facile interchange of the carbinol OD but not the ether CD with atmospheric H_2O during transfer to and through the mass spectrometer. These results clearly indicate that carbinol, and not THF, is the major source of the proton (deuteron) acquired by the carbanion during the course of this arrangement (eq 3) that follows pseudo-first-order kinetics. NaH in THF or t-BuO$^-$ in Me_2SO also effected the rearrangement.

$$\underset{1,\ R\,=\,H,\ D}{(Me_3Si)_3CCH_2CH_2OR} \xrightarrow[THF]{Na/K} \underset{2}{(Me_3Si)_2CRCH_2CH_2OSiMe_3} \quad (3)$$

Since δ-silylcarbinols have also recently been shown to undergo rearrangement[10] and some related silanols have now been shown to rearrange similarly[11] (eq 4), it is apparent that there is a large family of rearrangements involving similar oxyanion to carbanion interconversions, whose scope we are investigating.

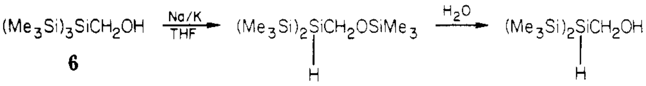
$$(Me_3Si)_3CSiR_2OH \rightarrow (Me_3Si)_3CSiR_2O^- \rightarrow (Me_3Si)_2C^-SiR_2OSiMe_3 \rightarrow (Me_3Si)_2CHSiR_2OSiMe_3 \quad (4)$$

It is already clear from our studies that substitution of silyl groups in $(Me_3Si)_3CCH_2CH_2OH$ by one or more phenyl or *tert*-butyl groups markedly slows down the rate of the rearrangement, fairly obviously because these groups fail to stabilize the intermediate carbanion as effectively as does a silyl group, a conclusion in accord with earlier findings by Eaborn of the higher kinetic acidity of $(Me_3Si)_3CH$ relative to Ph_3CH.[12]

We have now extended the breadth of this type of rearrangement by observing, for the first time as far as we are aware, examples of a related rearrangement involving oxyanion to silanion isomerization. Thus 2-(tris(trimethylsilyl)silyl)ethanol,[13] **3**, prepared in 81% yield (after sublimation) by treatment of (tris(trimethylsilyl)silyl)lithium[14] with ethylene oxide, when treated with a small droplet of 1:5 Na/K alloy (<1-mm diameter, ~5 mol %, much of which was not consumed) in dry THF for 1–2 h. gave the isomeric silyl ether[15] **4** in over 75% yield. If the compound and solvents were not thoroughly dry, traces of the hydrolysis product **5** were also present, as evidenced by weak infrared signals at 3400 (br, OH) and 2130 (SiH) cm^{-1}. The rearrangement followed pseudo-first-order kinetics, consistent with a mechanism in which the rate-controlling step involves isomerization of an initially formed oxyanion to a silanion, which is then rapidly protonated by unrearranged carbinol in the system, as observed in other cases.[1-3] No rearrangement of **3** to **4** was observed on treatment with Et_3N or triethylenediamine over several days, even at reflux temperatures.

$$\underset{3}{(Me_3Si)_3SiCH_2CH_2OH} \xrightarrow[THF]{} (Me_3Si)_3SiCH_2CH_2O^- \rightarrow (Me_3Si)_2Si^-CH_2CH_2OSiMe_3 \rightarrow \underset{4}{(Me_3Si)_2SiHCH_2CH_2OSiMe_3} \xrightarrow{H_2O} \underset{5}{CH_2CH_2OH(Me_3Si)_2SiH}$$

Similarly (tris(trimethylsilyl)silyl)methanol,[16] **6**, obtained by reduction of tris(trimethylsilyl)silanecarboxylic acid[17] in 92% yield, underwent rearrangement with Na/K in THF to yield the silyl ether[18] **7** accompanied by a small amount of its hydrolysis product **8**. Since separation of **7** from **8** could not be effected, **7** was hydrolyzed to **8** in near quantitative yield.[19]



$$\underset{6}{(Me_3Si)_3SiCH_2OH} \xrightarrow[THF]{Na/K} \underset{7}{(Me_3Si)_2\underset{\displaystyle H}{\underset{|}{Si}}CH_2OSiMe_3} \xrightarrow{H_2O} \underset{8}{(Me_3Si)_2\underset{\displaystyle H}{\underset{|}{Si}}CH_2OH}$$

In preliminary experiments we also found that treatment of tris(trimethylsilyl)silanol with Na/K led to several products containing SiH and SiO bonds (infrared), of which some were of higher molecular weight than the starting materials (mass spectrometry), suggesting, at least in part, the involvement of bimolecular processes. In view of the recent finding of Eaborn concerning silanone formation in related systems,[20] it is not clear in this case the extent to which these are the products of an oxyanion to silanion intramolecular rearrangement or of silanone formation followed by further reaction.

In summary, it appears that a family of rearrangements involving isomerization of silylcarbinols to alkoxysilanes exists which is well accounted for by invoking an oxyanion to silanion rearrangement, a sequence which parallels the well-known oxyanion to carbanion isomerizations. We are continuing to explore this family of rearrangements.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada.

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[10] Eaborn, C.; El-Kheli, MN.; Retta, N.; Smith, J. D. *J. Organomet. Chem.* **1983**, *249*, 23.

[11] Damrauer, R.; Eaborn, C.; Happer, D. A. R.; Mansour, A. I. *J. Chem. Soc., Chem. Commun.* **1983**, 348.

[12] Eaborn, C.; Eidenschink, R.; Jackson, P. M.; Walton, D. R. M. *J. Organomet. Chem.* **1975**, *101*, C40.

[13] Properties of **3**: mp 147–162 °C (varies with heating rate); IR (CCl_4) 3360 (br, OH) cm^{-1}; ^1H NMR (CCl_4) δ 0.34 (27 H, s, Me_3Si), 1.28 (2 H, t, CH_2), 1.61 (1 H, br s, OH), 3.78 (2 H, t, CH_2OH); ^{29}Si NMR ($CDCl_3$) δ −12.19 (Me_3Si), −87.74 (Si) ppm. The ^1H NMR spectra used external Me_4Si here and elsewhere.

[14] Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

[15] Properties of **4**: oil; IR (neat) 2075 (SiH), 1080 (SiOC) cm^{-1}; ^1H NMR (C_6D_6) δ −0.33 (9 H, s, Me_3SiO), −0.22 (18 H, s, Me_3Si), 0.83 (2 H, m, CH_2), 2.85 (1 H, t, SiH), 3.36 (2 H, t, CH_2O) ppm.

[16] Properties of **6**: mp 67–74 °C (after two sublimations); IR 3380 (OH) cm^{-1}; ^1H NMR (C_6H_6) δ −0.36 (27 H, s, Me_3Si), 0.12 (1 H, br, OH), 3.05 (2 H, s, CH_2O); ^{13}C NMR (C_6D_6) 1.22 (Me_3Si), 51.10 (CH_2O) ppm; ^{29}Si NMR (C_6D_6) −13.76 (Me_3Si), −81.34 (Si) ppm; mass spectrum, *m/e* 278 (M^+) 263 ($M - Me^+$) 173 (base).

[17] Brook, A. G.; Yau, L. *J. Organomet. Chem.*, in press.

[18] Properties of **7**: IR (neat) 2075 (SiH), 1070 (br, SiOC) cm^{-1}; ^1H NMR (C_6H_6) δ −0.32 (18 H, s, Me_3Si), −0.50 (9 H, s, Me_3SiO), 2.8 (1 H, t, SiH), 3.1 (2 H, d, CH_2O) ppm.

[19] Properties of **8**: IR (neat) 3300–3400 (br, OH), 2110 (SiH) cm^{-1}; ^1H NMR (C_6H_6) δ −0.29 (18 H, s, Me_3Si), 0.38 (1 H, br s, OH), 2.87 (1 H, t, J = 4 Hz, SiH), 3.10 (2 H, d, J = 4 Hz, CH_2O); ^{13}C NMR (C_6D_6) 0.24 (Me_3Si), 50.16 (CH_2O); ^{29}Si NMR (C_6D_6) −15.16 (Me_3Si), −67.75 (Si) ppm.

[20] Aiube, Z. H.; Chojnowski, J.; Eaborn, C.; Stanczyk, W. A. *J. Chem. Soc., Chem. Commun.* **1983**, 493.

Palladium-Catalyzed Addition of Hexamethylditin to Allenes

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Summary: Hexamethylditin adds readily to allenes in the presence of $Pd(PPh_3)_4$; unsymmetrically substituted allenes undergo kinetically controlled addition at lower temperatures, while at higher temperatures the thermodynamically more stable products are formed.

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Table I. Products of the Palladium(0)-Catalyzed Reaction between Hexamethylditin and Allenes RR'C=C=CHR"

R	R'	R"	reactn condtns	% consumptn of allene and ditin	% yield of distannyl-alkene	compositn of product mixture, %: 1	2a	2b
H	H	H	65 °C/2 h	100	89	100		
H	H	H	150 °C/3 days	100	90	67[a]		
Ph	H	H	25 °C/2 days	47	40	100[b]		
Ph	H	H	85 °C/12 days	80	73		100	
MeO	H	H	35 °C/14 days	95	81	62	17	22
MeO	H	H	95 °C/6 days	100	79		58	42
Me_3Sn	H	H	85 °C/15 h	95	62	77	23	
Me	Me	H	85 °C/15 h	95	63	59	41	
Ph	Me	H	80 °C/2 h	46	39	79	4	17
Me	Me	Me	80 °C/2 h	54	45	20[c]	80	

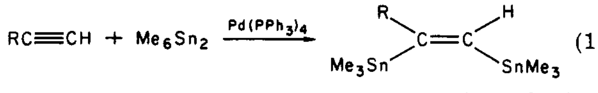
[a] 33% $[H_2C{=}C(SnMe_3)CH_2]_2$ formed. [b] Heating **1** in the presence of the catalyst at 125 °C for 1 h gives 100% **2a**/**2b**. [c] Apparently only the *Z* isomer.

Table II. ^{119}Sn NMR Data for Compounds $Me_3SnCR_1R_2C(SnMe_3){=}CR_3R_4$ (R_4 Cis to Sn)[a]

R_1	R_2	R_3	R_4	$\delta(Me_3Sn_{allyl})$	$\delta(Me_3Sn_{vinyl})$	$^3J(^{119}Sn-^{119}Sn)$
H	H	H	H	−7.8	−36.0	130
Ph	H	H	H	−0.6	−30.3	490
H	H	H	Ph	−2.4	−42.6	118
H	H	Ph	H	−6.8	−24.2	122
MeO	H	H	H	−20.6	−39.4	94
H	H	MeO	H	−9.1	−22.1	181
H	H	H	MeO	−7.6	−39.6	130
Me_3Sn	H	H	H	+11.5	−37.2	281
H	H	H	Me_3Sn[b]	−13.1	−71.3	157
Me	Me	H	H	+16.4	−35.3	161
H	H	Me	Me	−3.6	−45.7	118
H	H	Me	Ph[c]	−10.3	−44.0	105
H	H	Ph	Me[c]	−2.3	−42.4	112
Me	H	Me	Me	+2.8	−57.3	150
Me	Me	H	Me[c]	+14.4	−62.0	218

[a] Chemical shifts in ppm vs. Me_4Sn; coupling constants in Hz. [b] $\delta(R_4)$ −49.1 ppm, ^3J(SnSn) 517, ^4J(SnSn) 90 Hz. [c] Assignment tentative.

We recently reported[1] that hexamethylditin undergoes cis addition to 1-alkynes in the presence of tetrakis(triphenylphosphine)palladium(0) (eq 1). In the case of



(1)

propyne (R=CH_3), however, we obtained 2,3-bis(trimethylstannyl)-1-propene rather than the expected 1,2-bis(trimethylstannyl)-1-propene (eq 2). Since Japanese

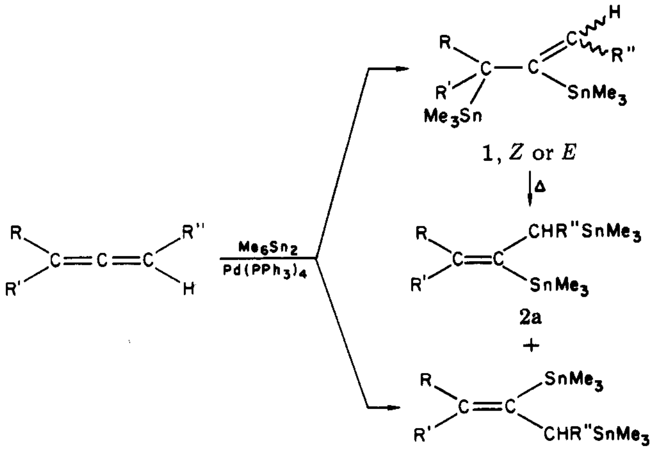
$$CH_3C{\equiv}CH + Me_6Sn_2 \xrightarrow{Pd(PPh_3)_4} Me_3SnCH_2C(SnMe_3){=}CH_2 \quad (2)$$

workers had previously reported that disilanes add to allenes[2] as well as to alkynes[3] in the presence of Pd(0), it seemed likely that allene was formed from propyne under the reaction conditions and reacted more readily than the latter.

We have thus investigated the palladium-catalyzed addition of hexamethylditin to several allenes and wish to present our preliminary results on this addition here.

A summary of the results is provided in Table I. All products have been fully characterised by NMR spectroscopy: ^{119}Sn NMR data are collected in Table II. In those cases in which a single product was formed, it was, where possible, purified by distillation and subjected to elemental analysis.

Four products, **1***Z*, **1***E*, **2a**, and **2b**, can in principle be formed when an unsymmetrically substituted allene reacts with the ditin (only three products when R" = H). Table I shows that the nature of the products formed depends on the reaction conditions: at lower temperatures addition to the more highly substituted double bond is preferred, leading to **1** as the sole or main product, while at higher temperatures and longer reaction times the thermodynamicly more stable products **2a** and **2b** are the main products. The apparent reversibility of the reaction leading to **1** is supported by the observation that attempted distillation of **1** can lead to decomposition to reform the allene and ditin as well as isomerization to **2**. In some cases (1-methoxy-1-(trimethylsilyl)allene, tetrakis(trimethylstannyl)allene) no reaction occurs. (1-Hydroxy-1-cyclo-



2b

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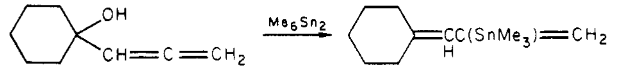
[1] Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45.

[2] Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inoue, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343.

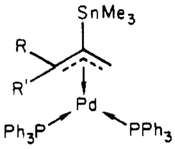
[3] Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149.

hexyl)allene gives the monostannylbutadiene **3**, possibly due to elimination of trimethyltin hydroxide. The regiospecific or regioselective addition noted here was indicated in the previous report of disilane addition:[2] allene and methylallene (1,2-butadiene) reacted with disilanes $X_{3-m}Me_mSiSiMe_nX_{3-n}$ (X = Cl, OMe; *m*, *n* = 0–3), methylallene giving only the product corresponding to the "kinetic" ditin adduct.



3

Though no mechanistic examination of the reaction has been carried out, we assume that (π-allyl)palladium intermediates such as **4** and/or **5** are involved. We can safely presume that the primary palladium species formed are PdL_2·allene[4] and $PdL_2·Me_6Sn_2$ (probably trans, as in the platinum case).[5] The existence of a species such as **4** is supported by the observation that at high temperatures allene itself gives a byproduct that is clearly formed by dimerization of the allyl groups. If **5** is formed with the cis geometry shown and with the π-allyl ligand in the plane of the complex, it can exist in two forms when the allene is not symmetrically substituted. When R and R′ are not too large, the form shown (which leads to the kinetic product) is likely to be favored on steric grounds, but heating can lead via the second form to the thermodynamic product.



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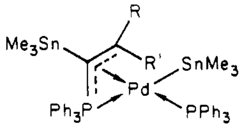

5

The products of addition of hexamethylditin to allenes offer considerable potential in organic synthesis, since they contain both vinylic and allylic trimethyltin residues: the chemistry of the 2,3-bis(trimethylstannyl)-1-propenes is under active investigation.

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Registry No. 1 (R = R′ = R″ = H), 90886-11-6; 1 (R = Ph, R′ = R″ = H), 90886-12-7; (*Z*)-^{1} (R = R′ = H, R″ = Ph), 90886-13-8; (*E*)-1 (R = R′ = H, R″ = Ph), 90886-14-9; 1 (R = MeO, R′ = R″ = H), 90886-15-0; (*E*)-1 (R = R′ = H, R″ = MeO), 90886-16-1; (*Z*)-1 (R = R′ = H, R″ = MeO), 90886-17-2; 1 (R = Me_3Sn, R′ = R″ = H), 90886-18-3; (*Z*)-1 (R = R′ = H, R″ = Me_3Sn), 90886-19-4; 1 (R = R′ = Me, R″ = H), 90886-20-7; (*Z*)-1 (R = R′ = R″ = Me), 90886-25-2; **2** (R = Ph, R′ = R″ = H), 90886-26-3; **2a** (R = Me_3Sn, R′ = R″ = H), 90886-27-4; **3**, 90886-29-6; $Pd(PPh_3)_4$, 14221-01-3; Me_6Sn_2, 661-69-8; $(H_2C{=}C(SnMe_3)(CH_2)_2$, 90886-28-5; $Me_3SnCH_2C(SnMe_3){=}CMe_2$, 90886-21-8; *cis*-$Me_3SnCH_2C(SnMe_3){=}C(Me)Ph$, 90886-22-9; *trans*-$Me_3SnCH_2C(SnMe_3){=}C(Me)Ph$, 90886-23-0; $Me_3SnCH(Me)C(SnMe_3){=}CMe_2$, 90886-24-1; $H_2C{=}C{=}CH_2$, 463-49-0; $PhCH{=}C{=}CH_2$, 2327-99-3; $MeOCH{=}C{=}CH_2$, 13169-00-1; $Me_3SnCH{=}C{=}CH_2$, 4104-88-5; $Me_2C{=}C{=}CH_2$, 598-25-4; $PhC(Me){=}C{=}CH_2$, 22433-39-2; $Me_2C{=}C{=}CHMe$, 3043-33-2; 1-(1,2-propadienyl)cyclohexanol, 34761-56-3.

Supplementary Material Available: Tables of elemental analyses and ^1H and ^{13}C NMR data (7 pages). Ordering information is given on any current masthead page.

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Silylene–Disilene Isomerizations. A Theoretical Study

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Summary: Transition states and barrier heights for the title reactions via 1,2-silyl and 1,2-methyl shifts are investigated through ab initio calculations. The 1,2-silyl shift in silylenes to disilenes is found to proceed at room temperature, this being in agreement with the recent experiment. Also discussed are the structures of disilenes.

There is considerable current interest in the possible interconversion of divalent and doubly bonded silicon compounds. Several examples of the silylene–silene isomerizations (via 1,2-hydrogen[1] and 1,2-silyl[2] shifts) have been documented in the last few years. However, the unimolecular reactions are likely to proceed only at high temperature, as the calculated barrier heights[3] as well as the further experimental studies[4] reveal. In contrast, recently Sakurai and co-workers[5] have found that a silylene, $Me\ddot{S}iSiMe_2(SiMe_3)$ (**1**), isomerizes rapidly to a disilene, $(SiMe_3)MeSi{=}SiMe_2$ (**2**): this is the first example at room temperature. We report here the ab initio calculations of the transition states and barrier heights for the interconversion reactions (1) and (2).[6]

$$\underset{\mathbf{3}}{\mathrm{H\ddot{S}iSiH_2(SiH_3)}} \rightleftharpoons \underset{\mathbf{4}}{\mathrm{(SiH_3)HSi{=}SiH_2}} \qquad (1)$$

$$\underset{\mathbf{5}}{\mathrm{H\ddot{S}iSiH_2(CH_3)}} \rightleftharpoons \underset{\mathbf{6}}{\mathrm{(CH_3)HSi{=}SiH_2}} \qquad (2)$$

All calculations were for closed-shell singlets. Geometries were fully optimized at the Hartree-Fock level with the 6-31G[7] energy gradient method. Energies were improved with the larger 6-31G* basis set[7] using third-order Møller–Plesset perturbation theory.[8]

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