

or ammonia and carbon dioxide; if it takes place in alcohol solution an allophanic ester will be produced.

The dry salts of the acyl esters of the alkoxyhydroxamic acids described above, when heated, rearranged to give new isocyanates: methoxymethyl isocyanate; ethoxymethyl isocyanate; β -methoxyethyl isocyanate. The rearrangement of these salts in water solution did not yield *sym*-disubstituted ureas, since methoxymethyl isocyanate and ethoxymethyl isocyanate, upon hydrolysis, yield amines, ROCH_2NH_2 , which dissociate at once to give ammonia, formaldehyde and an alcohol, while β -methoxyethyl isocyanate was unaffected by water and was isolated as such when the compound, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{—CON}(\text{K})\text{OCOC}_6\text{H}_5$, was heated with water.

During the investigation new methods for the preparation of methoxyethyl chloride and methoxyethyl iodide were developed, and the following additional new compounds were synthesized: methoxymethyl isocyanate, ethoxymethyl isocyanate, β -methoxyethyl isocyanate, β -methoxypropionic acid and β -methoxypropionyl chloride.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 95]

THE PREPARATION OF METHYL-ISOPROPYL-ANTHRAQUINONE¹

BY MAX PHILLIPS

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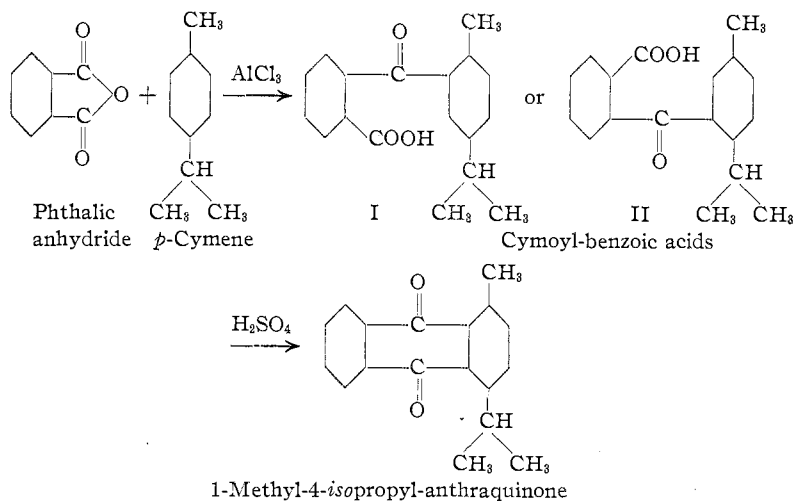
Several alkyl derivatives of anthraquinone are described in the literature.² The method generally followed in their preparation consists in first combining the alkyl-aromatic hydrocarbon with phthalic anhydride in the presence of aluminum chloride, forming an alkyl derivative of benzoyl-benzoic acid and subsequently condensing this, in the presence of sulfuric acid, to the corresponding anthraquinone substitution product. A derivative of anthraquinone containing both the methyl and *isopropyl* groups has not heretofore been described in the literature, although Elbs³ made an unsuccessful attempt to prepare such a compound. In connection with some work on *p*-cymene which has been under way in the Color Laboratory for some time, it appeared desirable to prepare a methyl-*isopropyl*-anthraquinone. Accordingly, the experiments described in this paper were conducted.

¹ Presented before the Division of Dye Chemistry of the American Chemical Society at its meeting, Washington, D. C., April 21–26, 1924.

² *Ann.*, **234**, 238 (1886). *Ber.*, **20**, 1361, 1364 (1887). *Ann. chim.*, [6] **14**, 446 (1888). *J. prakt. Chem.*, [2] **41**, 4 (1890). *Ann.*, **311**, 181 (1900). *Ann.*, **312**, 99 (1900). *Ber.*, **41**, 3627 (1908). *Ber.*, **43**, 2891 (1910). *J. prakt. Chem.*, [2] **82**, 205 (1910). *Monatsh.*, **32**, 687 (1911). *J. Chem. Soc.*, **119**, 1573 (1921).

³ Elbs, *J. prakt. Chem.*, [2] **33**, 318 (1886).

The reactions involved in this synthesis may be represented by the following structural formulas.



When *p*-cymene is condensed with phthalic anhydride, two isomeric cymoyl-benzoic acids may be formed, one having the structure represented by Formula I and the other that represented by Formula II. The cymoyl-benzoic acid described in this paper is believed to have the structure represented by Formula I, for the following reason: when *p*-cymene is halogenated, nitrated or sulfonated and, in fact, when any substituent is introduced into the cymene molecule, substitution takes place largely in the position *ortho* to the methyl group, the position adjacent to the *isopropyl* group being much more difficult to attack. It may therefore reasonably be expected that in this case also the acid most readily formed would probably be the one represented by Formula I. Presentation of direct proof of the constitution of this acid is, however, reserved for a future communication.

Experimental Part

Cymoyl-benzoic Acid.—A mixture of 50 g. of powdered phthalic anhydride and 100 g. of powdered aluminum chloride was placed in a flask provided with a reflux condenser, at the end of which was attached a calcium chloride tube; 200 g. of *p*-cymene was added to this in small portions, the rather vigorous reaction being allowed to subside each time before further addition. When all of the cymene had been added, the flask was heated on the steam-bath until the evolution of hydrogen chloride ceased (about eight hours). After the reaction product had cooled to room temperature, it was poured into ice water, 100 cc. of concd. hydrochloric acid was added, and the mixture was steam-distilled to remove the cymene not used up in the reaction. The quantity of cymene thus recovered varied from 140 to 150 g. The residue in the flask was washed with water and then digested on the steam-bath with dil. ammonia. The ammoniacal solution was boiled with animal charcoal and filtered, and the filtrate was made acid with dil. sulfuric

acid. The product thus obtained was amorphous. It was dried at 100°; yield, 80 g., or 84%.

In order to obtain this condensation product in pure and crystalline form, it was dissolved in sodium carbonate solution and evaporated to dryness on the steam-bath. This residue was transferred to a Büchner funnel and washed with ether until a colorless product was obtained. This was subsequently dissolved in water and the solution was made acid with dil. sulfuric acid, whereupon a colorless oil separated which on standing solidified. It was crystallized from benzene from which it separated as colorless prismatic crystals; m. p., 124° (corr.).

Anal. Subs., 0.1835, 0.1002: CO₂, 0.5119, 0.2808; H₂O, 0.1017, 0.0567. Calc. for C₁₈H₁₈O₃: C, 76.56; H, 6.42. Found: C, 76.07, 76.42; H, 6.20, 6.33.⁴

The silver salt of this acid was prepared from the ammonium salt in the usual manner.

Anal. Subs., 0.3686, 0.3076: Ag, 0.1012, 0.0846. Calc. for C₁₈H₁₇O₃Ag: Ag, 27.72. Found: 27.45, 27.50.

Methyl-isopropyl-anthraquinone.—Eighty g. of cymoyl-benzoic acid was treated with 500 g. of fuming sulfuric acid (20% SO₃) and the mixture was heated on the steam-bath for two hours. The reaction product was allowed to cool to room temperature and then poured into ice water. A yellow precipitate separated. This was filtered off and crystallized from 95% alcohol from which it separated as yellow needles; yield, 32 g., or 43%; m. p., 113.8° (corr.).

Anal. Subs., 0.2278, 0.1677: CO₂, 0.6834, 0.5032; H₂O, 0.1254, 0.0891. Calc. for C₁₈H₁₈O₂: C, 81.78; H, 6.10. Found: C, 81.80, 81.82; H, 6.11, 5.94.

Methyl-isopropyl-anthracene Picrate.—Five g. of methyl-isopropyl-anthraquinone, 500 cc. of aqueous ammonia and 30 g. of zinc dust were heated together on the steam-bath until the solution, which at first was red, became colorless. The reaction mixture was filtered and the residue on the filter paper was extracted with boiling 95% alcohol. On concentrating the alcoholic solution no crystallization of the hydrocarbon took place. Accordingly, a saturated alcoholic solution of picric acid was added to it, and after a few minutes the picrate separated as brown needles; m. p., 131° (corr.).

Anal. (modified Kjeldahl). Subs., 0.2376, 0.1052: 15.1 cc., 6.7 cc. of 0.1 N HCl. Calc. for C₁₈H₁₈.C₆H₃(NO₂)₃O: N, 9.07. Found: 8.90, 8.94.

Dinitro-methyl-isopropyl-anthraquinone.—Five g. of methyl-isopropyl-anthraquinone was dissolved in 30 cc. of concd. sulfuric acid and a nitrating mixture, consisting of 12 g. of nitric acid (d., 1.4) and 12 g. of sulfuric acid (d., 1.84), was added gradually to it. The mixture was subsequently placed on the steam-bath for one-half hour to complete the reaction, whereupon it was allowed to cool to room temperature and then poured into ice water. The nitration product that separated was filtered off and crystallized from acetic acid as yellow needles; yield of pure product, 1.64 g.; m. p., 232° (decomp.).

Anal. (modified Kjeldahl). Subs., 0.1057, 0.1085: 5.9 cc., 6.0 cc. of 0.1 N acid. Calc. for C₁₈H₁₄O₂N₂: N, 7.90. Found: 7.82, 7.74.

1,4-Dicarboxy-anthraquinone and 1,4-Dicarboxy-anthracene.—Three g. of methyl-isopropyl-anthraquinone and 25 cc. of nitric acid (d., 1.1) were heated together in a sealed tube at 210° to 220° for five hours. The crystalline product thus obtained was filtered off, dissolved in dil. ammonia, the solution filtered, and the dicarboxy-anthraquinone precipitated by the addition of dil. sulfuric acid. The product was crystallized

⁴ The carbon, hydrogen and nitrogen determinations reported in this paper were made by Mr. R. M. Hann, of the Bureau of Chemistry.

from dil. alcohol; m. p., 315–316° (decomp.). Elbs,⁵ who prepared 1,4-dicarboxyanthraquinone by oxidizing 1,4-dimethyl-anthraquinone with nitric acid, states that this acid melts above 300° and that 1,4-dicarboxy-anthracene melts at 320°. Accordingly, the acid was dissolved in ammonia and reduced by the addition of zinc dust. The reduction was known to be complete when the ammoniacal solution became colorless. The zinc dust was filtered off and the filtrate was made acid with dil. sulfuric acid, whereupon a colorless precipitate was obtained. The acid thus obtained was crystallized from dil. alcohol. It melted (with noticeable decomposition) at 320°. This acid was undoubtedly identical with the 1-4-dicarboxy-anthracene of Elbs. Inasmuch as it was prepared from methyl-*isopropyl*-anthraquinone, the relative positions occupied by the methyl and *isopropyl* groups must be the 1 and 4.

Summary

1. 1-Methyl-4-*isopropyl*-anthraquinone has been synthesized from *p*-cymene and phthalic anhydride. The reaction proceeds in two stages: *p*-cymene and phthalic anhydride combine to form cymoyl-benzoic acid; this when condensed in the presence of sulfuric acid yields methyl-*isopropyl*-anthraquinone.

2. Several derivatives of this anthraquinone have been prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

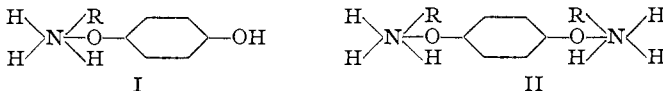
ADDITION COMPOUNDS OF HYDROQUINONE WITH ALIPHATIC AMINES

BY ROLLA N. HARGER^{1,2}

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Aromatic amines have been found to form with hydroquinone double compounds³ which may be formulated as aryl derivatives of mono-ammonium hydroquinone I, or diammonium hydroquinone II,



So far as the writer has been able to ascertain, the only investigation of the behavior of aliphatic amines with hydroquinone is the work of H. D. Gibbs,⁴ in a study of the action of liquid methylamine upon various phenols. At a moderately low temperature hydroquinone was found to combine with

⁵ Elbs, *J. prakt. Chem.*, [2] **41**, 1 (1890).

¹ National Research Fellow in Chemistry.

² Constructed from a Dissertation presented by Rolla N. Harger to the Faculty of the Graduate School of Yale University in June, 1922, in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson.)

³ (a) Hebebrand, *Ber.*, **15**, 1973 (1882). (b) Niemyer, *Ann.*, **228**, 322 (1885); *Ger. pat.* 174,689, 1906. (c) E. Lumière, A. Lumière and Seyewetz, *Mon. Sci.*, [4] **13**, I, 168 (1899). (d) Dollinger, *Monatsh.*, **31**, 643 (1910). (e) Hock, *Ber.*, **16**, 885 (1883).

⁴ Gibbs, *THIS JOURNAL*, **28**, 1395 (1906).