

after the ether was removed was distilled under reduced pressure. At 97° under 1 mm. pressure a small amount of dioxide oil was distilled.

Anal. Calcd. for $C_{10}H_{10}O_2$: H, 6.22; C, 74.04. Found: H, 6.06, 6.35; C, 74.23, 74.06.

The residue in the distilling flask was taken up in benzene and the solution allowed to stand overnight. Crystals of a dihydroxydibenzoate separated and were recrystallized from hot benzene; their melting point after recrystallization was 186°.

Anal. Calcd. for $C_{24}H_{22}O_6$: H, 5.42; C, 70.93. Found: H, 5.20, 5.35; C, 70.86, 70.75. *Mol. wt.* Calcd. for $C_{24}H_{22}O_6$: mol. wt., 406. Found: mol. wt. (boiling point method), 371.4.

The dibenzoate is only slightly soluble in most organic solvents but moderately soluble in chloroform and acetone.

Summary

1. The 3,4-hydroxybenzoate of phenylbutadiene was isolated as the primary product of the oxidation of *cis*-phenylbutadiene by means of perbenzoic acid, when the reaction was carried out at 0°. A dihydroxybenzoate was obtained from the same reagents at 25°.

2. The 3,4-hydroxybenzoate of phenylbutadiene was hydrolyzed with alkali to 3,4-dihydroxyphenylbutadiene and derivatives of the dihydroxy compound were prepared.

3. The 3,4-hydroxybenzoate of phenylbutadiene was decomposed by acids to the monoxide or the dimer of the monoxide of phenylbutadiene. The product obtained depended upon the acid used and the conditions under which the reaction took place.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ORIENTING INFLUENCES IN THE BENZENE RING. THE SULFONATION OF BENZOIC ACID¹

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Generally speaking, previous work has shown that benzoic acid may be sulfonated readily with strong sulfuric acid at high temperatures (*ca.* 200°) and by long duration of heating (two to twenty-four hours).² In this way about 90% of the product is the *m*-sulfobenzoic acid and the balance is the *para* isomer. Furthermore, Maarse,² incidental to a lengthy investigation of this problem, demonstrated that the *meta* isomer may be converted under the ordinary reaction conditions into the *para* isomer

¹ From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy. Presented before the Division of Organic Chemistry at the 82d Meeting of the American Chemical Society, Buffalo, N. Y., September, 1931.

² Maarse, *Rec. trav. chim.*, **33**, 207-238 (1914).

to the extent of about 15% although the reverse reaction was found to occur to about a three-fold greater degree. Now despite the fact that ortho substitution had been reported as totally absent and that metallic sulfates had no effect upon the sulfonation reaction, Dimroth and Schmaedel³ have stated that the presence of mercuric sulfate not only increases the degree of sulfonation but also permits sulfonation in the ortho position to the extent of 5%.³ Furthermore, Auger and Vary,⁴ sulfonating variously in the presence of iodine, always obtained all three isomeric sulfo-benzoic acids, of which the ortho amounted to only 1%. Although the main facts as presented above appear to be quite satisfactory, there are a few questions which are as yet unsettled. If the influence of such catalysts as iodine and mercuric sulfate is correctly reported, why does no ortho substitution normally take place? Why are the meta and para isomers so closely associated whereas all theories regarding orienting influences in the benzene ring demand that only the ortho and para isomers be so related? In addition, however, there were other rather interesting aspects which caused this problem to be investigated.

Without going thoroughly into the matter here, it was observed by the author from an extended study of the general problem of orienting influences that there was no substantial basis for the assumption that ortho and para substitution are closely related and opposed to meta substitution. Nevertheless it is perhaps well to present some of the more significant evidence for this particular point of view.

Although a superficial consideration of the evidence indicates that ortho substitution occurs frequently and perhaps always together with para substitution, whereas meta substitution takes place alone, a thorough examination will reveal that in nearly every case where an exhaustive study of the reaction products has been made, all three isomers are simultaneously formed.⁵ Indeed it is rather the great number of cases in which all three isomers do occur that leads one to believe that such is the normal circumstance. True enough the amount of meta substitution is almost negligible in cases where para substitution predominates, yet when meta substitution is the greatest, para substitution is always less than the accompanying ortho substitution. Table I clearly illustrates the argument.

The above figures show that whether para or meta substitution predominates it is accompanied principally by ortho substitution and consequently that ortho is no more closely related to para than to meta substitu-

³ Dimroth and Schmaedel, *Ber.*, **40**, 2411 (1907).

⁴ Auger and Vary, *Compt. rend.*, **173**, 239 (1931).

⁵ Exceptions are those such as sulfonation of nitrobenzene and benzene sulfonic acid where only the ortho isomer is absent. In such cases molecular rearrangements are known to occur and possibly account for the absence of the ortho isomer. Where halogenation gives no meta isomer, nitration shows that all three can occur as with toluene, and *vice versa* as with chlorobenzene.

TABLE I
NITRATION OF MONO-SUBSTITUTED BENZENES

Original substituent	% Meta	% Ortho	% Para
—COOH	76.5	22.3	1.2 [a]
—NO ₂	90.9	8.1	1.0 [b]
—SO ₃ H	68.3	19.9	6.2 [c]
—CH ₃	4.4	58.8	36.8 [d]
—OH	2.7	59.2	38 [e]
—Cl (bromination)	1.2	17.5	81.3 [f]
—NH(CH ₃ CO)	2.1	19.4	78.5 [g]

[a] Holleman, *Ber.*, **39**, 1716 (1906); [b] Holleman and de Bruyn, *Rec. trav. chim.*, **19**, 79 (1900); [c] Obermiller, *J. prakt. Chem.*, [2] **89**, 70 (1914); [d] Holleman and Vermeulen, *Chem. Centr.*, I, 1820 (1912); [e] Arnall, *J. Chem. Soc.*, **125**, 811 (1924); [f] Holleman and van der Linden, *Chem. Zentr.*, II, 640 (1910); [g] Arnall, *J. Soc. Chem. Ind.*, **48**, 1597 (1929).

tion. Furthermore, the simultaneous formation of the ortho and the meta isomer to the exclusion of the para is illustrated by the nitration of benzaldehyde in the presence of acetic anhydride, where 70% of the meta and 30% of the *o*-nitrobenzaldehyde were obtained.⁶ Also, Reddelien⁷ has found that benzaldehyde forms under certain conditions an addition compound with nitric acid which may be isolated as such. He then showed that this addition compound when treated with sulfuric acid alone yielded pure *m*-nitrobenzaldehyde. This, of course, was to be expected since the aldehyde group is a strong meta orienting substituent. But when this same benzaldehyde nitrate was treated with acetic anhydride in addition to the sulfuric acid, he obtained pure *p*-nitrobenzaldehyde. He further showed that whereas traces of *o*-nitrobenzaldehyde were found in both cases, at neither time did the para and the meta derivatives occur together. This experiment certainly suggests that ortho substitution takes place in any case and may be accompanied by either para or meta substitution. Generally, therefore, a careful examination of the evidence indicates that ortho substitution is midway between and equally related both to para and meta substitution and consequently this conception is proposed in place of the old and accepted one.

Closely related to the above aspect is the conclusion reached by Blanksma⁸ that indirect substitution occurs only when the substituents —OH, —NH₂, —NHR, —OR or —CH₃ are present in the ring. Furthermore, it has been stated by Holleman⁹ that indirect substitution leads always to ortho-para substitution, whereas direct substitution may lead to either ortho-para or to meta substitution, though principally to the latter. Now, as it

⁶ Holleman, *Rec. trav. chim.*, **33**, 1 (1914).

⁷ Reddelien, *J. prakt. Chem.*, **91**, 213 (1915); *Z. angew. Chem.*, **35**, 580 (1922).

⁸ Blanksma, *Rec. trav. chim.*, **21**, 282 (1902).

⁹ Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, p. 214.

will be shown later, it appears quite probable that in the sulfonation of benzoic acid, not only are ortho and meta substitution closely related but also they do occur indirectly. It may therefore be readily understood that the present investigation offered an opportunity to throw considerable light not only upon the specific question of the sulfonation of benzoic acid but also upon the general problem of orienting influences.

Indeed the available evidence suggests that the sulfonation of benzoic acid is actually an indirect substitution involving several intermediate compounds. Thus the first step, formation of an addition compound with the sulfuric acid, $C_6H_5COOH \cdot H_2SO_4$, is suggested by the work of Kendall and Carpenter,¹⁰ who have indicated the existence of this addition compound by cryoscopic measurements. Support for a second step, a condensation under the influence of excess sulfuric acid to form benzoyl sulfuric acid, is given by Oppenheim's¹¹ preparation of this latter compound from benzoyl chloride and sulfuric acid. As for a third step, Oppenheim observed that benzoyl sulfuric acid changed on long standing to sulfobenzoic acid though he did not specify exactly which isomer. This scheme, involving an addition compound, a condensation, and a rearrangement, is by no means uncommon, being known to take place in the sulfonation of aniline,¹² and in all probability in the sulfonation of both toluene and phenol.¹³ Yet these examples all lead to ortho and para substitution whereas no similar case of meta substitution is definitely known. Assuming, however, that with benzoic acid such a course of reaction does occur, a significant question is still unanswered. Are the para and meta isomers formed by a direct rearrangement of the benzoyl sulfuric acid or by a rearrangement of a possible intermediate *o*-sulfobenzoic acid? Indeed, it was the probability of the latter scheme that suggested the first step of this investigation.

Thus to determine whether the *o*-sulfobenzoic acid would rearrange to another isomer under the reaction conditions, it was heated with a large excess of concentrated sulfuric acid at 200° for various intervals of time from one-half hour to twelve hours. Upon recovering the potassium salts of the sulfobenzoic acids, they were converted to the hydroxybenzoic acids by fusion with caustic potash and the salicylic acid or the ortho isomer was removed from the mixture by extraction with chloroform in which it is readily soluble whereas the meta and para isomers are not. In this way it was found that the *o*-sulfobenzoic acid was converted solely to the meta isomer and the rate of conversion was thus quite readily determined.

¹⁰ Kendall and Carpenter, *THIS JOURNAL*, **36**, 2500 (1914).

¹¹ Oppenheim, *Ber.*, **3**, 736 (1870).

¹² See Gattermann, "Die Praxis des org. Chemikers," 21st ed., 1928, pp. 156-157.

¹³ Holleman and Caland, *Ber.*, **44**, 2509 (1911); Olsen and Goldstein, *Ind. Eng. Chem.*, **16**, 66 (1924); Baumann, *Ber.*, **11**, 1909 (1878).

Plotting the percentage of meta isomer against the time gave a regular curve approaching a maximum of about 85% in twelve hours (see Fig. 1). On the other hand, the natural logarithm of the concentration of the unchanged ortho isomer against the time gave a straight line as demanded by a monomolecular reaction. Similarly, with a view to the reported effect of mercuric sulfate on the sulfonation reaction, its influence upon this isomerization was studied. The rate of conversion was found to be greatly increased, over two-fold up to four hours of heating. The plot for the natural logarithm of unchanged ortho-isomer against the time was a straight line, suggesting as is very probable that this also is a mono-molecular reaction.

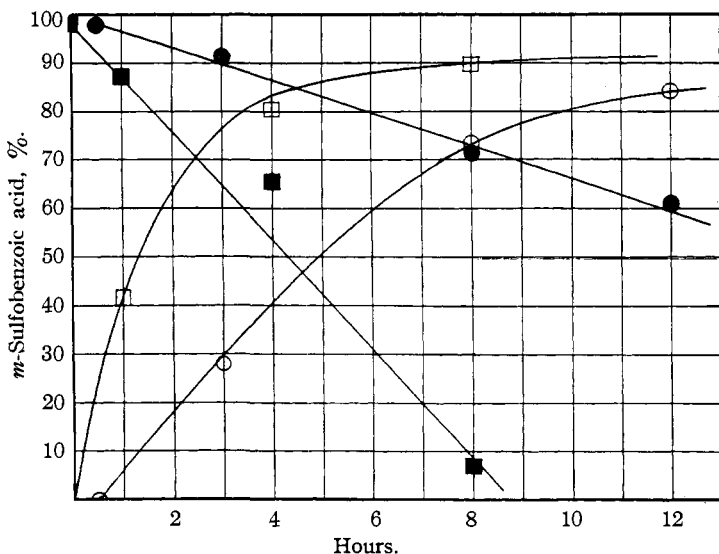


Fig. 1.—Isomerization of *o*-sulfobenzoic acid: ○ and ●, without mercuric sulfate; □ and ■, with mercuric sulfate; ● and ■, logarithm of the concentration of *o*-sulfobenzoic acid.

The sulfonation of benzoic acid at 200° both in the absence and presence of mercuric sulfate and for intervals of time where incomplete sulfonation would be obtained was then investigated. Thus, excepting that the unreacted benzoic acid was removed before fusion by extraction with ether of the solution of sulfobenzoic acids, an exactly similar procedure was followed and the degree of sulfonation and proportion of the isomers was determined for three, one, one-third and one-twelfth hours. The following results were obtained.

It is perfectly apparent that the sulfonation proceeds far more rapidly than is indicated by previous work. Furthermore, the percentage of recovered product decreases markedly from the percentage of sulfonation

TABLE II

Time, hrs.	SULFONATION OF BENZOIC ACID AT 200°			
	% Sulfonation (reacted C_6H_5COOH)	Recovered product, %	Ortho substitution, % Without Hg	With Hg
3	99.1	98.3	6.3 (high)	2.3
1	95.5	93.3	5.8	3.8
1/3	81.0	75.0	14.3	7.3
1/12	35.9	11.6	^a	^a

^a Only a trace of hydroxybenzoic acid was obtained (less than 0.05 g.).

calculated from the recovered unreacted benzoic acid. At five minutes practically no products were obtained although an apparent 36% sulfonation is definitely indicated. The same results are obtained when mercuric sulfate is present; but an explanation of this anomaly is suggested by a study of reaction velocity curves (see Fig. 2). The curve for the percent-

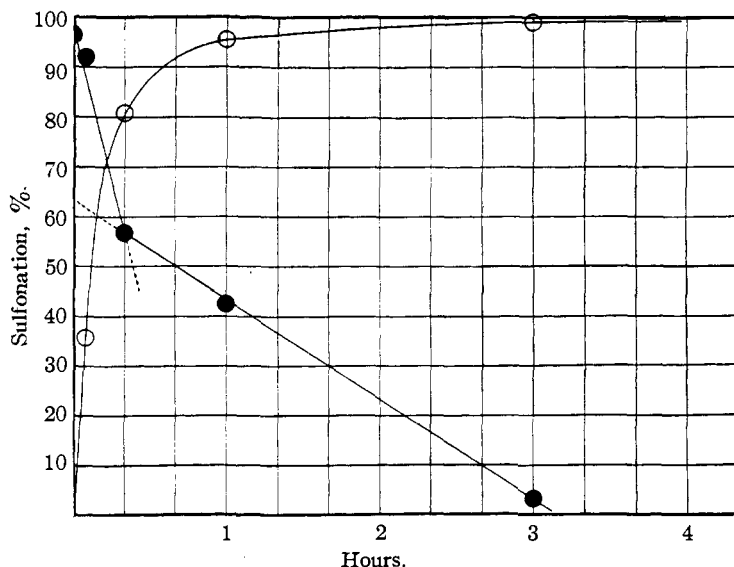


Fig. 2.—Sulfonation of benzoic acid at 200°: O, % sulfonation; ●, logarithm of the concentration of unreacted benzoic acid.

age of sulfonation against time is perfectly regular in every respect. However, the plot of the natural logarithm of the concentration of the unreacted benzoic acid against the time breaks rather abruptly at about twenty minutes. This great divergence can scarcely be attributed to an experimental error since a correction in the direction of less sulfonation would only increase it, whereas a correction in the other direction would indicate entirely too great a degree of sulfonation to be on the curve at all. Furthermore, the twenty-minute sulfonation as well as the others also was virtually run in duplicate since it has been shown that the presence of

mercuric sulfate in no way influences the degree of sulfonation. To continue, therefore, from twenty minutes to three hours, the plot is a perfect straight line, whereas from zero time to twenty minutes it is probably a slight curve though of a decidedly greater slope. It is scarcely to be doubted therefore that this curve represents two distinct reactions, a primary and a subsequent one. Indeed, the most plausible explanation of these facts is that the portion of the curve up to twenty minutes represents the condensation of the addition compound to the benzoyl-sulfuric acid, possibly accomplished through the agency of the excess sulfuric acid. This part of the line though not indicated in this way should curve where the inevitable shading off to the subsequent reaction takes place. From this point on the straight line demands a monomolecular reaction and probably represents the isomerization of the benzoyl-sulfuric acid not to the *m*-sulfobenzoic acid but to the ortho isomer. An examination of the figures in the table above reveals this fact since increasingly larger amounts of the ortho isomer are formed in the absence of mercuric sulfate than in its presence as the sulfonation becomes more incomplete. This fact coupled with the effect of mercuric sulfate on the conversion of the ortho to the meta isomer indicates very strongly that the ortho isomer is actually an intermediate product.

The above interpretation presents a fairly probable picture of the reaction mechanism and agrees with the scheme as originally proposed. For a complete explanation, however, one must consider the formation of the para isomer. Yet recalling the work of Maarse,² it appears very likely that this isomer is formed by a conversion of the *m*-sulfobenzoic acid. Indeed, preliminary work on the isomerization of the meta isomer reveals that certainly no more than a trace of the ortho isomer is formed although it is perfectly obvious from a regular decrease in the melting point that a slight admixture of another substance is present in increasingly larger amounts as the time of heating is lengthened. Although further study would be of considerable interest, it is believed nevertheless that a clear insight into the nature of this reaction has already been obtained.

In conclusion, however, it may be added that the above work bears directly on the general problem of orienting influences. Not only has the total absence of ortho substitution as previously reported been explained, but it has also been shown that the apparently simultaneous and exclusive formation of the meta and para isomers is not an anomalous case. Indeed, considerable support has been obtained for a more nearly correct view of the relation of the three isomeric positions among di-substituted benzenes. Inasmuch as direct conversion of the ortho to the para isomer is a well-known reaction (see above) and since the present work offers the conversion of the ortho to the meta isomer as a complementary case, it at once appears that ortho substitution occupies a unique place between meta and

para substitution and is equally related to both. This proposition is obviously not in harmony with the long-accepted and time-honored point of view upon which has been based all previous and present hypotheses to explain orienting influences in the benzene ring. Closely related to this aspect of the question are the contention of Holleman and also the proposition of Blanksma concerning the occurrence of direct and indirect substitution. However, it is perfectly obvious from the present investigation that the sulfonation of benzoic acid, a well-recognized case of meta substitution, is actually an example of indirect substitution. Thus with all due respect to the weight and value of Holleman's opinion, this study is offered as support for ideas which are at complete variance with his. In addition it must be mentioned that in the light of this investigation, the work of Dimroth and Schmaedel as previously presented is apparently in error.

Experimental Part

Pure *o*-sulfobenzoic acid was prepared by the hydrolysis of *o*-sulfobenzoic anhydride, recrystallized from benzene (m. p. 118.5°).¹⁴ Five grams of *o*-sulfobenzoic acid and 30 cc. of concentrated sulfuric acid (1.84) were placed in an Erlenmeyer flask and heated at 200° in an oil-bath for the desired length of time. The contents of the flask were run into about 800 cc. of water and neutralized with either barium carbonate or barium hydroxide. The precipitate of barium sulfate was removed by decantation of the supernatant liquid and filtration. The barium sulfate was also thoroughly washed with water, the washings being added to the filtrate. The residual barium contained in the filtrate as the barium salts of the sulfobenzoic acids was precipitated completely by addition of the necessary amount of dilute sulfuric acid. Following evaporation to about 400 cc. the barium sulfate was removed by decantation and filtration, the filtrate further evaporated, neutralized with potassium carbonate and finally evaporated to complete dryness.

The potassium salts of the sulfobenzoic acids thus obtained were powdered and fused with 10–15 g. of potassium hydroxide at 200–210° for two hours. The melt was completely dissolved with about 200 cc. of water and acidified with concentrated hydrochloric acid. The acidified solution was then extracted four times in a separatory funnel with 40 cc. of ether and the hydroxybenzoic acids obtained as a residue by distilling off the ether. This residue was then purified by extraction with absolute ether and a practically pure residue of hydroxybenzoic acids was thus obtained. Upon powdering this residue was extracted with 25 cc. of chloroform and removal of the chloroform by distillation gave a residue consisting of the *o*-hydroxybenzoic acid with a slight admixture of the meta isomer. The portion insoluble in chloroform was found to be practically pure *m*-hydroxybenzoic acid. The isomers were identified by their melting points and mixed melting points with the pure isomers. After weighing, a correction determined through solubility measurements was made for the admixture of the meta with the ortho isomer. It was thus readily possible to calculate the percentage conversion of the ortho to the *m*-sulfobenzoic acid.

The influence of mercuric sulfate was studied in a precisely similar fashion by the addition of 0.5 g. of this salt to the *o*-sulfobenzoic acid and sulfuric acid before heating.

The sulfonation of benzoic acid was investigated in the same way by dissolving 2.34

¹⁴ Obtained from Hynson, Westcott and Dunning, Baltimore, Md., through the courtesy of Dr. F. Dunning.

g. of benzoic acid (C. P.) in 30 cc. of concentrated sulfuric acid (1.84) and heating for the desired length of time, namely, three, one, one-third and one-twelfth hours. The influence of mercuric sulfate was again studied in a similar fashion by the addition of 0.5 g. of this salt to the reaction mixture. The subsequent procedure was identical with the isomerization experiments except for the removal of the unreacted benzoic acid. This was accomplished by extraction of the acid solution of the sulfobenzoic acids reduced to about 125 cc. three times with 25 cc. of ether. The benzoic acid was weighed and the percentage sulfonation calculated. Finally, to identify absolutely the presence of the ortho isomer, the chloroform soluble residue was powdered in the small extraction flask, placed on a boiling water-bath with a water filled test-tube held in the neck of the flask through a stopper, and the ortho isomer or salicylic acid allowed to sublime onto the outside of the test-tube. In this way the presence of the least trace of salicylic acid could be demonstrated, since it gave the characteristic purple color in a water solution when tested with ferric chloride. This procedure was found necessary both on account of the slight amount of residue and since the melting point method was not completely satisfactory.

The percentage sulfonation was determined not only by the recovered unreacted benzoic acid, but also by the recovered potassium salts and the yield of hydroxybenzoic acids.

The author herewith desires to express his appreciation and gratitude for the generous advice and kindly encouragement of E. Emmet Reid, Professor of Chemistry, Johns Hopkins University.

Summary

A reaction scheme for the sulfonation of benzoic acid has been proposed and supported by a study of the isomerization of *o*-sulfobenzoic acid and the actual sulfonation reaction.

A new relation between ortho, meta and para substitution has been proposed and evidence from the sulfonation of benzoic acid added to that already found in the literature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

ORGANIC REACTIONS WITH BORON FLUORIDE. I. THE PREPARATION OF ESTERS

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Bowlus and Nieuwland¹ found that boron fluoride united with acetic acid in the proportion of one mole of boron fluoride to two moles of acetic acid. This compound is a heavy liquid, fuming strongly in moist air. Analyses pointed to the formula $(\text{CH}_3\text{COOH})_2\text{BF}_3$. By the use of this compound as a catalytic agent a series of esters has been prepared. The question as to whether the catalytic effect observed is due to the acid-boron fluoride compound, or to the reaction of this substance with some of the alcohol to form the boron fluoride compound, is at present unanswered.

¹ Bowlus and Nieuwland, *THIS JOURNAL*, 53, 3835 (1931).