Acknowledgment.—Only the ability to utilize the considerable competence of a large number of people at Humble Research and Development has permitted the successful conclusion of this work. In particular the author's thanks are due L. Westerman and J. O. Brewer for the molecular weights, N. F. Chamberlain and T. Hines for the n.m.r. spectra, and S. H. Hastings, H. W. Kinsey, and T. Reid for the ultraviolet spectra. The author is grateful to the Humble Oil and Refining Company for permission to publish these results.

Reactions of (Chloromethyl)alkylsilanes and Quinoline[1]

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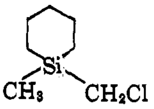
A reassignment of the structures of the (α-chloro)dimethylsilacyclopentanes has been made on the basis of n.m.r. spectra. Upon reflux with quinoline, (chloromethyl)alkylsilanes undergo cleavage of the chloromethyl group to yield chlorosilanes or, with water work-up, disiloxanes.

In a previous study,[2] we investigated the free-radical chlorination of dimethylsilacyclopentane and dimethylsilacyclohexane and assigned structures to the monochlorinated products. After completion of that work, it was brought to our attention that the n.m.r. spectrum of the compound designated 1-chloromethyl-1-methylsilacyclohexane (1) was not in agreement with our assigned structure.[3] Since the structure assigned to this compound was based upon analogy from the more extensively investigated 1-chloromethyl-1-methyl-silacyclopentane (2) and 1,1-dimethyl-2-chlorosilacyclopentane (3), we were prompted to investigate the n.m.r. spectra of the two isomers and to reinvestigate the chemistry leading to our original structure assignments.



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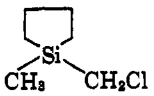

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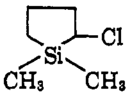
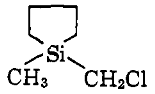
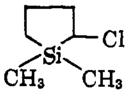


3

An assignment of structures to 2 and 3 can be made with the aid of the characteristic chemical shifts and splitting patterns of the chloroalkyl protons observed in the n.m.r. spectra. The n.m.r. spectra of some reference compounds along with the n.m.r. spectra of the (monochloroalkyl)dimethylsilacyclopentanes are summarized in Table I. The (chloromethyl)silanes show a sharp singlet in the region of interest while the (α-chloroethyl)silanes (examined to determine the chemical shift rather than the splitting pattern) exhibit a quartet. In the spectra of the (α-chloro)dimethylsilacyclopentanes, the isomer previously assigned structure 2, b.p. 156–157°, showed a well defined triplet; the isomer previously assigned structure 3 exhibited a sharp singlet. It is apparent from this spectral data that the original structure assignments were reversed.

TABLE I

CHEMICAL SHIFTS AND SPLITTING PATTERNS OF SOME (CHLOROALKYL)SILANES[a]

Compound	Chemical shift of the chloroalkyl protons, p.p.m.	Splitting pattern
$(CH_3)_3SiCH_2Cl$	2.68	Singlet
$CH_3(C_2H_5)_2SiCH_2Cl$	2.68	Singlet
	2.75	Singlet
$C_2H_5(CH_3)_2SiCH(Cl)CH_3$	3.25	Quartet J = 7 c.p.s.
	3.30	Triplet J = 5 c.p.s.

[a] Ref. 9.

In our original work,[2] the key step in the structure proof was a quinoline dehydrohalogenation. It was reasoned that 3 would react to yield an olefin while 2 would not react. Indeed, when the reaction was carried out, one of the α-chloro isomers underwent reaction with quinoline while the other was recovered from the reaction mixture along with some olefinic material. In that it later became apparent that 2 reacts with quinoline at a faster rate than does 3, it was of interest to determine the nature of this reaction.

It was observed that (chloromethyl)trimethylsilane (4) and (chloromethyl)diethylmethylsilane (5) both undergo cleavage of the chloromethyl group when heated under reflux with quinoline. With 4, after a 3-day reflux with quinoline, trimethylchlorosilane was isolated in 70% yield. Shorter reflux periods resulted in substantially lower yields of the chlorosilane. With 5, a 24-hr. reflux with quinoline and water work-up resulted in a 75% yield of the disiloxane (6).

$$\underset{\mathbf{4}}{(CH_3)_3SiCH_2Cl} \xrightarrow{\text{quinoline}} (CH_3)_3SiCl$$

$$\underset{\mathbf{5}}{CH_3(C_2H_5)_2SiCH_2Cl} \xrightarrow[\text{2. } H_2O]{\text{1. quinoline}} \underset{\mathbf{6}}{[CH_3(C_2H_5)_2Si]_2O}$$

Under the same conditions as used with 5, (α-chloroethyl)dimethylethylsilane yielded only traces of vinyl(dimethyl)ethylsilane, while 70% of the starting (α-chloroethyl)silane was recovered.

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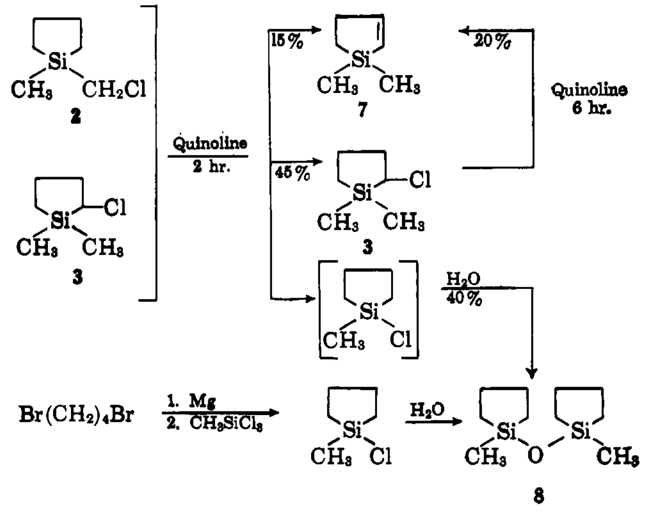
(1) This work was supported by a grant (NSF-G14554) from the National Science Foundation.

(2) R. J. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961).

(3) (a) We are grateful to S. Brownstein, National Research Council, Canada, for bringing to our attention the incompatibility of the n.m.r. spectrum of **3** and our previously assigned structure. (b) Although the (chloro)dimethylsilacyclohexane was not completely characterized, the position of the chloroalkyl proton multiplet (3.2 p.p.m.) in the n.m.r. spectrum indicates that the chlorine is attached to the 2-position of the ring rather than the 3-position of the ring. The multiplicity of this band is attributed to the conformations of the ring.

It is apparent that while the quinoline dehydrohalogenation synthesis of vinylsilanes is applicable in systems such as X-$CH_2CH_2SiX_3$ or $RCH(X)SiX_3$,[4] it is not reliable in systems of the type $CH_3CH(X)SiR_3$.

On the basis of these observations, reinvestigation of the reactions of **2** and **3** with quinoline was undertaken. In contrast to the open-chain analogs, only a 2-hr. reflux with quinoline was necessary for complete disappearance (g.l.p.c.) of one of the α-chlorodimethylsilacyclopentane isomers, now known to be **2**, from a mixture of the two isomers. Water work-up and distillation of the reaction mixture resulted in a 40% yield of *sym*-dimethylbis(cyclotetramethylene)disiloxane (**8**), a 15% yield of 1,1-dimethylsilacyclo-2-pentene (**7**), and a 45% recovery of **3**. The identity of the higher boiling disiloxane **8** was shown by independent synthesis using the method of West.[5] The chloro isomer **3**, isolated from the distillation, was resubjected to a 6-hr. quinoline reflux. From this reaction there was obtained a 20% yield of **7**.



The path of the cleavage remains obscure. Distillation of the quinoline residue yielded, besides quinoline, N-methyl-1,2,3,4-tetrahydroquinoline indicating some type of oxidation–reduction reaction. 2-Methylquinoline was not observed in the volatile material indicating that if the initial step is a displacement of the chlorine by the quinoline, the second step is not a thermal rearrangement followed by cleavage of the type observed with 2-trimethylsilylmethylpyridine.[6] Most of the quinoline material could not be distilled easily. Thin layer chromatography of this residual material revealed the presence of at least fifteen different compounds, characterization of which was not attempted.

Experimental[7]

Reactions of (Chloroalkyl)silanes and Quinoline. A. (Chloromethyl)trimethylsilane (4).—A mixture of 57.3 g. (0.47 mole) of (chloromethyl)trimethylsilane, b.p. 97–98°, and 60.0 g. (0.47 mole) of freshly distilled quinoline, b.p.121° (23 mm.), was heated at reflux for 3 days. The mixture became progressively darker during the reflux and at the end of the reflux period a dark red precipitate was noted. Fractional distillation of the reaction mixture yielded 35.5 g. (70%) of trimethylchlorosilane, b.p. 59–63°, $n^{25}\text{D}$ 1.3876–1.3884 (lit.[8] b.p. 57°, $n^{20}\text{D}$ 1.3884), and 4.5 g. of a mixture of recovered (chloromethyl)trimethylsilane and hexamethyldisiloxane (identified by gas phase chromatography), b.p. 90–97°, $n^{25}\text{D}$ 1.4054.

Continued distillation using vacuum yielded 13.9 g. of a yellow liquid, b.p. 108–119° (9 mm.), $n^{25}\text{D}$ 1.5862–1.5864. A center cut of this distillation fraction, b.p. 108–112° (9 mm.), $n^{25}\text{D}$ 1.5864, was used for further investigation. Thin layer chromatography of the distillate on silica gel with 50% petroleum ether (b.p. 30–60°)–50% chloroform as developing solvent showed one major spot, R_f 0.53, and no spot at R_f 0.14. On the same plate, an authentic sample of N-methyl-1,2,3,4-tetrahydroquinoline exhibited a spot at R_f 0.53, 2-methylquinoline exhibited a spot at R_f 0.14, and quinoline, at R_f 0.11. The n.m.r. spectrum[9] and the infrared spectrum of the distillate were identical with those of an authentic sample of N-methyl-1,2,3,4-tetrahydroquinoline [lit.[10] b.p. 112° (8.5 mm.), $n^{17.5}\text{D}$ 1.5827]. Bands in the spectrum were observed at 1.92 (pentuplet); 2.65, 3.15 (triplets, J = 6 c.p.s.); 2.75 (singlet); and 6.6 p.p.m. (multiplet). The bands at 1.92, 2.65, and 3.15 were identical in chemical shifts and splitting patterns with those of the aliphatic ring protons of 6-methoxy-1,2,3,4-tetrahydroquinoline.[11]

The residue after vacuum distillation was black and tarry. Thin layer chromatography (silica gel) using benzene–chloroform (1:1) as developing solvent showed eight distinct spots while a chromatogram using chloroform–methanol (99:1) revealed the presence of an additional seven components.

In other runs, the yield of trimethylchlorosilane ranged from 4% (1.5-hr. reflux) to 50% (3-day reflux).

B. (Chloromethyl)diethylmethylsilane (5).—Direct chlorination[2] of 456 g. (3.5 moles) of dimethyldichlorosilane yielded 185 g. (57%) of (chloromethyl)methyldichlorosilane, b.p. 122° (lit.[12] b.p. 122°). Treatment of the (chloromethyl)dichlorosilane with 2.0 moles of commercial ethylmagnesium bromide followed by water work-up and fractional distillation yielded 63.3 g. (65% based upon the chloromethyldichlorosilane) of (chloromethyl)diethylmethylsilane, b.p. 155–156°, $n^{25}\text{D}$ 1.4371.

Anal. Calcd. for $C_6H_{15}SiCl$: C, 47.84; H, 9.96; Cl, 23.58. Found: C, 47.95; H, 9.94; Cl, 23.78.

A mixture of 40.0 g. (0.27 mole) of the (chloromethyl)silane and 69.0 g. (0.58 mole) of quinoline was heated at reflux for 24 hr. Direct distillation of the mixture yielded 35.5 g. of material boiling up to 210°. This distillate was mixed with 30 ml. of water and heated at reflux for 2 hr. At the end of this period only one high-boiling component was observed in a gas phase chromatogram. The organic layer was then extracted with ether, washed with bicarbonate solution, and dried. Fractional distillation yielded 21.6 g. (75%) of *sym*-tetraethyl(dimethyl)-disiloxane (6), b.p. 192–193°, $n^{25}\text{D}$ 1.4175. The infrared spec-

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(4) (a) L. H. Sommer, D. L. Bailey, G. M. Goldberg, D. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954); (b) C. L. Agre and W. Hilling, *ibid.*, **74**, 3895 (1952); (c) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2869 (1948); (d) D. T. Hurd, *ibid.*, **67**, 1813 (1945); (e) V. A. Ponomarenko and A. D. Snegova, *Zh. Obshch. Khim.*, **27**, 2067 (1957); *Chem. Abstr.*, **52**, 6146 (1958); (f) A. D. Petrov, V. F. Mironov, V. G. Glukhovtsev, and Uy. P. Egorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1091 (1957); *Chem. Abstr.*, **52**, 6163 (1958); (g) A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and Uy. P. Egorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 310 (1957); *Chem. Abstr.*, **51**, 14588 (1957); (h) A. D. Petrov, V. F. Mironov, and D. Mashantsker, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 550 (1956); *Chem. Abstr.*, **51**, 1819 (1957); (i) V. F. Mironov, V. G. Glukhovtsev, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **104**, 865 (1955); *Chem. Abstr.*, **50**, 11234 (1956); (j) A. N. Pines and E. R. York, U. S. Patent 2,735,860 (1956); *Chem. Abstr.*, **50**, 13986 (1956).

(5) R. West, *J. Am. Chem. Soc.*, **77**, 6012 (1954).

(6) C. Eaborn and R. A. Shaw, *J. Chem. Soc.*, 3306 (1955).

(7) All boiling points are uncorrected. Distillations, unless otherwise noted, were made at atmospheric pressure using a 3-ft. modified Podbeilniak column (*cf.* J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, New York, N.Y., 1950, p. 237). The infrared spectra were recorded using a Beckman IR-4 instrument. The carbon, hydrogen, and chlorine analyses were performed by the Berkeley Micro-analytical Laboratory. Gas phase analyses were accomplished using an Aerograph gas phase chromatography unit (Wilkens Instrument and Research Co.) equipped with a 5-ft. silicone column.

(8) (a) W. F. Gilliam and R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1793 (1944); (b) B. O. Bray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. DiGiorgio, and F. C. Whitmore, *ibid.*, **70**, 433 (1948).

(9) N.m.r. spectra were recorded on a Varian Associates A-60 n.m.r. spectrometer, using carbon tetrachloride solutions (15%). Chemical shifts are given in parts per million downfield from tetramethylsilane (internal standard).

(10) Beilstein, F. K., "Beilstein's Handbuch der Organischen Chemie," Vol. XX, 1920, p. 174.

(11) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 266.

(12) R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945).

trum of this material showed bands at 7.95 (Si–CH$_3$), 8.10 (Si–C$_2$H$_5$), and 9.35 μ (Si–O).

Anal. Calcd. for C$_{10}$H$_{26}$Si$_2$O: C, 55.04; H, 11.92. Found: C, 54.94; H, 11.92.

An authentic sample of this disiloxane was prepared from diethyldichlorosilane and methylmagnesium bromide. The two samples showed identical physical and spectral properties.

C. **(α-Chloroethyl)dimethylethylsilane.**—Direct chlorination[2] of 264 g. (1.68 moles) of diethyldichlorosilane yielded 56.8 g. (17.6%) of (α-chloroethyl)ethyldichlorosilane, b.p. 160–165°, n^{25}_{D} 1.4541–1.4575 (lit.[13] b.p. 160°); 34.6 g. (11%) of (β-chloroethyl)ethyldichlorosilane, b.p. 175–183°, n^{23}_{D} 1.4621–1.4645 (lit.[13] b.p. 178°); and 104 g. (25%) of recovered diethyldichlorosilane. Treatment of the (α-chloroethyl)ethyldichlorosilane (56.8 g., 0.29 mole) with 1.34 moles of methylmagnesium bromide followed by water work-up and distillation yielded 27.1 g. (53%) of (α-chloroethyl)dimethylethylsilane, b.p. 143–145°, n^{24}_{D} 1.4340. A redistilled sample, b.p. 144–144.5°, n^{24}_{D} 1.4341, was used for analysis.

Anal. Calcd. for C$_6$H$_{15}$SiCl: C, 47.84; H, 9.96; Cl, 23.58. Found: C, 47.70; H, 9.69; Cl, 23.88.

A mixture of 13.5 g. (0.09 mole) of the (α-chloroethyl)silane and 23.0 g. (0.18 mole) of quinoline was heated at reflux for 24 hr. The material boiling up to 200° was removed by direct distillation of the reaction mixture. Fractional distillation of this material yielded 9.5 g. (70%) of recovered (α-chloroethyl)dimethylethylsilane, b.p. 142–143°, n^{25}_{D} 1.4302. Only 0.2 g. of material boiling in the range of 85–95°, n^{26}_{D} 1.4012, was obtained. Gas phase analysis revealed that this fraction consisted of one major component which had a retention time the same as that of an authentic sample of vinylethyldimethylsilane, b.p. 88°, n^{25}_{D} 1.4062, prepared in 35% yield by the method of Sommer (lit.[13] b.p. 88°, n^{25}_{D} 1.4089).

D. **(Chloro)silacyclopentanes.** 1. **Mixture of Isomers.**—To a 50-g. mixture of 1-chloromethyl-1-methylsilacyclopentane (**2**) and 1,1-dimethyl-2-chlorosilacyclopentane[14] (**3**), was added 110.0 g. (0.85 mole) of quinoline. The resulting solution was heated at reflux for 2 hr. and distilled to remove material boiling up to 210°. The milky white distillate was washed carefully with 6 *N* hydrochloric acid, diluted with ether, washed with water, and finally dried with potassium carbonate. Fractional distillation yielded 2.9 g. (*ca.* 15%) of 1,1-dimethylsilacyclo-2-pentene (**7**), b.p. 94–100°, n^{25}_{D} 1.4439 (lit.[15] b.p. 100–106°, n^{24}_{D} 1.4425); 11.3 g. (*ca.* 45%) of 1,1-dimethyl-2-chlorosilacyclopentane (**3**) (previously assigned structure **1**[2]), b.p. 158°, n^{25}_{D} 1.4687; and 7.1 g. (*ca.* 40%) of *sym*-dimethylbis(cyclotetramethylene)disiloxane (**8**), b.p. 215–217°, n^{23}_{D} 1.4615 (lit.[5] b.p. 221°, n^{26}_{D} 1.4573). The infrared spectrum of this disiloxane was identical with that of an authentic sample, prepared in 24% yield, using the method of West.[5]

2. **1,1-Dimethyl-2-chlorosilacyclopentane** (**3**).—To 52.0 g. (0.40 mole) of quinoline was added 20.0 g. (0.135 mole) of the 2-chlorosilacyclopentane **3**, isolated as in part D, and the mixture was heated at reflux for 6 hr. Direct distillation followed by fractional distillation yielded 3.0 g. (20%) of 1,1-dimethylsilacyclo-2-pentene (**7**),[15] b.p. 97–100°, n^{22}_{D} 1.4438; and 1.7 g. (10%) of recovered starting material, b.p. 153–158°, n^{22}_{D} 1.4650.

N.m.r. Spectra. A. **1-Chloromethyl-1-methylsilacyclopentane** (**2**).—**2** was isolated from the mixture of isomers using a 15 ft. × $^1/_8$ in. 20% silicone preparative gas chromatographic column,[16] n^{22}_{T} 1.4741.

Anal. Calcd. for C$_6$H$_{13}$SiCl: C, 48.46; H, 8.81; Cl, 23.81. Found: C, 48.43; H, 8.77; Cl, 23.68.

The n.m.r. spectrum[9] showed the following bands (p.p.m.): 0.02 (singlet), 0.65 (unresolved multiplet), 1.60 (pentuplet), and 2.75 (singlet). The integrated areas under these peaks appeared in the ratios of 2.8:4.0:4.0:2.0, which are in agreement with the expected ratios of 3:5:4:2.

B. **1,1-Dimethyl-2-chlorosilacyclopentane** (**3**).—The n.m.r. spectrum[9] was run on the sample isolated from reaction D1. The following bands were observed (p.p.m.): 0.15 (singlet), 0.25 (singlet), 0.65 (unresolved multiplet), 1.85 (unresolved multiplet), and 3.30 (triplet). The ratios of the integrated areas under the peaks (2.9:3.0:2.0:4.0:1.2) are in agreement with the expected ratios 3:3:2:4:1.

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[13] L. H. Sommer, D. L. Bailey, G. M. Goldberg, D. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

[14] (a) Gas phase chromatography at 150° indicated that the mixture was composed of an approximately equal ratio of the two α-chloro isomers. In contrast to our previous work, this mixture was distilled prior to the quinoline reflux to remove any higher-boiling disiloxanes which would be expected to arise from the hydrolysis of the 3-chlorodimethylsilacyclopentane during water work-up. (b) Yields are based upon the estimated weight of the isomer in the mixture.

[15] (a) R. J. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961). (b) V. F. Mironov and V. V. Nepomnia, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1231 (1959); *Chem. Abstr.*, **54**, 1268 (1960). (c) Three attempts to analyze for carbon and hydrogen were prevented by explosions during combustion. The reason for this behavior is not apparent.

[16] Specially prepared for the Aerograph Model A-90-C by the Wilken Instrument and Research Co., Walnut Creek, Calif.

Reactions of Enamines. III.[1] Chlorothionacetamides

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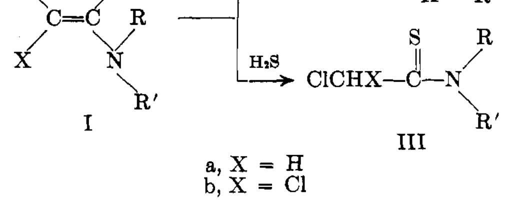
A synthesis of α-chloro- and α,α-dichlorothionacetamides by reaction of 1,2-dichloro- and 1,2,2-trichlorovinylamines with hydrogen chloride–hydrogen sulfide is reported. A similar reaction of 1,2,2-trichlorovinylamines with chlorine–hydrogen sulfide produces trichlorothionacetamides. The ultraviolet, infrared, and n.m.r. spectra of the thionamides and the mechanism of their formation are discussed.

The hydrolysis of N,N-disubstituted 1,2-dichlorovinylamines (Ia) or 1,2,2-trichlorovinylamines (Ib) has been shown to yield the corresponding chloro- and dichloroacetamides (IIa and IIb), respectively.[2]

Since this reaction leads to high yields of chloroacetamides at low temperatures, the analogous reaction with hydrogen sulfide appeared to be a promising method for the preparation of the unreported N-substituted α-chlorothionacetamides (III).



The recent preparations of α-chlorothionacetamide and α,α,α-trichlorothionacetamide by reaction of the respective nitriles with thionophosphoric acid derivatives followed by treatment with hydrogen chloride

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[1] For paper II of this series, see A. J. Speziale and G. H. Alt, *Tetrahedron Letters*, **No. 2**, 111 (1963).

[2] (a) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 909 (1960); (b) A. J. Speziale and L. R. Smith, *ibid.*, **84**, 1868 (1962).