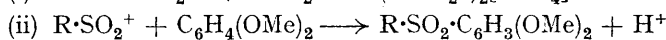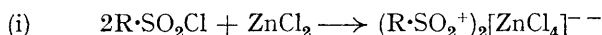**854.** *Acylation and Allied Reactions catalysed by Strong Acids. Part VII.* Evidence for the Existence of Sulphonyl Cations* $(R \cdot SO_2{}^+)$.
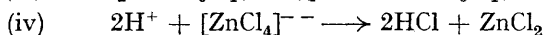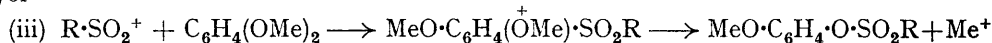
By H. Burton and H. B. Hopkins.

Previous results (*J.*, 1945, 14) on the reaction between sulphonyl chlorides and the dimethoxybenzenes in the presence of zinc chloride are explained by postulating the intermediate production of sulphonyl cations $(R \cdot SO_2{}^+)$. " Sulphonyl perchlorates " $(R \cdot SO_2{}^+ClO_4{}^-)$ are shown to be formed less readily, and to be less active, than the " acyl perchlorates." Sulphones are obtained under suitable experimental conditions, showing the existence of the sulphonyl cations : the yields are, however, generally not good.
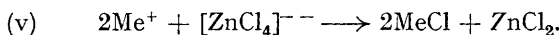
It was shown by Burton and Hoggarth (*J.*, 1945, 14) that sulphonyl chlorides $(R \cdot SO_2Cl)$ react with the dimethoxybenzenes in presence of zinc chloride in one or both of two ways, namely, elimination of hydrogen chloride to give the dimethoxyphenyl sulphone, $R \cdot SO_2 \cdot C_6H_3(OMe)_2$, or elimination of methyl chloride to yield the methoxyphenyl sulphonate, $R \cdot SO_2 \cdot O \cdot C_6H_4 \cdot OMe$. In general the *o*- and *p*-dimethoxybenzenes and the more reactive, especially aliphatic, sulphonyl chlorides gave almost exclusively the esters. In view of the results obtained with mixtures of acetyl chloride or acetic anhydride and zinc chloride (Burton and Praill, *J.*, 1951, 726 ; 1952, 755) it becomes clear that the above results with sulphonyl chlorides are adequately explained as a consequence of the following series of reactions :

(i) $\qquad 2R \cdot SO_2Cl + ZnCl_2 \longrightarrow (R \cdot SO_2{}^+)_2[ZnCl_4]^{--}$

(ii) $R \cdot SO_2{}^+ + C_6H_4(OMe)_2 \longrightarrow R \cdot SO_2 \cdot C_6H_3(OMe)_2 + H^+$

and/or

(iii) $R \cdot SO_2{}^+ + C_6H_4(OMe)_2 \longrightarrow MeO \cdot C_6H_4 (\overset{+}{O}Me) \cdot SO_2R \longrightarrow MeO \cdot C_6H_4 \cdot O \cdot SO_2R + Me^+$

(iv) $\qquad 2H^+ + [ZnCl_4]^{--} \longrightarrow 2HCl + ZnCl_2$

and/or

(v) $\qquad 2Me^+ + [ZnCl_4]^{--} \longrightarrow 2MeCl + ZnCl_2$.

In accordance with these reactions, *m*-dimethoxybenzene (resorcinol dimethyl ether), which must possess an extremely reactive position at $C_{(4)}$, showed preferential sulphone formation.

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Evidence for the existence of sulphonyl cations has also been adduced by Bourne, Randles, Tatlow, and Tedder (*Nature*, 1951, **168**, 942) who suggest that trifluoro-acetic anhydride and sulphonic (or carboxylic) acids give a mixed anhydride, $CF_3 \cdot CO \cdot O \cdot X$ (X = $R \cdot SO_2$ or $R \cdot CO$), which exists to a small degree as the ions X^+ and $CF_3 \cdot CO_2^-$. We agree with this view but would point out that the implication that sulphonic acids are weak acids is certainly not true. It is possible that sulphonic acids are much weaker acids in, *e.g.*, trifluoroacetic acid than in water, and we assume that this view is implicit in the suggested mechanism. We are informed by one of the authors (Tedder, personal communication) that the production of the mixed anhydride from trifluoroacetic acid and acetic anhydride or from trifluoroacetic anhydride and acetic acid, is a very fast reaction : this would follow from the results obtained by Bourne *et al.*

In view of the successful preparation of " acyl perchlorates " from silver perchlorate and acyl halides (Burton and Praill, *J.*, 1950, 2034; 1951, 529) we decided to investigate the possible extension of the procedure to " sulphonyl perchlorates " ($R \cdot SO_2^+ ClO_4^-$). We realised that in comparison with acyl halides, the sulphonyl halides are much less reactive and this is evident in the experiments we have carried out. Generally, the reaction proceeds slowly and incompletely in a solvent of low dielectric constant, *e.g.*, benzene, and more rapidly but still incompletely in nitrobenzene or nitromethane. Preliminary experiments with benzenesulphonyl chloride and silver perchlorate in mesitylene (or anisole) also showed that dark tarry products, similar to those obtained from the sulphonyl chloride and mesitylene in presence of aluminium chloride, were formed. In order to minimise this type of effect we used *m*-xylene as the reactive hydrocarbon but even then the production of coloured by-products was not prevented. In view of this somewhat unexpected complication we studied initially the amount of silver chloride produced from (*a*) benzene- or *p*-bromobenzene-sulphonyl chloride (1 mol.) and silver perchlorate (1·5 mols.) in benzene at 17—18° during 18 hours and (*b*) benzene- or toluene-*p*-sulphonyl chloride and silver perchlorate in nitrobenzene at 20—21° during 2 hours. The yields of silver chloride were : (*a*) 0·89, 0·6, (*b*) 0·73, 0·85 mol., respectively, indicating that for $Ar \cdot SO_2Cl$ the rate of the reaction increases, as expected, in the order of electron release of the group Ar. Thus the rate of reaction (1)

$$Ar \cdot SO_2Cl + AgClO_4 \longrightarrow Ar \cdot SO_2 \cdot ClO_4 + AgCl \quad . \quad . \quad . \quad (1)$$
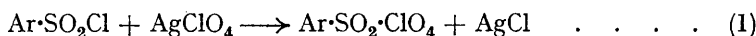
is evidently determined by the ease of separation of the chlorine atom of $Ar \cdot SO_2Cl$ as the chloride ion. The results also show quite clearly, again as expected, that the reaction proceeds much more rapidly in the solvent of higher dielectric constant.

We have also determined in several experiments the number of g.-ions of hydrogen in the initial aqueous phase after carrying out a reaction with the sulphonyl perchlorate and an active aromatic compound (Ar'H). We deemed this to be necessary in view of the obvious incompleteness of the reactions studied, since reaction (2) if it occurred exclusively would give rise to 1 g.-ion for each molecule of the perchlorate :

$$Ar \cdot SO_2 \cdot ClO_4 + Ar'H \longrightarrow Ar \cdot SO_2Ar' + H^+ + ClO_4^- \quad . \quad . \quad (2)$$
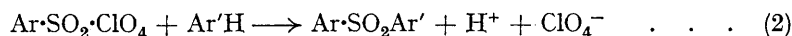
If the sulphonyl perchlorate were not to react as in (2) then on decomposition with water it would give 2 g.-ions of hydrogen :

$$Ar \cdot SO_2 \cdot ClO_4 + H_2O \longrightarrow Ar \cdot SO_3H + HClO_4.$$
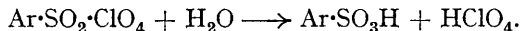
The results obtained are only of significance for Ar = Ph and possibly C_6H_4Me, since we were able to show that unchanged sulphonyl chloride was not hydrolysed to any significant extent under the experimental conditions used. (This method was not applicable to methanesulphonyl chloride which underwent partial hydrolysis.) The value obtained averaged *ca.* 1·2 g.-ions per g.-mol. of the sulphonyl perchlorate which may suggest that reaction (1) is faster than reaction (2).

In those cases where a solid product was obtained it proved to be the expected sulphone in accordance with reactions (1) and (2) : no other crystalline compound could be isolated. Thus benzenesulphonyl perchlorate and *m*-xylene in benzene, nitrobenzene, or nitromethane gave increasing amounts (7, 15, and 25%, respectively) of pure phenyl *m*-4-xylyl sulphone.

Toluene-*p*-sulphonyl perchlorate and *m*-xylene in nitrobenzene gave 46% of *p*-tolyl *m*-4-xylyl sulphone. In both cases, an identical sulphone was also obtained by the appropriate Friedel–Crafts reaction using aluminium chloride. The last-named sulphone, as obtained in both cases, was found to have m. p. 51—52°, a value which differs widely from that (121°) reported by Meyer (*Annalen*, 1923, **433**, 343), who states that this compound was synthesised by the Friedel–Crafts method and also by passing toluene vapour through *m*-xylene-4-sulphonic acid at 170—180° for 24 hours. We had great difficulty in obtaining crystalline material from the Friedel–Crafts experiment carried out exactly as described by Meyer : we found that a substance other than the true sulphone was produced and although we attach some reserve to our result—in view of the very small amount of the material available—it is probable that some disulphone was also formed. It is also possible that the *m*-xylene used by Meyer was not pure.

In view of the apparent formation of mixtures in our procedure we also investigated the nature of the secondary products. We found that extraction of a chloroform solution of the total reaction product with cold 2N-sodium hydroxide removed small but definite amounts of a phenolic product which may be originally present as such or may have arisen from an easily hydrolysable ester. We were able to prove that some ester was also present in the alkali-washed product since hydrolysis with boiling aqueous-alcoholic potassium hydroxide gave a further quantity of phenolic material and also an acid fraction. It is possible that during the reactions, especially those carried out for 18 hours or so, that the sulphonyl perchlorate is oxidising the aromatic component to a limited extent :

$$R{\cdot}SO_2{}^+ClO_4{}^- + ArH \longrightarrow R{\cdot}SO^+ClO_4{}^- + Ar{\cdot}OH \ (\longrightarrow Ar{\cdot}O{\cdot}SO_2{\cdot}R)$$
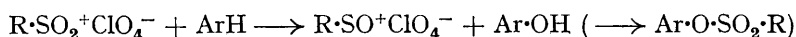
It is almost certain that the phenol does not arise from the arylsulphonyl cation since we found that the use of methanesulphonyl perchlorate also led to the formation of phenolic material. Furthermore, the use of nitrobenzene (or benzene) as solvent still resulted in phenol formation. It is also possible that phenol and ester may both arise by the direct attack of the sulphonyl cation on the aromatic component through oxygen, *i.e.*, that the cation exists to a small extent as a hybrid * (cf. I) :
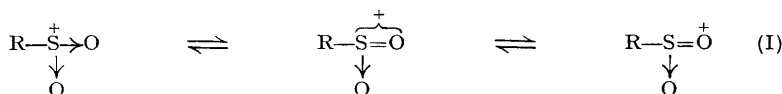
The attack of (I) on ArH would thus lead to Ar·O·SO·R, *i.e.*, an aryl sulphinate, which might be partly hydrolysed by cold, and certainly by hot, 2N-sodium hydroxide. Unfortunately we have not been able to devise a satisfactory method for identifying small amounts of sulphinic and sulphonic acids in admixture.

It will be seen that various by-products are possible and are almost certainly formed : it appears doubtful, therefore, whether the perchlorate technique is really suitable for the preparation of sulphones. The results are however not without some theoretical interest and in view of the fact that one of us is no longer able to take part in the work, we deem it worth while to place them on record.

We have also carried out a few experiments on the reaction of toluene-*p*-sulphinyl chloride on silver perchlorate in *m*-xylene–benzene and find that the reaction is much more rapid than with the sulphonyl chloride. The reaction product was again a viscous gum (? mixture) ; we were not able to identify *p*-tolyl *m*-4-xylyl sulphoxide as a constituent.

EXPERIMENTAL

Materials.—Silver perchlorate was dried as previously described (*J.*, 1950, 2036). Anisole, mesitylene, *m*-xylene, nitromethane, and nitrobenzene were all dried and redistilled. Benzene was purified by repeated shaking with concentrated sulphuric acid, washed with water, dried, and fractionated (the distillate gave a negative result for thiophen by the isatin test). Benzene- (b. p. 129°/20 mm.) and methane-sulphonyl chloride (b. p. 63·5—64°/19 mm.) were fractionated.

* The work of Bennett and Youle (*J.*, 1938, 1816) and Bennett and Grove (*J.*, 1945, 378) on the formation of phenolic by-products during nitration could be similarly explained by postulating that NO₂⁺ reacts to a small extent in the mesomeric form, ON:O⁺, which would lead to an aryl nitrite and thence the phenol.

Toluene-*p*-sulphonyl chloride was twice recrystallised from light petroleum (b. p. 40—60°) and had m. p. 67·5—68°. *p*-Bromobenzene sulphonyl chloride, similarly purified, had m. p. 74·5—75°. Toluene-*p*-sulphinyl chloride was obtained as a yellow oil from sodium toluene-*p*-sulphinate and thionyl chloride.

General Technique.—Silver perchlorate (7·8 g., 0·0376 g.-mol.) was dissolved in a mixture of the aromatic compound (*e.g.*, *m*-xylene; 20 g., 0·19 g.-mol.) and a diluent (*e.g.*, benzene, 40 g.) and the sulphonyl chloride (0·025 g.-mol.), dissolved in the same diluent (~10 g.), was added gradually to the cooled solution. Silver chloride separated slowly from the reaction mixture which slowly developed a colour (usually reddish). The mixture was then either filtered through a sintered-glass funnel on to crushed ice or poured on to ice and subsequently filtered; in either case, the precipitate of silver chloride was well washed with chloroform and then with water.

The chloroform layer was separated and washed repeatedly (~6 times) with water. These aqueous washings were combined with the main aqueous layer. The chloroform layer was then extracted four times with 2N-sodium hydroxide (except when nitromethane was the diluent), twice more with water, and dried (Na$_2$SO$_4$). The chloroform and the other solvents were removed by distillation in a vacuum and the resulting dark oil or gum was kept, or alternatively, refluxed with ~10% aqueous-alcoholic potassium hydroxide. The alcohol was removed by distillation and the residue extracted with chloroform and dried (Na$_2$SO$_4$). The dark oil or gum obtained on removal of the chloroform was set aside for several days, or in some cases, weeks, to crystallise. Any solid which separated was filtered off, washed with a little ether, and recrystallised to constant m. p. from aqueous ethanol. The filtrate was evaporated and again left to stand, the process being repeated until no further solid could be obtained.

Treatment of the aqueous layers. All silver ions were removed by addition of excess of sodium chloride solution. Aliquots of the filtrate were titrated to phenolphthalein with 0·1N-sodium hydroxide to determine the number of g.-ions of hydrogen present.

Treatment of the sodium hydroxide extracts. The strongly coloured alkaline extracts were acidified with hydrochloric acid, which discharged most of the colour and gave rise to an immediate turbidity and phenolic odour. In some cases the phenolic compound was isolated as a black gum by ethereal extraction. It amounted to 0·2 g. (expt. 10), 0·1 g. (expt. 12), 0·3 g. (expt. 15).

Treatment of the aqueous layer from the aqueous-alcoholic potassium hydroxide reflux. Acidification with hydrochloric acid caused a turbidity and phenolic odour. Ether-extraction yielded 0·2 g. of a dark oil (expt. 14) and 0·09 g. of a gum (expt. 15) which could be separated by the usual procedure into acid and phenolic fractions.

Further details of some of the experiments are as follows :

Expt. 8. Solid separated from the dark oil (3·4 g.) obtained from benzenesulphonyl chloride and *m*-xylene in nitrobenzene at 22° for 2 hours. Recrystallisation gave colourless plates (0·91 g.) of phenyl *m*-4-xylyl sulphone, m. p. 86° (Found : C, 67·7, 67·5; H, 5·7, 5·9; S, 13·4, 13·4. Calc. for C$_{14}$H$_{14}$O$_2$S : C, 68·3; H, 5·7; S, 13·0%). When the experiment was carried out at −1° for 6 hours, 0·7 g. of sulphone, m. p. and mixed m. p. 86°, was obtained. The sulphone obtained from benzenesulphonyl chloride, *m*-xylene, and aluminium chloride in nitrobenzene had m. p. 85—86°, alone or in admixture. Steinkopf and Hübner (*J. pr. Chem.*, 1934, **141**, 198) give m. p. 87° for the sulphone synthesised from magnesium, bromobenzene, and *m*-xylene-4-sulphonyl fluoride.

Expt. 9. Repetition of expt. 8, with nitromethane as the diluent at 16° for 4·5 hours, gave 1·5 g. of recrystallised sulphone, m. p. and mixed m. p. 85—86°.

Expt. 10. In a modification of expt. 8, benzene was used as the diluent at 18° for 18 hours. The sulphone (0·41 g.) had m. p. and mixed m. p. 86°.

Expt. 18. Toluene-*p*-sulphonyl chloride and *m*-xylene in nitrobenzene at 21° for 2 hours gave an oil (4·3 g.) which gradually deposited crystals (3 g.). Two crystallisations from light petroleum (b. p. 60—80°) gave colourless prisms of p-*tolyl* m-4-*xylyl sulphone*, m. p. 51—52° (Found : C, 69·5; H, 6·3; S, 12·1. C$_{15}$H$_{16}$O$_2$S requires C, 69·2; H, 6·2; S, 12·3%). The same compound was obtained by the Friedel–Crafts procedure from the chloride, *m*-xylene, and aluminium chloride in nitrobenzene.

Control Experiments.—(i) The appropriate amounts of benzenesulphonyl chloride, *m*-xylene, and nitrobenzene dissolved in chloroform were added to an aqueous solution of silver perchlorate. After 1 hour, the mixture was worked up as described above. The chloroform layer gave a mere trace of residue and the aqueous layer contained not more than 0·0004 g.-ion of hydrogen.

(ii) Methane- and benzene-sulphonyl chloride (0·0087 g.-mol.) were dissolved separately in chloroform and poured on to ice. After *ca.* 4 hours the chloroform layer was separated and washed four times with water. The combined aqueous layers were titrated with 0·1N-sodium hydroxide. Hydrolysis of the methanesulphonyl chloride had occurred to the extent of 29% whereas hydrolysis of the benzenesulphonyl chloride was negligible.

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