

ORGANIC PRECIPITANTS FOR POTASSIUM, 5-NITRO-6-CHLOROTOLUENE-
3-SULFONIC ACID AND RELATED SALTS

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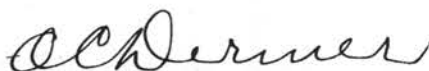
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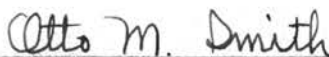
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In Partial Fulfillment of the Requirements
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1937

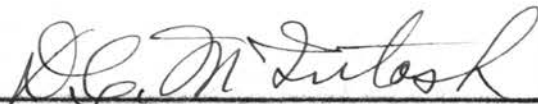
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In Charge of Thesis



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FOREWORD

Sodium 5-nitro-6-chlorotoluene-3-sulfonate appears to be the best organic reagent, with one possible exception, for the quantitative determination of potassium ion. The sodium salt is about 32 times as soluble as the potassium salt. The absolute solubility of the potassium salt, however, is too great to permit ordinary quantitative precipitation.

The purpose of this investigation is to study the effect on solubility exerted by the various groups on the benzene ring in the compound mentioned. The method involves varying the nature of the groups present and comparing solubilities of the salts.

HISTORICAL

Most of the organic compounds which have been proposed as analytical reagents for potassium may be classified as nitrophenols or aromatic sulfonic acids. Among nitrophenols recommended have been o-nitrophenol (63), 2, 4-dinitrophenol (63), 2, 6-dinitrophenol (63), 2, 4, 6-trinitrophenol (picric acid) (5, 11, 13, 45, 54, 55, 59, 64, 77), 2, 4, 6-trinitro-m-cresol (63), 2, 4, 6-trinitroresorcinol (styphnic acid) (63), and 2, 4, 6, 2', 4', 6'-hexanitrodiphenylamine (dipicrylamine) (50, 56, 69, 83), which closely resembles a nitrated phenol. Classified as sulfonic acids are 1-naphthalene sulfonic acid (63), 1-amino-2-naphthol-6-sulfonic acid (4, 45), 2, 4-dinitronaphthol-7-sulfonic acid, also called flavianic acid (18a), 2-nitro-4-chlorobenzene sulfonic acid (23a), and 2-chloro-3-nitrotoluene-5-sulfonic acid (20, 21, 27, 30, 40, 41, 79). Closely related are "Dreft," "Gardinol," and other salts of alkyl sulfuric acids (29, 60, 81). Reagents which cannot be listed as either nitrophenols or sulfonic acids include picrolonic acid (76), 5-nitrobarbituric acid (dilituric acid) (25a), and tartaric acid (2, 3, 6, 7, 10, 12, 14, 15, 16, 17, 18, 19, 22, 32, 37, 38, 39, 44, 45, 46, 47, 48, 51, 57, 58, 62, 65, 66, 67, 72, 73, 78, 80, 84, 85). Although 2, 4-dinitronaphthol-7-sulfonic acid and 5-nitrobarbituric acid give promise of becoming quantitative reagents for potassium only the following have been used for that purpose: Tartaric acid, picric acid, dipicrylamine, and 2-chloro-3-nitrotoluene-5-sulfonic acid.

Of these three organic reagents tartaric acid gives the least accurate results. Probably the best procedure for its use is that of Clarke and Davidson (18), in which the potassium is precipitated as potassium bitartrate by the addition of tartaric acid and sodium bitartrate. The potassium bitartrate is filtered out, washed with dilute alcohol, dissolved in hot water and titrated with standard sodium hydroxide solution. Since a rough approximation of the percentage of potassium can thus be made in a short time (one half hour), the method is popular where accuracy is not essential.

According to the procedure used by Caley (13), potassium is precipitated from water by a saturated solution of picric acid in 95 per cent alcohol. The potassium picrate is filtered out, washed with ether to remove picric acid, and dissolved in a large volume of water. The yellow solution is compared in a colorimeter to a standard solution of potassium picrate containing about the same concentration of potassium. This procedure was found to give good results within only a narrow range of concentrations; too much potassium makes it difficult to match the deepened color, and too little is not completely precipitated.

Winkel and Maas (83) have recently outlined a method whereby potassium is quantitatively precipitated and determined by use of magnesium dipicrylamine. The method is said to give results reproducible to 0.5% of the potassium present, and to be applicable in the presence of moderate amounts of sodium, magnesium, or ammonium ions.

The English chemist Davies (20) first prepared 2-chloro-3-nitrotoluene-5-sulfonic acid and noted the slight solubility of its potassium salt. The details of its use in determining potassium were worked out by Davies and Davies (21). It has been used by Wiggins and Wood (79)

for determining potassium in oil well brines colorimetrically by estimating the nitro groups in the precipitated salt by reducing them, diazotizing and coupling with R salt. Langham (40) and Schempf (66a) have tried to effect the micro-determination of potassium by dissolving the precipitated salt in concentrated alkali and estimating the depth of color produced (by the nitro group) by comparison with standards. The method is not, however, very satisfactory, owing to the solubility of the potassium salt (30). Efforts have been made (41) to decrease this solubility by using various non-aqueous solvents, as is done in potassium analysis by the perchlorate and the chloroplatinate methods; but the results are not promising.

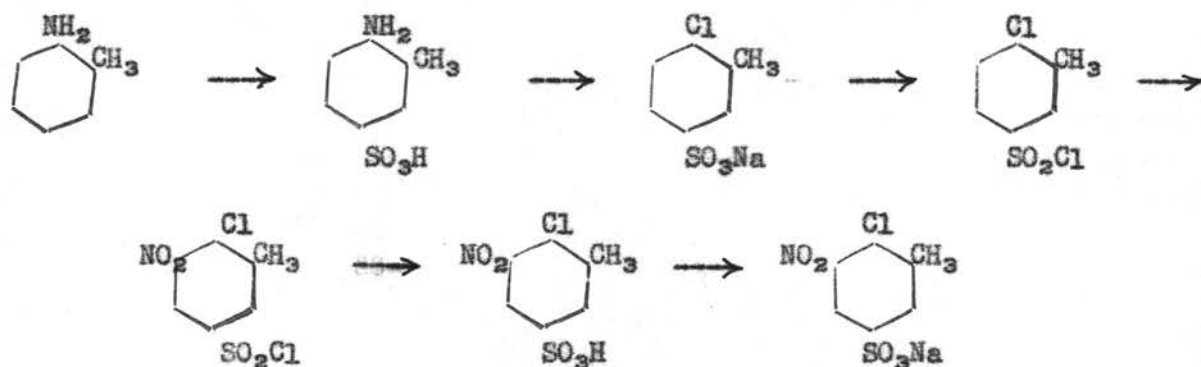
EXPERIMENTAL

The experimental work on this problem may be divided into three phases:

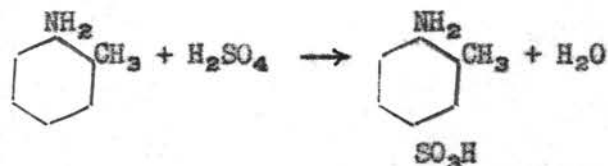
1. Synthesis of sodium and potassium salts, in pairs.
2. Analysis of the salts for alkali metal, to determine their degree of purity.
3. Determination of the solubilities of the salts.

Synthesis

For the preparation of salts there was used the method of Davies (20), more or less modified, by Schultz and Lucas (68) and by the authors. For Davies' reagent, sodium 2-chloro-3-nitrotoluene-5-sulfonate, the following steps are required:



In the sulfonation of o-toluidine

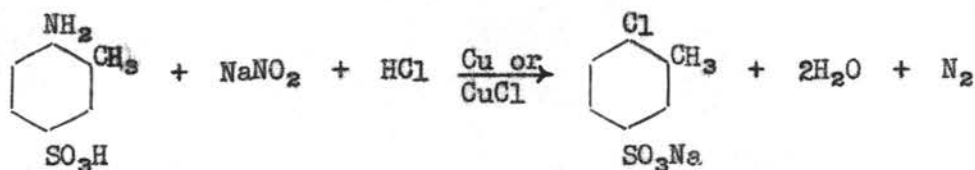


750 g. of the amine were stirred and heated with 2250 g. of conc. sulfuric acid for 9 hours at about 160°, and then poured into a large volume of cold water. It was impossible to filter out the crude product from the wash water until the mixture had been boiled and then chilled. After

*All temperatures are recorded in degrees Centigrade

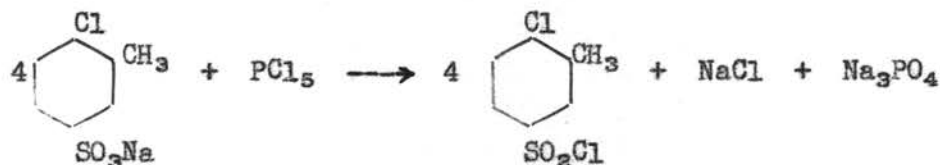
this product has been boiled with charcoal and recrystallized from water, it weighed 900 g. (82% theoretical—the highest to be reported for this step).

Several small portions (50 g. each) of this 2-aminotoluene-5-sulfonic acid were converted into sodium 2-chlorotoluene-5-sulfonate by reactions represented as



At this stage we were unable even to approach the yield (98%) of 2-chlorotoluene-5-sulfonic acid claimed by Schultz and Lucas although we tried both the Sandmeyer and the Gattermann method. Since the free acid is very soluble in water and since a mol of sodium ions was present, the precipitated crystals which Schultz and Lucas obtained must actually have been the sodium salt, not the free acid.

The sodium salt was heated with excess phosphorus pentachloride or oxychloride (both were tried) for several hours,

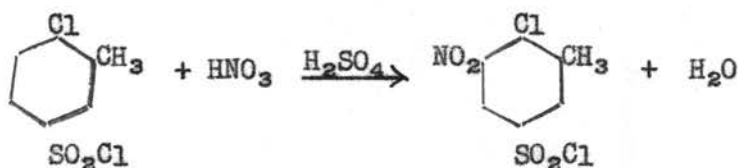


the mixture poured into ice water, and the sulfonyl chloride recrystallized by extracting with ligroin in a Soxhlet apparatus and then cooling; melting point 59–61°. The literature gives 60–65° (86), 64–6° (20), 65° (68), and 64° (23).

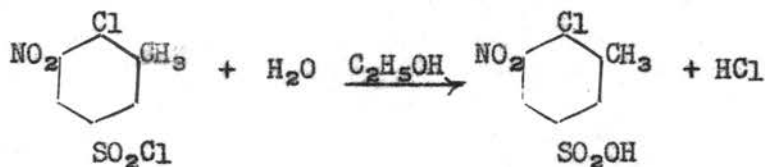
We also tried to shorten the time of preparation of the sulfonyl chloride and to improve the yield by starting with o-chlorotoluene. This modification is discussed as the first step in preparing salts of 2-chloro-

toluene-5-sulfonic acid.

The nitration and hydrolysis of the sulfonyl chloride were performed according to the published directions of Davies. 2-chlorotoluene-5-sulfonyl chloride was gradually added to a mixture of two volumes of concentrated sulfuric acid and one volume of fuming nitric acid. The reaction mixture was stirred well and held for about 90 minutes between 25° and 35° in temperature.

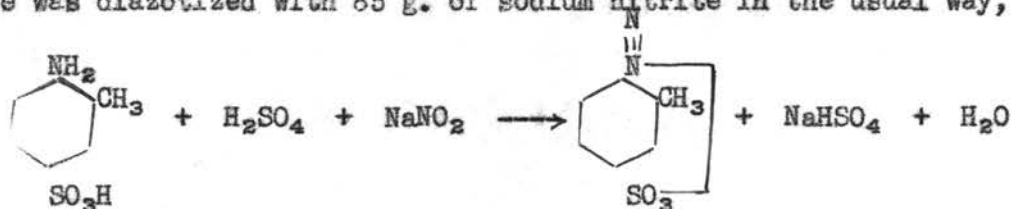


The mixture was then poured into ice water and the nitrated compound filtered out, dried, and recrystallized from ligroin. The pure 2-chloro-3-nitrotoluene-5-sulfonyl chloride was then hydrolyzed by refluxing with 90% alcohol for three hours, after which it was concentrated and repeatedly evaporated with fresh water to expel hydrogen chloride. This method of hydrolysis avoids any danger of removing the ring halogen, and also prevents contamination of the salts with alkali halide.

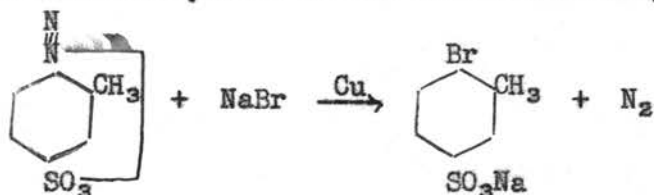


The acid was then separated into portions which were neutralized with sodium hydroxide and potassium hydroxide to form the respective salts. These were purified by several recrystallizations, the sodium salt from 50-90% alcohol, the potassium salt from water. Since the yield of purified salts was rather small, we also recrystallized and used Eastman's sodium 2-chloro-3-nitrotoluene-5-sulfonate (No. 3405), made by the above method, for some of our work.

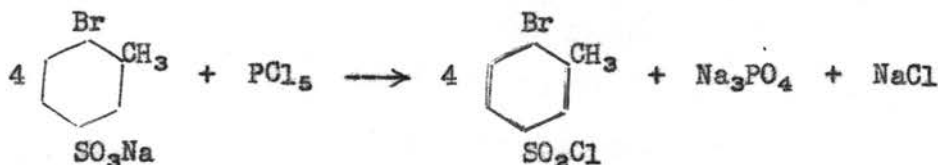
2-Bromo-3-nitrotoluene-5-sulfonic acid. This compound was prepared by a method analogous to that of Davies. 187 g. (1 mol) of 2-aminotoluene-5-sulfonic acid was suspended in 100 g. of concentrated sulfuric acid, 150 g. of sodium bromide dihydrate, and about 50 cc. of water. The amine was diazotized with 85 g. of sodium nitrite in the usual way,



and then treated with copper powder (ca 80g.) freshly prepared from copper sulfate and zinc. (A preliminary run had indicated that the Gattermann catalyst is better than the Sandmeyer for this step.)



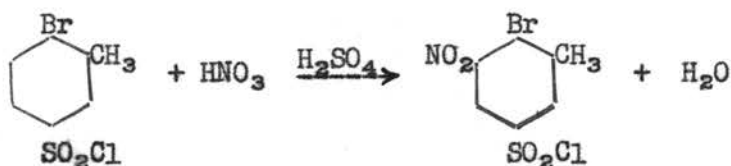
After the persistent foam was gone (this required standing overnight, followed by warming) the solution was filtered and concentrated to obtain sodium 2-bromotoluene-5-sulfonate. The salt, badly contaminated with copper salts and sodium sulfate, was air and oven-dried and treated with PCl_5 as usual.



The 2-bromotoluene-5-sulfonyl chloride, when well purified by recrystallization from ligroin, weighed 66 g. and melted at 56-57°. Wynne (86) gives 61°.

65 g. of this sulfonyl chloride were slowly added to a mixture of 80 cc. of concentrated sulfuric acid and 40 cc. fuming nitric acid which

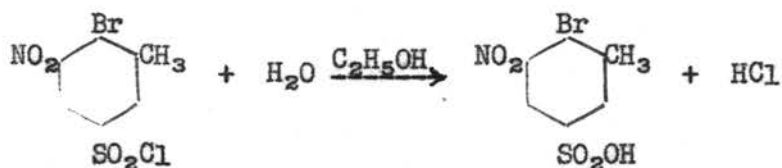
was stirred constantly for two hours at temperatures between 25° and 35°



The 2-bromo-3-nitrotoluene-5-sulfonyl chloride was isolated as usual and recrystallized, first from ligroin, then from ether. Yield 36 g.

M. P. 64-64.5°.

The nitrated sulfonyl chloride was refluxed with 50 cc. of 90% alcohol for three hours

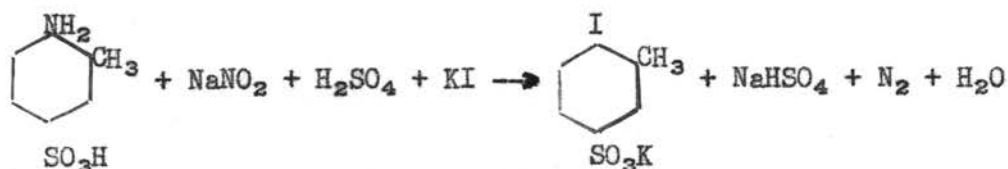


and the 2-bromo-3-nitrotoluene-5-sulfonic acid purified by repeated evaporations with distilled water. The salts obtained by neutralization were recrystallized, the potassium salt from water and the sodium salt by Soxhlet extraction and crystallization using 90% alcohol.

It should be mentioned that Hübner and Müller (35) long ago carried out a nitration of barium 2-bromotoluene-5-sulfonate. The reaction did not proceed normally, however, for the salts formed were all very soluble, the potassium more so than the sodium.

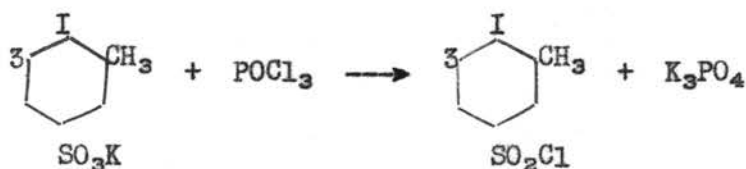
2-Iodo-3-nitrotoluene-5-sulfonic acid. This compound could not be secured because of the repeated failure of the nitration of 2-iodotoluene-5-sulfonyl chloride, but the synthesis up to that point will be described.

One mol of 2-aminotoluene-5-sulfonic acid was diazotized as usual, stirred for 15 or 20 minutes to remove excess nitrous acid, and then treated with a saturated solution of one mol of potassium iodide in water. Slight darkening and immediate evolution of gas began.



After two hours the mixture was stirred and heated until all separated solid dissolved; on cooling, potassium 2-iodotoluene-5-sulfonate readily crystallized out. A further quantity was obtained by concentrating the mother liquor. Total yield, 247 g.; this is 74 per cent of theoretical yield. This acid was also obtained, as its sodium salt, by preparing o-iodotoluene by the Gattermann reaction and sulfonating the product. 53 g. of o-toluidine thus produced 59 g. of o-iodotoluene, of boiling point 203-208°; this when sulfonated with 10% fuming sulfuric acid yielded 67 g. of sodium 2-iodotoluene-5-sulfonate.

The oven-dried salts were found to liberate iodine when treated with phosphorus pentachloride, to give oily decomposition products when acted upon by chlorosulfonic acid, and to fail to react with boiling thionyl chloride (B. P. 75°). Consequently phosphorus oxychloride was used to form the sulfonyl chloride.



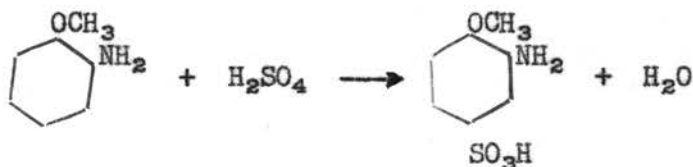
247 g. of this potassium salt were refluxed with 225 g. of phosphorus oxychloride for three hours in an oil bath. After excess oxychloride had been recovered by distillation the residue was worked up as usual. The 2-iodotoluene-5-sulfonyl chloride, when recrystallized from ether, amounted to 157 g. of best quality, M. P. 63.5-64.5°, and 15 g. of second quality.

Practically all of this sulfonyl chloride was used up in futile attempts to effect its nitration by Davies' method. If the temperature

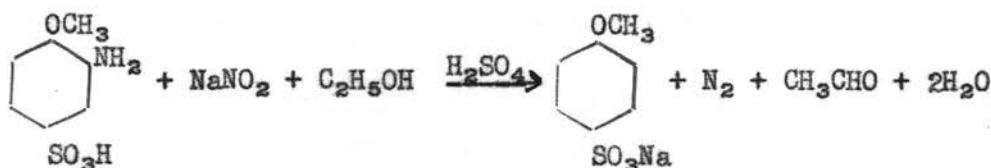
was held low, no reaction occurred; if it was raised a few degrees, the reaction mixture yielded no insoluble material at all when poured into water. On two occasions only, small amounts of a product, melting after recrystallization at 172° or $178-82^{\circ}$, were obtained. Nitration in acetic acid solution also failed. The attempt was finally abandoned when solubility results indicated that sodium 2-iodo-3-nitrotoluene-5-sulfonate would probably not be superior to the bromine derivative as a potassium precipitant.

2-Chloro-6-nitroanisole-4-sulfonic acid. This acid was the product of an attempt to obtain 2-chloro-3-nitroanisole-5-sulfonic acid.

50 g. of *o*-anisidine was stirred with 150 g. of 15% fuming sulfuric acid at 150° for an hour, and then poured into ice water. The crude product obtained by filtration was too insoluble to be recrystallized from water; therefore, it was dissolved in alkali and reprecipitated by acid. Yield 56 g. A similar run starting with 150 g. of *o*-anisidine produced 170 g. of sulfonic acid. The reaction was eventually found to have taken the course

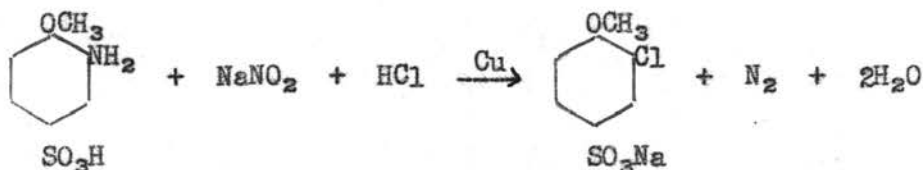


This was proved by removal of the amino group and identification of the resulting anisole sulfonic acid. 20 g. of the acid was diazotized in ethyl alcohol, treated with a little copper powder, and boiled several hours.

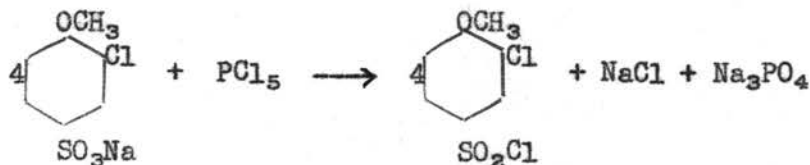


Upon concentration, the solution deposited a sodium salt which was converted to the sulfonyl chloride by using phosphorus pentachloride (thionyl chloride gave very poor results). The sulfonyl chloride, by treatment with ammonium hydroxide, yielded an amide which, after recrystallization from alcohol, melted at 115°. Since p-anisole sulfonamide melts at 112-116° (26, 70) whereas m-anisole sulfonamide melts at 128° (71) the original aminosulfonic acid must have had the formula assigned above. This confirms a German patent claim (1) as to the product of sulfonating o-anisidine under other conditions.

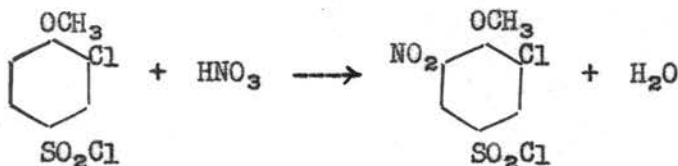
We chose to complete the procedure of Davies to permit a comparison of the salts with the others synthesized. By the usual method of diazotization and Gattermann introduction of chlorine,



treatment with thionyl chloride or phosphorus pentachloride,

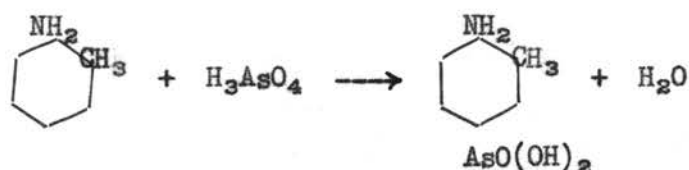


and recrystallization from ligroin, we obtained from 68 g. of the amino acid 32 g. of pure 2-chloroanisole-4-sulfonyl chloride, melting at 77°. This 32 g. lot, stirred with 20 g. of fuming nitric acid and 40 g. of concentrated sulfuric acid at 45-50° for 90 minutes, gave 20 g. (after recrystallization from ligroin) of 2-chloro-6-nitroanisole-4-sulfonyl chloride, melting at 44°.

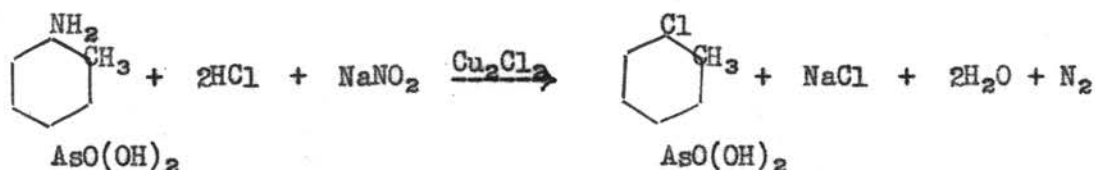


This was hydrolyzed and converted into pure potassium and sodium salts as usual by the method of Davies.

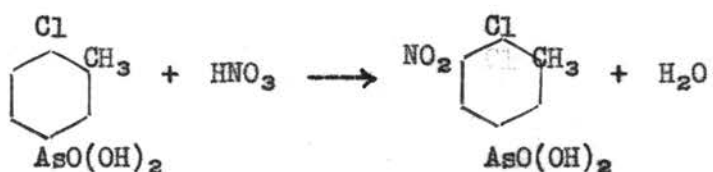
2-Chloro-3-nitrotoluene-5-arsonic acid. 320 g. of o-toluidine were arsonated by heating with 345 g. of syrupy arsenic acid according to the procedure recommended for arsonilic acid (43).



186 g. (41 %, based on arsenic acid) of 2-aminotoluene-5-arsonic acid were obtained. By means of the Sandmeyer reaction 52 g. of this acid were converted to 2-chlorotoluene-5-arsonic acid (14 g.),



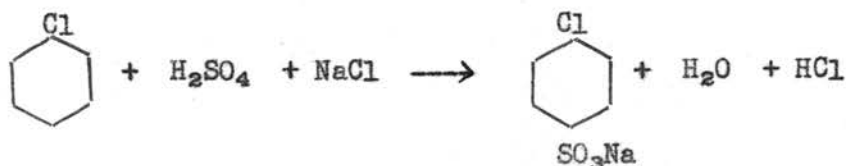
and thence by nitration in hot fuming nitric acid to 2-chloro-3-nitrotoluene-5-arsonic acid (15 g.).



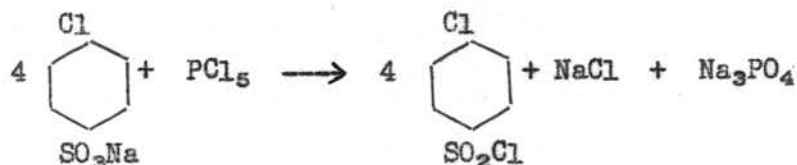
Since qualitative tests showed that this dibasic acid gives very soluble sodium and potassium salts, no further work was done on purifying these salts or proving their structure.

2-nitrochlorobenzene-4-sulfonic acid. 150 g. of chlorobenzene (Eastman No. 70) were sulfonated by stirring with 470 g. of 15 % fuming sulfuric acid until the reaction mixture was homogeneous. When this was poured into water and sodium chloride added, 316 g. of sodium

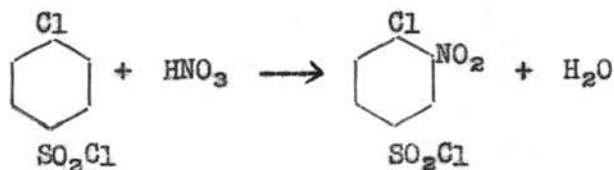
p-chlorobenzene sulfonate separated.



158 g. of this salt were converted to the sulfonyl chloride as usual;

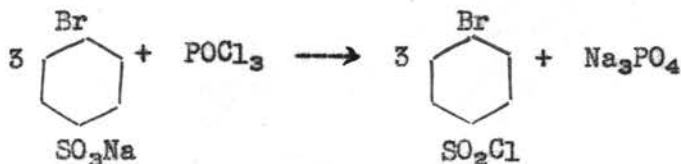


after recrystallization from ligroin and ether the p-chlorobenzene sulfonyl chloride melted at 52-3°. (Literature gives 55° (28), 53.3° (49), 50.5-51.5° (53)). By the procedure of Davies, this chloride was nitrated (M. P. 39°); literature gives 40-41 (25))



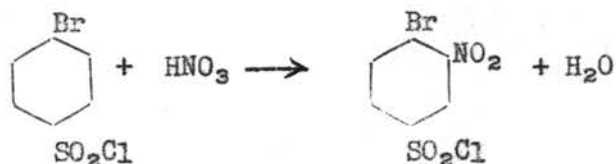
and converted into sodium- and potassium -2-nitrochlorobenzene-4-sulfonates. An attempt to nitrate sodium p-chlorobenzene sulfonate directly produced a mixture which could not be separated into its components.

2-Nitrobromobenzene-4-sulfonic acid. 259 g. of crude sodium p-bromobenzene sulfonate (student preparation) and 170 g. of phosphorus oxychloride were mixed and heated together.



The crude p-bromobenzene sulfonyl chloride obtained by pouring the reaction mixture into water was recrystallized from ligroin; melting

point then was 74-74.5°; literature gives 74.5 (49) and 75-6 (9, 33). 100 g. of this sulfonyl chloride gave 70 g. of 2-nitrobromobenzene-4-sulfonyl chloride, melting after recrystallization at 57° (Goslich (28) gives 56-7°), by the nitration procedure of Davies.



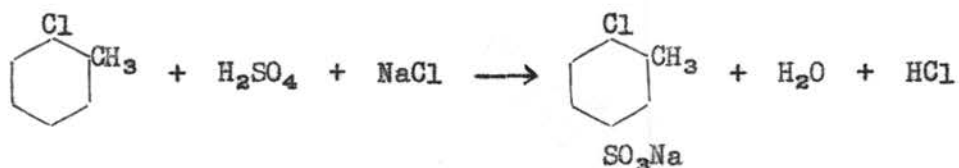
The salts were secured as usual by hydrolysis and neutralization of the sulfonic acid with alkali. The potassium salt has been made before, from the product obtained by nitrating barium p-bromobenzene sulfonate (28).

2-Nitroiodobenzene-4-sulfonic acid. Like 2-iodo-3-nitrotoluene-5-sulfonic acid, this acid was never obtained—and for the same reason. Eastman's iodobenzene (No. 152) was converted to p-iodobenzene sulfonyl chloride by either (a) sulfonating with fuming sulfuric acid and treating the sodium sulfonate with chlorosulfonic acid (31) or (b) treating iodobenzene itself with chlorosulfonic acid. The former produced the purer product of M. P. 80-81° after recrystallization; the literature gives values from 81.5° to 87° (42, 49, 53, 82, 87). However, Davies' nitration method failed to give any 2-nitroiodobenzene-4-sulfonyl chloride from either sample.

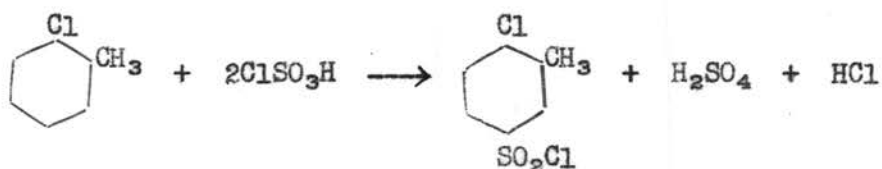
2-X-toluene-5-sulfonic acids, where X = F, Cl, Br or I. These four acids were obtained by Davies' method from the sulfonyl chlorides, which were in turn prepared in various ways.

2-chlorotoluene-5-sulfonyl chloride was synthesized by three different procedures. One of these has already been described on page 6: that which employed 2-aminotoluene-5-sulfonic acid as a starting material. In another,

144 g. of *o*-chlorotoluene, b. p. 154-6°, was stirred with 315 g. of 7% fuming sulfuric acid until it dissolved.

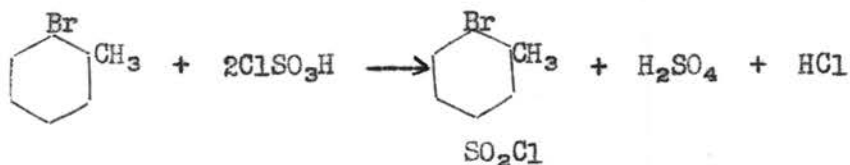


The sodium salt (170 g.) was isolated and treated with phosphorus pentachloride as usual to obtain 105 g. of crude 2-chlorotoluene-5-sulfonyl chloride, melting at 58-60°. Recrystallization from ligroin yielded 54 g. of pure product, m. p. 59-61°. The third alternative method involved sulfonation with chlorosulfonic acid to eliminate one step. 74 g. of *o*-chlorotoluene was dropped into 225 g. of stirred chlorosulfonic acid without cooling, the addition requiring about two hours.



The reaction mixture was cautiously poured into water and the crude sulfonyl chloride extracted with ligroin. After this solvent had been distilled off the chloride was fractionated through a 16 inch Vigreux column at 1 mm. pressure: B. P. 109-116° yield 92 g. This was then recrystallized from a mixture of ligroin and ethyl ether. Another similar run in which the chlorosulfonic acid was dropped into the *o*-chlorotoluene was more disagreeable to carry out and did not give so good a yield.

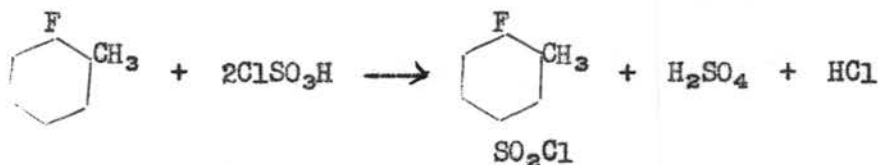
2-bromotoluene-5-sulfonyl chloride was obtained as described on page 8, and also by sulfonating *o*-bromotoluene. 100 g. of redistilled *o*-bromotoluene, B. P. 176-8°, was dropped into 200 g. of stirred chlorosulfonic acid within 1 hour, the temperature remaining below 50°.



The 2-bromotoluene-5-sulfonyl chloride was isolated by the method used for the chloro derivative; it was distilled at 4 mm. pressure and recrystallized from ether: M. P. 54-55°.

2-iodotoluene-5-sulfonyl chloride was prepared as outlined on page 10.

2-fluorotoluene-5-sulfonyl chloride was secured by sulfonating o-fluorotoluene with chlorosulfonic acid. 60 g. of o-fluorotoluene, prepared from o-toluidine via the diazonium fluoborate (24), B. P. 112-5°, was dropped into 200 g. of stirred chlorosulfonic acid during 2 hours.



The sulfonyl chloride, on extraction and distillation at 1 mm., was separated into two fractions, of boiling ranges 99-109° and 101-103°. Since these could not be crystallized by cooling, they were hydrolyzed separately according to Davies' method. When the solubilities of the salts from the two fractions later proved to be the same, we concluded that the fractions contained only one compound.

Analysis

To prove the purity of each salt obtained, it was analyzed for alkali metal by the sulfate method (8, 61, 74). The customary procedure involving simple evaporation with concentrated sulfuric acid in open crucibles could not be used for the nitrated salts because the initial decomposition was so violent as to cause losses of material. A preliminary digestion overnight with ammonium sulfide, intended to reduce the nitro group, did not help much. It was finally found that a modified Kjeldahl digestion would destroy organic matter safely.

Two or more samples of the oven-dried salt (about 0.2 g. each) were placed in 30 cc. Florence flasks, each of which contained 1-2 cc. of concentrated sulfuric acid. The mixtures were heated at about 200° until they became clear. This usually required 8-10 hours, but the time could be decreased by occasionally adding a drop of concentrated nitric acid, to aid in oxidizing the carbon. The clear cooled solutions were quantitatively transferred to weighed crucibles by rinsing with water, then cautiously evaporated dry and ignited to constant weight at a dull red heat.

This procedure failed when applied to salts containing fluorine, because the hydrofluoric acid attacked the glass reaction vessels and caused high results. In those cases, fortunately, the decomposition in platinum crucibles could be carried out without losses.

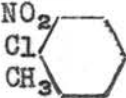
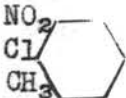
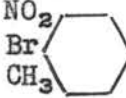
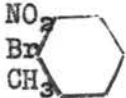
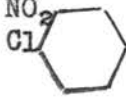
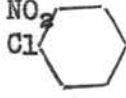
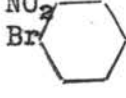
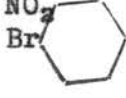
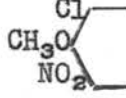
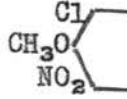
Determination of Solubility

The glass-stoppered bottles used in these determinations were first cleaned and tested for tightness; on some it was necessary to regrind the stoppers. Solutions of each of the salts studied were made up in these bottles, only enough distilled water being used to dissolve part of the solid. The stoppers were wired in and the bottles rotated end over end on a rack at about 35° for several hours. Then they were placed in a water thermostat at $30^{\circ} \pm 0.5^{\circ}$ and further rotated until equilibrium was reached in the solutions. By repeated sampling on each run we found that 24 hours were sufficient to guarantee saturated solutions.

The sampling was done by binding a tiny filter on the tip of a 5 cc. pipette, withdrawing a portion of solution through this filter, removing the filter, and delivering the solution into a weighed dish. The solution was then weighed and evaporated to dryness, and the residual salt dried to constant weight in an oven at 120° . A blank determination gave too small a residue to be weighed.

Results

Analyses and Solubilities of Salts

Salt	% metal calc.	% metal found		Solubility g/100 g. water		Mean Soly. mols/100g. water	Soly. Na Salt	Soly. K Salt
 SO ₃ Na	8.41	8.49,	8.54	20.4,	20.2 ^a	.0739		
								35
 SO ₃ K	13.50	13.68,	13.75	0.61,	0.61 ^b	.00211		
 SO ₃ Na	7.23	7.23,	7.24	17.2,	17.7	.0549		
								34
 SO ₃ K	11.71	11.59,	11.65	0.55,	0.54	.00162		
 SO ₃ Na	8.86	8.89,	8.87	19.2,	19.6,	.0748		
								10
 SO ₃ K	14.22	13.96,	14.15	2.04,	2.07 ^c	.00744		
 SO ₃ Na	7.57	7.64,	7.65	41.1,	40.9	.135		
								18
 SO ₃ K	12.19	12.16,	12.24	2.36	2.42 ^d	.00747		
 SO ₃ Na	7.94	7.87,	8.08	9.24,	9.34	.0523		
								2.7
 SO ₃ K	12.79	12.79,	12.84	3.62,	3.61	.0118		

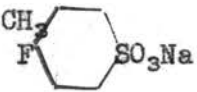
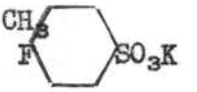
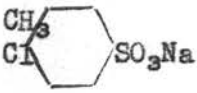
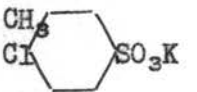
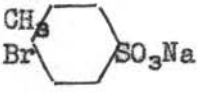
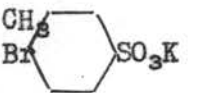
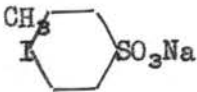
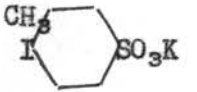
a Davies and Davies (21) gave the value 20.0 for 30°

b Davies and Davies (21) gave the value 0.57 for 30°

c Ullmann and Kuhn (76) gave the value 1.83 for 20°

d Goslich (28) gave the value 1.006 for 8.75°

Table of Results, Cont.

Salt	% metal calc.	% metal found	Solubility g/100 g. water	Mean Soly. mols/100g. water	Soly. Na Salt	Soly. K Salt
	10.85	11.00	27.5, 27.3	.129		1.6
	17.14	17.07	18.4, 18.2	.0811		
	10.06 ^e	10.05, 10.24	8.07, 8.16	.0355		0.84
	15.98 ^e	16.18, 16.21	10.2, 10.4	.0422		
	8.43 ^f	8.36, 8.52	6.92, 7.04 ^g	.0256		0.67
	13.53 ^f	13.38, 13.60	10.9	.0377		
	7.19	7.20, 7.29	4.99, 4.99	.0156		0.78
	11.63	11.75, 11.83	6.73, 6.81	.0201		

e It has been reported (34,86) that these salts exist as hydrates, the potassium salt containing one-half molecule of water and the sodium salt either one-half or one molecule of water per molecule of salt. This water is said to be expelled by drying at 140°-190°. Since our analyses showed no water present, the dehydration must occur upon drying even at 110°.

f Hubner and coworkers (36) reported that these salts also exist as hemihydrates. As before, we must conclude that the water is completely driven off at 110°.

g Hubner, Retschy, Muller, and Post (36) gave the value 5.3 for 14°.

Discussion of Results

Reagents for potassium are almost invariably judged by their ability to separate potassium from sodium. It is obvious, therefore, that essential characteristics of a good precipitant for potassium are (1) minimum solubility of the potassium salt (for quantitative work) and (2) maximum value of the ratio: Solubility of sodium salt/solubility of potassium salt.

Our results show that 2-bromo-3-nitrotoluene-5-sulfonic acid is slightly better than the chlorine derivative in the first respect, and slightly poorer in the second. This does not agree with the findings of O'Leary and Papish (52), who reported that the bromine compound is relatively insensitive to potassium, but gave no details of preparation or testing procedure.

The results are too few to permit much generalization, but it seems clear that the presence of the nitro group and the methyl group simultaneously is desirable. Of the two the nitro group is far more important, however, since without it solubilities of potassium salts increased tenfold and ratios dropped to less than 1. This might have been predicted from the almost universal presence of the nitro or the nitrite group in potassium precipitants. Yet, curiously enough, 2,6-dinitrochlorobenzene-4-sulfonic acid gives a potassium salt more than twice as soluble as the salt of the mononitro derivative, 2-nitrochlorobenzene-4-sulfonic acid (75).

The amisol derivative is worthless as a potassium reagent—and of course there is no structural reason why it should be valuable. The absolute solubilities of the salts containing different halogens and the solubility ratios (except in the case of iodine) both decrease with increasing atomic weight of the halogen. It may be pointed out that if

2-fluorotoluene-5-sulfonic acid maintains the same relative ranking in ratio after nitration, it should surpass anything yet tried. This possibility remains to be tested, as does the effect of omitting the halogen altogether.

SUMMARY

Some preliminary work is reported on improving 2-chloro-3-nitro-toluene-5-sulfonic acid as a precipitant for potassium by changing the nature of the groups present. A series of sodium and potassium salts has been prepared, some containing halogens other than chlorine, some no methyl group, and some no nitro group; nearly all are new compounds. All were synthesized by a more or less modified method of Davies, improved by Schultz and Lucas. Each salt was analyzed for metal to verify its purity and then evaluated by measuring its solubility in water at 30°.

Results indicate that 2-bromo-3-nitrotoluene-5-sulfonic acid is about equal in value to the chlorine compound. It is suggested that the effectiveness of the reagents depends on the presence of at least the nitro and the methyl groups simultaneously.

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