

initial rate of formation of VIII depends linearly on light intensity indicating a normal one-photon mechanism.

The barrier in the photochemical process VI \rightarrow VIII is higher than had been expected from simple theory.² In terms of correlation diagrams, this may be related to the fact that the MO's of acenaphthylene involved, although of correct nodal properties, have relatively small expansion coefficients at the double bond where their assistance is needed during the reaction.^{2b}

Further work along these lines as well as exploration of synthetic possibilities opened by the availability of VI and VII are in progress.

Acknowledgment is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(7) Alfred P. Sloan Fellow, 1971-1973.

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Received November 10, 1973

Stereochemistry of Chloride Displacement from Silacyclobutanes

Sir:

The stereochemistry of reactions at asymmetric silicon atoms has been studied in a number of different chiral organosilane systems with results which have indicated that the stereochemical outcome depends on the nature of entering and leaving groups and sometimes the solvent but not normally on organosilane structure.¹ The first significant deviation from this type of behavior was recently reported.^{2,3} In the 1-phenyl-1-silaacenaphthene ring system, both inversion and retention are reasonable stereochemical possibilities, but only retention is observed, even in reactions which proceed with predominant or complete inversion of configuration at Si in other chiral organosilanes. Sommer postulated² that the stereochemical crossover is associated with angle strain at Si. This observation demands confirmation in other angle strained systems. We now wish to report the stereochemistry of reactions in the strained 1,2-dimethyl-1-silacyclobutane ring system.

Dubac, *et al.*, have reported⁴ the displacement of *tert*-butoxide from 2-methyl- and 3-methyl-1-silacyclobutanes by methylmagnesium iodide or *n*-butyllithium or LiAlH₄, all of these reactions being proposed to be stereospecific with retention. However, similar reactions involving displacement of alkoxide in nonstrained systems also proceed with retention.^{1a,b,5} The same authors reported the reduction of 1,2-dimethyl-1-chloro-1-silacyclobutane by LiAlH₄ to be nonstereoselective.⁴

(1) (a) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965; (b) R. Corriu and J. Massé, *Bull. Soc. Chim. Fr.*, 3491 (1969); (c) H. Sakurai and M. Murakami, *J. Amer. Chem. Soc.*, **94**, 5080 (1972).

(2) D. N. Roark and L. H. Sommer, *J. Amer. Chem. Soc.*, **95**, 969 (1973).

(3) Certain resonance-stabilized organolithium and magnesium reagents are reported to give different results in cyclic systems for reasons unrelated to those under discussion here: R. Corriu and J. Massé, *J. Organometal. Chem.*, **34**, 221 (1972).

(4) J. Dubac, P. Mazerolles, and B. Serres, *Tetrahedron Lett.*, 3495 (1972).

(5) R. Corriu and G. Royo, *Bull. Soc. Chim. Fr.*, 1497 (1972); R. Corriu and J. Massé, *J. Organometal. Chem.*, **35**, 51 (1972).

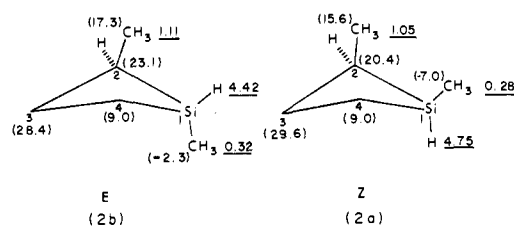


Figure 1. ¹H (underlined) and ¹³C (in parentheses) chemical shifts for (*E*)- and (*Z*)-1,2-dimethyl-1-silacyclobutane, in CDCl₃ relative to TMS.

We have reinvestigated this latter reaction and find it to be greater than 95% stereospecific.

Silacyclobutane ring closure by the method of Damrauer⁶ afforded in 75% yield a 60:40 mixture, **1a** and **1b**, respectively, of the two isomers of 1,2-dimethyl-1-chloro-1-silacyclobutane. The ratio of the two isomers was determined from the relative intensities of the SiMe protons in the nmr (CCl₄), **1a** (δ 0.55) and **1b** (δ 0.62). Enrichment to an 80:20 mixture was accomplished by careful distillation on a 7-cm Vigreux column. Reduction of the 80:20 mixture of **1a** and **1b** with LiAlH₄ in diethyl ether gave an 80:20 mixture, **2a** and **2b**, respectively, of the two isomers of 1,2-dimethyl-1-silacyclobutane, as determined by glpc.⁷ Similarly, reduction of the original 60:40 mixture of **1** gave a 60:40 mixture of **2** indicating the reaction is stereospecific.

In order to determine the stereochemistry of the reaction, **2a** and **2b** were separated by preparative glpc.⁸ The structures of **2a** and **2b** were assigned from ¹H and ¹³C chemical shifts (Figure 1).⁹ No attempt has been made to judge the relative stabilities of silacyclobutane conformers. The silacyclobutane ring is known to be puckered but also to be flipping extremely rapidly on an nmr time scale.¹⁰ In many substituted cycloalkanes, substituents exert an influence on the chemical shifts of protons on an adjacent carbon that is stereospecific and greater when the substituent and proton are cis to one another than when they are trans.¹¹ Methyl groups generally show the effect of shielding cis protons on adjacent carbons,¹² and, in the *E* isomer in our system, shielding of the proton on Si by the cis C₂-Me gives rise to a resonance at substantially higher field (δ 4.42) than the Si-H of the *Z* isomer (δ 4.75). Also, the Si-Me and C₂-Me protons appear at higher field (slightly, but consistently) in the *Z* isomer where they are cis to one another. The proton on C₂ could not be resolved from

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(7) Glpc analysis was carried out using a 16 ft \times 1/8 in. column of 15% Apiezon L on 60-80 mesh Chromosorb W at 85°.

(8) Preparative glpc was carried out on a Perkin-Elmer Model 21 using a 5 ft 4 in. \times 3/4 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W operating at a temperature of 85° and a carrier gas flow rate of 270 ml/min.

(9) Nmr spectra were obtained on approximately 25% CDCl₃ solutions employing Varian HA-100 and CFT-20 spectrometers for pmr and cmr determinations.

(10) L. V. Vilkov, V. S. Mastryukov, Yu. V. Baurava, V. M. Vdovin, and P. L. G. Grinberg, *Dokl. Akad. Nauk SSSR*, **117**, 1084 (1967); J. Laane and R. C. Lord, *J. Chem. Phys.*, **48**, 1508 (1968); W. C. Pringle, Jr., *ibid.*, **54**, 4979 (1971).

(11) H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 149 (1969).

(12) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 747 (1962); E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Lett.*, 741 (1962); H. Booth, *Tetrahedron*, **22**, 615 (1966); R. C. Fort and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

the other ring protons so that no useful coupling constant data is available. On these bases, **2a** was assigned the *Z* structure and **2b** the *E* structure. The stereochemical assignments were confirmed by ^{13}C chemical shifts for which a reasonably close analogy to the present system exists in a study of methyl-substituted phosphetanes.¹³ Steric interaction between the methyl groups of the *Z* isomer gives rise to resonances at higher field for both the SiMe ($\delta -7.0$) and the $\text{C}_2\text{-Me}$ ($\delta 15.6$) relative to the SiMe ($\delta -2.3$) and $\text{C}_2\text{-Me}$ ($\delta 17.3$) of the *E* isomer. This high field shift is also observed for the C_2 resonance of the *Z* isomer. The assignments made here are contrary to those proposed by Dubac and Mazerolles, who had in hand only a 50:50 mixture of **2a** and **2b**.⁴

Free radical chlorination using CCl_4 and benzoyl peroxide was carried out on **2a** to give **1a**. The reaction was greater than 95% stereospecific, as determined by nmr. Similarly, **2b** gave **1b**. Since this reaction goes through a silyl radical intermediate,¹⁴ **2a** can be presumed to arise from **1a** with retention of configuration.¹⁵⁻²⁰ ^1H chemical shifts of the Si-Me groups in the chlorides offer some additional evidence, using reasoning similar to that applied to the hydrides, that **1a** has the *E* structure and **1b** the *Z* structure. This assignment again is in contrast to one made previously.²¹ Perhaps surprisingly, the assignment means that the original ring closure to form silacyclobutane gives a somewhat greater amount of *E* isomer, with cis methyl groups, than of *Z* isomer, whereas conformational analysis indicates that methyl is appreciably larger than chlorine.²²

The stereochemical assignments lead to the firm conclusion that reduction of Si-Cl by LiAlH_4 in the silacyclobutane ring system proceeds with retention of configuration. Acyclic^{1a} and nonstrained cyclic^{1b} silicon chlorides in contrast undergo reduction with almost complete inversion. The angle strain effect is thus confirmed, and we offer the following simple rationalization. "Normal" (SN_2 Si)^{1a} attack on the backside of

Si (relative to the leaving group) occurs with the same stereochemical constraints as SN_2 attack on carbon; namely, the entering and leaving groups are apical and the other substituents equatorial. Attack on one of the other three faces of the approximate tetrahedron about silicon (flank attack)²³ leads to retention of configuration. Flank attack can be induced by coordination of the leaving group to some portion of the entering group ($\text{S}_{\text{Ni}}\text{Si}$)^{1a,24} or, as in the angle strain cases, by the inability of the substituents about Si to occupy their normal equatorial positions in the SN_2 Si transition state because of prohibitive increase in angle strain.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged. Cmr spectral data were obtained by Miss Barbara Ervine of Varian Associates during the visit of the CFT-20 mobile laboratory on the LSU campus.

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(25) Experimental work done at Louisiana State University.

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Received November 12, 1973

Unusual Metalloporphyrins. XXIII.¹ Fluxional Behavior of Out of Plane Organometalloporphyrins²

Sir:

Fluxional molecules³ of both transitional³⁻⁵ and non-transitional^{6,7} organometallic compounds have received considerable attention in the past decade. Most

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(15) A referee has suggested that an interpretation which is at least plausible is that both Si-H chlorination and Si-Cl reduction go with inversion. We disagree. It is true that the two examples in which the stereochemistry of silyl radical reactions have been investigated are both retentions;^{14,16} also both theoretical¹⁷ and experimental¹⁸ studies indicate that silyl radicals are pyramidal in all cases investigated. The foregoing is relevant but is not at the crux of our argument. Our work shows that both **2a** and **2b** react stereospecifically to give **1a** and **1b**, respectively. There are stereoselective free radical reactions in which there is bias for attack on one side of a radical center arising from molecular asymmetry¹⁹ and there are known examples of stereospecific retention reactions in unusual cases²⁰ but there are no known examples of stereospecific inversion reactions at a radical center when it is carbon, silicon, or anything else. Our reactions would have to be an example of the latter unless the chlorination goes with retention and the reduction with retention.

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