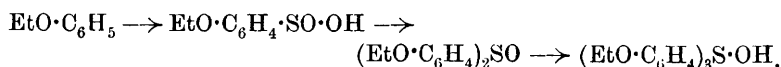


LXX.—*The Sulphination of Phenolic Ethers and the Influence of Substituents.*

By SAMUEL SMILES and ROBERT LE ROSSIGNOL.

IN a previous paper (Trans., 1906, 89, 696), the authors showed that the interaction of thionyl chloride and phenetole takes place in three successive stages, which are marked by the formation of the sulphinic acid, sulphoxide, and sulphonium salt. The whole reaction may be formulated thus :



To this process, where quadrivalent sulphur is introduced, we propose to apply the term sulphination in distinction to the name sulphonation which is given to the substitution of that element in the sexavalent condition.

In the communication above referred to, we were unable to isolate the phenetolesulphinic acid which should form the primary product of the reaction. We were limited to showing that this acid could be transformed by condensation with phenetole to a sulphoxide and sulphonium base, which were identical with the products obtained by the interaction of phenetole and thionyl chloride. It seemed desirable therefore to obtain a more direct proof that the sulphinic acid is the initial stage of sulphination. The object with which these experiments were undertaken was twofold, namely, (1) to show that a sulphinic acid is formed during the sulphination of an aromatic compound, and (2), since this result was achieved by employing a substituted phenolic ether, to study the effect of substitution on the course of this reaction. These may be considered separately.

Owing to the somewhat violent action of thionyl chloride and aluminium chloride on the phenolic ethers, we found it necessary to

devise a milder sulphinating reagent which could be more easily controlled. We found gaseous sulphur dioxide and aluminium chloride to be the most suitable reagent. Whilst our experiments with this reagent were nearing completion, we communicated in June, 1906 (Proc., 1906, **22**, 158), an outline of the results to the Society. A few weeks later, we heard from Prof. Knoevenagel that he also was engaged on similar work, and he directed our attention to the fact that at his instance a patent had already been taken out (Knoll & Co. D.R.-P. 171789 Sept. 16, 1905) for the preparation of sulphinic acid by this method; but here no mention was made of the formation of sulphoxides or sulphonium bases. Since our experiments had for the greater part not dealt with the substances examined by Prof. Knoevenagel, we agreed with him roughly to divide the field of investigation.

The action of this reagent on benzene has been previously noticed by Friedel and Crafts (*Ann. Chim. Phys.*, 1888, [vi], **14**, 443), by Adrianowsky (*J. Russ. Phys. Chem. Soc.*, 1879, **11**, 119), and by Colby and Loughlin (*Ber.*, 1887, **20**, 195). The first-named investigators merely state that they obtained benzenesulphinic acid by passing gaseous sulphur dioxide into a warm mixture of benzene and aluminium chloride; they do not give the quantities of the reagents or the yield of acid. Adrianowsky led sulphur dioxide over hot aluminium chloride and thus obtained the compound AlCl_3SO_2 ; this was found to react with warm benzene, giving benzenesulphinic acid. Colby and Loughlin, in describing their investigation of phenyl sulphoxide, mention that they obtained this substance by the action of sulphur dioxide on hot benzene and aluminium chloride. Finally, as above mentioned, Prof. Knoevenagel (*loc. cit.*) showed that sulphinic acids may be obtained in excellent yield by the action of gaseous sulphur dioxide on a mixture of an aromatic hydrocarbon and aluminium chloride; in the patent referred to, the example of benzenesulphinic acid is quoted. We have independently found (Proc., 1906, **22**, 158) that these reagents may be generally applied to the preparation of either aromatic sulphinic acids, sulphoxides, or sulphonium bases. It is shown in subsequent pages that the type and quantity of the products depend on the nature and position of the groups already attached to the aromatic nucleus. In some cases the reaction is confined to the preliminary stage, the sulphinic acid being then the sole product; in others the sulphination is more complete and the sulphonium base is formed, whilst with some substances the sulphination proceeds only as far as the intermediate stage, and with these the sulphoxide may preponderate.

The action of sulphur dioxide on a mixture of the aromatic substance and aluminium chloride takes place readily even at 0° . The mixture

rapidly absorbs the gas, and in a short time becomes warm, evolving hydrogen chloride.

With regard to the mechanism of the reaction, it might be supposed that the gas on entering the solution is converted by the aluminium chloride into thionyl chloride, which would then act in the nascent state on the aromatic compound. This view, however, seems untenable. Baud (*Ann. Chim. Phys.*, 1904, [viii], 1, 8) found that aluminium chloride and sulphur dioxide unite at the ordinary temperature, forming the compound $\text{Al}_2\text{Cl}_6 \cdot 2\text{SO}_2$ (see also Adrianowsky, *loc. cit.*); he also showed that when this substance is heated to 80° , it decomposes into sulphur dioxide and the compound $\text{Al}_2\text{Cl}_6 \cdot \text{SO}_2$, and the latter on further heating to about 200° yields sulphur tetrachloride; but according to the above hypothesis the compound $\text{Al}_2\text{Cl}_6 \cdot \text{SO}_2$ when heated should yield thionyl chloride and an oxychloride of aluminium. Furthermore, the interaction of thionyl chloride, benzene, and aluminium chloride at the ordinary temperature gives (Colby and Loughlin, *loc. cit.*) phenyl sulphoxide, whilst sulphur dioxide under the same conditions furnishes benzenesulphinic acid alone.

The contrast between the action of this reagent and that of thionyl chloride can be seen in the cases of benzene and *m*-5-xylenol methyl ether. In both instances, thionyl chloride furnishes less sulphinic acid and more sulphoxide than is obtained with gaseous sulphur dioxide, and with the xylenol ether the yield of sulphonium salt is also greatly increased. In spite of the milder action of sulphur dioxide, we have not been successful in isolating phenetolesulphinic acid from the products of sulphination of phenetole; nevertheless we have been able to obtain the acid from more complex phenolic ethers. *p*-Cresol methyl ether yields the sulphinic acid and sulphoxide, whilst the methyl ether of *m*-5-xylenol gives the three types of product: sulphinic acid, sulphoxide, and sulphonium base. These facts, together with those already advanced (*Trans.*, 1906, 89, 696), furnish definite proof that the sulphinic acids are the primary products of sulphination.

The influence of substitution on the course of the reaction was followed by examining the behaviour of various phenolic ethers. The experiments were conducted in a roughly quantitative manner, and a summary of the results is appended in the following table. In the first column, the compounds submitted to sulphination are given, whilst in the second, third, and fourth the yields of sulphinic acid, sulphoxide, sulphonium chloride from 20 grams of material are shown:

Twenty grams of	Yield in grams of sulphonic acid.	Yield in grams of sulphoxide.	Yield in grams of sulphonium salt.
Benzene	10	none	none
Toluene	8	<1	<1
Anisole	none	7—8	15—16
Phenetole	„	1—2	17—18
<i>m</i> -Cresol methyl ether	„	3	16
Resorcinol dimethyl ether	„	3*	12—16
Quinol dimethyl ether	„	4*	none
„ „ „ (SOCl ₂)	„	15*	„
<i>p</i> -Cresol methyl ether	3—4	12—14	„
<i>m</i> -5-Xylenol methyl ether	7	1·5	trace
„ „ „ (SOCl ₂)	1	12*	2

* Contain sulphide.

In each case the sulphination was carried out under as nearly as possible the same conditions; these together with the methods of isolating the products are described in the experimental part of this paper. The figures quoted for the yields are only approximate, but they are sufficient to show the relative amounts of each type of product formed during sulphination of each compound.

Constitution of the Products.

Before discussing the effect of substitution on the course of the reaction, it is necessary to consider the position taken up by the sulphinic group on combining with the aromatic nucleus in each of these substances.

Toluene.—The sulphinic acid obtained is identical with that prepared from *p*-toluidine; it is therefore the *para*-derivative.

Phenetole.—It has already been shown that with phenetole the sulphur group takes up the *para*-position with respect to the ethoxyl¹ (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 698). This was demonstrated from the facts that the phenetyl sulphoxide obtained is also formed by condensation of phenetole-*p*-sulphinic acid with phenetole, and that it may be oxidised to phenetole-*p*-sulphone.

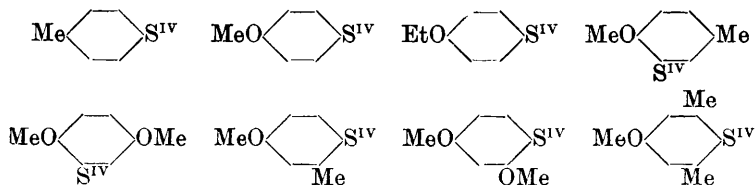
Anisole.—Similar facts have been collected to show that, also, with anisole, substitution takes place in the *para*-position. Anisylsulphoxide when oxidised yields the anisylsulphone which is obtained by methylation of phenol-*p*-sulphone. Further, Loth and Michaelis (*Ber.*, 1894, **27**, 2540), by the action of thionyl chloride and aluminium chloride in warm ethereal solution on anisole, obtained the anisyl sulphide which Mauthner (*Ber.*, 1906, **39**, 3593) has recently shown by synthesis from *p*-anisylmercaptan and *p*-iodoanisole to be the *para*-derivative.

p-Cresol Methyl Ether.—Here the sulphinic group enters the ortho-position with respect to the methoxyl group. This is proved as follows. The methyl ether of *p*-cresolsulphinic acid may be oxidised in alkaline solution to a sulphonic acid, which is identical with that obtained by sulphonation of the ether. The same chloride and amide are furnished by the sulphonic acid from either source. Now Alleman (*Amer. Chem. J.*, 1904, **31**, 25; see also Metcalf, *ibid.*, 1893, **15**, 320) has shown that sulphonation of the ether takes place in the ortho-position with respect to the methoxyl group, yielding *p*-methoxytoluene-*m*-sulphonic acid. Hence the sulphinic acid formed from *p*-cresol methyl ether is *p*-methoxytoluene-*m*-sulphinic acid. Additional strength is given to this conclusion by the fact that Gattermann (*Ber.*, 1899, **32**, 1144), on treating the diazonium salt of *p*-methoxy-*m*-toluidine with copper powder and sulphurous acid, obtained a sulphinic acid of the same melting point as that furnished by direct sulphination. We have not, however, submitted these two products to a closer comparison.

Quinol Dimethyl Ether.—Here the sulphinic group must occupy the ortho-position with respect to a methoxyl group.

From these instances, it is clear that on sulphinating the phenolic ethers the quadrivalent sulphur group enters the same position as the sulphonic group during sulphonation, and, indeed, this is to be expected from the general rules of substitution. It is well known that sulphonation of phenetole yields either the ortho- or para-sulphonic acids or both, according to the conditions of the reaction, and it is worth remarking that we have already observed (*Trans.*, 1906, **89**, 699) the formation of isomeric sulphonium salts during the interaction of thionyl chloride and phenetole.

Although in the three remaining ethers, resorcinol dimethyl ether, *m*-cresol methyl ether, and *m*-5-xylenol methyl ether, we have not been able to obtain direct proof of the position of the entrant sulphur group, there is little doubt from the behaviour of the ethers previously described that this is introduced in the para-position with respect to the methoxyl group. In the case of *m*-cresol, the conclusion is confirmed by the results of sulphonation, which yield *m*-hydroxytoluene-*o*-sulphonic acid (Claus and Krauss, *Ber.*, 1887, **20**, 3089). Beyond the analogy with other ethers, further evidence is lacking to show the structure of the sulphinic derivatives of *m*-5-xylenol; it is probable that the sulphur group occupies the para-position with respect to the methoxyl, but for the present purpose it is immaterial whether it takes the para or ortho situation, in either case the quadrivalent sulphur has two adjacent groups in the ortho-position. The following formulæ represent the constitution of these substances:



Discussion of Results.

The varying nature and amounts of the products obtained by sulphinating these ethers can be readily explained by considering the directing influence which the groups already attached to the benzene nucleus exert on the entrant quadrivalent sulphur group, and by the steric conditions under which the latter is placed. Although these influences are well known and often referred to by chemists, a few words on the sense in which we wish to apply them to the present question may not be out of place. By directing influence, we mean not only the guiding influence which a group exerts on another about to combine with the substance, but also the reactivity which it imparts to the benzene nucleus. On examining the parent substance, benzene, it seems that this is not very reactive, since only the sulphinic acid is formed; evidently, under the given conditions, benzene does not react with benzenesulphinic acid to give the sulphoxide. On the other hand, a derivative which contains a group of strong directing influence, such as methoxyl appears to be, will be inclined, by virtue of its increased reactivity to yield the later stages of the reaction; at the same time, the sulphinic group is directed to a special position, which, in this case, is ortho or para to the methoxyl. Thus anisole, in contrast to benzene, furnishes a large amount of the sulphonium salt, a small quantity of *p*-anisyl sulphoxide, and no sulphinic acid.

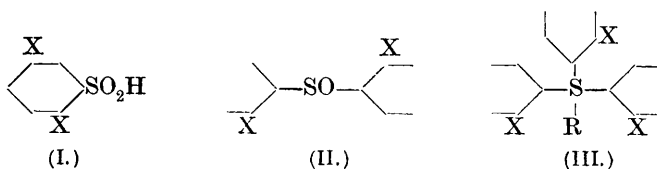
With regard to the influence of steric* conditions, it is well known that often in aromatic compounds the reactivity of a group seems to be lessened if the ortho-position is occupied. In many reactions, notably the semidine change (Jacobson, *Annalen*, 1895, 287, 97; 1898, 303, 290), and the formation of rosanilines (Noelting, *Ber.*, 1889, 22, 2573), these steric influences have been regarded from another standpoint: they are assumed to control the reaction in such a way as to avoid a product which contains accumulated ortho-substituents. It is this view which we adopt in the following discussion.

* We employ this term with some reserve, since Stewart and Baly (*Trans.*, 1906, 89, 489) have shown that the differences in reactivity of substituted quinones which have usually been ascribed to steric influences are due to quite different causes.

As already explained, it seems that in a substance which contains a group of strong directing influence the tendency will be to form the sulphonium base, but if the sulphur group enters the ortho-position with respect to a group already present, the reaction will be to a certain extent restrained, since ortho-substitution increases on passing through the successive stages. It is clear, then, that directing and steric influences will oppose one another, and, at any rate in the cases which we have examined, we think that by this conflict the varying products of sulphination can be satisfactorily explained.

With phenetole and anisole, substitution takes place in the para-position with respect to the methoxyl or ethoxyl group, and, there being no substituent in the ortho-position to the quadrivalent sulphur, the sulphination proceeds undisturbed by steric influences. The product is almost entirely sulphonium salt.

In the next pair of ethers, those of *p*-cresol and quinol, the sulphinic group takes up the ortho-position with respect to the methoxyl. The sulphinic acid (I), sulphoxide (II), and sulphonium base (III), which form the three successive stages of the reaction, would have the configurations :



and it is evident that, as the reaction proceeds, ortho-substituents are accumulated. With these ethers, the sulphonium salt is not formed during sulphination under the given conditions, the product consists chiefly of sulphoxide, and, in the case of *p*-cresol, an appreciable quantity of sulphinic acid. This suppression of the sulphonium salt is clearly due to the inhibiting action of the ortho-substitution, which attains the maximum at this stage.

Turning now to the ethers of resorcinol and *m*-cresol, we again find that the sulphinic group takes up an ortho-position with respect to methyl or methoxyl, and the configuration of the three products will be as before, the sulphoxide being doubly ortho-substituted, and the sulphonium salt trebly so. The steric relations in these substances are therefore similar to those in the above-mentioned ethers of *p*-cresol and quinol, but the products of sulphination are very different. In both cases, the chief product is the sulphonium salt, with a very small quantity of sulphoxide. Here it is evident that the steric inhibition is overcome by the directing influences of the methyl and methoxyl groups, and it will be seen in resorcinol and *m*-cresol methyl ether (I)

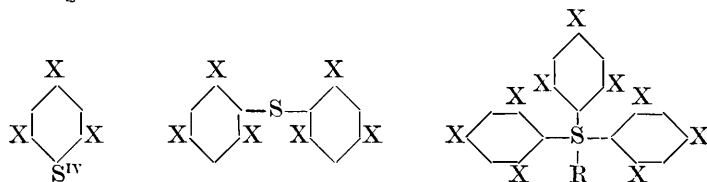
that these reinforce one another at the point of substitution,



whilst with quinol and *p*-cresol methyl ether (II) they do not. In the latter pair of ethers, the inhibiting effect of triple ortho-substitution is sufficient to overcome the comparatively weak directing influences but in the first-named ethers the directing influences are strengthened and the steric effect is in turn overcome.

The next ether, that of *m*-5-xylenol, shows yet a different behaviour.

The three stages in the sulphination of this substance would have the configuration :



whence it is seen that the sulphinic acid would contain two ortho-substituents, the sulphoxide four, and the sulphonium base six. In comparison with *m*-cresol ether, the directing influences are strengthened, since the three substituents reinforce one another; but at the same time the steric inhibition is greatly augmented by the increased ortho-substitution, and its action is now sufficient to affect the course of the sulphination. Thus it is found that the sulphinic acid appears as the chief product, whilst the sulphonium base is almost completely suppressed, less than 1 gram of this being formed from 20 grams of the ether. From the same amount of *m*-cresol ether, 16 grams of sulphonium salt were obtained, and the sulphinic acid could not be detected.

The ethers of phenol, *m*-cresol, and *m*-5-xylenol thus form a series in which both directing and steric influences increase. In the first two substances, the directing influences are dominant, but with the third, as mentioned above, steric hindrance comes into play. The effect of steric hindrance may also be brought out by lessening the directing influences, as on passing from *m*-cresol to *p*-cresol. The latter substance yields no sulphonium salt.

It is of some interest to compare the behaviour of toluene and phenetole. With the former substance the second and third stages of the reaction are almost suppressed, whilst with the ether the sulphonium salt is formed in large quantity. Evidently this is due to

the weaker directing influence of the methyl group, the steric relations in the two cases being similar.

Finally, we wish to remark that when it is stated that the sulphonium salt is not formed, we do not necessarily mean that this does not exist. Thus, in the case of *p*-cresol ether, it is shown that the use of a stronger condensing reagent than aluminium chloride readily furnishes the sulphonium base. It should be further noticed that a different sulphinating agent may lead to very different results, and this can be seen by comparing the action of sulphur dioxide with that of thionyl chloride in *m*-5-xylenol ether. The latter agent increases the yield of the sulphonium salt and lessens that of the sulphinic acid. In fact, what has been said of the sulphination of these phenolic ethers only refers to the reaction as carried out under the special conditions described in the experimental part of this paper.

EXPERIMENTAL.

In all the subsequent experiments, unless otherwise stated, the sulphination was carried out as follows. The liquid to be sulphinated was first gradually mixed with an equal weight of finely-powdered aluminium chloride. During the process, considerable heat was developed, hence the contents of the flask were thoroughly cooled in order to avoid hydrolysis of the phenolic ether. The vessel having been immersed in melting ice, gaseous sulphur dioxide was allowed to bubble through the liquid contents, the passage of the gas being regulated so as to confine the temperature of the solution below 15°. The process was continued until the mixture was saturated or had become solid. Finally, the product was set aside at the atmospheric temperature for two hours, and then decomposed with powdered ice or cold water. Usually the process of sulphination occupied from six to eight hours.

The method of isolating the products was varied according to the requirements of each case. Generally the acid liquid obtained by decomposing the product of sulphination was extracted with chloroform in which the three substances sulphinic acid, sulfoxide, and sulphonium chloride are soluble.

The presence of either of these products was established by the isolation and analysis of the substance in question. On the other hand, the conclusion that they were absent rests on a rather less firm basis. The absence of the sulphinic acid was inferred from the results of examining the alkaline extract from the chloroform solution. The sulphonium salts were tested for by adding aqueous chloroplatinic acid to the original acid liquid or to the aqueous extract from the chloroform solution; the platinichlorides of these bases are very sparingly soluble

in water, and if no precipitate was obtained in applying this test it was inferred that the base in question was absent. Since these tests are by no means quantitative, any negative conclusion drawn from them is clearly somewhat insecure. Hence, when it is mentioned that neither sulphinic acid nor sulphonium base are present, the statement is made with some reserve; the substances may occur in very small quantity, but far too small to be isolated, and certainly not sufficient to affect the general conclusions drawn from these experiments.

Benzene.

Benzenesulphinic Acid.—Sulphination as above. On treatment with ice and hydrochloric acid, the mass furnished a pale yellow solid, which was collected and dissolved in dilute aqueous sodium hydroxide. Benzenesulphinic acid was precipitated from this alkaline solution by the addition of dilute mineral acid. Twenty grams of benzene yielded 10 grams of the acid. Neither sulphoxide nor sulphonium salt were observed in the product of sulphination under the above conditions. On account of its cheapness and the ease with which it is carried out, this method of preparing benzenesulphinic acid is superior to the reduction of the sulphonic chloride or to the decomposition of benzenediazonium salts with copper powder.

Toluene.

Toluene-p-sulphinic Acid.—Sulphination as above. By decomposing the product with water and hydrochloric acid, a yellow, solid mass was obtained; this was dissolved in chloroform, and the solution was extracted with aqueous sodium hydroxide. The alkaline liquid was mixed with excess of dilute sulphuric acid and cooled; the toluenesulphinic acid which separated (8 grams) was collected and recrystallised, and it finally melted at 84—85°. A mixture of this with toluene-*p*-sulphinic acid, prepared from *p*-toluidine, melted at the same temperature. Small quantities, less than one gram, of sulphoxide and sulphonium chloride were respectively obtained from the chloroform solution and from the original acid liquid. The presence of the sulphonium salt in the latter was recognised by precipitation with chloroplatinic acid. These substances were not closely examined.

Anisole.

Anisyl Sulphoxide, $(C_6H_4 \cdot OMe)_2SO$, and *Trianisylsulphonium*,
 $(C_6H_4 \cdot OMe)_3S^+$.

—Sulphination as usual. The product was slowly poured into cold water, and the resulting liquid, after the usual addition of acid, was repeatedly extracted with ether. The united ethereal extracts were shaken with dilute aqueous alkali hydroxide, and, on acidifying this, a small quantity of phenol was obtained, but no sulphinic acid was detected.

Anisyl Sulphoxide.—The ethereal solution was evaporated, and, after anisole had been removed by distillation in a current of steam, the residue was collected and dried. The product, anisyl sulphoxide, was almost pure; when recrystallised from hot ethyl acetate, it formed colourless prisms which melted at $93-94^\circ$ (Loth and Michaelis, *Ber.*, 1894, **27**, 2540, give 96°). Analysis yielded the following data:

0.2390 gave 0.5599 CO_2 and 0.1251 H_2O . C = 63.89; H = 5.81.

0.2355 ,, 0.1884 $BaSO_4$. S = 12.59.

$C_{14}H_{14}O_3S$ requires C = 64.12; H = 5.34; S = 12.21 per cent.

Trianisylsulphonium.—The aqueous layer from the original ethereal extract was evaporated on the water-bath until a considerable quantity of oil had separated. The liquid was cooled, and then extracted with chloroform. Finally, the chloroform solution was distilled, and the oily residue of sulphonium chloride was dried in the steam-oven. Trianisylsulphonium chloride, when set aside at the ordinary temperature, gradually solidifies to a mass of colourless needles, which are soluble in water, alcohol, or chloroform. For analysis, the salt was converted into the platinichloride.

Trianisylsulphonium platinichloride separates from a warm mixture of alcohol and epichlorohydrin in orange needles which melt at 221° :

0.2197 gave 0.3629 CO_2 and 0.0789 H_2O . C = 45.04; H = 3.99.

0.2513 ,, 0.0438 Pt. Pt = 17.42.

$C_{42}H_{42}O_6Cl_6S_2Pt$ requires C = 45.24; H = 3.77; Pt = 17.5 per cent.

Twenty grams of anisole yielded 8 grams of anisyl sulphoxide and 15 grams of trianisylsulphonium chloride. In another experiment with the same quantity of anisole, 7 grams of sulphoxide and 16 grams of sulphonium chloride were obtained. In neither case was anisylsulphinic acid detected.

Anisylsulphone, $(C_6H_4 \cdot OMe)_2SO_2$. (1) *Oxidation of Anisyl Sulphoxide*.—The sulphoxide was treated with potassium permanganate in glacial acetic acid solution (see Smiles and Le Rossignol, *loc. cit.*). The product, when recrystallised from alcohol, formed colourless prisms which

melted at 129° (Loth and Michaelis, *loc. cit.*, give 120°, and Annaheim, *Annalen*, 1874, 172, 36, gives 130°).

(2) *Methylation of p-Phenolsulphone*.—The methylation was effected with an alkaline solution of methyl iodide in methyl alcohol. The re-crystallised product melted at 129°, and was identical with the above, since a mixture of the two melted at the same temperature :

0.2558 gave 0.2050 BaSO₄. S = 11.93

C₁₄H₁₄O₄S requires S = 11.51 per cent.

Phenetole.

Phenetyl Sulphoxide, (C₆H₄·OEt)₂SO, and *Triphenetylsulphonium*, (C₆H₄·OEt)₃S⁺.—Sulphination as above. The reaction product was worked up by a process similar to that described with anisole. The products, phenetyl sulphoxide and triphenetylsulphonium chloride, were found to be identical with those obtained with the action of thionyl and aluminium chlorides on phenetole (Smiles and Le Rossignol, *loc. cit.*). Two experiments, each with 20 grams of phenetole, furnished respectively 1 gram of sulphoxide with 17 grams of sulphonium chloride, and 2 grams of sulphoxide with 18 grams of sulphonium chloride.

m-Cresol Methyl Ether.

m-Methoxytolyl Sulphoxide, (C₆H₃Me·OMe)₂SO, and *Tri-m-methoxytolylsulphonium*, (C₆H₃Me·OMe)₃S⁺.—The sulphination and method of treatment were the same as with anisole. The sulphoxide was isolated as a pale yellow oil; this was covered with dry ether, and set aside at the ordinary temperature. After the lapse of two weeks, the substance crystallised in colourless prisms, which were collected and purified from ethyl alcohol. *m-Methoxytolyl sulphoxide* melts at 83—84°, is soluble in hot ethyl acetate or alcohol, and gives a deep violet solution with concentrated sulphuric acid :

0.1589 gave 0.3840 CO₂ and 0.0844 H₂O. C = 65.90; H = 5.90.

0.2264 „ 0.1484 BaSO₄. S = 11.32.

C₁₆H₁₈O₃S requires C = 66.20; H = 6.20; S = 11.03 per cent.

The crude sulphonium chloride formed a viscous liquid which did not show signs of crystallisation until it had remained four or five weeks under dry ether. It was converted into the platinichloride.

m-Methoxytolylsulphonium platinichloride forms orange-coloured plates which melt at 138—140° :

0.1990 gave 0.3501 CO₂ and 0.0829 H₂O. C = 47.9; H = 4.62.

0.1646 „ 0.0272 Pt. Pt = 16.52.

C₄₈H₅₄O₆Cl₆S₂Pt requires C = 48.08; H = 4.58; Pt = 16.27 per cent.

Twenty grams of *m*-cresol methyl ether furnished 3 grams of sulphoxide and 16 grams of sulphonium base. No sulphinic acid was detected.

Resorcinol Dimethyl Ether.

tris-*m*-Dimethoxyphenylsulphonium, $(C_6H_3 \cdot OMe)_3S^+$.—Sulphination as usual. The product was decomposed with ice-water, and then separated from unchanged phenolic ether by distillation in a current of steam. The residue was repeatedly extracted with hot water. The united extracts were filtered to remove small quantities of oily impurity, and were then set aside to cool.

The sulphonium chloride separated at first as an oil, but later in the crystalline form. When the liquid had cooled, the solid was collected.

tris-*m*-Dimethoxyphenylsulphonium chloride separates from warm moist acetone in flocculent aggregates of minute needles which melt at 129—130°. The substance is sparingly soluble in cold acetone or water, and extremely so in alcohol. It contains water of crystallisation; an air-dried sample was heated to constant weight at 110°, when it was found that:

0·1697 lost 0·0266 H_2O . $H_2O = 15·67$.

0·1663 „ 0·0262 H_2O . $H_2O = 15·75$.

$C_{24}H_{27}O_6ClS, 5H_2O$ requires $H_2O = 15·81$ per cent.

Determinations of halogen and of sulphur were made in the air-dried substance:

0·2481 gave 0·0652 $AgCl$. $Cl = 6·49$.

0·2419 „ 0·1076 $BaSO_4$. $S = 6·10$.

$C_{24}H_{27}O_6ClS, 5H_2O$ requires $Cl = 6·24$; $S = 5·63$ per cent.

The anhydrous salt was also analysed:

0·1431 gave 0·3134 CO_2 and 0·0762 H_2O . $C = 59·72$; $H = 5·91$.

$C_{24}H_{27}O_6ClS$ requires $C = 60·19$; $H = 5·64$ per cent.

This sulphonium chloride gives an intensely reddish-violet solution with concentrated sulphuric acid.

The *platinichloride* was isolated as a flesh-coloured, crystalline powder, which was insoluble in water. It melts at 153—155°:

0·1852 gave 0·0273 Pt . $Pt = 14·74$.

$C_{48}H_{54}O_{12}Cl_6S_2Pt$ requires $Pt = 15·06$ per cent.

The residue from which the chloride had been extracted with water consisted of a pale brown, amorphous mass. This apparently contained at least two substances, one of which was soluble in hot alcohol, and the other quite insoluble; but, since attempts to purify them were not successful, it remains doubtful at present whether either was the

required sulphoxide. Both substances imparted a reddish-violet colour to concentrated sulphuric acid.

In the above method of treatment, the product of sulphination is submitted to distillation with steam, and for this reason the process would not be suitable for isolating the sulphinic acid, should it be formed, since substances of this class are readily decomposed by hot aqueous mineral acids. Hence another experiment was performed in which the sulphinic acid was especially sought for, but none could be found.

Twenty grams of resorcinol dimethyl ether yielded in two different experiments 15—16 grams and 12 grams of sulphonium chloride. The formation of sulphoxide could not be proved, but it probably occurs in small amount.

Judging from analogy to quinol dimethyl ether (see later), the amorphous mass above referred to probably consists of a mixture of sulphide and sulphoxide.

p-Cresol Methyl Ether.

Sulphinic Acid, $\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_2\text{H}$ ($\text{Me}:\text{OMe}:\text{SO}_2\text{H} = 1:4:3$), and *Sulphoxide*, $(\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me})_2\text{SO}$.—Sulphination as usual. The mixture of aluminium salts was decomposed in the usual manner with ice-water and hydrochloric acid. The sulphinic acid and sulphoxide now appeared as a crystalline suspension in the acid liquid; they were removed by extraction with chloroform. *p*-Methoxytoluene-*m*-sulphinic acid was isolated by first shaking the chloroform solution with aqueous sodium carbonate and then acidifying the latter with dilute mineral acid. After recrystallisation from hot water, it melted at 96—97° (Gattermann, *Ber.*, 1899, 32, 1144, gives 97°):

0.2047 gave 0.3865 CO_2 and 0.0998 H_2O . C = 51.49; H = 5.40.

$\text{C}_8\text{H}_{10}\text{O}_3\text{S}$ requires C = 51.6; H = 5.37 per cent.

This acid gives a bright blue solution with concentrated sulphuric acid.

Oxidation of p-Methoxytoluene-m-sulphinic Acid to the Sulphonic Acid, $\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H}$.—A solution of the acid in excess of aqueous alkali hydroxide was warmed on the water-bath with the calculated amount of potassium permanganate. Towards the end of the reaction, alcohol was added to remove the green colour. The liquid was then successively filtered, neutralised with carbon dioxide, and evaporated to dryness. The sulphonyl chloride was prepared from the mixture of alkali salts; it separated from acetone in large, colourless plates which melted at 83—84°. When set aside with cold strong ammonia for forty-eight hours, the chloride furnished an amide melting at 182°.

Alleman (*loc. cit.*), by sulphonation of *p*-cresol methyl ether,

obtained a sulphonic acid which he showed to be of the structure $\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{H}$ ($\text{Me}:\text{OMe}:\text{SO}_3\text{H} = 1:4:3$). According to the same author, the chloride and amide of this acid melt respectively at $83\cdot5\text{--}84^\circ$ and $180\text{--}181^\circ$. We prepared these substances and were able to confirm the above temperatures of fusion. We also found that a mixture of the chloride or amide and the corresponding derivative prepared from the sulphinic acid melts at the same temperature as the pure substance from either source; hence oxidation of the sulphinic acid yields the sulphonic acid of the above constitution.

The chloroform solution from which the sulphinic acid had been extracted was dried and then distilled. The residue of almost pure sulphoxide was oily, but it immediately solidified on contact with dry ether. *p-Methoxytoluene sulphoxide*, $(\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me})_2\text{SO}$, forms shining prisms, which melt at $133\text{--}134^\circ$ and are soluble in hot ethyl acetate or alcohol. With concentrated sulphuric acid, it gives a deep violet solution, which is decolorised by the addition of *p*-cresol methyl ether:

0.2938 gave 0.7089 CO_2 and 0.1654 H_2O . C = 65.81; H = 6.26.

0.2268 ,, 0.1839 BaSO_4 . S = 11.13.

$\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$ requires C = 66.20; H = 6.2; S = 11.03 per cent.

No sulphonium chloride could be detected in the product of sulphination.

From 20 grams of *p*-cresol methyl ether, 4 grams of sulphinic acid and 14 grams of sulphoxide were obtained. In another experiment, the yield of acid was about 3.5 grams and of sulphoxide 12 grams.

tris-p-Methoxytolylsulphonium, $(\text{MeO}\cdot\text{C}_6\text{H}_3\text{Me})_3\text{S}^+$.—*p*-Cresol methyl ether was slowly mixed with a solution of the sulphoxide in concentrated sulphuric acid. When sufficient phenolic ether had been added to change the colour to pure red, the solution was poured into a large bulk of ice-cold water. The sulphonium sulphate then separated as a semi-solid precipitate, which was converted in aqueous solution into the chloride. The addition of chloroplatinic acid to the latter yielded *tris-p-methoxytolylsulphonium platinichloride* as a flesh-coloured precipitate which melted at $230\text{--}231^\circ$:

0.1511 gave 0.2653 CO_2 and 0.0590 H_2O . C = 47.88; H = 4.33.

0.1878 ,, 0.0300 Pt. Pt = 15.97.

$\text{C}_{48}\text{H}_{54}\text{O}_6\text{Cl}_6\text{S}_2\text{Pt}$ requires C = 48.08; H = 4.5; Pt = 16.27 per cent.

The substance is insoluble in water or alcohol.

Quinol Dimethyl Ether

A mixture of equal weights of the phenolic ether and finely-powdered aluminium chloride was covered with carbon disulphide. Sulphination was then conducted as usual, fresh carbon disulphide being added from time to time to keep the mass sufficiently liquid to allow the passage of the gas. The product was a stiff brown mass; it was decomposed with ice. Since special tests did not reveal the presence of sulphinic acid, the contents of the flask were distilled in a current of steam until the quinol ether ceased to pass over. The remaining oil was separated from the acid mother liquor by shaking with chloroform, in which it dissolved readily. The chloroform solution was evaporated after repeated washing with water, and the residual oil was covered with ether and set aside in a desiccator. In about two weeks, it had solidified to a pale yellow, amorphous mass, which on further investigation proved to be a mixture.

The more soluble constituent was removed by extraction with hot alcohol, from which it was precipitated by addition of water. The amorphous solid was redissolved in acetone, and, after the pale green solution had been boiled with animal charcoal, it was filtered and again precipitated with water. The substance was evidently *p*-dimethoxyphenyl sulphide, since analysis yielded the following result :

0.1573 gave 0.3594 CO₂ and 0.0797 H₂O. C = 62.3 ; H = 5.62.

C₁₆H₁₈O₄S requires C = 62.74 ; H = 5.88 per cent.

The colourless, amorphous substance thus obtained melts at 97—100°, and is soluble in acetone or hot alcohol. The insoluble constituent of the mixture was boiled with water to remove the aluminium salts, to which it clung tenaciously. Thus *p*-dimethoxyphenyl sulphoxide was obtained as a colourless, amorphous powder melting at about 200°. It dissolves in concentrated sulphuric acid with an intense emerald-green colour, which is removed by the addition of phenetole. It is insoluble in alcohol and sparingly so in hot acetone :

0.2048 gave 0.4470 CO₂ and 0.0980 H₂O. C = 59.52 ; H = 5.32 :

C₁₆H₁₈O₅S requires C = 59.62 ; H = 5.55 per cent.

The yield of these substances was comparatively small, the weight of the mixture obtained from 20 grams of phenolic ether being only 4 grams. No sulphonium salt could be detected.

The action of thionyl chloride and aluminium chloride on the quinol ether was also investigated. Thionyl chloride was gradually mixed with a solution of quinol dimethyl ether in carbon disulphide to which aluminium chloride had been added. The mixture of sulphide and sulphoxide furnished by 27 grams of the ether weighed 22 grams,

and, from this, 8 grams of sulphide and 12 grams of sulphoxide were isolated. Again, neither sulphinic acid nor sulphonium salt could be detected in the products.

m-5-Xylenol Methyl Ether.

Sulphinic Acid, $\text{MeO}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{SO}_2\text{H}$, *Sulphoxide*,
 $(\text{MeO}\cdot\text{C}_6\text{H}_2\text{Me}_2)_2\text{SO}$,

and *Sulphonium Base*, $(\text{MeO}\cdot\text{C}_6\text{H}_2\text{Me}_2)_3\text{S}^+$.—Sulphination as usual. The product was poured on broken ice, and, when the ensuing reaction had subsided, the mixture was extracted with chloroform. The sulphinic acid was removed from the chloroform solution by shaking with aqueous alkali carbonate, from which it was precipitated by the addition of mineral acid.

5-Methoxy-m-xylene-2-sulphinic acid crystallises from hot water in slender needles which melt at 94—95°. It is sparingly soluble in cold water and readily so in alcohol. The solution in concentrated sulphuric acid exhibits a characteristic violet colour :

0.1506 gave 0.2985 CO_2 and 0.0805 H_2O . C = 54.04 ; H = 5.93.

$\text{C}_9\text{H}_{12}\text{O}_3\text{S}$ requires C = 54.0 ; H = 6.0 per cent.

The original extract now contained sulphoxide together with a very small quantity of sulphonium chloride. The latter was separated by warming with water the residue left by evaporation of the chloroform. The sulphonium chloride crystallised from the cold aqueous solution in colourless needles, but the quantity furnished by this experiment was so small that a more complete examination of the substance was postponed until a further quantity had been obtained by another method. The viscous residue, now free from sulphonium chloride, was dried and then set aside in a vacuum, but it showed no tendency to crystallise until pure ether had been added. After the ethereal solution had remained about a week at the ordinary temperature, the crystalline precipitate of sulphoxide was collected and recrystallised from alcohol.

5-Methoxy-m-xylol sulphoxide forms colourless, flat prisms which melt at 154—155°. It is moderately soluble in cold alcohol and very sparingly so in ether. The solution in concentrated sulphuric acid is violet :

0.1494 gave 0.1128 BaSO_4 . S = 10.31.

$\text{C}_{15}\text{H}_{22}\text{O}_3\text{S}$ requires S = 10.06 per cent.

Ten grams of the phenolic ether yielded 3.5 grams of sulphinic acid, about 0.7 gram of the sulphoxide, and a very small quantity of the sulphonium chloride.

Action of Thionyl Chloride on m-5-Xylenol Methyl Ether.

A mixture of 10 grams of powdered aluminium chloride and an equal weight of phenolic ether was placed in a flask surrounded by ice. Five grams of thionyl chloride were then added, very slowly at first while the reaction was violent and more rapidly later. When shaken at intervals during the reaction, the mixture involved much hydrogen chloride. Finally, the deep violet product was set aside at the ordinary temperature for two hours and then decomposed in the usual way with powdered ice. The three products were isolated by the process which has already been described.

The yields of the products when compared with those obtained with sulphurous acid illustrate the stronger sulphinating powers of thionyl chloride. Only about half a gram of sulphinic acid was isolated, whilst the yield of crude sulphoxide was 6 grams, but this contained an oily impurity, probably sulphide. The amount of sulphonium chloride produced was also larger, 1 gram being formed by the sulphination of 10 grams of the ether.

tris-5-Methoxy-m-xylyl-2-sulphonium chloride, $(\text{MeO} \cdot \text{C}_6\text{H}_2\text{Me}_2)_3\text{SCl}$, crystallises from hot water in long, colourless needles, which melt at $103\text{--}105^\circ$ and contain 7 molecules of water of crystallisation. A sample which had been dried in the air at the ordinary temperature was heated to 110° until constant weight was attained :

0.2597 lost, at 110° , 0.0540 H_2O . $\text{H}_2\text{O} = 20.79$.

0.1386 gave 0.0314 AgCl . $\text{Cl} = 5.60$.

$\text{C}_{27}\text{H}_{33}\text{O}_3\text{ClS}, 7\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 21.05$; $\text{Cl} = 5.93$ per cent.

This sulphonium chloride dissolves with a violet-brown colour in concentrated sulphuric acid.

The *platinichloride* was obtained as an orange-coloured, crystalline powder melting at 160° :

0.1801 gave 0.3302 CO_2 and 0.0804 H_2O . $\text{C} = 50.0$; $\text{H} = 4.96$.

0.1244 ,, 0.0192 Pt . $\text{Pt} = 15.43$.

$\text{C}_{54}\text{H}_{66}\text{O}_6\text{Cl}_6\text{S}_2\text{Pt}$ requires $\text{C} = 50.54$; $\text{H} = 5.14$; $\text{Pt} = 15.21$ per cent.

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THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.