Fenske to have an efficiency of 11–12 plates. The inner tube containing the packings was surrounded by an electric heater which was in turn enclosed in a Pyrex vacuum jacket.

Solid *p*-acetamino derivatives of some of the alkylbenzenes were prepared according to the procedure of Ipatieff and Schmerling.[6]

In conclusion, amalgamated aluminum has been shown to have certain decided advantages over aluminum chloride in alkylation reactions of aromatic hydrocarbons. (a) Higher yields of the desired product are obtained in most cases than those cited in literature using aluminum chloride.[7] (b) The reaction proceeds smoothly with the formation of smaller amounts of rearranged products and tars.[8] (c) The use of this catalyst affords certain manipulative advantages.

1. Temperature remains fairly constant during the entire reaction and the use of the catalyst simplifies experimental procedures. 2. Reaction may be allowed to proceed overnight without observation.

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[6] Ipatieff and Schmerling, *J. Chem. Soc.*, **59**, 1056 (1937).

[7] Schreiner, *J. prakt. Chem.*, **81**, 558 (1910); Bert, *Ber.*, **36**, 3086 (1903); Radziewanowski, *ibid.*, **28**, 1137 (1895); **33**, 439 (1900); Boedtker, *Bull. Soc. Chim.*, **45**, 647 (1929); **25**, 844 (1901); **31**, 966 (1904); *Chem. Zentr.*, VIII, **12**, 1112 (1904).

[8] Calloway, *Chem. Rev.*, **17**, 327 (1935); Read, THIS JOURNAL, **49**, 3153 (1927); **48**, 1606 (1926); Wagner, *Ber.*, **11**, 1251 (1878).

DEPARTMENT OF CHEMISTRY
AGRICULTURAL MECHANICAL AND NORMAL COLLEGE
PINE BLUFF, ARKANSAS
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Simplified Method for the Preparation of Aromatic Sulfuric Acid Esters

BY J. FEIGENBAUM AND C. A. NEUBERG

The aromatic sulfuric acid esters are found in normal and especially in pathological urine. Since the discovery of pheno-sulfatase, which splits the aromatic sulfuric acid esters, the preparation of the esters has become significant.[1] The procedure generally used and improved by Neuberg and collaborators[2] is that according to Czapek.[3]

Analogous to this method chlorosulfonic acid is added to an ice-cooled solution of pyridine in chloroform and then a solution of phenol in pyridine. The chloroform is first distilled off *in vacuo*. The mixture is then made alkaline with strong aqueous potassium hydroxide and the pyridine is removed by a second distillation *in vacuo*. The ester potassium salt is obtained from the residue by extraction with hot alcohol, from which it separates in crystalline form upon cooling.

It should be remarked that, in view of the situation caused in some countries by the war, there is great difficulty in procuring pure pyridine. We, therefore, in the above-mentioned procedure, substituted for pyridine dimethylaniline, which is cheaper. As an immediate result we obtained bright, pure white crystals, whereas with the former method the substance sometimes remained colored even after several recrystallizations.

Therefore, in order to find a quicker and simplified method, we looked for a substitute for chloroform as a solvent that would enable us to maintain alkalinity without having to distill off the solvent as in the case of chloroform. With solvents such as petroleum ether, benzine, carbon disulfide, carbon tetrachloride and benzene (which itself reacts with chlorosulfonic acid), we obtained the pure ester salt, but the yield was rather poor.

We have therefore tried the reaction of chlorosulfonic acid directly in the solution of the phenol in dimethylaniline, and have not only obtained the pure white crystals of the potassium salt of the aromatic sulfuric acid esters, but also have succeeded in getting a better yield (average 90% instead of 70%) than by the former procedure. Thus, in this manner, we are *able to avoid all distillations in vacuo*. We only need to filter the separated substances and to wash them, preferably with ether. Petroleum ether, benzine, benzene, etc., may also be used.

Procedure.—Fifteen grams of technical chlorosulfonic acid is added drop by drop with constant stirring to an ice-cooled solution of 10 g. of phenol in about 40 cc. of dimethylaniline. The mixture is then made alkaline with strong aqueous potassium hydroxide (1:1). The solid portion is filtered off by suction and washed thoroughly with ether. The ester salt is extracted from the residue with hot alcohol (95%) and the alcoholic solution filtered through a heated funnel. The separated crystals thus obtained from the alcoholic filtrate are filtered with suction and washed with cold alcohol. By recrystallization from a minimum of hot water we get a pure sulfuric acid ester potassium salt, free from any chlorine and sulfate ions.

Further ester salt can be gained by evaporating on a water-bath the water-layer of the first filtrates. This no longer contains any tertiary amine, because it is present in the ether layer. The same can be done with the alcohol of the second filtrate. (The ether and dimethylaniline used in the preparation are recovered by simple distillation.)

By substituting in this simplified procedure pyridine for dimethylaniline the resulting substance was also white and well crystallized.

It seems that when working with this method the yield with some phenols, as α- and β-naphthol, is better if dimethylaniline is used, while with phenol itself, cresols and polyalkylated phenols better results are obtained with pyridine.

By the same simplified method we obtained good results with phenol when substituting quinoline for dimethylaniline or pyridine.

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[1] C. Neuberg and E. Simon, *Ergeb. Physiol.*, **34**, 896 (1932).

[2] Neuberg, *et al.*, *Biochem. Z.*, **156**, 368 (1925).

[3] Czapek, *Monatsh.*, **35**, 635 (1914).

Anal. Calcd. for $C_6H_5SO_4K$: S, 15.1. Found: S (from quinoline), 15.1, 15.05; (from dimethylaniline), 15.0, 15.0.

CHEMICAL DEPARTMENT OF THE CANCER RESEARCH INSTITUTE OF THE UNIVERSITY OF JERUSALEM, AND THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY
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The Change in Magnetic Susceptibility of Nickel Disalicylaldehyde on Hydrogenation

BY M. A. FOBES AND GEORGE N. TYSON, JR.

A mechanism that accounts for the uptake of hydrogen in copper disalicylaldehyde has been reported previously.[1] In the course of further magnetic susceptibility measurements of hydrogenated disalicylaldehydes it appears reasonable to extend the concept to the hydrogenated nickel compound. Green nickel disalicylaldehyde becomes yellow when hydrogenated, and both forms of the compound exhibit two unpaired electrons as shown in the experimental data.

Solutions and Hydrogenations.—The divalent nickel disalicylaldehyde used in this investigation has been described previously.[2] 1.9332 g. was diluted to 100 ml. using J. T. Baker and Co. C. P. grade pyridine. The solution so obtained was measured magnetically within a few minutes of mixing. The solution was then hydrogenated by placing approximately 50 ml. in a 250-ml. Florence flask, cooling to about 5° and evacuating to 15 mm. pressure, with subsequent introduction of hydrogen into the evacuated flask, to a pressure slightly greater than atmospheric. When the flask containing the hydrogen and the solution was heated to 90° for approximately 200 hours, hydrogenation occurred. The original solution was a light green, while the hydrogenated compound formed a yellow liquid with a brownish cast, which readily reverted to the green color when exposed to oxygen.

Magnetic Measurements.—The magnetic susceptibility measurements were made by the Gouy method. The susceptibilities due to the nickel disalicylaldehyde in the freshly prepared green solution (I) (measured at 24°) and the yellow brown hydrogenated nickel disalicylaldehyde (II) (measured at 26°) are shown in Table I. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital contribution to the magnetic moment. In the conversion of the experimental data into Bohr magnetons, a correction has been made for the diamagnetism of the nonmetal portion of the molecule.

TABLE I

Soln.	$\chi_g \times 10^6$	$\chi_m \times 10^6$	Bohr magnetons Exptl.	Bohr magnetons Calcd.	Unpaired electrons
I	12.32	3706	3.0	2.83	2
II	12.08	3625	3.0	2.83	2

CHEMISTRY DEPARTMENT
POMONA COLLEGE
CLAREMONT, CALIFORNIA
RECEIVED JUNE 30, 1941

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[1] Tyson and Vivian, THIS JOURNAL, **63**, 1403 (1941).

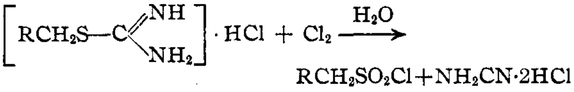
[2] Tyson and Adams, *ibid.*, **62**, 1228 (1940).

[CONTRIBUTION FROM MERCK AND CO., AND UNIVERSITY OF NORTH CAROLINA]

Explosion Hazard in the Chlorination of Alkyl Isothioureas to Prepare Alkyl Sulfonyl Chlorides

BY KARL FOLKERS, ALFRED RUSSELL AND R. W. BOST

In a series of papers, Sprague and Johnson[1] recently described a new and excellent method for the preparation of a considerable number of alkyl sulfonyl chlorides. The method consisted in the reaction of chlorine upon S-alkyl-isothiourea salts in aqueous solution according to the scheme



$$\left[\mathrm{RCH_2S{-}C}\begin{smallmatrix}{\nearrow}\mathrm{NH}\\ {\searrow}\mathrm{NH_2}\end{smallmatrix}\right]\cdot\mathrm{HCl} + \mathrm{Cl_2}\xrightarrow{\mathrm{H_2O}}\mathrm{RCH_2SO_2Cl}+\mathrm{NH_2CN}\cdot 2\mathrm{HCl}$$

It was stated that when R was the carboxyl group, the reaction did not produce the sulfonyl chloride derivative. In connection with one of the problems in the Merck Research Laboratory, one of the research chemists investigated the reaction of chlorine upon formamidine thiolacetic acid hydrochloride ($R=CO_2H$) since the corresponding sulfonyl chloride was desired. The first experiment gave a very hygroscopic product melting at 78–81° which was apparently sulfoacetic acid.[2] This result suggested that the reaction actually did go, but that the sulfonyl chloride was hydrolyzed to the sulfonic acid. In the next experiment, greater care was taken to have all the materials and apparatus more carefully cooled throughout, but the solution was refrigerated over the week-end. After further brief passage of chlorine, the oily globules were collected in a vial from a separatory funnel; they exploded violently. The chemist suffered severe

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[1] Sprague and Johnson, THIS JOURNAL, **58**, 1348 (1936); **59**, 1837 (1937); **59**, 2439 (1937); **61**, 176 (1939); "Sulfonic Halides," U. S. Patent 2,147,346 by T. B. Johnson, assignor to Röhm and Haas Company, Philadelphia, Pa.; "Process of Preparing Sulfonyl Halides and Sulfonic Acid from Pseudothioureas," U. S. Patent 2,146,744 by T. B. Johnson, assignor to Röhm and Haas Company, Philadelphia, Pa.

[2] Sulfoacetic acid monohydrate was hygroscopic and melted at 84–86° according to O. Stillich, *J. prakt. Chem.*, **73**, 538 (1906).