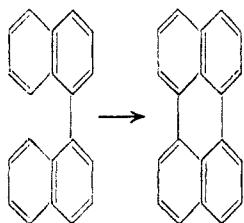


[CONTRIBUTION FROM THE U. S. BUREAU OF MINES, CENTRAL EXPERIMENT STATION, PITTSBURGH, PA.]

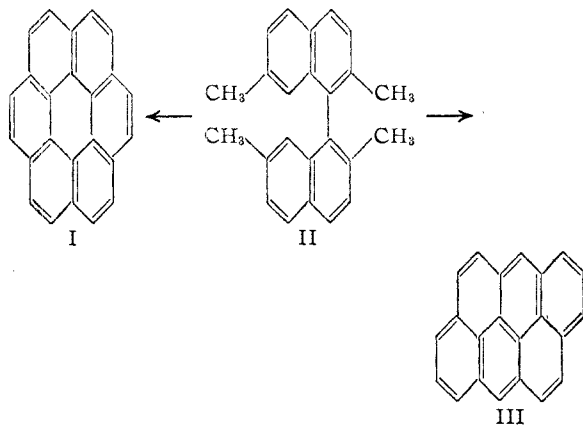
Aromatic Cyclodehydrogenation. IV. Experiments in the Dinaphthyl Series¹BY MILTON ORCHIN² AND ROBERT A. FRIEDEL³

In an extension of the cyclodehydrogenation reaction⁴ to the dinaphthyl series, 1,1'-dinaphthyl was passed over a palladium catalyst at 490° and gave in one pass a 10% conversion to perylene.^{4a}



This synthesis of perylene has the advantage over other methods^{5a} of closing down the rings of dinaphthyl in that the unconverted starting material can be recovered unchanged and utilized again.

The attractive possibility of obtaining coronene (I) in one step from 2,2'-7,7'-tetramethyl-1,1'-dinaphthyl (II) led to the study of the latter compound.



A one-gram sample of II, kindly furnished by Professor M. S. Newman, was treated with a palladium catalyst at 510°. Only 45 mg. of material survived this treatment. From this material it

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(4) For article III see Orchin, *THIS JOURNAL*, **68**, 571 (1946).

(4a) NOTE ADDED IN PROOF.—Since the original submission of this article, a sample of 3,4,3',4'-tetrahydro-1,1'-dinaphthyl became available through the courtesy of M. S. Newman. Treatment of this compound at 500° with a chromia on alumina catalyst gave perylene. Further experiments with this catalyst, which appears to be superior to palladium in the cyclodehydrogenation reaction, will be reported in a forthcoming paper.

(5a) Clar, "Aromatische Kohlenwasserstoffe," Julius Springer, Verlag, Berlin, 1941, p. 221.

was possible to isolate a pure compound in the form of crystalline yellow-gold plates. The ultraviolet absorption spectrum (Fig. 1), melting point and ultimate analysis indicated the probable structure of anthanthrene, III. The formation of III from II involves the loss of two methyl groups and the unusual formation of two new aromatic rings by loss of hydrogen between methyl groups and nuclear hydrogens.^{5b}

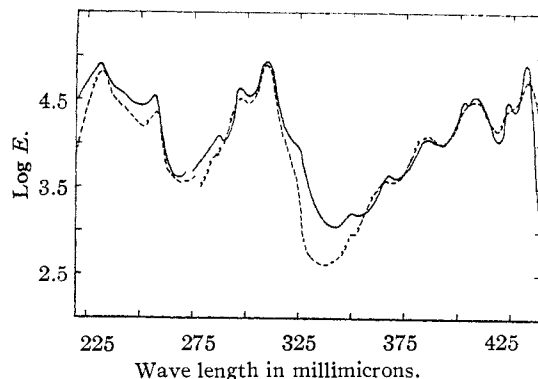


Fig. 1.—Ultraviolet absorption spectra: — anthanthrene (Clar, ref. 5 (a), p. 243); ---- reaction product. Both spectra from 220–275 in alcohol; from 275–440 in benzene.

Experimental⁶

1,1'-Dinaphthyl.—This compound was prepared by coupling 1-naphthylmagnesium bromide in the presence of cuprous chloride.⁷ There is some discrepancy in the literature regarding the melting point of 1,1'-dinaphthyl.⁸ This may be explained by the observation in the present work that this compound has two melting points. When crystallized from benzene-alcohol the compound had a melting point of 145.0–147.0°. When the melted compound solidified and was reheated the compound melted sharply at 159.5–160.5°. If the original crystallized material was heated slowly near its melting point only partial melting or sintering took place, and the material liquified completely and sharply at 159.5–160.5°. In some cases a heating rate of about 6° per minute was required to get crystallized material to melt at the lower temperature. When the compound was crystallized from acetic acid, the same double melting point behavior was noted. Prolonged drying *in vacuo* over phosphorus pentoxide of the benzene-alcohol or acetic acid recrystallized material did not change the characteristics. When the high melting form was recrystallized from solvents, the crystalline material which separated melted at the lower melting point.

Perylene.—Two grams of 1,1'-dinaphthyl was passed over a palladium-charcoal catalyst at 490° during two

(5b) The loss of a methyl group does not occur under the somewhat similar conditions (temperature 450°) used for the cyclodehydrogenation of 2,2'-dimethylbiphenyl to 4-methylfluorene: Orchin and Woolfolk, *THIS JOURNAL*, **67**, 122 (1945).

(6) Analyses by Dr. T. S. Ma, University of Chicago.

(7) Sakellarios and Kyrimis, *Ber.*, **57**, 325 (1924).

(8) The authors in reference 7 gave the m. p. as 154°; Schoepfle, *THIS JOURNAL*, **45**, 1566 (1923), gives the m. p. as 157°.

hours.⁹ The yellow solid product was crystallized from about 10 milliliters of benzene, whereupon 0.17 g. of perylene, m. p. 270°, was obtained. The mother liquor was passed over a column of alumina-Super-Cel. The yellow band at the top of the column on elution gave 0.05 g. of additional perylene. The balance of the column on elution gave 1.0 g. of unchanged dinaphthyl. The *sym*-trinitrobenzene complex of perylene crystallized from benzene as brick red needles, m. p. 248.0-249.0°. *Anal.* Calcd. for C₂₁H₁₅N₃O₆: N, 9.03; Found: N, 8.83.

Anthanthrene.—One gram of 2,2',7,7'-tetramethyl-1,1'-dinaphthyl was passed over palladium-charcoal⁹ at 510° during one hour. A small amount of a solid orange-yellow material was collected as product which, after crystallization from toluene, separated as orange plates. A benzene solution of this crystalline material was passed over a short column of alumina-Super Cel. The yellow band formed at the top of the column was separated and eluted with benzene. The benzene solution was treated with *sym*-trinitrobenzene and deep red needles of a trinitrobenzene complex, m. p. 250-253°, separated. The trinitrobenzene complex was dissolved in acetic acid and tin and hydrochloric acid added to the solution. The mixture was heated for five minutes in order to reduce the trinitro-

(9) For a description of the apparatus see *Ind. Eng. Chem., Anal. Ed.*, **17**, 673 (1945). For a description of the catalyst see *THIS JOURNAL*, **67**, 122 (1945).

benzene portion of the complex. The warm mixture was decanted into ice water and the precipitated hydrocarbon filtered and dried. The precipitate was dissolved in benzene, and the solution treated with norite, filtered, and the filtrate concentrated. On cooling, there separated gold-yellow plates, m. p. 255-257° with decomposition.¹⁰ *Anal.* Calcd. for C₂₂H₁₂: C, 95.62; H, 4.38. Found: C, 95.33; H, 4.84.

The catalyst used for the dehydrogenation was exhaustively extracted with benzene, but no material was extracted.

Summary

When 1,1'-dinaphthyl was treated with a palladium-charcoal catalyst at 490° it was converted to perylene.

When 2,2'-7,7'-tetramethyl-1,1'-dinaphthyl was treated with a palladium catalyst at 510° a small quantity of a compound whose properties were consistent with the structure of anthanthrene, was isolated, but most of the material was carbonized.

(10) Scholl and Meyer, *Ber.*, **67**, 1229 (1934), give the melting point as 257°; Clar, *Ber.*, **72**, 1645 (1939), gives the melting point as 261°.

PITTSBURGH, PA.

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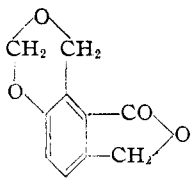
[CONTRIBUTION NO. 45 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Action of Formaldehyde on *m*-Hydroxybenzoic Acid. II

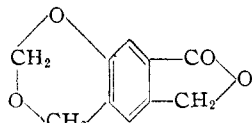
BY C. A. BUEHLER, JAMES O. HARRIS,¹ COMER SHACKLETT² AND BURTON P. BLOCK³

In the previous paper of this series⁴ it was stated that two products are formed when formaldehyde reacts with *m*-hydroxybenzoic acid in hydrochloric acid solution. While the structure of the product melting at 254° was proved in the former paper, the structure of the other compound, melting at 176° when highly purified, is now to be considered. Having the formula C₁₀H₈O₄, the compound contains dioxanyl and phthalide rings since it gives, respectively, an orange to red precipitate when heated with phloroglucinol in strong sulfuric acid solution and a fluorescence develops with resorcinol and sulfuric acid.

Three structures are possible for the dioxanyl phthalide



I



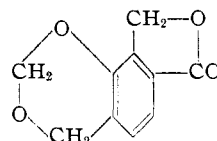
II

(1) Present address: Monsanto Chemical Company, Anniston, Alabama.

(2) Present address: Clinton Engineer Works, Tennessee Eastman Corporation, Oak Ridge, Tennessee.

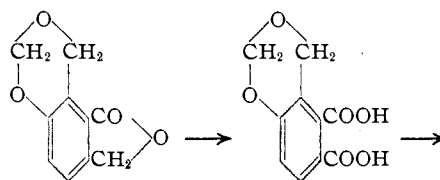
(3) Present address: Department of Chemistry, Purdue University, Lafayette, Indiana.

(4) Buehler, Powers and Michels, *THIS JOURNAL*, **66**, 417-418 (1944).



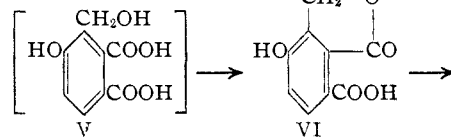
III

Oxidation with alkaline permanganate led to the formation of a product reconcilable only on the basis of formula I.



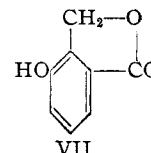
I

IV



V

VI



VII

The dicarboxylic acid, IV, which melts at 198°, could not be produced originally with certainty.