10 cc. of methanol was added and the solution was diluted with 10 cc. of acetone. After standing for two weeks, small wart-like clusters of crystals appeared. By using these as seeds, calcium (−)-pantothenate could be crystallized readily from 10% solution in 99.5% methanol. The crystals were washed with methanol and dried *in vacuo* at 100°; m. p. 187.5–189°; $[\alpha]^{25}D$ −27.8° (*C*, 1% in H_2O). The biological potency was practically zero.

Anal. Calcd. for $Ca(C_9H_{16}O_5N)_2$: C, 45.35; H, 6.77. Found: C, 45.30; H, 6.55.

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RAHWAY, N. J.
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The Preparation of 2-Bromonaphthalene

BY MELVIN S. NEWMAN AND PAUL H. WISE

Since the replacement of amino groups on the naphthalene nucleus by bromine according to the usual Sandmeyer technique often results in poor yields, we were interested in using the procedure of Schwechten[1] wherein the diazonium salt is treated with mercuric bromide and the solid complex thus produced is dried and heated with sodium bromide. Although Schwechten gave no details concerning the amount of mercuric bromide used, he represented the complex in the case of diazotized 2-naphthylamine as $(C_{10}H_7N_2Br)_2 \cdot HgBr_2$. A search of the literature revealed that investigators who have followed this procedure generally have used mercuric halides far in excess of that required by the formula.[2] In this communication we show that when the amount of mercuric bromide is reduced to that required for the formation of the complex $(C_{10}H_7N_2Br)_2 \cdot HgBr_2$ it is possible to obtain from 53 to 59% of pure 2-bromonaphthalene. Doubling the amount of mercuric bromide used raised the yield to 61–65%, and further increases had no effect.

Experimental

As the result of many experiments, we recommend the following procedure for the preparation of 2-bromonaphthalene. To the cold diazonium solution, prepared as usual from 50 g. (0.35 mole) of 2-naphthylamine, 670 cc. of water, 140 cc. of concentrated hydrochloric acid and 20% sodium nitrite solution, is added with stirring a cold suspension of mercuric bromide formed by treating 57 g. (0.175 mole) of mercuric nitrate with 83 g. of sodium bromide in a total volume of 250 cc. of water. The yellow insoluble complex which separates immediately is collected by filtration, washed with water and acetone, and air dried. The air-dried complex weighs from 137 to 149 g. (94–103% calculated on the basis of the formula $(C_{10}H_7N_2Br)_2 \cdot HgBr_2$). For decomposition, the complex is well mixed with 300 g. of finely ground sodium bromide and added in several portions through a wide rubber tube to a flask heated in a glycerol bath at 90° and fitted with a reflux condenser.[3] After each addition of complex a vigorous gas evolution occurs but no tendency to explode was ever noticed.

After the decomposition is complete, the organic matter is taken into benzene and washed with dilute acid and alkali. The 2-bromonaphthalene is twice vacuum distilled, b. p. 103–104° at 4 mm., and crystallized from 110 cc. of hot alcohol after addition of 4 cc. of hot water. In two crops, there is obtained 38.4–43.1 g. (53–59%) of almost colorless plates of 2-bromonaphthalene, m. p. 55.0–56.4°, cor. The remainder of the organic material is mostly accounted for as dark tar and high-boiling matter. Very little if any naphthol is produced.

Using a similar procedure, 1-chloro-2-bromonaphthalene, m. p. 55.0–56.5°, was obtained in 46% over-all yield from 1-chloro-2-acetylaminonaphthalene.[4]

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[1] Schwechten, *Ber.*, **65**, 1605 (1932).

[2] For example, see Ruzicka and Mörgeli, *Helv. Chim. Acta*, **19**, 377 (1936); and Bachmann and Boatner, THIS JOURNAL, **58**, 2194 (1936).

[3] See sketch in Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1935, p. 287.

[4] Hodgson and Leigh, *J. Chem. Soc.*, 1352 (1937).

CHEMICAL LABORATORIES
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The Action of *t*-Butylmagnesium Chloride on Propylene Oxide

BY PHILIP G. STEVENS[1] AND JAMES A. MCCOUBREY[2]

In view of the recent paper by Huston and Agett[3] on the reaction of the Grignard reagent with ethylene oxide, we wish to report briefly our work in the same field. As we were interested primarily in a stereochemical problem, we used propylene oxide and *t*-butylmagnesium chloride, hoping to obtain 4,4-dimethylpentanol-2.[4]

Our best results were obtained by allowing the oxide (220 g.) and the Grignard reagent (from 150 g. of magnesium) to stand at about 25° for seven weeks. The mixture was decomposed with ammonium sulfate, and most of the ether (5 liters) from the extractions, supernatant on one liter of 10% caustic, was removed by fractional distillation. To destroy the chlorhydrin, the residual liquor was refluxed with excess caustic for five hours and then steam-distilled. Thus a chlorine-free product was obtained. Fractional distillation yielded the following fractions boiling above 130° at 762 mm.: 1, 130–134, 0.5 g.; 2, 134–137, 11 g.; 3, 137–138, 39 g.; or a combined yield of 11%, and a residue of 42 g. Two grams of fraction 3 gave 4 g. of crude 3,5-dinitrobenzoate, which after repeated crystalliza-

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[3] Huston and Agett, *J. Org. Chem.*, **6**, 123 (1941).

[4] Levene and Walti, *J. Biol. Chem.*, **94**, 367 (1931).