comm., 1968, 229.

80. S. Hauptmann, L. Franke, K. Dietrich, G. Wild, and M. Schnitzker, Z.Chem., 1963, 3, 147.

81. "U.V. Atlas of Organic Compounds", Butterworths, London, 1966, Vol. II, spectrum E2/T2 (9,10-dimethylanthracene).

82. B. Hankinson, M.Sc. Thesis, University of Keele, 1967, p. 71-72.

83. See ref. 82, p. 74.

84. "Organic Syntheses", John Wiley and Sons, London, 1963, Collective Vol. IV, p. 651, D. M. Burness (synthesis of sodium methoxide; hydrolysis of this using D_2O, gives deuterated-methanol (CH_3OD)).

85. R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", Chapman and Hall, Ltd., London, 1953, p. 262.

86. A. I. Vogel, "A Text-book of Practical Organic Chemistry, Including Qualitative Organic Analysis", Longmans, Green and Co., London, Third Edition, 1956, p. 176.

87. G. Hugel, L. Lods, J. M. Mellor, D. W. Theobald, and G. Ourisson, Bull.Soc.chim.France, 1965, 2884.

88. C. Lieberman, Annalen, 1882, 212, 71; K. H. Meyer, Annalen, 1911, 379, 73.

89. R. Skowronski, W. Chodkiewicz, and P. Cadiot, Compt.rend., 1959, 249, 552.

90. See ref. 86, p. 332.

91. "The Merck Index of Chemicals and Drugs", Merck and Co. Inc., Rahway, N.J., U.S.A., Seventh Edition, 1960, p. 12.

92. F. M. Rossi, P. A. McCusker, and G. F. Hennion, J.Org.Chem., 1967, 32, 1233.

93. W. von E. Doering and L. Speers, J.Amer.Chem.Soc., 1950, 72, 5515.

94. J. L. Adelfang and G. H. Daub, J.Amer.Chem.Soc., 1958, 80, 1405.

INDEX OF COMPOUNDS DESCRIBED IN THE EXPERIMENTAL SECTION

---

† - tentative structure