

## 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.

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

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

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Received October 24, 1961

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.

(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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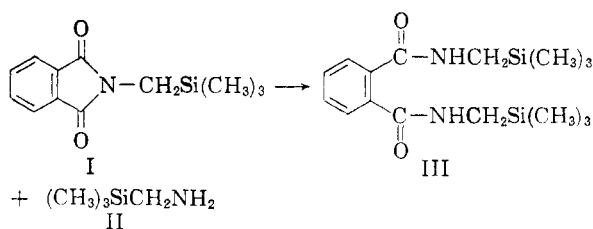
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Investigation of the solid revealed that it was the diamide III. The infrared spectrum of III exhibited the characteristic amide I and II bands at  $6.15 \mu$  and  $6.45 \mu$ .<sup>7</sup> Confirmation of the identification was obtained by the independent preparation of III from phthaloyl chloride and II.

Incomplete cleavage of I when the conditions of Ing and Manske were used would explain these results. Addition of base to the concentrated filtrates would free the amine II which in turn would react with I to yield III. However, evaporation to dryness of the acidified filtrate prior to the addition of base would complete the cleavage of I thus preventing the formation of III. That such a rationale is feasible is provided by the reaction of I and II to give a 77% yield of III.



#### EXPERIMENTAL<sup>8</sup>

*N,N'*-Bis(trimethylsilylmethyl)phthalamide (III). A. As a by-product from the Gabriel reaction. To a stirred solution of 125 ml. of absolute ethanol and 50.0 g. (0.215 mole) of *N*-trimethylsilylmethylphthalimide<sup>6</sup> was added over a 10-min. period 10.7 g. (0.215 mole) of hydrazine hydrate. The mixture was heated under reflux for 1.5 hr., 25 ml. of concentrated hydrochloric acid added to the refluxing solution, and the heating continued for an additional 2 hr. The mixture was then cooled and filtered. The precipitate was washed several times with 6*N* hydrochloric acid and finally refluxed with 100 ml. of 6*N* hydrochloric acid, then refiltered. All acid filtrates were combined and evaporated until *ca.* two-thirds of the volume remained; two phases were observed. The concentrated filtrates were then made basic with potassium hydroxide. A white solid formed and was extracted with several portions of ether. Removal of the ether by distillation gave 13.6 g. (36%) of III, m.p. 177–178°.

Anal. Calcd. for  $\text{C}_{16}\text{H}_{28}\text{Si}_2\text{N}_2\text{O}_2$ : C, 57.2; H, 8.34; N, 8.35; Si, 16.6. Found: C, 57.17; H, 8.35; N, 8.37; Si, 16.8.

B. From phthaloyl chloride. To 1.00 g. (9.70 mmoles) of aminomethyltrimethylsilane was added slowly 1.00 g. (4.92 mmoles) of phthaloyl chloride followed by 7 ml. of 10% sodium hydroxide. The resulting white solid was filtered, washed with 10 ml. of water, then crystallized from 95% ethanol, yielding 2.60 g. (80%) of III, m.p. 176–177°. A mixed melting point with the material obtained as described in part A showed no depression.

C. From *N*-trimethylsilylmethylphthalimide (I) and aminomethyltrimethylsilane (II). Upon the mixing of 1.00 g. (9.70 mmoles) of II and 2.3 g. (10.0 mmoles) of I, a cloudy solution resulted, which, upon warming, solidified. Crystallization from ethanol yielded 2.5 g. (77%) of III, m.p. 177–177.5°. A mixed melting point with the sample obtained as described in part A showed no depression.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, 1954, pp. 180–185.

(8) All melting points are uncorrected and were taken on a Fisher melting point stage. The infrared spectra were taken using a Beckman IR-5 recording spectrophotometer (KBr pellet). The carbon-hydrogen microanalysis was performed by the Berkeley Microanalytical Laboratory.

*Aminomethyltrimethylsilane hydrochloride.* The procedure described in part A was followed precisely through the combination of the acid filtrates. The combined acid filtrates were boiled to dryness and the resulting solid was then added to a potassium hydroxide solution. The resulting basic mixture was steam distilled as described by Sommer and Rockett,<sup>5</sup> yielding 16.8 g. (60%) of aminomethyltrimethylsilane hydrochloride, m.p. 245–246° (lit.<sup>5</sup> 242–243°).

*Acknowledgment.* The silicon analysis performed by Francis J. Freenor is gratefully acknowledged.

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### Studies in Organosilicon Chemistry. XLIII. An Investigation of Silicon-Containing *s*-Triazines

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Received October 30, 1961

Preliminary work by the writers and others has led to the conclusion that for the preparation and isolation of triazines with silyl side chains, good yields may be expected of those compounds in which an aromatic nucleus is found between triazine carbon and silicon.

Six of these compounds have been prepared through the use of the proper Grignard reagent acting on cyanuric chloride or of ammonia acting on a silicon containing product. Several new intermediates have also been prepared. For example, cyanuric chloride reacts with *p*-trimethylsilylphenylmagnesium bromide with replacement of a chlorine to give 2,4-dichloro-6-*p*-(trimethylsilylphenyl)-*s*-triazine. Dimethylallyl-*p*-bromophenylsilane was prepared by the action of *p*-bromophenyllithium on dimethylallylchlorosilane. Dimethyl-*p*-bromophenylsilane resulted from the interaction of dimethylvinylchlorosilane and *p*-bromophenylmagnesium bromide.

#### EXPERIMENTAL

Several intermediates were satisfactorily prepared, in accordance with methods outlined in the literature. These comprised 2-chloro-4,6-diphenyl-*s*-triazine,<sup>2</sup> trimethyl-*p*-bromophenylsilane,<sup>3a,b</sup> dimethyl-*p*-bromophenylphenylsilane,<sup>4</sup> and chloromethyldimethylfluorosilane.<sup>5</sup>

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