

served at  $5.30 \mu$  in both butene isomers, but it was quite weak.

Ultraviolet irradiation of either I or II in the gas phase in a quartz vessel resulted in the formation of a mixture of I and II in a ratio of about 3:2, together with sizable amounts of iodine, III and chlorotrifluoroethylene<sup>7</sup>; no coupling<sup>8</sup> occurred. In the liquid phase in the presence of a halogen getter such as mercury, coupling<sup>8</sup> but not isomerization took place; and the formation of III and chlorotrifluoroethylene was very much reduced. Photochemical chlorination of either I or II in the gas phase produced III in high yield.

The observation by Hauptschein *et al.*<sup>3</sup> that I was more reactive than II was also confirmed. When either the addition to ethylene or the ultraviolet-light-promoted coupling reaction was carried out on a mixture of roughly equal amounts of I and II, recovered starting material was always over 99% II.

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Lawrence Radiation Laboratory  
University of California  
Livermore, Calif.

(7) Hauptschein, (ref. 3) reported no isomerization occurred on heating either isomer at 40–50° with iodine monochloride in the presence of iron.

(8) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

(9) E. R. Bissell, *J. Org. Chem.*, 26, 5100 (1961).

## The Preparation of Phosphite and Phosphinite Decaboranes

R. J. POLAK AND T. L. HEYING

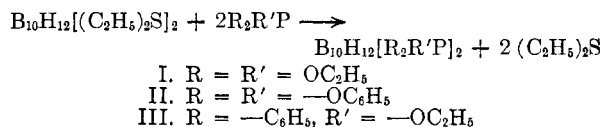
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In the course of some other work to be reported in detail in the near future, and encouraged by the work of Reetz<sup>1</sup> in preparing trialkyl phosphite boranes, we undertook the preparation of some phosphite and phosphinite derivatives of decaborane.

The reaction of decaborane with Lewis bases to produce  $B_{10}H_{12}(\text{Base})_2$  materials is well established<sup>2</sup> as is the replacement of the ligands with materials of higher base strengths in such molecules.<sup>3</sup> Accordingly it was found that organic phosphites would react with decaborane in refluxing benzene to produce the corresponding  $B_{10}H_{12}$  derivatives as exemplified by the following equation. It was sub-



sequently found that higher yields could be obtained when the replacement reaction with bis(acetonitrile)decaborane was employed, and the best yields were obtained when bis(diethyl sulfide)<sup>4</sup> decaborane was used in a similar reaction.



Although only compound I was prepared directly from decaborane it is thought that II and III<sup>5</sup> can likewise be prepared in this manner.

### EXPERIMENTAL

*Materials.* Bis(acetonitrile)decaborane, bis(diethyl sulfide)decaborane, and ethyl diphenylphosphinite were prepared in these laboratories by established literature procedures. Decaborane was obtained from the Olin Mathieson Chemical Corp. and repurified by sublimation shortly before use. Other chemicals were used as received from suppliers.

*Bis(triethyl phosphite)decaborane I.* To 5 g. (0.041 mole) of sublimed decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 15 g. (0.09 mole) of triethyl phosphite. The reactants were refluxed for 20 hr. in an inert atmosphere, cooled, and the solution was washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. The solvent was removed and the residue was sublimed to insure removal of any unchanged decaborane (no decaborane was recovered). The resultant viscous oil was dissolved in a minimum of methanol and cooled slowly to 0°. The white crystalline product (6.8 g.) was isolated by filtration (37%; m.p. 90–91°)

*Anal.* Calcd. for  $B_{10}C_{12}H_{42}P_2O_6$ : C, 31.8; H, 9.3; P, 13.7; B, 24.1. Found: C, 31.8; H, 9.5; P, 13.3; B, 24.4.

2. To 10 g. (0.033 mole) of bis(diethyl sulfide)decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 17 g. (0.1 mole) of triethyl phosphite. The reactants were refluxed for 10 hr. in an inert atmosphere, cooled, and washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. Upon removal of the solvent layer, 20.5 g. of a light brown solid was recovered. When recrystallized from methanol, 12.8 g. of white crystalline product was isolated (85%; m.p. 90°) which was demonstrated to be identical to the material prepared from decaborane.

3. To 5 g. (0.025 mole) of bis(acetonitrile)decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 10 g. (0.06 mole) of triethyl phosphite. The reactants were refluxed for 10 hr. in an inert atmosphere and washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. After removal of solvent from the organic layer, 11.0 g. of crude product was isolated. Upon recrystallizing from methanol 8.0 g. of the product was recovered (72%; m.p. 90°).

*Bis(triphenyl phosphite) decaborane II.* To 5 g. (0.017 mole) of bis(diethyl sulfide)decaborane and 100 ml. of benzene in a 250-ml., three-necked flask was added 12 g. (0.039 mole) triphenyl phosphite. On cooling after refluxing for 6 hr. in an inert atmosphere, a white solid precipitated. The solid (10 g.) was removed and since it was found to be virtually insoluble in common organic solvents it was washed several times with benzene and then washed with hot methanol to purify (81%; m.p. 209–210°).

(4) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 83, 2669 (1961).

(5) Substantiated later by Dr. H. A. Schroeder of these laboratories; to be published as part of a larger undertaking.

(1) T. Reetz, *J. Am. Chem. Soc.*, 82, 5039 (1961).

(2) R. Schaefer, *J. Am. Chem. Soc.*, 79, 1006 (1957) and others.

(3) For example: M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, 81, 5519 (1959).

*Anal.* Calcd. for  $B_{10}C_{36}H_{42}P_2O_6$ : C, 58.4; H, 5.7; P, 8.3; B, 14.6. Found: C, 56.4; H, 6.1; P, 8.3; B, 14.8.

*Bis(ethyl diphenyl phosphinite) decaborane III.* To 2.0 g. (0.0065 mole) of bis(diethyl sulfide)decaborane and 50 ml. of benzene in a 250-ml. three-necked flask were added 3.0g. (0.013 mole) of ethyl diphenylphosphinite and 25 ml. of benzene. The reaction was conducted at reflux for 7 hr. in an inert atmosphere. Upon cooling the solid which had precipitated was removed and the filtrate was evaporated to dryness to leave 3.9 g. of crude product. After recrystallization from ethyl acetate, 2.6 g. of white crystals were isolated (68%; m.p. 213–215°)

*Anal.* Calcd. for  $B_{10}C_{46}H_{52}P_2O_2$ : C, 57.9; H, 7.3; P, 10.7. Found: C, 58.1; H, 7.1; P, 10.6.

The material requires drying under vacuum at 160° to remove the last traces of ethyl acetate.

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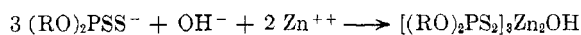
OLIN MATHIESON CHEMICAL CORP.  
ORGANICS DIV.  
NEW HAVEN, CONN.

### Basic Zinc Double Salts of *O,O*-Dialkyl Hydrogen Phosphorodithioates

W. E. BACON AND J. F. BORK

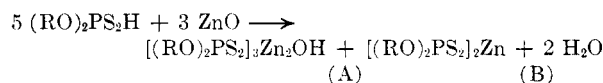
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The basic zinc double salts of *O,O*-di-*i*-propyl and *O,O*-di-*n*-butyl hydrogen phosphorodithioates have been prepared by metathesis of the sodium *O,O*-dialkyl phosphorodithioates and zinc chloride in aqueous solutions.<sup>1</sup> The formation of this product



depends upon excess hydroxyl ion during the reaction of the zinc ion with phosphorodithioate ion.<sup>1</sup>

It would appear that the use of molar quantities of zinc oxide with the dialkyl hydrogen phosphorodithioates would provide a new route to these salts. The reaction of a 33% excess (molar quantities) of zinc oxide over that required to form the basic zinc double salt with *O,O*-di-*n*-propyl hydrogen phosphorodithioate yielded 61% of the basic zinc double salt (A) and 37% of the normal zinc *O,O*-di-*n*-propyl phosphorodithioate (B). This



method provides a convenient method of preparing the basic zinc double salts in a neutral medium in good yields. The use of one tenth of a mole of excess of zinc oxide over that required to form the normal zinc salt (B) gave a product consisting of 31% basic

zinc double salt of *O,O*-di-*n*-propyl hydrogen phosphorodithioate and 65% of zinc *O,O*-di-*n*-propyl phosphorodithioate.

During the reaction of zinc oxide with *O,O*-dialkyl hydrogen phosphorodithioates the hydroxyl ion comes from the water formed during the reaction. The use of zinc dust to form the normal zinc salt provides an anhydrous system, and should yield none of the basic zinc double salt. *O,O*-Di-*n*-propyl hydrogen phosphorodithioate readily reacted with zinc dust to give only zinc *O,O*-di-*n*-propyl phosphorodithioate. This is a viscous liquid product at 25° and is soluble in benzene.

The use of molar quantities of water with the zinc oxide appears to increase the yield of basic zinc double salts. Thus the reaction of *O,O*-di-*n*-butyl hydrogen phosphorodithioate with molar quantities of zinc oxide containing an equivalent amount of water gave a 70% yield of the corresponding basic zinc double salt. The melting point of this product corresponds to the reported value.<sup>1</sup>

The basic zinc double salts and the normal zinc salts of *O,O*-di-*i*-propyl,<sup>1</sup> and *O,O*-di-*i*-butyl hydrogen phosphorodithioate are solids. These salts were separated by recrystallization from petroleum ether. By contrast, both the zinc *O,O*-di-*n*-propyl and *O,O*-di-*n*-butyl phosphorodithioates are liquids, while the corresponding basic zinc double salts are solids. Treatment of the basic zinc double salts with concentrated hydrochloric acid regenerates the starting phosphorus acid. Acidification of the basic zinc double salt of *O,O*-di-*n*-propyl hydrogen phosphorodithioate with hydrochloric acid gave *O,O*-di-*n*-propyl hydrogen phosphorodithioate (65%).

Electrometric titration of the basic zinc double salt with alcoholic potassium hydroxide and benzene-alcohol solvent gave a neutral equivalent of one third the molecular weight. This corresponds to the reaction of the three phosphorodithioate ions with the stronger base. To check this a purified sample of zinc *O,O*-di-*i*-propyl phosphorodithioate was titrated by the same procedure. The neutral equivalent obtained was one half of the molecular weight which corresponds to the reaction of two phosphorodithioate ions with the stronger base. The titration of the basic zinc double salt with potassium hydroxide to give a neutral equivalent one third of the molecular weight is in harmony with the tetrabutyl ammonium hydroxide titration of the basic zinc double salt reported previously.<sup>1</sup> Titration of the basic zinc double salt with aqueous hydrochloric acid using benzene-alcohol solvent and Bromphenol Blue as the indicator gave a neutral equivalent equal to the molecular weight. This presumably corresponds to the titration of the basic hydroxyl group, and parallels the results reported previously with perchloric acid in acetonitrile-dioxane solvent.<sup>1</sup>

(1) V. P. Wystrach, E. O. Hook, and G. L. M. Christopher, *J. Org. Chem.*, **21**, 705 (1956).