Anal. Caled. for $B_{10}C_{36}H_{42}P_{2}O_{6}$: 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 $B_{10}C_{40}H_{52}P_2O_2$: 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.

Acknowledgment. This work was supported by the Office of Naval Research.

Olin Mathieson Chemical Corp. Organics Div. New Haven, Conn.

Basic Zinc Double Salts of 0,0-Dialkyl Hydrogen Phosphorodithioates

W. E. BACON AND J. F. BORK

Received October 19, 1961

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.¹ The formation of this product

 $3 (RO)_2 PSS^- + OH^- + 2 Zn^{++} \longrightarrow [(RO)_2 PS_2]_3 Zn_2 OH$

depends upon excess hydroxyl ion during the reaction of the zinc ion with phosphorodithioate ion.¹

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

$$5 (\text{RO})_2 \text{PS}_2 \text{H} + 3 \text{ZnO} \longrightarrow$$

$$[(\text{RO})_2 \text{PS}_2]_3 \text{Zn}_2 \text{OH} + [(\text{RO})_2 \text{PS}_2]_2 \text{Zn} + 2 \text{H}_2 \text{O}$$
(A)
(B)

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.¹

The basic zinc double salts and the normal zinc salts of 0,0-di-i-propyl,1 and 0,0-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 0,0-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.¹ 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.¹

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

EXPERIMENTAL

O,O-Dialkyl hydrogen phosphorodithioates. These acids were prepared by a method outlined by Mastin, Norman, and Weilmuenster.² These crude acids are 80-90% purity as determined by titration with standard alkali, and were used as such or purified by the method of Bacon and LeSuer.³

Basic zinc double salt of O,O-di-n-propyl hydrogen phosphorodithioate. O,O-Di-n-propyl hydrogen phosphorodithioate, 214 g. (1.0 mole), was slowly dripped into a slurry of zinc oxide, 81.4 g. (1.0 mole) and benzene, 500 ml. at 35°. The reaction was exothermic. The mixture was stirred 2 hr. at 50°, then the water was removed by refluxing the benzene into a Dean-Stark tube. After all the water was removed the solution was cooled and filtered. The benzene was removed by distillation to 90° at 50 mm. The residue, consisting of solid and liquid, was diluted with petroleum ether, 250 ml., and the solid product removed by filtration. The white solid, 150 g. (61%), was recrystallized from *n*-propyl alcohol, m.p. 178-179°.

Anal. Calcd. for $C_{18}H_{43}P_3O_7S_6Zn_2$: P, 11.82; S, 24.42; Zn, 16.63; C, 27.50; H, 5.47; neut. equiv. (as a base), 788; neut. equiv. (as an acid), 263. Found: P, 11.74; S, 24.74; Zn, 16.70; C, 28.04; H, 5.09; neut. equiv. (as an acid) 257.

The petroleum ether was removed from the filtrate by distillation, and further concentrated by heating to 80° at 50 mm. The slightly cloudy residue was filtered through a sintered glass funnel and the filtrate, 90 g. (37%), was the normal zinc salt.

Anal. Caled. for $C_{12}H_{25}O_4P_2S_4Zn$: P, 12.60; S, 26.07; Zn, 13.29. Found: P, 12.30; S, 25.76; Zn, 12.82.

Zinc O,O-di-n-propyl phosphorodithioate by reaction with zinc dust. O,O-Di-n-propyl hydrogen phosphorodithioate, 216 g. (1.0 mole), was added rapidly to zinc dust. 36 g. (1.1 moles), suspended in benzene, 500 ml., at 35°. The reaction was exothermic and the mixture foamed briefly. The mixture was stirred 2 hr. at 50-70° and filtered. Only a trace of the zinc dust remained. The benzene was removed by distillation, 80° at 50 mm. The cloudy viscous liquid was filtered and the filtrate was the product.

Anal. Calcd. for $C_{12}H_{28}O_4P_2\hat{S}_4Zn$: P, 12.60; S, 26.07; Zn 13.29. Found: P, 12.30; S, 25.70; Zn, 12.54.

Basic zinc double salt of 0,0-di-n-butyl hydrogen phosphorodithioate. Crude 0,0-di-n-butyl hydrogen phosphorodithioate, 1620 g. (6.0 moles), water, 108 g. (6.0 moles), and benzene, 1740 g. (22.3 moles), were mixed at 35°. Zinc oxide, 488 g. (6.0 moles), was added slowly at 50-60° over a period of fifteen minutes. The mixture was stirred 2 hr. at 60°. The water was removed by refluxing the benzene through a Dean-Stark tube.

The benzene solution was filtered and the benzene removed by distillation to 100° at 35 mm. The residue was cooled and the crude product filtered; 962 g. was obtained. This product was recrystallized from naphtha and the mother liquors combined and retreated with zinc oxide and water as outlined previously. The solid obtained, 248 g., was combined with the previous batch giving 1210 g. (70%), m.p. 149-151°.

Anal. Calcd. for $C_{24}H_{45}P_3O_7S_6Zn_2$: P, 10.66; S, 22.07; Zn, 15.00; C, 33.06 H, 6.36; neut. equiv. (as a base), 872; neut. equiv. (as an acid), 291. Found: P, 10.60; S, 22.15; Zn, 15.33; C, 33.47; H, 6.07; neut. equiv. (as a base), 862 (using Bromophenol Blue as the indicator).

Basic zinc double salt of O,O-di-i-butyl hydrogen phosphorodithioate. Crude O,O-di-i-butyl hydrogen phosphorodithioate, 520 g. (2.0 moles); benzene, 652 g. (8.3 moles); and water 100 g. (5.5 moles), were mixed at 35°. The zinc oxide, 163 g. (2.0 moles), was slowly added at 35–50° over a period of 10 min. The mixture was stirred 1 hr. at 50°, then dried by refluxing the benzene through a Dean-Stark tube. After complete removal of the water (3–4 hr.), the product was filtered. The benzene was evaporated and the last trace of solvent was removed by heating to 100° at 30 mm. The residue was extracted with petroleum ether, 500 ml. Upon cooling the petroleum ether, 150 g. of white solid separated (25%), m.p. $138-140^{\circ}$.

Anal. Caled. for $C_{24}H_{55}P_3O_7S_6Zn_2$: P, 10.66; S, 22.07 Zn, 15.00. Found: P, 10.33; S, 22.03; Zn, 15.13.

Acknowledgment. The authors wish to thank Mr. Harry Ferber and members of his staff, who carried out the analytical determinations.

THE LUBRIZOL CORP. CLEVELAND 17, OHIO

A By-Product of the Gabriel Phthalimide Synthesis of Aminomethyltrimethylsilane¹

Ralph J. Fessenden, Dennis Yasuda,² and Marvin D. $$\rm Coon^3$$

Received October 24, 1961

In connection with another investigation,⁴ aminomethyltrimethylsilane (II) was prepared following the procedure of Sommer and Rockett,⁵ who utilized the Gabriel method with the Ing-Manske modification⁶ for the cleavage of the *N*-substituted phthalimide I.

Sommer and Rockett, after treatment of I with hydrazine hydrate, heated the mixture under reflux with concentrated hydrochloric acid, filtered the phthalhydrazide, and evaporated the filtrate to dryness. The resulting residue was then dissolved in water, made basic, and steam distilled into hydrochloric acid. This procedure differs slightly from the general method of Ing and Manske, who, after filtration, merely concentrated the filtrate, then made it basic, and extracted the desired amine.

When the procedure of Sommer and Rockett was followed precisely, the hydrochloride of II was obtained in 60% yield. However, when the work up method of Ing and Manske was used, a white solid of the formula $C_{16}H_{28}N_2O_2Si_2$ was isolated. No amine II was obtained.

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⁽¹⁾ This work was supported by a grant (NSF-G14554) from the National Science Foundation.

⁽²⁾ Participant in the National Science Foundation Undergraduate Research Participation Program (G11923), 1960-1961.

⁽³⁾ Participant in the National Science Foundation Undergraduate Research Participation Program (G15713), Summer 1961.

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