The biological potency against *S. aureus* is 983 U./mg. and as determined iodometrically is 986 U./mg. The calculated potency is 955 U./mg. and the optical rotation is $[\alpha]^{25}\text{D}$ +175° (1% in 50% aqueous acetone).

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The Friedel–Crafts Reaction of Benzene and 3,4-Dichlorohexane

BY KEIITI SISIDO AND HITOSI NOZAKI

The condensation of benzene with 3,4-dichlorohexane has been studied. The dichlorohexane was prepared from divinylacetylene by catalytic hydrogenation followed by chlorination.[1] The reaction product obtained by the usual procedure was composed of two fractions.

The analysis and molecular weight determination of the first fraction agreed with the formula $C_{12}H_{16}$, showing that it was a mono-cyclialkylated benzene. The dehydrogenation of this hydrocarbon with sulfur or with selenium under the condition not to be accompanied with anomalies[2] gave an oily product, whose picrate formed orange needles melting at 144–144.5°, alone or admixed with an authentic specimen of 1,4-dimethylnaphthalene picrate. It has often been observed, however, in the case of the picrates of naphthalene derivatives, that a mixture of two different isomers shows no depression of the melting point. But as all of the isomers of dimethylnaphthalene are already known, an examination of the literature about the characteristic data of the hydrocarbons and their picrates made it clear that the dehydrogenation product above mentioned was nothing else but 1,4-dimethylnaphthalene. From these observations, we concluded that the hydrocarbon $C_{12}H_{16}$ was a new compound, 1,4-dimethyltetralin.

In the alkylation of benzene with alkyl halogenides catalyzed by aluminum chloride, the isomerizations of the alkyl radicals are often observed. The mechanism of the present condensation is explained from this view-point that the chlorine atoms of the 3,4-positions migrate to the 2,5-positions and the resulting dichloride cyclialkylates benzene to form a six-membered carbon ring.

The second reaction product formed colorless liquid. Several attempts to crystallize it were unsuccessful. The results of its analysis and molecular weight determination gave a formula $C_{18}H_{26}$, showing that it was not 3,4-diphenylhexane[3] as expected at first, but a di-cyclialkylated benzene, *i. e.*, 1,4,5,8-tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene, -phenanthrene or a mixture of them.

Experimental

The Condensation of 3,4-Dichlorohexane with Benzene.—To a mixture of 105 g. of benzene and 24 g. of aluminum chloride was added 42 g. of 3,4-dichlorohexane in the course of about one hour under stirring, during which time the reaction temperature was maintained at 5–10°. After additional fifteen minutes the mixture was heated slowly so as to insure a uniform evolution of hydrogen chloride gas. Heating was continued for about two hours until the reaction temperature reached 25° and practically no more evolution of gas was observed. The reaction mixture was poured over crushed ice acidified with hydrochloric acid and treated as usual. The solvent was removed and the residue was distilled under reduced pressure. The following fractions were obtained.

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I	107–131	37	11	Colorless liquid
II	79–110	9	5	Colorless liquid
III	112–140	9	1	Colorless liquid
IV	140–170	9	5	Colorless viscous oil
V	170–184	9	3	Viscous sirupy oil
VI	Residue	..	3	Viscous sirupy oil

The Mono-cyclialkylated Product: 1,4-Dimethyltetralin.—Fractions I and II were combined and the mixture was redistilled. The main fraction boiling at 216–227° under atmospheric pressure weighed 14 g. occupying 50% of the total condensate. It formed a colorless liquid with characteristic odor. The boiling point determined by the Emich method was 226°.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06; mol. wt., 160. Found: C, 89.74; H, 10.21; mol. wt. (cryoscopy in benzene), 152.

The Dehydrogenation of 1,4-Dimethyltetralin with Sulfur.—A mixture of 2.4 g. of the hydrocarbon and 1.0 g. of sulfur was heated on a metal-bath at 180–250° for two and a half hours. The reaction product was immediately distilled and yellowish oil, boiling at 260–300° (bath temperature), was obtained. It was dissolved in hot alcohol and added a hot alcoholic solution of picric acid. On cooling, orange needles separated. After one recrystallization from alcohol, the picrate melted at 144–144.5° and repeated crystallizations changed the melting point no more. This fact showed that the material was already quite pure. When admixed with an authentic specimen of 1,4-dimethylnaphthalene picrate (m. p. 143–144°) it melted at 144–144.5°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_7N_3$: C, 56.10; H, 3.92. Found: C, 55.39; H, 4.17.

The Dehydrogenation of the Dimethyltetralin with Selenium.—To 1.58 g. of the substance was added 1.62 g. of selenium and the mixture was heated on a metal-bath at 250–300° for one hour. The reaction product was shaken out and heated for additional six and a half hours at 300–350° (bath temperature). Distillation of the dehydrogenation product gave 0.57 g. of yellowish oil, which yielded the same picrate as described above.

The Di-cyclialkylated Product.—Fraction IV was redistilled under reduced pressure and the main fraction boiling at 145–160° at 9 mm. was subjected to the following experiments.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.19; H, 10.81; mol. wt., 242. Found: C, 89.20; H, 10.81; mol. wt. (cryoscopy in benzene), 220.

A mixture of 4.5 g. of the substance and 2.3 g. of sulfur was heated for about three hours at 180–260°. The resulting black mass was distilled under reduced pressure. The red viscous oil, which distilled at 230–300° (bath temperature) at 5–6 mm., solidified immediately. On recrystallizations from alcohol, colorless prisms melting at 219–220°[4] separated. An analysis was impossible for lack of material.

Higher Boiling Fractions.—Fraction V and the residue separated a small quantity of crystals, melting at 197–

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[1] Spiegler and Tinker, THIS JOURNAL, **61**, 940 (1940).

[2] Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935).

[3] Lepin and Reich, *Chem. Zentr.*, **87**, I, 787 (1916).

[4] *Cf.* Ellison and Hey, *J. Chem. Soc.*, 1849 (1938).

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

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Two Derivatives of 9,10-Dimethylanthracene

BY KEIITI SISIDO AND TYÛZÔ ISIDA

In view of the fact that 9,10-dimethylanthracene[1] often cited in the literature erroneously as 9,10-dimethyl-9,10-dihydroanthracene since the discovery of this compound,[2] we have undertaken to obtain the real 9,10-dimethyl-9,10-dihydroanthracene.

9,10-Dimethylanthracene 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-dimethylanthracene.

The acetylation of anthracene[3] gives 9-, 1- and 2-acetylanthracenes, and the treatment of 9-acetylanthracene with aluminum chloride rearranges it into 1- and 2-acetyl compounds. Nenitzescu[4] acetylated 9,10-dihydroanthracene and obtained 9-acetyl-9,10-dihydroanthracene.

Acetylation of 9,10-dimethylanthracene in the presence of aluminum chloride gave 2-acetyl-9,10-dimethylanthracene. 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 β-position of the nucleus.[5] 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-dimethylanthracene may be attributed to the same steric factor, inasmuch as the free benzene ring in 9,10-dimethylanthracene 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[6]

9,10-Dimethyl-9,10-dihydroanthracene.—Into a boiling suspension of 0.62 g. of 9,10-dimethylanthracene 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, 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-dimethylanthracene.

2-Acetyl-9,10-dimethylanthracene.—When a mixture of 7.0 g. of 9,10-dimethylanthracene, 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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(1) Barnett and Matthews, *Ber.*, **59**, 1429 (1926); Bachmann and Chemerda, *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; *Friedlaender*, **16**, 1195.

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

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

(6) Microanalyses by Miss Meizyô of our Laboratory.

NEW COMPOUNDS

Di-(*p*-anisyl)-methylcarbinol

Although 1,1-di-(*p*-anisyl)-ethylene has been made from di-*p*-anisyl ketone and methylmagnesium bromide,[1,2] 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

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

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