THE CHEMISTRY OF TRICHLOROSILANE IN THE PRESENCE OF TERTIARY AMINES

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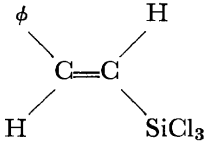
Silane (≡Si—H) additions to unsaturated hydrocarbons constitute an important reaction for the formation of the silicon–carbon bond, both from a synthetic[1] and industrial viewpoint[2]. Several catalyst systems have been employed and the literature is replete with reactions catalyzed by peroxide[1c], chloroplatinic acid and platinized charcoal. Less extensively covered has been the catalysis by organic tertiary bases. Trichlorosilane has been found to add to acrylonitrile using tertiary amines[3a,c], tertiary phosphines[3a], or substituted amides[4] to give β-cyanoethyltrichlorosilane. Pyridine[5], however, was found not to catalyze the addition of trichlorosilane to styrene, 1-octene, or vinyltrichlorosilane.

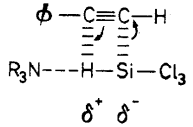
The mechanism of such reactions has been suggested as being akin to the cyanoethylation of chloroform by bases[5], involving silicon–amine complexes[3b,4], or a simple four-centred addition of trichlorosilane to the acetylene[3b]. Accordingly, we decided to undertake a broad study of the tri-*n*-butylamine catalyzed addition of trichlorosilane to arylacetylenes in order to elucidate the general mechanism of such reactions.

PHENYLACETYLENE

The first mechanistic insight on the tri-*n*-butylamine catalyzed hydrosilylation of phenylacetylene was provided by Pike[3b]. It was reported that the major product of the reaction was a diadduct, whose structure was undetermined. In addition to diadduct, one monoadduct was isolated, whose structure was determined as being *trans*-β-trichlorosilylstyrene.

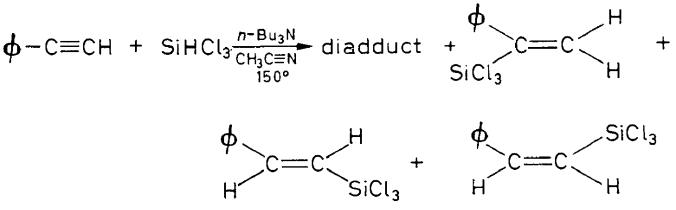


Its formation was rationalized in terms of a simple four-centred type reaction of amine and silane (or silicon amine complex) to the acetylene.



Such a mechanism would require that the product formed have a *trans* stereochemistry arising from a *cis* addition. The reaction was carried out in a bomb at 148° for four hours in acetonitrile-conditions which were claimed to be necessary for the reaction to occur.

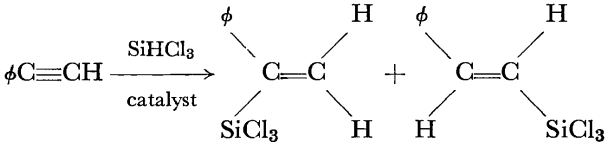
In our hands, the tri-*n*-butylamine catalyzed addition of trichlorosilane to phenylacetylene in a bomb at 150°, using acetonitrile as solvent, afforded diadduct as the major product in agreement with the published results[3b]. However, the monoadduct fraction was found to contain all three possible monoadducts—α-trichlorosilylstyrene, and *cis*- and *trans*-β-trichlorosilylstyrene[6].



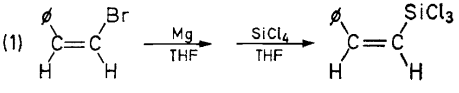
Eq. (1)

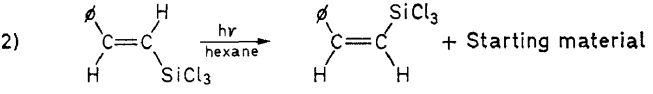
In two identical runs, the predominant monoadduct was the α-isomer. The identification of the products was made by comparison of spectral data provided from authentic samples.

Authentic samples of α- and *trans*-β-trichlorosilylstyrene were prepared by the following reaction:



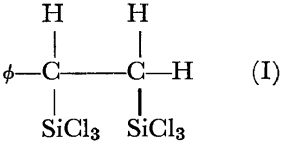
The *cis*-β-trichlorosilylstyrene was prepared in two ways:





The photoisomerization (Method 2) was found to produce the *cis* product in better yield than the Grignard route (Method 1).

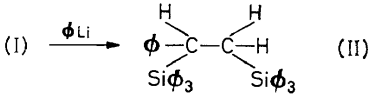
The diadduct produced in the trichlorosilane addition to phenylacetylene was shown unequivocally to have the α,β-bis trichlorosilyl structure:

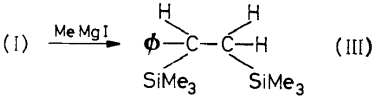


(I)

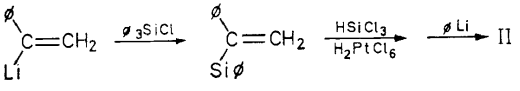
Structure proof for this compound was achieved both by chemical methods[7] and by the use of n.m.r. spectroscopy.

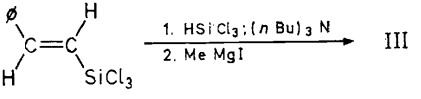
Very briefly the chemical proof of structure was accomplished as follows:



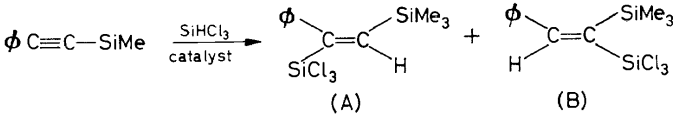


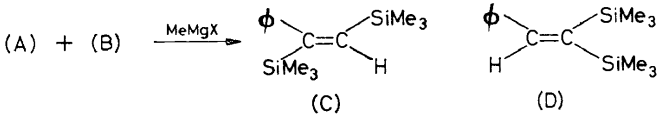
Compounds II and III proved identical in all respects to those prepared by the following sequence:

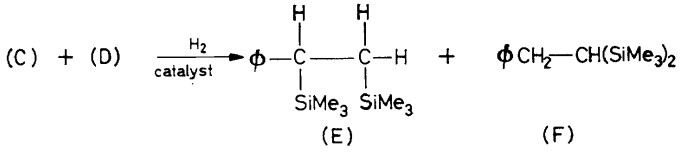




Additional proof was afforded by the synthesis of β,β-bis(trimethylsilyl) ethylbenzene[6]. This was achieved by the following reaction sequence:



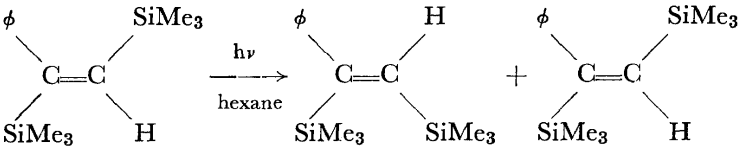




Compound E was identical in all respects with the methylated diadduct produced from the phenylacetylene reaction with trichlorosilane. The n.m.r. spectra of compounds E and F supported unequivocally the assigned

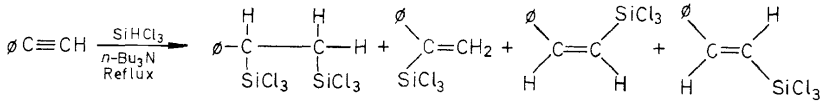
structures. Compound E shows two distinct singlets for the trimethylsilyl protons at 9·95 and 10·05 τ respectively, while compound F shows only one singlet at 9·92 τ.

That compounds C and D have the structure indicated was shown by the photoisomerization of pure *trans* C to a mixture of *cis*- and *trans*- isomers.



It is obvious that compound D could not undergo such an isomerization. The *cis*-isomer was characterized by its n.m.r. and infrared spectra as well as its elemental analysis.

While the above conditions (bomb; 150°; acetonitrile; tri-*n*-butylamine) can cause addition of trichlorosilane to phenylacetylene, we have found that much milder conditions are possible. By employing excess amine, we have been able to obviate the need for a solvent like acetonitrile. When equimolar quantities of phenylacetylene and trichlorosilane were refluxed under nitrogen with a 2·0 mole percent of amine, there was no detectable reaction. However, by using a 20 mole per cent of amine (based on silane), a 43 per cent yield of diadduct was obtained. The major product of this reaction, as before[3b], was the α,β-diadduct. The monoadduct fractions again contained all the possible isomers.



Eq. (2)

The reaction shown in equation (2) was followed by v.p.c. to determine, if possible, the initial mode of addition of the trichlorosilane. The first adduct which could be detected (after 3–5 hours) was the *cis*-β-trichlorosilylstyrene, followed by the α, β-diadduct. At longer reaction times, the *trans*-isomer appeared and occasionally traces of α-trichlorosilylstyrene could be detected.

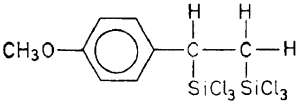
When the hydrosilylation of the monoadducts themselves was carried out[8], the following relative order of reactivity was observed: α-trichlorosilylstyrene $\gg$ *cis*-β-trichlorosilylstyrene $>$ *trans*-β-trichlorosilylstyrene $>$ phenylacetylene.

When a mixture of the *cis*- and *trans*-monoadducts was heated alone with tri-*n*-butylamine, a rather facile isomerization of the *cis*- to the *trans*- isomer was observed.

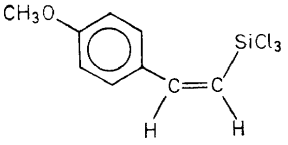
p-METHOXYPHENYLACETYLENE AND *m*-TRIFLUOROMETHYLPHENYLACETYLENE

In order to assess the influence of electronic factors on the amine catalyzed hydrosilylation of alkynes, the reaction with *p*-methoxyphenylacetylene

was examined carefully[6]. Again, the major product of the reaction was diadduct, identified as α,β-bis(trichlorosilyl)-*p*-methoxyethylbenzene.



Using the techniques developed for phenylacetylene, the reaction with *p*-methoxyphenylacetylene was followed by v.p.c. and identification of the initial adducts was made on the basis of a comparison of retention times with authentic samples. The latter were in general, synthesized by methods comparable to those described previously for the phenyl case. The first monoadduct to appear in this series was *cis*-β-trichlorosilyl-*p*-methoxystyrene.



This compound was often preceded by the appearance of the diadduct. The α-trichlorosilyl-*p*-methoxystyrene made its appearance after still longer reaction times. The overall reaction rate was slower with *p*-methoxyphenylacetylene than with phenylacetylene itself. For example, after 24 hours, phenylacetylene gave a 43 per cent yield of diadduct while *p*-methoxyphenylacetylene gave only 19 per cent diadduct (see *Table 1*).

Table 1. Tri-*n*-Butylamine catalyzed hydrosilylations of phenylacetylenes[a,d]

R—C₆H₄—C≡CH R=	*Solvent*	*Reflux Time* (Hrs.)	Mole % *Amine*[b]	*Diadduct*[c] (%)
H—	None	5	20	7
H—	None	24	20	43
H—	None	24	2	0
H—	CH_3CN	24	20	0
H—	CH_3CN	96	20	10
CH_3O—	None	24	20	19
CH_3O—	None	72	20	49

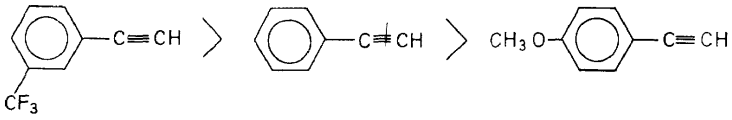
(a) Acetylene and trichlorosilane were in equimolar amounts (b) Based on silane (c) Yield is based on acetylene (d) All reactions in this table were carried out at the reflux temperature of the mixture—no bomb reactions were involved in any of these cases.

When mixtures of the monoadducts of *p*-methoxyphenylacetylene were hydrosilylated, the order of reactivity observed was again, as with phenylacetylene, $\alpha \gg$ *cis* $\beta >$ *trans* β. However, the conversion of monoadducts to diadduct was slower in the case of *p*-methoxyphenylacetylene than with the monoadducts of phenylacetylene.

Table 1 summarizes briefly the results we have obtained in the amine-catalyzed hydrosilylations of the aromatic acetylenes just discussed.

We are presently engaged in a study of the amine-catalyzed addition of

trichlorosilane to *m*-trifluoromethylphenylacetylene[9]. The purpose here is to investigate the effect of electron-withdrawing groups on the course of the reaction. It is eminently clear that the trifluoromethyl compound reacts faster than the unsubstituted phenyl and that. again, the α,β-diadduct is the predominant product. Hence the relative rate order for the acetylenes is:



OTHER ACETYLENES

It is perhaps of interest that phenyltrichlorosilylacetylene also adds trichlorosilane[6] in the presence of tri-*n*-butylamine to form a mixture of diadducts in the approximate ratio of 70/30.

$$\phi\text{—C}\equiv\text{C—SiCl}_3 \xrightarrow[\text{SiHCl}_3]{n\text{-Bu}_3\text{N}} \underset{70/30}{\phi\text{C}_2\text{H}_2(\text{SiCl}_3)_3} + \text{monoadducts}$$

The diadduct mixture is exceedingly difficult to separate but gives a correct elemental analysis for the proposed molecular formula. An n.m.r. spectrum suggests the following structures for the diadduct mixture:

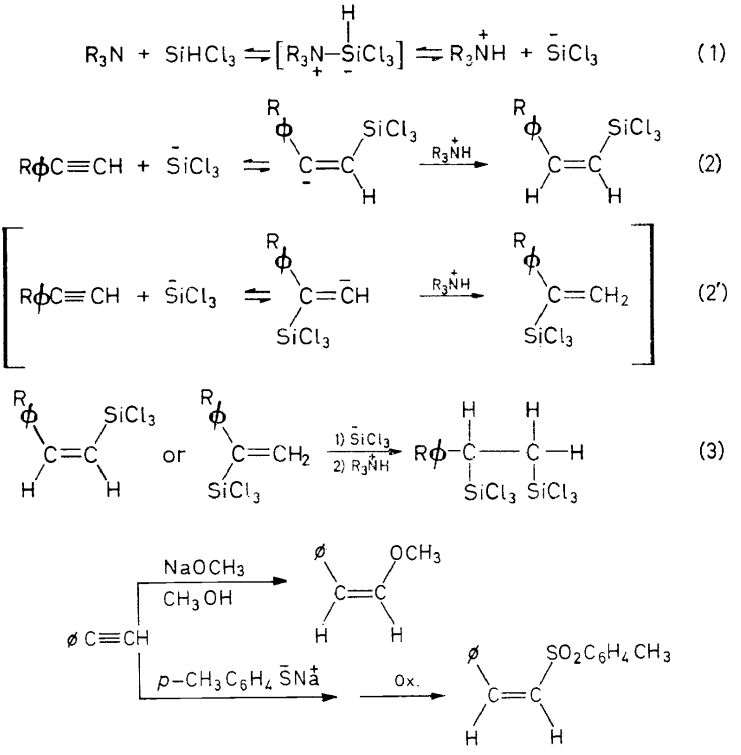
It must be emphasized, however, that the exact structures of these unusual compounds has yet to be verified.

MECHANISM

The finding that the rate of such addition reactions is facilitated by solvents like acetonitrile and excess amine strongly suggests that the reaction is ionic in nature. The stereochemistry which was found for the initial adducts, however, would seem to exclude the simple four-centred type process originally proposed[3b] since the latter would seemingly demand a *trans* configuration for the monoadducts.

At this point, our data seem more consistent with a mechanism proposed for the addition of trichlorosilane to acrylonitrile[3c] (see steps 1-3).

Such a reaction sequence would nicely explain several of the experimental observations described. As an ionic process, it would be facilitated by polar solvents. In step (2) the *trans* nucleophilic addition of an anion to an acetylenic linkage yielding a *cis*-product is well documented in the literature[10]. For example, sodium methoxide in methanol adds to phenylacetylene to give *cis*-β-methoxystyrene[11], while sodium *p*-tolylthiolate adds to the same substrate to yield *cis*-β-styryl-*p*-tolylsulphone after oxidation[12].



The substituent effects observed for the silane additions are nicely explained by the anionic addition postulated in step (2). Certainly such a process should be facilitated by an electron-withdrawing group on the phenyl ring like CF_3, and retarded by an electron supplying group like methoxy.

Unfortunately our relative rate studies do not allow us to make a decision at this time between the trichlorosilyl anion attack on the α or β- positions as shown in steps 2 and 2′ of the mechanism. While the *cis* isomer is the first monoadduct which can be detected in such additions, usually followed by the appearance of diadduct, we have demonstrated that the α-isomer proceeds to diadduct at a faster rate than the *cis* isomer. Hence, it is conceivable that some of the diadduct is arising from the α-monoadduct (step 2′). Our rate studies do eliminate, we believe, the possibility of the *trans*-monoadducts as intermediates for diadduct formation. The *trans*-isomer reacts the slowest of the three monoadducts to form diadduct (both in the methoxy and phenyl series) and invariably appears in the reaction product *after* the *cis*-isomer. We are inclined to believe that the *trans*- isomer arises principally from an isomerization of *cis*- in the presence the amine—a process which we have demonstrated experimentally occurs quite readily.

In passing, it should be noted that we have no evidence that the trichlorosilyl anion postulated in step (1) of our mechanism is formed *via* the silicon-amine complex which we have depicted. Such silicon-amine

complexes are now well known[13] and it seems attractive that, by a simple hydride shift, the trichlorosilyl anion might form from such a complex.

DEUTERIUM EXCHANGE EXPERIMENTS

It is reasonable to assume that certain tertiary amines are sufficiently basic to react with aromatic acetylenes†:

$$ArC{\equiv}CH + R_3N \leftrightharpoons R_3\overset{+}{N}H + ArC{\equiv}C^-$$

If such an equilibrium does exist[14], along with the one depicted in step (1) of the mechanistic sequence shown above, then deuterium scrambling would be expected if phenylacetylene-d_1 is treated with trichlorosilane in the presence of tri-*n*-butylamine.

$$\phi C{\equiv}CD + (n\text{-}Bu)_3N \leftrightharpoons \phi C{\equiv}C^- + (n\text{-}Bu)_3\overset{+}{N}D$$

$$SiHCl_3 + (n\text{-}Bu)_3N \leftrightharpoons [(n\text{-}Bu)_3\overset{+}{N}\text{-}\underset{\displaystyle H}{\underset{|}{Si}}Cl_3\overset{-}{]} \leftrightharpoons \overset{-}{S}iCl_3 + n\text{-}Bu_3\overset{+}{N}H$$

Stated another way, recovered trichlorosilane should contain some deuterium and recovered phenylacetylene-d_1 should be depleted of deuterium by the same amount. Accordingly, equimolar amounts of phenylacetylene-d_1 and trichlorosilane were refluxed with catalytic amounts of tri-*n*-butylamine[9]. The resultant mixture was separated into its components before the starting materials were consumed. The recovered phenylacetylene-d_1 was found depleted of deuterium (97 to 82 per cent). To facilitate handling, the recovered trichlorosilane was converted to triphenylsilane by treatment with phenylmagnesium bromide. The triphenylsilane thus produced was shown by low voltage mass spectroscopy to contain 16 per cent triphenylsilane-d_1.

$$SiDCl_3 \xrightarrow{\phi MgBr} \phi_3SiD$$

Two other components of such a reaction mixture were isolated and examined spectroscopically. The recovered tri-*n*-butylamine exhibited infrared and mass spectra which were identical to those of the starting material. Since the α- positions of tri-*n*-butylamine are highly efficient sites for radical attack[15], some deuterium incorporation at such positions might be expected from a radical process. The principal reaction product (α,β-di-(trichlorosilyl)ethylbenzene) contained approximately 21 and 35 per cent deuterium in the α- and β- positions‡ respectively.

† In partial substantiation of such an equilibrium, we observed the formation of small amounts of phenylethynyltrimethylsilane when trimethylchlorosilane was added to a normal reaction mixture of phenylacetylene, trichlorosilane and tri-*n*-butylamine.

$$\phi C{\equiv}CH \xrightarrow[SiHCl_3\ Me_3SiCl]{(n\text{-}Bu)_3N} \text{usual diadducts} + \phi\text{—}C{\equiv}C\text{—}SiMe_3$$

‡ These values were obtained by n.m.r. spectroscopy and should be considered only qualitative.

In blank experiments, it was shown that *no* deuterium exchange occurred if phenylacetylene-d_1 was simply refluxed with trichlorosilane in the *absence* of the amine catalyst. The isotopic composition of the starting materials had remained completely unchanged.

The results of these deuterium exchange experiments lend considerable support to our hypothesis that, in some manner, the amine is capable of removing the hydrogen from the trichlorosilane in these reactions as depicted in step (1) of the mechanism presented above. This could conceivably occur directly, in an acid-base type reaction, or via some type of silicon-amine type complex.

The concept of a trichlorosilyl anion as a discrete chemical entity which can be generated by treating trichlorosilane with a tertiary amine is an exciting concept which could conceivably have far-reaching synthetic applications for both the silicon and carbon chemist.

In conclusion, I wish to express my deepest appreciation to the National Science Foundation for their financial support of this work and to my graduate students, Drs Paul R. Jones and Stanley Dunny and Mr William E. Smith whose diligence and experimental skill made it possible.

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