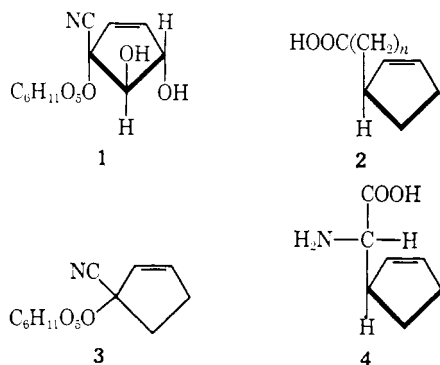


portance of steric resemblance in the biosynthesis of cyanohydrin glucosides is shown in the prevalent simultaneous synthesis from valine and isoleucine^{2,17} and by the fact that *O*-methylthreonine, an isoleucine analog, inhibits the conversion in flax of valine to linamarin.^{1,21} Since isobutyraldoxime accumulates in the blocked system and *O*-methylactaldoxime also is inhibitory, *O*-methylthreonine probably is carried at least to the aldoxime stage. We suggest that if a group of plants has the quirk of producing an L-2-cyclopentene-1-glycine, the passage to deidaclin and its additionally hydroxylated congeners involves little change in enzymatic specificities from the widespread synthesis of linamarin and methyllinamarin¹⁷ (lotaustralin).

The Passifloraceae, related tribes of Flacourtiaceae, and perhaps other, neighboring families (*e.g.*, Turneraceae¹⁰) promise to be a nest of cyclopentenones bearing a single, straight carbon chain in the 3 position. To understand the taxonomic limits of and biosynthetic pathways within this group of plants is a challenge.



Acknowledgment. We thank Professor R. Hegnauer for generously enabling us to work on this problem by supplying us with deidaclin (and gynocardase), Dr. G. O. Dudek, Harvard University, Cambridge, Mass., for the mass spectra, and F. H. Bissett for pmr spectra.

(20) R. L. Dennis, W. J. Plant, C. G. Skinner, G. L. Sutherland, and W. Shive, *J. Amer. Chem. Soc.*, **77**, 2362 (1955); R. M. Gipson, C. G. Skinner, and W. Shive, *Arch. Biochem. Biophys.*, **111**, 264 (1965).

(21) G. W. Butler, *Proc. Roy. Aust. Chem. Inst.*, **36**, 65 (1969).

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1,3,5,7-Tetrasiladamantanes. A Facile Synthesis via Catalyzed Ligand Redistribution

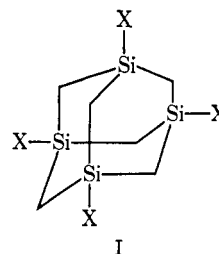
Sir:

The novel, highly symmetrical 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane (*i.e.*, I, X = Cl) was prepared in very low yield (<0.1%) several years ago¹ when an AlCl₃-catalyzed redistribution reaction of Me₃SiCl and SiCl₄ was inadvertently overheated to 500°. Fritz and coworkers² subsequently isolated the tetramethyl analog (I, X = Me) in the complex mixture

(1) A. L. Smith and H. A. Clark, *J. Amer. Chem. Soc.*, **83**, 3345 (1961).

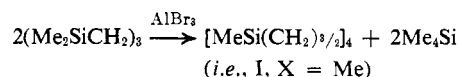
(2) (a) For a summary of Fritz's work, see G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, **7**, 349 (1965); (b) G. Fritz, F. Diem, H. Köhler, D. Kummer, and H. Scheer, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970).

of products arising from the pyrolysis of Me₄Si at 650°. Whereas the arrangement of carbon atoms in



adamantane³ is based on the diamond structure, silicon carbide is the structural parallel for the 1,3,5,7-tetrasiladamantanes.⁴

The unprecedented resistance to solvolysis¹ of cages such as I (X = Cl) is believed to derive from (a) their bridgehead structure which precludes backside attack, and (b) their markedly lessened strain which renders them much less susceptible to flank attack than earlier, highly strain-activated, bridgehead silicon derivatives.⁵ Regarding this latter point, examination of molecular models reveals that any distortion of the bond angles between a silicon and its three adjacent carbon atoms distorts the atomic arrangement throughout the whole cage, and would require the addition of substantial amounts of energy to the system. Thus the enhanced solvolytic stability of the tetrasiladamantane system is consistent with earlier inferences that flank attack at silicon involves a transition state with appreciably altered bond angles between the silicon center and the three nonleaving substituents. In order to facilitate further studies of the unique chemistry of this novel heterocyclic system, we have devised a markedly improved synthesis based on the catalyzed ligand redistribution reaction of appropriate tetraorganosilicon substrates, such as 1,3,5-hexamethyl-1,3,5-trisilacyclohexane; *i.e.*



A ligand redistribution approach to this problem was selected because (a) simple tetraalkylsilanes are known to undergo random exchange of alkyls in the presence of aluminum halides (thus BuSiMe₃ affords Bu₂SiMe₂, Bu₃SiMe, Bu₄Si, and Me₄Si),^{6,7} (b) the best route to adamantane itself is *via* the AlBr₃-catalyzed rearrangement of hydrocarbon precursors,³ and (c) appropriate

(3) For details concerning the nomenclature, synthesis, and chemistry of adamantanes, see R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(4) Based on this analogy, Fritz^{2b} has referred to the various silcarbane cage structures (including Si₄, Si₇, Si₉, and Si₁₀ examples) arising from Me₄Si pyrolysis as carborundanes. We suggest that use of the trivial name *carborundane* be reserved for the parent tetrameric silsesquimethylene structure (*i.e.*, I, X = H).

(5) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **79**, 1008 (1957); **81**, 251 (1959).

(6) (a) G. Calingaert, H. Soroos, and V. Hnizda, *ibid.*, **62**, 1107 (1940); (b) G. A. Russell, *ibid.*, **81**, 4185 (1959); (c) P. D. George, L. H. Sommer, and F. C. Whitmore, *ibid.*, **77**, 1677 (1955); (d) see also, A. J. Barry and J. W. Gilkey, U. S. Patent 2,647,912 (1953).

(7) The literature also contains a few examples of simple heterocyclic synthesis *via* the AlX₃-catalyzed redistribution of appropriate substrates. Thus, Me₃Si(CH₂)₄SiMe₃ afforded 1,1-dimethyl-1-silacyclopentane⁸ and Me₃SiCH₂CH₂SiMe₃ yielded Me₂Si(CH₂CH₂)₂SiMe₂.⁹

(8) N. S. Nametkin, V. M. Vdovin, and K. S. Pushchevaya, *Dokl. Akad. Nauk SSSR*, **150** (3), 562 (1963).

(9) Yu. P. Egorov, K. S. Pushchevaya, E. D. Lubuzh, V. M. Vdovin, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 822 (1963).

silcarbane substrates containing the requisite Si-CH₃ and SiCH₂Si moieties are readily prepared.¹⁰

Our preliminary efforts to convert (Me₂SiCH₂)₃ to the desired cage structure with modest amounts of AlBr₃ (i.e., 1–5% of substrate weight) were disappointing. Noting that Schleyer's adamantane syntheses often employed quite massive amounts of aluminum halide catalysts, we evaluated the effect of larger amounts (i.e., 20–200% of substrate weight) in the present system and this did indeed afford facile redistribution at moderate temperatures (e.g., 80–100°) producing Me₄Si and the desired cage structure (I, X = Me). Moreover, the "catalyst" is apparently a reactant and also gives rise to a substantial number of silicon-functional sites; i.e., depending on the conditions, cage structures are formed in which one or more of the methyl substituents have been replaced by Cl or Br.

Thus when a mixture of (Me₂SiCH₂)₃ (130.0 g; 0.61 mol) and AlBr₃ (22.5 g; 0.085 mol) was heated, the temperature rose to approximately 100°, then decreased as Me₄Si gradually formed; an 85% yield of Me₄Si (45 g) was distilled from the system during the ensuing 2-hr period. After the reaction product was diluted with benzene and washed with water to remove the aluminum salts, the organic layer was dried and examined *via* tandem glc-mass spectrometry. The overall yield of volatile tetrasilaadamantanes in this particular run was approximately 27% (in some recent runs, yields as high as 80% have been achieved); the major component was the Me₄ derivative admixed with lesser amounts of the Me₃Br and Me₂Br₂ derivatives. The individual components were resolved by preparative glc and characterized by nmr and/or mass spectroscopy. Like the substituted adamantane hydrocarbons, these silicon analogs exhibit very characteristic cracking phenomena;^{11,12} thus, their mass spectra generally show a parent-ion line accompanied by a very intense line corresponding to a fragment produced by the loss of one bridgehead substituent (or several such lines if more than one type of substituent is present) and little else of comparable intensity. To illustrate, the monobromide shows parent lines of moderate intensity (12%, relative intensity) at *m/e* values of 320 and 322 (corresponding to the two almost equally distributed isotopes of Br), very intense lines (100%) at 305 and 307 (parents – methyl), and a weak line (2%) at 241 (parents – bromine). The nmr spectrum (CCl₄ solution) of this species consists of three lines at τ 9.62 (BrSiCH₂SiCH₃), 9.84 (SiCH₃), and 10.19 (CH₃SiCH₂SiCH₃) in the expected intensity ratio of 6:9:6.

The above ligand exchange method thus constitutes a versatile route to a variety of 1,3,5,7-tetrasilaadamantanes (i.e., I, X = Cl, Br, Me). The derivative chemistry of these functional cages is currently under study, and will be described at an early date. Redistribution¹³ of organic ligands for the synthesis of

polycyclic heteroatom cage systems appears to be without precedent and should facilitate future studies of such systems. Thus, this general method may well be applicable to the synthesis of polycyclic heteroatom cages containing components such as SiCH₂CH₂Si, Si₃CH, GeCH₂, SnCH₂, etc.

in their relative position but not with respect to their total number or formal character.¹⁴ In contrast to the adamantane work in which deep-seated carbonium ion rearrangements are involved, the aluminum halide catalyzed redistribution of *n*-Pr_{1-x}SiEt_x was shown *not* to involve carbonium ion intermediates (i.e., the equilibrium mixture contained no *i*-Pr moiety).¹⁵

(14) H. A. Skinner and T. F. S. Tees, *J. Chem. Soc.*, 3378 (1953).

(15) P. D. George, L. H. Sommer, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 77, 1677 (1955).

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

Received June 20, 1970

Rotational Barriers of Alkyl Cations

Sir:

The structures and stabilities of carbonium ions are subjects of continuing interest.¹ Although a great deal of information has been obtained from spectroscopic and mechanistic evidence, quantum mechanical calculations provide insights not yet accessible experimentally.^{2–10} Semiempirical molecular orbital methods have already been used to study rotational barriers in a number of carbonium ions.^{11–15} How-

Table I. Extended *ab initio* Energies for the Propyl Cation^a

Compd	Conformation ^b	Total energy	Relative energy
1a		-117.25566	0.0
1b		-117.25206	2.26

^a Absolute energies in hartrees, relative energies in kilocalories per mole. ^b Bond lengths: *d*(CH), 1.096; *d*(C-H), 1.084; *d*(CC), 1.534; *d*(C⁺C), 1.48 Å. Bond angles: CH₃ and CH₂ tetrahedral and staggered; CH₂⁺ planar.

(1) See e.g., "Carbonium Ions," Vol. I, G. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968; Vol. 2, 1970; D. Bethell and V. Gold, "Carbonium Ions. An Introduction," Academic Press, New York, N. Y., 1967.

(2) J. E. Williams, R. Sustmann, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 91, 1037 (1969).

(3) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, 91, 5350 (1969).

(4) J. E. Williams, V. Buss, and L. C. Allen, submitted for publication.

(5) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, in press.

(6) J. E. Williams, V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, 92, 2141 (1970), and references therein cited.

(7) G. V. Pfeiffer and J. G. Jewett, *ibid.*, 92, 2143 (1970).

(8) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970).

(9) D. T. Clark and D. M. J. Lilley, *ibid.*, 603 (1970).

(10) V. Buss, P. von R. Schleyer, and L. C. Allen, to be published.

(11) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(12) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 1833 (1970).

(13) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

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(15) V. Buss, unpublished results.

(10) W. A. Kriner, *J. Org. Chem.*, 29, 1601 (1964).

(11) Z. Dolejšek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, 31, 435 (1966).

(12) However, see R. S. Gohlke and R. J. Robinson (*Org. Mass Spectrom.*, 3 (7), 967 (1970)), for the details of an interesting skeletal rearrangement which "carborundanes" undergo in a mass spectrometer.

(13) Lest our analogy to Schleyer's work be misinterpreted, we emphasize that we are dealing here with the conceptually much simpler redistribution reactions in which the organic moieties undergo changes