

198°. The detailed study of this crystalline substance was abandoned because of the low yield.

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## Two Derivatives of 9,10-Dimethylantracene

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In view of the fact that 9,10-dimethylantracene<sup>1</sup> often cited in the literature erroneously as 9,10-dimethyl-9,10-dihydroanthracene since the discovery of this compound,<sup>2</sup> we have undertaken to obtain the real 9,10-dimethyl-9,10-dihydroanthracene.

9,10-Dimethylantracene was reduced with sodium and the desired new compound was obtained. It was found that 9,10-dimethyl-9,10-dihydroanthracene on treatment with aluminum chloride is converted to 9,10-dimethylantracene.

The acetylation of anthracene<sup>3</sup> gave 9-, 1- and 2-acetylanthracenes, and the treatment of 9-acetylanthracene with aluminum chloride rearranges it into 1- and 2-acetyl compounds. Nenitzescu<sup>4</sup> acetylated 9,10-dihydroanthracene and obtained 9-acetyl-9,10-dihydroanthracene.

Acetylation of 9,10-dimethylantracene in the presence of aluminum chloride gave 2-acetyl-9,10-dimethylantracene. It was shown from this experiment that the acyl group can enter also directly into the 2-position of the anthracene nucleus, and that *meso*-acylanthracene is not always necessary as an intermediate.

In the Friedel-Crafts reaction of 1,2,3,4-tetramethylnaphthalene the substitution takes place only at the  $\beta$ -position of the nucleus.<sup>5</sup> This fact is probably due to the steric hindrance caused by the methyl groups at the 1- and 4-positions. The acetylation which takes place exclusively at the 2-position of 9,10-dimethylantracene may be attributed to the same steric factor, inasmuch as the free benzene ring in 9,10-dimethylantracene as well as in 1,2,3,4-tetramethylnaphthalene is attached to a tetra-substituted nucleus.

During this experiment we have experienced a slight skin-eruption, presumably caused by the acetyl compound. This fact may be of interest as compared with the similar poisoning effect of benzanthrone in view of the chemical constitution.

### Experimental<sup>6</sup>

**9,10-Dimethyl-9,10-dihydroanthracene.**—Into a boiling suspension of 0.62 g. of 9,10-dimethylantracene in 6 g. of ethyl alcohol was added 2.5 g. of metallic sodium in small portions. On addition of sodium the yellow crystals disappeared and a colorless solution resulted, which,

(1) Barnett and Matthews, *Ber.*, **59**, 1429 (1926); Bachmann and Chmerda, *J. Org. Chem.*, **4**, 583 (1939).

(2) Angelbis and Anschütz, *Ber.*, **17**, 165 (1884); Anschütz, *Ann.*, **235**, 305 (1886).

(3) I. G. Farbenindustrie A.-G., German Patent 492,247; *Friedländer*, **16**, 1195.

(4) Nenitzescu, *Ber.*, **72**, 819 (1939).

(5) Hewett, *J. Chem. Soc.*, 293 (1940).

(6) Microanalyses by Miss Meizyô of our Laboratory.

however, turned reddish brown due perhaps to the action of sodium alcoholate. After two and a half hours of boiling, the solution was decolorized with active carbon. On cooling a small quantity of colorless crystals separated out. The solution was added with water in order to precipitate the desired reaction product. On repeated recrystallizations of the material from alcohol and from glacial acetic acid colorless, rectangular or square leaflet crystals of m. p. 130° resulted, yield 0.2 g. The product is very soluble in ether, benzene, carbon disulfide, moderately soluble in alcohol and glacial acetic acid. The product gives no picrate and its solution does not show a fluorescence.

*Anal.* Calcd. for  $C_{16}H_{16}$ : C, 92.26; H, 7.74. Found: C, 92.45; H, 7.92.

When the crystals were mixed with aluminum chloride in the presence or absence of benzene and after thirty minutes of standing poured into water, characteristic yellow crystals separated. A benzene solution of this material exhibits a beautiful violet fluorescence and on addition of picric acid gave dark violet-brown needles, thus proving the formation of 9,10-dimethylantracene.

**2-Acetyl-9,10-dimethylantracene.**—When a mixture of 7.0 g. of 9,10-dimethylantracene, 150 cc. of carbon disulfide, 2.7 g. of acetyl chloride and 4.5 g. of aluminum chloride was stirred for four hours at room temperature, the reaction did not take place to any appreciable extent. But as soon as the temperature was elevated to 45° the reaction ensued. The progress of the reaction was traced by the liberation of hydrogen chloride. After an additional two hours at 45° the reaction product was poured into iced water acidified with hydrochloric acid, and treated in the usual way. There was obtained a brown solid which on repeated recrystallizations from alcohol using active carbon gave fine yellow crystals of m. p. 164.5°. The product developed blue coloration in concentrated sulfuric acid, yield 6.5 g.

*Anal.* Calcd. for  $C_{18}H_{16}O$ : C, 87.28; H, 6.45; mol. wt., 248. Found: C, 87.08; H, 6.45; mol. wt., 243.

A solution of 1.0 g. of the substance in glacial acetic acid was oxidized with 3.0 g. of chromic acid in the usual way and the product was recrystallized from glacial acetic acid. There was obtained an anthraquinonecarboxylic acid of m. p. 277–280°. The mother liquor yielded the same substance. As the isomers of the acid have nearly the same melting points, for the identification we have methylated the material by the E. Fischer method. An ester of m. p. 165–166.5° resulted, which, when admixed with an authentic sample of methyl ester of anthraquinone-2-carboxylic acid, did not depress the melting point.

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## NEW COMPOUNDS

### Di-(*p*-anisyl)-methylcarbinol

Although 1,1-di-(*p*-anisyl)-ethylene has been made from di-*p*-anisyl ketone and methylmagnesium bromide,<sup>1,2</sup> the corresponding tertiary alcohol, di-(*p*-anisyl)-methylcarbinol, was not isolated because the intermediate Grignard addition compound was hydrolyzed in acid solution. The alcohol has now been made by modification of the Grignard reaction.

In a dry 500-ml. 3-necked flask fitted with a stirrer, nitrogen inlet, reflux condenser and dropping funnel was placed 50 ml. of 1.2 *N* (0.058 mole) methylmagnesium bromide. To this solution was added dropwise during

(1) Pfeiffer and Wizinger, *Ann.*, **461**, 144 (1928).

(2) Bergmann and Bondi, *Ber.*, **64B**, 1455 (1931).