XCV.—*Arylsulphuric Acids.*

By GEORGE NORMAN BURKHARDT and ARTHUR LAPWORTH.

THE use of dialkylanilines in place of pyridine for the preparation of arylsulphuric acids by Verley's method [*Bull. Soc. chim.*, 1901, **25**, 46; compare Durand and Huguenin, Brit. Pat. 186057 (1922), 202630 and 202632 (1923)] has been found to lead to rather better yields and recovery of tertiary base is simplified.

Diethylaniline (100 g.; 2½ mols.) or the equivalent quantity of dimethylaniline in carbon disulphide (100 c.c.) was stirred mechanically and cooled to −10°. Chlorosulphonic acid (34 g.; 1·1 mols.) was run in steadily during 15 minutes, the temperature being maintained below 10°. Phenol (25 g.; 1 mol.) in carbon disulphide (50 c.c.) was then added all at once, the mixture stirred for an hour, and the disulphide thereafter removed by distillation on a steam-bath. The cold, viscous residue was run into a solution of sodium hydroxide (22 g.) in water (150 c.c.) containing 10 g. of hydrated barium hydroxide,* with vigorous shaking, the temperature being kept below 35°. A large proportion of the diethylaniline could

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* For certain purposes, the use of excess of ammonia instead of the hydroxide of an alkali metal is advantageous; but in this case, before removing the tertiary base in a current of steam, it is necessary to add sufficient barium hydroxide to convert all salts present into barium salts, as ammonium phenyl sulphate may suffer hydrolysis in the steam distillation process.

then be separated directly and the remainder removed by steam distillation or by extraction with benzene; the aqueous residue on direct evaporation yielded 90% of the theoretical quantity of sodium phenyl sulphate together with 7% of sodium chloride.

If the base and phenol were mixed before the chlorosulphonic acid was added, the yields never exceeded 60% of the theoretical.

Use of Sulphuric Anhydride in place of Chlorosulphonic Acid.—The authors carried out a number of experiments on the use of sulphuric anhydride in place of the chlorosulphonic acid employed by Verley (*loc. cit.*), as the formation of hydrogen chloride in the preparation is often disadvantageous. The experiments were completed before the patents of Durand and Huguenin (Brit. Pat. 202632 of 1923) came to their notice, but some of the observations made were not redundant and appear worthy of record.

As it was evident that the use of sulphuric anhydride as sulphating agent for phenols would render it easy to isolate pure products, trials of a number of organic media as solvents were made. The liquids were cooled and the anhydride was distilled slowly into them. Chloroform and carbon tetrachloride were decomposed rapidly, yielding carbonyl chloride even with most careful cooling, and carbon disulphide evolved carbonyl sulphide. Diethylaniline could not be made to dissolve the anhydride without charring and sulphonation; hexane did not appear to dissolve the anhydride as such, but was rapidly attacked when in contact with it: the nature of the reaction in the latter instance is under investigation. Experiments in which sulphuric anhydride was distilled into a cooled solution containing both phenol and diethylaniline in carbon tetrachloride gave more promising results, but even in presence of the tertiary base about 13% of the anhydride was destroyed by reaction with the tetrachloride, and the mixed salts obtained at the end of the operation contained 8% of inorganic chloride.

The only solvent found to dissolve sulphuric anhydride readily and without decomposition was liquid sulphur dioxide, and the following is an account of one of the experiments in which it was tried as solvent for sulphating phenols.

A solution of sulphuric anhydride (19 g.) in 80 c.c. of liquid sulphur dioxide was slowly added with vigorous stirring to phenol (20 g.) and diethylaniline (60 g.) in a wide-mouthed flask, cooled in a freezing mixture. After remaining over-night to allow most of the solvent to evaporate, it was found that much of the latter was obstinately retained and had to be removed by heating for an hour on a steam-bath. The product, after cooling, was neutralised with aqueous sodium hydroxide and sufficient barium hydroxide to precipitate inorganic sulphate. Nearly pure sodium phenyl sulphate in 60% yield was isolated on removal of diethylaniline and evaporation of the aqueous residue.

Use of Pyridine Sulphuro-anhydride in the Preparation of Salts of Phenylsulphuric Acids. [With FRANK ASHWORTH].—This method is virtually a modification of the process last described, inasmuch as sulphuric anhydride with a tertiary base, in this instance pyridine, is used. The following is an example of its application to a nitrophenol.

Sulphur trioxide (25 g.) is slowly distilled, with stirring and drastic cooling, into pyridine (29 g.; 1·75 mols.). Benzene (200 c.c.) is now added, and the whole heated to boiling * under a reflux condenser. *p*-Nitrophenol (30 g.; 1 mol.) is next introduced and the whole boiled for 4 hours, during which time the pyridine salt of *p*-nitrophenylsulphuric acid crystallises out. The mixture is cooled, poured into a slight excess of aqueous potassium hydroxide, the benzene distilled off under diminished pressure, the residual solution made just acid with acetic acid, and unchanged nitrophenol (2 g.) extracted with ether. The solution is rendered slightly alkaline once more and the water and pyridine evaporated off under diminished pressure, when potassium *p*-nitrophenyl sulphate is obtained in yields of 90—94% of the theoretical.

Eugenol under similar conditions gave a 70% yield of potassium eugenyl sulphate.

o-Nitrophenol proved much more difficult to attack than the para-isomeride. Yields of the sulphate up to 25% were obtained when equivalent proportions of *o*-nitrophenol and pyridine sulphuro-anhydride were used, and 56% yields with twice the theoretical amount of the latter.

Use of Pyrosulphate and Tertiary Bases in the Preparation of Phenylsulphuric Acids.—It is somewhat remarkable that there are no published records of attempts to extend or improve upon the results obtained by Baumann (*Ber.*, 1878, **11**, 1907), who succeeded in making potassium phenyl sulphate from phenol by means of potassium pyrosulphate. He worked with aqueous solutions only, however, with potassium hydroxide as condensing agent, and the yields were very poor. The present authors have found that good yields of the phenyl sulphates can be obtained by heating finely powdered potassium pyrosulphate with a solution of the phenol or naphthol in dry dimethylaniline, followed by extraction of the product with aqueous alkali.

A mixture of phenol (1 mol.) and dimethyl- or diethyl-aniline (1 mol.) was heated on a steam-bath and stirred mechanically while

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* Control experiments showed that pyridine sulphuro-anhydride has no appreciable action on boiling benzene.

finely powdered potassium pyrosulphate * (1½ mols.) was added; the suspension was stirred and heated for 8 hours. The reaction mixture was poured into a suspension of excess of baryta in cold water, the base being subsequently removed by steam distillation, the excess of baryta being precipitated by means of carbon dioxide. After filtering and evaporating, potassium phenyl sulphate in 80—85% yield was easily isolated.

Another experiment using phenol (1 mol.), base (3 mols.), and pyrosulphate (2½ mols.), heated and stirred for 4 hours, gave a yield of 90%.

The method was also found satisfactory for α- and β-naphthols, and for eugenol and *iso*eugenol, except that in all these cases it was impossible to use barium hydroxide on account of the low solubility of the salts of the products. A slight excess of potassium hydroxide was therefore added and the base separated while the solution was hot.

Notes on the Properties of the Salts of Arylsulphuric Acids.—Baumann and Verley (*loc. cit.*) recorded (*a*) that the potassium salts of the arylsulphuric acids are stable to alkalis, but are readily hydrolysed by acids; (*b*) that they decompose, with some isomerisation to sulphonates, at 150—200°; (*c*) one or two physical properties in a few instances. Heymann and Koenigs oxidised potassium *o*- and *p*-tolyl sulphates to the corresponding carboxylic acids (*Ber.*, 1886, **19**, 704). In the present investigation many of the above observations were confirmed and extended, and a variety of salts of arylsulphuric acids examined in some detail.

The salts show some variations in their ease of hydrolysis. The alkali salts are stable at 100° in neutral aqueous solution and require heating to boiling before rapid hydrolysis sets in in presence of mineral acid. The barium salt is decomposed on heating to 100° in aqueous solution for 1½ hours, after which the hydrolysis proceeds rapidly to completion in 2 hours. The ammonium and magnesium salts are of intermediate stability. All the salts are stable at 100° in an aqueous solution of sodium acetate even in presence of a considerable concentration of acetic acid. Hydrolysis of the potassium salt is also brought about by heating at 150° with strong alkali or with half-concentrated ammonia at 190—220° for 4 hours. In the latter case, no aniline is produced.

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* Potassium pyrosulphate was made by heating powdered potassium hydrogen sulphate, under 2—3 mm. pressure, in a bolthead flask on a sand-bath. The reaction proceeded at 270—330° and was stopped when the temperature began to rise rapidly. The mass was then poured on to an iron plate and allowed to cool in a desiccator; it contained 90% of pyrosulphate. The salt was powdered and sieved as rapidly as possible immediately before application in the above reactions, otherwise it deteriorated.

Heating with aniline gave no indication of replacement of the hydroxyl group. Diazo-compounds do not couple to an appreciable extent with salts of phenylsulphuric acid in alkaline solution, and nitrous acid is without action, even after several days. Concentrated nitric acid rapidly decomposes the alkali salts, producing a mixture of nitro-derivatives without tarring or much evolution of heat. The bromination of salts of phenylsulphuric acids is described in another communication. Potassium phenyl sulphate crystallises in anhydrous, rhombohedral or six-sided plates with apex angle 95°. It dissolves to the extent of 0·7% in alcohol and 14% in water at 17°, and is freely soluble in both media when hot (Found : K, 18·3. Calc. for $C_6H_5O_4SK$, K, 18·5%).

The sodium salt forms rhombic plates consisting of aggregates of twinned leaflets. It dissolves to the extent of 7% in alcohol and 31% in water at 17°, and is freely soluble in both media when hot (Found : Na, 9·3. Calc. for $C_6H_5O_4SNa,3H_2O$, Na, 9·2%). The barium salt forms fine granules and is rather less readily soluble in water than is barium chloride; in hot or cold alcohol, it dissolves to the extent of about 15%; when the moist salt is exposed in a steam-oven it is quantitatively decomposed in a few minutes, phenol being liberated, and the same change occurs at the ordinary temperature in the course of a few days. The ammonium salt is extremely soluble in cold water and crystallises in hydrated, rhombohedra composed of thin plates like the sodium salt. The magnesium salt forms small, nacreous, rectangular or six-sided plates; it is less soluble in cold water than any of the other salts examined.

Salts of the isomeric tolylsulphuric acids are very sparingly soluble in cold alcohol and acetone and only slightly soluble in hot; they can be recrystallised from 85% alcohol, and, in the case of the *p*-tolyl derivative, from acetone containing 2% of water. They are very freely soluble in acetone containing 5% of water. The *o*-salt is soluble to the extent of 22% in water at 17°, the *m*- 9%, and the *p*- 10%.

p-*Toluidine tolyl sulphates* are characteristic. They were prepared as follows : Potassium tolyl sulphate (5·5 g.) was added to a hot solution of *p*-toluidine (2 g.) in 50 c.c. of alcohol, the mixture stirred for a minute with the liquid just below the boiling point, and *p*-toluidine hydrochloride (3·5 g.) added. The solution was boiled and shaken for a few minutes, and the potassium chloride (1·8 g.) which separated was filtered off. On evaporation, the liquor gave an almost theoretical yield of the toluidine tolyl sulphate, which was washed with benzene and recrystallised from benzene containing 5% of alcohol. The salts from *o*- and *p*-cresols are fairly soluble in water and readily in alcohol and acetone but insoluble in benzene. On recrystallisation, they formed matted, woolly needles which on melting or heating for some time at 110° gave *p*-toluidine sulphate and free cresol. The salt from *o*-cresol melted sharply with decomposition at 125—127°, and the *p*-salt at 149—151°.

Potassium m-*carboxyphenyl sulphate* was prepared by oxidation of the *m*-tolylsulphate. The latter (30 g.) was dissolved in water (100 c.c.) containing a little potassium hydroxide. A hot saturated solution of potassium permanganate (60 g.) was added to the solution, and the mixture heated on the steam-bath for 8 hours, after which the excess permanganate was reduced by means of alcohol, and the precipitate removed by filtration. The filtrate after cooling was rendered slightly acid with hydrochloric acid. The flocculent precipitate formed was collected, washed, and recrystallised from 70% alcohol. The yield was 80%. The salt forms plates: 3·2 parts dissolve in 100 parts of water at 17°; it is readily soluble in acetone containing 10% of water (Found: K, 15·3. $C_7H_5O_6SK$ requires K, 15·3%). It gave no coloration with ferric chloride. It was hydrolysed, on boiling with mineral acid, yielding *m*-hydroxybenzoic acid and potassium hydrogen sulphate.

Salts of Naphthylsulphuric Acids.—These are readily obtained in yields of 80—90% by the methods described on pp. 684 and 686. High purity of the naphthols is important in using the latter method or the products are discoloured.

Potassium α-naphthyl sulphate crystallises from water as a coarse, crystalline powder or in long, soft needles. It dissolves in 40 parts of water at 17°, is freely soluble in hot water, and almost insoluble in most of the usual organic media (Found: K, 14·7. $C_{10}H_7O_4SK$ requires K, 14·9%).

Potassium β-naphthyl sulphate resembles its isomeride in general appearance and characters, but its crystals are hydrated. It dissolves in 70 parts of water at 17° (Found: K, 11·9. $C_{10}H_7O_4SK,4H_2O$ requires K, 11·7%).

Both these salts are stable to boiling alkalis and to boiling dilute acetic acid in presence of sodium acetate; they are easily hydrolysed, however, by hot dilute mineral acids. They are at once attacked in aqueous solution by bromine, and precipitates soluble in ether are formed together with free sulphuric acid; the elimination of the sulphate residue is not, however, complete after several minutes in presence of excess of bromine.

A considerable amount of time was spent in investigating the oxidation of the isomeric potassium naphthyl sulphates with alkaline permanganate in aqueous solution. It was found that rapid oxidation took place at 80°, and from the quantity of free inorganic sulphate formed, that about 42% of the α-salt underwent oxidation in the unsubstituted ring, and in the case of the β-isomeride about 62%. Numerous attempts to separate from the resulting mixtures the sulphates of the hydroxyphthalic, hydroxyphthalonic acids, or the corresponding products formed after elimination of the sulphate radicals were not successful, owing mainly to the excessive solubility of these acids and their derivatives.

From potassium α-naphthyl sulphate, a small amount of the hydroxyphthalic acid (m. p. 150°) and some phthalic acid were obtained (compare Miller, *Annalen*, 1881, **208**, 247).

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