

Acylation and Allied Reactions Catalysed by Strong Acids.
Part XIII. The Isomeric p-Tolyl Xylyl Sulphones.*

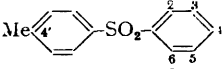
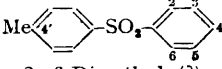
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The action of toluene-*p*-sulphonyl perchlorate on the xylenes is investigated with reference to the possible formation of xylyl toluene-*p*-sulphinates as by-products accompanying the *p*-tolyl xylyl sulphones. The results are not conclusive. It has been found that toluene-*p*-sulphonyl chloride, *m*-xylene, and aluminium chloride in the absence of a solvent give a product which yields some toluene-*p*-sulphonic acid on alkaline hydrolysis.

IN the course of some experiments on sulphonyl perchlorates (Burton and Hopkins, *J.*, 1952, 4457) it was shown that the properties of *p*-tolyl *m*-4-xylyl sulphone did not agree with those previously reported by Meyer (*Annalen*, 1923, 433, 343). The possibility that the *m*-xylene used by Meyer was not pure, was put forward. Since the isomeric sulphones from *o*- and *p*-xylene have not been reported, it seemed worthwhile to prepare them. The orientation of these compounds has not been rigidly established but they have been allotted the structures that would normally be predicted for them.

By Meyer's procedure with toluene-*p*-sulphonyl chloride and aluminium chloride, *p*-xylene gave an almost quantitative yield of *p*-tolyl *p*-2-xylyl sulphone, whilst *o*-xylene gave a mixture of isomeric compounds containing a higher proportion of *p*-tolyl *o*-4-xylyl sulphone. The melting points of these sulphones are listed for comparison :

	M. p. 135° 51—52 109		M. p. 121—122° (Meyer's compound) 131—132
2 : 3-Dimethyl- 2 : 4-Dimethyl- 2 : 5-Dimethyl-		2 : 6-Dimethyl- (?) 3 : 4-Dimethyl-	

Experiments were also carried out with the toluene-*p*-sulphonyl chloride-silver perchlorate mixtures. *p*-Xylene gave, as expected, a reasonable yield (*ca.* 70%) of almost pure *p*-tolyl *p*-2-xylyl sulphone after 24 hours at room temperature. *o*-Xylene under similar conditions gave a somewhat lower yield (56%) of a mixture of isomeric sulphones. This mixture appeared to contain rather more of the *p*-tolyl *o*-3-xylyl sulphone which, nevertheless, was formed in relatively small amount.

Burton and Hopkins (*loc. cit.*) also carried out some preliminary work on the small amounts of secondary products that accompany the sulphones in the sulphonyl perchlorate experiments. These secondary products were shown to be an acidic substance and some phenolic material, both of which could have arisen by the hydrolysis of an ester. It was suggested that this ester could have arisen by the direct attack of the sulphonyl cation on the aromatic component through the oxygen, thus leading to an aryl sulphinate, Ar·O·SO·R.

In a further attempt to identify these by-products we have studied the alkali-soluble material resulting from the treatment of the crude reaction product with potassium hydroxide in alcohol (or in dioxan). In the experiments with *m*-xylene and aluminium chloride, especially in the absence of solvent, it has been found that the alkali-soluble material contains toluene-*p*-sulphonic acid, identified by its ready addition to *p*-benzoquinone to form 2 : 5-dihydroxy-4'-methylidiphenyl sulphone. In no case was any phenolic material observed, but traces of thiocresol appear to have been formed. The mechanism of the reduction process by which these compounds have been produced has not been determined, but it is probable that the trace of thiocresol arises by the well-known conversion of a sulphonic acid into a sulphonic acid and thiolsulphonate.

The hydrolysis products from the perchlorate experiments yielded small amounts of

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resinous materials that had a strong phenolic smell. These were soluble in sodium hydroxide solution but not in sodium hydrogen carbonate. No positive colour reaction was obtained with ferric chloride. Attempts to isolate bromo-derivatives, phenylcarbamates, or 1-naphthylcarbamates from this fraction were unsuccessful. Traces of derivatives were occasionally obtained but these appeared to be mixtures. The small amount of acidic substance arising from the hydrolysis did not give identifiable amounts of 2 : 5-dihydroxy-4'-methylidiphenyl sulphone, nor a benzylthiuronium salt. However, the concentrate from an ethereal solution of the acid turned dark blue on keeping, as did a sample of *p*-toluenesulphonic acid.

Thus, while evidence for the formation of traces of toluenesulphonic esters has been obtained, it has not been possible to ascertain the exact constitution of these compounds.

EXPERIMENTAL

Materials.—Silver perchlorate was treated as before; aluminium chloride (laboratory reagent) was freshly powdered lump. Other reagents were dried and redistilled. *o*- and *m*-Xylene had b. p. 144° and 137—138°, respectively; *p*-xylene had m. p. 13—14°.

Reactions with m-Xylene.—*Method (A).* (i) Toluene-*p*-sulphonyl chloride (0.053 mole) was added all at once to a mixture of *m*-xylene (0.05 mole) and powdered aluminium chloride (0.082 mole). After a short induction period there was copious evolution of hydrogen chloride. The temperature rose to 30—40° and the mixture became almost homogeneous. After 30—45 min. it was heated to 40—50° for 30 min.; it became deep mauve. The cooled mixture was decomposed by 16% hydrochloric acid (50 ml.) and heating under reflux for 2—3 hr. The mixture was then steam-distilled until the distillate was clear. The gummy product failed to crystallise on cooling or on being seeded.

The gum was dried in a vacuum-desiccator (P_2O_5) and then dissolved in ether. After 2 months, the crystals that had separated were recrystallised from light petroleum (b. p. 60—80°). The colourless diamond-shaped prisms (0.2 g.) gave a clear melt by 74° (Found: S, 12.4. Calc. for $C_{15}H_{16}O_2S$: S, 12.3%). Several recrystallisations of this material from light petroleum, or light petroleum-ethanol, raised the m. p. to 110—112°, but there was insufficient material for a satisfactory analysis.

When the bulk of the material was kept for several months in a refrigerator, some large colourless prisms separated which, when washed free from gummy material, melted at 50—51°.

(ii) A similar reaction was carried out in nitrobenzene (27 ml.) with 0.025 mole of *m*-xylene. The mixture was heated at 80—90° for 4 hr. The crude product, which almost completely solidified on drying in the desiccator, was extracted with boiling light petroleum (b. p. 60—80°) to separate it from a little resinous material. The slightly brown crystalline product (4.1 g., 0.016 mole), m. p. 49—50°, crystallised from light petroleum as colourless prisms, m. p. 51—52° (Found: C, 69.2; H, 6.2; S, 12.6. Calc. for $C_{15}H_{16}O_2S$: C, 69.2; H, 6.2; S, 12.3%).

In subsequent experiments the boiling with hydrochloric acid and the steam-distillation were omitted. Instead, the crude gum was taken up in ether, and the solution was washed free from acid, dried (Na_2SO_4), and evaporated to dryness. The residual gum (*ca.* 11 g.) was boiled with excess of alcoholic potassium hydroxide for 2 hr. and the cooled solution was poured into 3—4 volumes of water. The oily material was again taken up in ether, and the ethereal solution washed with water and dried (Na_2SO_4). Evaporation of the ethereal solution gave a gum which proved to be as resistant to crystallisation as in earlier experiments.

The gum distilled at 174—175°/1.3 × 10⁻² mm.; the colourless distillate slowly crystallised to a slightly sticky solid, m. p. and mixed m. p. 42—43°. No separation of an impurity could be effected by chromatographic adsorption on an alumina column, ethanol being used as an eluant.

The alkaline washings from the hydrolysis were acidified with sulphuric acid (Congo-red), and extracted several times with small amounts of ether. The combined ethereal extracts were washed with saturated sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated to dryness. Small amounts of gum were obtained which had a smell resembling that of thiocresol.

The sodium hydrogen carbonate washings were warmed to remove dissolved ether and acidified with dilute sulphuric acid. A saturated aqueous solution of *p*-benzoquinone was added, and the mixture left at 0° for several hours. The light brown solid that separated (*ca.* 0.1 g.) melted at 209—210° (mixed m. p. with 2 : 5-dihydroxy-4'-methylidiphenyl sulphone, 209—210°) (Borsche and Frank, *Annalen*, 1926, 450, 75, give m. p. 211°) (Found: S, 11.6. Calc. for $C_{13}H_{12}O_4S$: S, 12.1%).

(iii) Another experiment was carried out with five times the original quantities. The main product was the low-melting *p*-tolyl *m*-4-xylyl sulphone, m. p. 51—52°, but repeated recrystallisation of the solid which separated first from the mixture gave material (0.51 g.) of m. p. 74—75°.

Attempted purification of this material by adsorption from benzene–light petroleum (b. p. 60—80°) (1 : 1) on an alumina column (16 × 1.5 cm.) and elution with ethanol, effected little change.

Five more recrystallisations from light petroleum gave colourless, diamond-shaped prisms (25 mg.), m. p. 120—121° (Found: C, 69.7; H, 5.8; S, 11.9. Calc. for C₁₅H₁₆O₂S: C, 69.2; H, 6.2; S, 12.3%) (Meyer, *loc. cit.*, reported m. p. 120—121° for *p*-tolyl *m*-4-xylyl sulphone).

Method (B). Toluene-*p*-sulphonyl chloride (0.05 mole) in nitromethane (20.0 g.) was added during 16—17 min. to a solution of silver perchlorate (0.05 mole) in *m*-xylene (0.27 mole) and nitromethane (53.5 g.). The temperature of the mixture rose to 25°. After 24 hr. at room temperature the mixture was filtered on to crushed ice. Recovery of silver chloride was 94% of the theoretical amount.

The mixture was then taken up in ether as in method (A). All nitromethane was removed from the reaction product (11.7 g.) before treating it with alcoholic potassium hydroxide. Alkaline washings from the hydrolysis yielded small amounts (0.1—0.2 g.) of a brown resin which had a phenolic smell: it was insoluble in sodium hydrogen carbonate solution. The dried residue was treated with phenyl isocyanate (or 1-naphthyl isocyanate) in sodium-dried light petroleum (b. p. 80—100°); little reaction occurred on warming even in the presence of a drop of triethylamine. Any substituted urea was removed from the mixture; the petroleum solution sometimes deposited traces of crystalline material.

The phenylcarbamate melted over a range, 70—80°, but did not depress the m. p. of the phenylcarbamate of *m*-4-xylenol, m. p. 102° (Heilbron's "Dictionary of Organic Compounds" gives m. p. 102°).

Reactions with o-Xylene.—Method (A). *o*-Xylene (0.05 mole) reacted with toluene-*p*-sulphonyl chloride (0.053 mole) and aluminium chloride (0.082 mole) under the conditions used for *m*-xylene. The crude sulphone (11.8 g.), recrystallised from ethyl alcohol and then from benzene–light petroleum, gave colourless flaky needles, m. p. 131—132° (Found: C, 69.0; H, 6.1; S, 12.5. C₁₅H₁₆O₂S requires C, 69.2; H, 6.2; S, 12.3%). This material, which was the major product, was probably *p*-tolyl *o*-4-xylyl sulphone.

The alcoholic mother-liquors slowly deposited a few long needles. On repeated recrystallisation from benzene–light petroleum (b. p. 60—80°) colourless prisms of (probably) *p*-tolyl *o*-3-xylyl sulphone, m. p. 135°, were obtained (Found: C, 69.3; H, 6.3; S, 12.4%). On admixture with the main product the m. p. was 107°.

Method (B). An experiment using silver perchlorate, carried out in the same way as for *m*-xylene, gave material (7.3 g.) of m. p. 107°. Slow crystallisation from benzene–light petroleum gave long colourless prisms (0.84 g.) and clusters of fine needles. The prisms were separated by hand picking and were recrystallised to constant m. p. (135°). This was unchanged by adsorption from a benzene solution on an alumina column (16 × 1.5 cm.) followed by elution with ethyl alcohol. The m. p. with the higher-melting material from method (A) was 135°. Chromatographic treatment of the remaining crystalline material did not effect complete separation but the product was mainly *p*-tolyl *o*-4-xylyl sulphone (mixed m. p.).

A small amount of phenolic by-product was obtained from this experiment but no derivative of known constitution was obtained.

Reactions with p-Xylene.—Method (A). This method, carried out as for the other xylenes, gave an almost quantitative yield (12.0 g.) of nearly pure *p*-tolyl *p*-xylyl sulphone, m. p. 105—106°. Recrystallisation from 96% ethyl alcohol gave clusters of colourless prisms, m. p. 109° (Found: C, 69.2; H, 6.0; S, 12.3%).

Method (B). The silver perchlorate technique being used, the crude product (11.0 g.) melted at 108—109° after one crystallisation from ethanol.

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