values and study the structure–reactivity relationship.

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Inversion at Tetracoordinate Silicon in Nucleophilic Media. Ligand Permutation in 3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′(3*H*,3′*H*)-spirobi[2,1-benzoxasilole]

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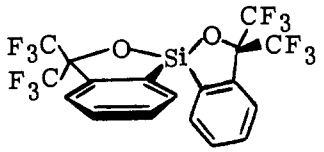
Intramolecular ligand permutation (inversion) at tetracoordinate silicon in nucleophilic media has been observed for a variety of halo- and aminosilanes.[1] As the inversion process is always second order (or higher-order) with respect to the nucleophile, the mechanism is generally thought to involve reversible stepwise attack of two molecules of nucleophile to give a symmetrical penta- or hexacoordinate intermediate or transition state. We wish to present the first example known to us of inversion at tetracoordinate silicon in nucleophilic media which occurs at a rate showing a first-order dependence on the concentration of the nucleophile.

The spirosilane **1**[2] exhibits an A_3B_3 ^{19}F NMR spectrum in nonnucleophilic solvents (e.g., chloroform, toluene) which, upon addition of weak nucleophiles, shows the coalescence of trifluoromethyl peaks expected for the interconversion accompanying inversion at silicon.



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Kinetic studies on **1** were carried out by visual fit of observed and calculated spectra[3] to determine the pseudo-first-order rate constant ($k_1 = k_2$ [Nu]^n). The order of inversion with respect to the nucleophile is given by the slope of a plot of ln k_1 vs. ln [Nu] and is clearly unity for nucleophiles tetrahydropyran (0.984 ± 0.009) or benzaldehyde (0.97 ± 0.02). Quoted errors are standard deviations, calculated from points for at least four different concentrations of nucleophile (ca. 0.05–0.5 M).

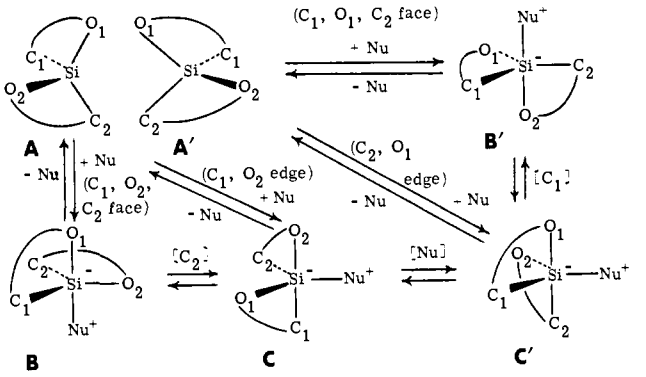

Figure 1. Selected pathways for the racemization of **1** by nucleophilic attack on a tetrahedral face opposite oxygen (A ⇄ B ⇄ C ⇄ C′ ⇄ B′ ⇄ A′), or on a C,O edge (A ⇄ C ⇄ C′ ⇄ A′) of the tetrahedral silicon, with intervening Berry pseudorotation steps about the pivot ligand indicated in brackets.

The effect of substituents on the rate of inversion was investigated by using a series of para-substituted benzaldehydes as nucleophiles.[4] The best correlation was obtained by using the Yukawa and Tsuno modification of the Hammett–Brown equation[5]: $\log k/k_0 = [\sigma + 0.39(\sigma^+ - \sigma)]\rho$ with a ρ value of −1.52 ± 0.03.[6] Activation parameters determined from the temperature dependence of k_2 with benzaldehyde as nucleophile are $\Delta H^* = 6.9 \pm 0.2$ kcal/mol, $\Delta S^* = -27.9 \pm 1.2$ eu, and $\Delta G^*_{298} = 15.2 \pm 0.4$ kcal/mol.

Inversion of **1** by ionization to a zwitterionic silicenium ion appears unlikely as the rate of inversion shows no relation to the polarity of the nucleophile.[7] A mechanism involving attack of one molecule of nucleophile at silicon to give a pentacoordinate intermediate is consistent with all of these findings, including first-order kinetics in the nucleophile and a moderately negative activation entropy (an ordered transition state). The transition state, with its developing positive charge at the nucleophilic center, is stabilized by electron-releasing substituents on benzaldehyde, giving rise to the negative value of ρ.

One plausible mechanism for the inversion of **1** involves attack of the nucleophile[8] on the O,O edge of the tetrahedron of **1** to give **2**, followed by the sequence of five pseudorotation steps necessary to invert the chirality of a trigonal-bipyramidal species.[9] Loss of the nucleophile then gives silane of inverted configuration. Although several such pseudorotation sequences are possible starting from **2**, all involve high energy intermediates[9,10] having two apical carbons or a diequatorial five-membered ring and one apical carbon ligand.

Pseudorotation mechanisms have been invoked to explain ligand permutation of a few fluorosiliconates[11] and most recently and most convincingly for the isolable siliconate **3** (the report of which[12] appeared shortly after this paper had been submitted). The structure of **3** was confirmed by an X-ray crystal structure determination and is essentially that which was proposed for similar siliconates prepared in this laboratory,[2] on the basis of data obtained on the solution phase.

While the reported nondissociative inversion of **3** most probably involves a sequence of five pseudorotation steps, such a mechanism

(1) (a) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1980**, *186*, 25. (b) Corriu, R. J. P.; Larcher, F.; Royo, G. *Ibid.* **1976**, *104*, 293. (c) Corriu, R. J. P.; Henner-Leard, M. *Ibid.* **1974**, *65*, C39. (d) Corriu, R.; Henner-Leard, M. *Ibid.* **1974**, *64*, 351. (e) Corriu, R. J. P.; Henner, M. *Ibid.* **1974**, *74*, 1. (f) Carre, F.; Corriu, R.; Leard, M. *Ibid.* **1970**, *24*, 101. (g) Corriu, R. J. P.; Leard, M. *J. Chem. Soc., Chem. Commun.* **1971**, 1086. (h) Corriu, R.; Henner, M. *Bull. Soc. Chim. Fr.* **1974**, 1447. (i) Corriu, R.; Leard, M.; Masse, J. *Ibid.* **1968**, 2555. (j) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7045. (k) Sommer, L. H.; Rodewald, P. G. *Ibid.* **1963**, *85*, 3898. (l) Tamao, K.; Ishikawa, M.; Kumada, M. *Chem. Commun.* **1969**, 73. (m) Kaufmann, K. D.; Ruhlmann, K. *Z. Chem.* **1967**, *7*, 391.

(2) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591. (b) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(3) Spectra were calculated by using modified LAOCOON 3 programs. See: Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 4701. Spectral parameters for **1** were $J_{FF} = 8.8$ Hz, $T_1 = 0.15$. The chemical shift difference between the trifluoromethyl groups in **1** was found to vary linearly with temperature, $\Delta\nu$ (Hz) = 33.7 − 0.0758T (°C), at 84.6 MHz.

(4) Para substituents were $(Me)_2N$, MeO, CH_3, H, Cl, NO_2.

(5) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971.

(6) Values of σ and σ^+ are those given by: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

(7) At 35 °C inversion of **1** is very fast in methanol and tetrahydrofuran, fast in acetone and tetrahydropyran, slow in acetic acid, and undetectable in nitrobenzene, 1,2-dichloroethane, and toluene.

(8) For a recent review on the mechanism of nucleophilic displacement at silicon, see: Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.

(9) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321.

(10) Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.

(11) (a) Gibson, J. A.; Ibbott, D. G.; Janzen, A. F. *Can. J. Chem.* **1973**, *51*, 3203. (b) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155.

(12) Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608.

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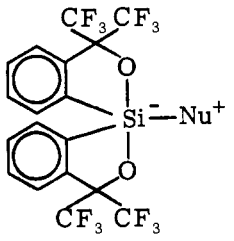

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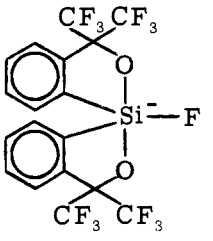

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is not necessary to explain the inversion of **1** promoted by weak nucleophiles. The structure of the initially formed intermediate is not known. Although **2** might be expected to be the most stable structure, it may not be the kinetically favored product of nucleophilic attack. If attack of nucleophile were to occur opposite one of the oxygen ligands, inversion of configuration could be obtained by a sequence of three pseudorotations (B ⇄ C ⇄ C′ ⇄ B′) followed by loss of the nucleophile (Figure 1). This sequence has an advantage energetically over the five-step sequence starting from **2** in that the intermediate having a diequatorial five-membered ring has two apical oxygens, one of them being a highly apicophilic oxonium ligand.

An even shorter (and possibly lower energy) pathway for racemization is possible if one invokes attack on the C_1, O_2 edge (or the C_2, O_1 edge) of the tetrahedron of **1**. This three-step inversion (A ⇄ C ⇄ C′ ⇄ A′) involves only one pseudorotation step interconverting enantiomers C and C′, energetically equivalent species with one apical carbon and without a diequatorial five-membered ring.

Some of these mechanisms for inversion propose edge (equatorial) attack of the nucleophile rather than face (apical) attack to give the initial intermediate. A similar mode of attack has been proposed to explain retention of configuration in nucleophilic substitution at silicon,[8] i.e., equatorial attack of the nucleophile to give a pentacoordinate intermediate followed by apical departure of the leaving group. Alkoxy-substituted silanes are thought to be particularly susceptible to equatorial attack, as these compounds usually give retention of configuration upon nucleophilic substitution. Apical attack on **1** may be strongly disfavored since it always leads to a high-energy intermediate having a five-membered rink linking equatorial sites. It may nevertheless be kinetically favored, with subsequent pseudorotation leading to more stable intermediates.[13]

Silane **1** is remarkably electrophilic, forming 1:1 adducts with such nucleophiles as pyrrolidine[14] and 4-(*N*,*N*-dimethylamino)-pyridine.[2] In contrast, **1** does not easily form hexacoordinate compounds by the addition of two nucleophiles—none have yet been isolated or observed spectroscopically. For example, the ^{29}Si spectra of **1** in the presence of 1–5 equiv of sodium methoxide show only a peak at −76.4 ppm (±0.3 ppm), characteristic of a pentacoordinate compound.[15] Furthermore, in solution with a large excess of the nucleophile pyrrolidine, the isolated stable adduct of pyrrolidine and **1** shows no evidence in its ^{19}F NMR spectrum of the inversion which could accompany nucleophilic displacement at silicon via a hexacoordinate transition state.[14]

The bidentate ligands of **1** are exceptionally well suited to stabilize pentacoordinate silicon, but they are less capable of stabilizing hexacoordinate structures. The reversible formation of pentacoordinate intermediates in weakly nucleophilic media is thus expected. Pseudorotation of these intermediates provides the most probable mechanism to account for the observed rapid nucleophile-induced inversion of configuration.

Acknowledgment. We are grateful to Professor A. J. Arduengo for assistance in adapting the LAOCOON programs and Professor R. Corriu for helpful suggestions. This research was supported in part by a grant from the National Science Foundation (CHE 81-13142). NMR experiments were conducted at the University of Illinois Midwest NSF Regional NMR Facility (CHE 79-16100).

Registry No. 1, 70091-69-9; **2** (Nu = pyrrolidine), 80145-68-2.

(13) Inversion of **1** by a series of fluoroalkoxy O–Si bond dissociation and recombination steps of the pentacoordinate intermediate cannot be rigorously excluded but seems unlikely. The rate of inversion shows no relation to solvent polarity, and the breaking of a relatively strong silicon–oxygen bond of a five-membered ring is expected to be energetically unfavorable.

(14) The pyrrolidine adduct was synthesized by addition of 1 equiv of pyrrolidine to **1** in dichloromethane, removal of the solvent under reduced pressure, and recrystallization from dichloromethane–pentane (72% isolated yield): mp 198–199 °C; ^1H NMR ($PhNO_2$-d_5) δ 8.4 (m, 2.0, H ortho to Si on spirobicyclic rings), 7.9–7.4 (m, 6.0, remaining *H* on spirobicyclic rings), 6.9–6.0 (br s, 1.3, HN), 3.5 (t, 4.1, CH_2N), 1.95 (m, 4.1, remaining H on pyrrolidine); ^{19}F NMR ($PhNO_2$-d_5) (A_3B_3) δ −74.5, −75.1, J_{FF} = 9.9 Hz; ^{29}Si NMR ($PhNO_2$-d_5) δ −82.4 (s); MS (70 eV) *m/e* (relative intensity) 512 (55.0, $M^+ - C_4H_9N$), 443 (100.0, $M^+ - C_4H_9N - CF_3$), 71 (23.2, $C_4H_9N^+$). Anal. ($C_{22}H_{17}F_{12}NO_2Si$) C, H, N.

(15) Silane **1** exhibits a ^{29}Si signal at δ 8.6 (downfield of tetramethylsilane); pentacoordinate compounds derived from **1** give signals between δ −64.1 and −82.4, an upfield shift characteristic of pentacoordinate silicon. See: Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* **1980**, *186*, 13.

Stereochemical Control of the Internal Michael Reaction. A New Construction of *trans*-Hydrindane Systems.

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Vicinal stereochemistry can often be controlled very effectively via cycloadditions: The Diels–Alder reaction immediately comes to mind. This vicinal control has been very important in the construction of bicyclic systems but has been somewhat limited in that it leads most directly to cis fusions. The important system represented by the trans "angularly methylated" hydrindanes is a case in point: they can be reached via Diels–Alder addition only by subsequent more or less elaborate further manipulation of the initial cis adducts.[1] We now report that the intramolecular Michael addition provides a new approach to the construction of bicyclic systems and illustrate this here with the synthesis of *trans*-hydrindanes. We show that, using **1** below, (a) the intramolecular Michael addition takes precedence over the formally possible vinylogous aldol condensation and (b) the stereochemical result can be controlled to give the very desirable trans arrangement of the two carbonyl chains, thus leading to a simple route to *trans*-hydrindenones (Scheme I).

The synthesis of the model system **1** is outlined in Scheme II.

Reaction of silyl enol ether **4**[2] with *m*-chloroperbenzoic acid in tetrahydrofuran at 0 °C followed by treatment of the intermediate α-silyloxy ketone with tetrabutylammonium fluoride furnished the α-hydroxy ketone[3] which was cleaved with $Pb(OAc)_4$ in methanol to provide the aldehydo ester **6** (in 57% yield from **4**): IR (neat) 1715, 1730, 2700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (3 H, d, *J* = 7 Hz, CH_3), 3.7 (3 H, s, CH_3), 9.75 (1 H, t, *J* = 2 Hz, CHO). Condensation of **6** with dimethyl (2-oxopropyl)-phosphonate in aqueous potassium hydroxide/methanol (0 °C) furnished enone ester **7** in 81% yield: IR (neat) 1630, 1680, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (3 H, d, *J* = 7 Hz), 2.25 (3 H,

†Present address: Department of Chemistry, University of Colorado, Boulder, CO 80302.

(1) Woodward, R. B.; Sondheimer, F.; Taub, D.; Heusler, K.; McLamore, W. M. *J. Am. Chem. Soc.* **1952**, *74*, 4223. Stork, G.; Stotter, P. L. *Ibid.* **1969**, *91*, 7780. Trans, as well as cis, hydrindanes are produced in internal Diels–Alder reactions (Jung, M. E.; Halweg, K. *Tetrahedron Lett.* **1981**, 3929. Bal, S.; Helquist, P. *Ibid.* **1981**, 3933. Roush, W.; Peseckis, S. *J. Am. Chem. Soc.* **1981**, *103*, 6696. Kametani, T.; Matsumoto, H.; Honda, T.; Fukumoto, K. *Tetrahedron Lett.* **1980**, 4847.

(2) Stork, G.; Hudrlik, P. *Ibid.* **1968**, *90*, 4462.

(3) Rubottom, G. M.; Vasquez, M. A.; Pelagrince, D. R. *Tetrahedron Lett.* **1974**, 4319. Rubottom, G. M.; Gruber, J. M.; Boeckman, R. K., Jr.; Ramaiah, M.; Medwid, J. B. *Tetrahedron Lett.* **1978**, 4603.

0002-7863/82/1504-0310$01.25/0