3 H nmr singlets at δ 0.99, 1.04, and 1.70 (broad), and signals at 2.8 (m, 1 H, C-1(H)), 3.5 (m, 1 H, C-5(H)), and 5.3–5.8 (m, 3 H, vinyl protons), in a 4:1 ratio. An alternative formulation for the bicyclic product, 2,2,7-trimethylbicyclo[3.2.0]hepta-3,6-diene, is excluded since a C(6)–H resonance well below the other olefinic absorptions is absent.

For the isomerization **5** → **7** at 200°, $k \leqq 2 \times 10^{-5}$ sec^{-1}; it is thus about 100 times slower than the conversion **1** → **2**,[1] but at least 10^{11}-fold faster than the degenerate and unobserved bicyclo[3.3.0]octa-2,6-diene rearrangement.[3,4] That a cis,trans,cis tropone might be more accessible, relative to its bicyclic precursor, than a cis,trans,cis tropilidene seems resonable, considering the larger bond angle and lower bending force constant for the C–CO–C unit.

Whatever the final resolution of this mechanistic controversy may be, the propensity shown by bicyclo[4.2.0]- and bicyclo[3.2.0]dienes **3** and **5** for this type of rearrangement, and the absence of rearrangement in bicyclo[3.3.0]octa-2,6-diene at 450° for 85 min,[4] does not deserve to be discounted as a pertinent fact through postulating that heteroatom functionality is essential. It is not.

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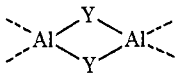
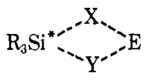
The SNi-Si Mechanism. Reductive Displacement of Good Leaving Groups with Retention of Configuration by Diisobutylaluminum Hydride. Stereochemical and Mechanistic Crossover with the Etherate Complex of Diisobutylaluminum Hydride

Sir:

A large number of dimeric aluminum compounds contain bridge 4 rings (I).[1] It is interesting to consider this



I



II

structural feature of formally trivalent aluminum compounds (R_3Al, etc.), together with the SNi-Si mechanism (II) in which the attacking reagent is EY.[2] Structure II may be an intermediate or transition state in which E is the electrophilic part and Y the nucleophilic part of the attacking reagent.

Comparison of I and II leads immediately to the interesting prediction that the use of organoaluminum reagents (R_2AlY), in which E in EY is a formally trivalent aluminum center, should greatly favor reactions at asymmetric silicon proceeding with retention of configuration.[3] Indeed, we have proposed that many *retention* reactions at asymmetric silicon proceed by mechanism SNi-Si, and we wish to report below stereochemical results which validate the above prediction and thereby provide strong additional evidence for the importance of the SNi-Si mechanism.[4]

We have found that a variety of functional groups on silicon can be reduced to give a silicon–hydrogen bond with i-Bu_2AlH. Reductions have been carried out using optically active R_3Si^*X, in which R_3Si^* is α-naphthylphenylmethylsilyl.[2a] Table I gives the stereochemical results for reduction of seven optically active silanes with i-Bu_2AlH in hexane solvent. In this solvent i-Bu_2AlH is trimeric and association involves hydrogen bridges.[5]

$$R_3Si^*X + i\text{-}Bu_2AlH \longrightarrow R_3Si^*H + Bu_2AlX$$

Table I. Reductions of R_3Si^*X with i-Bu_2AlH in n-Hexane

Reaction no.	Si*X	Product	Predominant stereochemistry,[a] %
1	(+)-Si*OCH$_3$	(+)-SiH	Retention, 100
2	(−)-Si*O(−)Men[b]	(+)-SiH	Retention, 100
3	(+)-Si*OPh	(+)-SiH	Retention, 99
4	(+)-Si*F	(+)-SiH	Retention, 98
5	(−)-SiSCH$_3$	(+)-SiH	Retention, 77
6	(−)-SiSC$_6$H$_4$-p-CH$_3$	(+)-SiH	Retention, 92
7	(−)-Si*Cl	(+)-SiH	Retention, 100

[a] For a definition of, and reasons for, the term "predominant stereochemistry," see L. H. Sommer, J. D. Citron, and G. A. Parker, *J. Amer. Chem. Soc.*, **91**, 4729 (1969). [b] Men is menthyl.

Retention of configuration for reactions 1–3 in Table I engenders no surprise since reductions of the designated compounds with lithium aluminum hydride, containing formally tetravalent aluminum, also proceed with *retention* of configuration.

However, reduction of the compounds designated in reactions 4–7 in Table I with lithium aluminum hydride proceeds with *inversion* of configuration.[2a] Thus, the change from $LiAlH_4$ to i-Bu_2AlH produces a dramatic change in stereochemistry favoring *retention* of configuration as predicted on the basis of an SNi-Si mechanism model. The most striking result of all in Table I is the entirely new finding of a reaction of acyclic R_3Si^*Cl proceeding with pure *retention* of configuration.

Previously,[6] based on reactions of acyclic R_3Si^*X with strong nucleophiles, we formulated the "SN2-Si stereochemistry rule" of inversion of configuration for good leaving groups X, whose conjugate acids have pK_a less than ~6, providing the entering group Y is more basic than the leaving group X.

The above rule does not always apply to F as a leaving group for special reasons already given.[6] Paralleling one of those reasons (the high capacity of F for coordination with an electrophilic center), the present work shows that the rule may also not apply to special

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(1) For an excellent review, see G. E. Coates and K. Wade, "Organometallic Compounds," 3rd ed, Vol. 1, Methuen, London, 1967, pp 295–343.

(2) (a) For references up to 1965, see: L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapters 3, 4, 6, 10, and 11; (b) for a later reference which also cites numerous pertinent references, see: L. H. Sommer and H. Fujimoto, *J. Amer. Chem. Soc.*, **91**, 7040 (1969).

(3) This prediction receives further support from the fact that the covalent radii of aluminum and silicon are closely similar, being 1.25 and 1.17 Å, respectively.

(4) Overall geometry for SNi-Si is postulated (see ref 2) to be either a tetragonal pyramid at Si with X and Y basal and cis, or a trigonal bipyramid with X and Y equatorial and apical, respectively. In the latter case, pseudorotation of II to a second intermediate II, in which X is apical and the 4-ring structure is still intact, is possible.[2b]

(5) Reference 1, pp 340–341.

(6) L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **89**, 857 (1967).

reagents whose special properties include having a very strong electrophilic center (E) and a much weaker nucleophilic center (Y).

With one exception, the compounds used in this study (Table I) have previously been synthesized and assigned absolute and relative configurations using the (+)-R_3Si^*H configuration as the reference configuration.[2,7] The exception is (−)-α-naphthylphenylmethyl(*p*-tolylthio)silane, mp 87–88°, [α]D −67° (*c* 0.8, *n*-hexane).[8] The method of preparation for this compound and assignment of relative configuration paralleled those for (−)-$R_3Si^*SCH_3$.[8]

Reactions in Table I were carried out under dry nitrogen and the reaction mixtures were colorless and homogeneous. Using 1 equiv of R_3Si^*X and 1 equiv of *i*-Bu_2AlH (both *ca.* 0.5 *M*) in *n*-hexane, a wide range of reactivities has been found during preliminary studies.

The reactivity with *i*-Bu_2AlH in *n*-hexane was: $R_3Si^*OCH_3$ > $R_3Si^*O(-)Men$ > R_3Si^*OPh > R_3Si^*F, $R_3Si^*SCH_3$ > $R_3Si^*SC_6H_4$-*p*-CH_3 > R_3Si^*Cl.

From examination of the reactivity pattern it is clear that the concepts of "good" and "poor" leaving groups, which we (and others) base upon idealized (pure "push") nucleophilic attack reactions, certainly do not obtain for the reactions in Table I with a reagent such as *i*-Bu_2AlH in *n*-hexane. For such reactions, then, it is not too surprising to find R_3Si^*Cl reacting with *retention* of configuration in apparent violation of the SN2-Si stereochemistry rule which really applies to reactions with reagents that are predominantly strong nucleophiles.

At room temperature in *n*-hexane, reaction with $R_3Si^*OCH_3$ is complete in less than 2 min, and reaction with R_3Si^*Cl is only 10% complete after 24 hr.

In sharp contrast to the above results, profound changes in stereochemistry result from use of the etherate complex of *i*-Bu_2AlH. The stereochemical results using *i*-Bu_2AlH–Et_2O in ether solvent are reported in Table II.

Table II. Reductions of R_3Si^*X with *i*-Bu_2AlH–Et_2O in Ether

Reaction no.	Si*X	Product	Predominant stereochemistry, %
1′	(+)-Si^*OCH_3	(+)-SiH	Retention, 99
2′	(−)-$Si^*O(-)Men$	(+)-SiH	Retention, 96
3′	(+)-Si^*OPh	(+)-SiH	Retention, 100
4′	(+)-Si^*F	(−)-SiH	Inversion, 90
5′	(−)-$SiSCH_3$	(−)-SiH	Inversion, 98
6′	(−)-$SiSC_6H_4$-*p*-CH_3	(−)-SiH	Inversion, 98
7′	(−)-Si^*Cl	(−)-SiH	Inversion, 90

Comparison of Tables I and II reveals dramatic stereochemistry crossover from *retention* of configuration for reactions 4–7 in Table I to *inversion* of configuration for reactions 4′–7′ in Table II. The stereochemical results in reactions 4′–7′ parallel those obtained with lithium aluminum hydride.[2a]

In addition to the etherate complex of *i*-Bu_2AlH, other donor–acceptor complexes of *i*-Bu_2AlH were studied and gave stereochemical results paralleling those in Table II. Among the complexes studied was *i*-Bu_2AlH–TMEDA (TMEDA is tetramethylethylenediamine) in *n*-hexane solvent and with this reagent relative rates gave the reactivity pattern: R_3Si^*Cl > $R_3Si^*OCH_3$ > $R_3Si^*O(-)Men$, R_3Si^*F. This is a pattern to be expected from attack of a strong nucleophile at a silicon center.

We believe that reactions 1–7 in Table I proceed by a four-center SNi-Si mechanism (II) and that the poor leaving groups in reactions 1′–3′ in Table II also react by an SNi-Si mechanism which involves a preliminary fast displacement of an ether molecule from aluminum by the silicon reactant.

We also feel that reactions 4′–7′ in Table II probably proceed by an SN2-Si mechanism because the reducing H in *i*-Bu_2AlH–Et_2O is far more hydridic and nucleophilic than the bridge H's in trimeric *i*-Bu_2AlH.[9]

Detailed studies of rates and rate law for *retentive* and *invertive* reductions of R_3Si^*X by *i*-Bu_2AlH, complexed and uncomplexed with donor substances, are presently under way.

Acknowledgment. We are grateful for support of this work by the National Science Foundation.

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(7) L. H. Sommer and J. McLick, *J. Amer. Chem. Soc.*, **89**, 5806 (1967).

(8) Analyses for C, H, and S were satisfactory and spectral data were consistent with the assigned structure.

(9) Support for the assumption of more nucleophilic character of H in donor–acceptor complexes of *i*-Bu_2AlH, compared to trimeric *i*-Bu_3AlH, is found in metalation of monoalkylacetylenes with *i*-Bu_3AlH–Et_3N compared to hydroalumination with trimeric *i*-Bu_2AlH; work of G. S. Zweifel and R. B. Steele; R. B. Steele, Ph.D. Thesis, University of California at Davis, 1966.

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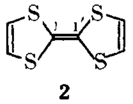
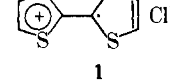
Electrical Conductivity by the Bis-1,3-dithiole–Bis-1,3-dithiolium System[1]

Sir:

Recently we reported the isolation and structure determination of bis-1,3-dithiolium chloride[2] (**1**) and also published an X-ray structure determination[3] of **2**.



2



1

In this communication we present some more intriguing properties of these molecules.

We were prompted to examine the electrical properties of **2** because X-ray crystallography revealed that, in a single crystal, the molecules were found to have their central double bonds (C_1–$C_{1'}$) lined up along one of the crystal's axes.[3] Thus, if the crystals were placed

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(1) Research supported by the Petroleum Research Fund administered by the American Chemical Society and by the Research Corporation.

(2) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1435 (1970). (b) Professor S. Hünig (Würzburg) also prepared bis-1,3-dithiolium chloride (private communication). (c) In ref 2a, the nmr chemical shift of **2** is in error; it should read CCl_4 (δ relative to TMS) 6.15 (s).

(3) W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *ibid.*, 889 (1971).