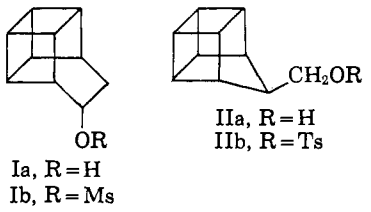
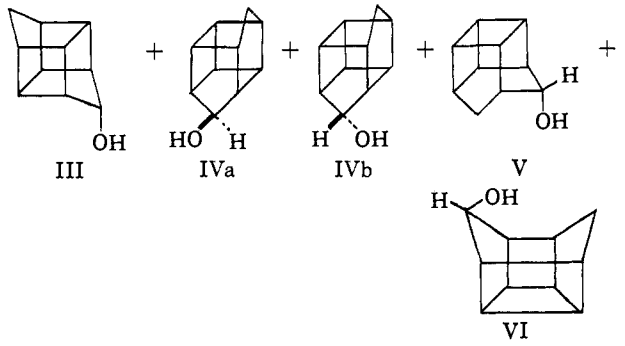
Solvolysis of Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-yl Methanesulfonate (1,1′-Bishomocubyl Mesylate) and Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-carbinyl *p*-Toluenesulfonate (Homocubylcarbinyl Tosylate)[1]

Sir:

The solvolyses of the 1,1′-bishomocubyl system I[2,3] and the related homocubylcarbinyl system II[3] are of interest because of the large amount of strain in the structures and the number of rearrangement pathways available.

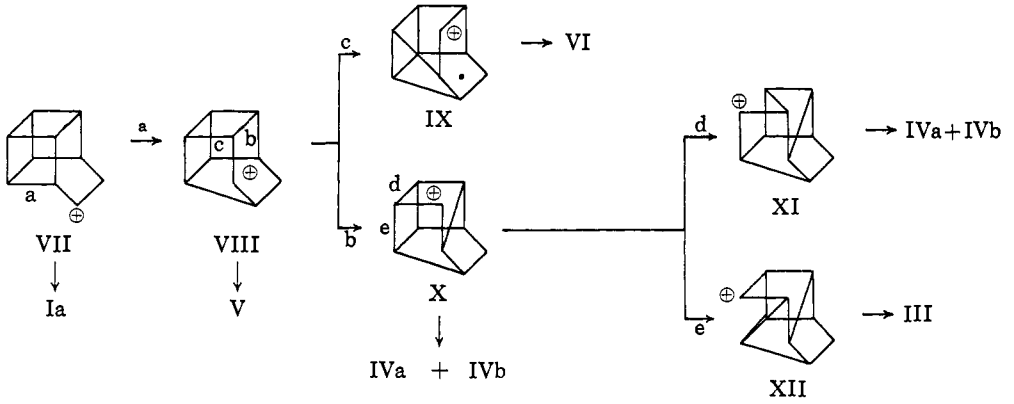




Acetolysis of Ib[3] in buffered acetic acid (2 hr, 105°, no methanesulfonate remains) yielded a mixture of acetates which was hydrolyzed. The mixture of saturated alcohols[4] was found by vpc to possess the following composition: Ia (10%), III (14%), IVa + IVb (18%), V (2%), and VI (56%).

The alcohols were separated by preparative vpc and their structures established in the following manner. Alcohol III (mp 137–140°) was oxidized to the known ketone[5] (mp 120–122°; nmr τ 8.58 (2 H, triplet, J = 1.4 cps)). The equivalency of the two methylene hydrogens at τ 8.58 and the triplet splitting is in accord with the symmetrical structure. Mixed isomeric alcohols IVa and IVb (mp 145–150°, not separable by vpc) were oxidized to the known ketone[6] (mp 124–126°). The ratio of the isomers present was shown to be 65:35 by comparison with an authentic mixture.[7] Alcohol VI (mp 223–225°; nmr τ 6.11 (1 H, triplet, J = 4.0 cps), 7.40 (1 H, doublet, J = 12.5 cps), 8.88 (1 H, doublet, J = 12.5 cps, fine structure in doublet) was oxidized to the related ketone (mp 180–182°; $\nu_{max}^{CCl_4}$ 1740 cm^{-1}) which on hydride reduction yielded solely starting alcohol VI, indicating an *endo* hydroxyl. The triplet structure for the proton on the carbinol carbon in VI speaks for the assignment of this symmetrical structure.

Further proof for the structure of VI was obtained in the following manner. The methanesulfonate Ib in buffered acetic acid at room temperature yielded an identical mixture of products after either 5 or 180 min, showing the initial reaction was very fast. The reaction mixture consisted of 45% acetates and 55% internal-returned mesylates. The internal-returned mesylates were reduced with sodium in liquid ammonia to yield (vpc analysis) 3% III, 7% IVa + IVb, and 90% of a material with a retention time similar to VI; the nmr spectrum of this last fraction showed it to be approximately a 1:1 mixture of V and VI. The nmr spectrum, at 100 Mc, clearly showed a quartet at τ 5.94 (J = 2.6 and 7.0 cps) and a triplet at τ 6.11 (J = 4.0 cps). Since there are only five possible pentacyclodecane nuclei (I, III–VI) containing only one methylene group and three (I, III, IV) have been prepared synthetically, the two alcohols in this mixture must have cage structures related to V and VI. The alcohol with the symmetrical structure of VI in the nmr should have a triplet for the hydrogen on the carbinol carbon while the unsymmetrical alcohol V should show a quartet; such is the case. Thus, although pure V cannot be obtained, its presence in this mixture establishes the structure VI assigned above to the major acetate formed on solvolysis. The composition of the acetates formed in this solvolysis of limited duration was essentially the same as that found for the extended reaction.



The products obtained from the acetolysis of Ib can be derived from the various carbonium ion intermediates (classical or nonclassical) shown below.

(1) This work was supported in part by Public Health Service Grant No. AM-709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) S. Masamune, H. Guts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966).

(3) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).

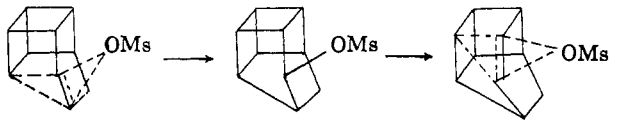
(4) The total alcohol mixture showed very low end absorption in the ultraviolet and no vinyl proton absorption in the nmr spectrum.

(5) An authentic sample was prepared by hydrolysis of the related ketal kindly supplied by Professor G. W. Griffin (G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964)).

(6) R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, **22**, 29 (1960).

(7) The mixture of alcohols was prepared by reduction of the ketone by sodium borohydride and the material used in the analysis was kindly supplied by Professor K. V. Scherer, Jr.

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).

William G. Dauben, Dale L. Whalen
Department of Chemistry, University of California
Berkeley, Califonia 94720
Received July 18, 1966

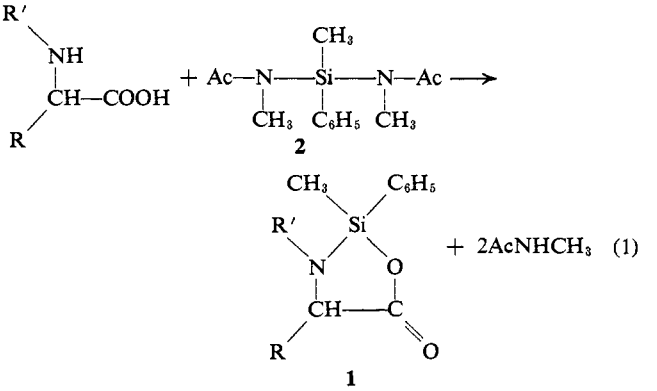
The Asymmetric Synthesis of an Optically Active Difunctional Silane

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.