Cooling to room temperature produced yellow crystals which were collected and washed with *n*-heptane (2 × 4 ml). The product was recrystallized from methylcyclohexane; yield 1.3 g (84 %), m.p. 287–290° with decomposition. (Found: C, 33.68; H, 8.47; B, 29.96; P, 17.51. $C_{20}H_{60}B_{20}NiP_4$ calcd.: C, 34.33; H, 8.64; B, 30.93; P, 17.71 %.)

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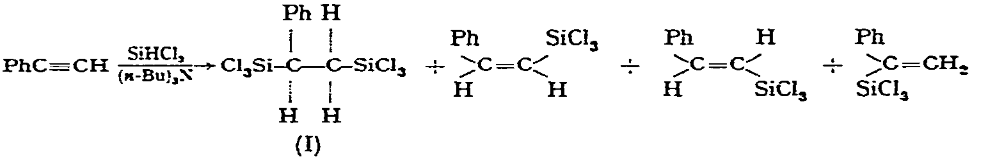
## PRELIMINARY NOTE

# Concerning the amine-catalyzed addition of trichlorosilane to phenylacetylene. The structure of the diadduct

While the hydrosilation of unsaturated hydrocarbons catalyzed by peroxides, platinum or chloroplatinic acid has been investigated intensively, relatively little attention has been given to additions catalyzed by organic bases[1–4]. Accordingly, we undertook a study of base-catalyzed silane additions to alkynes with the object of elucidating the general mechanisms of such reactions.

In agreement with earlier workers[3], we have found that the addition of trichlorosilane to phenylacetylene, catalyzed by tri-*n*-butylamine, gives a considerable amount of a diadduct. We have established conclusively that this diadduct is α,β-bis(trichlorosilyl)ethylbenzene* (I). We have identified the monoadducts of the reaction to be α-(trichlorosilyl)styrene and *cis*- and *trans*-β-(trichlorosilyl)styrene**. We have obviated the necessity for using acetonitrile as the solvent for this reaction by using

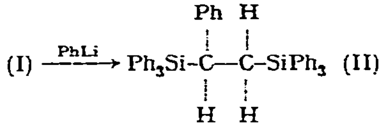


$$PhC{\equiv}CH \xrightarrow[(n\text{-}Bu)_3N]{SiHCl_3} Cl_3Si\text{-}\overset{Ph}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{-}SiCl_3 + \overset{Ph}{\underset{H}{>}}C{=}C\overset{SiCl_3}{\underset{H}{<}} + \overset{Ph}{\underset{H}{>}}C{=}C\overset{H}{\underset{SiCl_3}{<}} + \overset{Ph}{\underset{SiCl_3}{>}}C{=}CH_2 \qquad (1)$$

(I)

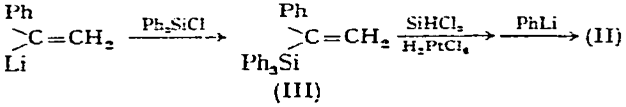
tri-*n*-butylamine in excess of the amount[4] required for catalysis. While equimolar quantities of phenylacetylene and trichlorosilane, when refluxed with 2.0 mole percent of tri-*n*-butylamine, gave no detectable reaction, 20.0 mole percent of amine gave a 38 % yield of the diadduct.

The structure of the diadduct was established unequivocally by chemical methods. Treatment of compound (I) with excess phenyllithium produced α,β-bis(triphenylsilyl)ethylbenzene (II); m.p. 174–5° (acetone–ethanol). (Found: C, 84.3; H, 6.1; Si, 9.2. $C_{44}H_{38}Si_2$ calcd.: C, 84.9; H, 6.1; Si, 9.0 %.)



$$(I) \xrightarrow{PhLi} Ph_3Si\text{-}\overset{Ph}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{-}SiPh_3 \; (II) \qquad (2)$$

Compound (II) was synthesized by an alternate route. Treatment of α-styryllithium[5] with triphenylchlorosilane produced α-(triphenylsilyl)styrene (III) in 21 % yield; m.p. 129–130° (95 % ethanol). (Found: C, 85.7; H, 6.06. $C_{26}H_{22}Si$ calcd.: C, 86.2; H, 6.08 %.) A cyclohexane solution of (III) was refluxed with excess trichlorosilane for ten hours in the presence of a catalytic quantity of chloroplatinic acid. When the product of this reaction was treated with excess phenyllithium, compound (II) was again obtained. The latter material was identical in every respect (m.p.; infrared spectrum; mixture m.p. undepressed) with the phenylated diadduct obtained in the hydrosilation of phenylacetylene. Since this synthesis started with α-styryllithium, the possibility of the diadduct (I) being β,β-bis(trichlorosilyl)ethylbenzene was eliminated.



$$\overset{Ph}{\underset{Li}{>}}C{=}CH_2 \xrightarrow{Ph_3SiCl} \overset{Ph}{\underset{Ph_3Si}{>}}C{=}CH_2 \xrightarrow[H_2PtCl_6]{SiHCl_3} \xrightarrow{PhLi} (II) \qquad (3)$$

(III)

Treatment of the diadduct (I) with excess methylmagnesium iodide produced α,β-bis(trimethylsilyl)ethylbenzene (IV); b.p. 91–3°/3.5 mm. (Found: C, 66.9; H, 10.5. $C_{14}H_{26}Si_2$ calcd.: C, 67.2; H, 10.4 %.)

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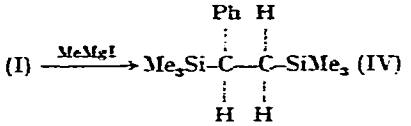
* In one earlier report[1] of this diadduct, the structure was surmised to be β,β-bis(trichlorosilyl)ethylbenzene. In a second report[3], the diadduct was referred to only in terms of its molecular formula. Two different molecular formulas were used for the diadduct, both of which were incorrect.

** The monoadducts were identified by conversion to methylated compounds and comparison of the retention times (VPC) and infrared spectra with compounds synthesized by known methods.



$$\text{(I)} \xrightarrow{\text{MeMgI}} \text{Me}_3\text{Si}-\overset{\text{Ph}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{SiMe}_3 \text{ (IV)} \qquad (4)$$

Compound (IV) was also prepared by methylation (with methylmagnesium iodide) of the product obtained by treating *trans*-$\beta$-(trichlorosilyl)styrene[6] with trichlorosilane and tri-*n*-butylamine.

(5)

Since the starting material for this synthesis was known to be the $\beta$-substituted styrene, the diadduct (IV) could *not* be $\alpha,\alpha$-bis(trimethylsilyl)ethylbenzene. The only remaining structure possible for compound (I) is $\alpha,\beta$-bis(trichlorosilyl)ethylbenzene.

The NMR spectrum of (IV) also bears out the $\alpha,\beta$-type structure proposed for this compound. The spectrum consists of a: singlet (2.60 $\tau$) aromatic protons; quartet (7.63 $\tau$) methylidyne proton; multiplet (8.78 $\tau$) methylene protons and *two* singlets (9.78 and 9.88 $\tau$) for the trimethylsilyl protons. The presence of two distinct singlets for the trimethylsilyl protons is indicative of the different environment of the two groups, a situation not compatible with either a di-$\alpha$ or a di-$\beta$ structure.

Of potentially considerable significance is the discovery of *cis*-$\beta$-(trichlorosilyl)-styrene among the monoadduct products of the hydrosilation reaction (eqn. 1). Such a product is not congruous with the mechanisms which have been suggested[2,3]: a simple four-centered type reaction between the silane–amine (or silicon–amine complex) and the alkyne. Also of significance is the large amount of diadduct which forms in this reaction. It becomes imperative to determine from which monoadduct the bulk of this material is formed. It is not inconceivable that one of the three possible monoadducts adds trichlorosilane much more rapidly than the other two and that the diadduct is formed preferentially from just this one monoadduct. For this reason conclusions concerning the stereochemistry of the initial addition cannot be drawn safely from a small quantity of a particular monoadduct which might be detected in the reaction products.

Additional experiments designed to shed light on the mechanism and stereochemistry of the addition and source of the diadduct are already underway.

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