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The Chemistry of Trichlorosilane–Tertiary Amine Combinations

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Trichlorosilane ($SiHCl_3$; bp 33°) is a relatively inexpensive, commercially available chemical. First reported[1] in 1857, its method of preparation has since been considerably refined.[2] Since one of its principal uses is in the preparation of transistor-grade silicon, it can be purchased in high purity.

In 1947 it was reported[3] that trichlorosilane adds to the olefinic linkage of 1-octene, forming *n*-octyltrichlorosilane under the influence of peroxide or ultraviolet light. This was an extremely important dis-

$$CH_3(CH_2)_5CH{=}CH_2 \xrightarrow{SiHCl_3} CH_3(CH_2)_7SiCl_3$$

covery since it constituted an entirely new method of forming a silicon–carbon bond.[4] In the intervening years the addition of the $\geqslant$SiH linkage to olefinic and acetylenic bonds has received considerable attention, and, aside from the so-called "direct process,"[5] today constitutes perhaps the most important method of synthesizing organosilicon compounds.

Two of the many reasons why these $\geqslant$SiH addition reactions are so important is that they are highly stereoselective[6] and that they can be effected under a wide variety of conditions. For example, the additions can be brought about thermally,[7] by noble metals on a solid support (Pt on carbon),[8] or by soluble metal complexes. Much of the intriguing chemistry exhibited by the latter systems has been explored and developed in commercial laboratories.[9]

Prior to 1962, there were only three reports of $\geqslant$SiH additions to olefins catalyzed by tertiary amine. Acrylonitrile was reported[10] to add trichlorosilane under these conditions to yield the β-silyl isomer. 2-Vinylpyridine added trichlorosilane at 160° without the

$$CH_2{=}CHCN \xrightarrow[R_3N]{HSiCl_3} Cl_3SiCH_2CH_2CN$$

assistance of additional base, and allyl cyanide underwent a similar addition in the presence of pyridine, but in poor yield.[11] It was a report[12] in 1962 that tertiary amines and phosphines could effect the addition of trichlorosilane to olefins and acetylenes which attracted our attention and provided the stimulus for our foray into tertiary amine–trichlorosilane chemistry.

Interaction between Tertiary Amines and Trichlorosilane. The literature contains numerous reports of amine complexes with silicon compounds[13] of the general formula $SiH_{4-n}X_n$. There can be little doubt that silanes can and do form complexes of varying compositions with amines like pyridine and trimethylamine.

While studying the addition of trichlorosilane to phenylacetylene in the presence of tertiary amines like tri-*n*-propyl- or tri-*n*-butylamine, we detected, by nmr spectroscopy, an interaction between the amine and silane which led us to postulate the existence of a tri-

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(1) H. Buff and F. Wöhler, *Justus Liebigs Ann. Chem.*, **104**, 94 (1857).
(2) C. A. Kraus and W. K. Nelson, *J. Amer. Chem. Soc.*, **56**, 195 (1934); H. S. Booth and W. D. Stillwell, *ibid.*, **56**, 1529 (1934); A. G. Taylor and B. V. Walden, *ibid.*, **66**, 842 (1944); F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *ibid.*, **69**, 2108 (1947).
(3) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *ibid.*, **69**, 188 (1947); see also H. C. Miller and R. S. Schreiber, U. S. Patent 2,379,821 (1945).
(4) See E. G. Rochow, "Introduction to the Chemistry of the Silicones," Wiley, New York, N. Y., 1946, pp 19–30, for a review of the synthetic methods then available.
(5) E. G. Rochow, *J. Amer. Chem. Soc.*, **67**, 963 (1945); U. S. Patent 2,380,995 (1945).
(6) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, **83**, 4385 (1961).
(7) A. J. Barry, L. DePree, J. W. Gilkey, and D. E. Hook, *ibid.*, **69**, 2916 (1947).
(8) G. H. Wagner, U. S. Patent 2,637,738 (1953); J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).
(9) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16, 1133 (1965).
(10) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Jap.*, **29**, 322 (1956).
(11) S. Nozakura, *ibid.*, **29**, 784 (1956).
(12) R. A. Pike, *J. Org. Chem.*, **27**, 2186 (1962).
(13) U. Wannagat, R. Schwarz, H. Voss, and K. G. Knauff, *Z. Anorg. Allg. Chem.*, **277**, 73 (1954); A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 2674 (1954); H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1508 (1966), 705 (1967).

chlorosilyl anion ($SiCl_3^-$). Trichlorosilane alone, in acetonitrile,[14] shows a sharp singlet (nmr) character-

$$SiHCl_3 + R_3N \overset{CH_3CN}{\rightleftarrows} [R_3\overset{+}{N}\text{-}\overset{-}{Si}HCl_3] \rightleftarrows R_3\overset{+}{N}H + \overset{-}{Si}Cl_3 \quad (1)$$

istic of the lone proton of the silane at δ 6.25. This singlet broadens considerably and diminishes in size as tri-*n*-propylamine is added. At the same time, a new signal appears and increases in size at δ 11.03, which we attribute to the NH resonance of $(n\text{-}C_3H_7)_3NH^+$.

Tri-*n*-propylammonium chloride shows a broad NH resonance at δ 11.48 in acetonitrile.[15] The peak-broadening effect noted for the silanic proton is typical of situations in which proton exchanges are occurring. The latter interpretation receives support from our observation that the broad $SiHCl_3$ resonance becomes a sharp singlet again as the spectrum is run at progressively lower temperatures. The Forsen–Hoffman technique[16] indicated that this rapid proton exchange was occurring between the silicon atom and the nitrogen of the amine. Thus, irradiation of the N–H proton directly with a strong decoupling field caused the Si–H resonance to disappear. Conversely, irradiation of the Si–H resonance greatly diminished the N–H signal.

These observations are consistent with the equilibrium depicted in eq 1, although they shed no light on the intermediacy of the trichlorosilane–amine complex shown. The most exciting consequence of eq 1 is the postulation of a $SiCl_3^-$ anion existing in appreciable concentration in acetonitrile when certain tertiary amines are brought into contact with $SiHCl_3$.

Work from another laboratory[17] has provided evidence which supports the idea of a silicon–nitrogen complex as an intermediate in eq 1. It was observed[17] that trichlorosilane undergoes amine-catalyzed hydrogen–deuterium exchange with tri-*n*-butylamine deuteriochloride in methylene chloride at 30°. This finding itself tends to support the overall equilibrium depicted in eq 1. More important, however, it was re-

$$HSiCl_3 \overset{R_3N}{\rightleftarrows} R_3\overset{+}{N}H + \overset{-}{Si}Cl_3$$

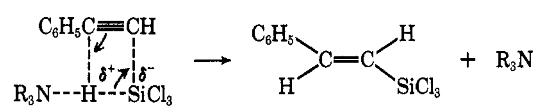
$$\overset{-}{Si}Cl_3 + R_3\overset{+}{N}DCl \rightleftarrows DSiCl_3 + R_3N + Cl^-$$

ported[17] that, within experimental error, there was no kinetic isotope effect for this exchange. It follows that the Si–H bond is not breaking during the rate-determining step. Hence it can be argued that complex formation as shown in eq 1 is likely the first and slow step in the reaction, followed by a rapid hydrogen shift from silicon to nitrogen.

It is also significant that equimolar mixtures of methyldichlorosilane and tri-*n*-propylamine in acetonitrile show[14] an unperturbed quartet for the silanic hydrogen (nmr) centered at δ 5.63. There is no down-field absorption whatsoever which can be attributed to the tri-*n*-propylammonium ion. Similarly, it has been reported[17] that *no* exchange occurs between methyldichlorosilane and tri-*n*-butylamine deuteriochloride even in the presence of 1 *M* tri-*n*-butylamine. Consistent with both of these observations, we have found that solutions of methyldichlorosilane and tertiary amines do not usually exhibit the chemistry characteristic of the corresponding trichlorosilane–tertiary amine combinations.

While the trichlorosilyl anion had been postulated earlier[10] as a reaction intermediate, the nmr and deuterium exchange data cited above constitute the first experimental evidence for its existence. A logical sequel to the concept of a discrete trichlorosilyl anion species[18] would be the postulation of a possible parallelism between its chemistry and that of the isoelectronic phosphines. It was in an attempt to establish such a parallelism that much of the chemistry which follows had its genesis in our laboratory.

Addition Reactions of Trichlorosilane Catalyzed by R_3N. It was reported[12] that trichlorosilane adds to various olefins and acetylenes in the presence of tertiary amines and phosphines. Polar solvents, like aceto- or adiponitrile, were essential for the reaction to proceed at any appreciable rate. A syn mode of addition of $SiHCl_3$ was claimed[12] on the basis of results obtained with phenylacetylene, wherein only *trans*-β-trichlorosilylstyrene was purportedly obtained in addition to a diadduct which was the major product. The trans product was rationalized[12] in terms of a solvated four-membered transition state.



A reinvestigation[19] of this work revealed that *all* possible mono adducts are in reality formed in this reaction and that the bis adduct (major product) was the α,β-bis(trichlorosilyl) compound ($C_6H_5CHSiCl_3$–CH_2SiCl_3, "bis product"). The need for a polar solvent was verified, but it was found that this requirement could be satisfied by eliminating the acetonitrile and using tri-*n*-butylamine in excess of catalytic amounts.

By competitive rate studies, it was also ascertained[20] that the three mono adducts reacted to form bis adduct in the order: $\alpha \gg$ cis > trans. Further, electron-withdrawing groups (m-CF_3) situated on the phenyl ring of phenylacetylene caused a more rapid rate of addition than electron-releasing (p-OCH_3) groups. Taken as a composite, these data are best explained by the mechanism comprising reactions 2–4. Since the trans mono

(14) R. A. Benkeser, K. M. Foley, J. B. Grutzner, and W. E. Smith, *J. Amer. Chem. Soc.*, **92**, 697 (1970).

(15) The difference between δ values of 11.03 and 11.48 is not unexpected in view of the difference of anions in the two cases.

(16) S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

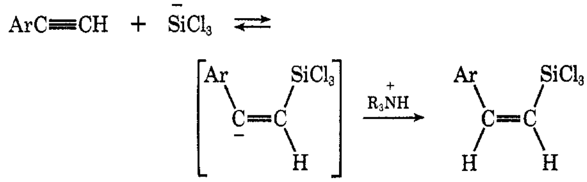
(17) S. C. Bernstein, *J. Amer. Chem. Soc.*, **92**, 699 (1970).

(18) It is noteworthy that salts like $KSiH_3$ [M. A. Ring and D. M. Ritter, *ibid.*, **83**, 802 (1961)], $(CH_3)_3NHGeCl_3$ [P. S. Poskozim and A. L. Stone, *J. Inorg. Nucl. Chem.*, **32**, 1391 (1970)], and $NaSnH_3$ [H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958)] have all been characterized.

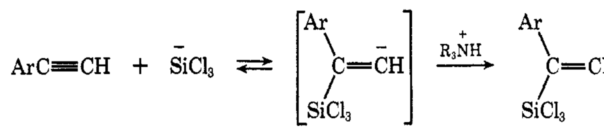
(19) R. A. Benkeser, S. Dunny, and P. R. Jones, *J. Organometal. Chem.*, **4**, 338 (1965).

(20) R. A. Benkeser, *Pure Appl. Chem.*, **19**, 389 (1969).

$$R_3N + SiHCl_3 \rightleftharpoons [R_3\overset{+}{N}-\overset{-}{Si}HCl_3] \rightleftharpoons R_3\overset{+}{N}H + \overset{-}{Si}Cl_3 \quad (2)$$



(3)



(4)

adduct is the slowest to form bis adduct, and since all three mono adducts are present, we do not feel that the trans mono adduct plays an important role as an intermediate[21] in bis adduct formation.

The concept of $SiCl_3^-$ formation (eq 2) as the first step in this sequence is useful. Certainly this step, as well as the ionic processes which follow, would be favored by polar solvents (acetonitrile or excess amine). Likewise, if this anion were the attacking species, the substituent effects could be explained since electron-withdrawing groups should favor such a process. Likewise, the stereochemistry of the addition may well be anti, leading to a cis product as shown in eq 3. The rule of "trans nucleophilic additions"[22] to acetylenes has been found to hold in numerous cases and may well apply here. The propensity for this reaction to form bis adducts preferentially can also be explained *via* the concept of $SiCl_3^-$. One might predict that the mono adducts, since they possess *two* electron-withdrawing groups (C_6H_5 and $SiCl_3$), would react more rapidly than the starting material, as is indeed the case.

It is of interest that we have found phenyltrichlorosilylacetylene ($C_6H_5C{\equiv}CSiCl_3$) also adds *two* trichlorosilanes in the presence of tri-*n*-butylamine to form two tris(trichlorosilyl) products (70:30). The structure of these adducts has not been determined. This result would indicate that the acidic H on the acetylenic group is not a necessary requirement[23] for the reaction.

Reactions of Trichlorosilane–Tertiary Amines with Organic Halides. Organic halides, in the presence of trichlorosilane–tertiary amines, undergo a variety of transformations depending upon the reaction conditions.

Benzylic halides react with essentially equimolar amounts of trichlorosilane and amine to form the corresponding benzylic trichlorosilane in good yield as exemplified by *p*-chlorobenzyl chloride. A wide variety of substituents can be tolerated in the aromatic ring.[24] At the present time this constitutes the best method for

$$p\text{-}ClC_6H_4CH_2Cl \xrightarrow[(C_3H_7)_3N]{SiHCl_3} p\text{-}ClC_6H_4CH_2SiCl_3\ (78\%)$$

synthesizing such benzylic silanes. Thus far, the method has not been successful when applied to simple alkyl halides like *n*-butyl chloride. It is possible that in such cases disproportionation of the trichlorosilane catalyzed by tetraalkylammonium chloride becomes the predominant reaction.[25]

Geminal dihalides usually react with the trichlorosilane–amine combination to produce *gem*-trichlorosilyl derivatives, often in high yield, provided the appropriate amounts of silane and amine are present. This is exemplified by the reaction of benzal chloride.[24]

$$C_6H_5CHCl_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} C_6H_5CH(SiCl_3)_2$$

This discovery has made a variety of *gem*-trichlorosilyl compounds readily available which hitherto had been virtually inaccessible. The reaction is influenced by the other groups attached to the carbon holding the two halogens. Apparently electron-withdrawing groups like phenyl favor the reaction, while electron-supplying groups retard it. For example, 1,1-dibromoethane produced only 28% of the corresponding bis(trichlorosilyl) product.

$$CHC_3HBr_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} CH_3CH(SiCl_3)_2\ (28\%)$$

Compounds containing more than two halogens attached to the same carbon can undergo several types of reactions with trichlorosilane–amine as demonstrated by eq 5–9. Two things are readily apparent from

$$CCl_4 \xrightarrow[\text{cat. }(C_4H_9)_3N]{SiHCl_3} CHCl_3\ (82\%) + SiCl_4 \quad (5)$$

$$CCl_4 \xrightarrow[\text{excess }(C_3H_7)_3N]{SiHCl_3} CH_2(SiCl_3)_2\ (55\%) + SiCl_4 \quad (6)$$

$$CHCl_3 \xrightarrow[\text{excess }(C_3H_7)_3N]{SiHCl_3} CH_2(SiCl_3)_2\ (60\%) + SiCl_4 \quad (7)$$

$$Cl_3CCO_2CH_3 \xrightarrow[\text{cat. }(C_4H_9)_3N]{SiHCl_3} CHCl_2CO_2CH_3\ (82\%) + SiCl_4 \quad (8)$$

$$Cl_3CCCl_3 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} Cl_2C{=}CCl_2\ (86\%) + SiCl_4 \quad (9)$$

these cases. Under certain circumstances stable silicon–carbon bonds are produced in the form of bis(trichlorosilyl) products. In other instances the halogens have been replaced by H rather than a trichlorosilyl moiety. In any event, the yield of either type of product is quite good and the procedures have considerable synthetic utility.

The mechanisms of reactions 5–9 must remain speculative at the present time. On the other hand, certain experimental observations have been made which are suggestive.

In reaction 5 approximately equimolar amounts of carbon tetrachloride and trichlorosilane were employed, but only catalytic quantities of amine.[26] In reaction 6

(21) We have also found that the cis monoadduct is isomerized to the trans under the reaction conditions employed.

(22) W. E. Truce, *Org. Sulfur Compounds*, **1**, 112 (1961).

(23) We must concede that diphenylacetylene and 1-phenylpropyne, for reasons not entirely clear, do not undergo amine-catalyzed addition of $SiHCl_3$ very readily.

(24) R. A. Benkeser, J. M. Gaul, and W. E. Smith, *J. Amer. Chem. Soc.*, **91**, 3666 (1969).

(25) D. R. Weyenberg, A. E. Bey, and P. J. Ellison, *J. Organometal. Chem.*, **3**, 489 (1965).

the ratio carbon tetrachloride:trichlorosilane:amine was approximately 1:5:2. When reaction 5 was repeated in a *solvent* of carbon tetrachloride (hence, large excess) at low temperature with a full equivalent of *N*-methyldicyclohexylamine,[27] the amine hydrochloride could be precipitated quantitatively by pentane. In addition, trichloromethyltrichlorosilane (Cl_3CSiCl_3) could be isolated from the pentane solution.[28]

It has been shown by others that the latter compound can be cleaved by amine hydrochlorides[29] to $CHCl_3$ and $SiCl_4$. Accordingly, we suggest that the reaction sequence for this reduction can best be rationalized as

$$CCl_4 + SiHCl_3 + R_3N \longrightarrow \underbrace{Cl_3CSiCl_3 + R_3NHCl}_{CHCl_3 + SiCl_4 + R_3N}$$

When a large excess of trichlorosilane is present, the chloroform which is produced *via* the sequence suggested above can react further and bis(trichlorosilyl)methane is formed. That this pathway is feasible is demonstrated by eq 7, wherein bis(trichlorosilyl)methane can be produced from chloroform directly.[30]

Examples 6 and 7 raise the interesting question of why only bis(trichlorosilyl) products are formed while the remaining halogens of the starting halocarbon are replaced by H. A simple steric argument does not seem adequate since compounds are known which contain three trichlorosilyl groups attached to the same carbon atom.[31] One might surmise that tris compounds are produced, but that cleavage of one of the silicon groups occurs under conditions of the reaction. For example, a transformation like the following might be envisioned.

$$RC(SiCl_3)_3 \xrightarrow[R_3N]{R_3NHCl} SiCl_4 + R\overset{H}{\overset{|}{C}}(SiCl_3)_2$$

Unfortunately, using benzotrichloride as the substrate and employing very mild conditions (solvents at low temperatures), we were unable to detect the presence of any tris product. Obviously, such negative evidence is not convincing, but at this time we favor the view that with most polyhalohydrocarbons like CCl_4 we are observing a nucleophilic displacement by $SiCl_3^-$ *on* halogen (eq 10–14). Such a sequence would explain

$$R_3N + SiHCl_3 \longrightarrow R_3\overset{+}{N}H + \overset{-}{Si}Cl_3 \quad (10)$$

$$CCl_4 + \overset{-}{Si}Cl_3 \longrightarrow [SiCl_4 + \overset{-}{C}Cl_3] \longrightarrow Cl_3CSiCl_3 + Cl^- \quad (11)$$

$$Cl_3CSiCl_3 + R_3N \longrightarrow R_3\overset{+}{N}SiCl_3 + \overset{-}{C}Cl_3 \quad (12)$$

$$\overset{-}{C}Cl_3 + R_3\overset{+}{N}H \longrightarrow CHCl_3 + R_3N \quad (13)$$

$$R_3\overset{+}{N}SiCl_3 + Cl^- \longrightarrow SiCl_4 + R_3N \quad (14)$$

the catalytic nature of the amine as well as the formation of Cl_3CSiCl_3 which (*vide supra*) can be isolated from such reaction mixtures. At first sight, step 11 would seem unlikely since it postulates a cation cage effect in which the CCl_3^- displaces Cl^- from silicon before it is protonated by the R_3NH^+. Such cage effects have been detected in other systems, so that it is not without precedent.[32] Moreover, direct protonation of CCl_3^- by R_3NH^+ could not explain the formation of Cl_3SiCCl_3.

On the other hand, several mechanisms can be written involving silylene[33] or carbene intermediates. Thus the following is conceivable.

$$\overset{-}{Si}Cl_3 \longrightarrow SiCl_2 + Cl^-$$

$$SiCl_2 \xrightarrow{CCl_4} Cl_3CSiCl_3$$

Although there is precedent for the insertion of $SiCl_2$ into the C–Cl bond[34] of CCl_4, the reaction is reported to proceed in very low yield which is contrary to our results. Two other observations make us skeptical of invoking silylene intermediates, at least in the halide displacements just described. (i) Up to this time, silylenes have been prepared only under rather vigorous thermal conditions, at least at temperatures well above those we employ. (ii) Disubstituted acetylenes have been used as "traps" for silylene intermediates,[35] while we have found most disubstituted acetylenes (*e.g.*, diphenylacetylene) to be relatively unreactive toward trichlorosilane–tertiary amine systems.

Similarly, one might invoke the intermediacy of dichlorocarbene (from $CCl_3^- \rightarrow CCl_2 + Cl^-$) and its subsequent insertion into the Si–Cl bond of $SiCl_4$[36] to form Cl_3CSiCl_3. Several experiments were carried out

$$SiCl_4 + CCl_2 \longrightarrow Cl_3SiCCl_3$$

in an attempt to shed some light on this possibility. While the results of these experiments were entirely negative, a few are worthy of mention.

When trichlorosilane, carbon tetrachloride, and tri-*n*-butylamine were allowed to react in the usual way in the presence of cyclohexene, a 72% yield of $CHCl_3$ was realized along with 73% of $SiCl_4$. Significantly, no 7,7-dichloronorcarane was detected nor any cyclohexyltrichlorosilane. The absence of the two latter products might cast some doubt on the transient existence of dichlorocarbene or a trichlorosilyl radical.

(26) The presence of *some* amine is essential. Trichlorosilane and carbon tetrachloride alone do not react with each other after refluxing for 6 hr.

(27) We have used this amine as well as tri-*n*-propyl- and tri-*n*-butylamine for most of our work. The solubility of the amine hydrochloride which forms in all of these reactions is an important factor in product purification.

(28) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **90**, 5307 (1968).

(29) G. D. Cooper and A. R. Gilbert, *ibid.*, **82**, 5042 (1960).

(30) R. A. Benkeser, J. M. Gaul, and W. E. Smith, *ibid.*, **91**, 3666 (1969).

(31) R. Müller and G. Seitz, *Chem. Ber.*, **91**, 22 (1958); E. Amberger and H. D. Boeters, *ibid.*, **97**, 1999 (1964).

(32) P. T. Lansbury and V. A. Pattison *J. Org. Chem.*, **27**, 1933 (1962).

(33) For an excellent review of divalent silicon intermediates (silylenes) see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(34) P. L. Timms, *Inorg. Chem.*, **7**, 387 (1968).

(35) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

(36) There is precedent for such insertion reactions. See D. Seyferth and E. G. Rochow, *Inorg. Syn.*, **6**, 37 (1960); D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, **85**, 2667 (1963).

In still another case, silicon tetrachloride was refluxed in benzene with phenyltrichloromethylmercury[37] for 18 hr. At the end of this period, 63% of phenylmercuric chloride could be isolated but there was no trace of Cl_3CSiCl_3. Hence, there was no dichlorocarbene insertion into silicon tetrachloride at least under these conditions.

Evidence was obtained for the feasibility of the CCl_3^- displacement on silicon in silicon tetrachloride as depicted in eq 11. A 31% yield of Cl_3CSiCl_3 was realized when trichloromethyllithium[38] was treated with silicon tetrachloride at $-100°$ in a mixture of hexane and tetrahydrofuran. While this result constitutes a dubious argument by analogy, in that the reaction conditions were quite different from those we usually employ, it does lend some credibility to the notion that a CCl_3^- moiety can displace halide from silicon even at very low temperatures.

We also found that $BrCCl_3$ could be reduced exclusively to $CHCl_3$ by trichlorosilane with catalytic amounts of $(n\text{-}C_4H_9)_3N$. Again the amine catalyst was

$$BrCCl_3 \xrightarrow[(n\text{-}C_4H_9)_3N;\ CH_2Cl_2]{SiHCl_3} CHCl_3 + SiBrCl_3$$

essential: there was no reaction when bromotrichloromethane was refluxed with trichlorosilane alone. This result not only supports the notion of attack on halogen by $SiCl_3^-$ but would cast further doubt on the dichlorocarbene intermediate. The latter might be expected to insert preferentially into the Si–Br bond, and subsequent cleavage of the dichlorobromomethyltrichlorosilane should form dichlorobromomethane. When

$$SiBrCl_3 \xrightarrow{CCl_2} Br\text{—}C(Cl)_2\text{—}SiCl_3$$

conditions were altered, and an attempt was made to isolate dichlorobromomethyltrichlorosilane, only trichloromethyltrichlorosilane was obtained.[39] These results are clearly consonant with a CCl_3^- displacement on silicon as depicted in eq 11, since one would expect a preferential displacement of Br^- relative to Cl^-.

A rather revealing experiment is shown by eq 15.

$$Cl_3SiSiCl_3 \xrightarrow[0.1\ \text{equiv of}\ (C_2H_5)_3N]{CCl_4\ (\text{solvent})} Cl_3CSiCl_3\ (41\%) + SiCl_4 \quad (15)$$

The intermediacy of a $SiCl_3^-$ anion has been postulated when tertiary amines react with hexachlorodisilane.[29]

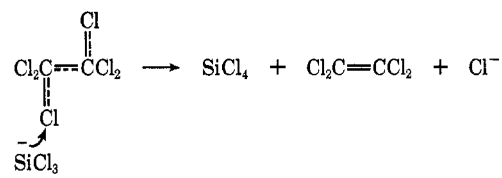
$$Cl_3SiSiCl_3 \xrightarrow{R_3N} R_3\overset{+}{N}SiCl_3 + \overset{-}{Si}Cl_3$$

Since trichloromethyltrichlorosilane can be isolated in this case as well, it seems likely that the *same* intermediate ($SiCl_3^-$) is being produced in the reaction between $SiHCl_3$ and tertiary amines and that it is being intercepted by CCl_4 in the same way.

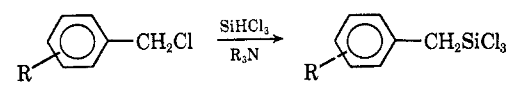
A final note with regard to our proposed step 11 in the reduction of carbon tetrachloride is in order. It is well documented that nucleophilic displacements on the chlorine atoms of carbon tetrachloride do occur.[40] Since we feel that we have good evidence for the existence of $SiCl_3^-$ under the conditions we employ, the attack of this species on the chlorine atoms of carbon tetrachloride seems eminently reasonable. It is noteworthy that reaction 16 also occurs readily. Such re-

$$Cl_3CCCl_3 \xrightarrow[(n\text{-}C_3H_7)_3N;\ C_4H_8O]{SiHCl_3} Cl_2C{=}CCl_2\ (86\%) + SiCl_4 + (n\text{-}C_3H_7)_3NHCl \quad (16)$$

ductive eliminations are commonly effected by nucleophilic substances like I^-,[41] organometallic compounds,[42] and phosphines.[43] The process can easily be envisioned as involving a nucleophilic attack on Cl by the $SiCl_3^-$.



It should be pointed out that there is no compelling reason to assume that the $SiCl_3^-$ moiety *must always* attack on a halogen atom. While we believe this to be true in many of the polyhalides cases, we are inclined to view the reaction with benzyl halides as a displacement on the benzylic carbon atom rather than on halogen. Competitive rate studies[44] with substituted benzylic halides indicate that electron-withdrawing groups have



only a *slight* accelerating effect which we feel is more in line with an S_N2 displacement on the carbon atom.

When 1,1,1-trichloro-2-propanone was treated with the trichlorosilane–amine combination, 1,1-dichloro-2-trichlorosilyloxypropene was isolated. Such a product could come about by an attack of $SiCl_3^-$ on *either* O

$$Cl_3C\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[(n\text{-}C_3H_7)_3N]{SiHCl_3} Cl_2C{=}\overset{OSiCl_3}{\overset{|}{C}}CH_3$$

or Cl, although the simplest view would be a direct attack on the carbonyl oxygen. In principle, then, $SiCl_3^-$ (like the phosphines) has the potential of attacking on halogen, carbon, or oxygen.

Reactions of Trichlorosilane–Tertiary Amines with

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(44) J. M. Gaul, Purdue University, unpublished studies.

Carbonyl Compounds. One of the most remarkable and useful transformations which the trichlorosilane–tertiary amine systems can effect is the removal of a carbonyl oxygen from a wide variety of compounds. Aromatic ketones, aldehydes, acid chlorides, acid amides, and aromatic acids all undergo such a reaction, which we have termed, "reductive silylation." Pictorially, the reaction can be represented as the replacement of a carbonyl oxygen by the $H\cdots SiCl_3$ moieties of trichlorosilane. Examples 17–19 illustrate this reaction with aldehydes and ketones.[45]

$$RC(=O)R' \xrightarrow[R_3N]{SiHCl_3} RCH(SiCl_3)R' + [-OSiCl_2]_n$$

$$C_6H_5C(=O)C_6H_5 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} (C_6H_5)_2CHSiCl_3\ (95\%) \quad (17)$$

$$p\text{-}ClC_6H_4C(=O)C_6H_5 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} p\text{-}ClC_6H_4CH(SiCl_3)C_6H_5\ (73\%) \quad (18)$$

$$2,6\text{-}Cl_2C_6H_3CHO \xrightarrow[(C_3H_7)_3N;\ CH_3CN]{SiHCl_3} 2,6\text{-}Cl_2C_6H_3CH_2SiCl_3\ (61\%) \quad (19)$$

Not only does the method provide an entirely new way of forming silicon–carbon bonds, but the products, being benzylic silanes,[46] can be cleaved by base to replace the trichlorosilyl group by H. This can be achieved in one operation without isolating the silicon intermediates.[47] Equations 20–22 are typical.

$$C_6H_5C(=O)C_6H_5 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} (C_6H_5)_2CH_2\ (72\%) \quad (20)$$

$$p\text{-}ClC_6H_4C(=O)C_6H_5 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} p\text{-}ClC_6H_4CH_2C_6H_5\ (79\%) \quad (21)$$

$$2,6\text{-}Cl_2C_6H_3CHO \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} 2,6\text{-}Cl_2C_6H_3CH_3\ (54\%) \quad (22)$$

Similar transformations are possible with tertiary amides. Aromatic tertiary amides seem most amenable to the reaction, but the silicon compounds which result are usually difficult to handle and characterize. N,N-Dimethylbenzamide undergoes reductive silylation smoothly, and the resulting aminosilane can be characterized without difficulty.[47] Spectral data (nmr), analysis, etc., indicate that the following reaction occurs.

$$C_6H_5C(=O)N(CH_3)_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} C_6H_5CH(SiCl_3)N(CH_3)_2\ (64\%)$$

Since such products are benzylic silanes, the silicon group can be removed by base treatment without isolation of the intermediate organosilane. Examples 23–25 illustrate the scope and overall yields of benzylamine which can be obtained in such a two-step process.[47] Aliphatic tertiary amide products are particularly difficult to handle. In the case of N,N-dimethylcaproamide, the intermediate trichlorosilyl compound was converted immediately, without isolation, to its trimethyl derivative (overall 22% yield) which could be characterized.[47]

$$C_6H_5CON(CH_3)_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} C_6H_5CH_2N(CH_3)_2\ (60\%) \quad (23)$$

$$p\text{-}ClC_6H_4CON(CH_3)_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} p\text{-}ClC_6H_4CH_2N(CH_3)_2\ (53\%) \quad (24)$$

$$p\text{-}CH_3OC_6H_4CON(CH_3)_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow[KOH]{C_2H_5OH} p\text{-}CH_3OC_6H_4CH_2N(CH_3)_2\ (55\%) \quad (25)$$

$$CH_3(CH_2)_4CON(CH_3)_2 \xrightarrow[(C_3H_7)_3N]{SiHCl_3} \xrightarrow{CH_3MgI} CH_3(CH_2)_4CH(Si(CH_3)_3)N(CH_3)_2\ (22\%)$$

Both aliphatic and aromatic acid chlorides react under reductive silylation conditions to produce 1,1-bis(trichlorosilyl) compounds in good yield as illustrated by eq 26–28. Possibly these reactions proceed through a two-step sequence, the first step involving reductive silylation in which the carbonyl oxygen is replaced as with ketones, and the second involving a halide displacement (*vide supra*). The example of benzoyl chloride provides some indication this may be the case. At short reaction times and with an approximate ratio of acid chloride to amine of 1:1, an excellent yield of α-chlorobenzyltrichlorosilane can be obtained.[45] With more trichlorosilane and extended reaction times, the α,α-bis(trichlorosilyl) product predominates.

$$CH_3COCl \xrightarrow[(C_3H_7)_3N;\ CH_3CN]{SiHCl_3} CH_3CH(SiCl_3)_2\ (55\%) \quad (26)$$

$$(CH_3)_2CHCOCl \xrightarrow[(C_3H_7)_3N;\ CH_3CN]{SiHCl_3} (CH_3)_2CHCH(SiCl_3)_2\ (41\%) \quad (27)$$

$$C_6H_5COCl \xrightarrow[SiHCl_3;\ CH_3CN]{(C_6H_{11})_2NCH_3} C_6H_5CH(SiCl_3)_2\ (46\%) \quad (28)$$

Perhaps even more amazing is the fact that aromatic acids[48] and their anhydrides can be reduced by the trichlorosilane–tertiary amine combination since only a limited number of chemical reagents are available which can bring about the reduction of the carboxyl group.[49]

$$C_6H_5CO_2H \xrightarrow[CH_3CN]{SiHCl_3;\ (C_3H_7)_3N} C_6H_5CH_2SiCl_3\ (58\%)$$

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$$p\text{-}ClC_6H_4CO_2H \xrightarrow[CH_3CN]{SiHCl_3;\ (C_3H_7)_3N} p\text{-}ClC_6H_4CH_2SiCl_3\ (69\%)$$

$$3,5\text{-}(CH_3)_2C_6H_3CO_2H \xrightarrow[CH_3CN]{SiHCl_3;\ (C_3H_7)_3N} 3,5\text{-}(CH_3)_2C_6H_3CH_2SiCl_3\ (51\%)$$

Again, since the products of this new reaction are benzylic silanes, a procedure has been developed which allows their cleavage by base to the corresponding toluene derivative without isolation of the intermediate silicon compound.[50] If one interrupts these reactions

$$C_6H_5CO_2H \xrightarrow[CH_3CN]{SiHCl_3} \xrightarrow[\Delta]{R_3N} \xrightarrow[aq\ CH_3OH]{KOH} C_6H_5CH_3\ (78\%)$$

$$p\text{-}ClC_6H_4CO_2H \xrightarrow[CH_3CN]{SiHCl_3} \xrightarrow[\Delta]{R_3N} \xrightarrow[aq\ CH_3OH]{KOH} p\text{-}ClC_6H_4CH_3\ (94\%)$$

$$o\text{-}C_6H_4(CO_2H)_2 \xrightarrow[CH_3CN]{SiHCl_3} \xrightarrow[\Delta]{R_3N} \xrightarrow[aq\ CH_3OH]{KOH} o\text{-}(CH_3)_2C_6H_4\ (64\%)$$

after the first step (heating with trichlorosilane in acetonitrile) and distils the product, a good yield of the acid anhydride can be obtained. Although we have shown that aromatic anhydrides can be reduced[50] in a similar fashion to benzylic silanes, one is not justified in assuming that anhydrides are intermediates in these acid reductions, since we have also shown that tribenzoyloxysilanes $[(ArCO_2)_3SiH]$ and benzoyloxychlorosilanes $[(ArCO_2)_xSiHCl_y]$ are also reduced under similar conditions to the corresponding benzylic silanes. Since it is known that anhydrides can be formed thermally[51] from acyloxysilanes and certain aroyloxysilanes, it is possible that the anhydrides obtained are formed *during* the distillation of the aroyloxy intermediates and play no significant role as intermediates in the formation of the benzylic silanes.

It would not be justifiable at this time to write detailed mechanisms for the varied "reductive silylations" described above since the necessary supporting experimental data are not yet available. We feel that in many cases, if not all of them, the trichlorosilyl anion plays an important, but as yet undefined, role. The oxygen which is removed from carbon is incorporated into a siloxane polymer. It is quite significant, we believe, that trichlorosilane alone, or in combination with certain tertiary amines, as well as hexachlorodisilane, have been used to deoxygenate phosphine oxides and sulfoxides in what mechanistically appears to be a closely related reaction.[52]

I wish to express my appreciation for the dedication and enthusiasm of my coworkers, most of whose names are included among the references. In addition, I wish to thank the National Science Foundation whose financial assistance provided support for a considerable portion of the work.

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Biosynthesis of the Hemlock and Related Piperidine Alkaloids

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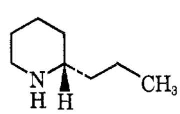
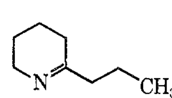
More than half of the known alkaloids contain piperidine rings.[1] However, in many of these compounds, the piperidine nucleus is fused to a carbocyclic or heterocyclic ring. Some of the simplest piperidine alkaloids are those found in the hemlock plant (*Conium maculatum*), and the structures of these are illustrated in Chart I. Most of these bases were identified a long time ago; in fact, coniine (**1**) was isolated in 1827[2] and was the first alkaloid to be synthesized.[3]

Modern methods for the isolation and separation of alkaloids (gas chromatography, thin-layer chromatography) have made it apparent that additional alkaloids of unknown structure are present in hemlock.[4–7] Also,

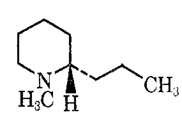
Chart I



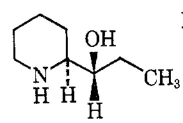
1 ((+)-coniine)



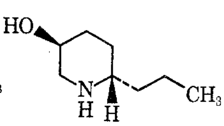
2 (γ-coniceine)



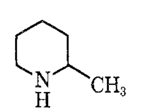
3 (*N*-methylconiine)



4 (conhydrine)



5 (ψ- conhydrine)



6 (2-methyl piperidine)

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(2) L. Giesecke, *Arch. Pharm.* (*Weinheim*), **20,** 97 (1827).

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