p-TOLUIDINE SALTS OF MONOARYL SULFATES

Monoaryl sulfate	M. p., °C.[a]	Formula	Analytical data[b] Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfate, % Calcd.	Sulfate, % Found	Equiv. wt. Calcd.	Equiv. wt. 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

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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).

chloride as the reaction progresses. The preparation of the Grignard reagent from 1-chloromethylnaphthalene and its hydrolysis proved to be very satisfactory. The following procedure is similar to the preparation of allylmagnesium bromide.[12,13]

In a three-neck 3-liter flask fitted with a mercury seal stirrer with nichrome wire paddles, efficient reflux condenser, dropping funnel and gas inlet tube was placed 63.2 g. (2.6 atoms) of magnesium turnings, 100 cc. of absolute ether, and a crystal of iodine. A slow current of dry, oxygen-free nitrogen is passed through the flask during the reaction. A 50-cc. portion of a solution of 150 g. (0.85 mole) of 1-chloromethylnaphthalene in 750 cc. of absolute ether is added from the funnel and the mixture is stirred. Usually the reaction starts readily, but if it does not the mixture should be heated to reflux and 2–3 cc. of methyl iodide added. When the initial reaction has subsided, 1080 cc. of absolute ether is added and the ether solution of the chloride added dropwise over a period of five hours. The addition of ether may stop the formation of Grignard reagent in which case it is necessary to add 2–3 cc. more of methyl iodide. Normally the ether solution of the Grignard reagent will become yellow-green in color at the end of the first one-half hour; if this color does not appear the reagent is not forming. When all of the ethereal solution has been added, the mixture is stirred and heated at reflux for an additional hour. The yield of Grignard reagent determined by titration was 88–92%.[14]

This Grignard reagent gave the usual color test with Michler ketone.[15] The anilide derivative, 1-naphthylacetanilide prepared from the Grignard reagent and phenyl isocyanate melted at 156–7°,[16] which corresponds with the value reported for the same compound prepared from aniline and 1-naphthylacetic acid.[17]

The aralkylmercuric chloride derivative, 1-naphthylcarbinylmercuric chloride, was prepared from the Grignard reagent and mercuric chloride.[18] After several crystallizations from 80% alcohol it melted at 126–128°.

Anal. Calcd. for $C_{11}H_9HgCl$: Cl, 9.39. Found: Cl, 8.94.

The naphthalide derivative, 1-naphthyl-1-acetonaphthalide, was obtained from the reaction of the Grignard reagent with 1-naphthyl isocyanate[19] and purified by crystallization from xylene; m. p. 175–177°.

Anal. Calcd. for $C_{21}H_{17}NO$: N, 4.41. Found: N, 4.26.

Hydrolysis of the Grignard Reagent.—The reagent was hydrolyzed by adding it to an ammonium chloride solution made from 54 g. of ammonium chloride and 400 cc. of water. To prevent the formation of oxidation products the hydrolysis is conveniently carried out by removing the stirrer and reflux condenser from the flask in which the reagent was made and fitting them to a three-neck 5-liter flask containing the aqueous solution. The two flasks are connected by 10-mm. glass tubing so that the application of nitrogen pressure will force the reagent over into the second flask. The hydrolyzing mixture is stirred and cooled and the Grignard reagent is added as rapidly as possible and then the mixture is heated to reflux for one hour. The ether layer is separated and distilled, the crude 1-methylnaphthalene being collected at 235–245°. Fifty cc. of petroleum ether (60–70°) is added to the product and it is dried over potassium carbonate. The dried solution is decanted directly into a distilling flask containing 1–2 g. of barium oxide and then distilled. The yield of 1-methylnaphthalene boiling 238–40° is 96–97 g., 80% of the theoretical based upon the 1-chloromethylnaphthalene. The picrate derivative melted at 140–141°.[20]

The reported values for the refractive index and density for 1-methylnaphthalene vary widely, probably because of contamination by the more refractive and more dense 2-isomer. The product prepared here was further purified by fractional distillation through a glass helix-packed column, 15 inches in length. The middle fraction showed $n^{25}\text{D}$ 1.6140 ± 0.0002 and $d^{25}{}_4$ 1.0163 ± 0.0002. Both values are somewhat lower than those reported earlier.[21,22,23]

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[13] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[14] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[15] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[16] Schwartz and Johnson, *ibid.*, **53**, 1063 (1931).

[17] Higginbottom and Short, *Rec. trav. chim.*, **53**, 1141 (1934).

[18] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[19] Gilman and Furry, *ibid.*, **50**, 1214 (1928).

[20] Baril and Hauber, *ibid.*, **53**, 1090 (1931).

[21] Beverage and Strieff, *J. Research Nat. Bur. Standards*, **24**, 395 (1940).

[22] Weiss and Downs, *Ind. Eng. Chem.*, **15**, 1022 (1923).

[23] McKittrich, *J. Institute Petroleum Tech.*, **23**, 630 (1937).

CLEVELAND, OHIO RECEIVED OCTOBER 30, 1942

The Chlorination of 4-Phenylphenyl Acetate in Acetic Acid

BY HAROLD R. SCHMIDT, CORA MAY SEGURA SAVOY AND JOHN LEO ABERNETHY

It was of interest in connection with the chlorination of 4-phenylphenyl acetate to see if the solvent had any appreciable effect on the position of entry of chlorine.[1] Bromination of 4-phenylphenyl acetate in glacial acetic acid is known to give 2-bromo-4-phenylphenyl acetate,[2] whereas chlorination of 4-phenylphenyl acetate in carbon tetrachloride yields 4-(4-chlorophenyl)-phenyl acetate.[3] There was the possibility that the solvent was causing the difference in mode of entry of chlorine. This was tested by substituting glacial acetic acid for the carbon tetrachloride in the latter chlorination.

A solution of 8 g. of chlorine in 50 cc. of glacial acetic acid was added, drop by drop, over a period of one hour, to a mixture of 10 g. of 4-phenylphenyl acetate dissolved in 50 cc. of glacial acetic acid, to which had been added a trace of iodine. The reaction mixture was stirred during this period and for an additional five hours. When the

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[1] Since this work was finished, Hazlet reported some rather interesting solvent effects in connection with the bromination of 4-phenylphenyl chloroacetate, at the meeting of the American Chemical Society at Buffalo, N. Y., September, 1942.

[2] Hazlet and Kornberg, THIS JOURNAL, **61**, 3037 (1939).

[3] Savoy and Abernethy, *ibid.*, **64**, 2219 (1942).