Since it seemed obvious that a solvate of lead chloride with ethylene glycol was being formed at high concentration of ethylene glycol, the samples in the range of high glycol concentration were prepared from lead chloride which was precipitated and washed with conductivity water as well as from lead chloride precipitated and washed in pure ethylene glycol.

The break in the solubility curve is no doubt due to the fact that the solid phase changed to a solvate of lead chloride. A crystalline product was obtained by washing the solvate with ether or acetone and drying it over sulfuric acid or anhydrous calcium sulfate. The lead chloride content of nine samples so prepared ranged from 68.5 or 71.8% and gave an average of 70.0%; this corresponds to the compound di-ethylene glycol lead (II) chloride, $PbCl_2 \cdot 2C_2H_4(OH)_2$ (theoretical per cent. of lead chloride is 69.1%). Evidence concerning the presence or absence of other solvates was inconclusive.

Information about the stability of the solvated product was obtained from cell data.[3,6] The measured potential for the cell

$$Pb(Hg),\ PbCl_2(\text{solvent}),\ AgCl,\ Ag$$

at saturation of lead chloride is 0.4842 volt in water[7] as well as in 20, 40, 60 and 80% (by weight) ethylene glycol–water solutions[3] but is 0.4963 volt in 100% ethylene glycol.[3] This corresponds to a free energy difference of only 520 calories and indicates a low stability of the solvate.

At the present time there seems to be no direct clue to the interpretation of the minimum.

1,2-Propylene glycol does not give these effects at 25° (see Table II).

Work is now in progress on the measurement of the electrical conductivity of lead chloride–ethylene glycol–water solutions.

[6] Results to be published soon.

[7] Carmody, THIS JOURNAL, 51, 2905 (1929).

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p-Toluidine Salts of Monoaryl Sulfates

BY A. D. BARTON AND LESLIE YOUNG

Since 1876, when Baumann[1] isolated potassium phenyl sulfate from urine, it has become evident that compounds of this type are formed in the animal body from many phenolic substances. Many monoaryl sulfates are unstable in the free acid form and they are usually prepared in the form of their alkali-metal salts. Such salts are unsatisfactory for identification purposes. They do not melt sharply, and only with difficulty can they be freed from inorganic impurities. In the hope of facilitating biochemical investigations involving the isolation and identification of monoaryl sulfates, a study of the preparation and properties of the organic base salts of monoaryl sulfates was undertaken.

A method for the preparation of the *p*-toluidine salts of *o*- and *p*-cresyl sulfates has been described.[2] In the present work a more convenient method of preparing *p*-toluidine salts of monoaryl sulfates has been developed, since preliminary experiments had shown that among the bases tested, *p*-toluidine consistently yielded crystalline derivatives which melted sharply.

Materials.—The potassium aryl sulfates were prepared by the method of Burkhardt and Wood.[3] Chlorosulfonic acid (1.4 moles) was added to a chilled solution of dimethylaniline (3.7 moles) in 500 ml. of carbon disulfide. The phenolic compound (1 mole) was then added and the mixture was stirred for one hour and allowed to stand overnight. The carbon disulfide was distilled off and the oil which remained was poured into aqueous potassium hydroxide (4 moles). The dimethylaniline was separated and the crude potassium aryl sulfate obtained by evaporation of the aqueous solution was crystallized from 80% ethanol and then from water. With the exception of potassium *p*-nitrophenyl sulfate, which crystallized as bright yellow prisms, the potassium salts were obtained in the form of colorless plates.

The *p*-toluidine hydrochloride was prepared by adding an excess of concentrated hydrochloric acid to a solution of *p*-toluidine in ethanol. The mixture was stirred thoroughly and chilled. The crystalline product was filtered off, and recrystallized from ethanol.

Procedure.—Solutions of equimolar portions of the potassium aryl sulfate and of *p*-toluidine hydrochloride in the minimum amounts of water at 60° were mixed quickly and chilled. The *p*-toluidine salt of the aryl sulfate separated almost immediately and was removed by filtration. The crude product was washed on the filter with a small amount of ice-water and crystallized from water, using charcoal, if necessary, to remove any colored impurities. The material was then crystallized once more from water and finally from aqueous ethanol, yielding in every case colorless needles.

The melting points and analyses of the *p*-toluidine salts of a series of monoaryl sulfates are given in the table.

Sulfate was determined gravimetrically as barium sulfate after acid hydrolysis of the *p*-toluidine salt. The equivalent weight was determined by titration with standard sodium hydroxide solution.

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[1] E. Baumann, *Pflügers Arch.*, 13, 285 (1876).

[2] G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.*, 684 (1926).

[3] G. N. Burkhardt and H. Wood, *ibid.*, 141 (1929).

p-TOLUIDINE SALTS OF MONOARYL SULFATES

Monoaryl sulfate	M. p., °C.[a]	Formula	Analytical data[b] Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found	Sulfate, % Calcd.	Found	Equiv. wt. Calcd.	Found
Phenyl	145–146	$C_{13}H_{15}NO_4S$	55.49	55.94	5.37	5.25	4.98	5.03	34.2	34.1	281	280
o-Cresyl	135.5–136.5	$C_{14}H_{17}NO_4S$	56.93	57.07	5.80	5.89	4.74	4.88	32.6	32.5	295	293
m-Cresyl	133–134	$C_{14}H_{17}NO_4S$	56.93	56.90	5.80	5.83	4.74	4.74	32.6	32.5	295	292
p-Cresyl	162–163	$C_{14}H_{17}NO_4S$	56.93	56.98	5.80	5.78	4.74	4.84	32.6	32.5	295	292
p-Bromophenyl	193–194	$C_{13}H_{14}NO_4SBr$	43.34	43.69	3.92	4.16	3.89	3.98	26.7	26.4	360	355
p-Nitrophenyl	167–168	$C_{13}H_{14}N_2O_6S$	47.85	47.60	4.32	4.32	8.59	8.38	29.4	29.1	326	325

[a] All melting points are uncorrected. The sample was placed in the bath 5° below the melting point. [b] The microanalyses were made by Michael Edson and Mrs. P. M. Marrian.

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A Synthesis of 1-Methylnaphthalene

BY OLIVER GRUMMITT AND ALLEN C. BUCK[1]

1-Methylnaphthalene, unlike the isomeric 2-methylnaphthalene, cannot be obtained readily in pure form from coal tar distillates. Physical methods of isolation are laborious because the concentration of 1-methylnaphthalene is relatively low and its boiling point and solubility are not very much different from that of 2-methylnaphthalene[2,3] and certain nitrogen[4] and sulfur compounds. Coulson[3] has, however, recently succeeded in obtaining pure 1-methylnaphthalene from a coal tar fraction by means of several fractional distillation and crystallization operations, including the preparation of the monosulfonic acids, crystallizations, and regeneration of the hydrocarbon by hydrolysis.

It appeared that 1-methylnaphthalene might be more accessible by direct synthesis. This work has shown that substantial amounts of the pure hydrocarbon can be prepared in good yields by the following steps: naphthalene → 1-chloromethylnaphthalene → 1-naphthylcarbinylmagnesium chloride → 1-methylnaphthalene. Since 1-methylnaphthalene and its intermediates may be of use in the synthesis of polycyclic compounds, an effort was made to establish optimum reaction conditions.

Experimental

1-Chloromethylnaphthalene.—Several preparations according to the procedure of Cambron[5] gave 45% yields instead of 56% as reported. Fieser and Novello[6] also obtained 45% yields with this method but by a modification of the procedure of Darzens and Levy[7] succeeded in obtaining 51% yields.[8] Attempts to duplicate the yields reported by Darzens and Levy were unsuccessful. The following procedure which is a modification of Cambron's method consistently gave yields of 70% or more.

In a three-neck 3-liter flask fitted with a mercury seal stirrer with nichrome wire paddles[9] and reflux condenser were placed 256 g. (2.0 moles) of naphthalene (technical grade), 110 g. (1.22 moles) of paraformaldehyde (Eastman Kodak Co.), 260 cc. of glacial acetic acid, 362 cc. of concentrated hydrochloric acid, and 165 cc. of 85% phosphoric acid. This mixture was heated with efficient stirring in a water-bath held at 80–85° for six hours. The crude product is transferred to a large separatory funnel and washed with two 1-liter portions of cold water, a solution of 20 g. of potassium carbonate in 500 cc. of cold water, and finally with 500 cc. of cold water. The product is the lower layer in these washings. About 200 cc. of ether is added to the oil layer and the solution is given a preliminary drying with 10 g. of anhydrous potassium carbonate for one hour. The lower aqueous layer which forms is separated and the ether solution again dried with 20 g. of potassium carbonate for eight to ten hours. Both the washing and drying operations must be carefully done because the presence of small amounts of acid or water may cause the 1-chloromethylnaphthalene to resinify during the final distillation. The ether solution is distilled first at atmospheric pressure to remove the ether and then at reduced pressure. The use of a clean, dry distilling flask and an even moderate rate of distillation help to overcome the tendency of the product to resinify during distillation. Approximately 40 g. of naphthalene distills at 90–110° (5 mm.) followed by 195–204 g. of 1-chloromethylnaphthalene at 128–133° (5 mm.) or 148–153° (14 mm.). The yield is 70–72% of the theoretical based on the naphthalene taken.

The distillation residue consists of some polymeric material, di-(chloromethyl)-naphthalenes, and di-(1-naphthyl)-methane.[10] Both 1-chloromethylnaphthalene and this residue are powerful skin irritants and should therefore be handled with care.

1-Naphthylcarbinylmagnesium Chloride.—The reduction of 1-chloromethylnaphthalene to 1-methylnaphthalene by zinc and hydrogen chloride is suitable for the preparation of small amounts of the hydrocarbon.[11] On a larger scale the method is impracticable because of the decreasing rate of reaction between the zinc and hydrogen

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[1] Sherwin-Williams Research Laboratory, Western Reserve University, Cleveland, Ohio.

[2] Morgan and Coulson, *J. Soc. Chem. Ind.*, **53**, T73 (1934).

[3] Coulson, *ibid.*, **60**, no. 5, 123 (1941).

[4] Kharasch, Kane and Brown, THIS JOURNAL, **62**, 2242 (1940).

[5] Cambron, *Can. J. Research*, **17B**, 10 (1939).

[6] Fieser and Novello. THIS JOURNAL, **62**, 1855 (1940).

[7] Darzens and Levy, *Compt. rend.*, **202**, 73 (1936).

[8] Fieser and Gates, THIS JOURNAL, **62**, 2335 (1940).

[9] Hershberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 313 (1936).

[10] Manske and Ledingham, *Can. J. Research*, **17B**, 14 (1939).

[11] Anderson and Short, *J. Chem. Soc.*, 485 (1933).