

CCCXLI.—*Extraction of the Isomeric Xylenes from Crude Xylol.*

By T. S. PATTERSON, ANDREW McMILLAN, and ROBERT SOMERVILLE.

DURING the war we worked out a method of separating *m*-xylene from coal-tar, and coke-oven, xylene, and from Borneo petroleum, a problem regarding which little appears in the literature, although it proved to be a very simple one. Our ultimate procedure was as follows : * A sample (2400 c.c.) of coke-oven xylene (b. p. 137—141°) was shaken on a machine in four bottles with 3600 c.c. of ordinary concentrated sulphuric acid (*d* 1.84) for about $\frac{3}{4}$ hour. The mixture became slightly warm—up to about 40°—and the time of shaking depended a little on the temperature developed. The residue amounted to 141 c.c., from which a stronger sulphuric acid absorbed 135 c.c. presumably of *p*-xylene; the remainder, we suppose, was petroleum. To the acid liquid, 2560 c.c. of water were slowly added with stirring. On standing over-night or by cooling to about 10°, the mass went almost solid. After vigorous shaking, the resulting pasty crystals were removed by filtration; yield of moist crystals = 5376 g.

Of this crude sulphonie acid, 1500 g. were heated in a 2-litre distilling flask on an oil-bath. At 130° (thermometer in acid), steam at 150—200° was blown through the liquid, and during the earlier part of the distillation 1 part of condensed steam brought over about 4 parts of *m*-xylene. In all, 472 c.c. of *m*-xylene were brought over in 1 $\frac{1}{4}$ hours by about 500 c.c. of condensed steam. Taking this as the true yield, the whole 5376 g. of sulphonie acid should produce 1691 c.c. of *m*-xylene, which, calculated on the

* Clarke and Taylor (*J. Amer. Chem. Soc.*, 1923, 45, 831) have recently published some work on the subject. Our results, whilst not overlapping, supplement and amplify theirs.

2259 g. originally absorbed by the sulphuric acid, is equivalent to 74.9%. The product was of a slightly better quality, as will be explained below, than a sample of Merck's pure *m*-xylene (pre-war). By crystallising the sulphonic acid as described below, the quality of the xylene could easily be improved.

The acid obtained is doubtless a mixture of *o*- and *m*-xylene-sulphonic acids. It is very soluble in water and in alcohol, but can easily be recrystallised by melting it and then adding about one-third of its bulk of 33% sulphuric acid. This would probably be the simplest procedure on a large scale. To obtain a pure specimen of the acid, which does not appear hitherto to have been described, it is best to recrystallise the crude product from chloroform, adherent water being removed by running the warm solution through filter-paper. After three crystallisations, it melted at 61–62°, and yielded a sulphonyl chloride which, with ammonia, gave a sulphonamide melting at 136–137° (Jacobsen, *Ber.*, 1878, **11**, 18). This identifies the acid as *m*-xylene-4-sulphonic acid, the sodium salt of which has already been obtained by Clarke and Taylor (*loc. cit.*).

The melting point of some *m*-xylene, prepared from a sample of acid which had been crystallised three times from chloroform, was determined by means of a pentane thermometer and liquid air. The uncorrected results along with those for other products were as follows :

Crude coke-oven xylene – 70°, Merck's pure *m*-xylene – 47°, xylene from sulphonic acid (not recrystallised) – 45.5°, *m*-xylene from sulphonic acid crystallised thrice from chloroform – 40.5°. By applying the proper correction to the last reading, a value close to – 53°, which is stated to be the m. p. of pure synthetic *m*-xylene, was obtained.

Calcium m-xylene-4-sulphonate forms light, flaky crystals. It is easily soluble in water at the ordinary temperature, but becomes much less soluble as the temperature rises. From the concentrated solution it therefore separates on heating.

o-Xylene-4-sulphonic acid was made, for purposes of comparison with the preceding acid, by the method described above, using a sample of Kahlbaum's *o*-xylene. From the sulphuric acid solution, the *o*-xylenesulphonic acid separates in the same manner as the *m*-xylenesulphonic acid, and it also can be crystallised from chloroform, but is much more difficult to obtain pure on account of its hygroscopic character. Long standing on a porous plate in a vacuum desiccator gave a product, m. p. 63–64°. It was converted into the chloride, and this into the sulphonamide, m. p. 143–144° (Jacobsen, *Ber.*, 1878, **11**, 22).

Calcium o-xylene-4-sulphonate, unlike the salt derived from *m*-xylene, is a fine, granular solid, soluble in hot water, but much less soluble in cold water than is the *m*-xylene derivative. It is thus differentiated markedly from the *m*-xylene derivative, and a simple method of separating the two acids is accordingly available. This method we applied to the separation of *o*-xylene from the crude coke-oven xylol referred to above. From 625 c.c. of the crude product there were obtained, by distillation with an ordinary rod and disc fractionating column, 45 c.c. of a fraction, b. p. 139—142°. This was converted into the corresponding calcium sulphonates. On concentrating the solution, a white, flaky mass of calcium *m*-xylenesulphonate separated at the boiling point, and was filtered off. This was repeated until all the calcium *m*-xylenesulphonate appeared to be removed. The filtrate was then cooled in ice and calcium *o*-xylenesulphonate crystallised out. The weight of the salt so obtained was 50 g., corresponding to a yield of 4.7% of *o*-xylene on the original sample.

The properties of these salts afford a simple test for determining roughly the purity of *o*-xylene. From a sample of *o*-xylene obtained from The British Drug Houses, Ltd., the calcium sulphonate was prepared. On concentrating the solution, a white solid separated at the boiling point, which redissolved on cooling the solution, thus showing the presence of an appreciable amount of *m*-xylene in the specimen.

These results suggest an interesting lecture experiment. By mixing together 2.5 g. of calcium *o*-xylenesulphonate, 0.5 g. of calcium *m*-xylenesulphonate, and 8 c.c. of water, a mixture is obtained which is liquid at 50°, and on cooling in ice-water goes almost solid owing to the separation of calcium *o*-xylenesulphonate, whereas on heating at 100° it again goes almost solid, but this time owing to the separation of calcium *m*-xylenesulphonate. Starting from a low temperature, the semi-solid mass passes gradually into solution, which is complete at 50°, and then, on heating to a higher temperature, the mixture goes almost solid again.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

[Received, July 3rd, 1924.]