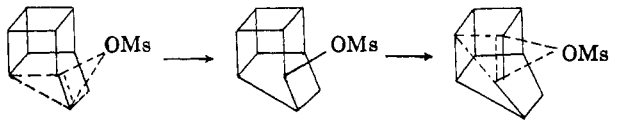
The rapid formation of mesylates of V and VI shows that ion-pair return with ions VIII and IX competes favorably with the further reaction of these species. Furthermore, the fact that the major solvolysis alcohol VI possesses the more hindered *endo* configuration indicates that the course of the reaction does not proceed entirely through classical intermediates such as IX in which the attack of solvent from the less-hindered side would lead to the *exo* isomer of VI. In this case, bridging in the nonclassical intermediates would account for the ion-pair return and the formation of the *endo* isomer VI.[8]



Hydride reduction of homocubanecarboxylic acid[3] afforded IIa, and its *p*-toluenesulfonate IIb (mp 82.0–83.5°) was solvolyzed in buffered acetic acid (67 hr, 117°). The resulting acetates were hydrolyzed and the mixture of alcohols had the following composition: IIa (52%), III (10%), IVa + IVb (15%, ratio 9:1), V (trace), and VI (23%).

The general pattern of the reaction of IIb is similar to that found for Ib. Three important differences are to be noted. First, the major solvolysis product resulted from displacement without rearrangement. Second, no 1,1′-bishomocubanol (Ia) was formed. Third, the ratio of the isomeric alcohols IVa:IVb was different. These latter two differences are most likely due to the formation of a carbonium ion VII which is vibrationally deformed[9] from the initial ion formed in the acetolysis of Ib. It also is noteworthy that, in the formation of III, four successive bond migrations must occur.

A more detailed description of the solvolyses of Ib and IIb will be published later.

(8) The stereospecificity of such a reaction also could be due to rapid interconversion of the classical ions; see H. C. Brown, K. Morgan, and F. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965)
(9) J. Berson and J. Gajewski, *ibid.*, **86**, 5020 (1964).

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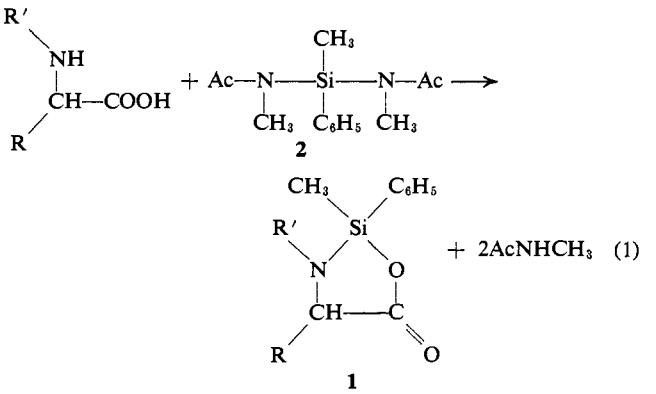
The Asymmetric Synthesis of an Optically Active Difunctional Silane

Sir:

In the course of work on silyamides[1,2] and amino acids,[3] we had occasion to consider the possibility of synthesizing silicon compounds analogous to 2,5-oxazolidinediones, replacing the carbonic acid portion of the anhydride by a silane. Since the silicon could easily be made an asymmetric center, it would be possible to study the effect of a carbon asymmetric center on the reactions of an asymmetric silicon. In addition, the polymerization of the amino acid portion might be possible in a fashion similar to that recently disclosed by Weygand, *et al.*,[4] for 2,2-bistrifluoromethyl-oxazolidone-5. At the same time the fate of the silane portion of the molecule would be of interest. We now wish to report the synthesis of the 2-silaoxazolidone ring system **1** and some of its reactions.

(1) J. F. Klebe, *J. Am. Chem. Soc.*, **86**, 3399 (1964).
(2) J. F. Klebe, H. Finkbeiner, and D. M. White, *ibid.*, **88**, 3390 (1966).
(3) H. Finkbeiner, *J. Org. Chem.*, 30, 3419 (1965).

The synthesis involved reaction of bis(N-methylacetamido)methylphenylsilane[5] (**2**) with an amino acid at room temperature (eq 1). Although simple amino acids seem to undergo the desired reaction, the product is a mixture of cyclic and linear material. However, N-phenyl amino acids react cleanly and smoothly to produce the desired compounds.



The reaction of optically active N-phenylalanine prepared by the procedure of Portoghese,[6] $[\alpha]^{25}D$ +65°, with the difunctional silylating agent in benzene was essentially complete after 15 min at room temperature. Since the product, 2-(methylphenylsila)-3-phenyl-4-methyloxazolidone-5 (**1**, R = CH_3, R′ = C_6H_5), contains two asymmetric centers, diastereomers are produced (in a ratio of about 2:1). The nmr spectrum shows two clearly separated silicon methyl peaks and two C-methyl doublets. On removing the solvent and the acetamide the liquid mixture spontaneously converted to the predominant diastereomer, thus obviating a separation step. The rearrangement is reversible; in solution, an equilibrium mixture of the two diastereomers is slowly attained. The product (mp 125–128°) showed only one Si-methyl peak (the upfield peak of the original pair) and one C-methyl doublet in the nmr spectrum, and its elemental analysis agrees with the proposed structure.

The specific rotation of the "stable" diastereomer, $[\alpha]^{25}D$ −27.5° (*c* 9.4, benzene), was obtained by measurement immediately after preparation of the solution. Mutarotation of the solution was observed for a period of 180 hr. From the nmr spectrum the relative amounts of the two diastereomers were determined and in turn the specific rotation of the unstable isomer, $[\alpha]^{25}D$ −96°.

Other silaoxazolidones obtained as the sole products from **2** and N-phenyl (or substituted N-phenyl) amino acids are included in Table I.

(4) F. Weygand, K. Burger, and K. Engelhardt, *Ber.*, **99**, 1461 (1966).
(5) Bis(N-methylacetamido)methylphenylsilane was prepared from dichloromethylphenylsilane and N-methylacetamide with triethylamine as acid acceptor; mp 66–68°. *Anal.* Calcd for $C_{13}H_{20}N_2O_2Si$: C, 59.1; H, 7.6; N, 10.6; Si, 10.6. Found: C, 59.5; H, 7.8; N, 10.7; Si, 10.7.
(6) P. S. Portoghese, *J. Med. Chem.*, **8**, 147 (1965). We wish to thank Professor P. S. Portoghese of the University of Minnesota for kindly supplying us with a sample of the quinine salt of (+)-N-phenylalanine.

Table I. Silaoxazolidones 1

No.	R	R′	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % Si	Found, % C	Found, % H	Found, % N	Found, % Si
1a[a]	H	C_6H_5	84–86	66.9	5.6	5.2		66.7	5.7	5.2	
1b	CH_3	C_6H_5	115–117								
1c[b]	CH_3	C_6H_5	125–128	67.8	6.1	5.0	9.9	67.7	6.1	5.0	9.9
1d	$C_6H_5CH_2$	C_6H_5	128–130	73.5	5.9	3.9	7.8	73.5	6.1	4.0	7.6
1e	C_6H_5	C_6H_5	171–175	73.0	5.5	4.1	8.1	73.3	5.6	3.8	8.6
1f	$(CH_3)_2CH$	C_6H_5	109–112	69.4	6.8	4.5		69.0	7.1	4.3	
1g[c]	$(CH_3)_2CH$	C_6H_5	120–125								
1h[d]	$(CH_3)_2CH$	C_6H_5	115–118								
1i[e]	CH_3	XC_6H_4									

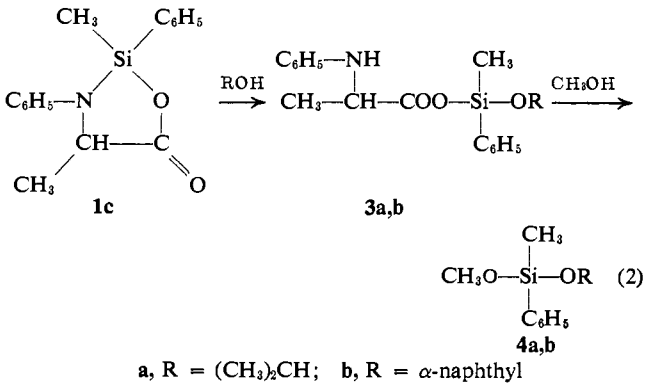
[a] Mol wt: calcd, 269; found, 268. [b] $[\alpha]^{25}D$ −27.5°. [c] $[\alpha]^{25}D$ −38.0°. [d] $[\alpha]^{25}D$ +32.6°. [e] X = *p*-CH_3O, *p*-CH_3, *p*-Cl, *p*-NO_2, *m*-NO_2 (pairs of diastereomers which have not crystallized to date).

The predominant diastereomer gave rise to the upfield silicon methyl peak in all cases except in those derived from N-phenylphenylglycine (**1e**) and N-phenylvaline (**1f–h**), where the signal remaining after crystallization was the downfield one of the original pair.

Since it was possible that the downfield silicon methyl absorbance was due to the silicon having the opposite configuration from that of the alanine derivative, N-phenylvaline was resolved through the quinine salt ($[\alpha]^{25}D$ +85° (*c* 5, EtOH)). The silaoxazolidone **1g** was prepared as in the alanine case, mp 120–125°, $[\alpha]^{25}D$ −38.0° (*c* 8.7, benzene). Its antipode, **1h**, starting with N-phenylvaline ($[\alpha]^{25}D$ −80°), was also prepared, mp 115–118°, $[\alpha]^{25}D$ +32.6°.

Reactions of 2-Methylphenylsila-3-phenyl-4-alkyloxazolidone-5. The silicon–nitrogen bond in the silaoxazolidone would be expected to be much more reactive than the silicon–oxygen bond. This suggested that successive reactions of the silaoxazolidone with two different alcohols could lead to separation of the optically active silicon from the carbon asymmetric center if both cleavage reactions were stereospecific.

Reaction of the 3-methylsilaoxazolidone **1c** with 2-propanol and methanol in successive steps led to the expected isopropoxymethoxymethylphenylsilane (**4a**) (eq 2).



1c 3a,b 4a,b (2)

a, R = $(CH_3)_2CH$; b, R = α-naphthyl

The specific rotation of **4a** was very small ($[\alpha]^{25}D$ −0.4°). From examination of the change of optical rotation during this reaction sequence we concluded that the silyl ester **3a** racemized rapidly during the reaction even though the two diastereomers of **3a** could not be detected by nmr. However, when 1-naphthol was used in the ring opening, the formation of two diastereomeric esters **3b** was readily determined by nmr which made it possible to choose reaction conditions that minimize the racemization. When an equivalent amount of 1-naphthol was added to silaoxazolidone **1c** (20% in benzene), the reaction was essentially complete at room temperature in 20 min. A short time later a new Si–CH_3 singlet appeared and grew at the expense of the original product. At equilibrium the two Si–CH_3 signals were of about equal intensity. The isomerization was accompanied by a change in specific rotation from +36.5° at 0.5 hr to +53.0° at 7 hr after addition of the 1-naphthol.

These results indicated that while a stereospecific ring opening could be achieved, any subsequent reaction must not only also be stereospecific but sufficiently rapid to minimize racemization. When a fivefold excess of methanol was added to the naphthoxysilyl ester **3b** the reaction was more than 90% complete in 3 min at 40°; less than 10% isomerization of **3b** was detected.

The isolated optically active naphthoxymethoxymethylphenylsilane **4b** had a specific rotation of +21.9° (*c* 5, benzene). *Anal.* Calcd for $C_{18}H_{20}SiO_2$: C, 73.45; H, 6.16; Si, 9.54. Found: C, 73.21; H, 6.08; Si, 9.75. (This compound is the first known case of an optically active silane with two oxygen atoms attached to silicon.) Previous preparations of optically active silanes have been limited to compounds having at most one Si–O bond. Sommer, *et al.*,[7] report a specific rotation of +16.5° for methoxymethylphenylnaphthylsilane.

A similar set of experiments was carried out using the silaoxazolidone derived from (+)-N-phenylvaline. Since the racemization of the naphthoxysilyl ester was considerably faster than in the case of the N-phenylalanine derivative, optical purity of the methoxynaphthoxymethylphenylsilane has not been high; $[\alpha]^{25}D$ −4.9° (*c* 19.5, benzene). However, the opposite configuration was obtained as expected from the nmr spectrum.

(7) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).

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Effect of Substituents on the Proton–Proton Coupling Constants of Monosubstituted Benzenes

Sir:

It has been well established experimentally that, among the several factors which determine the size of the vicinal coupling constants between a proton bonded