324. *Volume Effects of Alkyl Groups in Aromatic Compounds. Part V. The Monosulphonation of* p-*Cymene.*

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IN Part II of this series (J., 1933, 980) three instances were noted in which the order of orienting powers of the methyl and the *iso*propyl group required by current electronic theories was reversed; the results now to be recorded establish the sulphonation of *p*-cymene as a fourth example of the same phenomenon.

Such a conclusion was indicated qualitatively by the earlier literature dealing with this substitution. Jacobson (*Ber.*, 1878, **11**, 1059), by the direct action of sulphuric acid on the hydrocarbon, isolated a cymenemonosulphonic acid (the α-acid) and showed that its sodium salt gave carvacrol on potash fusion. Later, Claus (*Ber.*, 1880, **13**, 901; 1881, **14**, 2139) developed an improved method of separation *via* the barium salts and was thereby enabled to detect the formation also of an isomeric acid (the β-acid), the constitution of which was formally established by Kelbe and Koschnitzky (*Ber.*, 1886, **19**, 1733; cf. Dinesmann, D.R.P., 125097; or *Centr.*, 1901, ii, 1030) by its conversion into thymol; the yields of this second acid were evidently very small, and it is clear that substitution occurred almost entirely at the 2-position in the hydrocarbon. Quantitative repetitions of the process have verified this; the results are summarised in the table.

Sulphonation of p-*Cymene.*

Weight of cymene taken, g.	25	27	50	30	30	25
Approx. temp. of sulphonation ...	0—10°	0—10°	0—10°	50—80°	50—80°	90—100°
Yield of barium 2-sulphonate, g.	23·5	26·1	45·5	14·5	18·1	5·1
Vol. (l.) of cold saturated solution from which crystn. occurred ...	3	3	6	2	2	2
Corr. yield of barium 2-sulphonate, g.	83·5	86·1	165·5	54·5	58·1	45·1
Yield of barium 3-sulphonate, g.	5	5·5	12	9·5	11·5	12
Total yield of monosubstituted derivatives, g.	88·5	91·6	177	64·0	69·6	57·1
Yield of $Ba(C_{10}H_{13}SO_3)_2,3H_2O$, calc., g.	92	99·4	184	110	110	92
Yield, %, of 2-sulphonate on cymene taken	91	87	90	49·5	53	49

Details of a typical experiment are given on p. 1502. In working up the products, the method used was that of Claus (*loc. cit.*); very little unchanged cymene was recovered, and its amount was quite insufficient to explain the deficiencies in yield shown in the antepenultimate line of the table; these, in the lower-temperature experiments, may have been due to the formation of some cymenedisulphonic acid, the barium salt of which is soluble in alcohol and would therefore have been removed during the separation. The "corrected" yields in line 5 of the table are those actually isolated by crystallisation from water plus an allowance for aqueous solubility. Rough indications that the amount of 2-substitution becomes relatively less with rise of temperature were observed.

The barium salts of both 2- and 3-cymenesulphonic acids crystallise as trihydrates, and the chemical purities of the samples isolated in this work were therefore difficult to demonstrate. The first salt, however, had every property associated with homogeneity (large, well-formed plates) and in this respect differed from the second salt, which was always obtained only as a white powder; moreover, the latter appeared the more likely to have been a mixture, for, having the greater solubility, it may have contained a salt or salts of one or more of the possible isomeric side-chain substituted sulphonic acids; the solubility difference between the 2- and the 3-barium sulphonate themselves (see p. 1502), however, is such that a sharp separation should be possible.

In this connexion an attempt was made to synthesise barium cymene-3-sulphonate by the process $C_3H_7{\cdot}C_6H_3Me{\cdot}OH \longrightarrow C_3H_7{\cdot}C_6H_3Me{\cdot}SH \longrightarrow C_3H_7{\cdot}C_6H_3Me{\cdot}SO_3H$. 3-Thiol-*p*-cymene was readily obtained by the action of phosphorus pentasulphide on thymol (Fittica, *Annalen*, 1874, **172**, 325) and was subjected to oxidation by various reagents.

No conditions could be achieved under which oxidation was confined to the thiol group; the only isolable acid product was the acid (possibly 3-sulpho-*p*-toluic acid) previously noted by Fittica (*loc. cit.*), the formation of which is consistent with the oxidisability of the *iso*propyl radical in cymene compounds (cf. Parts III and IV; this vol., pp. 848, 852).

For purposes of further identification, barium cymene-2-sulphonate was converted *via* the chloride into the crystalline amide, which was also easily obtained from the crude total product from the action of chlorosulphonic acid on *p*-cymene at 0—10°, showing that substitution by the chlorosulphonyl group, like that by the sulphonyl radical, occurs very largely at position 2 (*i.e.*, ortho to methyl rather than to iso*propyl*).

EXPERIMENTAL.

Interaction of Fuming Sulphuric Acid and Cymene.—The action of fuming sulphuric acid seemed to be more satisfactory than that of the ordinary acid; the following is typical of the experiments summarised above in the table. The hydrocarbon (25 g.) was well stirred mechanically, and treated cautiously (1 hour) under ice–salt cooling with fuming sulphuric acid (15% SO_3; 30 c.c.), the stirring being prolonged for a further 3 hours. The reaction product was added to chopped ice, and diluted with water to about 2·5 l. Sufficient powdered barium carbonate for neutralisation was dusted in, and the mixture raised to 100° by passage of a current of steam. Filtration (hot-water funnel) and cooling then gave barium cymene-2-sulphonate (23·5 g.) as white shining plates (Found: loss at 150°, 8·3, 8·8, 8·5. Calc. for $C_{20}H_{26}O_6S_2Ba,3H_2O$: loss, 8·75%. Found, in anhydrous salt: Ba, 24·4. Calc.: Ba, 24·3%). The filtrate was evaporated to about 500 c.c. and cooled, a further quantity of the 2-sulphonate (*ca.* 48 g.) in obviously slightly less pure condition being obtained. This was removed, and the remaining liquor taken as far as possible towards dryness on the steam-bath. Repeated extraction of the resulting syrup with boiling alcohol left a white solid salt (5 g.), the aqueous solution of which had an intensely sweet taste (contrast the 2-salt, which was bitter). For analysis, the 3-sulphonate was dried over sulphuric acid in a vacuum (Found: Ba, 24·1; loss of weight at 150°, 8·4%).

The alcoholic extracts, which contained barium cymenedisulphonate along with the above salts in unknown amounts, were not examined, since the main point, *viz.*, that more 2- than 3-substitution occurs, was adequately established by the isolated yields of the former isomeride.

Solubilities of Barium Cymene-2- and -3-sulphonates in Water.—A pure specimen of the former salt was recrystallised from water and kept at room temperature for a day before decantation of the mother-liquor. This (25 c.c.), on evaporation to constant weight in a vacuum desiccator, afforded 0·5120, 0·5131, 0·5101 g. of the trihydrate; 100 c.c. of the saturated solution at 16—18° therefore contain 2·05 g. This value has been employed in making the corrections in the table above.

Determination of the solubility of the 3-isomeride was difficult because this salt did not crystallise when its aqueous solutions were evaporated; the barium salt was added in portions to 75 g. of distilled water at 18°, with repeated shaking; 24 g. appeared to dissolve, hence the solubility of this salt is about 16 times greater than that of the 2-isomeride.

The following experiment was performed as a check of the assumption, made in compiling the table, that the solubilities of the two salts will be individually maintained in a mutual mixture. The two salts (5 g. of each) were dissolved in 100 c.c. of boiling water, and the solution cooled. In two such experiments 2·8 and 2·9 g. of solid were deposited, whereas 2·95 g. of 2-sulphonate are to be expected.

Interaction of Chlorosulphonic Acid and Cymene.—To cymene (27 g.) under water cooling was slowly added an equal weight of chlorosulphonic acid. Some reddening of the solution and considerable frothing occurred. After 0·5 hour's standing, the viscous mass was diluted with ice and strongly basified with aqueous ammonia. After some hours, the sulphonamide was collected and crystallised from hot water, forming white plates, m. p. 114—115° (Kelbe, *Ber.*, 1886, **19**, 1969, quotes m. p. 115·5°); yield 26 g., *ca.* 60%.

In another experiment barium cymene-2-sulphonate (30 g.) was warmed with an equal weight of phosphorus pentachloride, etc., and the crude oily product transformed into the amide as above. After crystallisation from water, 16·1 g. (70%) of the sulphonamide were obtained, m. p. 114°. The isomeric 3-sulphonamide has m. p. 151° (Remsen and Day, *Amer. Chem. J.*, 1883, **5**, 150).

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