482. *The Configurations of Certain Isomeric 9,10-Substituted 9,10-Dihydroanthracenes.*

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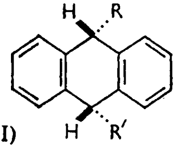
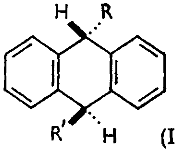
The configurations of the stereoisomeric 9,10-dihydro-9,10-dimethylanthracenes are established. The *cis*-isomer is prepared by a stereospecific reaction sequence from dimethyl *cis*-9,10-dihydroanthracene-9,10-dicarboxylate. A monoacid obtained by carboxylation of sodio-9-methylanthracene is shown to be *cis*-9,10-dihydro-9-methylanthracene-10-carboxylic acid.

Badger, Goulden, and Warren [1] appear to have been the first to isolate an authentic 9,10-dihydro-9,10-dimethylanthracene (I or II; R = R′ = Me); the compound melted at 101—102°. Mikhailov [2] later claimed to have prepared two other 9,10-dihydro-9,10-dimethylanthracenes, melting at 130° and 54—60° respectively, but while the former isomer was also reported by Sisido and Isida [3] and by Badger, Jones, and Pearce,[4] the latter compound has not been described elsewhere. Badger and his colleagues suggested,[4] and later assumed,[5] that the isomers melting at 101° and 130° were *cis*- and *trans*-respectively, but satisfactory evidence was lacking.



(I)



(II)

Since the configurations of dimethyl *cis*- and *trans*-9,10-dihydroanthracene-9,10-dicarboxylates (I and II; R = R′ = CO_2Me) had already been determined by Mathieu,[6] these esters were selected for conversion into methyl derivatives by the well-known stereospecific route: [7]

$$-CO_2Me \xrightarrow[LiAlH_4]{} -CH_2{\cdot}OH \xrightarrow[TsCl]{} -CH_2{\cdot}OTs \xrightarrow[LiAlH_4]{} -Me \quad (Ts = p\text{-}C_6H_4Me{\cdot}SO_2)$$

Because both carboxylate groups in the *cis*-diester (I; R = R′ = CO_2Me) were in the quasiaxial conformations [8,9] and therefore not seriously hindered sterically, ready conversion into *cis*-9,10-dihydro-9,10-dimethylanthracene was expected and confirmed, the final product melting at 130°.

Greater difficulty was expected in the reduction of the *trans*-isomer because one group is in the hindered quasiequatorial conformation. Reduction of one group and conversion into a methyl group as above seemed possible. However, the *trans*-dimethyl ester (II; R = R′ = CO_2Me) was not reduced by lithium aluminium hydride in ether, and a yellow polymeric product resulted when tetrahydrofuran was the solvent.

The 9,10-dihydroanthracene-*trans*-9,10-dicarboxylic acid for preparation of the *trans*-dimethyl ester used in the latter reduction was prepared by two methods. One route [8] involved addition of sodioanthracene in ether to a slurry of solid carbon dioxide in ether, conversion of the dicarboxylic acid in the mixed acids into the *cis*-anhydride and hydrolysis

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[1] Badger, Goulden, and Warren, *J.*, 1941, 18.

[2] Mikhailov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1946, 619.

[3] Sisido and Isida, *J. Amer. Chem. Soc.*, 1948, **70**, 1289.

[4] Badger, Jones, and Pearce, *J.*, 1950, 1700.

[5] Badger, "The Structures and Reactions of the Aromatic Compounds," Cambridge Univ. Press, 1954, p. 109.

[6] Mathieu, *Ann. Chim. (France)*, 1945, **20**, 215.

[7] Karrer, Portmann, and Suter, *Helv. Chim. Acta*, 1948, **31**, 1617; Karrer and Erhardt, *ibid.*, 1951, **34**, 2202; Karrer and Dinkel, *ibid.*, 1953, **36**, 122; Hussey, Liao, and Baker, *J. Amer. Chem. Soc.*, 1953, **75**, 4727; Dauben, Tweit, and MacLean, *ibid.*, 1955, **77**, 48.

[8] Beckett and Mulley, *J.*, 1955, 4159.

of the anhydride to the *trans*-dicarboxylic acid (II; $R = R' = CO_2H$) with aqueous alkali. An improved overall yield of the *trans*-dicarboxylic acid was achieved by treating the crude mixed acids with aqueous alkali to produce a mixture of *trans*-dicarboxylic and monocarboxylic acid, which were separated by making use of the poor solubility of the *trans*-acid in methanol or ether.

Because of the failure to prepare the *trans*-isomer (II; $R = R' = Me$) by an unequivocal route, 9,10-dihydro-9,10-dimethylanthracene melting at 101° was prepared by a modification of the method of Badger *et al.*;[4] its infrared spectrum (chloroform solution) differed from that of the isomer melting at 130°, indicating that the two compounds were geometrical isomers and not merely polymorphic forms. The configurations allocated by Badger to these isomers should therefore be reversed. If the compound of m. p. 54—56° isolated by Mikhailov[2] is a pure 9,10-dihydro-9,10-dimethylanthracene, it must be a polymorph.

Our configurational assignments facilitated the determination of the configuration of a monocarboxylic acid isolated in substantial yield from the product of addition of 9-methylsodioanthracene in ether to solid carbon dioxide. The melting point of this acid did not correspond with that of either of the dihydro-9-methylanthracenecarboxylic acids reported by Burtner and Cusic.[10]

The 9-methylanthracenemonocarboxylic acid was isolated from the crude mixture of carboxylic acids after treatment with acetic anhydride and removal of the *cis*-anhydride which crystallised. Treatment with diazomethane, followed by the stereospecific reactions outlined above, gave *cis*-9,10-dihydro-9,10-dimethylanthracene, m. p. 128—130°. The acid was therefore *cis*-9,10-dihydro-9-methylanthracene-10-carboxylic acid. This will be the thermodynamically most stable of the *meso*-monocarboxylic acids, since the *meso*-substituents are here subjected to the least non-bonded interactions. Whether it is formed as a primary product of carboxylation or as a result of inversion of the less stable *trans*-isomer has not yet been established.

EXPERIMENTAL

Methyl Hydrogen cis-9,10-*Dihydroanthracene*-9,10-*dicarboxylate*.—Finely powdered *cis*-9,10-dihydroanthracene-9,10-dicarboxylic anhydride[11] (5 g.) was heated in dry methanol (20 ml.) containing pyridine (10 drops) under reflux for ½ hr. The solution was poured into 10% hydrochloric acid (50 ml.) and extracted with ethyl acetate. Evaporation of the solvent gave white crystals (5·6 g.), m. p. 172—173°, which were ground and shaken with 5% aqueous sodium hydrogen carbonate (100 ml.) for 10 min. The solution was filtered and slowly acidified (stirring) with 10% sulphuric acid. The white solid which separated was filtered off, washed with water, and dried to give a white powder (4·7 g.), m. p. 179—181·5°. Crystallisation from di-n-butyl ether (55 ml.) gave the methyl hydrogen ester (4·4 g., 78%) as prisms, m. p. 183—184° (lit.,[12] m. p. 184—185°). With diazomethane in ether this gave dimethyl *cis*-9,10-dihydroanthracene-9,10-dicarboxylate (3·1 g., 70%), m. p. 166—166·5° (lit.,[6] m. p. 166—167°).

cis-9,10-*Dihydro*-9,10-*bishydroxymethylanthracene*.—Finely powdered dimethyl *cis*-9,10-dihydroanthracene-9,10-dicarboxylate (3 g.; m. p. 166—166·5°) in dry ether was stirred for 12 hr. with excess of lithium aluminium hydride. The product was decomposed with water and excess of 10% hydrochloric acid, and the aqueous layer extracted with ether. The combined ether solutions were dried ($MgSO_4$) and evaporated to give cis-9,10-*dihydro*-9,10-*bishydroxymethylanthracene* (2·4 g., 99%), prisms, m. p. 166—168° (from methanol) (Found: C, 80·1; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

This diol (2·18 g.) and toluene-*p*-sulphonyl chloride (8·7 g.) in ice-cold pyridine (30 ml.) at 0° (1 hr.) and then at room temperature (20 hr.) gave the *ditoluene*-p-*sulphonate* (4·0 g., 80%), needles, m. p. 177—177·5° (from dioxan) (Found: C, 65·7; H, 5·1; S, 11·7. $C_{30}H_{28}O_6S_2$ requires C, 66·3; H, 5·0; S, 11·7%).

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[9] *Idem, Chem. and Ind.*, 1955, 146.
[10] Burtner and Cusic, *J. Amer. Chem. Soc.*, 1943, **65**, 1582.
[11] Beckett, Lingard, and Mulley, *J.*, 1953, 3328.
[12] Rigaudy, *Ann. Chim. (France)*, 1950, **5**, 398.

cis-9,10-*Dihydro*-9,10-*dimethylanthracene*.—The preceding toluene-*p*-sulphonate (3·3 g.) in dry ether, was stirred with excess of lithium aluminium hydride for 3 days, then left with occasional shaking for 4 days. The product was rapidly filtered and the residue in the funnel washed with dry ether. The combined ether solutions were washed with 10% hydrochloric acid, then water, and dried (Na_2SO_4). Evaporation and crystallisation from ether gave *cis*-9,10-dihydro-9,10-dimethylanthracene (0·78 g., 62%) as rhombs, m. p. 130° (lit.,[2] m. p. 130—131°) (Found: C, 92·5; H, 8·0. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%).

trans-9,10-*Dihydroanthracene*-9,10-*dicarboxylic Acid*.—The acid was prepared as described by Beckett and Mulley,[8] and by the following route:

Anthracene (50 g.), powdered sodium (20 g.), and glass chips were shaken in dry ether (450 ml.) in a stoppered separatory funnel. After a few minutes, the mixture became a deep blue-black, and the stopper was rapidly replaced by a reflux condenser fitted with a calcium chloride guard-tube. The ether boiled and, when the reaction had subsided, the funnel was closed and shaken for 3 days. Then the contents were poured on carbon dioxide in dry ether (500 ml.), most of the excess of sodium being retained in the funnel. The flask and contents were allowed to warm overnight to room temperature. Water (100 ml.) was added, the ether layer was extracted with sodium hydroxide solution, and the acids were precipitated from the aqueous extracts by concentrated hydrochloric acid, filtered off, and washed with water and a little ether to give 9,10-dihydroanthracenecarboxylic acids (55 g.) as a white powder.

The mixed crude acids (80 g.) (titration indicated 28 g. of monocarboxylic acid and 52 g. of dicarboxylic acids) were heated in 5% aqueous sodium hydroxide (600 ml.) under reflux for ½ hr., and the solution was cooled, filtered, and acidified (stirring) with concentrated hydrochloric acid. The precipitated acids were filtered off, washed with water, dried, and ground to give a mixture (77·6 g.) of acids. These were shaken with methanol (750 ml.) for ½ hr. and filtered off, to give a white powder (31 g.), m. p. 305—307°. Further shaking of the powder with methanol (300 ml.) for ½ hr. left *trans*-9,10-dihydroanthracene-9,10-dicarboxylic acid (26 g.), m. p. 310—312° (decomp.) (Found: equiv., 133. Calc. for $C_{16}H_{12}O_4$: equiv., 134). Crystallisation from glacial acetic acid did not alter the m. p. Beckett and Mulley [8] reported m. p. 309—310° (decomp.).

The *trans*-dicarboxylic acid with excess of diazomethane in ether gave the dimethyl ester (19·3 g., 83%) as plates, m. p. 165—165·5° (lit.,[6] m. p. 166—167°); admixture with *cis*-9,10-dihydroanthracene-9,10-dicarboxylate, m.p. 165°, depressed the m. p.

trans-9,10-*Dihydro*-9,10-*dimethylanthracene*.—Anthracene (10 g.) in dry ether (450 ml.) was shaken with powdered sodium (10 g.) for 4 days in a flask fitted with a stoppered adaptor to the side arm of which was attached a Bunsen valve. The stopper was then replaced by a rubber cap that was pierced by the tip of a pipette through which methyl iodide was added until the blue colour was discharged and did not return after several minutes' shaking. The mixture was filtered, and the solid rapidly washed with dry ether. Evaporation of the combined ether solutions left a sticky, pale yellow solid (9·25 g.). This (5·0 g.), when cooled in ether (10 ml.) by ether–solid carbon dioxide, gave white crystals (0·7 g.), m. p. 95°. Recrystallisation from ethanol gave *trans*-9,10-dihydro-9,10-dimethylanthracene (0·6 g., 9·5%) as leaflets, m. p. 100—101° (lit.,[1] m. p. 101—102°).

cis-9,10-*Dihydro*-9-*methylanthracene*-10-*carboxylic Acid*.—9-Methylanthracene [13] (20 g.), powdered sodium (10 g.), and glass chips in dry ether (450 ml.) were shaken and added to solid carbon dioxide as described for the preparation of 9,10-dihydroanthracenecarboxylic acids; they gave crude 9,10-dihydro-9-methylanthracenecarboxylic acids (26 g.). The dicarboxylic acids were converted into the *cis*-anhydride.[11] Evaporation of the mother-liquor from the first crop of anhydride, to about half-volume, gave a less pure second crop of the anhydride, and the mother-liquor therefrom was evaporated down to an orange gum that was dissolved in ether and left overnight. A solid was precipitated; it was filtered off, washed with ether, and dried (yield, 1·7 g.; m. p. 153—154°) and crystallised from acetic acid (10 ml.), to give cis-9,10-*dihydro*-9-*methylanthracene*-10-*carboxylic acid* (1·5 g., 16%) as colourless plates, m. p. 225—226° (Found: C 80·6; H, 6·1%; equiv., 237. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%; equiv., 238). The ether filtrate from the crude monocarboxylic acid (m. p. 153—154°) was evaporated to a small volume, heated with dilute sodium hydroxide (40 ml.) under reflux for 10 min., cooled, and filtered. Slow acidification of the filtrate with concentrated hydrochloric acid gave a yellow, sticky solid which, crystallised from acetic acid, gave a further 1·7 g. (18%) of *cis*-9-methyl-10-carboxylic acid, m. p. 223—234° (total yield, 34%).

[13] Sieglitz and Marx, *Ber.*, 1923, **56**, 1619.

The monocarboxylic acid (3·5 g.) with diazomethane in ether gave the *methyl ester* (3·2 g., 86%), rhombs, m. p. 89—90° (Found: C, 80·5; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

cis-9,10-*Dihydro*-10-*hydroxymethyl*-9-*methylanthracene*.—Methyl *cis*-9,10-dihydro-9-methylanthracene-10-carboxylate (3·0 g.) in dry ether was stirred with excess of lithium aluminium hydride for 12 hr., then treated with water and dilute hydrochloric acid, and the aqueous layer was extracted with ether. Evaporation of the ether extracts gave very pale yellow plates (2·7 g., 100%), m. p. 136—137°. Recrystallisation from ether gave cis-9,10-*dihydro*-10-*hydroxymethyl*-9-*methylanthracene* (0·25 g.), plates, m. p. 137—137·5° (Found: C, 85·3; H, 7·2. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

This gave a *toluene*-p-*sulphonate*, prisms (from di-*n*-butyl ether), m. p. 133·5—134·5° (Found: C, 72·3; H, 5·7. $C_{21}H_{22}O_3S$ requires C, 73·0; H, 5·9%).

cis-9,10-*Dihydro*-9,10-*dimethylanthracene*.—The above monotoluene-*p*-sulphonate (3·2 g.) in dry tetrahydrofuran (100 ml.) was stirred with excess of lithium aluminium hydride for 12 hr. The solvent was evaporated until the volume of the solution was *ca.* 20 ml., and the residue treated with water and dilute hydrochloric acid. The aqueous layer was extracted with ether, and the ether evaporated to yield a yellow solid (1·74 g.), m. p. 109—110°. Crystallisation from ether gave *cis*-9,10-dihydro-9,10-dimethylanthracene (1·3 g., 74%) as rhombs, m. p. and mixed m. p. 128—130°.

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