evaporated to dryness. The residue was dissolved in warm isopropyl alcohol and thrown out by addition of acetone, m.p. 239–240° (dec.); solubility in water at 25° about 5%. *Anal.* Calcd. for $C_7H_6Cl_2N_2$: ionic Cl, 18.75. Found: Cl, 18.48, 18.71.

5(or 6)-Aminobenzimidazole Dihydrochloride.—Isopropyl alcohol was added to a saturated solution of 5(or 6)-aminobenzimidazole[6] in dilute HCl and the resulting light pink crystals were washed with isopropyl alcohol and with ether. A sample kept in a vacuum desiccator gave a low analysis, apparently because of gradual loss of HCl, but a sample dried at atmospheric pressure gave satisfactory analyses; m.p. 299° (dec.); water solubility at 25° > 20%. *Anal.* Calcd. for $C_7H_9Cl_2N_3$: Cl, 34.40. Found: Cl, 34.33, 34.63.

We wish to express our appreciation to Mr. Charles Chumley and Mr. Eddie Pace for the preparation of the 1,2-diamino-4,6-dinitrobenzene and 5-nitro-1,2,3-triaminobenzene used in these preparations and to Dr. Alfred Gellhorn of Columbia University College of Physicians and Surgeons for arranging to screen several of the products against tumors.

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[6] G. M. van der Want, *Rec. trav. chim.*, **67**, 45 (1948).

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Bromomethylation; Preparation of 2,6-Bis-(bromomethyl)-4-alkyl Phenols

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This paper presents a direct method for the preparation of crystalline monomeric bromomethyl alkyl phenols. In it the phenol, dissolved in glacial acetic acid, is allowed to react with paraformaldehyde and anhydrous hydrogen bromide. The generality of the method is attested to by the simple preparations of 2,6-bis-(bromomethyl)-4-methylphenol,[2] 2,6-bis-(bromomethyl)-4-*t*-butylphenol, and 2,6-bis-(bromomethyl)-4-*t*-octylphenol.[3]

There seems to have been no direct bromomethylation procedure reported in the literature, although chloromethylation of non-phenolic materials is routine. In the latter connection, it has been noted that employing the usual procedures, phenols react so readily that the reaction goes too far, yielding polymeric material.[4] Buehler[5] has chloromethylated substituted phenols containing such strongly polar groups as $-NO_2$ and $-COOH$ which have been found to retard the undesirable resinification reaction leading to polymeric materials. He treated the phenol in concentrated hydrochloric acid with formalin in the presence of a strong acid catalyst, such as H_2SO_4. A patent[6] exists in which it is claimed that monomeric, crystalline 2,6-bis-(chloromethyl)-4-methylphenol was obtained as a result of reaction of aqueous formaldehyde, cresol and concentrated hydrochloric acid. We were unable to confirm this claim, nor were we able to prepare the desired bromomethyl compound from aqueous systems.

The *t*-butyl and *t*-octyl compounds reported herein have not been described previously. They were characterized by direct comparison with samples prepared from 2,6-bis-(hydroxymethyl)-4-*t*-butylphenol[7] and 2,6-bis-(hydroxymethyl)-4-*t*-octylphenol,[8] by hydrogen bromide using the method of von Auwers.[2]

Experimental[9]

2,6-Bis-(bromomethyl)-4-methylphenol.—To 150 g. of glacial acetic acid was added 54 g. of *p*-cresol and 35 g. of paraformaldehyde. The flask containing the mixture was immersed in an ice-bath and anhydrous hydrogen bromide was passed into the reaction mixture. Heat was evolved and the admission of HBr was regulated in such a manner that the temperature of the mixture was never allowed to exceed 80°. Near the saturation point of HBr in acetic acid (evidenced by fuming at the mouth of the flask) the suspended paraformaldehyde disappeared and a clear solution was obtained. HBr addition was stopped when the solution was completely saturated and the *p*-cresol derivative precipitated immediately. After the solid product was filtered off, and recrystallized from heptane, approximately 60% yield was obtained; m.p. 115–117°.

Anal. Calcd. for $C_9H_{10}Br_2O$: C, 36.8; H, 3.4; Br, 54.4. Found: C, 36.7; H, 3.4; Br, 54.3.

Other Phenols.—2,6-Bis-(bromomethyl)-4-*t*-butylphenol was prepared in the same manner as the cresol derivative when 4-*t*-butylphenol was used; yield 50%, m.p. 92–93°.

Anal. Calcd. for $C_{12}H_{16}Br_2O$: C, 42.9; H, 4.8; Br, 47.6. Found: C, 42.6; H, 4.8; Br, 47.4.

2,6-Bis-(bromomethyl)-4-octylphenol was prepared similarly from the commercially available phenol, which was not further purified; yield 25%, m.p. 87–90°. Both the butyl and octyl derivatives required several hours of refrigeration to effect crystallization.

Anal. Calcd. for $C_{16}H_{24}Br_2O$: C, 49.0; H, 6.2; Br, 40.7. Found: C, 48.1; H, 6.3; Br, 40.0.

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[1] Address communications to: Clark Laboratory, The Kendall Company, Cambridge 39, Massachusetts.

[2] This compound has been previously prepared by reaction of 2,6-bis-(hydroxymethyl)-phenol. See K. von Auwers, *Ber.*, **40**, 2532 (1907), and F. Uhlman and K. Brittner, *ibid.*, **42**, 2540 (1909).

[3] Nomenclature for parent methylol phenol given variously as: (a) 2,6-bis-(hydroxylmethyl)-4-*t*-octylphenol, (b) 2,6-bis-(hydroxymethyl)-4-diisobutylphenol, (c) α,α'-*m*-xylenediol-2-hydroxy-5-1,1,3,3-tetramethylbutyl.

[4] R. C. Fuson and C. H. McKeever, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 65.

[5] (a) C. A. Buehler, *J. Tennessee Acad. Sci.*, **22**, 303 (1947); (b) C. A. Buehler, F. K. Kirchner and C. F. Deebel, *Org. Syntheses*, **20**, 59 (1940).

[6] I. G. Farbenind. A.-G., British Patent 347,887 (1931).

[7] F. Hanus, E. Fuchs and E. Ziegler, *J. prakt. Chem.*, **153**, 327 (1939).

[8] J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

[9] Analyses by Carol K. Fitz, 115 Lexington Ave., Needham Heights 94, Massachusetts.

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The Reaction between Niobium Pentachloride and Niobium Metal

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Recently Schäfer, Göser and Bayer[1] have shown niobium tetrachloride is produced, when niobium pentachloride and niobium metal (in a molar ratio greater than 4/1) are caused to react at 350°. Their results were in agreement with those obtained in our own rather extensive study of the reaction between niobium pentachloride and niobium. Presented here, however, are certain of our results and conclusions which were not covered in their paper.

Large needles (*ca.* 1 cm. long) are obtained directly, after removal of excess pentachloride by vacuum sublimation at 120°, when the penta-

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[1] H. Schäfer, C. Göser and L. Bayer, *Z. anorg. allgem. Chem.*, **265**, 258 (1951).