treated pyroabietic acid of Fleck and Palkin and hydrolyzing the crystalline sulfonic acid. Fusion of the sulfonic acid with alkali results in extensive alteration of the molecule and under the conditions studied gives a mixture of several products.

Methyl dehydroabietate reacts smoothly with acetyl chloride in nitrobenzene solution in the presence of aluminum chloride and gives a sharply melting product characterized as the 6-acetyl derivative. This was hydrolyzed to the free acid and oxidized with hypohalite to methyl 6-carboxydehydroabietate.

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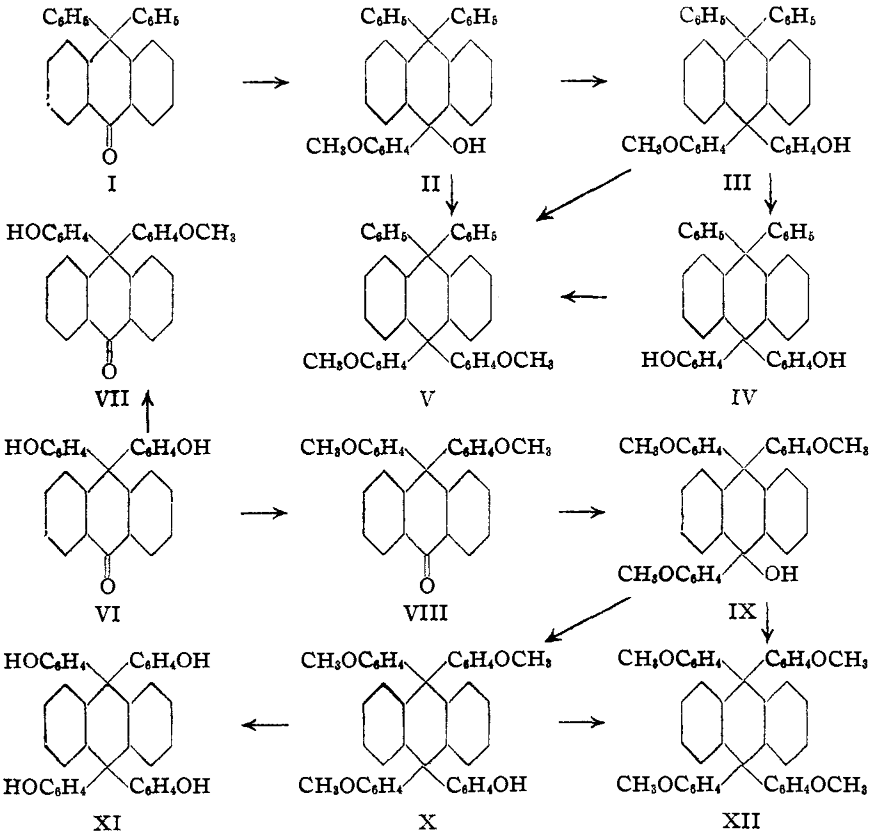
Hydroxy- and Methoxyphenyldihydroanthracenes

BY F. F. BLICKE AND R. A. PATELSKI[1]

Very few substitution products of 9,10-dihydroanthracene are known in which aryl groups occupy *meso* positions and it seems that hydroxyaryl derivatives such as 9,9,10-tri- and 9,9,10,10-tetra-(*p*-hydroxyphenyl)-9,10-dihydroanthracene, compounds in which we were especially interested, have never been prepared.



Since the carbonyl group in a 9,9-diarylanthrone-10 reacts toward an arylmagnesium halide in the characteristic manner, it was possible to convert the carbonyl compound into a tertiary carbinol which represents a 9,9,10-triaryl-10-hydroxy-9,10-dihydroanthracene. The hydroxyl group of the latter proved to be especially reactive toward phenol and anisole in the presence of a small amount of sulfuric acid, hence the hydroxyl group could be replaced by the hydroxyphenyl and anisyl nuclei and in this way a tetraaryl-9,10-dihydroanthracene could be obtained. Demethylation, in the case of the anisyl compounds, yielded the desired hydroxy derivatives.

It has been found that 9,9-diphenylanthrone-10 (I) reacts with *p*-anisylmagnesium iodide to yield 9,9-diphenyl-10-hydroxy-10-(*p*-anisyl)-9,10-dihydroanthracene (II); this product was converted readily into its carbinol methyl ether by methyl alcohol and hydrogen chloride. Compound II condensed with phenol, in the presence of a small amount of sulfuric acid, to yield 9,9-diphenyl-10-(*p*-hydroxyphenyl)-10-(*p*-anisyl)-9,10-dihydroanthracene (III), and with anisole to produce 9,9-diphenyl-10,10-di-(*p*-anisyl)-9,10-dihydroanthracene (V). Compound V was obtained also by methylation of compounds III and IV. By demethylation of the last named

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substance (III) there was produced 9,9-diphenyl-10,10-di-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (IV).

9,9-Di-(*p*-hydroxyphenyl)-anthrone-10 (VI) was converted by methyl sulfate into its monomethyl ether, 9-(*p*-hydroxyphenyl)-9-(*p*-anisyl)-anthrone-10 (VII), or into its dimethyl ether, 9,9-di-(*p*-anisyl)-anthrone-10 (VIII). Furthermore, the monomethyl ether (VII) was prepared by condensation of 9-hydroxy-9-(*p*-anisyl)-anthrone-10 with phenol in the presence of sulfuric acid.

Compound VIII reacted with *p*-anisylmagnesium iodide to form 9,9,10-tri-(*p*-anisyl)-10-hydroxy-9,10-dihydroanthracene (IX); condensation of the anthracene with phenol yielded 9,9,10-tri-(*p*-anisyl)-10-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (X). Upon demethylation of compound X there was obtained 9,9,10,10-tetra-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (XI).

9,9,10,10-Tetra-(*p*-anisyl)-9,10-dihydroanthracene (XII) was prepared by condensation of compound IX with anisole and by methylation of compound X.

Experimental Part

9,9-Diphenyl-10-hydroxy-10-(*p*-anisyl)-9,10-dihydroanthracene (II).—A solution of 30 g. of 9,9-diphenylanthrone (I)[2] in 100 cc. of dry benzene was added, gradually, to the Grignard reagent prepared from 35.4 g. of *p*-anisylmagnesium iodide, 3.7 g. of magnesium and 100 cc. of ether. The mixture was refluxed for five hours, decomposed with ice and ammonium chloride, the ether–benzene layer separated, filtered, steam distilled and the oily residue covered with methyl alcohol. After three days the product became crystalline; yield 22.5 g.; m. p. 142–144° after recrystallization from a mixture of ether and petroleum ether (30–60°).

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 87.18; H, 5.77. Found: C, 86.88; H, 5.79.

In order to obtain the carbinol methyl ether, a methyl alcohol solution of the anthracene was partially saturated with hydrogen chloride and after one hour the solvent was removed and the ether recrystallized from acetic acid; m. p. 191–193°.

Anal. Calcd. for $C_{34}H_{28}O_2$: C, 87.14; H, 6.03. Found: C, 87.18; H, 6.09.

9,9-Diphenyl-10-(*p*-hydroxyphenyl)-10-(*p*-anisyl)-9,10-dihydroanthracene (III).—A mixture of 20 g. of compound II, 30 g. of phenol and five drops of concd. sulfuric acid was heated on a steam-bath for two hours, the product washed thoroughly with hot water and the colorless crystals recrystallized from methyl alcohol; yield 23 g.; m. p. 250–252°.

Anal. Calcd. for $C_{39}H_{30}O_2$: C, 88.26; H, 5.73. Found: C, 87.96; H, 5.68.

9,9-Diphenyl-10,10-di-(*p*-anisyl)-9,10-dihydroanthracene (V).—This product was obtained when a mixture of 1.0 g. of compound II, 3.0 g. of anisole and one drop of sulfuric acid was heated on a steam-bath for one hour. After recrystallization from acetic acid the colorless material melted at 233–235°.

Anal. Calcd. for $C_{40}H_{32}O_2$: C, 88.19; H, 5.94. Found: C, 88.26; H, 5.92.

In order to prepare compound V by methylation of compound III, 2.0 g. of the latter, 6.0 g. of sodium hydroxide and 30 cc. of 50% alcohol were refluxed and 5 cc. of dimethyl sulfate added gradually. The mixture was heated for one hour. The product obtained weighed 1.9 g. and melted at 233–235° after recrystallization from acetic acid.

9,9-Diphenyl-10,10-di-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (IV).—A solution of 5 g. of compound III, 25 cc. of constant boiling hydrobromic acid and 150 cc. of acetic acid was refluxed for five hours, the precipitated material separated and the solution concentrated, whereupon more material separated; total yield 3.9 g.; m. p. 343–345° after recrystallization from acetic acid.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.33; H, 5.46. Found: C, 88.14; H, 5.52.

The di-3-bromobenzoyl derivative was prepared in the following manner: 2 g. of the anthracene and 5 g. of 3-bromobenzoyl chloride were heated for an hour at 190–200° and the mixture treated with hot alcohol. The ester was recrystallized from ethyl acetate; m. p. 231–233°.

Anal. Calcd. for $C_{52}H_{34}O_4Br_2$: Br, 18.13. Found: Br, 17.92.

The dimethyl ether was obtained when compound IV was methylated with dimethyl sulfate and alkali in dilute alcohol. It proved to be identical with compound V; mixed m. p. 233–235°.

9-(*p*-Hydroxyphenyl)-9-(*p*-anisyl)-anthrone-10 (VII).—A solution of 3.8 g. of 9,9-di-(*p*-hydroxyphenyl)-anthrone-10 (VI)[3] in 50 cc. of 20% sodium hydroxide solution was heated to 80° and treated, gradually, with 10 cc. of dimethyl sulfate. The precipitated product was recrystallized from acetic acid; m. p. 232–233°; yield 2.5 g.

Anal. Calcd. for $C_{27}H_{30}O_3$: C, 82.62; H, 5.14. Found: C, 82.51; H, 5.06.

We also prepared the anthrone by heating a mixture of 10 g. of 9-hydroxy-9-(*p*-anisyl)-anthrone-10 (XIII),[4] 25 g. of phenol and three drops of sulfuric acid for one hour on a steam-bath. The product was washed with hot water and recrystallized from acetic acid; yield 9 g.; mixed m. p. 232–233°.

9,9-Di-(*p*-anisyl)-anthrone-10 (VIII).—A mixture of 7.6 g. of 9,9-di-(*p*-hydroxyphenyl)-anthrone-10, 100 cc. of alcohol and 100 cc. of 10% sodium hydroxide solution was refluxed and 30 cc. of dimethyl sulfate added gradually. It was heated for one hour and the crystalline precipitate recrystallized from acetic acid; m. p. 208–209°.[5]

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[2] Barnett, Cook and Nixon, *J. Chem. Soc.*, 508 (1927).

[3] Scharwin and Kusnezof, *Ber.*, **36**, 2020 (1903); Scharwin, Naumof and Sandurin, *ibid.*, **37**, 3616 (1904).

[4] Blicke and Weinkauff, THIS JOURNAL, **54**, 1461 (1932).

[5] Scharwin, Naumof and Sandurin [*Ber.*, **37**, 3619 (1904)], who obtained the anthrone by another method, reported 208°.

The anthrone was prepared also by methylation of compound VII according to the procedure just described.

9,9,10-Tri-(*p*-anisyl)-10-hydroxy-9,10-dihydroanthracene (IX).—Sixteen grams of compound VIII, dissolved in 75 cc. of benzene, was added, gradually, to the Grignard reagent obtained from 18.9 g. of *p*-iodoanisole, 2.0 g. of magnesium and 75 cc. of ether. The mixture was refluxed for five hours, decomposed with ice and ammonium chloride, the ether–benzene layer filtered and the solution steam distilled. The crystalline residue was recrystallized from acetic acid; yield 15 g.; m. p. 226–228°.

Anal. Calcd. for $C_{35}H_{30}O_4$: C, 81.64; H, 5.91. Found: C, 81.42; H, 5.89.

The methyl ether was obtained when a methyl alcohol solution of the anthracene was partially saturated with hydrogen chloride; m. p. 205–206° after recrystallization from acetic acid.

Anal. Calcd. for $C_{36}H_{32}O_4$: C, 81.78; H, 6.11. Found: C, 81.52; H, 6.13.

9,9,10-Tri-(*p*-anisyl)-10-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (X).—A mixture of 5 g. of compound IX, 20 g. of phenol and three drops of sulfuric acid was heated on a steam-bath for three hours, the material washed with hot water and recrystallized from acetic acid; yield 5 g.; m. p. 310–312°.

Anal. Calcd. for $C_{41}H_{34}O_4$: C, 83.35; H, 5.81. Found: C, 83.07; H, 5.84.

9,9,10,10-Tetra-(*p*-hydroxyphenyl)-9,10-dihydroanthracene (XI).—Two grams of compound X, 20 cc. of constant boiling hydrobromic acid and 300 cc. of acetic acid were refluxed for five hours. The mixture was concentrated to a volume of about 75 cc. and poured into 200 cc. of water. The precipitated product was recrystallized from dilute alcohol; m. p. 371–374°.[6] The compound dissolves readily in dilute alkali.

Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.18; H, 5.15. Found: C, 82.92; H, 5.14.

One gram of the anthracene was heated with 5 g. of *m*-bromobenzoyl chloride for one hour at 190–200°. The material was washed with hot alcohol, then dissolved in hot acetic acid. When the solution cooled a small amount of colored by-product precipitated. The filtered solution was diluted with three volumes of methyl alcohol; the colorless precipitate, which was the tetra-*m*-bromobenzoyl derivative, melted at 163–168°.

Anal. Calcd. for $C_{66}H_{40}O_8Br_4$: Br, 24.99. Found: Br, 25.18.

9,9,10,10-Tetra-(*p*-anisyl)-9,10-dihydroanthracene (XII).—A boiling solution, obtained from 1 g. of compound X, 3 g. of sodium hydroxide and 20 cc. of 50% alcohol, was treated, gradually, with 5 cc. of dimethyl sulfate. The mixture was heated for one hour and the product recrystallized from acetic acid; m. p. 329–331°.[6]

Anal. Calcd. for $C_{42}H_{36}O_4$: C, 83.40; H, 6.01. Found: C, 83.38; H, 6.07.

The same anthracene was obtained when 1 g. of compound IX, 3 g. of anisole and one drop of sulfuric acid were heated for one hour on a steam-bath; mixed m. p. 329–331°.

Summary

A number of 9,9,10-tri- and 9,9,10,10-tetraaryldihydroanthracenes have been prepared in which the aryl groups are phenyl, *p*-hydroxyphenyl and *p*-anisyl.

(6) Determined in an air-bath with a 250–600° Palo–Myers mercury thermometer.

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Hydroxy- and Methoxyphenylanthrones. I.

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It is well known that interaction between phthalic anhydride and aromatic hydrocarbons or simple substitution products of the latter yields 2-acylbenzoic acids, diarylphthalides and anthraquinones; other products are formed also but their nature is not known.

It seems to us that in the reaction between phthalic anhydride and phenol, hydroxyphenylanthrones, such as 3,9-dihydroxy-9-(*p*-hydroxyphenyl)-anthrone-10, might be formed and that these anthrones, by further reaction with phenol, might be converted into hydroxy derivatives of diphenylanthrones, tri- and tetraphenyldihydroanthracenes. The hydroxyl groups can occupy either ortho or para positions in the phenyl nuclei and either a 1-, 2-, 3- or 4-position in the anthrone or anthracene nucleus. Since only a few representatives of such compounds have been described in the literature we have synthesized a number of them, often by several different procedures, in order to establish their structure definitely.

In many instances the desired substance has been prepared, with the aid of a Grignard reagent, in the form of its methyl ether; the hydroxy compound was then obtained by demethylation However, this procedure was not always successful since, occasionally, demethylation was accompanied by disruption of the molecule; hence

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