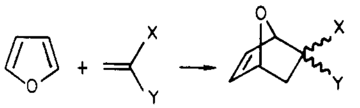
Å. The different conformations of the cyclohexyl groups probably play a role in determining the Sn-N distances (and the C-Sn-C angles as well). Some support for this notion is provided by a recently published structure of a hydrated tributyltin cation $Bu_3Sn(OH_2)_2^+$ in which more nearly identical Sn-O bond lengths of 2.295 (4) and 2.326 (5) Å were reported.[8]

Compounds 1 are effective promoters of Diels-Alder additions to furan (eq 3). The 7-oxabicyclo[2.2.1]heptene



2

(3)

system 2 has found considerable utility in organic synthesis.[9-12] However, eq 3 has typically required either very high pressures[9] or extended reaction times of up to 2-3 months.[10] Recently copper[11] or zinc[12] Lewis acids were reported to increase the rate of these reactions, though from the standpoint of large scale synthesis, both of these systems have practical drawbacks.[13] Using 0.2 M 1, R = cyclohexyl at 40 °C, the addition of either acrylonitrile or 2-chloroacrylonitrile to furan could be effected in 70-75% yield in 24 h (40% excess of furan; no solvent). The products had identical physical and spectroscopic properties to those of the (uncatalyzed) thermal reaction.[14] Interestingly, varying the steric size of the alkyl ligands in 1 from cyclohexyl to methyl had no discernible effect on the ratio of isomeric products (endo/exo) obtained from eq 3. Diels-Alder addition of methyl acrylate to furan was also promoted by 1, but the reaction additionally produced ca. 5% of resinous side products.

Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, and structure factor amplitudes (observed and calculated) (34 pages). Ordering information is given on any current masthead page.

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(8) Davies, A. G.; Goddard, J. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1983**, 597-598. For a review on the structure of organotin compounds, see: Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251-475.

(9) Dauben, W. G.; Krabbenhoft, H. O. *J. Am. Chem. Soc.* **1976**, *98*, 1992-1993.

(10) Nelson, W. L.; Allen, D. R. *J. Heterocycl. Chem.* **1972**, *9*, 561-568.

(11) Moore, J. A.; Partain, E. M., III *J. Org. Chem.* **1983**, 1105-1106.

(12) Brion, F. *Tetrahedron Lett.* **1982**, *23*, 5299-5302.

(13) Specifically, the procedure in ref 3 still requires up to 14 days to achieve a 33% yield while that in ref 4 is faster but requires the use of 40% by weight of Lewis acid in the reaction mixture.

(14) Kienzle, K. *Helv. Chim. Acta* **1975**, *58*, 1180-1183. Schmidt, R. R.; Beitzke, C.; Forrest, A. K. *J. Chem. Soc., Chem. Commun.* **1982**, 909-910.

A New Anion Rearrangement Involving Silyl Migration to Oxygen

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Summary: The proton that is added to carbon during rearrangements of $(Me_3Si)_3CCH_2CH_2OH$ to $(Me_3Si)_2CHCH_2CH_2OSiMe_3$ has been shown, by deuterium labeling, to originate from the hydroxyl group of the parent carbinol and not the solvent. Examples of a related new intramolecular rearrangement that appears to involve oxyanion to silanion isomerization are described.

The metal-(Na/K etc.) and base-catalyzed conversions of α-silylcarbinols to alkoxysilanes (eq 1) that involve oxyanion to carbanion rearrangements (Brook rearrangement) have been thoroughly investigated.[1-3] More recently a related rearrangement has been shown to occur when β-hydroxy silanes are treated with strong base in protic medium.[4] Under these conditions the carbanion intermediate, instead of losing silanolate ion as in the well-known Peterson olefination reaction,[5] is protonated to give the related alkoxysilane (eq 2). (β-Hydroxyvinyl)silanes similarly rearrange to allyl silyl ethers by using sodium hydride in HMPA.[6]

$$R_3SiCR_2OH \xrightarrow{Na/K} R_3SiCR_2O^- \rightarrow R_3SiOC^-R_2 \rightarrow R_3SiOCHR_2 \quad (1)$$

$$R_3SiCR_2CR_2OH \xrightarrow{B} R_3SiCR_2CR_2O^- \rightarrow {}^-CR_2CR_2OSiR_3 \rightarrow HCR_2CR_2OSiR_3 \quad (2)$$

A related rearrangement of a γ-hydroxy silane has recently been described, where the proton that becomes attached to carbon was said to arise from the attack of the carbanion intermediate on THF, the only solvent found in which rearrangement occurred by using NaH or potassium *tert*-butoxide as isomerizing agents. In our view a more probable source of the hydrogen was unrearranged carbinol present in the reaction mixture, and this has now been confirmed by deuteration studies.

Thus, a 0.56-g sample of 3,3,3-tris(trimethylsilyl)-1-propanol,[7,8] 1, was exchanged twice with solutions of 0.5 mL of 99.7% D_2O in 5 mL of THF. On evaporation to dryness, mass spectrometric studies, using the ratio of the abundance of the $(M - Me)^+$ ions for deuterated (*m/e* 262) and protonated (*m/e* 261) species, showed that the carbinol was at least 80.1% deuterated (after taking account of the D, ^{13}C, and ^{29}Si natural abundance isotopes).[9] After rearrangement at about 5% concentration in dry THF using a small droplet of Na/K (<1-mm diameter) for 1 h at room temperature, workup by evaporation after removal of the largely unconsumed Na/K yielded the isomeric 3,3-bis(trimethylsilyl)-3-deuterio-1-(trimethylsiloxy)propane, 2, in quantitative yield, shown by mass spectrometry (after taking account of natural abundance isotopes) to be 92.2% deuterated. That the carbinol appears to be less deuterated than the derived silyl ether is accounted for by the

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(1) Brook, A. G.; Pascoe, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 6224.

(2) Brook, A. G.; Warner, C. M.; Limburg, W. W. *Can. J. Chem.* **1967**, *45*, 1231.

(3) Brook, A. G.; LeGrow, G. E.; MacRae, D. M. *Can. J. Chem.* **1967**, *45*, 239.

(4) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809.

(5) Peterson, D. *J. Org. Chem.* **1968**, *33*, 780.

(6) Sato, F.; Tanaka, Y.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1983**, 165.

(7) Fleming, I.; Floyd, C. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 969.

(8) The ^1H NMR, IR, and mass spectra of this compound were essentially the same as recorded in ref 7. In addition for **1**: ^{29}Si NMR ($CDCl_3$) δ 2.95; ^{13}C NMR ($CDCl_3$) 2.68 (MeSi), 3.77 ($(Me_3Si)_3C$), 34.06 (CH_2), 62.99 (CH_2OH) ppm. For **2**: ^{29}Si NMR (C_6D_6) δ 3.33 (MeSi), 15.7 ($OSiMe_3$). For $(Me_3Si)_2CHCH_2CH_2OH$ (from **2** by hydrolysis): ^{29}Si NMR (C_6D_6) δ 3.35; ^{13}C NMR ($CDCl_3$) -0.03 (Me), 9.28 (CH), 29.08 (CH_2), 64.76 (CH_2OH) ppm.

(9) Thus $(262/261)_{exptl} = M_D/M_H + M_{nat.\ isotopes}/M_H$.

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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.

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

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.

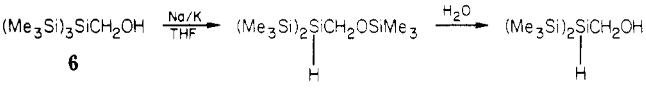
$$(Me_3Si)_3CSiR_2OH \rightarrow (Me_3Si)_3CSiR_2O^- \rightarrow (Me_3Si)_2C^-SiR_2OSiMe_3 \rightarrow (Me_3Si)_2CHSiR_2OSiMe_3 \quad (4)$$

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.

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

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]



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

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.

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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.