

THE SULFONATION OF ORTHO TOLUIDINE
AND THE PREPARATION OF
SODIUM 6-CHLORO-5-NITRO-META-TOLUENE SULFONATE

THESIS

BY

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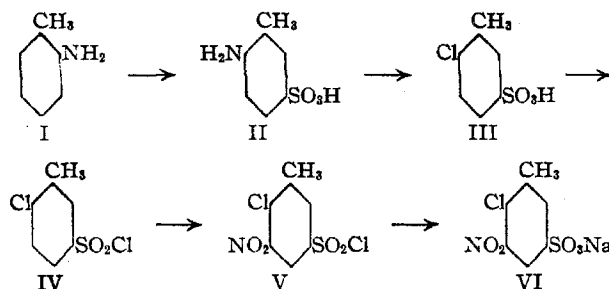
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Introduction

Davies¹ has pointed out that 6-chloro-5-nitro-*m*-toluenesulfonic acid may be used for separating potassium and rubidium on the one hand from lithium, sodium and cesium on the other, since the salts of the acid with the two former metals are very slightly soluble in water, while those with the three latter are quite soluble. It seemed desirable to study in more detail the steps involved in the preparation of the acid with the purpose of improving the procedures and increasing the yields at the different steps. We did not attempt to obtain the acid itself, but converted it instead into its sodium salt, which possesses a solubility markedly lower than that of the free acid and on that account separates more readily from aqueous solution.

The operations involved are as follows.



o-Toluidine is first sulfonated to *o*-toluidine-5-sulfonic acid (II), which through the diazo reaction is converted into 6-chloro-*m*-toluenesulfonic acid (III). This with phosphorus pentachloride yields 6-chloro-*m*-toluenesulfonoylchloride (IV) and the latter on nitration gave 6-chloro-5-nitro-*m*-toluenesulfonoylchloride (V) which is easily converted into sodium 6-chloro-5-nitro-*m*-toluenesulfonate (VI).

The first step, namely, the sulfonation of *o*-toluidine, was studied in detail. It was found that the presence of iodine, the use of which has been recommended by Ray and Dey,² is a decided detriment, since it catalyzes the oxidation of the toluidine by the sulfuric acid and leads to considerable charring with decreased yields. Best results were obtained by the use

¹ Davies, *J. Chem. Soc.*, 121, 785 (1922).

² Ray and Dey, *ibid.*, 117, 1405 (1920).

of fuming sulfuric acid³ (20%) in the ratio of two moles of acid to one of toluidine, and heating on an oil-bath for ten hours at 180°.

In the second step, the replacement of an amino group by a chlorine atom through the diazo reaction with cuprous chloride present, practically quantitative results were obtained. It is not necessary, as Davies recommends, to remove copper from the filtrate in order to obtain subsequent crops of the chlorosulfonic acid (III), since the latter crystallizes in fairly pure condition as the liquid is evaporated.

In the third step, the conversion of the sulfonic acid (III) to the sulfonechloride (IV), Davies obtained a practically quantitative yield, using, however, the sodium salt instead of the acid. His result is more satisfactory than that obtained with the free acid, but his procedure involves an additional step, namely, the conversion of the sulfonic acid to its sodium salt. The reaction of the acid with phosphorus pentachloride is carried out in the usual way.

The nitration of the sulfonechloride (IV) was done by following the directions of Davies and gave similar results.

The hydrolysis of the nitrated sulfonechloride (V) to the acid was also carried out as he directs, and the conversion of the latter to its sodium salt (VI) was a simple matter.

It is possible to obtain a 37% yield of the sodium salt (VI) from *o*-toluidine (I) by following the modified procedures as described below.

Experimental Part

Sulfonation of *o*-Toluidine.—Table I shows the results obtained by sulfonating *o*-toluidine (Eastman) with sulfuric acid at different temperatures and for different periods of time. The product from most of the runs was purified by one crystallization from water. In some cases, especially where it was evident that the yield was low, the crude material was not crystallized from water. The pronounced evolution of sulfur dioxide, accompanied by more or less extensive carbonization when iodine is present, shows conclusively that this element catalyzes the oxidation by sulfuric acid and causes a decreased yield of the sulfonic acid. The best results were obtained by heating the base with two molecular proportions of fuming sulfuric acid at 180° for ten hours in the absence of iodine. A modification of the conditions, that is, a shorter or longer time of heating, a higher or lower temperature, a larger amount of fuming sulfuric acid, the use of ordinary sulfuric instead of the fuming acid or the presence of iodine, resulted in a decreased yield.

In this method the acid should be added to the toluidine in small portions at a time and during cooling, in order to avoid charring. After the mixture had been heated for a few hours in the oil-bath, crystals of the

³ Gerver [*Ann.*, **169**, 374 (1873)] used fuming sulfuric acid. His yields were low.

sulfonic acid separated. At the end of ten hours the semi-solid mass is poured into a dish, two and one-half times its volume of water is added slowly during stirring and the mixture allowed to set overnight. The mass of crystals is filtered off, the filtrate cooled to 0° and a second small crop is obtained. The solid acid is purified by dissolving it in a minimum amount of hot water (300–400 cc.), boiling the solution with animal charcoal, filtering while hot and cooling. Fine white needles separate, which appear pure. After being filtered, the liquid is evaporated to 100 cc., and a second crop obtained. Since the solubility of the acid is only 26 g.⁴ in 100 cc. of water at 11°, it is not worth while to obtain a third crop. The acid was dried by heating for a few hours at 100°; yield, 78%.

The equivalent weight of the sulfonic acid after drying for three hours at 120° was determined by titration against a standard solution of alkali, and found to be 187.4 and 187.2. The value calculated for C₇H₇O₃NS is 187.1.

Diazotizing *o*-Toluidine-5-sulfonic Acid.—The procedure of Davies, which works well, was improved by using a mechanical stirrer and taking

TABLE I
SULFONATION OF *o*-TOLUIDINE

Strength of acid	Molecular ratio, acid to toluidine	Molecular ratio, iodine to toluidine	Average temp. of oil-bath, °C.	Time, hours	Sulfonic acid, yield, %	Remarks	
						Odor of SO ₂	Carbonization
96% H ₂ SO ₄	1.5	0.00	180	10	51	Slight	Slight
96% H ₂ SO ₄	2	.04	155	8	21 ^a	Slight	Moderate
96% H ₂ SO ₄	2	.00	180	9	72	Slight	Slight
96% H ₂ SO ₄	2	.00	180	10	62	Slight	Slight
96% H ₂ SO ₄	3	.04	155	8	39 ^a	Slight	Moderate
100% H ₂ SO ₄	3	.04	160	5	48	Slight	Moderate
20% SO ₃	1.5	.04	180	12	48 ^b	Slight	Slight
20% SO ₃	1.5	.04	180	10	48 ^b	Slight	Slight
20% SO ₃	2.0	.04	140	13	53	Slight	Moderate
20% SO ₃	2.0	.04	153	8	43	Strong	Moderate
20% SO ₃	2.0	.04	158	2.5	48	Strong	Moderate
20% SO ₃	2.0	.04	172	3.25	54	Strong	Moderate
20% SO ₃	2.0	.04	178	7	71	Strong	Moderate
20% SO ₃	2.0	.04	180	10	53	Strong	Moderate
20% SO ₃	2.0	.00	180	9	72	Slight	Negligible
20% SO ₃	2.0	.00	180	10	78	Slight	Negligible
20% SO ₃	2.0	.00	180	12	69	Slight	Slight
20% SO ₃	2.0	.00	190	10	65	Moderate	Moderate
20% SO ₃	3.0	.04	155	5	61 ^b	Strong	Extensive
20% SO ₃	3.0	.04	177	6.5	58	Strong	Extensive
20% SO ₃	3.0	.04	180	7	61	V. strong	Extensive
20% SO ₃	3.0	.04	180	10	51	V. strong	Extensive
20% SO ₃	3.0	.00	180	11	57	Moderate	Moderate

^a Toluidine not all sulfonated. ^b Impure.

⁴ Hasse, *Ann.*, **230**, 287 (1885).

two hours instead of one and one-half for introducing the sodium nitrite solution. The reaction was finished as soon as oxides of nitrogen were evolved continuously, showing that an excess of nitrite had been added.

Replacement of the Diazonium Group by Chlorine.—The diazo solution obtained from 200 g. of sulfonic acid is placed in a large evaporating dish, and to it is added slowly a solution of 200 g. of cuprous chloride dissolved in 1000 cc. of concd. hydrochloric acid and 200 cc. of water. Much frothing accompanies the reaction. After being heated for two hours on the water-bath the mixture is allowed to stand until morning, when the crop of colorless plates is filtered off and washed first with dil. hydrochloric acid, then with water. The filtrate on evaporation yields two small crops of thin plates which, added to the previous one, give a total weight of 216 g. of thoroughly dried 6-chloro-*m*-toluenesulfonic acid (III); yield, 98.2%.

6-Chloro-*m*-toluene-sulfonechloride (IV).—Instead of converting III to its sodium salt, the acid itself is treated with phosphorus pentachloride. The phosphorus chloride (500 g.) is added to the well-ground, thoroughly dried sulfonic acid (216 g.) and heated on a boiling water-bath for two hours during occasional shaking. The product is poured upon ten times its weight of finely crushed ice, following which the dark brown liquid soon changes to a coarsely granular, grayish solid. On filtering off the aqueous phase and grinding the residue with fresh portions of water, the solid can be freed from phosphorus chlorides. After drying, the product weighs 235 g. and melts at about 65°;⁵ yield, 85%.

6-Chloro-5-nitro-*m*-toluenesulfonechloride (V).—The nitration of IV above is carried out as described by Davies. It is essential that the material be thoroughly dried before nitrating. It may be done by heating the sulfonechloride at 45° for six hours; yield, 75%.

Sodium 6-Chloro-5-nitro-*m*-toluenesulfonate (VI).—The hydrolysis of V with alcohol followed by evaporation with water is done according to the directions of Davies. The solution is then diluted, neutralized with sodium hydroxide and boiled with animal charcoal. The salt is recovered by crystallizations and evaporations; yield, 80%.

In Table II a comparison is made between the results of Davies and those obtained by us.

TABLE II
SODIUM 6-CHLORO-5-NITRO-*m*-TOLUENESULFONATE FROM *o*-TOLUIDINE

Product	Per cent. yield per step		Per cent. yield in process	
	Davies	S. and L.	Davies	S. and L.
<i>o</i> -Toluidine-5-sulfonic acid	57	77	57	77
6-Chloro- <i>m</i> -toluenesulfonic acid	59.8	98.2	34	75
6-Chloro- <i>m</i> -toluenesulfonechloride (from Na salt)	96	85	33	63.5
6-Chloro-5-nitro- <i>m</i> -toluenesulfonechloride	70.8	75	23	47.5
Sodium 6-chloro-5-nitro- <i>m</i> -toluenesulfonate	?	80	?	37

Summary

An investigation has been made of the sulfonation of *o*-toluidine and optimum conditions have been determined.

A study has also been made of the operations involved in preparing from

⁵ Davies gives 64–66°.

o-toluidine-5-sulfonic acid, sodium 6-chloro-5-nitro-*m*-toluenesulfonate, a compound recently shown to be suitable for the separation of the rarer alkali metals. This has resulted in an improvement of the methods and in obtaining a 37% yield of the sodium salt calculated to the *o*-toluidine.

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