

sion with authentic  $[(C_2H_5)_3NH]_2B_{10}H_{10}$ , and both infrared and  $B^{11}$  n.m.r. spectra were identical. Evaporation of the ethanolic filtrate deposited 2.0 g. of additional material which melted at  $254^\circ$  (lit. for triethylammonium bromide  $253^\circ$ ) and its infrared spectrum was identical with Sadtler spectrum 9771 for  $(C_2H_5)_3NHB_{10}H_{10}$ .

**Reaction of 2-Bromodecaborane with Triethylamine in Ethylene Glycol Dimethyl Ether (Monoglyme).**—A solution of 2.0 g. of 2-bromodecaborane and 5.0 g. of triethylamine in 35 ml. of ethylene glycol dimethyl ether was refluxed for 6 hr. The white solid which had formed was separated from the yellow solution. This solid was dissolved in acetonitrile and on cooling 0.6 g. of triethylamine hydrobromide precipitated. The filtrate was evaporated to dryness and the residue was recrystallized from acetonitrile-acetone. The solid was removed and refluxed for a short time in ethanol and the remaining solid (2.25 g., 75%) was removed by filtration and melted at  $235.5^\circ$ . It was demonstrated to be  $[(C_2H_5)_3NH]_2B_{10}H_{10}$ . An additional small amount of  $(C_2H_5)_3NHB_{10}H_{10}$  was recovered from the alcoholic filtrate. The original filtrate was examined, but nothing could be isolated which could be identified as a  $B_{12}H_{12}^{2-}$ ,  $B_{10}H_{10}^{2-}$ , or  $B_{10}H_{12}$  product.

**Phosphonium Decahydrodecaborate Salts.**—Five unreported phosphonium decahydrodecaborate salts were prepared. The preparation of bis(ethyltriphenylphosphonium) decahydrodecaborate is given. Others were prepared in an analogous manner and the results of these preparations are summarized in Table I.

One gram ( $3.1 \times 10^{-3}$  mole) of bis(triethylammonium) decahydrodecaborate was dissolved in 5 ml. of warm dimethylformamide (DMF). To this was added a solution of 2.6 g. ( $6.2 \times 10^{-3}$  mole) of ethyltriphenylphosphonium iodide dissolved in 5 ml. of warm DMF. The mixture was warmed on the steam bath for a few minutes, then 25 ml. of water was added. A white precipitate formed immediately. After cooling to room temperature, the precipitate was filtered, and the residue was recrystallized from DMF-water and dried.

**Reaction of 2-Bromodecaborane with Trimethylamine in Toluene.**—Trimethylamine was bubbled through a refluxing solution of 4.0 g. of 2-bromodecaborane in 35 ml. of toluene for 7 hr. The mixture was cooled and the toluene was decanted from the gummy residue. This residue was dissolved in acetonitrile and on cooling a solid separated which was collected and recrystallized from acetonitrile to give 1.0 g. of a white solid. Repeated recrystallization afforded two products (A and B) as yet unidentified. A, which is probably a double salt (see Discussion), melted at  $274-275^\circ$ . *Anal.* Found: C, 23.87, 23.60; H, 8.91, 8.95; B, 23.94, 24.19; N, 8.91, 8.70. B decomposed gradually on heating above  $250^\circ$ . *Anal.* Found: C, 21.10, 21.18; H, 7.12, 6.90; B, 19.64, 19.68; N, 7.40, 7.70; Br, 45.0.

The original acetonitrile filtrate was evaporated and treated with acetone to give a white solid which was recovered. This was recrystallized from a small amount of acetonitrile and then from a minimum of water to give 3.1 g. of white plates of bis(trimethylammonium) bromononahydrodecaborate melting at  $259-260^\circ$ .

*Anal.* Calcd. for  $B_{10}C_6H_{26}N_2Br$ : C, 22.7; H, 9.1; B, 34.1; N, 8.8; Br, 25.3. Found: C, 23.0, 23.2; H, 10.1, 9.8; B, 33.4, 33.7; N, 9.1, 8.9; Br, 24.1, 24.1.

**Bis(trimethylammonium) Ethylnonahydrodecaborate.**—A solution of 4.5 g. of monoethyldecaborane (60% 2- and 40% 1-substituted) and 15 g. of triethylamine in 60 ml. of benzene was refluxed for 24 hr. The mixture was cooled and the supernatant liquid was decanted from the yellow gum which had formed. This gum was treated with ethanol, whereupon it solidified. It was recrystallized several times from a large volume of ethanol to give 9.0 g. (85%) of a white solid melting at  $193-194^\circ$ . Its infrared spectrum was quite similar to that of bis(trimethylammonium) decahydrodecaborate.

*Anal.* Calcd. for  $B_{10}C_{14}H_{48}N_2$ : C, 47.7; H, 13.6; B, 30.8. Found: C, 48.3, 48.0; H, 14.2, 14.0; B, 30.9, 31.1.

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CONTRIBUTION FROM CLIMAX MOLYBDENUM COMPANY  
OF MICHIGAN, RESEARCH LABORATORY,  
DETROIT 38, MICHIGAN

## Synthesis of Molybdenum Tetrachloride

BY M. L. LARSON AND F. W. MOORE

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Molybdenum tetrachloride has been difficult to prepare pure in appreciable quantities.<sup>1</sup> This is the result of the ease of its thermally-induced disproportionation and its oxidative instability.

It is then of interest that molybdenum tetrachloride can be prepared easily by the reaction of molybdenum pentachloride with refluxing benzene. Substantial quantities (300 to 400 g.) have been prepared routinely by this method to give products of 98 to 99% purity. No purification is required other than a simple benzene wash. This process, though developed independently in this laboratory, appears to be formally similar to the reduction of ferric chloride by chlorobenzene reported by Kovacic and Brace.<sup>2</sup>

The reaction of molybdenum pentachloride with refluxing benzene yields a small amount of black, polymeric, carbonaceous solid as impurity. This solid resembles the poly-*p*-phenylene which Kovacic and Lange have recently reported<sup>3</sup> to result from the treatment of benzene with a cocatalytic system of molybdenum pentachloride and water. Therefore, it is important that the molybdenum pentachloride intermediate be freed of oxychloride hydrolysis products and that the reaction system be anhydrous. Under these conditions, variable benzene reflux periods extended beyond the time (8 to 10 hr.) required to achieve complete reduction to tetrachloride do not cause formation of substantial poly-*p*-phenylene. Furthermore, the rate of benzene reduction past the tetrachloride stage is very slow. Kovacic and Lange report<sup>3</sup> that molybdenum trichloride was formed when a concentrated mixture of molybdenum pentachloride and benzene was refluxed for 1 hr. Their sole evidence for the formation of molybdenum trichloride was a potentiometric ceric titration of a 3 *N* hydrochloric acid extract of the reaction mixture. This conclusion can be discounted for two reasons: (1) molybdenum trichloride is insoluble in dilute hydrochloric acid<sup>1b</sup>;

(1) (a) W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936); (b) D. E. Couch and A. Brenner, *J. Res. Natl. Bur. Std.*, **63A**, 185 (1959); (c) S. A. Shechukarev, J. V. Vasilkova, and B. N. Sharupin, *Vestn. Leningr. Univ.*, **14**, No. 10, Ser. Fiz. i Khim., No. 2, 72 (1959); (d) S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 947 (1962).

(2) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

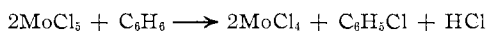
(3) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

(2) Mo(IV) in hydrochloric acid solution is known to undergo oxidative-reductive decomposition to form Mo(V) and Mo(III) species.<sup>4</sup>

It was also found possible to obtain molybdenum tetrachloride using chlorobenzene, but substantial formation of trichloride occurred after extended reflux periods (greater than 10 hr.). However, the use of temperatures below the boiling point and careful control of the extent of reduction by titration of the effluent HCl has allowed the formation of quite pure molybdenum tetrachloride.

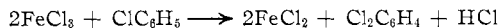
Reaction could also be effected using paraffinic solvents (cyclohexane, *n*-heptane, petroleum ether (40–43°)), but the product was invariably contaminated with 3 to 4% carbonaceous impurity, assumed to be dehydrochlorination-polymerization products. The use of paraffin wax at 145° and *n*-hexadecane at 160° has also been found to give considerable carbonaceous impurity.<sup>1b</sup>

Gas-liquid chromatographic analysis of the filtrate from the benzene reduction revealed that the reaction followed the stoichiometry



In the case of the chlorobenzene reduction, dichlorobenzenes are formed in nearly quantitative yield with a *para:ortho* isomer ratio of 2.1:1.

Molybdenum pentachloride is only slightly soluble in benzene, and the tetrachloride is insoluble. Edwards and Fowles report<sup>5</sup> that molybdenum pentachloride, which is a chlorine-bridged dimer in the crystalline state,<sup>6</sup> gives a cryoscopic monomeric molecular weight in benzene (0.15% solution). Therefore, it would be inferred that the reduction proceeds by a nucleophilic attack of benzene on pentacoordinate molybdenum pentachloride. The reaction stoichiometry, however, suggests that one benzene reduces two molybdenum pentachlorides. This is analogous to the chlorobenzene reduction of ferric chloride developed by Kovacic and Brace<sup>2</sup>



They conclude from the order of activity of other substituted aromatics and from the *para:ortho* isomer ratio of the substitution products that the rate-determining step occurs by an ionic mechanism.

### Experimental

All reductions were carried out under a prepurified nitrogen atmosphere, using glassware flamed dry in a stream of nitrogen. Material transfers were conducted in a drybox under nitrogen (dew point –45 to –50°). The MoCl<sub>5</sub> (Climax Molybdenum Company commercial grade packaged in flame-sealed ampoules) was purified by fractional sublimation to obtain a black, crystalline sublimate, m.p. 201–202° (cor.). Reagent benzene was dried by distillation from the sodium ketyl complex of benzophenone.<sup>7</sup> Chlorobenzene, Matheson Coleman and Bell reagent, was treated with Drierite and distilled.

(4) A. A. Bergh and G. P. Haight, Jr., *Inorg. Chem.*, **1**, 688 (1962).

(5) D. A. Edwards and G. W. A. Fowles, *J. Chem. Soc.*, 24 (1961).

(6) D. E. Sands and A. Zalkin, *Acta Cryst.*, **12**, 723 (1959).

(7) M. S. Kharasch and O. E. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 25.

**Benzene Reduction of Molybdenum Pentachloride.**—A stirred suspension of 12.65 g. (0.046 mole) of MoCl<sub>5</sub> in 100 ml. of benzene was heated at reflux in an oil bath for 9.33 hr. A slow stream of prepurified nitrogen was swept over the reaction mixture—successively through the reflux condenser, a Dry Ice-Trichloro slush-cooled trap, and a suck-back safety flask—into water to allow titration of 0.021 mole (91% of theory) of HCl. The evolution of HCl was very slow toward the end of the reflux period. The black solid product was separated by filtration and washed with benzene, using vacuum and nitrogen atmosphere conditions. After vacuum (oil-pump) drying, the product weighed 11.2 g. (102% yield).

*Anal.* Calcd. for MoCl<sub>4</sub>: Cl, 59.65; Mo, 40.35. Found: Cl, 58.98; Mo, 40.26; Cl:Mo atom ratio, 3.96. Treatment with 1:1 hydrochloric acid showed that 0.53% was insoluble.

Gas-liquid chromatographic analysis of the reaction mixture filtrate revealed the presence of 0.022 mole of chlorobenzene (94% of theory).

**Chlorobenzene Reduction of Molybdenum Pentachloride.**—The chlorobenzene reduction was performed similarly to the benzene reduction. The reaction mixture of 33.47 g. (0.123 mole) of MoCl<sub>5</sub> and 100 ml. of chlorobenzene was heated at 130 to 140° for 3.25 hr. Titration showed that 0.060 mole (98% of theory) of HCl was evolved. After benzene washing and vacuum drying, the solid product weighed 28.0 g. (96% yield).

*Anal.* Calcd. for MoCl<sub>4</sub>: Cl, 59.65; Mo, 40.35. Found: Cl, 58.69; Mo, 41.04; Cl:Mo atom ratio, 3.87. Treatment with 1:1 hydrochloric acid revealed that only 0.04% was insoluble. The X-ray powder diffraction pattern is similar to that obtained by Couch and Brenner.<sup>1b</sup>

Gas-liquid chromatographic analysis of the reaction mixture filtrate demonstrated the presence of 0.055 mole of dichlorobenzenes (90% of theory) with a *para:ortho* isomer ratio of 2.1:1.

**Properties of the Molybdenum Tetrachloride Product.**—Molybdenum tetrachloride, obviously a polymeric compound with extensive coupling of the 4d<sup>2</sup> electrons (spin-only  $\mu_{\text{eff}}$  of 0.934 B.M.<sup>8,9</sup> at 25°), has no melting point but undergoes disproportionation to MoCl<sub>3</sub> and MoCl<sub>5</sub> at moderate temperatures<sup>10</sup> (greater than 127° according to the thermodynamic calculations of Brewer and associates<sup>11</sup>). Attempts at purification and crystallization by vacuum sublimation were unsuccessful because of the lack of sufficient vapor pressure below this thermal decomposition point. The use of high vacuum (10<sup>-5</sup> mm.) has demonstrated thermal dissociation to MoCl<sub>3</sub> and chlorine at these moderate temperatures (less than 150°).<sup>12</sup>

Molybdenum tetrachloride is essentially insoluble in nonpolar organic solvents.<sup>13</sup> It was found possible, however, to employ a benzene suspension for quantitative and specific reaction with pyridine at room temperature to give MoCl<sub>4</sub>·2C<sub>6</sub>H<sub>5</sub>N (spin-only  $\mu_{\text{eff}}$  of 2.52 B.M. at 25°). Further reaction with pyridine in more polar media, such as *N,N*-dimethylformamide, gives some MoCl<sub>4</sub>·3C<sub>6</sub>H<sub>5</sub>N.<sup>12</sup> Reaction of MoCl<sub>4</sub> with acetylacetone solvent give an air-stable, insoluble, nonvolatile, red-purple solid, m.p. 253–255° dec., the elemental and infrared analysis of which closely approximates MoCl<sub>2</sub>(C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>. Its properties indicate a polymeric character with a coordination number higher than six.<sup>12</sup> Reaction with nonchelating, oxygen-donor solvents is ordinarily accompanied by oxidative-reductive decompositions. Horner and Tyree have found that triphenylarsine oxide was unique in giving a neutral octacoordinate Mo(IV) complex, MoCl<sub>4</sub>·4(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsO.<sup>14</sup>

(8) We are indebted to Professor Stanley Kirschner, Wayne State University, for the magnetic susceptibility measurements.

(9) Klemm reported a  $\mu_{\text{eff}}$  value of 2.1 B.M. at 20°, using a product which analyzed as MoCl<sub>4</sub>.<sup>11</sup>

(10) W. Biltz and C. Fendius, *Z. anorg. allgem. Chem.*, **172**, 385 (1928).

(11) L. Brewer, L. A. Bromley, P. W. Gilles, and N. F. Lofgren, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, Inc., New York, N. Y., 1950, paper 8, p. 291.

(12) M. L. Larson, unpublished work.

(13) Horner and Tyree<sup>14</sup> employed a very dilute solution in carbon tetrachloride (approximately 0.15%) for their syntheses studies.