

ether (V) by both chemical and instrumental analysis.

Attempts to prepare more highly chlorinated dimethyl ethers by the chlorination of V were unsuccessful. The reaction with chlorine was very sluggish and no products boiling higher than V could be isolated.

Both pentachlorodimethyl ether⁷ (VI) and hexachlorodimethyl ether^{5,8} (VII) have been reported. However, Regnault's and Sonay's values for the boiling point and density of VII are not in agreement with the values to be expected based on the other chlorinated dimethyl ethers.

EXPERIMENTAL

Chlorination of chloromethyl methyl ether. A 2-liter, 3-necked flask which was equipped with a mechanical stirrer, condenser and ice trap, thermometer, and sintered-glass disk inlet tube was charged with 322 g. (4.0 moles) of chloromethyl methyl ether and 1232 g. (8.0 moles) carbon tetrachloride. The flask was illuminated with a 275-watt ultraviolet bulb. Chlorine was admitted through the sintered disk at a rate of 200 ml./min. until 142 g. (2.0 moles) had been introduced. The heat of reaction maintained the system at reflux. Fractionation of the product produced 163 g. (1.4 moles) bis(chloromethyl) ether (I); b.p. 103–105°, n_D^{20} 1.4421 and 24 g. (0.2 mole) dichloromethyl methyl ether (II); b.p. 82–84°, n_D^{20} 1.4353.

Anal. Calcd. for $\text{ClCH}_2\text{OCH}_2\text{Cl}$: Sapon. Equiv., 57.5; Cl, 61.68. Found: Sapon. Equiv., 57.3; Cl, 61.81.

Calcd. for $\text{CH}_2\text{OCHCl}_2$: Sapon. Equiv., 38.3; Cl, 61.68. Found: Sapon. Equiv., 38.4; Cl, 61.77.

Chlorination of bis(chloromethyl) ether (I). The equipment described under chlorination of chloromethyl methyl ether was charged with 460 g. (4.0 moles) (I) and 1232 g. (8.0 moles) carbon tetrachloride. After heating to reflux, chlorine was passed in at a rate of 407 ml./min. until 212 g. (2.98 moles) had been introduced. The heat of reaction maintained the system at reflux. Fractionation of the product yielded 190 g. (1.27 moles) (42.6% yield) of (III) with b.p. 129°, n_D^{20} 1.4622 and d_4^{20} 1.464.

Anal. Calcd. for $\text{ClCH}_2\text{OCHCl}_2$: mol. wt., 149.4; Cl, 71.19. Found: mol. wt., 150; Cl, 70.5.

Chlorination of dichloromethyl methyl ether (II). The equipment described under chlorination of chloromethyl methyl ether was charged with 196 g. (1.7 moles) (II) and 616 g. (4.0 moles) carbon tetrachloride. After heating to reflux, chlorine was admitted at a rate of 275 ml./min. until 64 g. (0.90 mole) had been introduced. Only initial heating was necessary to hold the temperature at reflux. Upon fractionation, 109 g. (0.73 mole) (81.1% yield) of chloromethyl dichloromethyl ether (III) was obtained with b.p. 128–129°, n_D^{20} 1.4630, and d_4^{20} 1.464. No methyl trichloromethyl ether was isolated. The physical constants and analysis of this product agreed well with those obtained by the chlorination of bis(chloromethyl) ether.

Chlorination of dichloromethyl chloromethyl ether (III). The equipment described under chlorination of chloromethyl methyl ether was charged with 284 g. (1.9 moles) (III) and 616 g. (4.0 moles) carbon tetrachloride. The solution was heated to reflux and chlorine was bubbled in at a rate of 114 ml./min. until 81g. (1.15 moles) had been introduced. The heat of reaction maintained the system at reflux. By fractionation at reduced pressures, 63 g. (0.34 mole)

(29.6% yield) of bis(dichloromethyl) ether (V) was obtained having b.p. 143°, n_D^{20} 1.4728 and d_4^{20} 1.558.

Anal. Calcd. for $\text{CHCl}_2\text{OCHCl}_2$: mol. wt., 183.9; Cl, 77.13. Found: mol. wt., 190; Cl, 76.4.

Only one product resulted from this reaction whereas two products are possible. Since neither of the two expected products is reported in the literature, the identity of the product was confirmed by mass spectrometer and infrared patterns.⁹ The mass pattern showed relative peak heights at 83, 85, and 87 of 1.00:0.64:0.116 which is in good agreement with the values expected for CHCl_2 based on the relative abundance of the chlorine isotopes. The ratios of the heights of the 117, 119, 121, and 123 peaks are 1.00:4.67:4.00:1.17. These values are not in agreement with the heights expected for a CCl_3 group which should be 1.0:1.0:0.3:0.04. The infrared pattern as interpreted by Dr. W. H. Calkins is in agreement with the pattern to be expected for the *sym*-tetrachloro derivative. Furthermore, the relative areas from a gas chromatogram indicated that the sample was about 95% pure.

Chlorination of bis(dichloromethyl) ether (V). The equipment described under chlorination of chloromethyl methyl ether was charged with 616 g. (4.0 moles) carbon tetrachloride and 368 g. (2.0 moles) (V). The solution was heated to reflux and chlorine was introduced at a rate of 142 ml./min. until 43 g. (0.6 mole) had been admitted. It was necessary to apply external heat to maintain reflux. Fractionation of the product at reduced pressures resulted in the recovery of phosgene, unreacted (V) and 709 g. (4.6 moles) carbon tetrachloride. The excess carbon tetrachloride over that charged presumably resulted from the same decomposition which produced phosgene. No chloroform or more highly chlorinated ether was recovered.

This experiment was repeated reducing the temperature to 50° and the chlorine flow to 100 ml./min. Again phosgene, unreacted V, and 115% of the charged carbon tetrachloride were obtained by fractionation at reduced pressures.

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Preparation of 1,5-Dibromo-4,8-diiodonaphthalene¹

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We have recently prepared 1,5-dibromo-4,8-diiodonaphthalene according to the method of Whitehurst.² Some observations upon this synthesis are pertinent.

(1) Abstracted from a thesis presented to the Graduate School, University of North Dakota, by Robert W. Bayer in partial fulfillment of the requirements for the Master of Science degree in chemistry.

(2) J. S. Whitehurst, *J. Chem. Soc.* 222 (1951).

(7) I. Rabcewicz-Zabkowski, and S. Chwalinski, *Roczniki Chem.*, **10**, 686 (1930).

(8) V. Regnault, *Ann.*, **34**, 24 (1840).

EXPERIMENTAL

In this six-step process, the intermediate products were accumulated in several runs, in which the reaction conditions were varied in attempts to improve the yields. Only the significant departures from Whitehurst's work are given in any detail. The best experimental conditions are described.

A mixture³ of 40 g. of 1,5-dinitronaphthalene (K and K Laboratories, reagent grade), 120 g. of iron powder, 12 g. of ferrous sulfate, and 400 ml. of water was put into a 1-liter 3-neck flask equipped with a mechanical stirrer, and refluxed for 5 hr., cooled in an ice water bath, and filtered. The residue was returned to the reaction flask and refluxed with 250 ml. of pyridine for about 5 min., treated with Norite A, and filtered hot. The residue was extracted twice more with pyridine. To the hot extracts 30 g. of *p*-toluenesulfonyl chloride was added, the mixture kept hot for 30 min., then cooled, and 250 ml. of water added. The crude 1,5-bis(*p*-toluenesulfonamido)naphthalene was recrystallized once more from pyridine-water. The yield was 30.4 g. (35.5%). A purer sample had a melting point of 325–327° (decomp., corr.; lit.: 318° C., uncorr.).

The 4,8-dibromo-1,5-bis(*p*-toluenesulfonamido)naphthalene was prepared from the above intermediate on a ten-gram scale according to the method of Whitehurst.² The crude product was washed with boiling ethanol (95%). The yield was 8.1 g. (60%) and the material had a melting point of 245–250° (decomp., corr.; lit. 248°, decomp., uncorr.).

The 1,5-dibromo-4,8-diiodonaphthalene was prepared² by hydrolyzing ten-gram quantities of the above intermediate in concentrated sulfuric acid for 36 hr., followed by tetrazotization and reaction with potassium iodide. The crude product was extracted with acetic acid. The yield in the best run after one such extraction was 2.0 g.

A solution of 4.2 g. of the crude 1,5-dibromo-4,8-diiodonaphthalene dissolved in a minimum quantity of a 7:1 by volume *n*-heptane/benzene mixture was placed upon a 67 × 2.2 cm. activated alumina column (Alcoa, F-20). This mixture was fractionated using *n*-heptane (Phillips 66, pure grade) as the eluant. The course of the process was followed by infrared spectrometry. The first 4750 ml. of eluant contained an impurity, compound I. The pure 1,5-dibromo-4,8-diiodonaphthalene was taken off the column with 350 ml. of benzene. The yield was 1.9 g. and the pure product had a melting point of 163.5–164.5° (corr.; lit. 148°, uncorr.).

Anal.: Calcd. for C₁₀H₄Br₂I₂: C, 22.33; H, 0.75; halogen, 76.92. Found: C, 22.37; H, 0.87 halogen, 76.15, 76.40.

The infrared spectrum possessed an intense absorption at 823 cm.⁻¹, and hence was consistent with that of a 1,4,5,8-tetrasubstituted naphthalene.

The impurity, compound I, had intense absorption bands at 823 and 796 cm.⁻¹, consistent with that of a 1,4,5-trisub-

stituted naphthalene. The melting point was 106–109°. Its ultimate analysis is given in Table I.

DISCUSSION

In the preparation of the diamine it was found that the yields could be improved almost twofold by increasing the reduction time from 3 to 5 hr., and by extracting the material with pyridine rather than with boiling alcohol. While the bromination of the 1,5-bis(*p*-toluenesulfonamido)naphthalene is evidently incomplete, it does not appear that it can be improved upon. The procedure involves a 100% excess of bromine; compare Whitehurst's discussion.² Attempts to purify the 4,8-dibromo-1,5-bis(*p*-toluenesulfonamido)naphthalene through recrystallization from nitrobenzene,² led only to a black residue.

The method used in the preparation of the 1,5-dibromo-4,8-diiodonaphthalene from the 4,8-dibromo-1,5 bis(*p*-toluenesulfonamido)naphthalene leaves a great deal to be desired. The best yield obtained from 10 grams of this starting material can be estimated to be approximately one gram of pure product (11%). Using the method of Whitehurst, our yields were less than those he reported. In attempting to improve these yields, the time of tetrazotization was varied. The best results were obtained when the entire tetrazotization and iodination were carried out as rapidly as possible. Increasing the time of tetrazotization over the 5 min. recommended by Whitehurst caused a substantial decrease in the yield.

Extreme precautions were taken to keep the temperature of the tetrazotization and iodination reaction below 0°. The amount of urea added to decompose the excess nitrous acid was varied from 0 to 4 grams. The acidity of the solution was doubled. These last two variations gave no significant improvement over Whitehurst's procedure. The difficulty in the last step would then appear to be in the long hydrolysis of the 4,8-dibromo-1,5-bis(*p*-toluenesulfonamido)naphthalene to obtain the 4,8-dibromo-1,5-diaminonaphthalene.

The impurity, compound I, in the 1,5-dibromo-4,8-diiodonaphthalene, had a negative qualitative test for nitrogen. While the ultimate analysis is far from conclusive, the constant agreement of the carbon and of the total halogen analysis (if it is assumed that the 3.3% error in sample one is an error in the halogen analysis) seems to indicate that it is primarily 4-bromo-1,5-diiodonaphthalene. This is the logical impurity since it was not possible to purify the 4,8-dibromo-1,5-bis(*p*-toluenesulfonamido)naphthalene. It was thought that the compound I may have been caused by the loss of iodine from the tetrahalide in an acid solution or under the influence of ultraviolet light, since the acetic acid solutions used for initial recrystallizations became colored. However, compound I was found in the infrared spectrum of the crude product before recrystallization. The infrared spectrum of a sample of Professor Whitehurst's 1,5-dibromo-4,8-diiodonaphthalene showed the presence of compound I.

The behavior of the 1,5-dibromo-4,8-diiodonaphthalene upon recrystallization from acetic acid is anomalous. While it is possible to obtain a spectroscopically pure sample in three recrystallizations, the melting point of the crystals is 90–145°.

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TABLE I
ANALYSIS OF COMPOUND I

	Sample 1 ^a	Sample 2 ^a		C ₁₀ H ₅ BrI ₂	C ₁₀ H ₅ Br ₂ I
C	26.23	26.08	25.99	26.17	29.16
H	0.93	1.26	1.32	1.10	1.22
Br		12.79	13.32	17.42	38.80
I		59.63	59.68	55.31	30.81
Total	69.55,	(72.42) ^b	(73.00) ^b	72.73	69.61
halo- gen	69.45				
Total	96.71	99.96	100.31		

^a 50 mg. samples. ^b Calculated quantities are in parentheses.

(3) H. H. Hodgson, J. S. Whitehurst, *J. Chem. Soc.*, 2, 202 (1945).