TABLE II

Intermediates in the Conversion of Cyclic Ketones to α,ω-Diamino Acids

Compound	M.P.[a]	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Ref.
2,5-Dioximinocyclopentanone	214 d.[b]	42.25	4.26	19.72	42.41	4.23	19.97	(3)
2,6-Dioximino-4-methylcyclohexanone	[c]	49.40	5.92	16.47	49.72	5.64	16.22	(3)
4-Cyano-2-oximinobutyric acid	123–125	42.25	4.26	19.72	42.24	4.11	19.84	(3)
5-Cyano-4-methyl-2-oximinovaleric acid	109–111	49.40	5.92	16.47	49.30	5.72	16.56	(3)
2,5-Diacetoximinocyclopentanone	177 dec.	47.79	4.46	12.39	48.02	4.42	12.38	(4)
2,6-Diacetoximino-4-methylcyclohexanone	171–172	51.96	5.55	11.02	51.80	5.64	11.32	(4)
Ethyl 4-cyano-2-oximinobutyrate	Liq.[d]	49.40	5.92	16.47	49.31	6.14	16.29	(5)
Ethyl 5-cyano-4-methyl-2-oximinovalerate	61	54.53	7.12	14.14	54.71	6.87	14.25	(5)
DL-Ornithine monohydrochloride	205–211 dec.	[e]						(5)
DL-4-Methyllysine monohydrochloride	229–230	42.74	8.71	14.25[f]	42.71	8.71	14.46[f]	(5)

[a] All melting points are uncorrected. [b] Lit.[7] m.p. 215° dec. [c] Decomposed at about 200°. [d] Not distilled, n_D^{25} 1.4750. [e] Infrared spectrum identical to that of authentic DL-ornithine monohydrochloride. [f] Calcd.: Cl, 18.03. Found: Cl, 18.10.

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Neopentyl Group Analogs. IV. Trimethylsilylmethyldichlorophosphine[1]

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Our recent work on the tris(trimethylsilylmethyl) derivatives of the Group VB elements[2] has prompted further work in the area of silicon-substituted phosphorus compounds. Of particular interest as a possible intermediate in the synthesis of silicon-substituted phosphonitrilic compounds was trimethylsilylmethyldichlorophosphine.

Conventional methods used to synthesize alkyldichlorophosphines utilize the reaction of phosphorus trichloride with mild alkylating agents, such as dialkylmercury[3] or tetraalkyllead[4] compounds. Accordingly, bis(trimethylsilylmethyl)mercury and tetrakis(trimethylsilylmethyl)lead, both new compounds, were prepared by the usual Grignard procedure, and their action on phosphorus trichloride was investigated. The mercurial did not react with phosphorus trichloride either when a mixture of the reactants was refluxed in hexane solution, or in the absence of solvent at *ca.* 76°. In contrast, the lead compound was cleaved by phosphorus trichloride, giving crystalline, sublimable tris(trimethylsilylmethyl)lead chloride and trimethylsilylmethyldichlorophosphine. However, the isolated yield of the phosphine was not very high, and a better synthesis was desired.

$$[(CH_3)_3SiCH_2]_4Pb + PCl_3 \longrightarrow [(CH_3)_3SiCH_2]_3PbCl + (CH_3)_3SiCH_2PCl_2$$

Although the Grignard procedure is not generally applicable to the synthesis of pure $RPCl_2$ compounds because mixtures of mono-, di-, and trisubstituted products result, it seemed possible that with the relatively bulky trimethylsilylmethyl group, monosubstitution could be realized in acceptable yield. Indeed, our previous work[2] showed that complete substitution of all three chlorine atoms of phosphorus trichloride with trimethylsilylmethyl groups by the Grignard procedure requires drastic conditions. It was found in the present work that addition of one equivalent of trimethylsilylmethylmagnesium chloride to one mole of phosphorus trichloride in ether at low temperature resulted in the desired trimethylsilylmethyldichlorophosphine in *ca.* 40% yield.

Attempted conversion of trimethylsilylmethyldichlorophosphine to trimethylsilylmethyltetrachlorophosphorane was not successful. Even at −20° in the dark addition of a solution of chlorine in *sym*-tetrachloroethane to trimethylsilylmethyldichlorophosphine caused cleavage of the carbon-silicon bond to form trimethylchlorosilane. This facile cleavage of the carbon-silicon bond may be due to the inductive effect of the PCl_4 group; electron withdrawal by this group would make the Si-C bond more polar, hence more susceptible toward ionic fission.

Investigation of the solid formed in the chlorination reaction showed it to be impure phosphorus pentachloride rather than the expected chloromethyltetrachlorophosphorane. The hydrolysis product of this solid formed a barium salt of very low carbon content, and an anilinium salt could be prepared which was shown to be $[C_6H_5NH_3][H_2PO_4]$. It is not known at what point fission of the

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[1] Part III: D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

[2] D. Seyferth, *J. Am. Chem. Soc.*, **80**, 1336 (1958).

[3] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, 1950, p. 42.

[4] M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*, **14**, 429 (1949).

the P-C bond took place, nor is the fate of the methylene group of the trimethylsilylmethyldichlorophosphine known. It is, however, very likely that such cleavage took place after cleavage of the Si—C bond, since initial cleavage of trimethylsilylmethyldichlorophosphine at the P—C linkage would have given chloromethyltrimethylsilane, a compound which is stable to Si—C cleavage under these conditions, although side chain chlorination does take place.

EXPERIMENTAL[5]

(1) *Bis(trimethylsilylmethyl)mercury.* The Grignard reagent, prepared from 0.6 g.-atom of magnesium turnings and 0.6 mole of chloromethyltrimethylsilane in 450 ml. of tetrahydrofuran (THF), was cooled to −10°, and a solution of 0.28 mole of mercuric chloride in 125 ml. of tetrahydrofuran was added slowly with stirring. The mixture subsequently was heated at reflux for 1 hr., cooled, and hydrolyzed with 50 ml. of saturated ammonium chloride solution. The organic layer was separated; the aqueous phase was extracted with ether. The combined organic layer and ether washings were dried over anhydrous sodium sulfate. Fractional distillation gave 51 g. (48.5%) of bis(trimethylsilylmethyl)mercury, b.p. 49–50° at 0.35 mm., n_D^{25} 1.4869.

Anal. Calcd. for $C_8H_{22}Si_2Hg$: C, 25.62; H, 5.91; Hg, 53.49. Found: C, 25.89; H, 6.04; Hg, 53.43.

(2) *Tetrakis(trimethylsilylmethyl)lead.* To the vigorously stirred solution of *ca.* 0.6 mole of trimethylsilylmethylmagnesium chloride in 450 ml. of tetrahydrofuran at −10° was added a suspension of 83.5 g. (0.3 mole) of lead dichloride in tetrahydrofuran. The mixture became deep red-brown immediately. In order to effect the complete disproportionation of the divalent lead species formed initially, the solution was heated at reflux for 5 hr. until the reaction mixture was gray-green in color. The mixture was cooled to −10° and hydrolyzed with 100 ml. of saturated ammonium chloride solution. The metallic lead formed in the reaction was filtered off, and the organic layer was separated. The dried organic phase was fractionally distilled to give colorless liquid which became turbid on standing. Filtration and a second distillation gave 31 g. (37%) of tetrakis(trimethylsilylmethyl)lead, b.p. 104–105° at 0.01 mm.

Anal. Calcd. for $C_{16}H_{44}Si_4Pb$: C, 34.57; H, 7.97. Found: C, 34.14; H, 7.86.

(3) *Trimethylsilymethyldichlorophosphine.* (a) *Attempted preparation via the mercurial.* A solution of 90 g. (0.65 mole) of freshly distilled phosphorous trichloride in 100 ml. of hexane was heated at reflux while 50 g. (0.13 mole) of bis(trimethylsilylmethyl)mercury was added slowly. The resulting solution was heated for 12 hr. at reflux. Since no reaction appeared to have occurred, the hexane and the phosphorus trichloride were distilled off, and 90 g. of fresh phosphorus trichloride was added to the residue. This mixture was heated at reflux for 12 hr. Distillation led to a 96% recovery of the mercurial.

(b) *Preparation via the lead derivative.* A mixture of 39 g. (0.7 mole) of tetrakis(trimethylsilylmethyl)lead and 480 g. (3.5 moles) of phosphorus trichloride was heated at reflux for 16 hr. During this time white needles precipitated. After filtration of the reaction mixture, the excess of phosphorus trichloride was distilled from the filtrate; fractional distillation of the residue gave only 2.2 g. of trimethylsilylmethyldichlorophosphine. The filtered solid was washed with hexane and sublimed at 1 mm. (bath temperature 225°) to give 19.5 g. (55%) of tris(trimethylsilylmethyl)lead chloride; m.p. 214–216° after two sublimations.

Anal. Calcd. for $C_{12}H_{33}Si_3PbCl$: C, 28.6; H, 6.60; Cl, 7.04. Found: C, 28.38; H, 6.79; Cl, 6.75.

(c) *Preparation by the Grignard method.* The Grignard reagent prepared from 0.6 g.-atom of magnesium turnings and 0.6 mole of chloromethyltrimethylsilane in 450 ml. of diethyl ether was filtered through glass wool and added, with stirring, to a solution of 68.5 g. (0.6 mole) of phosphorus trichloride in 300 ml. of ether at −10°. The initially white solid formed turned deep yellow as the reaction progressed. The reaction mixture was stirred at room temperature for 1 hr. The solution was cooled, and anhydrous hydrogen chloride was bubbled into it for 0.5 hr. (Omission of this step resulted in very low yields of product; possibly destruction of a solid $(CH_3)_3SiCH_2PCl_2$-$MgCl_2$ complex is involved in the hydrogen chloride treatment). The mixture was filtered, and the salts were washed thoroughly with ether. Distillation of the ether solution gave 49 g. (43%) of trimethylsilylmethyldichlorophosphine, b.p. 50° at 1.5 mm., a liquid that fumed when exposed to moist air.

Anal. Calcd. for $C_4H_{11}Cl_2PSi$: C, 25.41; H, 5.85. Found: C, 25.75; H, 6.15.

(4) *Chlorination of trimethylsilylmethyldichlorophosphine.* A solution of 47 g. (0.25 mole) of trimethylsilylmethyldichlorophosphine in 100 ml. of 1,1,2,2-tetrachloroethane was cooled to −20° and protected from the light. The slow addition of a solution of 0.5 mole of chlorine in the same solvent was carried out in an atmosphere of nitrogen. A pale yellow solid precipitated (24 g.). The mixture was filtered under nitrogen. Fractional distillation gave 22 g. (81%) of trimethylchlorosilane, b.p. 55–56°, n_D^{25} 1.3855 (Dow Corning Corp. purest grade trimethylchlorosilane: n_D^{25} 1.3860), further identified by its infrared spectrum and the infrared spectrum of its hydrolysis product, hexamethyldisiloxane.

Two grams of the solid formed during the chlorination reaction was added in portions to 15 ml. of ice-cold water; a vigorous reaction was apparent. The resulting solution was treated with decolorizing charcoal and filtered. Evaporation of the filtrate at reduced pressure gave a noncrystallizable oil. This was diluted with 5 ml. of water. The acidic solution was neutralized to *p*H 6 with aqueous ammonia and treated with barium chloride solution. The resulting crystalline barium salt was washed well with hot water and dried.

Anal. Calcd. for $ClCH_2PO_3Ba$: C, 4.5; H, 0.75. Found: C, 0.49; H, 0.55.

Treatment of an aqueous solution of the hydrolysis product of the solid chlorination product with aniline caused precipitation of an anilinium salt, m.p. 183–184° after recrystallization from absolute alcohol. This was not the anilinium salt of chloromethylphosphonic acid, m.p. 198–199°, rather the monoanilinium salt of phosphoric acid.

Anal. Calcd. for $C_6H_{10}O_4NP$: C, 37.8; H, 5.25; N, 7.32. Found: C, 37.73; H, 5.12; N, 7.46.

A mixture of the anilinium salts prepared from the chlorination product and from phosphoric acid did not have a depressed melting point.

The reaction of trimethylsilylmethyldichlorophosphine with chlorine in 1:1 molar ratio also appeared to result in cleavage, since instead of trimethylsilylmethyltetrachlorophosphorane (18.5% C and 4.23% H), solids containing 8–9.5% C and 2.2–2.5% H were obtained.

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(5) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All reactions were carried out under an atmosphere of prepurified nitrogen.