

The Action of Chlorosulphonic Acid on Phenol and p-Cresol, etc. 337

89. The Action of Chlorosulphonic Acid on Phenol and p-Cresol at Low Temperatures.

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PREVIOUS publications concerned with the action of chlorosulphonic acid on phenol deal with the products when the reaction takes place without strong cooling, and usually when it is completed by heating (Engelhardt, *Z. Chem.*, 1869, 297; Mazurowska, *J. pr. Chem.*, 1876, 13, 169; Klason, *ibid.*, 1879, 19, 236). The reaction was considered to be analogous to the action on aliphatic alcohols, but the products described were undoubtedly sulphonates and not aryl sulphates. Haworth, Lapworth, and Wilson (J., 1924, 125, 1300) showed that when chlorosulphonic acid acted on *m*-cresol at low temperatures some tolylsulphuric acid was formed.

It has now been shown that when chlorosulphonic acid is added to phenol in carbon disulphide at -15° , phenylsulphuric acid and phenol-*p*-sulphonic acid are formed. No phenol-*o*-sulphonic acid was detected. Slow addition of the chlorosulphonic acid or long periods for reaction favoured the production of sulphonate. Under the conditions which gave most phenylsulphuric acid, the mixed barium salts obtained on extraction corresponded to 75% of the phenol used and contained 50% of barium phenylsulphate which could be separated from the barium phenol-*p*-sulphonate by precipitating the latter as the basic barium salt. From this the normal sulphonate was regenerated by the action of carbon dioxide.

Under similar conditions *p*-cresol gave a product (80% yield based on cresol) containing more than 90% of *p*-tolylsulphate, as was to be anticipated from the fact that phenol-*o*-sulphonic acid was not detected among the products obtained from phenol.

EXPERIMENTAL.

Experiment 6.— $\text{Cl}\cdot\text{SO}_3\text{H}$ (31 g. = 1.25 mol.) was added during 20 min. to $\text{Ph}\cdot\text{OH}$ (20 g. = 1 mol.) in CS_2 (100 g.) cooled to -15° and stirred. After 2.5 hrs.' stirring, the CS_2 was decanted (it contained nearly all the HCl which remained but gave no appreciable residue of $\text{Ph}\cdot\text{OH}$ on evaporation) and the acid layer was poured on ice, neutralised with BaCO_3 and filtered. The residue (A) was washed well with H_2O , and the filtrate (after extraction with CHCl_3) and washings were evaporated together under reduced press. until no more $\text{Ph}\cdot\text{OH}$ came over (distillate B). The conc. solution on boiling for 1 hr. with dil. HCl in presence of BaCl_2 gave BaSO_4 (23.7 g.) corresponding to the barium phenylsulphate. The $\text{Ph}\cdot\text{OH}$ unattacked by $\text{Cl}\cdot\text{SO}_3\text{H}$ was estimated as tribromophenol in the distillate B and the CHCl_3 extract. The BaSO_4 in the residue (A) was isolated after prolonged extraction with hot dil. HCl (11.5 g. = $\text{Cl}\cdot\text{SO}_3\text{H}$ which had not attacked $\text{Ph}\cdot\text{OH}$). These wts. indicate that the product contained approx. equimol. proportions of phenylsulphuric and phenolsulphonic acids.

Further Experiments.—The $\text{Cl}\cdot\text{SO}_3\text{H}$ was added in (1) 1 hr., (2) 0.5 hr., (3) 2.5 hr. and the extraction liquors were poured on ice (1) immediately, (2) after 12 hr., (3) immediately. Fractions of the cryst. Ba salts from the extractions were examined microscopically before and after decomp. of the $\text{Ba}(\text{Ph}\cdot\text{SO}_3)_2$ which was brought about by heating the moist solid in a steam-oven for a few min. None of the characteristic barium phenol-*o*-sulphonate was observed, and the proportion of phenol-*p*-sulphonate was higher in (2) and (3) than in the other expts. The products obtained under the conditions used in Expt. 6 were also fractionated and examined as K and Ba salts. When the $\text{Cl}\cdot\text{SO}_3\text{H}$ was added in less than 20 min. the CS_2 was appreciably attacked.

Salts of the phenolsulphonic acids (Obermiller, *Ber.*, 1907, 40, 3623) and phenylsulphuric acid (Burkhardt and Lapworth, J., 1926, 684) were prepared for comparison. The sulphonates are not significantly hydrolysed by dil. HCl in 1 hr. (in 24 hr. 20% HCl hydrolyses 59% of *o*- and 5% of *p*-isomeride; Obermiller, *loc. cit.*). The solubilities and microcryst. structures particularly of the Ba salts are characteristically different: barium phenol-*o*-sulphonate, rosettes of rhombohedral flakes with angles 110° and 70° ; *p*-sulphonate, feathery needles; potassium phenol-*o*-sulphonate, needles or elongated hexagons having apex angles 120° ; *p*-sulphonate, elongated hexagons, apex angles 73° .

Separation of the Products.—The cold aq. extract from a reaction as in Expt. 6 was shaken

with finely ground $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (100 g.) until it was alk. throughout, and then heated to complete the formation of basic $\text{Ba}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)$. After cooling, filtration gave a solution containing $\text{Ba}(\text{Ph} \cdot \text{SO}_4)_2$ with excess hydroxide and traces of chloride and sulphonate, and a residue containing excess hydroxide, BaSO_4 , and the basic sulphonate, from which the normal sulphonate was regenerated by suspension in water, passage of CO_2 , filtration, and crystn.

Action on p-Cresol.— $\text{Cl} \cdot \text{SO}_3\text{H}$ (20 g.) was added during 20 min. to *p*-cresol (15 g.) in CHCl_3 (70 g.) cooled to -10° and stirred mechanically. The whole was then run into ice-cold KOH aq. (20 g. in 150 c.c.), shaken until alk., warmed to complete solution, and the CHCl_3 layer separated. The aq. solution deposited potassium *p*-tolylsulphate (20 g.) on cooling; 2 g. were obtained by further evaporation, accounting for 11 g. of *p*-cresol. Ether extraction of the acidified liquor gave 1.5 g. of *p*-cresol and on evaporation of the aq. solution to dryness and extraction with EtOH , 2 g. of solid were isolated containing *p*-cresol (0.5 g.) and cresolsulphonate (1.5 g.), leaving 1 g. of cresol unaccounted for, *i.e.*, 5% of cresol was sulphonated and 75% converted into *p*-tolylsulphuric acid.

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