The Nuclear Magnetic Resonance and Stereochemistry of 9,10-Derivatives of 9,10-Dihydroanthracene

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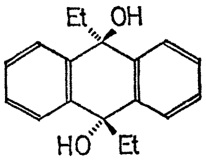
Summary The stereochemistries of the *cis*- and *trans*-9,10-diethyl-9,10-dihydro-9,10-dihydroxyanthracenes have been established by their method of preparation and their conformations deduced from their n.m.r. spectra.

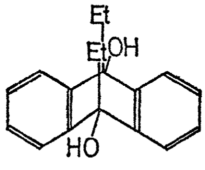
IN connection with the dimerisation of isoelemicin[1] we have prepared the *cis*- and *trans*-isomers of 9,10-diethyl-9,10-dihydro-9,10-dihydroxyanthracene and examined their n.m.r. spectra at 100 MHz. Contrary to the views of Cohen *et al.*,[2] we find that the major product[3] from the reaction of anthraquinone and ethylmagnesium bromide is the *trans*-isomer (I), m.p. 177—177·5°. The *trans*-stereochemistry follows from the preparation of the *cis*-isomer (II) in the following rational manner. Phenylhydrazine reduction[4] of the *trans*-isomer (I) gave 9,10-diethylanthracene which, on irradiation in methanol in a stream of oxygen, gave the epidioxide (III). Mild hydrogenolysis of the latter, under conditions which did not affect the *trans*-isomer (I), gave the *cis*-isomer (II) m.p. 146—148°.

Of especial interest in the n.m.r. spectra of these *cis*- and *trans*-isomers are the chemical shifts of the methyl triplet and methylene quartet signals. These shifts are shown in the Table together with similar data for three model compounds. In the absence of acid, the n.m.r. spectra of the *trans*-(I)- and *cis*-(II)-isomers were temperature independent and neither isomer showed intramolecular hydrogen-bonding in its i.r. spectrum (*cf.* ref. 2). The strikingly high-field methyl triplet shown by the *trans*-isomer (I) is not connected with the hydroxy functions since the cation (IV)[5] and di-isoelemicin[1] also show a high-field methyl triplet. We interpret these chemical shifts for the isomers (I) and (II) in the following way.

The *cis*-isomer must exist in the boat conformation (II) with the two ethyl groups in ψ-axial positions; in this conformation the methylene protons are slightly shielded by the magnetic anisotropy of the benzene rings but the methyl protons are not. This reasoning is supported by the data in the Table for the 9,10-ethanoanthracene (V);[6] in the fixed conformation (V), the methyl protons experience little shielding while the adjacent methine protons do. The conformation (II) for the *cis*-isomer is also in accord with the conclusion[7] that the ψ-axial methyl protons are shielded relative to the ψ-equatorial methyl protons in derivatives of 9,9-dimethyl-9,10-dihydro-10-methyleneanthracene (VI). In the *trans*-isomer (I), however, it is suggested that the central ring is flat at least on an n.m.r. time-scale. This planar conformation is indicated both by the equivalence of the methyl protons and by their high-field chemical shift. Dreiding models show that in flipping from a ψ-axial to a ψ-equatorial position, the methyl protons pass through a zone of maximum shielding when the tricyclic ring system is planar. Support for these arguments is provided by the n.m.r. spectrum of the cation (IV) in which the methyl groups are equivalent and resonate at high field (see Table). At the two extremes the methyl protons appear to be either deshielded in ψ-equatorial ethyl groups (see III) or unaffected in ψ-axial ethyl groups; the ψ-axial and ψ-equatorial methylene protons are respectively shielded and deshielded to a small extent.



(I)



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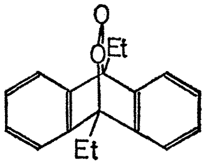

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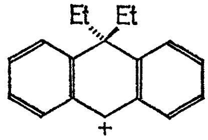

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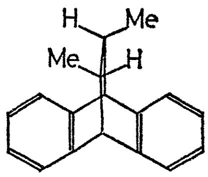
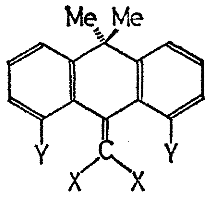


(V)



(VI)

TABLE

Chemical shift (τ) *for chloroform solutions with* Me_4Si *as internal standard*

Protons	*trans*-Isomer (I)	*cis*-Isomer (II)	Epidioxide (III)	Cation (IV)[5]	(V)
CH_3	9·78	9·18	8·69	9·8	9·25
CH_2	7·85	8·28	7·35	7·2	8·5—9·0

The *cis*- and *trans*-isomers (II) and (I) are readily equilibrated by acetic acid to a mixture containing *ca.* 90% of the *cis*-isomer (II). Careful control of pH is therefore necessary in the work-up of the Grignard complex in the preparation of the *trans*-isomer. For the same reason, it was not possible to reduce the epidioxide (III) cleanly to the *cis*-isomer (II) with lithium aluminium hydride. It is suggested that the lower stability of the *trans*-isomer is connected with torsional strain and the inability to minimise the interaction of the peri-hydrogens with the 9,10-substituents, simultaneously at both the 9- and 10-centres.

The relevance of these results to the work of Cohen *et al.*,[1,8] Nicholls and Schwarc,[9] and Carruthers and Hall[10] will be discussed in the full paper.

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