THE ELBS PERSULFATE OXIDATION

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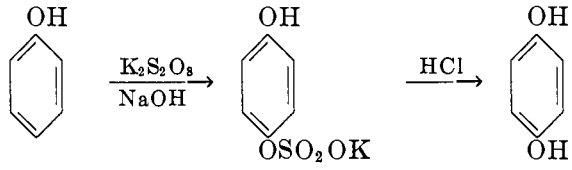
CONTENTS

I. INTRODUCTION

In 1893 Elbs (15) reported the oxidation of *o*-nitrophenol to nitroquinol by the action of ammonium persulfate in the presence of alkali. Later, potassium persulfate was substituted for ammonium persulfate and the reaction was extended to other substituted phenols (12). It was also shown that a hydroxyphenyl alkali sulfate is formed as an intermediate product, which is subsequently hydrolyzed in acid solution to quinol (12).



When the position para to the hydroxyl group is free, quinol derivatives are produced, but if that position is occupied, reaction takes place at the ortho position and a catechol derivative is obtained. The yields of the latter are, however, very poor.

Although this reaction affords a convenient method for the introduction of a hydroxyl group in the position para to the one present, it has been little used except in recent years. Its applicability has been studied recently in the case of many simple and substituted phenols, naphthols, coumarins, and flavones, and the success achieved suggests its more extensive use in synthetic work. The yields are often low but the products are usually isolated in a state of purity, owing to the fact that the intermediate hydroxyphenyl alkali sulfates are not extracted by ether from alkaline or acidified aqueous solutions so that the other organic products can readily be removed from the reaction mixture.

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In a few cases it has been noticed that oxidative coupling of the phenol nuclei takes place and biphenyl derivatives are formed. The formation of more complex products has also been noticed in some cases. A considerable amount of the unreacted material is generally recovered.

II. GENERAL REACTION CONDITIONS

Baker and Brown (3) have made a systematic study of this reaction and have established the following general reaction conditions:

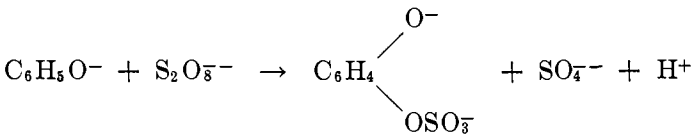
The phenolic compound (1 mole) is dissolved in a 10 per cent solution of sodium hydroxide (5 moles) and oxidized by the slow addition during 3–4 hr. of a saturated aqueous solution of potassium persulfate (1 mole). The reaction mixture is stirred continuously and the temperature not allowed to rise above 20°C. The reaction mixture is kept overnight and the next day acidified to Congo red, filtered if there is a precipitate, extracted with ether, and the unreacted starting material thus recovered. The aqueous layer is treated with excess of hydrochloric acid and heated on a steam bath for half an hour, and cooled. If there is any precipitate of the dihydric phenol it is filtered off, and the filtrate is extracted with ether to get a further quantity of the oxidation product.

The same authors find that no significant advantage is gained by using ammonium persulfate in place of potassium persulfate or by the addition of ferric chloride and that the yield is sometimes improved by carrying out the oxidation in solutions saturated with sodium chloride or sodium sulfate. When the dihydric phenol is easily soluble in water, it is an advantage to saturate the solution with carbon dioxide after the oxidation, extract it with ether (or alternately, if flocculent material is to be removed, acidify to Congo red, filter, extract with ether, and make alkaline to litmus with sodium hydrogen carbonate), evaporate the aqueous layer to dryness under diminished pressure, dissolve out the phenyl potassium sulfate derivative with 90 per cent alcohol, distil off the alcohol, and hydrolyze the residue with a small volume of 2 *N* acid, preferably under a layer of benzene or ether.

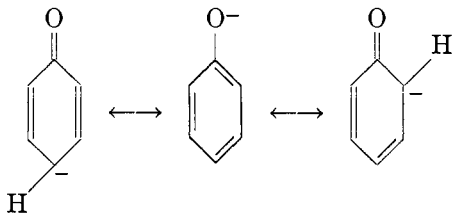
When the starting material is sparingly soluble in alkali, Rao and Seshadri (34) have found that the difficulty can be overcome by the judicious addition of pyridine. Addition of a small quantity of ferrous sulfate to the reaction mixture has been practiced (18, 47), but this does not appear to have any special advantage.

III. MECHANISM OF THE REACTION

Baker and Brown (3) have pointed out that the initial and final products of the Elbs persulfate oxidation of phenols must be represented by the following overall ionic equation, since the reaction is carried out in an alkaline aqueous solution:



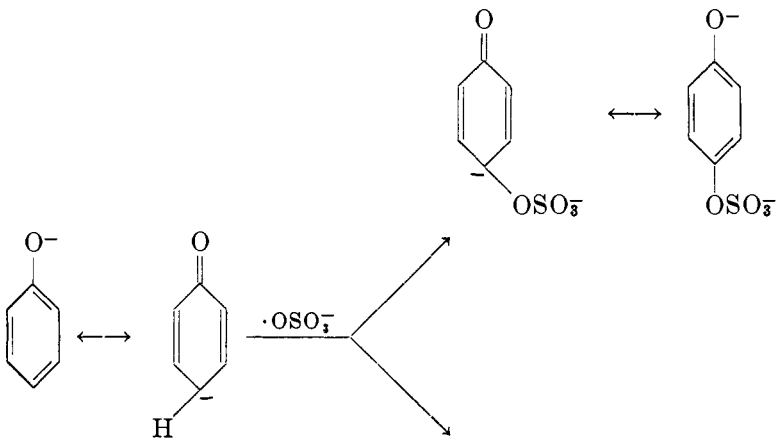
The direct introduction of the acid sulfate grouping, $—OSO_3^-$, in place of a hydrogen atom para or ortho (but never meta) to the phenolic oxygen atom, strongly suggests that resonance hybrids of the phenoxide ion may be involved.



If the persulfate ion is converted to a sulfate ion-radical, perhaps by interaction with a trace of a metal ion, e.g., a ferrous ion, then this reactive ion-radical can

$$Fe^{++} + S_2O_8^{--} \rightarrow Fe^{+++} + SO_4^{--} + \cdot OSO_3^-$$

attack one of the above resonance structures according to the following scheme:



4a

$$H\cdot \xrightarrow{S_2O_8^{--}} SO_4^{--} + H^+ + \cdot OSO_3^-$$

The slow rate of the reaction can be correlated with the requirement in the above mechanism that the sulfate ion-radical has to attack an anion. Reactions of this general type, i.e., those involving collisions between anions, are known, and the kinetics of such reactions and effect of added salts have been discussed in a number of texts (1a).

The oxidative coupling of the phenol nuclei which occasionally occurs may be due to the production of hydroxyl radicals by the following mechanism:

$$\cdot OSO_3^- + H_2O \rightarrow HSO_4^- + \cdot OH$$

Substituted phenyl radicals may then be formed which undergo dimerization.

$$C_6H_5O^- + \cdot OH \rightarrow {}^-OC_6H_4\cdot + H_2O \rightarrow {}^-OC_6H_4C_6H_4O^-$$

In this connection, the studies of Mertz and Waters (18b) on the oxidation

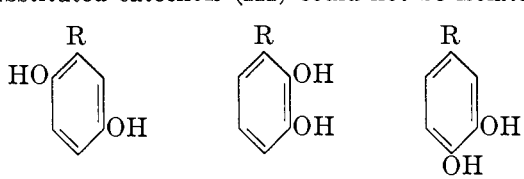
of aromatic compounds by hydrogen peroxide in the presence of ferrous salts showed that benzene was converted to phenol and biphenyl. A free-radical mechanism was suggested.

IV. OXIDATION OF PHENOLS AND NAPHTHOLS

A. Monohydric phenols

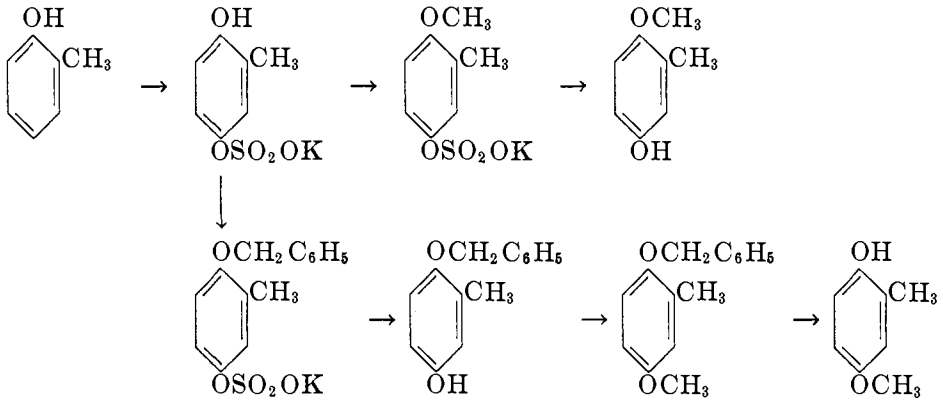
Oxidation of *o*-, *m*-, and *p*-cresols, *p*-chloro-, *p*-bromo-, and *p*-nitrophenols, salicylic acid, *p*-hydroxybenzoic acid, and *o*-, *m*-, and *p*-cresotic acids has been mentioned in the early patent literature (12). Gentisaldehyde, which is obtained in poor yield by the action of chloroform and alkali on quinol, can be obtained in good yield by oxidizing salicylaldehyde, the aldehyde group remaining intact (25). The same aldehyde was obtained in even better yield by the oxidation of *m*-hydroxybenzaldehyde (17). Baker and Brown (3) have studied systematically the application of this reaction to phenol, salicylaldehyde, *m*-5-xylenol, *m*-2-xylenol, *p*-xylenol, and *o*-chlorophenol. The highest yield (50 per cent) of the quinol derivative was obtained in the case of *o*-chlorophenol and the lowest (18 per cent) in the case of phenol. The original product recovered was highest (48 per cent) in the case of phenol and lowest (20 per cent) in the case of *o*-chlorophenol. The figures for the yields and recovery of the starting material were intermediate for the others. The same workers have studied the application of this reaction to phenols in which the position para to the hydroxyl group is substituted. The oxidation in these cases takes place in the ortho position but the yields are very poor. Thus in the case of *p*-cresol, vanillin, and *p*-hydroxybenzoic acid the yields were 9, 1.9, and 0.6 per cent, respectively, a large amount of the original product being recovered in the last two cases. That the simultaneous formation of the isomeric catechol derivatives along with the quinol derivatives is not precluded in this reaction is shown by the work of Forrest and Petrow (16). These workers found that in the preparation of gentisic acid by the persulfate oxidation of salicylic acid the purification of the crude product was difficult, owing to the presence of a persistent acidic impurity. They esterified the crude product and on fractional distillation of the derived methyl esters obtained methyl gentisate and methyl catechuate in the ratio of 6:1. In the case of other substances the ratios of the quinol to catechol derivatives were: phenol, 10:1; *o*-nitrophenol, 6:1; *o*-chlorophenol, 10:1; salicylaldehyde, 7:1; and *m*-hydroxybenzaldehyde, 22:1. These were separated by fractionation under reduced pressure.

m-Substituted phenols like *m*-hydroxybenzaldehyde and *m*-hydroxybenzoic acid gave compounds of type I with smaller quantities of the compounds of type II, but 4-substituted catechols (III) could not be isolated.



I II III

Baker and Brown (3) have shown that the stability of *p*-hydroxyphenyl potassium sulfate under alkaline conditions may be taken advantage of to prepare quinol monoalkyl ethers of known orientation by alkylating the *p*-hydroxyphenyl potassium sulfate. The synthetic possibilities are illustrated by them by the preparation of 5-benzyloxy-*m*-2-xylenol and the two isomeric monomethyl ethers of toluquinol and of 2,6-dimethylquinol. A further synthetic possibility is the preparation of both of the isomeric monoalkyl ethers of quinol from the same starting material by taking advantage of the fact that a benzyloxy group is much less readily hydrolyzed by acids than is the phenyl sulfate group.



B. Polyhydric phenols

In the oxidation of polyhydric phenols all except one hydroxyl group must usually be methylated in order to protect the molecule against general oxidation. The reaction has been applied to a number of such partially methylated phenols, generally with a view to obtaining the appropriate derivative required for further synthetic work. This reaction has simplified the synthesis of a number of naturally occurring products or their degradation products.

The phenol derivatives shown in table 1 have been subjected to this reaction and the corresponding para oxidation products obtained.

2-Hydroxy-5-methoxyacetophenone on similar oxidation gave the ortho oxidation product, 2,3-dihydroxy-5-methoxyacetophenone, in 1 per cent yield (4).

In the oxidation of 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-5-methoxyacetophenone, the diphenyl derivatives—4,4′-dihydroxy-3,3′-dimethoxydiphenyl-5,5′-dialdehyde and 2,2′-dihydroxy-5,5′-dimethoxy-3,3′-diacetylbiphenyl—formed as a result of oxidative coupling have been isolated.

It is found in general that the yields are increased by the presence of electron-attracting groups, by increasing substitution, and by the effect of substituents on the activity of the position para to the hydroxyl group. Thus, whereas 2-hydroxy-6-methoxyacetophenone gives a 38 per cent yield, 2-hydroxy-3-methoxyacetophenone gives only a 4 per cent yield of the oxidation product (3).

C. Naphthols

Desai and Sethna (14) have oxidized α- and β-naphthol and their derivatives. α-Naphthol, 2-acetyl-α-naphthol, and 1-hydroxy-2-naphthoic acid gave good

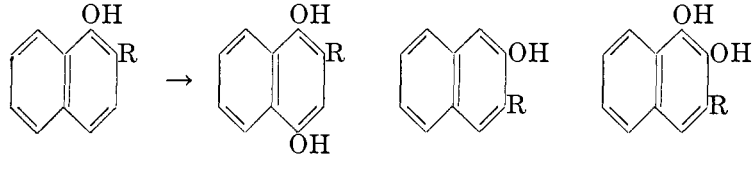
yields of the corresponding 4-hydroxy compounds. In the case of α-naphthol a large amount of a complex product was also formed. β-Naphthol and 2-hydroxy-3-naphthoic acid gave very poor yields of the corresponding 1,2-dihydroxy compounds. This is in agreement with the observations made in the case of phenol derivatives that where the position para to the hydroxyl group is

TABLE 1

Phenols oxidized by persulfate

PHENOL	REFERENCES
2,3-Dimethoxyphenol	(5)
2,3-Methylenedioxyphenol	(5)
2-Hydroxy-3,4-methylenedioxyallylbenzene	(5)
3-Hydroxy-4-methoxy-α-propenylbenzene	(44)
2-Hydroxy-3-methoxybenzaldehyde	(4)
2-Hydroxy-4-methoxybenzaldehyde	(31)
5-Hydroxy-4-methoxybenzaldehyde	(31)
2-Hydroxy-3-methoxyacetophenone	(4)
2-Hydroxy-4-methoxyacetophenone	(8)
2-Hydroxy-6-methoxyacetophenone	(1)
2-Hydroxy-6-benzyloxyacetophenone	(4)
2-Hydroxy-3,4-dimethoxyacetophenone	(2, 7)
2-Hydroxy-4,6-dimethoxyacetophenone	(42)
2-Hydroxy-4-benzyloxy-6-methoxyacetophenone	(22)
2-Hydroxy-3,4,6-trimethoxyacetophenone	(2)
2-Hydroxy-ω,4,6-trimethoxyacetophenone	(38)
2-Hydroxy-4-ethoxy-ω,6-dimethoxyacetophenone	(30)
2-Hydroxy-ω,4,6-triethoxyacetophenone	(39)
2-Hydroxy-ω,3,4,6-tetramethoxyacetophenone	(40)
2-Hydroxy-ω,3,6-trimethoxy-4-benzyloxyacetophenone	(43)
2-Hydroxy-3,4-dimethoxybenzophenone	(7)
2-Hydroxy-4-methoxybenzoic acid	(31)
5-Hydroxy-4-methoxybenzoic acid	(31)
2-Hydroxy-3,4-dimethoxybenzoic acid	(5)
2-Hydroxy-3,4-methylenedioxybenzoic acid	(5)
2-Hydroxycinnamic acid	(25)
2-Hydroxyphenylglyoxalic acid	(25)

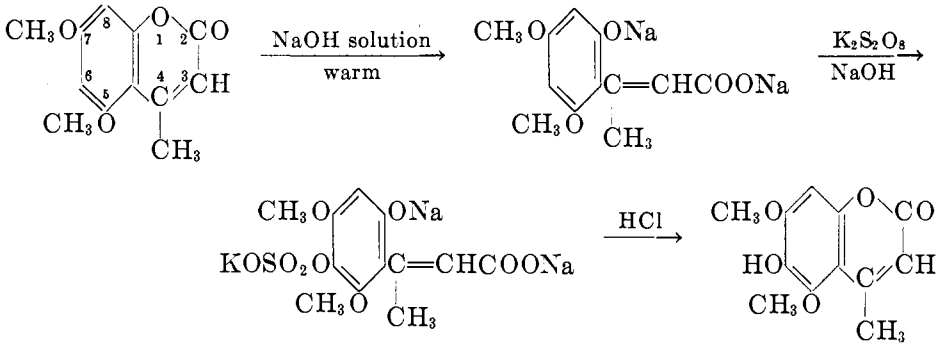
occupied the oxidation takes place in the ortho position but the yields are very poor.



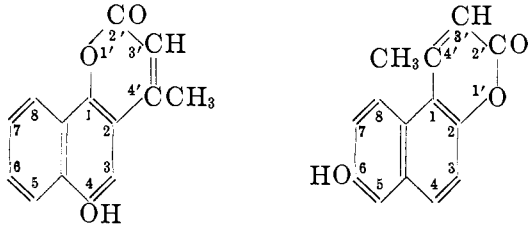
V. OXIDATION OF COUMARINS

The reaction was first applied to coumarins by Bargellini and Monti (9). Coumarin on oxidation gave 6-hydroxycoumarin and 7-methoxycoumarin gave

6-hydroxy-7-methoxycoumarin. 6-Hydroxycoumarin derivatives were also obtained in the oxidation of 7,8-dimethoxycoumarin, 7-methoxy-8-ethoxycoumarin, 7,8-diethoxycoumarin (7, 47), and 8-methoxycoumarin (18). Recently, Sethna and coworkers (13, 14, 26) have made a systematic study of the application of this reaction to coumarins. 4-Methyl-, 7-methoxy-4-methyl-, 5-methoxy-4-methyl-, 5-methoxy-4,7-dimethyl-, 5,7-dimethoxy-4-methyl-, and 7-8-dimethoxy-4-methylcoumarins have been oxidized and the corresponding 6-hydroxycoumarin derivatives obtained in good yields. They were thus able to synthesize the unknown 5,6-dihydroxy-4-methyl-, 5,6-dihydroxy-4,7-dimethyl-, 5,6,7-trihydroxy-4-methyl-, and 6,7,8-trihydroxy-4-methylcoumarins. The oxidation was carried out with completely methylated coumarins because the hydroxycoumarins generally gave pasty, uncrystallizable products and wherever a definite product could be isolated the yield of the oxidation product was very poor. The completely methylated coumarins were dissolved in alkali by warming on a steam bath, their dissolution being presumably due to the opening of the α-pyrone ring and the formation of an *o*-hydroxycinnamic acid derivative. The position para to the hydroxyl group formed by the opening of the ring is the 6-position in the original coumarin and therefore oxidation takes place in this position. In actual practice, therefore, it is the *o*-hydroxycinnamic acid derivative which is oxidized, the coumarin ring being formed again when the reaction mixture is acidified.



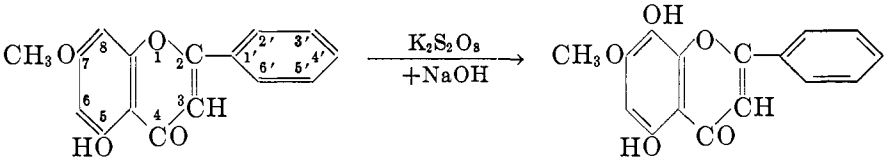
Further, 4′-methyl-1,2-naphtho-α-pyrone has been oxidized in good yield to 4-hydroxy-4′-methyl-1,2-naphtho-α-pyrone (I). Similar oxidation of 4′-methyl-2,1-naphtho-α-pyrone gave a product in poor yield, to which the tentative structure of 6-hydroxy-4′-methyl-2,1-naphtho-α-pyrone (II) has been assigned.



6-Methoxy-4-methyl- and 4,6-dimethylcoumarins were subjected to this reaction after opening the α-pyrone ring in hot alkali; in the former case only a pasty, uncrystallizable product was obtained and in the latter a small quantity of a product was obtained to which the 8-hydroxy-4,6-dimethylcoumarin structure has been assigned. 5-Hydroxy-4-methyl- and 5-hydroxy-4,7-dimethylcoumarins were dissolved in cold alkali and subjected to this reaction to determine whether the reaction takes place in the 8-position. Only complex products with high and indefinite melting points were obtained, probably owing to oxidative coupling taking place at the 6-position. The oxidation of 5-hydroxy-4-methylcoumarin-6-carboxylic acid was next tried; a product was obtained in poor yield to which the structure of 5,8-dihydroxy-4-methylcoumarin-6-carboxylic acid has been assigned. Oxidation of 5,7-dimethoxycoumarin gave the natural coumarin, fraxinol (6-hydroxy-5,7-dimethoxycoumarin) (13), previously obtained (46) by a longer method. In a note published recently Bhavsar and Desai (11) claim to have oxidized a number of coumarin derivatives by this method. Their detailed results are, however, not yet available.

VI. OXIDATION OF FLAVONES

Seshadri and coworkers have applied this reaction extensively with great success to the flavones and have converted the 5-hydroxyflavone derivatives into the 5,8-dihydroxy compounds with ease. This has led to a simpler synthesis of some flavones, e.g., wogonin, primetin, gossypetin, herbacetin, calycopterin, and nobiletin, which have been previously synthesized by other methods, and also to the synthesis of new flavone derivatives. Prior to oxidation the polyhydroxyflavones are usually partially methylated, leaving only the hydroxyl in the 5-position free. The difficulty arising out of the sparing solubility of these partial methyl ethers in aqueous alkali has been overcome by the addition of pyridine. In the case of some 5,7-dihydroxyflavones it is found that methylation is not necessary and that their ready solubility in alkali is an added convenience. The flavone derivatives shown in table 2 have been subjected to this reaction and the corresponding para oxidation products obtained.



The oxidation of ethyl 5-hydroxy-2-methylchromone-7-*O*-acetate to the 5,8-dihydroxy compound was carried out as a step in the synthesis of khellin (23).

The possibility of ortho oxidation in the flavone series has been tested. The oxidation of 7-hydroxy- and 7-hydroxy-3-methoxyflavones gave the 7,8-dihydroxy- and 7,8-dihydroxy-3-methoxyflavones in 10 and 20 per cent yields, respectively (24). Attempts to oxidize 5-hydroxy-3,7,8,3′,4′-pentamethoxyflavone were, however, unsuccessful (28). It appears from these results that although oxidation with persulfate does not proceed satisfactorily in the position

ortho to the phenolic hydroxyl group in general, it takes place better when the 8-position of the flavones is involved. 7-Hydroxyflavanols with one, two, and three methoxyl groups in the side phenyl nucleus have been oxidized in 10–15 per cent yield and the resulting products considered by analogy to be members of the 7,8-dihydroxyflavanol group (41). Attempts to carry out ortho oxidation in the side phenyl nucleus failed, however. Oxidation of 4′-hydroxy-3,7-dimethoxy-, 4′-hydroxy-3,5,7-trimethoxy-, 4′-hydroxy-3,5,7,3′-tetramethoxy-, and 4′-hydroxy-3,7,3′-trimethoxyflavones was attempted but only minute quantities of impure products were obtained (41). A free hydroxyl group in the 4′- or 3-position is detrimental to smooth oxidation with persulfate (37). Thus 5,7,4′-trihydroxyflavone gave an extremely small quantity of an impure product which

TABLE 2

Oxidation of flavones by persulfate

FLAVONE	REFERENCES
5-Hydroxy-	(27)
5-Hydroxy-3-methoxy-	(45)
5-Hydroxy-7-methoxy-	(32)
5-Hydroxy-7-benzyloxy-	(33)
5-Hydroxy-3,6-dimethoxy-	(6)
5-Hydroxy-3,7-dimethoxy-	(34)
5-Hydroxy-6,7-dimethoxy-	(19)
5-Hydroxy-3,7,4′-trimethoxy-	(35)
5-Hydroxy-7,3′,4′-trimethoxy-	(37)
5-Hydroxy-6,7,4′-trimethoxy-	(19)
5-Hydroxy-3,7,3′,4′-tetramethoxy-	(34)
5-Hydroxy-6,7,3′,4′-tetramethoxy-	(21)
5-Hydroxy-7,3′,4′,5′-tetramethoxy-	(37)
5-Hydroxy-3,6,7,3′,4′-pentamethoxy-	(28)
5-Hydroxy-3,7,3′,4′,5′-pentamethoxy-	(35)
5,7-Dihydroxy-	(32)
5,7-Dihydroxy-3-methoxy-	(34)
5,7-Dihydroxy-3,3′,4′-trimethoxy-	(34)

could not be purified, but 5,7-dihydroxy-4′-methoxyflavone and its 7-methyl ether underwent oxidation very satisfactorily.

VII. MISCELLANEOUS OXIDATIONS

Persulfate oxidation of *o*-hydroxychalcones has been successfully effected and a new hydroxyl group introduced in the 5-position, which corresponds to the 6-position in flavanones and flavones. Thus 2-hydroxy-4-methoxy- (29), 2-hydroxy-4,6-dimethoxy- (29), and 2-hydroxy-3,4,6-trimethoxychalcones (36) have been oxidized and the 2,5-dihydroxy compounds obtained in good yield.

p-Hydroxyphenylarsinic acid has been oxidized and a dihydroxyphenylarsinic acid obtained (15a).

8-Hydroxyquinoline has been successfully oxidized to 5,8-dihydroxyquinoline

(13). The latter decomposes rapidly on heating the aqueous solution and so a modified technique of working up the reaction mixture is used. The yield is, however, poor.

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