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

BY WILLARD M. BRIGHT[1] AND PETER CAMMARATA

RECEIVED JANUARY 22, 1952

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

BY C. H. BRUBAKER, JR., AND R. C. YOUNG

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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).

chloride and metal are heated together at 350–400° for one week in a sealed, evacuated tube.

The results of the present investigation are summarized in Table I.

TABLE I

THE REACTION OF NIOBIUM PENTACHLORIDE WITH NIOBIUM

Approximately 0.6 g. of niobium metal powder was used in each experiment

Expt.	$NbCl_5$/ Nb	Temp., °C.	Products	Cl/Nb in products after removal of any excess $NbCl_5$
1	5/1	350	Lg. needles of $NbCl_4$ with $NbCl_5$	4.0/1
2	5/1	400	Lg. needles of $NbCl_4$ with $NbCl_5$	4.0/1
3	4/1	400	$NbCl_4$ needles with $NbCl_3$, some $NbCl_5$	3.6/1
4	2/1	450–500	Inert $NbCl_3$ and Nb	2.70/1
5	3/2	400–450	Inert $NbCl_3$ and Nb	2.71/1
6	1/1	475–500	Inert $NbCl_3$ and Nb	2.68/1

The tetrachloride is somewhat soluble in ethanol, methanol, champhor, diisobutyl ketone and acetone and sparingly soluble in ethyl ether. It is believed that the tetrachloride reacts with these solvents, because hydrogen chloride vapor could be detected coming from the solutions, even when the solvents were carefully dried. Niobium tetrachloride is also moderately soluble in the monomethyl ether of ethylene glycol: no hydrogen chloride could be detected above these violet solutions.

It is surprising that the products from the last three experiments cited in Table I had an almost constant composition (approximately Nb_3Cl_8) in view of the varying conditions employed and the different ratios of pentachloride to metal. However, X-ray analyses showed that the material was a mixture of trichloride and metal. Moreover, although the trichloride can be sublimed (*in vacuo*) at about 500°,[2] the trichloride could not be removed from these mixtures by vacuum sublimation. Rather, at about 600°, a black sublimate of niobium tetrachloride appeared on a cold-finger condenser in a sublimation apparatus. If no condenser is employed, the tetrachloride disproportionates immediately and gives the tri- and pentachlorides.

Therefore, one must assume that niobium trichloride and niobium react at elevated temperatures and form some lower chloride (perhaps Nb_3Cl_8), which disproportionates and forms the metal and tetrachloride near 600°.

Analyses of samples from experiments 1, 2 and 3 were carried out by hydrolysis of the product in dilute ammonia. These solutions were acidified with nitric acid in order to oxidize the niobium. The niobium pentoxide, thus formed, was precipitated with ammonia, filtered, ignited and weighed and the chlorine was determined as silver chloride in the acidified filtrate. Samples from experiments 4, 5 and 6 were fused with sodium carbonate and the cooled melts were dissolved in water. These solutions were acidified with nitric acid, the pentoxide was precipitated with ammonia and chlorine was determined as silver chloride from the acidified filtrate.

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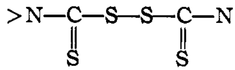
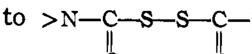
[2] C. H. Brubaker and R. C. Young, THIS JOURNAL, 73, 4179 (1951).

Dimethylcarbamyldimethylthiocarbamyl Disulfide

BY EARL C. GREGG, JR.

RECEIVED FEBRUARY 27, 1952

The novel method by which the subject compound may be prepared prompted this note.

The action of bromine on bis-(dimethylthiocarbamyl) sulfide is to precipitate the sulfide completely as a rust colored solid of unknown structure which is comprised of one mole of the sulfide and five gram-atoms of bromine as determined by the weight of the product. This rust colored solid reacts with cold water to form a relatively unstable, colorless solid (I), m.p. 108–110° (uncor.). Elemental analysis and molecular weight determination of I require an empirical formula $C_6H_{12}N_2OS_3$. A polarogram of I exhibits a well-defined reduction wave, Fig. 1, characteristic of bis-(diethylthiocarbamyl) disulfide.[1] The reduction potential and adsorption wave character suggest the presence of the  $>N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N<$ group.[1] However, an infrared spectrum of I, Fig. 2 center, exhibits both a carbonyl band at 5.94 μ and a thiocarbonyl band at 6.62μ.[2] To fit this evidence the above structural group may be modified to  $>N-\underset{\underset{O}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N<$. The infrared spectrum of I has bands common to

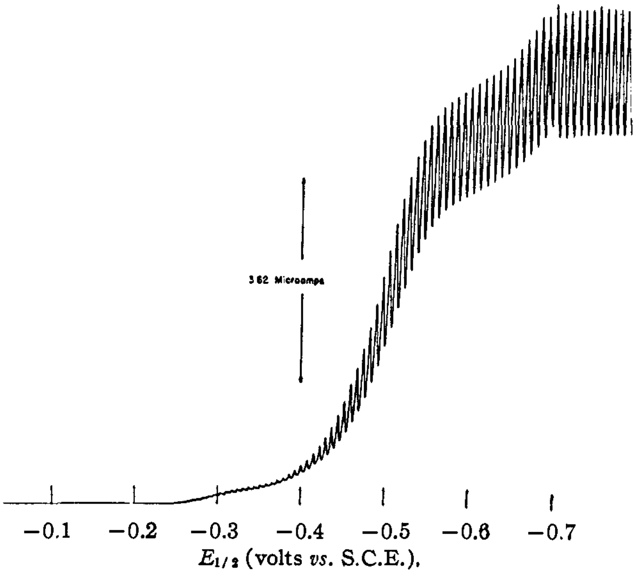


Fig. 1.

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[1] E. C. Gregg and W. P. Tyler, THIS JOURNAL, 72, 4561 (1950).

[2] Private communication. This assignment is in agreement with the extensive work not yet published on the thiocarbonyl absorption band by Mr. J. J. Shipman.