Conclusions and Summary

1. Benzyl alcohol reacts with phenol at low temperatures in the presence of aluminum chloride to form *p*-benzylphenol.

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH + H_2O$$

2. The methyl and ethyl ethers of *p*-benzylphenol may be prepared in good yield by condensing benzyl alcohol with anisole or phenetole.

3. The phenolic hydroxyl group does not interfere with the substitution of the benzyl group in the benzene ring by means of aluminum chloride under the described conditions.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

NAPHTHALENE AND THE CENTROID STRUCTURE

BY REYNOLD C. FUSON[1]

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Using the Lewis theory of atomic structure[2] as a basis, Huggins has recently evolved a new theory of conjugated double bonds.[3] Applying this theory to benzene (regarded as a triply conjugated system), he has arrived at the conclusion that the centroid model first proposed by Körner[4] is the correct configuration for benzene, naphthalene and other aromatic nuclei. The X-ray experimental data of Hull[5] and of Debye and Scherrer[6] for graphite have been interpreted by Huggins as constituting a *proof* of the correctness of this model;[7] and the more recent measurements made by Mark and Weissenberg[8] on triphenylmethane crystals are also in agreement with this theory.

Considering the centroid structure as *proved* for benzene, Huggins has applied it to numerous benzene derivatives including naphthalene, to which he has assigned a structure differing from that of Kekulé[9] in several

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[1] The work described in this paper formed a part of a thesis presented by Reynold C. Fuson in June, 1924, to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The original thesis is on file in manuscript in the Library of the University of Minnesota.—W. H. Hunter.

[2] Lewis, THIS JOURNAL, **38**, 762 (1916).

[3] Huggins, *ibid.*, **44**, 1607 (1922).

[4] Körner, *Gazz. chim. ital.*, **4**, 444 (1874). See also Marsh, *Phil. Mag.*, **26**, 426 (1888). Vaubel, *J. prakt. Chem.*, [2] **44**, 137 (1891); **49**, 308 (1894); **50**, 58 (1894).

[5] Hull, *Phys. Rev.*, [2] **10**, 692 (1917).

[6] Debye and Scherrer, *Physik. Z.*, **18**, 294 (1917).

[7] Huggins, THIS JOURNAL, **45**, 264 (1923).

[8] Mark and Weissenberg, *Z. Physik*, **17**, 347 (1923).

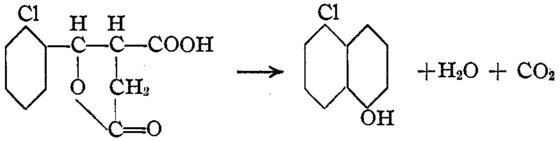
[9] The Kekulé structure is referred to here merely as a *type* of structure; this type includes most of the models which have received any considerable favor among chemists.

important respects. In particular, he has shown that the two rings composing naphthalene having two carbon atoms in common cannot lie with their principal planes coincident as is the case in the Kekulé model but must be so placed that these planes form an angle of 60° with each other.

As Huggins has pointed out, this throws the 1 and 8 positions far apart in space while the 1 and 5 positions are drawn close together. Bridge formation between groups in the first named positions is, therefore, not to be expected if the centroid model is correct. In this model, on the other hand, the 1 and 5 positions being close together might be expected to form bridges readily. And it is only on the assumption that these bridges are 1,5 that Huggins can explain their existence on the basis of his centroid model. This assumption must be regarded as a *necessary consequence* of his theory. With reference to this point, he makes the following statement: "In view of the present evidence, we may conclude that the numbering of many substitution products of naphthalene is in error, the 5 and 8 positions being interchanged and likewise the 6 and 7."

It is clear that this necessity for interchange of numbering is fundamental to the centroid structure for naphthalene and, indirectly, to that of benzene itself. Obviously, then, this structure for naphthalene (and benzene) must stand or fall with this proposition: *that peri bridges in the naphthalene series involve Positions 1 and 5 and not Positions 1 and 8.*

A search of the literature disclosed at least one compound of which it can be said that it *must* have the 1,5 orientation. This is the 1,5 chloronaphthol prepared by Erdmann and Kirchhoff[10] from *o*-chloro-phenylparaconic acid by the Erdmann ring closure.



On treatment with phosphorus pentachloride this compound yields 1,5-dichloronaphthalene. The 1,8-dichloronaphthalene whose orientation is thus established has been related to a large number of 1,8 derivatives including naphtho-sultone and naphtho-sultam each of which contains a peri bridge. These facts seem to show that bridge formation is related to the 1,8 positions.

Some doubt, however, is thrown upon the validity of this work by the fact that it depends upon the *normal* replacement of the sulfonic group. Now, sulfonic acids are known to undergo rearrangement in many replacements of this sort and are, accordingly, not well suited to rigorous study of orientation. Further, the orientation of the reference substance,

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[10] Erdmann and Kirchhoff, *Ann.*, **247**, 372 (1888).

1,8-dichloronaphthalene, has been laid open to question by the discovery of Armstrong and Wynne[11] that *1,8-dichloronaphthalene rearranges to 1,5-dichloronaphthalene* on treatment with hydrochloric acid or sulfur at 250–290°.

It occurred to the writer that the whole question could be decisively tested by a study of the orientation of naphtholactone, a substance containing a peri bridge and whose synthesis could be effected by reactions known to proceed normally. It is believed that the experimental data set forth in the present paper show that it has the 1,8 and not the 1,5 orientation required by Huggins' model. It has, accordingly, been concluded that the centroid model does not correctly represent the naphthalene molecule; from this it may be inferred that this structure for benzene is likewise erroneous.

The Orientation of Naphtholactone

The orientation of naphtholactone has been determined by a study of the so-called "1,5" and "1,8" hydroxynaphthoic acids. These acids are characterized by the fact that each has an hydroxyl group and a carboxyl group in alpha positions not in the same ring. Only two such isomers are possible—the 1,5 and the 1,8. Both of these acids are well known—one, the so-called "1,8," melts[12] at 169° and the other, known as the "1,5," melts[13] at 235–236°. But, as far as the writer has been able to learn, there is nothing in the literature which shows which of these two acids is really the 1,5 and which is the 1,8. The so-called "1,8" hydroxynaphthoic acid has been assigned the 1,8 orientation because it forms a bridge.[14] The only point of evidence involved here has been the one now called in question: the relative nearness of the two pairs of positions.

If, now, the 1,8-hydroxynaphthoic acid could be synthesized by a method which would leave no doubt as to its orientation it would, of course, be found to be identical with either the "1,5" or the "1,8" acid. Similarly, if the 1,5 acid could be prepared by unequivocal methods it also would be identical with one of the known acids. Now, since there can be but two such acids, if we could fix the orientation of either of them, that of the other would follow by the principle of exclusion. The unequivocal synthesis of either the 1,5 or the 1,8 acid would, therefore, enable us to assign an orientation to the "1,8" acid and, hence, to naphtholactone itself. The problem thus resolves itself into the preparation by unequivocal methods of either the 1,5 or the 1,8 hydroxynaphthoic acid.

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[11] Armstrong and Wynne, *Proc. Chem. Soc.*, No. **182**, 154–156 (1896–1897); *Chem. Zentr.*, **1897**, II, 553.

[12] Ekstrand, *J. prakt. Chem.*, [2] **38**, 278 (1888).

[13] Royle and Schedler, *J. Chem. Soc.*, **123**, 1641 (1923).

[14] Ref. 12, p. 280.

From a preliminary investigation it appeared that the synthesis of the 1,8 would involve considerable experimental difficulty. Accordingly, the 1,5 has been chosen and its synthesis has been carried out. The method of synthesis which has been used constitutes, it is believed, a proof of its orientation.

It is clear that by starting with the 1,5-chloronaphthol of Erdmann it would only be necessary to replace the chlorine atom by a carboxyl group in order to obtain the 1,5-hydroxynaphthoic acid desired. Although there seemed to be no direct method for doing this, it seemed probable that the corresponding 1,5-*bromo*naphthol could be synthesized in a similar way and the bromine atom then replaced by the carboxyl group by means of the Grignard reaction.

This general plan has been carried out and will now be described in some detail. An outline of the work is shown in Fig. 1. Arrows have been inserted in the figure to indicate in the case of each compound the substance from which it has been derived.

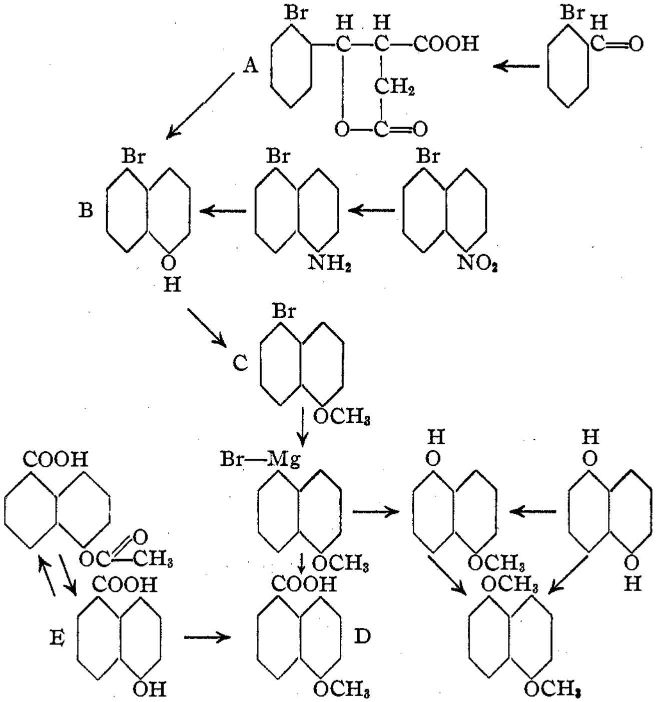
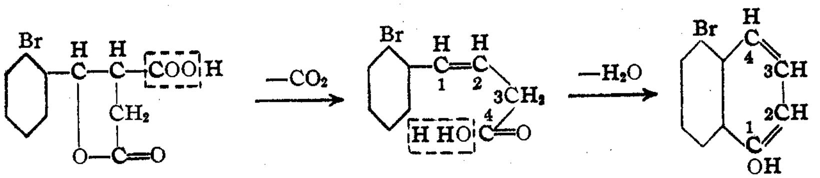


Fig. 1. Diagram of the experimental work.

o-Bromophenyl-paraconic acid (A) was prepared by the condensation of *o*-bromobenzaldehyde with succinic anhydride. The *o*-bromophenyl-paraconic acid on being heated gave 1,5-bromonaphthol (B). 1,5-Methoxy-bromonaphthalene (C), obtained from the bromonaphthol by methylation, was transformed into 1,5-methoxynaphthoic acid (D) by means of the Grignard reaction.

The so-called "1,5"-hydroxynaphthoic acid (E) was then prepared by known methods and its methylation product, "1,5"-methoxynaphthoic acid, isolated and characterized. It was found to be identical with the 1,5-methoxynaphthoic acid obtained by the ring-closure method outlined above, that is, it was found *to have the 1,5 orientation.* It follows that the "1,5"-hydroxynaphthoic acid itself is a 1,5 compound.



o-Bromophenyl-paraconic acid. *o*-Bromo-*β*-benzal-propionic acid. 1,5 Bromonaphthol.

***o*-Bromophenyl-paraconic Acid (Fig. 1-A).**—The first step in the synthesis was that of preparing *o*-bromophenyl-paraconic acid by a method which would leave no doubt as to the position of the bromine atom in the ring. This was accomplished by condensing *o*-bromobenzaldehyde with succinic anhydride. The *o*-bromophenyl-paraconic acid which resulted was a white, crystalline compound melting at 133–135°. From its method of formation, it follows that it must hold the bromine atom in the position *ortho* to the side chain, that is, it must be *ortho*-bromophenyl-paraconic acid.

1,5-Bromonaphthol (Fig. 1-B).—The second step in the synthesis was the condensation of *o*-bromophenyl-paraconic acid to 1,5-bromonaphthol. This reaction was found to take place in a manner entirely similar to that described by Erdmann and Kirchhoff[10] for the chlorine analog. When the air-dried acid was distilled the bromonaphthol passed over as a yellow liquid which solidified in the receiver. The pure substance melted at 137°. It gave the usual naphthol reactions and was shown by analysis to be a monobromonaphthol. From the mode of its formation it can only be the 1,5 compound.

The position taken by the hydroxyl group was determined in the following way. In the first place, the work of Erdmann and others shows that the reaction takes place in two steps. The first step is the formation of *o*-bromo-*β*-benzal-propionic acid from the *o*-bromophenyl-paraconic acid by the elimination of carbon dioxide. This compound then loses water and passes into the bromonaphthol. Now, in the *o*-bromo-*β*-benzal-propionic acid which is the mother substance of the naphthol, there are but two oxygen atoms and *both of these are tied to*

Carbon 4. The elimination of the molecule of water, obviously, involves the removal of one of them and requires that Carbon 4 becomes tied to the ring, that is, this carbon atom must take up Position 1 in the resulting naphthol. Now, it was the *only carbon atom in the original o-bromo-β-benzal-propionic acid which held oxygen.* The oxygen atom which remains must, therefore, be on this carbon atom and, consequently, the hydroxyl group containing the oxygen atom must occupy Position 1.

1,5-Methoxy-bromonaphthalene (Fig. 1-C).—The next step in the synthesis was the replacement of the bromine atom in the naphthol by the carboxyl group. Before this could be done, however, it was necessary to protect the hydroxyl group. This was done by methylation. The naphthol was dissolved in dil. alkali and treated with dimethyl sulfate. The 1,5-methoxy-bromonaphthalene formed in this way was a white crystalline solid melting at 67–68°.

1,5-Methoxy-naphthoic Acid (Fig. 1-D).—From the methoxy-bromonaphthalene the magnesium compound was obtained in the usual way. By treating this with carbon dioxide, 1,5-methoxynaphthoic acid was prepared. It formed in heavy plates melting at 227–228.5°.

The "1,5"-hydroxynaphthoic acid (Fig. 1-E) was then prepared by the method of Royle and Schedler[13] and its methylation product isolated and characterized. The "1,5"-methoxynaphthoic acid thus prepared was found to be identical with the 1,5-methoxynaphthoic acid just described. Since their methyl derivatives were found to be identical, it was concluded that the "1,5"- and 1,5-hydroxynaphthoic acids were the same. As a corollary of this, it follows that the "1,8"-hydroxynaphthoic acid and naphtholactone must have the 1,8 structure. The latter, however, contains a bridge. We may, therefore, conclude that bridge formation is concerned with the 1 and 8 and not the 1 and 5 positions as required by the centroid model. Naphthalene, therefore, cannot have the centroid structure and by inference at least, this structure for benzene is made doubtful.

Experimental Part

The Preparation of *o*-Bromophenyl-paraconic Acid.—This acid was prepared by the general method used by Erdmann[15] for the chlorine analogs. Eighty-five g. of *o*-bromobenzaldehyde was placed in a mixture of 47 g. of powdered succinic anhydride and 39 g. of freshly fused sodium acetate (molecular proportions) in a 1-liter round-bottom flask fitted with an upright air condenser. The flask was heated in an oil-bath to 140° and kept at this temperature until darkening and evolution of carbon dioxide showed that the reaction had begun; the temperature was then allowed to fall to 120° where it was kept nearly constant for six hours. Water was then introduced and the mixture steam-distilled. About one-fifth of the aldehyde used was recovered unchanged in the distillate. The paraconic acid was precipitated by the addition of hydrochloric acid, filtered off, dissolved in hot water and treated with an excess of sodium hydroxide. The

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[15] Ref. 10, p. 368.

barium salt of *o*-bromophenyl-itamalic acid separated as a heavy, white, crystalline mass. This was filtered off, washed with water and treated with concd. hydrochloric acid in which it dissolved to form a turbid liquid containing the free *o*-bromophenyl-itamalic acid. This when heated lost water almost at once, giving *o*-bromophenyl-paraconic acid which separated in colorless crystals. After repeated recrystallization from water the acid melted at 133–135°; yield, 50%.

Anal. Subs., 0.2151: AgBr, 0.1439. Calc. for $C_{11}H_9O_4Br$: Br, 28.04. Found: 28.47.

DETERMINATION OF THE MOLECULAR WEIGHT.—*o*-Bromophenyl-paraconic acid was titrated with sodium hydroxide solution using phenolphthalein as the indicator. When the titration was carried out in the cold, an end-point was reached when approximately 60% of the acid had been neutralized. An excess of the alkali was added, the solution boiled for a few minutes and then titrated back with standard hydrochloric acid solution.

	Subs.	Total amount of NaOH (0.1021 *N*) used	Equiv. wt.
1	0.7979	54.82	142.5
2	.4080	27.76	143.9

Mol. wt.: Calc., 285.05. Found: 286.4 (assuming the acid to be dibasic).

The Preparation of 1,5-Bromonaphthol.—Air-dried *o*-bromophenyl-paraconic acid was placed in a distilling flask and heated rapidly. The acid melted to a clear liquid and then began almost at once to give off carbon dioxide in large quantities. After the effervescence had subsided somewhat a yellow oil passed over and solidified almost immediately in the receiver. There remained a large residue that became black at the end of the distillation but the amount of material which came over after the carbonization had begun was very small. The temperature of the decomposition lies between 250° and 300°.

The distillate was dissolved in dil. alkali and this solution was washed with ether to remove a slight amount of oily substance insoluble in the alkali. By passing in a stream of carbon dioxide the 1,5-bromonaphthol was obtained in fine, white needles which after recrystallization from water melted at 137°. It had a distinctly phenolic odor and with ferric chloride gave a white precipitate which after a few hours turned to a deep purple.

Anal. Subs., 0.2281, 0.0931: AgBr, 0.1936, 0.0785; Calc. for $C_{10}H_7OBr$: Br, 35.85. Found: 36.11, 35.88.

The 1,5-bromonaphthol was also prepared from α-nitronaphthalene. Guareschi[16] has shown that when α-bromonaphthalene is brominated 1,5-bromonitronaphthalene is the chief product. This on reduction gives the 1,5-bromonaphthylamine.[17] It was found that by diazotizing the hydrochloride of this amine and hydrolyzing the resulting diazonium compound, 1,5-bromonaphthol could be obtained.[18] Although the diazotization took place very readily, the hydrolysis of the resulting diazonium salt presented difficulties. It was found that when the hydrolysis was carried out in solutions whose acid strength was less than normal a red dye was the only product obtained. By

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[16] Guareschi, *Ann.*, **222**, 290 (1884).

[17] Ullmann and Consonno, *Ber.*, **35**, 2803 (1902).

[18] This proved to be a much more convenient source than the *o*-bromophenyl-paraconic acid and was used almost exclusively after the constitution of the 1,5-bromonaphthol had been established by the Erdmann method and the products from the two sources had been shown to be identical.

use of 4 *N* sulfuric acid solutions a small amount of the naphthol was obtained, but even in this case the greater part of the material was recovered in the form of the dye. The following procedure was developed; it gave yields of 20 to 25%.

To a hot solution of 41 g. of 1,5-bromonaphthylamine in a liter of dil. hydrochloric acid solution (about 0.5 *N*), prepared by boiling the mixture for a few minutes, was quickly added a solution of 75 cc. of concd. sulfuric acid in 425 cc. of water whereupon the insoluble sulfate of the amine was precipitated in very fine, white crystals. The mixture was cooled rapidly to 0° and diazotized by the gradual addition of 11 g. of sodium nitrite in 75 cc. of water. A clear solution resulted. This was poured very slowly into a 10% solution of sulfuric acid which was kept boiling vigorously during the addition and then kept at the boiling point until the evolution of nitrogen had ceased. The whole process required about an hour. After the reaction mixture had cooled, the mixture of dye and naphthol which separated was filtered off, washed and extracted with alkali which removed the naphthol in the form of its soluble sodium salt. On acidification of the alkaline solution the naphthol precipitated in fluffy, white masses which were purified by recrystallization from hot water.

Anal. Subs., 0.1331: AgBr, 0.1132. Calc. for $C_{10}H_7OBr$: Br, 35.85. Found: 36.19.

Methylation of 1,5-Bromonaphthol.—To a solution of 5 g. of 1,5-bromonaphthol in 100 cc. of 1% sodium hydroxide solution was added two or three times the calculated amount of dimethyl sulfate and the mixture shaken vigorously. At the end of a minute the solution had become warm and crystals began to appear. The reaction was complete in about 15 minutes. The 1,5-methoxybromonaphthalene was filtered off and purified by recrystallization from alcohol. It forms in colorless plates; m. p., 67–68°; yield, 80%.

Anal. Subs., 0.1659: AgBr, 0.1324. Calc. for $C_{11}H_9OBr$: Br, 33.73. Found: 33.96.

The Preparation of 1,5-Methoxy-naphthoic Acid from 1,5-Methoxy-, Bromonaphthalene.—In the preparation of the naphthoic acid the bromine atom was replaced by the carboxyl group by means of the Grignard reaction.[19] A solution of 5.4 g. of 1,5-methoxy-bromonaphthalene in 15 cc. of absolute ether (dried over sodium) was placed in a half-liter round-bottom flask containing 0.5 g. of magnesium turnings. In order to keep out the air as completely as possible, the flask was equipped with a reflux condenser and the ether kept boiling vigorously during the course of the reaction. The condensation was so adjusted that a continuous stream of ether vapor was allowed to sweep out through the condenser, thus preventing the air from entering the apparatus. It was necessary, of course, to replenish the supply of ether in the flask from time to time. The reaction was initiated by the addition of a small amount of ethyl bromide. The Grignard compound which formed was almost insoluble in ether and was deposited in the form of a white paste so that it was difficult to tell when all of the magnesium had been used up.

The reaction was allowed to continue for several hours or until the magnesium had disappeared and then without removing the condenser a slow stream of carbon dioxide was passed into the mixture of Grignard compound and boiling ether. The Grignard reagent added rapidly to the carbon dioxide to form a thick paste which tended to collect in the mouth of the inlet tube and in order to prevent the tube from being closed it was fitted with a flaring mouth. The gas was passed in for four or five hours and the paste decomposed by hydrochloric acid. The ether solution containing the naphthoic acid was removed and evaporated to dryness; the crude acid was then dissolved in dil.

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[19] Compare Acree, *Ber.*, **37**, 625 (1904). Bodroux, *Bull. soc. chim.*, **31**, 32 (1904).

alkali and treated with carbon dioxide to remove the naphthol.[20] The methoxynaphthoic acid was obtained nearly pure by treating the solution with **dil.** hydrochloric acid. It formed in slightly yellow plates; m. p., 227–228.5°; yield, about **25%**.

Anal. Subs., 0.1624: CO_2, 0.4233; H_2O, 0.0711. Calc. for $C_{12}H_{10}O_3$: C, 71.26; H, 4.99. Found: C, 71.09; H, 4.91.

The Preparation of 1,5-Hydroxynaphthoic Acid.—The 1,5-hydroxynaphthoic acid was made by the method of Royle and Schedler.[21] 1,5-Aminosulfonic acid (Laurent's Acid) was used as the starting material. It was first diazotized and the diazo group then replaced by the cyano group by means of the Sandmeyer reaction. The resulting nitrile was hydrolyzed to the sulfonaphthoic acid which on fusion with alkali gave 1,5-hydroxynaphthoic acid. This acid was purified by recrystallization from hot water from which it separated in long, slender needles. Repeated treatment failed to remove all of the color. The final product, obtained after a long series of recrystallizations from water and alcohol, had a light buff tint and melted[22] at 231.5–233°.

Anal. Subs., 0.2306: CO_2, 0.5913; H_2O, 0.0881. Calc. for $C_{11}H_8O_3$: C, 70.19; H, 4.29. Found: C, 69.97; H, 4.28.

Methylation of 1,5-Hydroxynaphthoic Acid.—1,5-Hydroxynaphthoic acid was dissolved in an excess of 5% sodium hydroxide solution and the solution shaken with an excess of dimethyl sulfate, care being taken to prevent the mixture from becoming acid. The reaction was carried out at 40–60° and was found to go to completion in about 15 minutes. The solution was filtered while still alkaline and the filtrate then acidified by the addition of hydrochloric acid. The methyl ether which was thrown out by this treatment was filtered off and recrystallized from 95% alcohol. It crystallized in heavy, glistening plates; m. p., 227–228.5°.

Anal. Subs., 0.2301: CO_2, 0.5982; H_2O, 0.0991. Calc. for $C_{12}H_{10}O_3$: C, 71.26; H, 4.99. Found: C, 70.90; H, 4.82.

The writer wishes to take this opportunity to express his indebtedness to Professor W. H. Hunter for constant assistance and invaluable criticism both during the course of the work and in the preparation of the manuscript.

Summary

1. *o*-Bromophenyl-paraconic acid has been prepared and characterized and from it the 1,5-bromonaphthol has been made by the Erdmann ring closure, thereby establishing its orientation.

2. From the bromonaphthol so obtained 1,5-bromomethoxynaphtha-

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[20] This compound was the 1,5-methoxy-naphthol and was formed by oxidation of the Grignard reagent by the oxygen of the air. By recrystallization from hot water it was obtained in long, white needles melting at 139°. The melting point given in the literature [Bentley, Robinson and Weizmann, *J. Chem. Soc.*, **91,** 104 (1907)] is 140°. In order to settle conclusively the identity of the compound, it was methylated. The dimethoxynaphthalene so obtained melted at 183–184° which is the melting point given in the literature for "1,5"-dimethoxy-naphthalene.

[21] Ref. 13, p. 1647.

[22] The melting point given by Royle and Schedler for this compound (prepared by the same method) is 235–236°. Both their melting point and that observed by the writer are uncorrected. They reported an acetyl derivative melting at 202°. The writer has prepared this derivative from the acid melting at 231.5–233° and finds that it melts at 202–203°.

lene has been prepared by methylation. It has in turn been transformed into 1,5-methoxynaphthoic acid by use of the Grignard reaction.

3. The hydroxynaphthoic acid known as the "1,5" has been methylated and the resulting methoxynaphthoic acid has been found to be identical with that made from the bromonaphthol.
4. The so-called "1,5"-hydroxynaphthoic acid is, therefore, the 1,5 acid as has been assumed and the so-called "1,8" acid is shown to be the true 1,8 acid.
5. It has been concluded, accordingly, that the 1,8- and not the 1,5-hydroxynaphthoic acid forms the lactone.
6. Naphthalene cannot, therefore, have the centroid structure proposed by Huggins and by inference, at least, his structure for benzene is made doubtful.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

POLYHYDROXY-METHYLANTHRAQUINONES. IV. CONDENSATION OF OPIANIC ACID WITH SUBSTITUTED PHENOLS. ORIENTATION IN THE PREPARATION OF ANTHRAQUINONES

BY R. A. JACOBSON[1] WITH ROGER ADAMS

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Satisfactory methods for the synthesis of polysubstituted, in particular, polyhydroxy and polyhydroxy-methyl substituted anthraquinones are of interest on account of the large number of natural products and commercially important synthetic products belonging to this class of compounds. Many natural products are isomeric trihydroxy-methylanthraquinones, the most important containing two hydroxyl groups in one ring and one hydroxyl with one methyl in the other. A study of the methods which make possible the synthesis of many of these latter compounds has been undertaken in this Laboratory and the successful preparation of emodin has already been accomplished.[2] However, not all of the isomeric forms may be synthesized by the methods available. In this communication is reported a further development in the methods which will allow the production of many hitherto unavailable polyhydroxy- and polyhydroxy-methylanthraquinones.

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[1] This communication is an abstract of part of a thesis submitted by R. A. Jacobson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] (a) Graves and Adams, THIS JOURNAL, **45**, 2439 (1923). (b) Gardner and Adams, *ibid.*, **45**, 2455 (1923). (c) Jacobson and Adams, *ibid.*, **46**, 1312 (1924).