which may or may not be the ground electronic state.[6] A similar insertion reaction for dimethylsilene,[7,8] trimethylsilylsilene,[9] and SiH$_2$[1] has been postulated earlier. In these, as in the present study, the silenes exhibited a strong preference for Si–H over C–H bond insertion. This preference is not restricted to silenes; it has been observed with singlet methylene from the photolysis of ketene[10] and with singlet-D sulfur atom from the photolysis of COS. This increased reactivity of the Si–H bond in insertion reactions may be related to its hydridic character and the availability of the vacant d orbitals of the silicon atom.

The Xe-sensitized decomposition of CH$_3$SiH$_3$ has also been examined; it appears to be indistinguishable from the direct photolysis.

The effect of wavelength on the photolysis has been studied using the 1236-Å resonance line of Kr. While the nature of products remained unaltered, a marked increase in the hydrogen yield resulted, an effect which has been observed with paraffins[2] and can be attributed to the greater importance of atomic hydrogen production in the primary step.

A preliminary vacuum uv ($\lambda > 1200$ Å) flash photolysis study with kinetic mass spectrometry[11] of some other silanes indicated a similar though less efficient reaction for dimethylsilane (products H$_2$, CH$_4$, C$_2$H$_6$, and ((CH$_3$)$_2$SiH)$_2$), and, interestingly, an even less efficient decomposition for trimethylsilane. This feature of the silane photolysis is a significant departure from the behavior of paraffins and can possibly be understood only in the light of sufficient spectral data.

The vacuum uv photolysis of a series of other silicon compounds are currently under study.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[6] A recent semiempirical calculation predicts a $^1A_1$ ground state for SiH$_2$ with a lowest excited state, $^3B_1$, lying at ~48 kcal/mole; *cf.* P. C. Jordan, *J. Chem. Phys.*, **44**, 3400 (1966).

[7] O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **3**, 226 (1964).

[8] P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

[9] P. S. Skell and P. W. Owen, *ibid.*, **89**, 933 (1967); *cf.* also P. P. Gaspar, B. D. Pate, and W. Eckelman, *ibid.*, **88**, 3878 (1966); J. H. Purnell and R. Walsh, *Proc. Roy. Soc.* (London), **A239**, 543 (1966).

[10] M. A. Nay, K. S. Sidhu, H. E. Gunning, and O. P. Strausz, to be published.

[11] W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966).

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Biosynthesis of Lycopodine[1]

Sir:

The hypothesis that the lycopodium alkaloids are of polyketide origin[2] has gained general currency.[3–6] The carbon skeletons of the structural variants found among these alkaloids (*e.g.*, lycopodine (**12**), α-obscurine (**10**), and annotinine (**13**)) may be formally derived[2,4] from two tetraacetyl chains (**11**).[7] This hypothesis lacks experimental foundation.[10] We now propose a new hypothesis of the origin of the lycopodium alkaloids and offer experimental evidence in its support.

In separate experiments samples of lysine-2-^{14}C and -6-^{14}C were administered to *Lycopodium flabelliforme*. In each case radioactive lycopodine was isolated which, after purification to constant radioactivity, was converted to phenyldihydrolycopodine.[11] Permanganate oxidation then gave benzoic acid, representing the carbonyl carbon of lycopodine. One-fourth of the activity of the intact alkaloid derived from lysine-2-^{14}C as well as from lysine-6-^{14}C was localized at this carbon atom (Table I). In a further experiment labeled lycopodine was obtained from plants which had been infused with lysine-4,5-^{3}H-6-^{14}C (^{3}H:^{14}C 10.7 ± 0.2). The alkaloid showed a ^{3}H:^{14}C ratio (^{3}H:^{14}C 8.4 ± 0.1) which was 22% lower than that of the doubly labeled lysine.

Table I

	DL-Lysine-2-^{14}C[a] SA[b]	DL-Lysine-2-^{14}C[a] RSA[c]	DL-Lysine-6-^{14}C[a] SA[b]	DL-Lysine-6-^{14}C[a] RSA[c]
Lycopodine	1.30 ± 0.03	100 ± 2	1.22 ± 0.03	100 ± 2
Benzoic acid	0.33 ± 0.01	26 ± 1	0.31 ± 0.01	25 ± 1

[a] Precursor. [b] Specific activity (counts min^{-1} mmole^{-1}) × 10^{-4}. [c] Per cent relative specific activity.

The results demonstrate that lysine (**1**) serves as a specific precursor of lycopodine (**12**). This is compatible with the hypothesis that the lycopodium alkaloids are generated from two isopelletierine (**4**) units, whose piperidine nucleus is derived from lysine.[12] The steps of a plausible reaction sequence are shown in Scheme I. Recovery at the carbonyl carbon of 25% of the activity of the intact lycopodine, obtained from lysine-2-^{14}C and -6-^{14}C, is consistent with the view that the alkaloid represents a modified dimer of isopelletierine and that incorporation of lysine into this isopelletierine takes place by way of a symmetrical intermediate. Such symmetrical incorporation of lysine-4,5-^{3}H-6-^{14}C into lycopodine would be expected to be accompanied by loss of one-fourth to one-half of the tritium from C-5, *i.e.*, by a loss of 12.5–25% of the tritium, relative to ^{14}C, of the doubly

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[1] This investigation was supported by a grant from the National Research Council of Canada.

[2] H. Conroy, *Tetrahedron Letters*, No. 10, 34 (1960).

[3] K. Wiesner, *Fortschr. Chem. Org. Naturstoffe*, **20**, 271 (1962).

[4] E. Leete in "Biogenesis of Natural Compounds," P. Bernfeld, Ed., Pergamon Press, Inc., New York, N. Y., 1963, p 739.

[5] J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins," W. A. Benjamin, Inc., New York, N. Y., 1964, p 116.

[6] J. H. Richards in "Plant Biochemistry," J. Bonner and J. E. Varner, Ed., Academic Press Inc., New York, N. Y., 1965, p 526.

[7] Mention has been made also of several compounds other than acetate as possible precursors of lycopodium alkaloids.[3,8,9]

[8] E. Leete, *Tetrahedron*, **3**, 313 (1958).

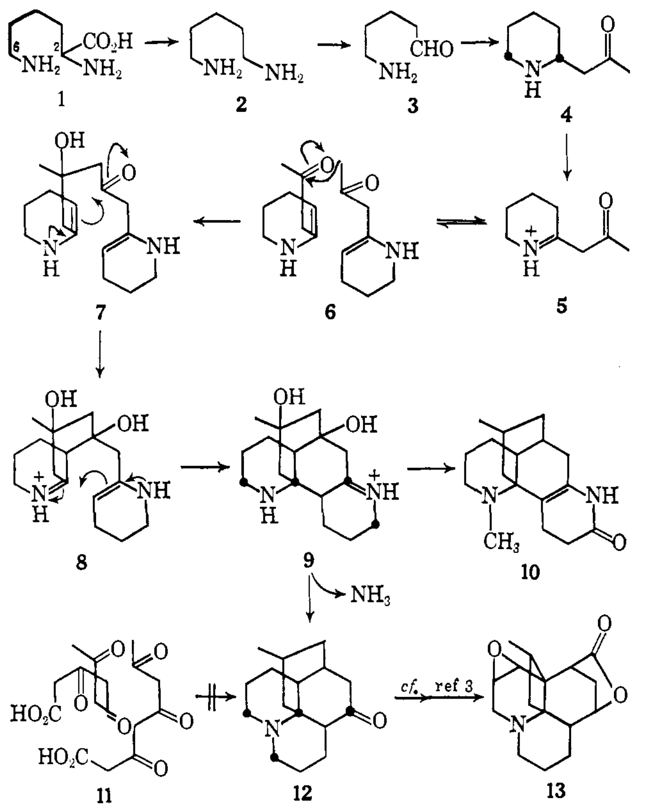
[9] E. Leete and M. C. L. Louden, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstract 1-C.

[10] Label from acetate-1-^{14}C was indeed incorporated nonrandomly into annotinine (13) in *Lycopodium annotinum*. However, the observed distribution of this activity was not in accord with the polyketide hypothesis.[9]

[11] D. B. MacLean, R. H. F. Manske, and L. Marion, *Can. J. Res.*, **28B**, 460 (1950).

[12] In *Sedum sarmentosum*, lysine-6-^{14}C was shown to be incorporated specifically into the piperidine ring of N-methylisopelletierine (R. N. Gupta and I. D. Spenser, *Chem. Commun.*, in press).

Scheme I



labeled lysine. The observed loss of 22% is in accord with this prediction.

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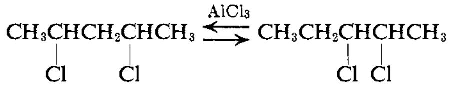
Diastereomeric Equilibration of the Dichloropentanes. A Model System for Polyvinyl Chloride

Sir:

Stereochemical equilibrium in chain molecules possessing two or more asymmetric centers is of considerable interest. Flory[1] has recently developed an excellent statistical mechanical theory capable of predicting the stereochemical equilibrium of such molecules. Since the same factors that determine the frequency of incidence of the conformations of a chain molecule also determine the diastereomeric equilibrium distribution of its lower homologs, it becomes of immediate interest to find suitable methods for equilibrating such species.[2]

The importance of the 2,4-dichloropentane system as a model for the structure of polyvinyl chloride has been recognized by other workers,[3] who have given conclusive evidence for the most stable conformers of each of the *meso* or *dl* varieties. What is lacking is the experimental verification of the relative stabilities of the *meso* and *dl* diastereomers, such as has been reported for the 2,4-diphenylpentanes.[2] In connection with our research program[4] on the isomerization of chloro- and dichloroparaffins with Friedel–Crafts catalysts we had the occasion to observe the facile equilibration of the dichloropentanes, thus providing a simple experimental tool for determining the relative stabilities of the 2,4-dichloropentane diastereomers.[5]

A suspension of aluminum chloride in carbon disulfide was used for equilibration.[6] *A priori*, one would also expect the 2,3-dichloropentane diastereomers to be produced in the equilibration, and this turns out to be the case. The same equilibrium mixture can be obtained starting with either the 2,3-dichloropentane or 2,4-dichloropentane diastereomers.[7] Table I shows the equilibrium distribution of the various diastereomers.[8] Equilibrium was rapidly attained (usually within 0.5 hr).



$$\text{CH}_3\underset{\text{Cl}}{\text{CH}}\text{CH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_3 \xrightleftharpoons{\text{AlCl}_3} \text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}\underset{\text{Cl}}{\text{CH}}\text{CH}_3$$

Table I. Equilibration of the Dichloropentanes at 25°

	% composition of dichloropentanes			
	dl-2,4-	*meso*-2,4-	*erythro*-2,3-	*threo*-2,3-
2,4-Dichloropentane[a]	64.3	26.1	5.0	4.6
2,3-Dichloropentane[b]	64.2	25.9	4.4	5.5

[a] 49% *dl*, 51% *meso*. [b] 52% *erythro*, 48% *threo*.

Capillary gas chromatography was necessary for complete resolution of all the diastereomers.[9] Since calibration samples prepared by mixing the appropriate amounts of the 2,3-dichloropentanes and 2,4-dichloropentanes confirmed that the response of the flame ionization detector was proportional to the concentration of the isomers, it was assumed the various diastereomers had nearly identical response factors.

In rationalizing the relative stabilities of the diastereomers it becomes necessary first to determine the stable rotational conformers. This has been studied by both infrared[3] and high-resolution nuclear magnetic reso-

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(1) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1798 (1967).

(2) While this manuscript was in preparation the epimerization of 2,4-diphenylpentane was reported: A. D. Williams, J. I. Brauman, N. J. Nelson, and P. J. Flory, *ibid.*, **89**, 4807 (1967).

(3) T. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).

(4) Unpublished work.

(5) An examination of the literature reveals that relatively little experimental information is available on the relative stabilities of diastereomers. For example, see L. I. Peterson, *J. Am. Chem. Soc.*, **89**, 2677 (1966), and references therein. See also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 138–139.

(6) H. Nozaki, M. Kawanisi, M. Okazaki, M. Yamae, Y. Nisikawa, T. Hisida, and K. Sisido, *J. Org. Chem.*, 30, 1303 (1965), have equilibrated the dichlorocyclohexanes with aluminum chloride.

(7) 2,3-Dichloropentane (mixture of diastereomers) was prepared by the ionic chlorination of mixed 2-pentene isomers using the general procedure described by Poutsma for the chlorination of the butenes. See M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 2172 (1965). *threo*-2,3-Dichloropentane was prepared by the chlorination of pure *cis*-2-pentene. The 2,4-dichloropentane diastereomers were prepared by the method of J. G. Pritchard and R. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

(8) Equilibrations were run by adding 0.10 mole of the dichloride to 25 ml of CS_2 containing 0.01 mole of anhydrous aluminum chloride. The mixture was stirred for the appropriate time under a nitrogen purge and quenched in ice water. The organic layer was separated and dried over anhydrous Na_2SO_4. The carbon disulfide solution was analyzed directly by gas chromatography. In general, polymerization to the extent of some 20–30% accompanies this isomerization–equilibration; however, we feel certain that polymerization does not affect the relative proportions of isomers since we approach the same equilibrium composition "from both sides;" *i.e.*, the rate of equilibration is greater than the rate of polymerization.

(9) Perkin-Elmer Model 226 with flame ionization detector. A 150 ft × 0.01 in. i.d. column coated with DC-550 silicone oil and operated at 25–150° at 2.5°/min and 50 psi (helium) was used.