pectedly slower; e.g., aryl or primary acyl radicals,[12] useful yields of stoichiometric acyl radical–olefin intermolecular addition products may be obtained. Since existing methods for promoting the free radical chain addition of aldehydes to alkenes commonly employ a substantial excess (4–10 molar equiv) of aldehyde relative to alkene,[1-3] phenyl selenoesters can serve as a useful alternative and complementary source of acyl radicals in instances when this component is economically or synthetically valuable. The mild and controlled reaction conditions for acyl radical generation may permit applications in instances where the presence of sensitive functionality would prohibit the use of conventional[9] or related methodology involving ionic acyl equivalents.[16]

Acknowledgment. Financial support of the National Institutes of Health (CA42056) and the Alfred P. Sloan foundation is gratefully acknowledged.

Supplementary Material Available: Full details of the preparation and characterization of phenyl selenoesters 1 and the free radical addition products 3–4 (8 pages). Ordering information is given on any current masthead page.

Dale L. Boger,*[17] Robert J. Mathvink
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907
Received January 20, 1989

(16) Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. Groves, J. K. *Chem. Soc. Rev.* **1972**, *1*, 73.

(17) National Institutes of Health research career development award recipient, 1983–88 (CA01136). Alfred P. Sloan Foundation research fellowship recipient, 1985–1989.

Axial Chirality by Asymmetric Induction. Diastereomeric Allene Formation via Silicon as a Chiral Auxiliary†

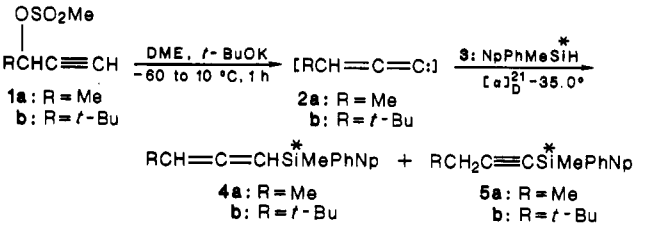
Summary: Interaction of alkenylidenecarbenes, RCH=C=C:, R = CH_3 and *t*-Bu, with chiral α-NpPhMeSi*H results in chiral allenes with a 3.5 ± 0.5% and 10.5 ± 0.5% diastereomeric excess, respectively. Hence the transfer of central chirality to axial chirality, via silicon as a chiral auxiliary, has been established. These results are discussed, and a transition state is proposed.

Sir: The practice and understanding of asymmetric synthesis is a major challenger and objective of modern organic chemistry.[2] A common means of achieving this goal is asymmetric induction via chirality transfer from one stereogenic center to another with the aid of a chiral auxiliary, most often a chiral carbon center.[2] Although numerous examples of asymmetric induction exist,[2] little, if anything, is known[3] about the possibility of generating axial chirality by way of asymmetric induction.

Silicon chemistry and its application in synthesis is burgeoning.[4] In spite of this interest and activity in silicon chemistry, the possible application of optically active organosilanes in synthesis and, especially, the use of optically active silicon as a chiral auxiliary have been rarely exploited, with only a few examples reported.[5] Hence, with the dual aim of examining the creation of axial chirality via asymmetric induction and the use of optically active silicon as the chiral auxiliary in chirality transfer, we investigated the interaction of dyssymmetrically substituted alkenylidenecarbenes **2** (Scheme I) with optically pure α-NpPhMeSi*H.[6]

Both enantiomers of optically pure α-NpPhMeSi*H are readily available by the procedure of Corriu and Moreau.[7] By a process exactly analogous to one previously reported,[8] we firmly established[1] that the insertion of $H_2C{=}C{=}C$: into the Si–H bond of optically pure (−)-(*S*)-α-NpPhMeSi*H proceeds with at least 98% stereospecificity, resulting in chiral allenylsilane of *retained* absolute con-

Scheme I



figuration with a specific rotation of $[\alpha]^{20}_D$ −6.32 ± 0.03° (pentane).

Interaction of the known methanesulfonate[9] **1** derived alkenylidenecarbenes **2** with **3** in glyme gave the silaallene

(1) Abstracted in part from: Learned, A. E. Ph.D. Dissertation, The University of Utah, 1987.

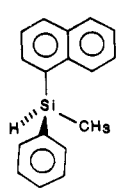
(2) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983–1985; Vols. 1–5. Nogradi, M. *Stereoselective Synthesis*; VCH Verlag: Weinheim, Germany, 1986.

(3) Jean, A.; Lequan, M. *J. Organomet. Chem.* **1973**, *50*, 75. Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062.

(4) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag: New York, 1983. Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(5) Larson, G. L.; Torres, E. *J. Organomet. Chem.* **1985**, *293*, 19. Larson, G. L.; Sandoval, S.; Cartledge, F.; Fronczek, F. R. *Organometallics* **1983**, *2*, 810. Paquette, L. A.; Hathaway, S. J. *J. Org. Chem.* **1983**, *48*, 3351. Paquette, L. A; Daniels, R. G. *Organometallics* **1982**, *1*, 1449. Fristad, W. E.; Bailey, T. R.; Paquette, L. A.; Gleiter, R.; Bohm, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4420. Fry, J. L.; Adlington, M. G. *Ibid.* **1978**, *100*, 7641.

(6) (*S*)-α-NpPhMeSi*H =



(7) Corriu, R. J. P.; Moreau, J. J. E. *Bull. Soc. Chim. Fr.* **1975**, *3*, 901.

(8) Stang, P. J.; Learned, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 5019.

† Dedicated to Professor Jerome A. Berson on the occasion of his 65th birthday.

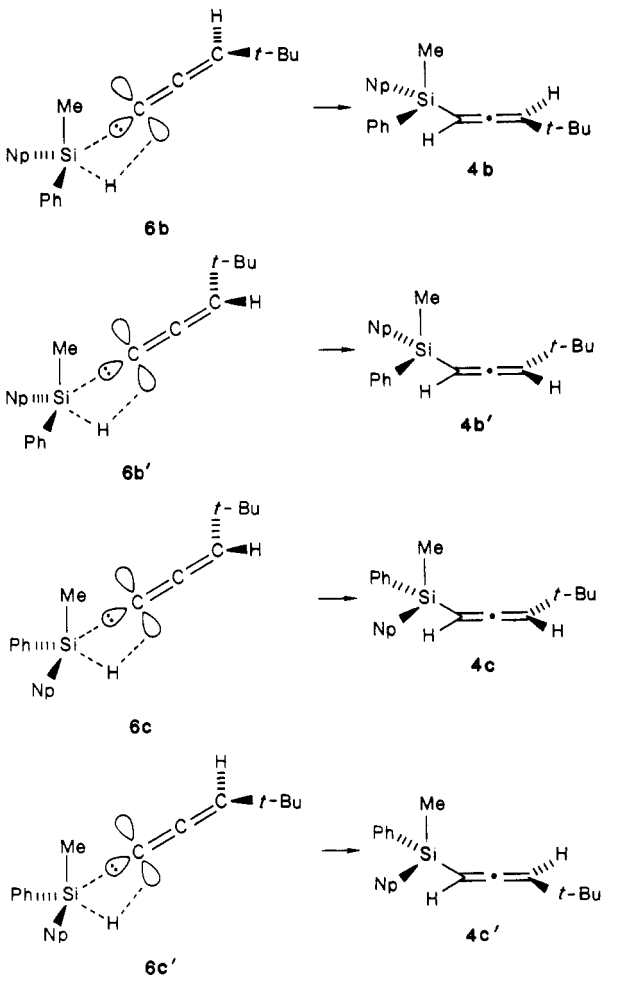
0022-3263/89/1954-1779$01.50/0

insertion products 4[10] along with rearranged[11] silaalkynes 5.[12] Examination of both the proton and carbon-13 in each sample. Careful, multiple integration of appropriate NMR signals[13] for *duplicate* runs for each reaction indicate a diastereomeric excess of 3.5 ± 0.5% for the methyl isomer **4a** and 10.5 ± 0.5% for the *tert*-butyl isomer **4b**. Isolation of recovered, excess starting silane **3** indicated no loss of optical activity. Hence, the data clearly establish that chirality transfer from silicon to the axial chirality of allene via 1,3-asymmetric induction occurs albeit with low diastereomeric preference. The extent of asymmetric induction, as expected, is a function of the steric bulk of the substituent on the carbene-derived nascent allene and increases as the size of R increases.

Our attempts to separate the diastereomers of **4a** and **4b**, in hopes of assigning absolute configuration to the respective chiral allenes by Brewster's rules,[14] have to date failed. However, a stereochemical assignment may be proposed, based upon examination of molecular models and reasonable assumptions based upon analogy, for the transition states of alkenylidenecarbene Si–H insertions. Concomitant theoretical and experimental results have established[15] that alkylidenecarbenes interact with substituted olefins in a manner that minimizes the steric interaction between the respective carbene and olefin substituents. Moreover, we have established (vide supra) that all unsaturated carbene insertions into the Si–H bond of a chiral silane occur by retention of absolute configuration about the silicon center. On the basis of these observations, one can propose two plausible transition states, **6b** and **6b′**, for the reaction of **2b** with (–)-(*S*)-α-NpPhMeSi*H leading to diastereoisomers **4b** and **4b′**, respectively, as shown in Scheme II. Because of the lower *tert*-butyl–phenyl as opposed to a *tert*-butyl–naphthyl interaction, transition state **6b** might be favored over **6b′**, predicting the *R,S* diastereoisomer **4b** as the one preferentially formed. This hypothesis can be tested by examining the interaction of **2b** with the opposite enantiomer of the chiral silane, namely, (+)-(*R*)-α-NpPhMeSi*H. By arguments similar to those above, transition state **6c** leading to the *S,R* diastereomer **4c** should be favored over **6c′**, which yields allenylsilane **4c′**. Since diastereoisomers **4b** and **4c** constitute an enantiomeric pair, they should exhibit identical spectral properties (^{1}H and ^{13}C NMR) and the same magnitude but the opposite sign for their respective specific rotations. Indeed reaction of **2b** with either optically pure (–)-(*S*)-α-NpPhMeSi*H or optically pure (+)-(*R*)-α-NpPhMeSi*H gave products with identical NMR spectra, but the rotations of the allenylsilane products were $[\alpha]^{19}_D$ +3.27° from **3*S*** and $[\alpha]^{20}_D$ –3.22° from **3*R***, respectively. Hence, these data are consistent with our transition-state models and stereochemical assignments.[16]

In conclusion, we have established that the creation of axial chirality via 1,3-asymmetric induction using silicon

Scheme II



(9) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(10) Adduct **4a** in 24% and **4b** in 48% yield, respectively. For **4a**: HRMS (EI, M$^+$) calcd for $C_{21}H_{20}Si$ 300.1342, found 300.1340; IR (neat) 3060, 2960, 2920, 1940 (C=C=C), 1590, 1505, 1430, 1250, 1110, 825, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05–7.25 (m, 24 H), 5.37 (dq, *J* = 6.9, 3.6 Hz, 2 H), 4.81 (dq, *J* = 6.9 Hz, 2 H), 1.57 (dd, *J* = 6.6, 3.6 Hz, 6 H), 0.77 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 212.96, 137.14, 136.96, 135.35, 134.62, [134.14, 134.09], 133.37, 130.45, 129.27, 128.86, 128.78, 127.84, 125.64, 125.41, 125.06, 79.83, 79.13 [12.85, 12.76], [–2.32, –2.38] (brackets indicate duplicate signals due to diastereomers). For **4b**: $[\alpha]^{19}_D$ +3.27; HRMS (EI, M$^+$) calcd for $C_{24}H_{26}Si$ 342.1803, found 343.1801; IR (neat) 3045, 2960, 2900, 1940 (C=C=C), 1588, 1387, 1360, 1250, 1205, 1105, 820, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05–7.25 (m, 24 H), [5.51, 5.50] (d, *J* = 7.0 Hz, 2 H), [4.86, 4.84] (d, 7.0 Hz, 2 H), [0.93, 0.92] (s, 18 H), [0.77, 0.76] (s, 6 H); ^{13}C NMR ($CDCl_3$) δ [209.83, 209.74], 137.26, 136.98, [135.42, 135.37], [134.69, 134.64], [134.38, 134.18], 133.37, [130.43, 130.38], 129.62, 129.13, 128.84, 127.83, 125.63, 125.39, 125.06, 82.48, [97.01, 96.97], 31.02, 30.38, –2.36 (brackets indicate duplicate signals due to diastereomers).

(11) The base-promoted isomerization of allenes to alkynes via a "conducted tour" process is well established. Cram, D. J.; Bosser, L. *J. Am. Chem. Soc.* **1964**, *86*, 2950. Bushby, R. J. *Q. Rev., Chem. Soc.* **1970**, *24*, 585. Theron, F.; Verny, M.; Vessiere, R. *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; p 381.

(12) Alkyne **5a** in 29% and **5b** in 21%, respectively. For **5a**: IR (neat) 3045, 2955, 2920, 2170 (C≡C), 1590, 1505, 1425, 1250, 1110, 820, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10–7.25 (m, 12), 2.33 (q, *J* = 7.3 Hz, 2 H), 1.19 (t, *J* = 7.3 Hz, 3 H), 0.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 136.72, 136.20, 135.35, 134.55, 133.38, 133.13, 130.64, 129.45, 128.80, 128.71, 127.91, 125.69, 125.45, 125.08, 113.11, 80.58, 13.86, 13.67, –0.71. For **5b**: MS (EI, *m/z*) 342 (M$^+$, 63) 327 (100), 247 (11); IR (neat) 3050, 2960, 2175 (C≡C), 1590, 1505, 1460, 1387, 1360, 1250, 1105, 820, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.20–7.15 (m, 12 H), 2.21 (s, 2 H), 1.03 (s, 9 H), 0.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 136.72, 136.31, 135.23, 134.53, 133.36, 133.26, 130.61, 129.42, 128.80, 128.76, 127.89, 125.72, 125.45, 125.05, 110.24, 82.97, 35.14, 31.37, 29.08, –0.65.

(13) The homonuclear decoupled C_{sp^2}–CH_3 groups were integrated for **4a**. Homonuclear decoupling was unnecessary for **4b**, and the product ratios were determined by straightforward integration of the diastereomeric Si–CH_3 groups.

(14) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 33. Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475.

(15) Apeloig, Y.; Karni, M.; Stang, P. J.; Fox, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 4781.

(16) The change in sign of rotation from levorotatory for the parent system CH_2=C=CHSi* to dextrorotatory for the substituted molecule *t*-BuCH=C=CHSi* indicates that the allenic portion of **4b** is dextrorotatory in accord with the Lowe–Brewster analysis[14,17] and our proposed transition states.

(17) Lowe, G. *Chem. Commun.* **1965**, 411. More, W. R.; Anderson, H. W.; Clark, S. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1971**, *93*, 4932.

as a chiral auxiliary is feasible. The extent of asymmetric induction is small and varies as a function of the steric bulk of the carbene/allene substituents with a diastereomeric excess of 3.5 ± 0.5% for R = CH_3 and 10.5 ± 0.5% for R = *t*-Bu. These values correspond to a difference in energy between diastereomeric transition states of only 22 cal/mol for the methyl-substituted system and 75 cal/mol for the *tert*-butyl system.

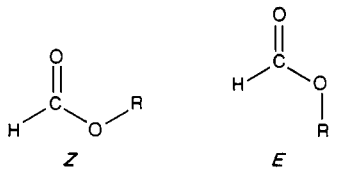
Acknowledgment. We are grateful to the NSF (CHE-8802622) for financial support.

Peter J. Stang,* Alan E. Learned[1]
Department of Chemistry
The University of Utah
Salt Lake City, Utah 84112
Received November 7, 1988

Dynamic Nuclear Magnetic Resonance Study of Vinyl Formate

Summary: Low-temperature carbon-13 NMR spectra of vinyl formate show that the populations of the *E* and *Z* conformations are 0.05 and 0.95 at −110 °C, with free energy barriers to interconversion at −87 °C of 8.3$_4$ and 9.2$_9$ kcal/mol.

Sir: Esters, amides and many related compounds have a strong preference for the *Z* conformation.[1] For methyl formate, the percentage of the *E* isomer in a favorable solvent (1:1 DMF/acetone-d_6) is only 0.3% at −83 °C,[2] and



Z *E*

1, R = CH_3; **2**, R = $(CH_3)_3C$; **3**, R = C_6H_5; **4**, R = CH_2=CH

several factors may be responsible for the large free energy difference of 2.2 kcal/mol between conformations: (1) Dipole–dipole interactions are more favorable for the *Z* conformation.[3] (2) The *Z* conformation may be stabilized by the interaction between a lone pair of electrons on the "ether" oxygen and σ^* of the carbonyl group.[4] (3) A cyclic "aromatic" system of six electrons is possible for the *Z* conformation, with two electrons each coming from the carbonyl π-bond, a lone pair of electrons on the "ether" oxygen, and a π-type orbital of the methyl group.[5]

"Aromaticity" also appears to be important for other alkyl groups; steric interactions in (*Z*)-**2** between oxygen and *tert*-butyl should be larger than the corresponding repulsion between the formyl hydrogen and *tert*-butyl in the *E* conformation, and the *E* − *Z* free energy difference in DMF/acetone-d_6 is smaller than for methyl formate, but the *Z* conformation is still favored by 0.48 kcal/mol.[2]

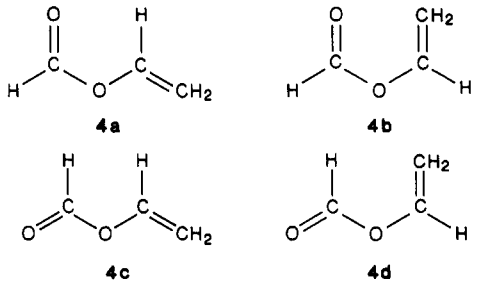
Aryl groups cannot complete an aromatic sextet in the *Z* conformation, and we have found a large population of the *E* conformation for phenyl thiolformate[6] and, more recently, for phenyl formate[7] (Table I). Vinyl esters should also be "nonaromatic", and we report here a dynamic NMR study of vinyl formate.

Table I. Populations of the *E* Isomers and *E* − *Z* Conformational Free Energy Differences for Esters of Formic Acid

ester	temp, °C	solvent	P_E	$\Delta G°$, kcal/mol	ref
1	−83	*a*	0.003	2.2	2
2	−105	*a*	0.19	0.48	2
2	−116	*b*	0.14	0.57	7
3	−117	*b*	0.20	0.43	7
4	−110	*b*	0.05	0.95	this work

[a] DMF/acetone-d_6 (1:1). [b] Acetone/acetaldehyde (1:3).

Four planar conformations are possible for vinyl formate, as shown in structures **4a–d**. Although several studies of this compound have been reported,[8–12] no experimental



4a **4b**

4c **4d**

evidence for the existence of the *E* conformations (**4c** or **4d**) has been described. The room-temperature 60-MHz proton NMR spectrum has been recorded[8] and shows long-range coupling to the formyl hydrogen. The microwave spectrum[9] of **4** was interpreted in terms of the planar conformation **4a**, and it was not possible to assign lines for any other conformation, although there were many lines that were not assigned. A later microwave study,[12] an electron-diffraction study,[12] and ab initio molecular orbital calculations[11,12] are in agreement with planar **4a** being the major conformation of vinyl formate, and the vibrational spectrum[10] and dipole moment[11] have also been interpreted in terms of this structure. The apparent planarity of this ester is in contrast to phenyl formate, which is reported[13,14] to have the phenyl group tilted by about 60°.

Because the *E* conformations are more polar than the *Z* isomers and are favored by polar solvents, we have taken

(1) For reviews, see: (a) Exner, O. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S.; Ed.; Interscience; London, 1977; p 1. (b) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.
(2) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.
(3) (a) For a listing of references discussing this effect, see ref 1a. (b) Recent calculations emphasize the importance of dipole–dipole interactions: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.
(4) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713.
(5) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1. See also ref 6 and references cited therein.
(6) Noe, E. A.; Sanders, T.; Garahi, M.; Hosseini, H.; Young, R. *J. Am. Chem. Soc.* **1985**, *107*, 4785.
(7) Mark, H. L.; Baker, T.; Noe, E. A. *J. Am. Chem. Soc.*, in press.
(8) Schaefer, T. *J. Chem. Phys.* **1962**, *36*, 2235.
(9) Rao, V. M.; Curl, R. F., Jr. *J. Chem. Phys.* **1964**, *40*, 3688.
(10) Gardenina, A. P.; Kotorlenko, L. A. *Opt. Spectrosc.* (*Engl. Transl.*) **1968**, *24*, 495.
(11) Aroney, M. J.; Bruce, E. A. W.; John, I. G.; Radon, L.; Ritchie, G. L. D. *Aust. J. Chem.* **1976**, *29*, 581.
(12) Pyckhout, W.; Van Alsenoy, C.; Geise, H. J.; Van Der Veken, B.; Coppens, P.; Traetteberg, M. *J. Mol. Struct.* **1986**, *147*, 85.
(13) Schaefer, T.; Penner, G. H. *Can. J. Chem.* **1987**, *65*, 2175.
(14) Schaefer, T.; Sebastian, R.; Penner, G. *Can. J. Chem.* **1988**, *66*, 1787.

0022-3263/89/1954-1781$01.50/0