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## CHEMISTRY OF ALKALI METAL-UNSATURATED HYDROCARBON ADDUCTS

### X \*. ELECTRON-TRANSFER REACTIONS OF $\alpha, \beta$ -UNSATURATED ORGANOSILANES

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#### Summary

The chemical behavior of alkali metal adducts of  $\alpha, \beta$ -unsaturated organosilanes was investigated by generating the adducts with lithium or potassium metal in donor solvents at  $-78^\circ\text{C}$  and studying the ensuing reduction, bimolecular coupling, cleavage and isomerization processes. Chosen for study were the triphenylvinyl derivatives of silicon, germanium and tin, as well as other vinyl-, phenyl-, allyl-, 1,3-alkadienyl-, 1-alkynyl- and cyclopropyl-silanes. By assessing gradations in substituent reactivity toward alkali metal, an empirical ordering of electron affinity for these substituents on silicon was determined: 1,3-alkadienyl > 1-alkynyl > 1-alkenyl > phenyl  $\gg$  2-alkenyl or cyclopropyl. Where available, ESR data were used to explain the reactivity and the reaction pathway observed for radical anion intermediates. Where such information was unobtainable, the behavior of unstable radical anions was ascribed to variations in  $p_\pi \rightarrow d_\pi$  stabilization.

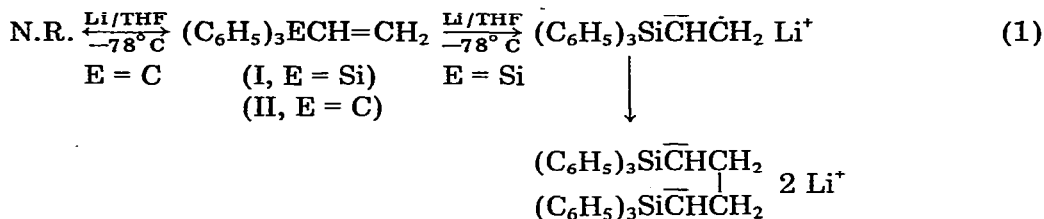
#### Introduction

The ready addition of alkali metals to carbon-carbon unsaturation generally requires the presence of multiple  $\pi$  bonds in the organic substrate, such as those in alkynes, 1,3-alkadienes or aromatic systems [1]. Isolated unsaturation of the monoolefinic or unconjugated alkadiene type usually does not suffice to yield metal adducts \*\*. After such experimental factors as the specific metal and the

\* For Part IX see ref. 13.

\*\* In recent work [31] a cesium-potassium-sodium alloy has been used with great success in generating less stable radical anions, such as those of arenes.

donor solvent have been taken into account, the intrinsic capability of the organic substrate to react can be ascribed to its electron affinity [2]. Thus it is useful to view these metal additions as involving electron transfer to the lowest-lying antibonding orbitals of the hydrocarbon. In this light the ready reductive coupling of triphenylvinylsilane (I) by lithium metal in tetrahydrofuran (THF), compared with the inertness of 3,3,3-triphenylpropene (II), indicates that silicon enhances the electron affinity of the vinyl group (eq. 1) [3]:



Many subsequent studies, involving the metal-promoted isomerizations of *Z*-1-propenylsilanes [4], the halfwave reduction potential and ESR spectra of 1,2-disilyl- and trisilyl-ethylenes [5] and the photoelectron spectra of vinyl- and allyl-silanes [6], have corroborated this effect of silicon on an adjacent double bond.

Moreover, even though the attachment of a silicon on an aromatic ring does not exert such a dramatic influence (for both benzene and trimethylphenylsilane (III) form radical anions with sodium at  $-78^\circ\text{C}$ ), an extensive series of studies has shown silicon to display electron-withdrawing characteristics in the radical anion [7]. Thus the total width of the hyperfine spectrum of the radical anion derived from III is 18.63 gauss [8]; the corresponding width of the spectrum of the benzene radical anion is 22.50 gauss [9]. If the McConnell relation [10] for the proportionality between hyperfine splitting and electron spin density be valid for III, then this narrowing of spectral width indicates considerable spin density on silicon. In addition, the large *para* proton hyperfine (8.13 gauss), compared with smaller *ortho* and *meta* couplings (2.66 and 1.06 gauss), implies that the  $\text{Me}_3\text{Si}$  group is strongly electron-withdrawing. Finally, in a qualitative sense, III displays a greater electron affinity than benzene, since it reacts preferentially with alkali metals in the presence of benzene. Also, these radical anions display differences in thermal stability: that of benzene is not stable above  $-50^\circ\text{C}$ , while that of III persists for several hours at  $25^\circ\text{C}$  [8].

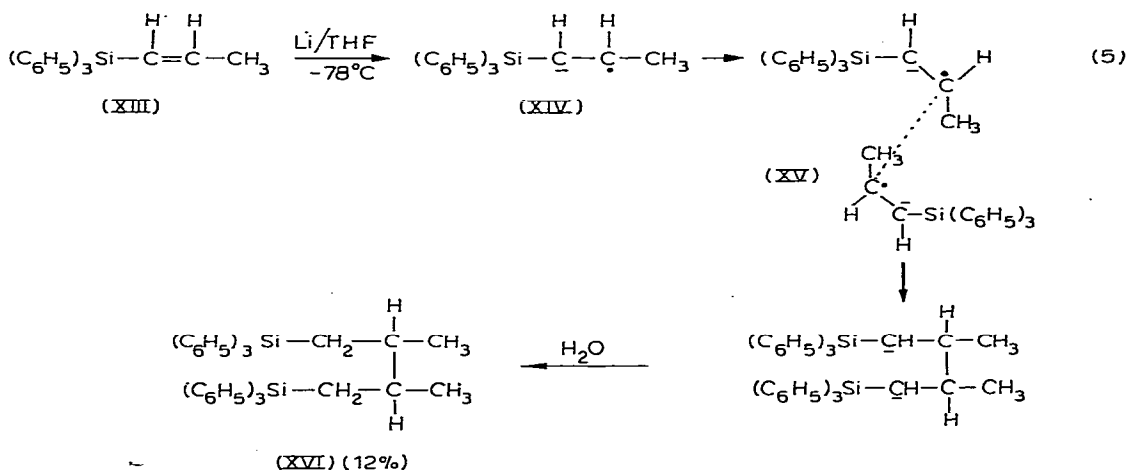
Although these numerous studies have investigated the formation and detailed structure of organosilyl radical anions, little attention has been paid to the chemical reactions of these intermediates. The present work, therefore, was conceived with an eye to delineating the chemical behavior of such radical anions. To this end, a series of vinyl-, aryl-, allyl-, 1,3-alkadienyl-, 1-alkynyl- and cyclopropyl-silanes was examined, together with some vinyl derivatives of other Group IV congeners. Cyclopropylsilanes were especially chosen [11], in order to learn whether the  $\pi$  like bonding of the ring might interact with the available silicon  $3d$  orbitals, similar to the delocalization suggested for vinylsilanes [3, 5, 12, 13].



The mode and ease of bimolecular reduction were also dependent upon the substituents borne by the vinylic group. Triphenyl-1-propenylsilane (XIII) underwent coupling  $\beta$  to the silicon much less readily than did I. Since the recovered XIII was enriched in the proportion of the more stable *E* isomer ( $E/Z = 30/70 \rightarrow 50/50$ ), it can be concluded that the *Z* form of XIII underwent coupling preferentially. Although the isomerization of the *E* and *Z* forms of XIII is possible (cf. ref. 4), under these experimental conditions (lithium pieces in THF at  $-78^\circ\text{C}$ ) nothing approaching equilibration of the *E* and *Z* isomers had occurred. For trimethyl-1-propenylsilane and also for XIII, equilibration would have formed ca. 100% of the *E* configuration. The resulting 1/1 mixture points to the lack of much *Z/E* isomerization under the reaction conditions.

In the absence of significant isomerization at  $-78^\circ\text{C}$ , and under pseudo first-order conditions, the resulting *E/Z* ratio could only result if the *Z* form had coupled preferentially. For, had the *E* and *Z* forms coupled with the same rate constant, the *E/Z* ratio would have remained unchanged; had the *E* form coupled more readily, the *Z* content of the recovered XIII would have been enriched.

The configuration of the dimer (XVI) was not determined but, in the absence of special ion-pair clustering effects (cf. the coupling of radical anions of benzalaniline [16a]) the radical anions XIV are assumed to have coupled in a *meso* configuration (XV) so as to minimize group repulsions\* (eq. 5):

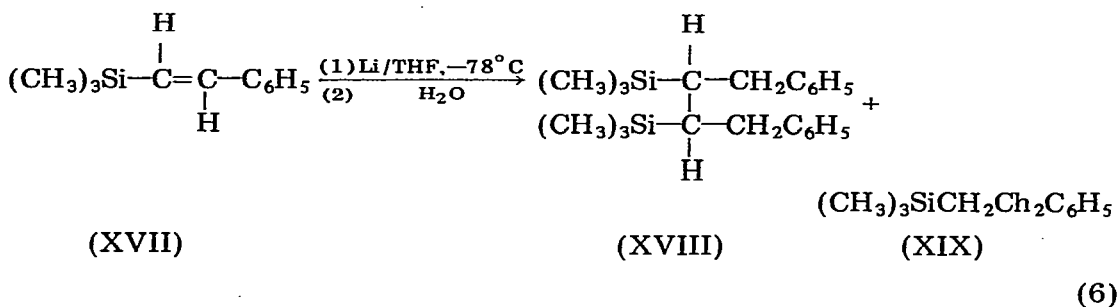


From multiplets observed in the 5.3–5.9 ppm region of the NMR spectrum of the crude product, it can also be concluded that a very small amount of XIII underwent coupling through the aryl groups (cf. section on Arylsilanes).

In contrast, trimethyl-*E*- $\beta$ -styrylsilane (XVII) underwent reduction to give coupling preferentially  $\alpha$  to the silicon (XVIII), together with considerable amounts of the monomeric reduction product (XIX); again, a *meso* configura-

\* The authors consider that suggesting the *meso* configuration for XVI is justified, even though no structural determination has yet been carried out. It is noteworthy that only one dimer of XVI was detected. In instances where such coupling involves special ion-pair clustering effects [16a], both the *meso* and *d,l* forms of the dimer can be discerned.

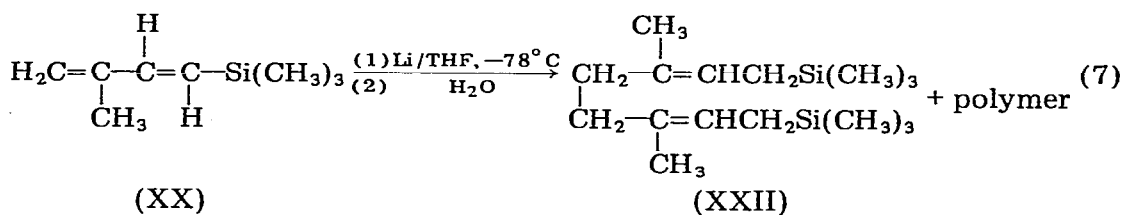
tion is assumed for XVIII (eq. 6):



A careful ESR study has been made of the radical anion formed from the action of various alkali metals on trimethyl(phenylethynyl)silane and the hyperfine coupling constants have been determined for the methyl and aromatic protons [16b]. These same authors report that this radical anion undergoes coupling at the carbon adjacent to the trimethylsilyl group to yield 1,4-diphenyl-2,3-bis(trimethylsilyl)-1,3-butadiene. Curiously, they offer no experimental or spectral information on this compound, but rather refer to analogous results obtained by Professor M.D. Rausch (University of Massachusetts, Amherst) and reported at the Fourth International Conference on Organometallic Chemistry held at Bristol, England, in 1969. To our knowledge, details on the stereochemical purity and structural assignment of this dimer have not been published in the refereed literature.

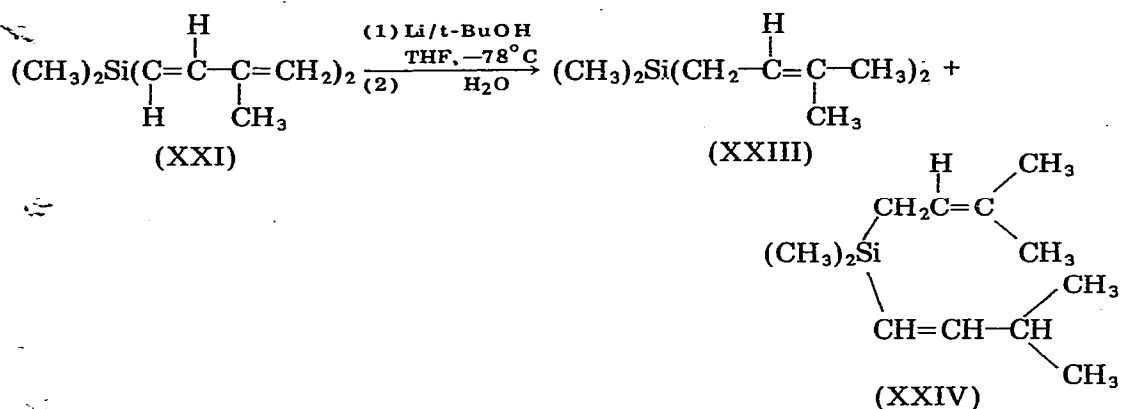
### 1,3-Alkadienylsilanes

The test substrates, trimethyl-*E*-3-methylbuta-1,3-dien-1-ylsilane (XX) and dimethylbis(*E*-3-methylbuta-1,3-dien-1-yl)silane (XXI), proved to be most prone to lithium metal-promoted polymerization. By conducting the reaction at  $-78^\circ\text{C}$ , XX was found to yield a significant amount of dimer, 3,6-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene (XXII) (NMR, parent peak at 282 in the mass spectrum), but at least four other volatile components accompanied this product. These products seemed to be stereoisomers or position isomers of the  $\text{C}_{10}$  skeleton (eq. 7):



Similarly, when XXI was subjected to such reducing conditions, in the hope of bringing about cyclization to a nine-membered silicon heterocycle (cf. eq. 4), only reduction of the dienyl system occurred. A 62% yield of dimethylbis(3-methylbut-2-en-1-yl)silane (XXIII, 42%, 6-proton singlets at 1.70 and 1.82 ppm and a 2-proton triplet at 5.28 ppm) and dimethyl(3-methylbut-2-en-1-yl)3-methylbut-3-en-1-ylsilane (XXIV, 20%, a 6-proton doublet at 1.01 ppm and

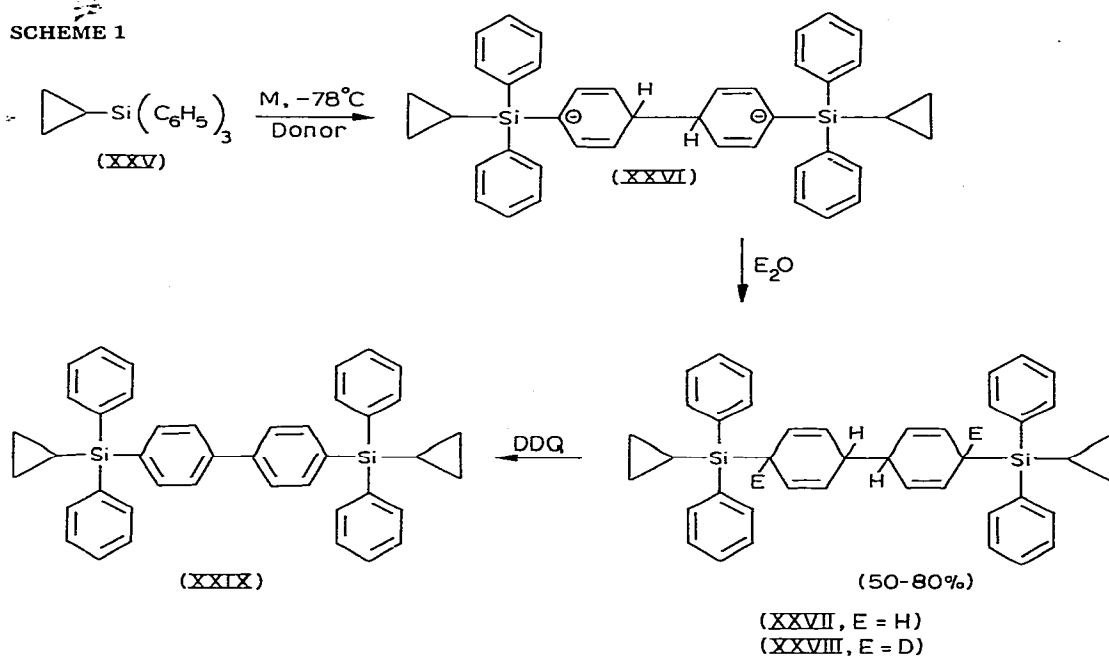
3-proton singlets at 1.55 and 1.65 ppm) was obtained:



### Arylsilanes

In an attempt to learn whether the cyclopropylsilyl group might form a radical anion through the assistance of cyclopropyl  $p_\pi$ -silicon  $d_\pi$  conjugation, cyclopropyltriphenylsilane (XXV) was treated with potassium metal in 1,2-dimethoxyethane or with lithium metal in tetrahydrofuran at  $-78^\circ\text{C}$ . Under these conditions no scission of the cyclopropyl ring or the cyclopropyl-silicon bond was observed, but rather efficient intermolecular coupling of the phenyl rings occurred at their *para* position (Scheme 1). The positions of highest nega-

SCHEME 1

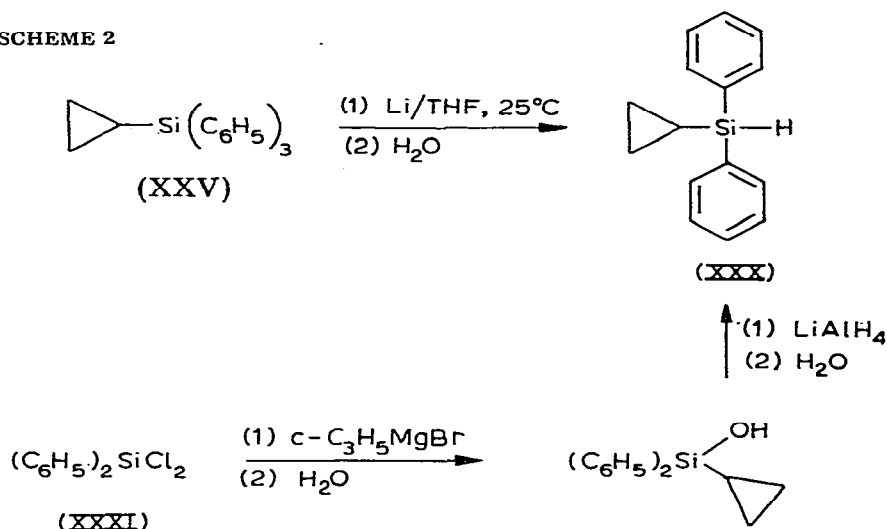


tive charge in intermediate XXVI were ascertained by deuteration to yield XXVIII and the overall skeletons of XXVI and XXVII were determined by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to yield 4,4'-bis(cyclopropyldiphenylsilyl)biphenyl (XXIX). The efficiency with

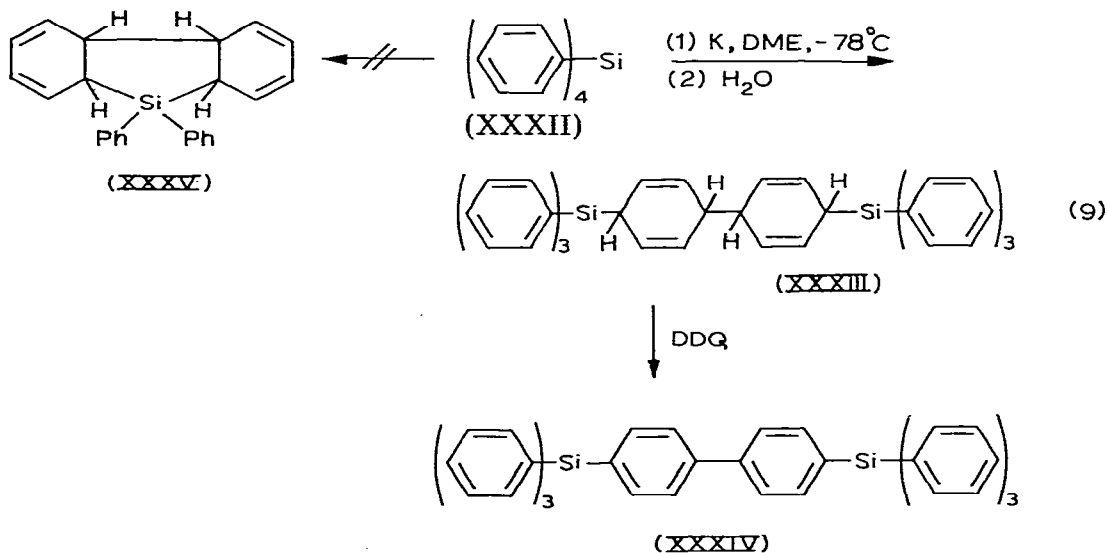
which the silyl substituent activates the benzene ring for coupling is remarkable.

The importance of low temperature was appreciated when the reaction of XXV with lithium metal in THF was carried out at 20–25°C. Under these conditions little coupling was achieved but extensive scission of the phenyl–silicon bond occurred instead. The cyclopropyldiphenylsilane (XXX) obtained upon hydrolysis was identified by an independent synthesis from dichlorodiphenylsilane (XXXI) (Scheme 2).

SCHEME 2



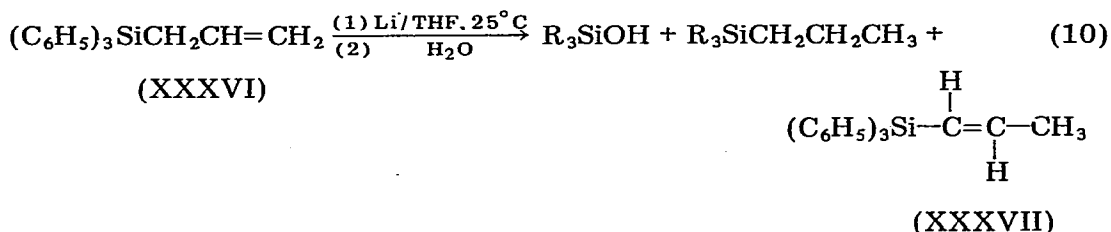
When an attempt was made with tetraphenylsilane (XXXII) itself to induce intramolecular *ortho* coupling, analogous in the behaviour of diphenyldivinylsilane (X, eq. 4), coupling occurred instead through the *para* positions (XXXIII) (eq. 9).



Dehydrogenation of the crude product XXXIII yielded XXXIV, but no trace of 5,5-diphenyldibenzosilole [17], the dehydrogenation product of XXXV, was detected.

### Allylic silane

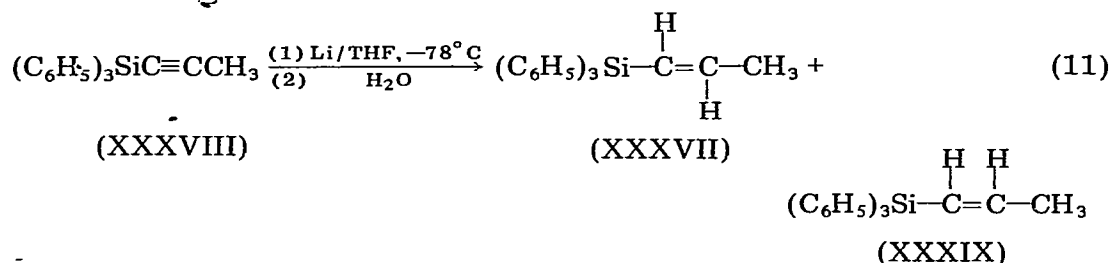
At low temperatures allyltriphenylsilane (XXXVI) reacted with lithium metal essentially like an arylsilane (cf. XXV and XXXII), undergoing *para* coupling to yield, after DDQ dehydrogenation, 4,4'-bis(allyldiphenylsilyl)biphenyl. At room temperature, on the other hand, a combination of silicon-carbon bond scission, allyl-propenyl isomerization and propenyl group reduction took place (eq. 10):



The principal product was the isomer of XXXVI, triphenyl-*E*-1-propenylsilane (XXXVII).

### Alkynylsilane

In a similar outcome, the interaction of triphenyl-1-propynylsilane (XXXVIII) with lithium metal at low temperatures led to reduction of the C<sub>3</sub> group and the formation of principally XXXVII, accompanied by a lesser amount of its *Z*-isomer, XXXIX (eq. 11).



## Discussion

### Chemical reactivity of substituents as a measure of their electron affinity

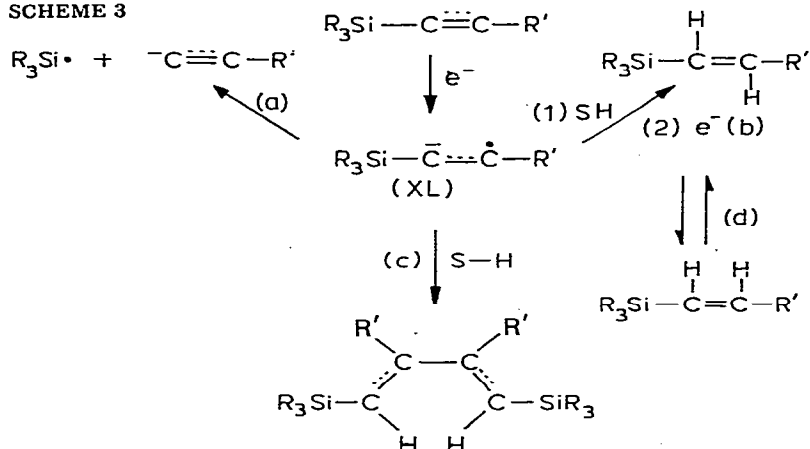
The study of the behavior of the foregoing organosilanes towards alkali metals has uncovered a noteworthy trend: the tendency of a substituent on silicon to undergo reaction decreases in the series, 1,3-alkadienyl > 1-alkynyl > 1-alkenyl > phenyl >> 2-alkenyl or cyclopropyl. This qualitative gradation is based upon: (a) the behavior of those silanes whose substituents offer the possibility of competitive reactions (e.g., (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCH=CH<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiC≡CCH<sub>3</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCH<sub>2</sub>CH=CH<sub>2</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si-c-C<sub>3</sub>H<sub>5</sub>, where a phenyl group is pitted



against an unsaturated group); (b) the rapidity with which, and the conditions under which, the organosilanes react with metals (e.g.,  $(\text{CH}_3)_3\text{SiCH}=\text{CHC}(\text{CH}_3)=\text{CH}_2$  more readily than  $(\text{C}_6\text{H}_5)_3\text{SiC}\equiv\text{CCH}_3$ , and the latter more readily than  $(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CHCH}_3$  at  $-78^\circ\text{C}$ ); and (c) the observation of which group is cleaved from silicon when such alkali metal reactions are conducted at  $25^\circ\text{C}$ .

Although the kind of reaction that ensues can be variously (a) silicon-carbon bond cleavage; (b) monomolecular reduction, (c) bimolecular reduction, or (d) isomerization (Scheme 3), all these processes can stem from an initial electron transfer step (XL).

SCHEME 3



With the assumption that substituent reactivity depends upon the ease of forming XL, then the foregoing reactivity sequence for substituents on silicon can be taken as an ordering of their electron affinities. Now it is readily granted that other factors than intrinsic electron affinity may play a role in the formation of XL and its subsequent reactions (solvation, steric factors and degree of association of anions and cations [2]), so this order should be considered as only empirical and qualitative. Since 1,3-alkadienyl, alkynyl and phenyl derivatives readily undergo reaction with alkali metals, regardless of the presence of an adjacent silicon center (so-called Birch reductions [18]), the vinylic group is most profoundly activated by the attached silicon. It is important to note that neither an allyl group nor a cyclopropyl group attached to silicon shows any electron affinity toward alkali metals. At low temperatures both XXV and XXXVI couple through the *para* positions, just like any other phenylsilane (cf. eq. 9 and Scheme 1). This observation indicates that the phenyl groups in XXV and XXXVI exhibit a greater electron affinity than the allyl or cyclopropyl groups. If such electron affinity be ascribed to the efficacy of carbon  $p_\pi$ -silicon  $d_\pi$  interaction, then one would conclude that such interaction with silicon's  $d$ -orbitals would be more effective with the phenyl  $\pi$ -like bonding of either an allyl or cyclopropyl group.

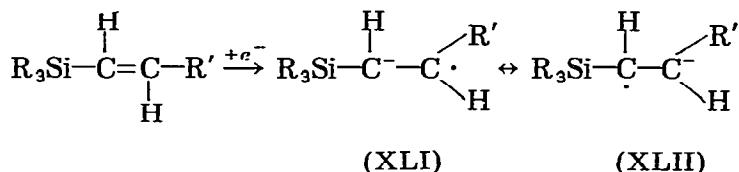
#### *Electron spin density and the site of reactivity*

In addition to considering the relative reactivities and electron affinities of substituents on silicon, one should also give some attention to the electron dis-

tribution in the resulting radical anions. The distribution of the free spin is especially relevant for those organosilanes where bimolecular reduction is observed. The tendency of phenylsilanes of the type  $(C_6H_5)_3SiR$  where  $R=C_6H_5$ ,  $CH_3$ ,  $c-C_3H_5$  and  $CH_2CH=CH_2$ , to couple uniformly through the *para* positions, and not intramolecularly through the *ortho* positions (eq. 9), can be correlated with the ESR spectra of such silanes, in which the hyperfine splitting by the phenyl protons shows the free spin to be maximum at the *para*, and minimum at the *ortho* and *meta*, positions [19]. This finding suggests that, in the absence of steric constraints, coupling will occur most rapidly at the sites of highest spin density.

Although it would be advantageous to correlate ESR data for radical anion intermediates with the course of their subsequent reactions, many radical anions are too reactive, even at low temperatures, to persist long enough to give well-resolved ESR spectra. Thus, all attempts to detect the radical anion derived from triphenylvinylsilane (I) have failed and the first reproducible and well-resolved signal is clearly that of a secondary product [19].

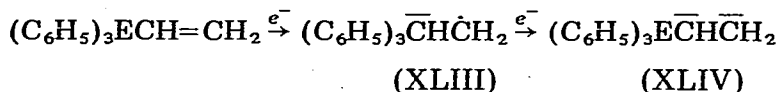
In the absence of ESR data, one might be prompted to assign electron spin density in the radical anion intermediate on the basis of the observed sites of coupling. The mode of coupling of vinylsilanes clearly depends upon the substituents, as evidenced by the behavior of triphenylvinylsilane (I), triphenyl-1-propenylsilane (XIII) and trimethyl-*E*- $\beta$ -styrylsilane (XVII). That I and XIII undergo coupling  $\beta$  to silicon and XVII couples  $\alpha$  to silicon suggests that XLI is a more important resonance representation in the former cases, while XLII is more important with XVII.



Where  $R' = \text{H}$  or alkyl, build-up of the anionic charge adjacent to silicon (XLI) would foster stabilization by a  $p_\pi \rightarrow d_\pi$  overlap between carbon and silicon. Where  $R' = C_6H_5$ , better delocalization of the anionic charge could be attained by having the charge adjacent to phenyl (XLII). An alternative explanation of such coupling modes might seek to invoke steric factors. Although such a steric argument might satisfactorily account for the  $\beta$  coupling of I and XIII ( $\text{Ph}_3\text{Si}$  much larger than  $\text{H}$  or  $\text{CH}_3$ ), it does not offer a satisfactory explanation for the behavior of XVII ( $\text{Me}_3\text{Si}$  equivalent to, or larger than,  $\text{Ph}$ ).

In connection with the stabilization of radical anions derived from vinylsilanes, the behavior of triphenylvinylmetallics of silicon, germanium and tin (I, IV and VIII) provides an instructive comparison. Under analogous reaction conditions (lithium in THF at  $-78^\circ\text{C}$ ) the silane underwent smooth reductive coupling (eq. 1), the germane was polymerized and the stannane was extensively cleaved at the vinyl-tin bond (eq. 3). Compared with the silane and the germane, the presumed radical anion of stannane was very unstable (XLIII,  $E = \text{Sn}$ ), possibly because the more electropositive tin is less effective in stabilizing the adjacent anion by a  $p_\pi \rightarrow d_\pi$  interaction. The polymerization observed with

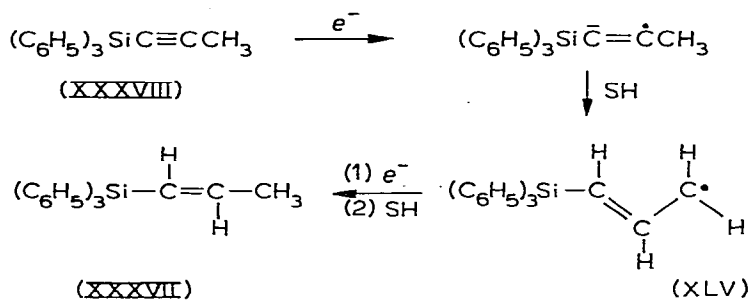
the germane, on the other hand, might have been due to the formation of dianion XLIV (E = Ge), whose generation would have been fostered by the greater electronegativity of germanium (Allred-Rochow values: Si = 1.74; Ge = 2.02;



and Sn = 1.72) and a  $p_\pi \rightarrow d_\pi$  stabilization. Such a dianion could be a potent initiator of anionic vinyl polymerization [20]. Support for this interpretation is seen in the reaction of germane(IV) with lithium in the presence of a weak proton source, t-butyl alcohol. In this case polymerization was suppressed completely and a mixture of reductive dimer VII and ethyltriphenylgermane (VI) was isolated (eq. 4). The protonation of XLIII would prevent the formation of XLIV; the resulting radical could either couple to form VII or undergo further reduction to yield VI. A similar suppression of dianions leading to polymers seems to underlie the successful cyclization of X, the coupling of XX and the monomolecular reduction of XXI by a combination of lithium and t-butyl alcohol\*.

#### Electron transfer and protonation

By maintaining the temperature below  $-70^\circ\text{C}$  the formation and the stabilization of radical anion intermediates are favored. Many metal reactions of organosilanes that involve reduction or coupling at  $-78^\circ\text{C}$  lead, instead, to silicon-carbon bond cleavage at  $25^\circ\text{C}$ . Consider the behavior of  $(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CH}_2$ ,  $(\text{C}_6\text{H}_5)_3\text{SiC}\equiv\text{CCH}_3$ , and  $(\text{C}_6\text{H}_5)_3\text{Si-c-C}_3\text{H}_5$ . But even at  $-78^\circ\text{C}$  many radical anion intermediates can abstract protons from the solvent or the substrate. Triphenyl-1-propynylsilane (XXXVIII) forms a radical anion that undergoes rapid conversion to the 1-triphenylsilylallyl radical [19] (XLV) by proton transfer.



The source of the protons, SH, is most likely the acidic protons of XXVIII [22].

Similarly, the isomerization of allyltriphenylsilane (XXXVI) to triphenyl-E-

\* For the previous use of t-butyl alcohol in such metal reductions see ref. 21a. Whether the t-butyl alcohol protonates the radical anion XLIII or the dianion XLIV (formed either on the lithium surface or by the disproportionation of XLIII) is an extraordinarily complex question. For studies of this aspect with aromatic anions, the reader is referred to recent articles by Garst [21b], Szwarc [21c], and Dye [21d].



tive addition of ice water, 10% aqueous HCl and pentane. Usual separation of the organic layer, washing with aqueous NaHCO<sub>3</sub>, removal of solvent and distillation of the product under reduced pressure gave a semi-solid material, which crystallized from pentane as a colorless solid, melting range 63–73°C [25]. By NMR integration this product was shown to be a 70/30 mixture of *Z*- and *E*-isomers. NMR of *Z*-XIII (CHCl<sub>3</sub>): δ 1.56 (d, of d 3 H, *J* 6 Hz and *J* 1 Hz), 6.10 (d of m, 1 H, *J* 15 Hz) 6.5–7.1 (m, 1 H) and 7.1–7.8 (two m, 15 H); NMR of *E*-XIII (CHCl<sub>3</sub>): δ 1.82 (m, 3 H), 6.20 (m, 2 H) and 7.1–7.8 (two m, 15 H) [25].

*Triphenyl-1-propynylsilane (XXXVIII)*. This compound was prepared by slowly passing propyne gas into a 200 ml ethereal solution of ethylmagnesium bromide (from 21.8 g (0.2 mol) of ethyl bromide and 4.9 g (0.2 g-atom) of magnesium turnings) until no more was absorbed and two liquid layers were formed. With cooling, 43.5 g (0.2 mol) of solid chlorotriphenylsilane were added, the mixture stirred at reflux for 18 h and then 200 ml of 10% aqueous HCl added. Usual work-up gave a semi-solid material, which was taken up in 100 ml of pentane and filtered to remove the precipitated triphenylsilanol. Subsequent pentane removal and recrystallization of the residue from methanol gave 35 g (58%) of XXXVIII, m.p. 114–115°C (lit. [26] 115.5–116°C); IR-(CS<sub>2</sub>): 3100, 2210 (C≡C), 1440, 1120, 1028, 742, 714 and 700 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>): δ 1.97 (s, 3 H) and 7.17–7.75 (two m, 15 H).

*Cyclopropyltriphenylsilane (XXV)*. Solid chloro triphenylsilane (43.5 g, 0.2 mol) was added to the Grignard reagent resulting from 24.2 g (0.2 mol) of cyclopropyl bromide and 4.9 g (0.2 g-atom) of magnesium turnings in tetrahydrofuran. After the mixture was stirred at reflux for 15 h and worked up by hydrolysis in the usual way, the resulting oily residue was distilled under reduced pressure to yield a viscous oil, b.p. 195–200°C (0.1 mmHg), which was crystallized from methanol, m.p. 80–81°C (37%); IR(CCl<sub>4</sub>): 3030, 3000, 1430, 1125 and 900 cm<sup>-1</sup>; NMR(CDCl<sub>3</sub>): δ 0.1–0.45 (m, 3 H), 0.49–1.05 (m, 2 H) and 7.10–7.68 (two m, 15 H). Anal.: Found: C, 83.97; H, 6.66. Calcd. for C<sub>21</sub>H<sub>20</sub>Si: C, 84.42; H, 6.35%.

*Allyltriphenylsilane (XXXVI)*. Solid chlorotriphenylsilane (19.5 g, 66 mol) was added to the Grignard reagent obtained from 5.18 g (67 mmol) of allyl chloride and 1.7 (68 mg-atom) of magnesium turnings in 100 ml of tetrahydrofuran. Stirring at reflux for 17 h, hydrolytic work-up and recrystallization from ethanol afforded 17.5 g (88%) of XXXVI, m.p. 89–90°C (lit. [27], 91–92°C).

*Dimethylbis(3-methylbut-3-en-1-yn-1-yl)silane*. A solution of 90.0 g (1.36 mol, 99%, Farchan) of 2-methylbut-1-en-3-yne in 200 ml of diethyl ether was added dropwise to ethylmagnesium bromide prepared from 149 g (1.36 mol) of ethyl bromide and magnesium turnings in 600 ml of ether. After a 24 h stirring period at 20–25°C the reaction mixture was treated dropwise with a solution of 88 g (0.71 mol) of dichlorodimethylsilane in 200 ml of ether. The resulting mixture was heated at reflux for 24 h, cooled and hydrolyzed with an aqueous NH<sub>4</sub>Cl solution. Washing of the organic layer with a saturated aqueous NaHCO<sub>3</sub> solution, drying the layer over anhydrous MgSO<sub>4</sub> and removal of solvent gave a residue whose fractional distillation yielded 94 g (73%) of product, b.p. 61–62°C/2 mmHg (lit. [28] b.p. 75°C/4 mmHg). This liquid had to be stored in the dark and the cold under nitrogen to retard polymerization. IR

(neat): 2175, 1275, 1250 and 985  $\text{cm}^{-1}$ ; NMR (neat):  $\delta$  5.02–5.35 (m, 2 H), 1.68 (s, hyperfine triplet,  $\text{CH}_3$ ) and 0.20 (s,  $(\text{CH}_3)_2\text{Si}$ ).

*Dimethylbis(E-3-methylbuta-1,3-dien-1-yl)silane (XXI)*. To 26.4 g (0.14 mol) of the foregoing butenylnylsilane, which was cooled in an ice bath, were added dropwise 40 g (0.28 mol) of diisobutylaluminum hydride. The orange-red reaction mixture was stirred at 20–25°C for 20 h. Thereupon the mixture was diluted with 100 ml of hexane and cautiously hydrolyzed with 10 ml of water. The hexane layer was filtered and then dried over anhydrous  $\text{MgSO}_4$ . Stripping the solvent from the organic layer and fractional distillation provided 13.5 g (51%) of colorless product, b.p. 72–74°C/8 mmHg; IR (neat): 3090, 2950, 1575, 1243, 1200 and 985  $\text{cm}^{-1}$  (*trans*-CH=CH); NMR (neat):  $\delta$  6.41 (d,  $J$  18 Hz, *trans*-CH=CHSi), 5.55 (d,  $J$  18 Hz, *trans*-CH=CHSi), 4.70–4.90 (m, 4 H), 1.75 (s, 2 $\text{CH}_3$ ) and 0.18 (s,  $(\text{CH}_3)_2\text{Si}$ ). Anal.: Found: C, 74.79; H, 10.49. Calcd. for  $\text{C}_{12}\text{H}_{20}\text{Si}$ : C, 74.90; H, 10.50%.

*Trimethyl-E- $\beta$ -styrylsilane (XVII)*, *triphenylvinylgermane (IV)*, *triphenylvinylstannane (V)* and *trimethyl(E-3-methylbuta-1,3-dien-1-yl)silane (XX)* These compounds were prepared according to published procedures (ref. 29 for XVII and XX) or were commercially available.

*Tetraphenylsilane (XXXII)* and *diphenyldivinylsilane (X)*. Both these compounds were available commercially. The former was recrystallized before use; the latter, which was shown by GC to contain 30% of diethyldiphenylsilane, was used as received.

#### *Metal reactions with Group IV organometallics*

*Diphenyldivinylsilane (X)*. A mixture of 5.0 g (70% pure, 14.8 mmol) of X and 3.1 g (42 mmol) of *t*-butyl alcohol was added dropwise over a period of 30 min to a vigorously stirred suspension of 290 mg (4.22 mg-atom) of finely divided lithium wire in 30 ml of anhydrous tetrahydrofuran, which was cooled to  $-78^\circ\text{C}$  by a bath of solid  $\text{CO}_2$  in acetone. The resulting mixture was stirred at  $-78^\circ\text{C}$  for an additional 21 h and then treated with water and 100 ml of diethyl ether. The organic layer was washed repeatedly with water to remove the THF and then dried over anhydrous  $\text{MgSO}_4$ . Removal of solvent gave 4.9 g of crude product which by GC was shown to be a 65/35 mixture of diethyldiphenylsilane (XI) and 1,1-diphenylsilacyclopentane (XII). Isolation by preparative GC yielded 1.75 g (50%, after adjusting for the initial content of diethyldiphenylsilane) 1,1-diphenylsilacyclopentane, whose spectral properties were identical with those previously reported [30]: IR ( $\text{CCl}_4$ ): 1425, 1125, 1080 and 1050  $\text{cm}^{-1}$ , inter alia; NMR ( $\text{CCl}_4$ ):  $\delta$  6.75–7.50 (m, 10 H), 1.50–1.90 (m, 2 H) and 0.83–1.33 (m, 2 H).

*Triphenylvinylgermane (IV)*. A solution of 1.0 g (3.0 mmol) of IV and 215 mg (2.9 mmol) of *t*-butyl alcohol was added dropwise to a stirred suspension of 20 mg (2.9 mg-atom) of finely divided lithium wire in 15 ml of anhydrous tetrahydrofuran maintained at  $-78^\circ\text{C}$ . After stirring at the same temperature for 24 h the mixture was decomposed by water. By the work-up procedure described above, 0.8 g of crude product was obtained, whose IR and NMR spectra showed the presence of triphenylgermane (2074  $\text{cm}^{-1}$  (Ge–H) and  $\delta$  5.68 ppm). Short path distillation gave 60% of ethyltriphenylgermane (b.p. 100–110°C/1 mmHg). Recrystallization of the distillation residue from hexane

afforded 350 mg (35%) of 1,4-bis(triphenylgermyl)butane, m.p. 195–196°C, whose mixture melting point with an authentic sample was undepressed.

*Triphenylvinylstannane (V)*. A solution of 2.0 g (5.3 mmol) of V and 370 mg (5.3 mmol) of *t*-butyl alcohol was added dropwise to a stirred suspension of 40 mg (5.7 mg-atom) of lithium dispersion in 30 ml of anhydrous tetrahydrofuran maintained at  $-78^{\circ}\text{C}$ . After stirring at the same temperature for 22 h and the usual hydrolytic work-up 1.5 g of a crude product was obtained whose IR and NMR spectra showed the presence of triphenylstannane (IR:  $1845\text{ cm}^{-1}$ , Sn—H; NMR:  $\delta$  6.8 ppm, s). Addition of hexane to this product precipitated a solid (m.p.  $> 360^{\circ}\text{C}$ ) that seemed to be polymeric. Attempted distillation under reduced pressure caused the deposition of tin metal.

*Triphenyl-1-propenylsilane (E/Z = 30/70) (XIII)*. To a vigorously stirred solution of 7.8 g (26 mmol) of XIII in 150 ml of anhydrous THF were added 200 mg (28 mg-atom) of lithium metal chips. As soon as the solution took on an orange color it was cooled to  $-78^{\circ}\text{C}$  and stirred at this temperature for 23 h. The mixture was then treated with water and 100 ml of ether and worked up in the foregoing manner. The resulting 6.4 g of crude product was chromatographed on 200 g of neutral alumina and elution was conducted with hexane/benzene mixtures. The starting material XIII was first eluted in pure condition (50%) and this was followed by intermediate fractions and finally by 12% of pure 2,3-dimethyl-1,4-bis(triphenylsilyl)butane (XVI), m.p. 165.5–166°C, from cyclohexane; IR ( $\text{CCl}_4$ ): 3060, 2975, 2900, 1430, 1160, 725 and  $702\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  7.1–7.6 (m, 10 H), 1.7–2.0 (m, 2 H), 1.15–1.30 (m, 4 H) and 0.76 (d,  $J = 6\text{ Hz}$  6 H); MS (70 eV)  $M/e$  598.

Anal.: Found: C, 83.94; H, 7.13. Calcd. for  $\text{C}_{42}\text{H}_{42}\text{Si}_2$ : C, 83.69; H, 6.97%.

Interestingly, the recovered XIII was shown to be a 50/50 mixture of the *E*- and *Z*-isomers. Moreover, the NMR spectrum of the crude product exhibited multiplets in the region  $\delta$  5.3–5.9 ppm, indicative of partial reduction or coupling of the phenyl groups.

*Cyclopropyltriphenylsilane (XXV)*. (a) *Lithium in tetrahydrofuran*. After a solution of 1.1 g (3.6 mmol) of XXV in 30 ml of anhydrous THF and 30 mg (4.6 mg-atom) of finely cut lithium chips had begun to form an orange color, the mixture was cooled to  $-78^{\circ}\text{C}$  and stirred at that temperature for 20 h. The usual hydrolytic work-up and the column chromatography on silica gel with a hexane eluent gave 4,4'-bis(cyclopropyldiphenylsilyl)-1,1',4,4'-tetrahydrobi-phenyl (XXVII). After recrystallization under a nitrogen atmosphere from diethyl ether, XXVII (89 mg, 80%) melted at 148–151°C; NMR ( $\text{CS}_2$ ):  $\delta$  8.47 (m, 10 H), 5.69 (br. d of d, 1 H), 5.2 (br. d of d, 1 H), 2.95 (br. d, 1 H) 2.17 (br. d, 1 H) 0.70 (2 H) and 0.17 (3 H). Anal.: Found: C, 83.49; H, 6.90. Calcd. for  $\text{C}_{42}\text{H}_{42}\text{Si}_2$ : C, 83.69; H, 6.97%.

Reaction of XXV (1.4 g, 4.6 mmol) in 25 ml of THF with 16.5 mg (23.5 mg-atom) of lithium dispersion for 45 h at 20–25°C gave upon hydrolytic work-up with 1 *N*  $\text{H}_2\text{SO}_4$ , 1.21 g of a yellow oil. Column chromatography on silica gel and elution with hexane provided 313 mg (30%) of cyclopropyl(diphenyl)silane (XXX); IR ( $\text{CCl}_4$ ): 3175, 3000, 2125, 1430, 1290, 1185, 1110, 1030 and  $930\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  7.0–7.75 (10 H) 4.71 (d,  $J$  3 Hz, 1 H) and 0.10–0.90 (m, 5 H). Anal.: Found: C, 80.21; H, 7.21. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{Si}$ : C, 80.29; H, 7.18%.

(b) *Potassium in 1,2-dimethoxyethane.* An analogous reaction of 1.1 g (3.6 mmol) of XXV in 25 ml of anhydrous and prepurified 1,2-dimethoxyethane with 200 mg of potassium metal for 25 h at  $-40^{\circ}\text{C}$  gave 50% of XXVII, m.p.  $149\text{--}150^{\circ}\text{C}$ ; IR( $\text{CS}_2$ ): 3050, 3000, 1405, 1100, 902, 826, 740 and  $705\text{ cm}^{-1}$ , with an NMR spectrum identical with the product of part (a).

Repetition of this reaction with work-up by  $\text{D}_2\text{O}$  yielded XXVIII, whose NMR spectrum lacked the broad doublet at 2.95 ppm and displayed a broad singlet at 2.17 ppm and a narrowed doublet at 5.69 ppm.

*Dehydrogenation of 4,4'-bis(cyclopropyldiphenylsilyl)-1,1',4,4'-tetrahydrobiphenyl (XXVII).* Heating 150 mg (0.30 mmol) of XXVII with 130 mg (0.60 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 15 ml of benzene for 6 h and diluting with petroleum ether (b.p.  $30\text{--}60^{\circ}\text{C}$ ) precipitated the hydroquinone of DDQ. The mixture was filtered, the filtrate evaporated and the residue recrystallized from diethyl ether to give 65 mg (44%) of 4,4'-bis(cyclopropyldiphenylsilyl)biphenyl (XXIX), m.p.  $159.5\text{--}160^{\circ}\text{C}$ ; IR ( $\text{CS}_2$ ): 3090, 1150, 810, 740 and  $700\text{ cm}^{-1}$ ; NMR( $\text{CS}_2$ ): 6.80–7.70 (m, 28 H), 0.50–1.0 (m, 4 H) and 0.15–0.40 (m, 6 H); MS (70 eV):  $M/e$  598 *P. Anal.*: Found: C, 84.09; H, 6.40. Calcd. for  $\text{C}_{42}\text{H}_{38}\text{Si}_2$ : C, 84.26; H, 6.34%.

*Trimethyl-*E*- $\beta$ -styrylsilane (XVII).* Freshly cut pieces of lithium metal (380 mg, 54.8 mg-atom) were added to a vigorously stirred solution of XVII (8.88 g, 54 mmol) in 125 ml of THF, which had been cooled to  $-78^{\circ}\text{C}$ . An additional amount of lithium (390 mg, 55 mg-atom) was added in three portions at 30 min intervals. After 14 h at  $-78^{\circ}\text{C}$  the reaction mixture was hydrolyzed in the usual way. The organic layer, augmented with ether, was washed with ether and dried over anhydrous  $\text{MgSO}_4$ . Removal of solvent and distillation provided 2.7 g (30%) of trimethyl-2-phenylethylsilane (XIX), b.p.  $55\text{--}60^{\circ}\text{C}/2\text{ mmHg}$ ; NMR:  $\delta$  7.25 (s, 5H), 2.51–2.90 (m, 2 H), 0.80–1.16 (m, 2 H) and 0.13 (s, 9 H). A second fraction, b.p.  $170\text{--}175^{\circ}\text{C}/2\text{ mmHg}$ , proved to be 1,4-diphenyl-2,3-bis-(trimethylsilyl)butane (XVIII), which upon recrystallization from methanol melted at  $65.5\text{--}66^{\circ}\text{C}$ ; IR ( $\text{CCl}_4$ ): no bands at 985 or  $1585\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  7.15 (s, 5 H), 2.45–3.20 (m, 2 H), 1.29–1.67 (m, 1 H) and 0.15 (s, 9 H). *Anal.*: Found: C, 74.59, H, 9.75. Calcd. for  $\text{C}_{22}\text{H}_{34}\text{Si}_2$ : C, 74.50; H, 9.66.

*Triphenyl-1-propynylsilane (XXXVIII).* (a) *Lithium in tetrahydrofuran.* To a suspension of 35 mg (5.0 mg-atom) of lithium dispersion in 30 ml of anhydrous THF was added XXXVIII (1.3 g, 4.37 mmol). After the mixture assumed a dark brown color, it was cooled to  $-78^{\circ}\text{C}$  and maintained there with stirring for 20 h. Hydrolytic work-up with 1 *N*  $\text{H}_2\text{SO}_4$  and addition of ether gave, after the usual treatment, 1.04 g of crude product, which was chromatographed on neutral alumina, with hexane as an eluent, to yield 230 mg (18%) of triphenyl-*E*-1-propenylsilane (XXXVII) (40%, from an NMR spectral integration of the crude product), m.p.  $92\text{--}93^{\circ}\text{C}$ ; IR ( $\text{CCl}_4$ ): 1610, 1425, 1105 and  $985\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  7.10–7.60 (m, 15 H), 6.1–6.3 (m, 2 H) and 1.91 (d, 3 H, *J* 4.5 Hz). Further elution with hexane afforded a 1/1 mixture of triphenyl-*E*- and *Z*-1-propenylsilane and unreacted XXXVIII.

(b) *Potassium in 1,2-dimethoxyethane.* An analogous reaction between 120 mg (3.0 mg-atom) of potassium metal and 750 mg (2.5 mmol) of XXXVIII in 25 ml of 1,2-dimethoxyethane at  $-78^{\circ}\text{C}$  for 21 h yielded, upon hydrolytic work-up, 90 mg (16%) of triphenylsilanol, m.p.  $151\text{--}152^{\circ}\text{C}$ , and triphenyl-



silane (400 mg, 53%); NMR ( $\text{CCl}_4$ ):  $\delta$  5.45 ppm.

*Tetraphenylsilane (XXXII)*. A solution of 5.0 g (14.8 mmol) of XXXII in 50 ml of 1,2-dimethoxyethane and 600 mg (15.3 mg-atom) of potassium metal shavings were stirred vigorously while being cooled to  $-78^\circ\text{C}$  for 21 h and then treated with 1 N  $\text{H}_2\text{SO}_4$ . Usual work-up gave 3.7 g of crude product. Because of the ease of air oxidation of the tetrahydro dimer (XXXIII) (38% based upon the NMR spectral integration of the vinyl multiplet centered at 5.5 ppm), a 2.49 g portion of crude product was allowed to react with 1.54 g (3.69 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 35 ml of refluxing benzene. After a reaction period of 12 h and the precipitation of the DDQ hydroquinone with petroleum ether (b.p.  $30-60^\circ\text{C}$ ) the filtrate was evaporated and the residue evaporated. Chromatography on neutral activated alumina and elution with hexane afforded 4,4'-bis(triphenylsilyl)biphenyl (XXXIV), m.p.  $289-290^\circ\text{C}$ , recrystallized from cyclohexane; IR ( $\text{CS}_2$ ): 3050, 1112, 900, 800 and 700  $\text{cm}^{-1}$ ; MS (70 eV):  $M/e$  670. Anal.: Found: C, 85.76; H, 5.37. Calcd. for  $\text{C}_{48}\text{H}_{38}\text{Si}_2$ : C, 85.92; H, 5.70%.

*Allyltriphenylsilane (XXXVI)*. (a) *Lithium at  $-78^\circ\text{C}$* . A solution of 2.1 g (7.1 mmol) of XXXVI in 35 ml of anhydrous THF and 50 mg (7.1 mg-atom) of lithium dispersion were allowed to react for 24 h at  $-78^\circ\text{C}$ . Usual hydrolysis and work-up gave a crude product, whose NMR spectrum showed it to be a 40/60 mixture of XXXVI and dimeric coupling product. Heating this product with 1.3 g (6.25 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 60 ml of benzene for 4 h and usual work-up yielded a mixture that was chromatographed on 60 g of neutral alumina with a hexane eluent. In this way 4,4'-bis(allyldiphenylsilyl)biphenyl was obtained, m.p.  $120-136^\circ\text{C}$ . Successive recrystallizations from a hexane/methanol pair raised the m.p. to  $150-151^\circ\text{C}$ ; IR ( $\text{CCl}_4$ ): 3050, 1450, 1250, 1162, 1000 and 905  $\text{cm}^{-1}$  ( $\text{CH}=\text{CH}_2$ ): NMR ( $\text{CCl}_4$ ):  $\delta$  6.80–7.40 (m, 14 H), 5.64 (m, 1 H), 4.30–4.58 (m, 2 H) and 2.27 (d, 2 H); MS (70 eV):  $M/e$  598,  $P$ , 557, 516. Anal.: Found: C, 84.26; H, 6.59. Calcd. for  $\text{C}_{42}\text{H}_{38}\text{Si}_2$ : C, 84.22; H, 6.39%.

(b) *Lithium at  $20-25^\circ\text{C}$* . An interaction of 50 mg (7.1 mg-atom) of lithium metal and 2.0 g (6.6 mmol) of XXXVI in 35 ml of anhydrous THF for 22 h at  $20-25^\circ\text{C}$  gave, upon the usual hydrolytic work-up, a crude oil that was chromatographed on neutral alumina using cyclohexane as an eluent. A mixture of triphenyl-*E*-1-propenylsilane (ca. 40%) and XXXVI was obtained. Repeated recrystallization of the former gave 585 mg (30%) of pure product, m.p.  $80-81^\circ\text{C}$ . Further chromatographic elution gave products that by IR and NMR spectral analysis appeared to be a mixture of silanols and propylsilanes.

*Trimethyl(E-3-methylbuta-1,3-dien-1-yl)silane (XX)*. A solution of 2.8 g (20 mmol) of XX in 75 ml of anhydrous THF was allowed to react with 154 mg (22 mg-atom) of lithium pieces at  $20^\circ\text{C}$  until a yellow color developed. The reaction mixture was then cooled to  $-78^\circ\text{C}$  and allowed to proceed for 8 h. After hydrolysis and usual work-up the crude oil was analyzed by gas chromatography on a 12 ft silicone gum rubber column. Of the five high-boiling components the major one was collected and shown to have a parent peak at 282 in the mass spectrum and an NMR spectrum in agreement with the structure of XXII.

*Dimethylbis(E-3-methylbuta-1,3-dien-1-yl)silane (XXI)*. A mixture of 1.0 g

(5.2 mmol) of XXI and 400 mg (5.4 mmol) of *t*-butyl alcohol was added dropwise over 60 min to a suspension of 75 mg (10.7 mg-atom) of finely cut lithium metal in 70 ml of anhydrous THF with the maintenance of vigorous stirring at  $-78^{\circ}\text{C}$ . After a 20 h stirring period at this temperature the usual hydrolytic work-up was undertaken. Distillation gave 620 mg (62%) of a 67/33 mixture of dimethylbis(3-methylbut-2-en-1-yl)silane (XXIII) and a positional isomer (GC). Gas chromatographic separation yielded XXIII; IR( $\text{CCl}_4$ ): 2990, 1245 and  $1160\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  5.28 (t, 2 H, br), 1.82 (s, 6 H), 1.70 (s, 6 H), 1.54 (d, 4 H,  $J$  8 Hz) and 0.10 (s, 6 H). The other isomer had the following properties: IR( $\text{CCl}_4$ ): 2990, 1245 and  $1160\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ):  $\delta$  5.30–6.32 (m, 3 H), 2.25 (m, 1 H), 1.65 (s, 3 H), 1.57 (s, 3 H), 1.45 (d, 2 H, br), 1.10 (d, 6 H,  $J$  7 Hz) and 0.01 (s, 6 H); MS (70 eV):  $M/e$  196 P, 127, 99, 85 and 73 (XXIV).

*Préparation of cyclopropyldiphenylsilane (XXX).* Cyclopropylmagnesium bromide, which was prepared from 4.7 g (38.8 mmol) of cyclopropyl bromide and magnesium turnings in 35 ml of anhydrous THF, was added dropwise to a solution of 10.0 g (40 mmol) of dichlorodiphenylsilane in 50 ml of THF over a period of 4 h. The mixture was stirred at  $25^{\circ}\text{C}$  for 25 h and at reflux for 5 h. Hydrolysis and usual work-up gave 4.3 g (46%) of crude cyclopropyldiphenylsilanol; IR ( $\text{CCl}_4$ ): 3750, 3350, 3100, 1435, 1120 and  $900\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ): 7.40–7.75 (m, 10 H), 4.18 (s, 1 H), 0.10–0.79 (m, 5 H).

This crude product in 50 ml of THF was added dropwise to a well-stirred solution of  $\text{LiAlH}_4$  (3.0 g, 80 mmol) in 50 ml of THF. The mixture was stirred for 90 min at  $25^{\circ}\text{C}$  and 24 h at reflux. Treatment with water and ether and usual work-up gave a crude oil whose distillation gave a fraction, b.p.  $145\text{--}155^{\circ}\text{C}/0.1\text{ mmHg}$ . Column chromatography on 30 g of silica gel using hexane as an eluent gave 600 mg (18%) of cyclopropyldiphenylsilane, whose spectral properties agreed with those found for XXX (cf. supra).

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### References

- 1 H.F. Ebel and A. Lüttringhaus, in E. Müller (Ed.), *Methoden der Organischen Chemie*, Vol. XIII/1, George Thieme Verlag, 1970, pp. 422–430.
- 2 J.J. Eisch, *The Chemistry of Organometallic Compounds*, Macmillan, New York, 1967, pp. 13–17.
- 3 J.J. Eisch and R.J. Beuhler, *J. Org. Chem.*, **28** (1963) 2876.
- 4 D. Seyferth, L.G. Vaughan and R. Suzuki, *J. Amer. Chem. Soc.*, **88** (1966) 286.
- 5 H. Bock and H. Seidl, *J. Organometal. Chem.*, **13** (1968) 87.
- 6 P. Mollère, H. Bock, G. Becker and G. Fritz, *J. Organometal. Chem.*, **46** (1972) 89.
- 7 (a) S.P. Solodovnikov and E.A. Chernyshev, *J. Struct. Chem (USSR. Eng. trans.)*, **3** (1962) 642; (b) J.A. Bedford, J.R. Bolton, A. Carrington and R.H. Prince, *Trans. Faraday Soc.*, **59** (1963) 53; (c) R.D. Cowell, G. Urry and S.I. Weissman, *J. Amer. Chem. Soc.*, **85** (1963) 822; (d) A.L. Allred and L.W. Bush, *J. Amer. Chem. Soc.*, **90** (1968) 3352; (e) H. Bock, H. Alt, F. Gerson and J. Heinzer, *Angew. Chem., Intern. Ed.*, **6** (1967) 941.
- 8 F. Gerson, J. Heinzer, H. Bock, H. Alt and H. Seidl, *Helv. Chim. Acta*, **51** (1968) 707.
- 9 (a) T.R. Tuttle and S.I. Weissman, *J. Amer. Chem. Soc.* **80** (1958) 5342; (b) M.G. Townsend and S.I. Weissman, *J. Chem. Phys.*, **32** (1960) 309; (c) J.R. Bolton and A. Carrington, *Mol. Phys.*, **4** (1961) 497; (d) J.R. Bolton, A. Carrington, A. Forman and L.E. Orgel, *Mol. Phys.*, **5** (1962) 43.

- 10 (a) H.M. McConnell, *J. Chem. Phys.*, 24 (1956) 764; (b) H.M. McConnell and D.B. Chestnut, *J. Chem. Phys.*, 28 (1958) 107.
- 11 J.J. Eisch and G. Gupta, *J. Organometal. Chem.*, 20 (1969) P9.
- 12 C.J. Attridge, *Organometal. Chem. Rev. A*, 5 (1970) 323.
- 13 J.J. Eisch and G. Gupta, *J. Organometal. Chem.*, 50 (1973) C23.
- 14 L.E. Smith, Doctoral Dissertation, The Catholic University of America, Washington, D.C., 1972.
- 15 J.J. Eisch and L.L. Libit, unpublished results, University of Michigan, 1962.
- 16 (a) J.J. Eisch, D.D. Kaska and C.J. Peterson, *J. Org. Chem.*, 31 (1966) 463; (b) A.G. Evans, J.C. Evans and T.J. Phelan, *J. Chem. Soc. Perkins II*, (1974) 1216.
- 17 H. Gilman and R.D. Gorsich, *J. Amer. Chem. Soc.*, 77 (1955) 6380.
- 18 H.O. House, *Modern Synthetic Reactions*, W.A. Benjamin, Menlo Park, Calif., 2nd ed., 1972, pp. 145-227.
- 19 J.J. Eisch and L.E. Smith, *J. Organometal. Chem.*, 50 (1973) C18.
- 20 (a) M. Swarc, M. Levy and R. Milkovich, *J. Amer. Chem. Soc.*, 78 (1956) 2656; (b) G. Geacintov, J. Smid and M. Swarc, *J. Amer. Chem. Soc.*, 84 (1962) 2508.
- 21 (a) D.H. Richards, N.F. Scully and F.J. Williams, *Chem. Ind.*, (1970) 1298; (b) J.F. Garst and J.A. Pacifici, *J. Amer. Chem. Soc.*, 97 (1975) 1802; (c) G. Levin, C. Sutphen and M. Swarc, *J. Amer. Chem. Soc.*, 94 (1972) 2652; (d) E.R. Minnich, L.D. Long, J.M. Ceraso and J.L. Dye, *J. Amer. Chem. Soc.*, 95 (1973) 1061.
- 22 E.J. Corey and H.A. Kirst, *Tetrahedron Lett.*, (1968) 5041.
- 23 R.J.P. Corriu, J. Masse and D. Samate, *J. Organometal. Chem.*, 93 (1975) 71.
- 24 J.J. Eisch and W.C. Kaska, *J. Org. Chem.*, 27 (1962) 3745.
- 25 H. Gilman and D. Aoki, *J. Organometal. Chem.*, 2 (1964) 89.
- 26 A.D. Petrov and L.L. Shehukovskaya, *Zh. Obshch. Khim.*, 25 (1955) 1083.
- 27 D. Seyferth and M.A. Weiner, *J. Org. Chem.*, 26 (1961) 4791.
- 28 I.A. Shikhiev, M.F. Shostakovskii and L.A. Kayutenko, *Zh. Obshch. Khim.*, 29 (1959) 2137.
- 29 J.J. Eisch and M.W. Foxton, *J. Org. Chem.*, 36 (1971) 3520.
- 30 R.A. Benkeser, Y. Nagai, J.L. Noe, R.F. Cunico and P.H. Gund, *J. Amer. Chem. Soc.*, 86 (1964) 2446.
- 31 E. Grovenstein, Jr., in F.G.A. Stone and R. West (Ed.), *Advances in Organometallic Chemistry*, Vol. 16, Academic Press, New York, 1977, pp. 199-202.