



## EXPERIMENTAL

*O,O-Dialkyl hydrogen phosphorodithioates.* These acids were prepared by a method outlined by Mastin, Norman, and Weilmuenster.<sup>2</sup> 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.<sup>3</sup>

*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  $C_{18}H_{43}P_2O_7S_6Zn_2$ : 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.* Calcd. 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  $C_{12}H_{25}O_4P_2S_4Zn$ : P, 12.60; S, 26.07; Zn, 13.29. Found: P, 12.30; S, 25.70; Zn, 12.54.

*Basic zinc double salt of O,O-di-n-butyl hydrogen phosphorodithioate.* Crude *O,O*-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  $C_{24}H_{55}P_2O_7S_6Zn_2$ : 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°.

*Anal.* Calcd. for  $C_{24}H_{55}P_2O_7S_6Zn_2$ : P, 10.66; S, 22.07 Zn, 15.00. Found: P, 10.33; S, 22.03; Zn, 15.13.

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## A By-Product of the Gabriel Phthalimide Synthesis of Aminomethyltrimethylsilane<sup>1</sup>

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In connection with another investigation,<sup>4</sup> amino-methyltrimethylsilane (II) was prepared following the procedure of Sommer and Rockett,<sup>5</sup> who utilized the Gabriel method with the Ing-Manske modification<sup>6</sup> 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  $C_{16}H_{23}N_2O_2Si_2$  was isolated. No amine II was obtained.

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