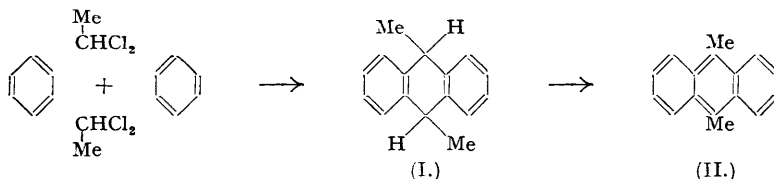


344. Substituted Anthracene Derivatives. Part I. *cis*- and *trans*-9 : 10-Dimethyl-9 : 10-dihydroanthracene.

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9 : 10-Dimethyl-9 : 10-dihydroanthracene (II) has been shown to exist in *cis*- and *trans*-forms.

At least five erroneous descriptions of 9 : 10-dimethyl-9 : 10-dihydroanthracene (I) have appeared in the literature. For example, Angelbis and Anschütz (*Ber.*, 1884, **17**, 165) claimed to have obtained the hydrocarbon by interaction of ethylidene chloride and benzene in the presence of aluminium chloride. Somewhat similar preparations have been described by Anschütz (*Annalen*, 1886, **235**, 299), by Böeseken and Bastet (*Rec. Trav. chim.*, 1913, **32**, 184), by Cook and Chambers (*J. Amer. Chem. Soc.*, 1921, **43**, 334), and by Davidson and Lowy (*J. Amer. Chem. Soc.*, 1929, **51**, 2978). However, in a paper describing the preparation of 9 : 10-dimethylantracene (II), Barnett and Matthews (*Ber.*, 1926, **59**, 1429; cf. Friedel and Crafts, *Bull. Soc. chim.*, 1884, **41**, 322; Anschütz and Romig, *Ber.*, 1885, **18**, 662) pointed out that the compound isolated by Anschütz and others could not be the dihydride as its properties (the relatively high melting point of 181°, the yellow colour, and the formation of a picrate) are those associated with a completely aromatic structure. They described Anschütz's hydrocarbon as 9 : 10-dimethylantracene (II) and attributed its formation to the dehydrogenating action of aluminium chloride on the dihydride (I) initially formed.



Authentic 9 : 10-dimethyl-9 : 10-dihydroanthracene (I) was first prepared by Badger, Goulden, and Warren (*J.*, 1941, **18**) by the action of methyl iodide on the 9 : 10-disodio-addition product with anthracene. This compound, unlike that of Anschütz, had m. p. 101–102° and was readily dehydrogenated with sulphur. In Egloff's compilation ("Physical Constants of Hydrocarbons," Vol. 4, 1947), this work has been overlooked, Anschütz's hydrocarbon still being listed as 9 : 10-dimethyl-9 : 10-dihydroanthracene.

The work of Badger, Goulden, and Warren also appears to have been overlooked by Sisido and Isida (*J. Amer. Chem. Soc.*, 1948, **70**, 1289) who recently prepared a new 9 : 10-dimethyl-9 : 10-dihydroanthracene, m. p. 130°, by reduction of 9 : 10-dimethylantracene with sodium and alcohol. This was very readily dehydrogenated to (II), even by treatment with aluminium chloride at room temperature. It seemed likely that the two dihydrides are *cis-trans*-isomers and, in order to clarify the position, the preparation of 9 : 10-dimethyl-9 : 10-dihydroanthracene has been re-investigated.

First, the preparation of the lower-melting dihydride by the above method was confirmed. This product was colourless, did not fluoresce in ultra-violet light, and did not form a picrate. Its dehydrogenation with sulphur to 9 : 10-dimethylantracene was also confirmed, but it was

not dehydrogenated with aluminium chloride at room temperature. There seems no reason to doubt that this product is 9 : 10-dimethyl-9 : 10-dihydroanthracene, and its ultra-violet absorption spectrum (see Fig. 1) is consistent with this conclusion. Sisido and Isida's preparation of the higher-melting dihydride and the behaviour with aluminium chloride have also been confirmed. In our hands, however, this method gave a mixture from which *both* dihydrides were isolated. The higher-melting dihydride was also colourless, non-fluorescent, and did not form a picrate. The ultra-violet absorption spectrum (Fig. 2) of this dihydride is also consistent with its formulation as 9 : 10-dimethyl-9 : 10-dihydroanthracene.

There can be little doubt that the two dimethyl dihydrides discussed in this paper are *cis-trans*-isomers. The lower-melting form is provisionally regarded as the *cis*-compound. Incidentally, its less ready dehydrogenation indicates that the preparation of 9 : 10-dimethylanthracene by the methods of Anschütz and others proceeds *via* the higher-melting (*trans*)-dihydride.

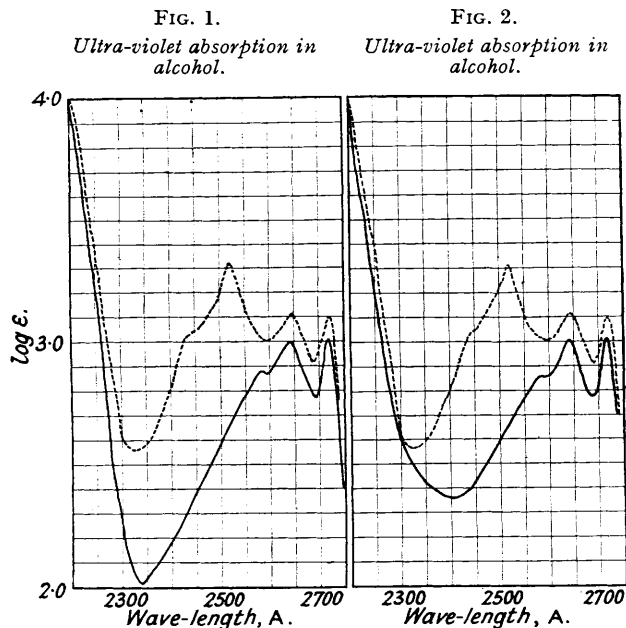


FIG. 1. - - - - - 9 : 10-Dihydroanthracene. Max. at 2520 (3.33), 2640 (3.10), 2710 Å. (3.09).
 ———— *cis*(?)-9 : 10-Dimethyl-9 : 10-dihydroanthracene, *m. p.* 101–102°. Maxima at 2580 (2.85), 2640 (2.99), 2710 Å. (3.01).

FIG. 2. - - - - - 9 : 10-Dihydroanthracene.
 ———— *trans*(?) 9 : 10-Dimethyl-9 : 10-dihydroanthracene, *m. p.* 130°. Maxima at 2580 (2.87), 2640 (3.01), 2710 Å. (3.02).

A few *cis-trans*-isomers of this type have been reported previously. For example, Barnett, Cook, and Matthews (*Rec. Trav. chim.*, 1925, **44**, 728) described the isomeric 1 : 5-dichloro-9 : 10-dihydroxy-9 : 10-dihydroanthracenes, and dipole moment measurements confirmed the configurations assigned to them (Bergmann and Weizmann, *J. Amer. Chem. Soc.*, 1938, **60**, 1801).

If the configurations of the dimethyl dihydrides are correctly assigned, addition of sodium to anthracene is a pure *cis*-reaction, as is the addition of chlorine to 1 : 5-dichloro- and 9 : 10-diphenyl-anthracene. In the case of 1 : 8-dichloroanthracene, however, addition of chlorine is a *trans*-reaction, for the dipole moment of the dichloride is smaller than that of the parent compound (Bergmann and Weizmann, *loc. cit.*).

The disodio- and dilithio-derivatives of anthracene hydrocarbons are usually very different in colour, and Bachmann and Pence (*J. Amer. Chem. Soc.*, 1937, **59**, 2339) made the interesting hypothesis that this might be associated with *cis*-addition in one case, and *trans*- in the other. We therefore investigated the reduction of 9 : 10-dimethylanthracene by first forming the 9 : 10-disodio-(or lithio-)addition product, at room temperature, followed by treatment with methanol (*cf.* Bachmann and Pence, *loc. cit.*). In both cases, however, a mixture of the two dihydrides was formed, and in this instance, therefore, the hypothesis is incorrect. Treatment

with sodium ethoxide sometimes brings about stereochemical inversion (*e.g.*, at centres adjacent to an enolisable group; cf. Linstead and Doering, *J. Amer. Chem. Soc.*, 1942, **64**, 1991), but it does not do so in the present case, for the lower-melting dihydride was recovered unchanged after 2 hours' boiling with a concentrated solution of sodium ethoxide.

The ultra-violet absorption curves of the two dimethyl dihydrides, compared with that of 9 : 10-dihydroanthracene, are given in the accompanying Figures. The absorption curves of the isomers are almost identical, except that the lower-melting isomer has an absorption minimum of $\log \epsilon_m$ 2.02 at 2340 Å., while the corresponding minimum of the higher-melting isomer is 2.35 at 2400 Å. The minimum in the curve for 9 : 10-dihydroanthracene is $\log \epsilon_m$ 2.55 at 2320 Å.

EXPERIMENTAL.

9 : 10-Dimethylantracene.—Several useful methods for the preparation of this compound have already appeared (*e.g.*, Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583; Badger, Goulden, and Warren, *loc. cit.*). The following method has also been found useful.

9 : 10-Bischloromethylantracene (2 g.; Badger and Cook, *J.*, 1939, 802) in dioxan (350 c.c.) was hydrogenated over 30% palladised asbestos (0.25 g.). Removal of solvent and crystallisation from alcohol gave yellow needles of 9 : 10-dimethylantracene, m. p. 180°.

cis(?)-9 : 10-Dimethyl-9 : 10-dihydroanthracene.—Prepared by the method of Badger, Goulden, and Warren (*loc. cit.*), this formed colourless blades, m. p. 101–102° (from alcohol). It was not fluorescent in ultra-violet light, and was recovered unchanged after prolonged irradiation in thin layers.

trans(?) -9 : 10-Dimethyl-9 : 10-dihydroanthracene.—The following procedure was more satisfactory than that recommended by Sisido and Isida (*J. Amer. Chem. Soc.*, 1948, **70**, 1289). To a suspension of 9 : 10-dimethylantracene (0.7 g.) in boiling alcohol (50 c.c.), sodium was added in small portions until the solution became non-fluorescent in ultra-violet light. More alcohol was added, if required, to dissolve the sodium, until the disappearance of the fluorescence indicated the completion of the reaction. The resulting colourless solution was diluted with a large volume of water. After some time, the precipitate was collected and fractionally recrystallised from alcohol. The larger portion (0.4 g.) consisted of *trans*(?) -9 : 10-dimethyl-9 : 10-dihydroanthracene, which formed colourless rectangular plates, m. p. 130–131°. From the liquors of the first recrystallisation a little of the lower-melting dihydride was isolated; after recrystallisation, it formed colourless blades (50 mg.), m. p. and mixed m. p. 101°. The relative proportions of the two isomers varied considerably with the experimental conditions.

Reduction of 9 : 10-Dimethylantracene via Alkali-metal Addition Compounds.—A solution of dimethylantracene (0.5 g.) in dry benzene (50 c.c.) and anhydrous ether (50 c.c.) was shaken with powdered sodium (1 g.) and chips of broken glass for 36 hours. The intense deep-blue colour of the disodio-derivative was discharged by the gradual addition of methanol, the glass and unchanged sodium were filtered off, and the solvent was evaporated. Fractional crystallisation of the product gave small amounts of the *trans*-, m. p. 130°, and the *cis*-dihydride, m. p. 101°. Both compounds were identified by mixed m. p.

Lithium gave a deep-violet addition complex with 9 : 10-dimethylantracene which, after interaction with methanol, yielded a similar mixture of the two dihydrides.

Action of Aluminium Chloride on the Dihydrides.—(a) A solution of the dihydride, m. p. 101° (0.5 g.), in benzene (5 c.c.) was treated with aluminium chloride (2 g.). After 2 hours, the mixture was poured into water, and the organic layer evaporated. The dihydride, m. p. 100°, was recovered almost quantitatively.

(b) A similar experiment with the dihydride, m. p. 130°, yielded 9 : 10-dimethylantracene, m. p. 178°, alone or mixed with an authentic specimen.

Ultra-violet Absorption Spectra.—The curves were determined with a Beckman D U Spectrophotometer, using a constant spectral band width of 10 Å. We are grateful to the Director of Chemistry, South Australian Government Department of Chemistry (S. D. Shield, Esq.), for permission to use the spectrophotometer.

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