Thus, the unquenched product ratio is

$$R_u = \frac{\Phi_{10}}{\Phi_{12}} = \frac{\mathbf{10}}{\mathbf{12}} = \frac{k_1(k_{dt} + k_3)}{k_3 k_{ISC}}$$

Since the quantum yield for production of **12** in the presence of quencher is

$$\Phi_{12} = \frac{k_3 k_{ISC}}{(k_{dt} + k_3 + k_q[Q])(k_{ds} + k_1 + k_{ISC})}$$

the quenched product ratio becomes

$$R_q = \frac{\Phi_{10}}{\Phi_{12}} = \frac{\mathbf{10}}{\mathbf{12}} = \frac{k_1(k_{dt} + k_3 + k_q[Q])}{k_3 k_{ISC}}$$

Thus, the ratio of the quenched and unquenched quantum yield or the product ratios will depend upon the quencher concentration according to eq 1.

If the original assumptions are correct, *i.e.*, that photoproduct **10** results from the singlet and **12** from the triplet of **5**, a plot of R_q/R_u *vs.* quencher concentration should be that of a straight line.

The Kinetics, Stereochemistry, and Mechanisms of the Silaallylic and Silapropynylic Rearrangements

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Abstract: The unimolecular, gas-phase reaction kinetics of the silaallylic rearrangement, the complete absence of β-substituent rate effects, the lack of influence on the activation parameters in substituting phenyl for methyl at the silicon reaction center, and the failure to realize a bimolecular isomerization mode all point to a concerted, symmetrical transition state of silicon migration. The only substituent rate effects observed are readily correlated with steric strain relief (in the α position of the allyl side chain) and conjugation influences which reflect in the transition state the energy differences between products and reactants. These results stand in sharp contrast to those noted in the thiaallylic rearrangement where d orbital involvement in the formation of a dipolar reaction intermediate has been implicated. Stereochemical studies using optically active as well as deuterium labeling of the course of rearrangement show that every act of migration is accompanied by inversion of the silicon configuration. This indicates a preference for utilizing a 3p orbital in bridging the allylic structure with conservation of orbital symmetry. It is the first case of 1,3 or 1,5 migration of silicon in which the preference for 3p orbital utilization has been identified. The corresponding silapropynylic rearrangement involving silicon migration across the termini for a propargyl–allenyl grouping has also been realized (for the first time) in these investigations. The kinetic characteristics of this reaction indicate a symmetrical, concerted transition state, similar in all respects to the silaallylic rearrangement despite the need for bending of the propargyl–allenyl framework in the activation step. Moreover, stereochemical studies confirm that the process of migration again takes place with complete inversion of the silicon configuration, apparently uncontaminated by any competing pathways which might lead to retention and racemization. A carboallylic migration in simple olefinic analogs of silaallylic substrates does not take place with sufficient mobility to compete with homolytic fragmentation reactions. The vastly greater activation barrier of the carboallylic *vs.* the silaallylic perhaps may be correlated with the dissociation energy of the critical bond of the sigmatropic process.

The identification of a 1,3 sigmatropic migration of silicon in allylsilanes has been reported[1] in a preliminary communication. Therein, also, the importance of determining the stereochemistry of the rearrangement course was pointed out. Orbital symmetry[2] considerations require that thermal, suprafacial 1,3 rearrangements[3] of carbon undergo inversion of configuration at the migrating center in a process involving both lobes of an antisymmetric 2p orbital. On the other hand, 1,5 migrations[4] proceed with retention of configuration in utilizing only one lobe of the 2p orbital.

For migrations of silicon, the group IVb neighbor of carbon, the situation is more complex because of the availability of low-lying, empty 3d orbitals, and schemes which predict either retention or inversion can be readily conceived. The involvement of the analogous 3d orbitals in sulfur has been established[5] in the case of

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the formally related thiaallylic rearrangement of phenyl allyl sulfides.

Prior to the earlier communication[1] only the 1,5 migrations[6,7] of silicon along a carbon skeleton had been known. However, no stereochemical studies of the nature carried out for the analog rearrangements of carbon, by means of which the essential orbital transformations in the silicon isomerizations might be characterized, have yet been reported. It was apparent from these examples, furthermore, that silicon possessed superior migratory abilities which qualified it as a good candidate for observing a 1,3 shift in a simple acyclic, allylic substrate. For instance, in 1,5 rearrangements of 5-substituted cyclopentadienes $\Delta G^{\ddagger}_{300^\circ\mathrm{K}} = 15.2$ (kcal/mol) for silicon migration,[6b] 22.2 for hydrogen,[8] and 41.8 for carbon (methyl);[9] for 1-substituted indenes $\Delta G^{\ddagger}_{300^\circ\mathrm{K}} = 23.6$ for silicon[7d] and 36.7 for hydrogen.[8]

A number of 1,3 and 1,5 migrations of silicon to heteroatom centers have been reported. These include 1,3 migrations from carbon to oxygen,[10] nitrogen to oxygen,[11,12] nitrogen to nitrogen,[12,13] nitrogen to sulfur,[12] and 1,5 migrations from oxygen to oxygen,[14] and nitrogen to nitrogen.[15] Here some stereochemical studies have been carried out. Retention of configuration at the migrating silicon center has been identified for both the 1,3 rearrangements of the β-ketosilanes[10b] as well as the (mono)-*O*-silyl enols of β-dicarbonyl compounds.[14b] On the basis of these results it would seem as if silicon migration utilizes one lobe of an antisymmetric 3p orbital, or an empty 3d orbital is involved in the rearrangement as is the case in the thiaallylic isomerizations.[5]

Many sigmatropic rearrangements of alkenes are known to take place as well with the corresponding alkynes. Examples include Cope rearrangements of vinyl propargyl ethers[16a–c] and of 1,5-hexadiynes,[16d,e] Claisen rearrangements of phenyl propargyl ethers,[16f,g] retroene reactions of β-hydroxyacetylenes,[17a,b,k] alkyl-1-alkynyl ethers,[17c–g] and alkyl propargyl ethers,[17h–j] and other related reactions.[18a–k] In general, corresponding double and triple bond structures are virtually interchangeable in pericyclic reactions. Their rates and activation parameters are very similar, with the alkynes generally reacting very slightly faster due to a slight lowering of the activation entropy.[17a,b,h,i,k] Some investigators[17a,b] have assumed that alkynes react *via* a unique, planar transition-state geometry, constrained by the linearity of ground-state propargylic and allenic groups. However, others[17h,i] have held that a relatively low energy bending mode[19a] permits alkynes to accommodate the geometric requirements of the conventional, nonplanar pericyclic transition state.[19b] In consideration of these alternative viewpoints, as well as the need to fully elucidate the pattern of orbital transformations in thermal reactions involving migration of silicon, the possibility of a silapropynylic rearrangement was also investigated.

Results and Discussion

Kinetics of Gas Phase Thermal Rearrangement of Allylsilane. Thermolysis of α-methylallyltrimethylsilane (**1**) in a gas-phase flow system utilizing a gold tube coil reactor[20] led to an equilibrium mixture consisting mainly (95%) of the γ(crotyl) isomers. The identical equilibrium mixture resulted from thermolysis of either *trans*- (**1a**) or *cis*-crotyltrimethylsilane (**1b**). The reaction followed a unimolecular rate law up to (at least) 90% completion and analysis of the rate data gave $E_a = 47.7$ kcal/mol and $\Delta S^{\ddagger} = -6.2$ eu at 500° (see Table I). The negative value of the activation entropy suggested a cyclic, concerted transition state,

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Table I. Rates and Activation Parameters for 1,3 Rearrangements of Allylic and Propargylic Silanes[a]

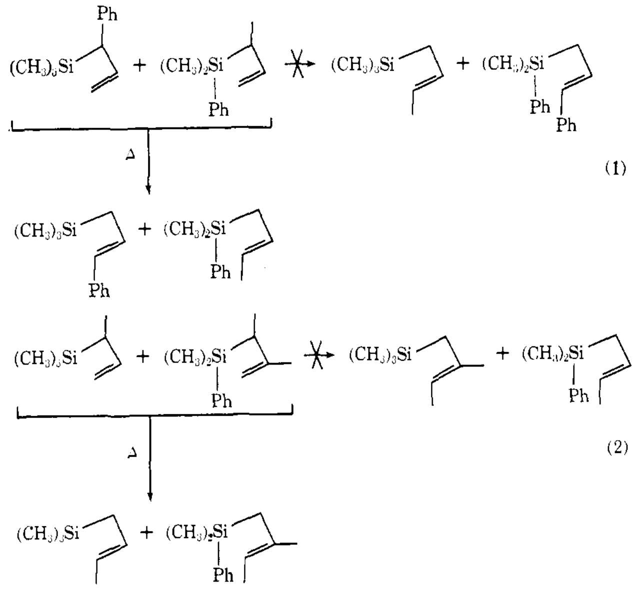
Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
Trimethyl-α-methylallyl (**1**)		Dimethylphenyl-α-methylallyl (**2**)	
506.2	0.0933, 0.0919	500.4	0.0732, 0.0713
516.8	0.126, 0.128	509.0	0.102, 0.100
526.0	0.191, 0.197	516.6	0.133, 0.134
536.6	0.280, 0.285	536.7	0.283, 0.285
547.0	0.417, 0.400	552.1	0.481, 0.475
557.1	0.595, 0.589	561.9	0.685, 0.685
567.2	0.843, 0.839	571.9	0.447, 0.469
577.3	1.20, 1.18		
E_a = 47.7 ± 0.3 kcal/mol		E_a = 47.2 ± 0.2 kcal/mol	
$\Delta S^{\ddagger}_{500}$ = −6.2 ± 0.3 eu		$\Delta S^{\ddagger}_{500}$ = −6.8 ± 0.3 eu	
log A = 12.32 ± 0.07		log A = 12.19 ± 0.16	
C_e = 5.4%		C_e = 5.5%	
Dimethylphenyl-α,β-dimethylallyl (**3**)		Trimethyl-α-phenylallyl (**4**)	
515.8	0.110, 0.110	419.9	0.0378, 0.0376, 0.0378
526.2	0.172, 0.163, 0.169	431.5	0.0633, 0.0629, 0.6269
536.1	0.242, 0.237, 0.239	440.2	0.0923, 0.0904
546.5	0.347, 0.349, 0.347	451.6	0.140, 0.144, 0.143
557.1	0.495, 0.487, 0.494	466.1	0.254, 0.264, 0.256
567.1	0.734, 0.726, 0.737	479.5	0.440, 0.430, 0.437
577.1	1.02, 1.00, 1.01		
E_a = 47.7 ± 0.3 kcal/mol		E_a = 42.5 ± 0.2 kcal/mol	
$\Delta S^{\ddagger}_{500}$ = −6.6 ± 0.3 eu		$\Delta S^{\ddagger}_{500}$ = −7.4 ± 0.3 eu	
log A = 12.26 ± 0.07		log A = 11.97 ± 0.07	
C_e = 5.3%		C_e = 1.9%	
Trimethylpropargyl (**9**)			
525.9	0.269, 0.266, 0.268		
546.5	0.386, 0.379		
556.8	0.557, 0.559, 0.565		
567.0	0.814, 0.818		
580.1	1.33, 1.36		
E_a = 49.9 ± 0.6 kcal/mol			
$\Delta S^{\ddagger}_{500}$ = −4.0 ± 0.8 eu			
log A = 12.89 ± 0.17			
C_e = 13.9%			

[a] $\Delta S^{\ddagger}$ calculated at 500° by the equation $A = (ekT/h)\exp(\Delta S^{\ddagger}/R)$; C_e = % unrearranged starting material at equilibrium, $k = -\log[(C - C_e)/(C_0 - C_e)]/t$; E_a, calculated by linear regression analysis of plot of log k *vs.* $10^3/T$.

as opposed to a homolytic or heterolytic dissociation and recombination mechanism. The course of rearrangement was tested by varying substituents on both the allylic framework and the migrating silicon center. When a methyl on the silicon in **1** was replaced by phenyl (in **2**) no significant effect on rate and activation parameters could be seen. This result is in best accord with a concerted migration. Moreover, the addition of a β-methyl group in the allyl moiety (**3**) also exerted little influence on the rate and activation parameters, providing further support for a concerted process. This is in contrast to the thiaallylic rearrangement where a dipolar mechanism has been identified.[5] In fact, the only substrate in which substitution on silicon or in the allyl side chain had a rate effect is **4**, which has an α-phenylallyl group being converted through the isomerization process to a (conjugated) phenylpropenyl arrangement representing a considerable (*ca.* 5 kcal) gain in resonance energy.[21a] Here the activation energy was diminished by about 5 kcal/mol without significant alteration of the activation entropy. This observation is clearly in keeping with a much discussed[21b] characteristic of reactions possessing a symmetrical transition state, where the activation energy grossly reflects the difference in energy between products and reactants. It must also be emphasized that the bond dissociation energy (*ca.* 69 kcal/mol) of the Si–C bond is considerably higher than the energy of activation.

1, $R_1 = CH_3$; $R_2 = CH_3$; $R_3 = H$ — **1a** (*trans*) + **1b** (*cis*)
2, $R_1 = Ph$; $R_2 = CH_3$; $R_3 = H$ — **2a** (*trans*) + **2b** (*cis*)
3, $R_1 = Ph$; $R_2 = CH_3$; $R_3 = CH_3$ — **3a** (*trans*) + **3b** (*cis*)
4, $R_1 = CH_3$; $R_2 = Ph$; $R_3 = H$ — **4a** (*trans*) + **4b** (*cis*)

Additional evidence supporting the unimolecular, cyclic nature of the reaction was gained through cross-product experiments.[5] When two differently substituted allylsilanes (eq 1 and 2) were cothermolyzed, only the products of the (separate) intramolecular reactions were formed.



The equilibrium constants encountered in this study are substantially larger than could have been anticipated from differences in enthalpy and entropy arising from changes in substitution between reactants and products. Using 3-methylbut-1-ene as a model for **1** and a 50:50 mixture of *cis*- and *trans*-pent-2-enes as a model for **1a** and **1b**, a value of $\Delta G°_{527}$ = 1.9 kcal/mol[22] can be calculated using group additivity principles.[23a,b] The computed experimental value $\Delta G°_{527}$ = 4.5 kcal/mol[24] therefore reflects *ca.* 2.6 kcal/mol of strain relief in going from the highly branched **1** to **1a** + **1b**.[25,26] In the instance of substrate **4**, the lower E_a (5.2 kcal/mol) has been attributed to the increase in conjugation at-

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[22] This calculation simply reflects the greater stability of the more substituted olefin; $\Delta(\Delta H_f°) + T(\Delta S_f°)$.

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[24] Calculated according to the relationship $\Delta G° = RT \ln K$.

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[26] Molecular mechanics calculations indicate 2.5–3.0 kcal/mol more strain in 2,2,3-trimethylbutane than in 2,2-dimethylbutane: E. M. Engler, J. D. Andose, and P. v. R. Schleyer, private communication to appear in a forthcoming article.

tending the activation process. However, the available data[21a] indicate that the difference between ground-state energies of product and reactant is *ca.* 5 kcal/mol. If it is assumed that only half of that amount is reflected in the lowering of the transition-state energy, the residual 2.5 kcal/mol can be correlated with the magnitude of (excess) strain energy relieved in the transformation of **4** compared to the corresponding reaction of **1**.

The occurrence of steric strain as a rate factor, aside from the normal conjugative substituent influence exerted in the symmetrical transition state of the silaallylic rearrangement, also came to light in connection with studying the stereochemical course of this reaction. The data in Table I demonstrate that replacement of methyl by the bulkier phenyl as a substituent on silicon does not alter the reaction rate. The evidence indicates, however, that a greater accumulation of even larger substituents in the vicinity of the central silicon produces a measurable degree of steric hindrance and rate retardation. Thus, it was found that β,γ-dideuterioallyl-α-naphthylphenylmethylsilane (**6**) undergoes silaallylic rearrangement somewhat more slowly (*ca.* a factor of $\sim$2) than the simplest member of the series, β,γ-dideuterioallyltrimethylsilane. The fact that a smaller steric effect is realized from increasing the bulk of substitution on the silicon than on the allyl side chain is to be correlated with the much greater carbon–silicon bond length.

Stereochemistry. Optically active α-naphthylphenylmethylallylsilane (**5**), $[\alpha]^{23}$D 7.2°, was prepared and thermolyzed at a series of temperatures. The thermolysis was carried out by metering and volatilizing a dilute solution of known concentration in toluene into a temperature-regulated quartz tube functioning as a gas flow reactor. This assembly was equipped for controlling the space velocity of the reactive component of the influent stream, utilizing dry nitrogen as the carrier gas. A sample of the partially reacted (recovered) silane (**5**) was then examined in an electronic polarimeter. In a parallel undertaking the deuterated analog **6** was prepared by partial, catalytic reduction of propargyl-α-naphthylphenylmethylsilane (**7**) with gaseous deuterium, using a catalyst palladium on barium sulfate poisoned with quinoline. This preparation was then thermolyzed in the quartz flow reactor under the identical conditions applied to the optically active substrate **5**, and the progress of its isomerization, corresponding to scrambling of the deuterium label, was followed by nmr.

If the migration in **5** proceeds with inversion of the silicon configuration, then racemization and scrambling should occur simultaneously; that is to say every act which resulted in scrambling is accompanied by inversion and therefore, $k_{\text{rac}} = k_{\text{scram}} = 2k_{\text{rearr}}$. If the silicon migration proceeded with retention of configuration, the silane **5** should be recovered with essentially unchanged optical activity concomitantly with the γ deuterium of **6** becoming scrambled between the α and γ allylic positions.

Table II. Relative Velocities of Racemization and Rearrangement in Deuterated Allylic Silanes

A. α-NpPhMeSiCH$_2$CD=CHD (**6**) $\rightleftarrows$ (**6a**) α-NpPhMeSiCHDCD=CH$_2$

Temp, C°	Relative nmr integration[a] methylene/vinyl	% scrambling[b,c]
500 ± 1	2.10	
520	1.98	10.9
540	1.84	23.6
560	1.49	56.4
580	1.31	71.8
590	1.08	92.8

B. (−)-α-NpPhMeSiAllyl (**5**) $\rightleftarrows$ (+)-α-NpPhMeSiAllyl

Temp, °C	$-[\alpha]^{23}$D	% racemization[d,e]
500 ± 1	6.2	
520	5.8	6.4
540	4.5	27.4
560	3.2	48.3
580	1.4	74.3
590	0.6	90.4

C. Me$_3$SiCH$_2$CD=CHD $\rightleftarrows$ Me$_3$SiCHDCD=CH$_2$

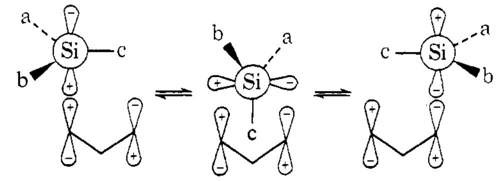
Temp, °C	Relative nmr integration[f] methylene/vinyl
None	2.2
480	1.8
490	1.5
500	1.3
540	1.1

[a] Determined on recovered, partly reacted substrate. [b] % conversion of **6** to **6a**. [c] A plot of *T vs.* % scrambling is a linear relation with least-squares slope = 1.17, intercept = −598, and correlation coefficient *R* = 0.988. This is to be compared with the plot *T vs.* % racemization in part B of this table. [d] % loss of initial optical activity. [e] Plot of *T vs.* % racemization gives a least-squares slope = 1.18 and intercept = −612 with a correlation coefficient *R* = 0.997. [f] Determined on recovered, partly reacted substrate.

The data (Table II) indicate that the allylic silane **5** is substantially unracemized at temperatures less than required to effect rearrangement under the selected quartz reactor conditions. The onset of rearrangement, as evidenced by the deuterium scrambling in **6**, occurs at temperatures producing measurable racemization. For the full temperature range over which the extents of racemization and scrambling, respectively, were compared at constant flow rate of substrate and carrier gas in the quartz reactor, it can be shown that a simple, linear relation is followed; $T = \text{f}(Y) + \text{constant}$. This expresses T, the reactor temperature, as a function (f) of the extent of (either) the scrambling or racemization. The linear plots of the data in Table II as well as a regression analysis of each of these lines show them to be superimposable within the limits of experimental error. Consequently, it can be stated that inversion of configuration and silaallylic rearrangement occur simultaneously.

As represented in the orbital diagram in Scheme I orbital symmetry in this sigmatropic process is conserved if silicon utilizes an antisymmetric 3p orbital in bridging across the allylic framework. Although the participation of 3d orbitals in this process cannot

Scheme I



definitely be ruled out, the fit of the data to the conclusion, that every act of rearrangement produces inversion at the migrating center, makes this seem less probable. Among the variety of 3d orbital geometries which are available to the silicon for effecting this concerted reaction with orbital symmetry conservation, only one (3dz^2) can participate with equivalent aptitude. Mixing of 3d orbital character into the 3p orbitals of silicon[27a-c] without significantly altering the geometry of the latter seems, therefore, a more likely possibility, if there is any 3d involvement at all in this reaction. Recent discussions[27d] of the requirements for use of 3d orbitals in bonding would also support these conclusions.

Finally, it must be emphasized that these are the first cases in which it has been established that a 1,3[10b] (or 1,5)[13b] migration of silicon has taken place with inversion of configuration.

Silapropynylic Rearrangement. Propargyltrimethylsilane, **9**, was found to undergo a reversible unimolecular rearrangement represented in eq 3. At

$$\underset{\mathbf{9}}{(CH_3)_3SiCH_2OC{\equiv}CH} \rightleftharpoons \underset{\mathbf{10}}{CH_2{=}C{=}CHSi(CH_3)_3} \qquad (3)$$

555° the composition consisted of 86.1% of the allenic isomer **10**. The activation parameters, $E_a = 49.9 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger}_{500} = -4.0 \pm 0.8$ eu, are very similar to those observed for the corresponding silaallylic rearrangement. The activation energy for rearrangement of **9** is slightly larger than for **1**, the α-methylallylsilane, which possesses an α-methyl substituent providing a small amount of acceleration stemming from resonance and steric strain (relief) effects. The free energy difference between **9** and **10**, −2.9 kcal/mol,[25] is to be correlated with *ca.* 1 kcal/mol[24] for the greater stability of an allenyl *vs.* a propargyl group, and *ca.* 2 kcal/mol of stabilization energy gained as silicon becomes bonded to an sp^2 center.[28a]

To the best of our knowledge this is the first report of a metallotropic, intramolecular migration of silicon to a triply bonded carbon. The near identity of the activation parameters of corresponding silapropynylic and silaallylic isomerizations suggests a strong similarity in transition-state structures of these reactions.

The implications of these observations for alkyne rearrangements in general are of considerable interest. The exactly analogous situation where corresponding alkene and alkyne substrates in six-centered pericyclic reactions possess nearly identical activation parameters[17h,i] is no mere coincidence. Evidently the low energy bending vibrations of propargyl and allenyl configurations allow the formation of activated states entirely similar to those proposed for related olefins. In the present instance the bending permits the silicon to "feel" the presence of the electron density of the p lobe at the γ carbon. It appears to be quite unlikely that a bulky silicon could bridge across a linear array of carbons, a situation which, in the symmetrical transition state of the concerted process, locates the heteroatom with its substituents directly atop the central carbon of the triad.

Stereochemistry of the Silapropynylic Rearrangement. Optically active propargyl-α-naphthylphenylmethylsilane, **7a**, containing 15% allenyl-α-naphthylphenylmethylsilane (**8**) was synthesized and subjected to gas-phase thermolysis in the quartz flow reaction under conditions (previously described) identical with those applied to allylic substrates. At temperatures between 480 and 570° the silane **7a** rearranges to a mixture consisting mainly (80%) of the allenyl isomer **8**. To ascertain the stereochemical change, if any, attending the rearrangement, **7a** and **8** were reduced catalytically to the same product, propyl-α-naphthylphenylmethylsilane, **11**. Samples of **7a** and **8**, both with highly measurable amounts of optical activity, afforded products (**11**) with opposite signs of rotation (and therefore configurations). Thus, as in the case of the silaallylic rearrangement, the migration of silicon in the silapropynylic rearrangement also occurs with inversion of configuration.

The resemblance between these isomerization reactions is emphasized by a comparison of reaction kinetics. The data in Table III represent a measure of the rate of change of optical activity and of composition as a function of the quartz flow reactor temperature under the same conditions of space velocity of the influent substrate (here **7a**) as applied to **5** and **6** (see Table II). Again, a simple, linear relationship is followed in which both the % **7a** and the optical rotation are a direct function of the reactor temperature with a high correlation coefficient. Moreover, the fact that little or no racemization is occurring and that inversion of configuration is the exclusive result of rearrangement can be readily perceived by comparison of the rotations of the hydrogenation products (**11**) from reaction compositions containing 80% of **7a** ([α]^{23}D +1.4°) and 80% of **8** ([α]^{23}D −1.4°).

Table III. Stereochemical Change in the Silapropynylic Rearrangement as a Function of the Extent of Reaction[a]

$$\underset{\mathbf{7a}}{(+)\text{-}\alpha\text{-NpPhMeSiCH}_2\text{C}{\equiv}\text{C}} \rightleftarrows \underset{\mathbf{8}}{(-)\text{-}\alpha\text{-NpPhMeSiCH}{=}\text{C}{=}\text{CH}_2}$$

Temp, °C	% **7a**	[α]^{23}D (**7a** + **8**)	[α]^{23}D (**11**)
480	85	9.2	1.7
490	79	7.9	
510	68	6.3	
530	54	3.8	0.2
550	35	1.1	
570	20	−1.8	−1.4

[a] A plot of *T vs.* % **7a** is linear with a least-squares slope = −0.73 and intercept = 436. The correlation coefficient *R* of the line is 0.996. A plot of *T vs.* [α]D constitutes a line with least-squares slope = −0.12 and intercept = 67.1. The correlation coefficient *R* of the line is 0.996.

The Possibility of a 1,3 Carboallylic Migration. Some 1,3 sigmatropic migrations of carbon have been reported in bicyclo[3.2.0]hept-2-enes[3a-f] and in 2-methyl-3,3-dicyano-4-phenylpent-1-ene.[3g] It was, there-

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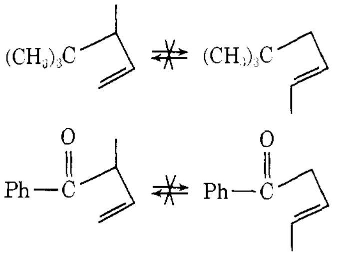
[27] See, for discussion of such orbital mixing, (a) J. D. Dunitz, *Acta Crystallogr.*, **9**, 579 (1956); (b) O. Foss and O. Tjomsland, *Acta Chem. Scand.*, **12**, 44 (1958); (c) I. Lindquist, *J. Inorg. Nucl. Chem.*, **6**, 159 (1958); (d) T. Brill, *J. Chem. Educ.*, **50**, 392 (1973).

[28] (a) For example, we have found that heating allyltriphenylsilane in quinoline at reflux results in its isomerization to propenyltriphenylsilane (cis and trans). (b) Allylic stabilization (10 kcal/mol) − benzhydryl stabilization[29] (15 kcal/mol) + 2 × cyano stabilization[30] (8 kcal/mol) = 41 kcal/mol. (c) I. M. T. Davidson and I. L. Stephenson, *Chem. Commun.*, 764 (1966). (d) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, **34**, 53 (1972).

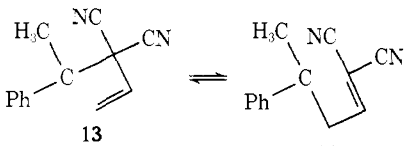
[29] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[30] S. F. Sarner, D. M. Gale, H. K. Hall, Jr., and A. B. Richmond, *J. Phys. Chem.*, **76**, 2817 (1972).

fore, of interest to determine whether hydrocarbon analogs of the active silanes (**1** → **3**) could undergo the related 1,3 carboallylic rearrangement. It was found that both 3,4-dimethyl-1-pentene and 3,4,4-trimethyl-1-pentene did not experience rearrangement during short time exposures to temperatures in the range of 600° where fragmentation reactions became evident. Moreover, no indications of a 1,3 rearrangement were found in thermolysis of 2-methyl-1-phenyl-3-buten-1-one (**12**) which would involve migration of a benzoyl group. In view of the reported[3g] 1,3 migration of an α-methylbenzyl group in **13** (eq 5), in contrast to



(4)



(5)

13 **14**

the failures of the potential[1,3] carboallylic rearrangements expressed in eq 4, we may speculate very briefly on the driving forces for 1,3 sigmatropic processes. The decisive factor may be the dissociation energy of the critical bond, namely, the bond that ties the allylic framework to the (potential) migrating center in the substrate. The normal carbon–silicon bond dissociation energy[28c,d] (*ca.* 69 kcal/mol) is evidently well below the threshold value necessary to foster the rearrangement reaction in competition with homolytic fragmentation modes. The normal carbon–carbon bond energies (*ca.* 80–85 kcal/mol) are considerably (*ca.* 10 kcal) above this threshold. Lowering of this energy by some 40 kcal[28b] through sufficient electronegative group substitutions is apparently crucial to the occurrence of the rearrangement of **13** to **14**.

Experimental Section

General. The gas-phase thermolysis apparatus utilizing a gold coil reactor has been previously described.[20] Preparative scale gas-phase thermolysis was accomplished in a quartz reactor (1 in. i.d. diameter) with a 12-in. heated zone and utilizing nitrogen carrier gas. The sample in each case was 0.15 *M* in dry toluene solution injected at 0.1 ml/min with N_2 flowing at 70 ml/min. Nmr spectra were recorded on a Varian Associates A-60A spectrometer and data are given in δ (ppm) with reference to tetramethylsilane (TMS, δ 0). Ir spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Samples were taken as neat liquid films between sodium chloride plates. Mass spectra were recorded at 70 eV on a C.E.C. 21-110B double-focusing, high-resolution spectrometer. Melting points were determined using a Mel-Temp melting point apparatus and are uncorrected, as are boiling points. Polarimetric measurements were made with an ETL-NPL automatic electronic polarimeter Type 143A.

The silanes **1** → **4** and **9** were prepared *via* allylic or propargylic Grignard reagents and a mixture of allylic isomers always resulted. These silanes were purified by twice distilling through a Nester/Faust NFT-51 adiabatic, annular, Teflon spinning band column. Analytical samples were collected from the exit port of an F&M Model 500 gas chromatograph. The column used was a 12 ft × 0.25 in. 10% Chromosorb W-AW, except for **3a** and **3b** which were collected from a 12 ft × 0.25 in. 10% 1,1,1-tris(2-cyanoethoxy)propane on a 60–80 Chromosorb W-AW column.

3,4-Dimethyl-1-pentene and 3,4,4-trimethyl-1-pentane were purchased from The Chemical Samples Co.

Trimethyl-α-methylallylsilane (1). Crotylmagnesium chloride was prepared by the dropwise addition (4 hr) of 54 g (0.6 mol) of crotyl chloride (Aldrich) in 200 ml of dry tetrahydrofuran (THF) to a rapidly stirred suspension of 15 g (0.6 mol) of magnesium turnings in 400 ml of THF. The Grignard was initiated with 2 g of crotyl chloride in 50 ml of THF and then an additional 350 ml of THF was added. During the addition of the halide the internal temperature remained *ca.* 40–45°. The mixture was refluxed for 20 min, cooled to 30°, and then 55 g (0.5 mol) of chlorotrimethylsilane (Aldrich, redistilled) in 50 ml of THF was added dropwise. The reaction was exothermic and the addition was at such a rate as to maintain *ca.* 40–50°. An additional 150 ml of THF was added before the silane addition was completed because the formation of a thick slurry prevented efficient stirring. The mixture was refluxed for 12 hr, cooled, and filtered to remove the salts ($MgCl_2$). Ethyl ether was added, followed by saturated ammonium chloride solution and extraction with water. The ethereal solution was dried ($MgSO_4$) and distilled through a long Vigreux column giving 58 g (90%) of product, bp 106–112°. The product was redistilled through a spinning band column and fractions of like composition were again distilled. The initial product mixture consisted roughly of 75% **1**, 10% **1a**, and 15% **1b**: nmr (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 1.09 (d, 2, J = 7 Hz, $CHC\mathit{H}_3$), 1.59 (quintet, 1, J = 7 Hz, $C\mathit{H}CH_3$), 4.82 (complex m, 2, $CH{=}C\mathit{H}_2$), 5.87 (complex m, 1, $C\mathit{H}{=}CH_2$); ir (neat) 1630 ($C{=}C$), 1255 and 840 ($Si(CH_3)_3$), 895 cm^{-1} ($CH{=}CH_2$).

Trimethyl-*cis*-crotylsilane (1b): nmr (CCl_4) δ 0.02 (s, 9, $Si(CH_3)_3$), 1.50 (m, 5, $C\mathit{H}_2CH{=}CHC\mathit{H}_3$), 5.36 (complex m, 2, $CH{=}CH$); ir (neat) 1640 ($C{=}C$), 1250 and 850 ($Si(CH_3)_3$), 718 cm^{-1} ($CH{=}CH$, cis), no strong bands at *ca.* 965 or 900; mass spectrum (70 eV) *m/e* (rel intensity) 128 (10), 113 (7), 93 (6), 85 (5), 74 (9), 73 (100), 59 (12), 58 (7), 45 (9), 43 (21), 41 (8).

Trimethyl-*trans*-crotylsilane (1a): nmr (CCl_4) δ 0.10 (s, 9, $Si(CH_3)_3$), 1.25 (d, 2, J = 5 Hz, $CH_2C{=}C$), 1.54 (d, 3, J = 5 Hz, $C{=}CH_3$), 5.39 (complex m, 2, $CH{=}CH$); ir (neat) 1640 ($C{=}C$), 1250 and 850 ($Si(CH_3)_3$), 968 cm^{-1} ($CH{=}CH$, trans).

Dimethylphenyl-α-methylallylsilane (2c). Chlorodimethylphenylsilane was prepared by the reaction of phenylmagnesium bromide with dichlorodimethylsilane in ether. The mixture was refluxed for 4 hr, cooled, filtered, and concentrated. Distillation twice through a Vigreux column resulted in nearly complete removal of the higher boiling impurity, dimethyldiphenylsilane, from the desired chlorodimethylphenylsilane which was obtained in 50% yield, bp 50° (2.5 mm): nmr (CCl_4) δ 0.62 (s, 6, $Si(CH_3)_3$) and 7.43 (complex m, 5, aromatic).

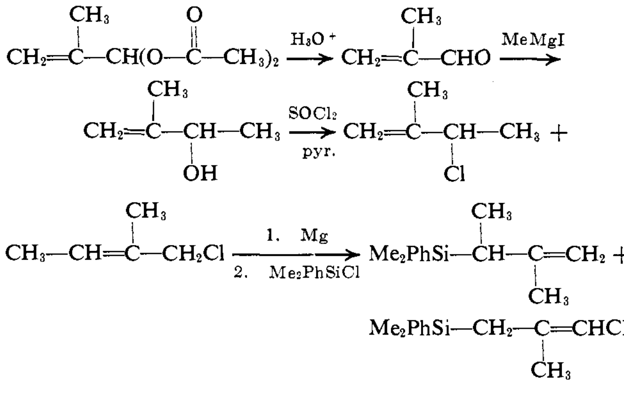
Dimethylphenyl-α-methylallylsilane (2). A solution of 41 g (0.24 mol) of chlorodimethylphenylsilane in 50 ml of THF was added over a period of 8 min (with cooling) to a stirred solution of crotylmagnesium chloride (from 32 g of crotyl chloride, 0.35 mol) in 600 ml of THF. The mixture was stirred at room temperature 2 hr and then refluxed for 12 hr. The solvent was removed on a rotary evaporator, ethyl ether was added, and the reaction mixture was worked up as usual. Distillation through a Vigreux column gave an 86% yield of product (bp 67° (0.6 mm)) which was redistilled through a spinning band column. The initial product mixture had roughly the same isomer composition as in **1** (see above): nmr (CCl_4) δ 0.22 (s, 6, $Si(CH_3)_2$), 1.02 (d, 2, J = 7 Hz, $CHCH_3$), 1.77 (quintet, 1, J = 7 Hz, $CHC\mathit{H}_3$), 4.81 (complex m, 2, $CH{=}C\mathit{H}_2$), 5.86 (complex m, 1, $C\mathit{H}{=}CH_2$), 7.38 (complex m, 5, aromatic); ir (neat) 1625 ($C{=}C$), 1420 and 1115 (SiPh), 1245 and 837 ($Si(CH_3)_2$), 897 ($CH{=}CH_2$), 736 and 700 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 190 (4), 137 (4), 136 (14). 135 (100), 121 (2), 119 (3), 107 (4), 105 (7), 69 (2), 59 (3), 53 (3), 43 (7).

Dimethylphenyl-*cis*-crotylsilane (2b): nmr (CCl_4) δ 0.28 (s, 6, $Si(CH_3)_2$), 1.61 (m, 5, $C\mathit{H}_2CH{=}CHC\mathit{H}_3$), 5.40 (complex m, 2, $CH{=}CH$), 7.40 (complex m, 5, aromatic); ir (neat) 1650 ($C{=}C$) 1420 and 1117 (SiPh), 1255 and 840 ($Si(CH_3)_2$), 732 and 700 (monosubst benzene), 725 cm^{-1} ($CH{=}CH$, cis), *no* strong band at *ca.* 965 or 900 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 191 (2), 190 (10), 137 (4), 136 (14), 135 (100), 121 (4), 119 (3), 107 (4), 105 (6), 91 (2), 59 (3), 53 (3), 43 (6).

Dimethylphenyl-*trans*-crotylsilane (2a): nmr (CCl_4) δ 0.26 (s, 6, $Si(CH_3)_2$), 1.66 (m, 5, $C\mathit{H}_2CH{=}CHC\mathit{H}_3$), 5.38 (complex m, 2, $CH{=}CH$), 7.40 (complex m, 5, aromatic); ir (neat) 1650 ($C{=}C$), 1420 and 1115 (SiPh), 1250 and 835 ($Si(CH_3)_2$), 970 ($CH{=}CH$, trans), 735 and 700 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 191 (2), 190 (8), 175 (5), 137 (4), 136 (14), 135 (100), 121 (6), 119 (3), 107 (5), 105 (9), 59 (4), 53 (4), 43 (11).

Dimethylphenyl-α,β-dimethylallylsilane (3). The silane **3** was prepared according to Scheme II.

Scheme II



Methacrolein was prepared by the hydrolysis of methallylidene diacetate. Into a 1-l. three-necked flask was charged 225 ml of water and 0.68 g of concentrated sulfuric acid (0.3% based on H_2O). The mixture was stirred and heated to 80° and then methylallylidene diacetate (Union Carbide) was added dropwise from an addition funnel. Heating was adjusted to maintain an internal temperature of 93–95° (exothermic reaction). Methacrolein–water azeotrope (92.3% methacrolein–7.7% water) was distilled out of the reaction mixture at 64° through a specially constructed still packed with 1/8-in. glass helices. A 5% hydroquinone solution was slowly dripped down through the still to prevent polymerization. The distillate was returned to a separator which allowed the water, which separated from the methacrolein, to be returned to the pot. The methacrolein was collected in a receiver containing hydroquinone and cooled in an ice bath. Ethyl ether was added to the methacrolein, followed by drying ($MgSO_4$).

The ethereal solution of methacrolein was added to methylmagnesium iodide in ether. Hydrolysis with saturated ammonium chloride solution and work-up gave 2-methyl-1-buten-3-ol: bp 112°; nmr (CCl_4) δ 1.21 (d, 3, *J* = 7 Hz, CHC*H*$_3$), 1.72 (s split, 3, *J* = 1 Hz, C=CCH$_3$), 3.30 (broad s, 1, OH), 4.14 (q, 1, *J* = 7 Hz, CHCH$_3$), 4.72 and 4.92 (two broad s with fine splitting, each 1, CH$_2$=C).

The alcohol (134 g, 1.56 mol), pyridine (123 g, 1.56 mol), and methylene chloride solvent (150 ml) were cooled in an ice bath and then a solution of thionyl chloride (119 g, 1.56 mol) in CH_2Cl_2 (75 ml) was added dropwise over a period of 5 hr. The ice bath was removed and the mixture stirred for 4 hr at room temperature and then refluxed for 8 hr. The mixture was extracted successively with water, 5% NaOH, and water and dried ($MgSO_4$). Distillation gave a mixture of (*ca.* 50:50) 3-chloro-2-methyl-1-butene and 1-chloro-2-methyl-2-butene: nmr (CCl_4) (mixture) 1.67 (complex m, 9, all CH$_3$), 3.98 (nearly s, 1, CH$_2$Cl), 4.51 (q, 0.5, *J* = 7 Hz, ClCHCH$_3$), 4.92 and 5.01 (two s with fine splitting, each 0.5, CH$_2$=C), 5.60 (q with fine splitting, 0.5, C=CH).

A solution of 20 g (0.2 mol) of chloride and 34 g (0.2 mol) of chlorodimethylphenylsilane (see **2c**) in 200 ml of dry THF was added to 4.8 g (0.2 mol) of magnesium turnings in 150 ml of THF (initiation with 3 g of halide in 50 ml of THF). The mixture was refluxed for 6 hr and then worked up as usual. Distillation through a Vigreux column gave a 60% yield of product: bp 54° (0.4 mm); nmr (CCl_4) δ 0.27 (s, 6, Si(CH$_3$)$_2$), 1.10 (d, 3, *J* = 7 Hz, CHC*H*$_3$), 1.57 (s with fine splitting, 3, C=CCH$_3$), 1.72 (m, 1, CHCH$_3$), 4.49 and 4.58 (two s with fine splitting, each 1, C=CH$_2$), 7.38 (complex m, 5, aromatic); ir (neat) 1630 (C=C), 1420 and 1117 (SiPh), 1247 and 820 (Si(CH$_3$)$_2$), 877 (C=CH$_2$), 738 and 700 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 205 (3), 204 (15), 189 (2), 137 (5), 136 (15), 135 (100), 121 (2), 107 (3), 105 (2), 69 (2), 43 (4).

Dimethylphenyl-*cis*-β,γ-dimethylallylsilane (3b): nmr (CCl_4) δ 0.30 (s, 6, Si(CH$_3$)$_2$), 1.42 (d, 3, *J* = 7 Hz, C=CHCH$_3$), 1.59 (s with fine splitting, 3, CH$_2$(CH$_3$)C=C), 1.72 (broad s, 2, SiCH$_2$), 5.09 (q, 1, *J* = 7 Hz, C=C*H*), 7.41 (complex m, 5, aromatic); ir (neat) 1660 (C=C), 1420 and 1105 (SiPh), 1240 and 827 (Si(CH$_3$)$_2$), 728 and 693 cm^{-1} (monosubst benzene).

Dimethylphenyl-*trans*-β,γ-dimethylallylsilane (3a): nmr (CCl_4) δ 0.30 (s, 6, Si(CH$_3$)$_2$), 1.42 (d, 3, *J* = 7 Hz, C=CHCH$_3$), 1.59 (s with fine splitting, 3, CH$_2$(C*H*$_3$)C=C), 1.72 (broad s, 2, SiCH$_2$), 5.09 (q, 1, *J* = 7 Hz, C=CH), 7.41 (complex m, 5, aromatic); ir (neat) 1650 (C=C), 1415 and 1110 (SiPh), 1240 and 830 (Si(CH$_3$)$_2$), 730 and 695 cm^{-1} (monosubst benzene).

Trimethyl-α-phenylallylsilane (4). Into a 1-l. round-bottomed flask was charged 134 g of cinnamyl alcohol (1 mol, Eastman), 79 g of pyridine (1 mol, Fisher) and 200 ml of methylene chloride. The mixture was cooled in an ice bath and 119 g of thionyl chloride (1 mol, Aldrich) in 100 ml of $CHCl_3$ was added dropwise over a period of 4 hr. The mixture was refluxed for 10 hr while SO_2 evolved. Upon cooling, water was added and the layers were separated. The methylene chloride layer was then extracted twice with 5% KOH and twice with water, dried ($MgSO_4$), concentrated, and distilled through a Vigreux column to give cinnamyl chloride in 94% yield, bp 65° (0.6 mm). The initial product mixture consisted roughly of 5% **4**, 75% **4a**, and 20% **4b**: nmr (CCl_4) δ 4.07 (d, 2, *J* = 6 Hz, CH$_2$Cl), 6.28 (m, 2, CH=CH), 7.22 (s, 5, aromatic).

The Barbier procedure[31] was used to prepare silane **4**. A solution of 15 g (0.1 mol) of cinnamyl chloride and 11 g (0.1 mol) of chlorotrimethylsilane in 200 ml of THF was added dropwise to a suspension of 2.4 g (0.1 mol) of magnesium turnings in 60 ml of THF (initiation with 1 g of cinnamyl chloride) over a period of 2 hr. The mixture was refluxed for 6 hr and worked up as usual. Distillation gave 15 g (80%) of product, bp 63° (0.5 mm), which was redistilled through a spinning band column: nmr (CCl_4) δ 0.05 (s, 9, Si(CH$_3$)$_3$), 2.99 (d, 1, *J* = 9 Hz, PhC*H*), 5.00 (complex m, 2, CH=CH$_2$), 6.21 (complex m, 1, CH=CH$_2$), 7.18 (complex m, 5, aromatic); ir (neat) 1630 (C=C), 1250 and 840 (Si(CH$_3$)$_3$), 990 and 900 (CH=CH$_2$), 740 and 700 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 191 (5), 190 (24), 175 (11), 115 (4), 75 (4), 74 (9), 73 (100), 59 (6), 45 (7).

Trimethyl-*cis*-cinnamylsilane (4b): nmr (CCl_4) δ 0.09 (s, 9, Si(CH$_3$)$_3$), 1.79 (d with allylic fine splitting, 2, *J* = 9 Hz, SiCH$_2$), 5.69 (m, 1, CH=CHPh), 6.35 (d with fine splitting, 1, *J* = 12 Hz, CH=C*H*Ph), 7.26 (s, 5, aromatic); ir (neat) 1630 (C=C), 1250 and 860 (Si(CH$_3$)$_3$), 745 and 698 cm^{-1} (monosubst benzene), no strong band at *ca.* 980, 965, or 920 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 191 (4), 190 (19), 175 (9), 125 (4), 75 (4), 74 (9), 73 (100), 59 (6), 45 (8).

Trimethyl-*trans*-cinnamylsilane (4a): nmr (CCl_4) δ 0.13 (s, 9, Si(CH$_3$)$_3$), 1.64 (complex m, 2, SiCH$_2$), 6.18 (complex m, 2, CH=CH), 7.21 (m, 5, aromatic); ir (neat) 1640 (C=C), 1250 and 860 (Si(CH$_3$)$_3$), 965 (CH=CH, trans), 742 and 693 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 191 (4), 190 (21), 175 (9), 117 (3), 116 (3), 115 (5), 91 (5), 75 (4), 74 (9), 73 (100), 59 (5), 45 (6), 43 (3).

Trimethylpropargylsilane (9). Into a 1-l. round-bottomed flask was charged 12 g of magnesium turnings (0.5 mol), 0.15 g of chloride (anhydrous), 75 ml of dry ether, and 2 g of propargyl bromide (Aldrich, freshly distilled). The mixture was heated at reflux until an exothermic reaction began. Then 125 ml of ether was added and the mixture cooled to *ca.* −20° with a Dry Ice–acetone bath. A solution of 58 g of propargyl bromide (0.5 mol) in 250 ml of ether was added dropwise over a period of 3 hr with cooling to maintain *ca.* −20°. The mixture was stirred 30 min longer and then 54 g of chlorotrimethylsilane (0.5 mol) in 175 ml of ether was added over a period of 90 min with cooling to maintain −20°. The mixture was allowed to warm to room temperature with stirring over a period of 90 min. After filtering, the reaction mixture was worked up as usual. The product was distilled through a Vigreux column at atmospheric pressure and then through a spinning band column, bp 90°. The initial product mixture was composed roughly of 80% **9** and 20% **9a**: nmr (CCl_4) δ 0.10 (s, 9, Si(CH$_3$)$_3$), 1.40 (d, 2, *J* = 3 Hz, CH$_2$C≡CH), 1.68 (t, 1, *J* = 3 Hz, CH$_2$C≡CH); ir (neat) 3300 (≡CH), 2120 (C≡C) and 1250 and 850 cm^{-1} (Si(CH$_3$)$_3$).

Trimethylallenylsilane (9a): nmr (CCl_4) δ 0.07 (s, 9, Si(CH$_3$)$_3$), 4.27 (d, 2, *J* = 7 Hz, CH=C=CH$_2$), 4.87 (t, 1, *J* = 7 Hz, C*H*=C=CH$_2$); ir (neat) 1950 (C=C=CH$_2$) and 1260 and 850 cm^{-1} (Si(CH$_3$)$_3$).

Trimethyl-β,γ-dideuterioallylsilane (11). Propargyltrimethylsilane (19 g) was reduced with deuterium gas in a Brown hydrogenator. Into the hydrogenation flask was charged 120 ml of pentane, 0.40 g of 5% palladium on barium sulfate, and 64 drops of quinoline. Deuterium gas was generated by adding D_3PO_4 (prepared by adding P_2O_5 slowly and cautiously with cooling to D_2O

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[31] F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 270 (1962).

in a glove bag) to a stirred suspension of magnesium turnings in D_2O. After the system was flushed with deuterium, the silane **9** was injected into the hydrogenation flask. Uptake of deuterium by the silane continued for a period of 7 hr. The mixture was stirred an additional 8 hr and then filtered, washed with water, dried ($MgSO_4$), and distilled through a long Vigreux column giving 12 g (63%) of the silane **11**: bp 86°; nmr (CCl_4) δ 0.00 (s, 9, $Si(CH_3)_3$), 1.50 (broad s with fine splitting, 2, $SiCH_2$), 4.82 (broad s with fine splitting, CD=CDH); ir (neat) 2230 (CD), 1620 (C=C), 1260 and 850 ($Si(CH_3)_3$), 920 cm^{-1} (C=CH), no band present at *ca.* 980 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 117 (3). 116 (6). 102 (4), 101 (7), 75 (4), 74 (10), 73 (100), 70 (11), 59 (11), 58 (6), 45 (15), 44 (6), 43 (11).

(−)-α-Naphthylphenylmethylallylsilane (5). α-Naphthylphenylmethoxysilane was prepared according to the method of Sommer[32] by the reaction of α-naphthylmagnesium bromide (from α-naphthyl bromide, Eastman) with phenylmethyldimethoxysilane (Roc Ric) in a mixed solvent consisting of benzene, ethyl ether, and THF in the ratio of 3:2:1 by volume. The product was recrystallized from hexane: mp 61.5–62.0° [lit.[31] mp 62.5–63.5°]; nmr (CCl_4) δ 0.71 (s, 3, $SiCH_3$), 3.50 (s, 3, OCH_3), 7.10–8.32 (complex m, 12, aromatic); ir (neat) 2800, 1180 and 1080 ($SiOCH_3$), 1590, 1500, 1210, 1140 and 989 (α-NpSi), 733 and 695 (SiPh), 1245 cm^{-1} ($SiCH_3$).

A solution of 110 g of the methoxysilane in 200 ml of dry ether was added to 13 g of lithium aluminum hydride in 250 ml of ether over a period of 1 hr. The mixture was refluxed for 16 hr and the excess $LiAlH_4$ destroyed by adding 84 ml of acetone. The mixture was poured into a beaker containing 125 ml of concentrated HCl, 125 ml of H_2O, and 300 g of ice. Extraction with ether followed by drying ($MgSO_4$) and distillation gave α-naphthylphenylmethylsilane: bp 145° (0.1 mm); 81 g recrystallized from pentane; nmr (CCl_4) δ 0.67 (d, 3, J = 4 Hz, $SiCH_3$), 5.40 (q, 1, J = 4 Hz, SiH), 7.05–8.25 (complex m, 12, aromatic); ir (neat) 2120 (SiH), 1590, 1500, 1210, 1140 and 980 (αNpSi), 1320, 1105, 733 and 695 (SiPh), 1245 cm^{-1} ($SiCH_3$).

Tetraallyltin, a precursor of allyllithium, was prepared next. A solution of 97 g (0.6 mol) of allyl bromide in 150 ml of ether was added dropwise to a stirred suspension of 19 g (0.6 mol) of magnesium turnings in 500 ml of ether over a period of 4 hr. The reaction was initiated with 3 g of halide in 75 ml of ether. During the addition of the halide solution, the reaction was cooled in an ice bath. The mixture was then refluxed for 15 min and a solution of 28 g (0.11 mol) of stannic chloride ($SnCl_4$) in 50 ml of benzene was added over a period of 90 min. The mixture was refluxed for 90 min, filtered, and worked up as usual. Distillation gave 24 g (80%) of tetraallyltin: bp 64° (0.6 mm); nmr (CCl_4) 1.92 (d, 2, J = 8 Hz, $SnCH_2$), 4.83 (complex m, 2 $CH{=}CH_2$), 5.97 (complex m, 1, $\mathit{CH}{=}CH_2$).

The published procedure[33] for the synthesis of the allylsilane resulted in a mixture of the desired allylsilane and the butylsilane. By a modification of that procedure the amount of butylsilane contamination was reduced to less than 10%. The following reaction was conducted in a glove bag under a nitrogen atmosphere. To a stirred solution of 0.025 mol of butyllithium (10 ml of 2.5 *M* butyllithium in pentane (Alfa)) in 125 ml of pentane was added 7.0 g (0.025 mol) of tetrallyltin. The mixture was stirred for 30 min, during which time allyllithium precipitated. Upon the addition of *ca.* 15 ml of dry ether, the flocculent white precipitate formed a gummy mass adhering to the bottom of the flask. The pentane was decanted off and an additional 100 ml of pentane added, the mixture stirred, and the pentane decanted off again. This procedure was repeated twice. The residue was dissolved in 100 ml of ether and a solution of 4.0 g of α-naphthylphenylmethylsilane in 50 ml of ether was added. The mixture was stirred for 30 min and then cautiously poured onto an ice–water mixture. Extraction with ether, followed by drying ($MgSO_4$), concentrating, and distilling gave 3.5 g of racemic silane **5**, bp 156° (0.1 mm).

The optically active silane **5** was prepared from (−)-α-naphthylphenylmethylsilane: $[\alpha]_D$ −7.2° (*c* 7.52, pentane); nmr (CCl_4) δ 0.67 (s, 3, $SiCH_3$), 2.23 (d, 2, J = 8 Hz, $SiCH_2$), 4.90 (complex m, 2, $CH{=}CH_2$), 5.78 (complex m, 1, $CH{=}CH_2$), 7.10–8.18 (complex m, 12, aromatic); ir (neat) 1630 (C=C), 990 and 895 ($CH{=}CH_2$), 1590, 1500, 1208, 1140 and 980 (αNpSi), 1310, 1100, 732 and 697 (SiPh), 1245 cm^{-1} ($SiCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 228 (12), 248 (23), 247 (100), 177 (23), 169 (17), 167 (111), 128 (26), 121 (45), 105 (8).

Allyltrimethylsilane. This compound was synthesized *via* the Barbier procecure.[33] An ethereal solution of allyl bromide (0.22 mol) and chlorotrimethylsilane (0.20 mol, Aldrich) was slowly added to a stirred suspension of magnesium turnings in ether after initiation with 1 g of allyl bromide. The mixture was refluxed for 3 hr, filtered, extracted with saturated ammonium chloride solution and water successively, dried ($MgSO_4$), and distilled giving **18** in 85% yield: bp 86° [lit.[34] bp 85°]; nmr (CCl_4) 0.00 (s, 9, $Si(CH_3)_3$), 1.45 (d, 2, J = 8 Hz, $SiCH_2$), 4.78 (complex m, 2, $CH{=}CH_2$), 5.77 (complex m, 1, $CH{=}CH_2$); ir (neat) 1640 (C=C), 1415 and 1220 ($SiCH_2$), 1250, 840, and 760 ($Si(CH_3)_3$), 980 and 920 cm^{-1} ($CH{=}CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 114 (10), 99 (10), 75 (4), 74 (9), 73 (100), 71 (4), 59 (12), 45 (11), 43 (11), 39 (4).

(+)-Propargyl-α-naphthylphenylmethylsilane (7a). Propargylmagnesium bromide was prepared (see **9**) from 4.8 g of propargyl bromide in a total of 40 ml of ether. Then 25 ml of THF was added slowly (exothermic), followed by 10 ml of benzene and 4.2 g of α-naphthylphenylmethylchlorosilane ($[\alpha]_D$ 10.1): nmr (CCl_4) δ 0.80 (s, 3, CH_3Si), 1.72 (t, 1, J = 3 Hz, C=CH), 2.12 (d, 2, J = 3 Hz, $CH_2C{=}C$), 7.05–7.95 (complex m, 12, aromatic); mass spectrum (69 eV) *m/e* 226 (parent peak); ir (neat) 3280 (=CH). 2115 (C=C). 1585, 1500, 1230, 1140, 980 (α-NpSi), 735, 700 (SiPh), 1255 ($SiCH_3$), 1115 cm^{-1} ($SiOCH_3$).

Allenyl-α-naphthylphenylmethylsilane (8): nmr (CCl_4) δ 0.77 (s, 3, CH_3Si), 4.33 (d, 2, J = 7 Hz, $C{=}CH_2$), 5.38 (t, 1, J = 7 Hz, SiCH=C), 7.05–7.95 (complex m, 12, aromatic); mass spectrum (70 eV) *m/e* 226 (parent peak); ir (neat) 1930 ($C{=}C{=}CH_2$), 1585, 1500, 1230, 1140, 980 (α-NpSi), 735 and 700 (SiPh), 1255 ($SiCH_3$), 1115 cm^{-1} ($SiOCH_3$).

A solution of 4.0 g of propargyl-α-naphthylphenylmethylsilane in 15 ml of pentane was added to 0.1 g of 5% palladium on barium sulfate and 16 drops of quinoline in 20 ml of pentane in a Brown hydrogenator, previously flushed with deuterium gas. The reaction was stirred 8 hr, the work-up (see **11**) and distillation gave 3.6 g: bp 160° (0.1 mm); nmr (CCl_4) δ 0.67 (s, 3, $SiCH_3$), 2.23 (s, 2, $SiCH_2$), 4.91 (broad s, 1, C=CHD), 7.10–8.10 (complex m, 12, aromatic).

2-Methyl-1-phenyl-3-buten-1-one (12). A solution of benzaldehyde (0.25 mol) in THF was added to a solution of crotylmagnesium chloride (from 0.3 mol of crotyl chloride) in the THF over a period of 15 min with cooling. The mixture was stirred at room temperature for 6 hr and then refluxed for 15 min. Work-up gave 2-methyl-1-phenyl-3-buten-1-ol in 90% yield: bp 59° (0.3 mm); nmr (CCl_4) δ 0.73, 0.92 (two d, 3, J = 7 Hz, $CH\mathit{CH}_3$), 2.38 (sextet, 1, J = 7 Hz, $CHCH_3$), 3.60 (broad s, 1, OH), 4.27 (m, 1, PhCH), 4.95 (complex m, 2, $CH{=}CH_2$), 5.73 (complex m, 1, $CH{=}CH_2$), 7.20 (s, 5, aromatic); ir (neat) 3400 (OH), 1640 (C=C), 1010 (CO), 910 ($CH{=}CH_2$), 755 and 695 cm^{-1} (monosubst benzene).

The alcohol (above) was oxidized by the method of Meinwald.[35] To a solution of Jones reagent from 7 g of chromium trioxide in 30 ml of acetone was added dropwise 16 g of alcohol in 30 ml of acetone with cooling so that the internal temperature remained *ca.* 15°. The mixture was stirred at room temperature for 2 hr and then sodium bisulfite was added to discharge the brown color. Work-up and distillation gave the ketone product in 86% yield: bp 62° (0.3 mm); nmr (CCl_4) δ 1.27 (d, 3, J = 7 Hz, $CHCH_3$), 4.10 (quintet, 1, J = 7 Hz, $CHCH_3$), 5.10 (complex m, 2, $CH{=}CH_2$), 5.99 (complex m, 1, $CH{=}CH_2$), 7.30 (complex m, 3, aromatic), 6.83 (complex m, 2, aromatic); ir (neat) 3450, 1600, and 1500 (NH), 1315 and 1260 (CN), 990 and 910 ($CH{=}CH_2$), 745 and 688 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 148 (3), 147 (15), 107 (10), 106 (100), 104 (4), 79 (6), 78 (5), 77 (21), 65 (4), 51 (27), 50 (3), 41 (3).

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