

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°, which corresponds with the value reported for the same compound prepared from aniline and 1-naphthylacetic acid.¹⁷

The aralkylmercuric chloride derivative, 1-naphthylcarbonylmercuric 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 C₁₁H₉HgCl: 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 isocyanate¹⁹ and purified by crystallization from xylene; m. p. 175-177°.

Anal. Calcd. for C₂₁H₁₇NO: 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_D^{25} 1.6140 ± 0.0002 and d_4^{25} 1.0163 ± 0.0002. Both values are somewhat lower than those reported earlier.^{21,22,23}

(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

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The Chlorination of 4-Phenylphenyl Acetate in Acetic Acid

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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

(12) Gilman and Kirby, *THIS JOURNAL*, **51**, 3475 (1929).

(13) Gilman and McGlumphy, *Bull. soc. chim.*, **63**, 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).

(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).

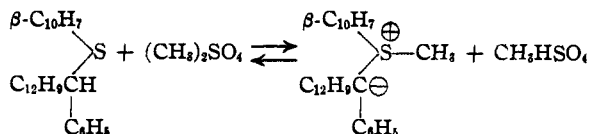
(3) Savoy and Abernethy, *ibid.*, **64**, 2219 (1942).

period of stirring had elapsed, the solution was poured into ten volumes of cold water. The white semi-solid mass was dissolved in carbon tetrachloride and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid material was recrystallized several times from ethanol. One and one-half grams of 4-(4-chlorophenyl)-phenyl acetate was isolated from this material.

The same product was therefore obtained as with carbon tetrachloride, showing that the solvent, in this instance, did not affect the point of entry of the chlorine.

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β -Naphthylsulfanylphenylxenylmethane.—This sulfoxide was prepared by treating the sulfide in glacial acetic acid with 30% hydrogen peroxide. After standing for four days the solution was diluted with an equal volume of water and extracted with ether. Recrystallization from acetic acid yielded the sulfoxide melting at 220° in a yield of 90%.

Anal. Calcd. for $\text{C}_{29}\text{H}_{22}\text{SO}$: S, 7.65. Found: S, 7.76.

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NEW COMPOUNDS

Mixed β -Naphthyl Thioethers

In the continuance of our investigation of sulfonium compounds,¹ we required several mixed sulfides not reported previously.

β -Naphthyl *n*-hexyl sulfide was prepared by mixing 5 g. of thio- β -naphthol with sodium ethylate (0.8 g. of sodium in 50 cc. of alcohol) and slowly adding 5.1 g. of *n*-hexyl bromide. After heating for one hour on the water-bath, the sodium bromide was removed by filtration and the alcoholic solution was distilled. The β -naphthyl *n*-hexyl sulfide is a light yellow oil that boils at 160° (20 mm.). The yield was 4.7 g. or 69%.

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{S}$: S, 13.11. Found: S, 13.53.

β -Naphthyl *n*-heptyl sulfide was prepared similarly from 10 g. of thio- β -naphthol and 11.1 g. of *n*-heptyl bromide. A crystalline substance melting at 34° was obtained. The yield was 13.2 g. or 82%.

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{S}$: S, 12.40. Found: S, 12.61.

β -Naphthylthiophenylxenylmethane.—Forty-five grams of phenylxenylchloromethane was dissolved in 82 g. of dry thiophene-free benzene. To this was added 30 g. of thio- β -naphthol dissolved in an equal amount of benzene. After refluxing for two hours and standing overnight, a white crystalline compound was obtained. It was recrystallized from glacial acetic acid and white needles were obtained. They melted at 155°. The yield was 60.5 g. or 95%.

Anal. Calcd. for $\text{C}_{23}\text{H}_{22}\text{S}$: S, 7.96. Found: S, 8.01.

Attempted Preparation of β -Naphthylphenylxenylmethylmethylsulfonium Sulfate.—A solution of 10 g. of β -naphthylthiophenylxenylmethane in 30 g. of benzene was mixed with 3 g. of dimethyl sulfate. A light blue color resulted which deepened to a dark purple on refluxing. The color was immediately destroyed by the addition of water and the β -naphthylthiophenylxenylmethane was recovered unchanged.

An application of the theories of Hughes² and Ingold³ would result in the following formulation.

- (1) Ray and Levine, *J. Org. Chem.*, **2**, 267 (1937).
- (2) Hughes and Kuriyan, *J. Chem. Soc.*, 1609 (1935).
- (3) Ingold and Jessop, *ibid.*, 713 (1930).

Fatty Derivatives of Salicylic Acid and α -Naphthol

Methyl-(2-capryloxy)-benzoate.—This compound was prepared by the reaction of methyl salicylate with capryl chloride at 200–225° until no more hydrogen chloride was evolved (about five hours); b. p. 217–219° (12 mm.), n_D^{25} 1.4888, yield, 71%.

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_4$: C, 70.56; H, 8.55. Found: C, 70.66; H, 8.29.

Methyl (4-Capryl)-salicylate.—Prepared by carrying out a Fries rearrangement on the above ester according to the procedure of Cox¹ except that light petroleum ether was used as a solvent instead of carbon disulfide. The material distilled at 180–190° (1.5 mm.) and after two recrystallizations from light petroleum ether melted at 66.5–67.5°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_4$: C, 70.56; H, 8.55. Found: C, 70.42; H, 8.60.

4-Caprylsalicylic Acid.—Hydrolysis of the preceding compound by refluxing with 15% sodium hydroxide solution yielded 4-caprylsalicylic acid which was crystallized to constant melting point from benzene, m. p. 120.5–121.5°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.46; H, 8.24.

α -Naphthylcaprylylate.—This compound was prepared according to the procedure used by Stoughton for the lower esters² except that a longer reaction time was necessary (three hours on the steam-bath); yield about 60%. The ester boiled at 156–157° (1 mm.), n_D^{25} 1.5442.

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.98; H, 8.12.

2-Caprylyl- α -naphthol.—Stoughton's procedure (*loc. cit.*) for the rearrangement of the lower esters was also used for this compound. It was first crystallized from alcohol and then twice from slightly diluted glacial acetic acid, m. p. 68–68.5°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.62; H, 8.17.

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- (2) Stoughton, *ibid.*, **57**, 202 (1935).
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