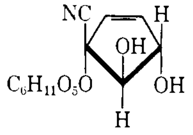
portance of steric resemblance in the biosynthesis of cyanohydrin glucosides is shown in the prevalent simultaneous synthesis from valine and isoleucine[2,17] and by the fact that *O*-methylthreonine, an isoleucine analog, inhibits the conversion in flax of valine to linamarin.[1,21] Since isobutyraldoxime accumulates in the blocked system and *O*-methyllactaldoxime 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 methyllinamarin[17] (lotaustralin).

The Passifloraceae, related tribes of Flacourtiaceae, and perhaps other, neighboring families (*e.g.*, Turneraceae[10]) promise to be a nest of cyclopentenes 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.



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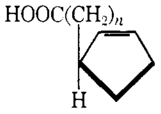

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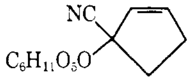

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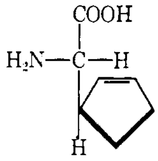

4

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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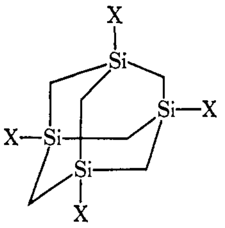
Received August 5, 1970

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

Sir:

The novel, highly symmetrical 1,3,5,7-tetrachloro-1,3,5,7-tetrasilaadamantane (*i.e.*, I, X = Cl) was prepared in very low yield (<0.1%) several years ago[1] when an $AlCl_3$-catalyzed redistribution reaction of Me_3SiCl and $SiCl_4$ was inadvertently overheated to 500°. Fritz and coworkers[2] subsequently isolated the tetramethyl analog (I, X = Me) in the complex mixture of products arising from the pyrolysis of Me_4Si at 650°. Whereas the arrangement of carbon atoms in adamantane[3] is based on the diamond structure, silicon carbide is the structural parallel for the 1,3,5,7-tetrasilaadamantanes.[4]



I

The unprecedented resistance to solvolysis[1] 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 tetrasilaadamantane 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.*

$$2(Me_2SiCH_2)_3 \xrightarrow{AlBr_3} [MeSi(CH_2)_{3/2}]_4 + 2Me_4Si$$
$$(i.e.,\ I,\ X = Me)$$

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 $BuSiMe_3$ affords Bu_2SiMe_2, Bu_3SiMe, Bu_4Si, and Me_4Si),[6,7] (b) the best route to adamantane itself is *via* the $AlBr_3$-catalyzed rearrangement of hydrocarbon precursors,[3] and (c) appropriate

(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).

(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 Si_4, Si_7, Si_9, and Si_{10} examples) arising from Me_4Si 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 AlX_3-catalyzed redistribution of appropriate substrates. Thus, $Me_3Si(CH_2)_4SiMe_3$ afforded 1,1-dimethyl-1-silacyclopentane[8] and $Me_3SiCH_2CH_2SiMe_3$ yielded $Me_2Si(CH_2CH_2)_2SiMe_2$.[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–CH_3 and $SiCH_2Si$ moieties are readily prepared.[10]

Our preliminary efforts to convert $(Me_2SiCH_2)_3$ to the desired cage structure with modest amounts of $AlBr_3$ (*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 Me_4Si 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 $(Me_2SiCH_2)_3$ (130.0 g; 0.61 mol) and $AlBr_3$ (22.5 g; 0.085 mol) was heated, the temperature rose to approximately 100°, then decreased as Me_4Si gradually formed; an 85% yield of Me_4Si (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 Me_4 derivative admixed with lesser amounts of the Me_3Br and Me_2Br_2 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 (CCl_4 solution) of this species consists of three lines at τ 9.62 ($BrSiCH_2SiCH_3$), 9.84 ($SiCH_3$), and 10.19 ($CH_3SiCH_2SiCH_3$) 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. Redistribution[13] 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 $SiCH_2CH_2Si$, Si_3CH, $GeCH_2$, $SnCH_2$, etc.

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

(11) Z. Dolejsek, 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 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 $n\text{-}Pr_{4-x}SiEt_x$ 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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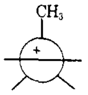
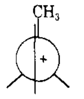
Rotational Barriers of Alkyl Cations

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: CH_3 and CH_2 tetrahedral and staggered; CH_2^+ planar.

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(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).

(14) T. Yonezawa, H. Hakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

(15) V. Buss, unpublished results.