# STERIC EFFECTS AND π-BONDING IN ORGANOSILICON CHEMISTRY: THEIR ASSESSMENT BY MEANS OF COMPARATIVE ORGANIC CHEMISTRY OF CARBON AND SILICON

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The subject of C→ Si π-bonding, i.e. overlap between a filled carbon $sp^n$ hybrid orbital or a carbon $p$-orbital and a vacant silicon $3d$ orbital has been of some interest during the past 12 years. Despite all the attention devoted to the subject[1], the question of precisely what contributions such π-bonding can and does make to organosilicon reactions remains without a satisfactory answer. It has become rather common practice to attribute unusual stabilities of various organosilicon structures, unexpected lack of reactivity of organosilicon compounds and other anomalies of organosilicon chemistry to the intervention of such π-bonding if an at all reasonable case can be made in its support. In some of these cases the explanation presented no doubt is the correct one; in others it is not. C→ Si π-bonding has not yet been put on a quantitative basis, and in fact, it is not always certain whether the physical data purported to support such π-bonding in organo-silicon compounds do indeed provide proof for this concept as conclusively as is claimed. It is, in fact, dangerous to postulate such π-bonding on the limited basis of observed chemical reactivity of organosilicon structures alone. Only if the behaviour of the analogous carbon structure has been examined and found to be different, does such a postulate rest on any half-way firm basis.

The reason that such precautions of "comparative organic chemistry" of silicon and carbon are advisable is that steric factors are often of overriding importance in organosilicon chemistry. One may find "anomalous" behaviour in the reactions of a functional organic substituent attached to a silicon atom, but this silicon atom always bears three other substituents. In most cases these are organic groups, very often three methyl groups, and the steric consequences of their presence (i.e. of the bulky triorganosilyl group) are what determine the "anomalous" reactivity that is observed for the functional substituent, rather than a π-bonding effect. If such "anomalous" reactivity also is found in the analogous carbon compound, then an explana-tion in terms of π-bonding in the organosilicon case in most cases is unten-able. If, on the other hand, the behaviour of the organosilicon system is truly "anomalous" when compared with the behaviour of the analogous

carbon structure under identical conditions, then $\pi$-bonding in the organosilicon case may well be the important factor. At any rate, further experiments designed to provide additional information on this question will have some purpose.
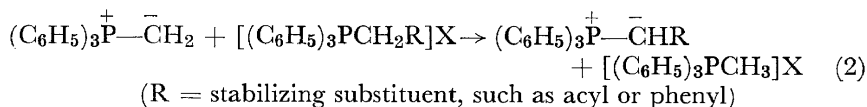
It is the purpose of this paper to stress the importance of steric effects in organosilicon chemistry and to present two examples of the "comparative organic chemistry" of carbon and silicon from our research of the past two years. In both cases, an initial postulation of $\pi$-bonding in an organosilicon system seems to provide a satisfactory explanation of the organosilicon reaction observed, but only in one case did such an explanation remain worth pursuing after the analogous carbon compound reactions had been investigated.
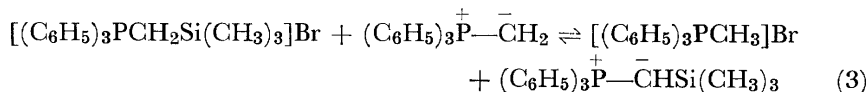
## I. TRIPHENYLPHOSPHINETRIMETHYLSILYLMETHYLENE

In 1961, we reported on the nucleophilic displacement of halide ion from various Group IVB organometallic halides by triphenylphosphinemethylene[2]. In the case of trimethylbromosilane, for instance, the reaction was formulated as given in equation (1).

$$(C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}H_2 + (CH_3)_3SiBr \rightarrow [(C_6H_5)_3PCH_2Si(CH_3)_3]Br \qquad (1)$$
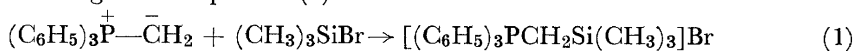
Characteristic of most of these reactions was the presence of methyltriphenylphosphonium bromide during crystallization of the crude products from aqueous solution. In 1962, Bestmann[3] discovered that proton transfer from a phosphonium salt to a phosphinealkylidene reagent ("transylidation") occurs readily and that formation of the more highly stabilized phosphinealkylidene reagent is favoured
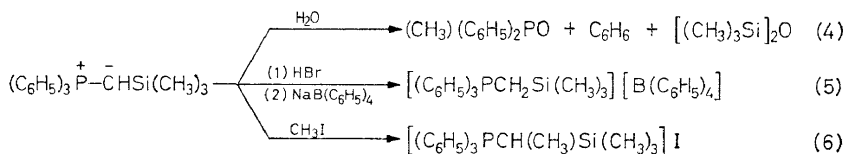
$$(C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}H_2 + [(C_6H_5)_3PCH_2R]X \rightarrow (C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}HR$$
$$+ [(C_6H_5)_3PCH_3]X \qquad (2)$$

$$(R = \text{stabilizing substituent, such as acyl or phenyl})$$

In these Laboratories it was demonstrated[4] that such transylidations were equilibrium processes, and that in the system involving triphenylphosphinemethylene and triphenylphosphineethylidene and their respective phosphonium salts, the $(C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}H_2/(C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}HCH_3$ ratio was about 17. A consideration of the facility with which such transylidations proceed prompted us to reexamine the triphenylphosphinemethylene-trimethylhalosilane reaction as a representative case of those reactions studied previously[2]. It seemed possible that the complications encountered in the isolation of pure $[(C_6H_5)_3PCH_2Si(CH_3)_3]Br$ may have been due to intervening transylidation equilibria, that is, reaction (1) may have been followed by reaction (3). Thus on working up with aqueous hydrobromic acid a mixture of methyl- and trimethylsilylmethylphosphonium halides would result.

$$[(C_6H_5)_3PCH_2Si(CH_3)_3]Br + (C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}H_2 \rightleftharpoons [(C_6H_5)_3PCH_3]Br$$
$$+ (C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{C}HSi(CH_3)_3 \qquad (3)$$

A transylidation such as reaction (3) was considered a distinct possibility. Although one would expect the $+I$ inductive effect of the trimethylsilyl group to destabilize the silicon-substituted phosphinealkylidene relative to
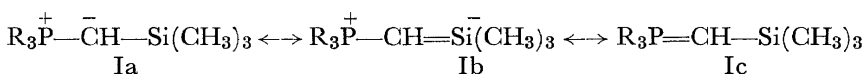
triphenylphosphinemethylene, a stabilization of the former by delocalization of negative charge into the silyl substituent by $p_\pi$—$d_\pi$ overlap also seemed a possibility. For this reason, the action of triphenylphosphinemethylene on (trimethylsilylmethyl)triphenylphosphonium iodide was studied.

It was found that virtually quantitative transylidation occurred when triphenylphosphinemethylene and (trimethylsilylmethyl)triphenylphosphonium iodide were stirred in 1 : 1 molar ratio in ether at room temperature for 15 h. Filtration of the reaction mixture gave methyltriphenylphosphonium iodide in nearly 100 per cent yield. The formation of triphenylphosphinetrimethylsilylmethylene and its presence in the yellow filtrate were demonstrated by the reactions given in equations (4) to (6).

$$(C_6H_5)_3 \overset{+}{P}-\overset{-}{C}HSi(CH_3)_3$$

$$\xrightarrow{\;H_2O\;} (CH_3)(C_6H_5)_2PO + C_6H_6 + [(CH_3)_3Si]_2O \quad (4)$$

$$\xrightarrow[\text{(2) NaB}(C_6H_5)_4]{\text{(1) HBr}} \left[(C_6H_5)_3PCH_2Si(CH_3)_3\right]\left[B(C_6H_5)_4\right] \quad (5)$$

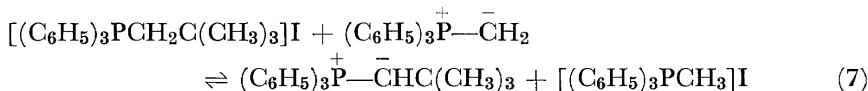$$\xrightarrow{\;CH_3I\;} \left[(C_6H_5)_3PCH(CH_3)Si(CH_3)_3\right]I \quad (6)$$

Thus our original preparative procedure was indeed complicated by competition of as yet unreacted trimethylbromosilane and already formed (trimethylsilylmethyl)triphenylphosphonium bromide for the phosphinemethylene reagent as it was being added.

It was of interest to inquire why the transylidation studied [reaction (3), but with I⁻ as the halide ion] proceeded essentially quantitatively as written, i.e. what factors contributed to the preferential formation of the silylsubstituted phosphinemethylene. An explanation involving C→ Si πbonding seemed attractive as well as fashionable in terms of current ideas about bonding in organosilicon compounds. Indeed, Miller[5] reported recently the isolation of trimethylphosphine-trimethylsilylmethylene as a colourless liquid and wrote resonance structures Ia, Ib and Ic (R = $CH_3$)

$$R_3\overset{+}{P}-\overset{-}{C}H-Si(CH_3)_3 \longleftrightarrow R_3\overset{+}{P}-CH=\overset{-}{S}i(CH_3)_3 \longleftrightarrow R_3P=CH-Si(CH_3)_3$$
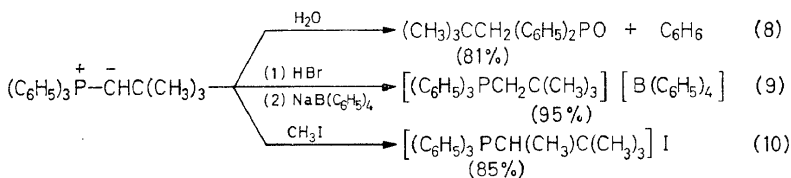$$\quad Ia \qquad\qquad\qquad Ib \qquad\qquad\qquad Ic$$

to describe this molecule. It is, however, as mentioned before, dangerous to interpret the results of reactions of organosilicon species in terms of πbonding effects if the possibility of steric effects being operative has not been eliminated. In the present case we are dealing with a "siliconeopentyl"phosphonium salt in which the quaternary silicon and phosphorus atoms separated by only a methylene group, and in such a structure one may find unusual reactivity caused not by electronic factors, but rather by steric factors. To obtain further information relating to this question, we prepared neopentyltriphenylphosphonium iodide [$(C_6H_5)_3PCH_2C(CH_3)_3$]I, the carbon analogue in whose derived phosphinealkylidene analogous π-bonding effects (i.e. Ib, with Si replaced by C) would not be operative, and examined its reaction with triphenylphosphinemethylene.

As in the case of the silicon analogue, transylidation between triphenyl-phosphinemethylene and neopentyltriphenylphosphonium iodide proceeded essentially quantitatively as shown in equation (7). After the methyl-

$$[(C_6H_5)_3PCH_2C(CH_3)_3]I + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2$$

$$\rightleftharpoons (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HC(CH_3)_3 + [(C_6H_5)_3PCH_3]I \qquad (7)$$

triphenylphosphonium iodide (yield 90–95 per cent) had been filtered, the deep orange filtrate was quenched in three separate experiments with water, anhydrous hydrogen bromide and methyl iodide in order to establish the identity of the species present in solution. The results are given in the following equations.
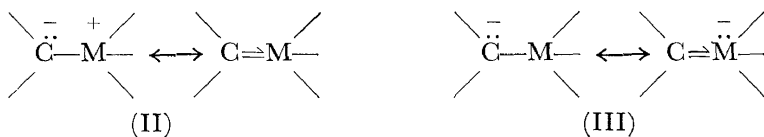


$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HC(CH_3)_3 \begin{cases} \xrightarrow{H_2O} (CH_3)_3CCH_2(C_6H_5)_2PO + C_6H_6 \qquad (8) \\ \qquad\qquad\qquad (81\%) \\ \xrightarrow[(2) NaB(C_6H_5)_4]{(1) HBr} \left[(C_6H_5)_3PCH_2C(CH_3)_3\right]\left[B(C_6H_5)_4\right] \qquad (9) \\ \qquad\qquad\qquad (95\%) \\ \xrightarrow{CH_3I} \left[(C_6H_5)_3PCH(CH_3)C(CH_3)_3\right]I \qquad (10) \\ \qquad\qquad\qquad (85\%) \end{cases}$$

On the basis of inductive effects alone, one would not expect triphenyl-phosphine-*tert*-butylmethylene to be favoured in an equilibrium as described by equation (7). As mentioned above, in transylidations triphenylphosphi-nemethylene is favoured over triphenylphosphineethylidene, and further experiments showed that triphenylphosphinemethylene is favoured over triphenylphosphineisopropylidene and triphenylphosphineisobutylidene. However, the adjacent quaternary phosphorus and carbon centres in neo-pentyltriphenylphosphonium iodide should cause severe steric crowding of the methylene protons. It is possible that such crowding could elongate the methylene C—H bonds. The result would be a weaker methylene C—H bond and an increased acidity of the methylene protons*. Furthermore, loss of a methylene proton in conversion to triphenylphosphine-*tert*-butyl-methylene should help to relieve this crowding. The structure of a phosphine-alkylidene in which the negative charge on the methylene carbon can only be displaced into phosphorus $d$ orbitals by a $\pi$-bonding mechanism has yet to be determined, and so no information is available concerning the geo-metry of substituents on the methylene carbon (a planar or nonplanar



system?). Any deviation of the methylene carbon hybridiza-

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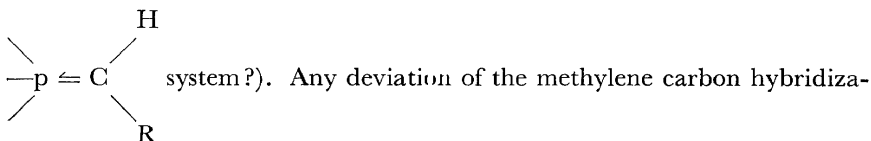
* An explanation in terms of an elongation of the N—H bond in phosphoramides of type

$$O{=}P{-}NH{-}R^2$$

with $R^1$ and $R$ attached to P, as the bulk of $R^2$, due to increasing branching, increased was given to account for the decrease of $\nu_{N-H}$ from 3441 cm$^{-1}$ for $R^2{=}CH_3$ to 3418 cm$^{-1}$ for $R^2 = $ iso-propyl to 3400 cm$^{-1}$ for $R^2 = $ *tert*-butyl[6].

tion from $sp^3$ (as it must be in the phosphonium salt) toward ($sp^2 + p$) as a result of C→ P π-overlap also would contribute to the relief of steric crowding at the methylene carbon. We conclude that in reaction (7) we are dealing with a case of "steric assistance"[7].

With the larger silicon atom (covalent radius 1·17 Å vs. carbon's 0·77 Å) in the (trimethylsilylmethyl)triphenylphosphonium salt such "steric assistance" in reaction (3) should not be as great as in the case of the neopentyl compound, but the steric factor still should result in a noticeable effect. It is not possible to assess the individual contributions of such a steric effect and C→ Si π-bonding of the type mentioned to the observed transylidation reaction. We feel, however, that the π-bonding contribution is much less important than the steric factor. Of the two possibilities for delocalizing negative charge on the methylene carbon atom, Ib and Ic (R = phenyl), the latter should be more important by far, since by C→ P π-bonding one is neutralizing the positive charge on phosphorus, while by C→ Si π-bonding one is placing excess charge on a silicon atom whose three other substituents cannot help with the accommodation of this negative charge. The greater importance of π-bonding in a system such as (II) as compared to π-bonding in a system such as (III) is well documented.



$$\overset{\displaystyle -}{\underset{\diagup\hspace{0.5em}\diagdown}{\text{C}}}\!\!-\!\!\overset{\displaystyle +}{\underset{\diagdown\hspace{0.5em}\diagup}{\text{M}}}\!\!-\ \longleftrightarrow\ \underset{\diagup\hspace{0.5em}\diagdown}{\text{C}}\!\!=\!\!\underset{\diagdown\hspace{0.5em}\diagup}{\text{M}}\!\!- \qquad\qquad \overset{\displaystyle -}{\underset{\diagup\hspace{0.5em}\diagdown}{\text{C}}}\!\!-\!\!\underset{\diagdown\hspace{0.5em}\diagup}{\text{M}}\!\!-\ \longleftrightarrow\ \underset{\diagup\hspace{0.5em}\diagdown}{\text{C}}\!\!=\!\!\overset{\displaystyle -}{\underset{\diagdown\hspace{0.5em}\diagup}{\ddot{\text{M}}}}\!\!-$$

(II)                                                 (III)

As one example may be cited the extremely facile Michael-type additions of nucleophilic reagents to vinylsulphonium[8] and vinylphosphonium[9, 10] salts as compared with the much more sluggish (but still significant) addition of nucleophiles to vinylsilanes[11]. In a system where an alkyl-substituted, neutral silicon atom and a positively charged phosphorus atom are adjacent to a carbon atom bearing a lone electron pair, charge delocalization should occur principally from carbon to phosphorus (form Ic). We conclude that C→ Si π-bonding is not a decisive factor in the stabilization of triphenylphosphinetrimethylsilylmethylene.


## II. LITHIUM-INDUCED ISOMERIZATION OF PROPENYLTRIMETHYLSILANE, -GERMANE AND -TIN

A study of the action of metallic lithium on tetra-*cis*- and tetra-*trans*-propenyltin in diethyl ether showed that isomerization of propenyl groups attached to tin occurred in addition to the expected metal displacement reaction (equation 11)[12].

$$(CH_3CH{=}CH)_4Sn + 4\ Li \longrightarrow 4\ CH_3CH{=}CHLi + Sn \qquad (11)$$
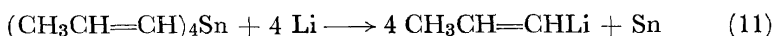
This interesting observation prompted a study of the action of metallic lithium on the propenyltrimethyl derivatives of carbon, silicon, germanium and tin.

Neither *cis*- nor *trans*-4,4-dimethyl-2-pentene (propenyltrimethylmethane) was isomerized by the action of lithium dispersion containing 2 per cent sodium in tetrahydrofuran, nor were any higher boiling products formed. In diethyl ether solution neither pure lithium nor sodium-containing lithium caused any isomerization of the pure *cis* or *trans* isomers of propenyltrimethylsilane[13] or propenyltrimethylgermane[13] during a 28 day contact time. In tetrahydrofuran, however, lithium dispersion caused isomerization of *cis*-propenyltrimethylsilane to the pure *trans* isomer within six hours. The *trans* isomer was itself unaffected with respect to isomerization by lithium in this solvent. In both cases, after hydrolysis, the recovery of propenyltrimethylsilane was only 45–50 per cent, and other products were present as well. *n*-Propyltrimethylsilane was formed in low yield. Three high boiling organosilicon compounds were isolated, but were not identified. It was established during their attempted characterization that they were not reductive dimerization products which might have been expected, either 1,4-bis-(trimethylsilyl)-2,3-dimethylbutane or 3,4-bis(trimethylsilyl)hexane.
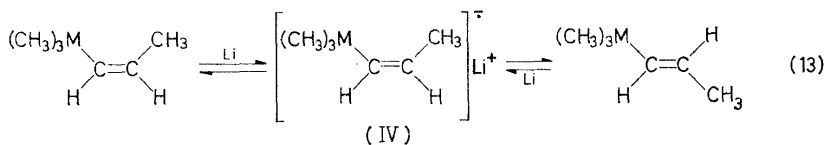
In tetrahydrofuran both propenyltrimethylgermane isomers were converted by the action of lithium dispersion to an equilibrium mixture containing 92 per cent *trans* and 8 per cent *cis*-propenyltrimethylgermane. Here, however, recovery of propenyltrimethylgermane was high (80–86 per cent), and neither *n*-propyltrimethylgermane nor high boiling organogermanium compounds were found.

Propenyltrimethyltin (in contrast to tetrapropenyltin) did not undergo metal displacement when treated with metallic lithium in diethyl ether medium. In this solvent pure lithium or sodium-containing lithium (2 per cent maximum) caused a relatively rapid isomerization of both *cis*- and *trans*-propenyltrimethyltin to an equilibrium mixture composed of 79 per cent of the *trans* isomer and 21 per cent of the *cis* isomer. In tetrahydrofuran, on the other hand, complete destruction of the propenyltrimethyltin resulted on treatment with lithium at room temperature. The reaction mixture was in this case quenched with triethylchlorosilane and hydrolyzed. Among the products identified (in the case of *cis*-propenyltrimethyltin) were *cis*- (38 per cent yield) and *trans*-propenyltriethylsilane (23 per cent yield), triethylmethylsilane (18 per cent) and triethylsilyltrimethyltin (45 per cent), in addition to higher boiling products not isolated in the pure state. These products indicated that the displacement reaction of tetraorganotin compounds by lithium occurs stepwise. In the present case the first step involved formation of propenyllithium and trimethyltinlithium (equation 12).

$$(CH_3)_3SnCH{=}CHCH_3 + 2\ Li \longrightarrow (CH_3)_3SnLi + CH_3CH{=}CHLi \quad (12)$$
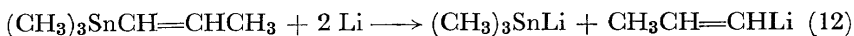
Methyllithium could be formed either by further attack by lithium on trimethyltinlithium or by partial methyl group displacement from propenyltrimethyltin.

The results of this study were consistent with an isomerization mechanism involving a radical anion intermediate (IV) (equation 13), in which an electron has been donated from a lithium atom into a $\pi$-antibonding orbital of the olefin. The resulting weakening of the $C_{2p}$—$C_{2p}$ $\pi$ overlap would permit rotation about the C—C axis, and isomerization could occur.

$$\underset{H}{\overset{(CH_3)_3M}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}} \quad \xrightarrow{\text{Li}} \quad \left[\underset{H}{\overset{(CH_3)_3M}{\diagdown}}C=C\underset{H}{\overset{CH_3}{\diagup}}\right]^{\overline{\cdot}}Li^+ \quad \underset{\overline{\text{Li}}}{\rightleftharpoons} \quad \underset{H}{\overset{(CH_3)_3M}{\diagdown}}C=C\underset{CH_3}{\overset{H}{\diagup}} \qquad (13)$$

$$(IV)$$

Alkali metal-induced isomerization of olefins is rare. The isomerization of *cis-* to *trans-*stilbene by lithium in tetrahydrofuran and similar isomerization of *cis-cis* and *cis-trans*-1,2,3,4-tetraphenylbutadiene to the *trans-trans* isomer was reported recently by Doran and Waack[14], and for those cases a radical anion mechanism was proposed. The observed isomerization of the propenyl compounds of silicon, germanium and tin (but not of carbon) by the action of metallic lithium suggests that the radical anions formed in these cases are stabilized in some manner. The formation of the radical anion from tri-phenylvinylsilane (*via* lithium in tetrahydrofuran at −75°C.) and the reductive dimerization of the latter species (giving $(C_6H_5)_3Si(CH_2)_4$—$Si(C_6H_5)_3$ after hydrolysis) have been described recently[15], and stabilization of the radical anion by C→ Si π-interaction was discussed.

$$(C_6H_5)_3Si\overset{\ominus}{-}\overset{\cdot}{C}H-\overset{\cdot}{C}H_2 \quad \longleftarrow \;\;- \quad (C_6H_5)_3\overset{\ominus}{Si}\dot{=}CH-\dot{C}H_2$$

The uninegative radical anions derived from 4-trimethylsilyl- and 4-tri-methylgermylbiphenylene have been studied by Curtis and Allred using electron spin resonance spectroscopy and oscillopolarographic analysis[16]. The e.s.r. spectra were interpreted and discussed in terms of a simple molecular orbital model involving $d$ orbitals of the group-IV substituent; and for the C—Si and C—Ge bonds, π-bond orders of 0·18 and 0·13, respectively, were calculated. Thus it seems reasonable to suggest that the decisive factor which permits isomerization of the propenyl compounds of silicon, germanium, and tin, but not of carbon, is the stabilization through $d\pi$—$p\pi$ bonding of the radical anions of the former. Such stabilization is, of course, not possible for the radical anion derived from propenyltrimethyl-methane, carbon not having available $d$ orbitals of suitably low energy, and thus electron transfer may not be energetically favourable in this particular system.

The fact that reduction or reductive dimerization products were obtained not at all or only in low yield suggests that only a small fraction of the olefin was converted to its radical anion. However, this is sufficient for complete isomerization to occur with time through electron transfer reactions between radical anion and olefin. (A concise discussion of the mechanism for geo-metric isomerization of olefins *via* their radical anions is given in the paper by Doran and Waack[14])

In summary, we have presented two cases of reactions of silicon com-pounds in which the observations made on the silicon compounds alone could be explained in terms of the action of C→ Si π-bonding. Control experiments with the analogous carbon compounds were carried out in both cases, and in one case strong evidence was obtained in this manner that steric factors, not π-bonding effects, in fact bore major responsibility for the observations made. We suggest that any time that reactions of a nearby

functional group in a substituent Z in an $R_3SiZ$ compound are studied, steric factors will be important and, in many cases, will swamp out completely the electronic effects one might have hoped to study. Ideally, such investigations should be carried out with $H_3SiZ$ compounds so as to avoid these complicating steric factors. The problems associated with this approach are, however, severe due to synthetic difficulties and also from the point of view of the high reactivity of the $H_3Si$ group.

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