

not be surprising if the geometry were intermediate between these two extremes. Berry, *et al.*, do not believe 3d orbital participation is important in the occupied orbitals.

Bonding in the Organohalophosphines. The argument presented above for the bonding in PCl_4 can also be used for the radical produced in irradiated $\text{CH}_3\text{-PCl}_2$. The large hyperfine splitting of the phosphorus strongly implies a geometry similar to the fully halogenated radicals. This species may be formulated as CH_3PCl_3 , where the dominant contribution to the line width is the unresolved chlorine splittings. It may be noted that some variation of line width was observed, depending on sample history, and is suggestive of important lattice effects. Further, the phosphorus hyperfine splitting is about 10% lower than in PCl_4 . The result may be rationalized with a simple model. Again, it is assumed that the geometry is nearly trigonal bi-

pyramidal and that the orbital composition of the equatorial PCl bond would be expected to be comparable in CH_3PCl_3 and in PCl_4 . The more electropositive P-CH_3 bond would likely have more s character than the P-Cl bond in the remaining equatorial bond.^{2a} Thus, the amount of s character in the orbital or the unpaired electron should be greater for PCl_4 than $\text{CH}_3\text{-PCl}_3$. This is a possible origin of the greater value of $A(\text{P})$ in PCl_4 compared to the organohalo radical. Difference in geometry may also influence the relative values. Again, with reference to the Higuchi tables, the smaller value of $A(\text{P})$ would suggest a geometry slightly closer to C_{4v} for CH_3PCl_3 than for PCl_4 . Indeed, since the values for $A(\text{P})$ decrease for the series PF_4 , PCl_4 , and CH_3PCl_3 , it is not unreasonable to associate this change with relative electronegativities and a sterically more closed structure. The question of 3d orbital participation must be left open as before.

Pentacoordinate Silicon Derivatives. IV.¹ Alkylammonium Siliconate Salts Derived from Aliphatic 1,2-Diols

Cecil L. Frye

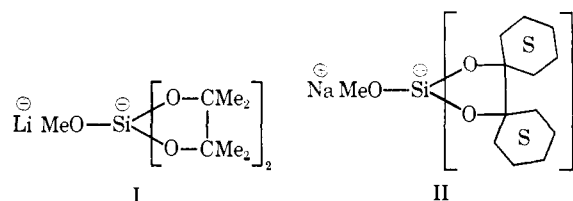
Contribution from the Chemical Research Department,
Dow Corning Corporation, Midland, Michigan 48640.
Received September 6, 1969

Abstract: Although stable, easily isolable, extracoordinate silicon derivatives of catechol and other aromatic 1,2-diols are well known, the literature contains relatively little information concerning analogous derivatives of *aliphatic* 1,2-diols. This paper describes the preparation of such a series consisting of alkylammonium siliconate salts derived from 1,2-diols as diverse as ethylene glycol, pinacol, and perfluoropinacol; also included are several examples of related α -hydroxycarboxylic acid derivatives of silicon. Compared to the catechol siliconates, the aliphatic diol siliconates are generally less robust thermally and solvolytically, except for the perfluoropinacol derivatives, in which the pentacoordinate silicon hybridization is maintained even in media as acidic as glacial acetic acid. Because of their extraordinary solvolytic stability, these perfluoropinacol siliconate anions are of special significance, since they should permit solution studies of pentacoordinate silicon species uncomplicated by equilibria involving merely tetracoordinate structure. Especially interesting was the chemistry of the novel strained heterocyclic $\text{Ph}(\text{OMe})\text{Si}(\text{OCMe}_2\text{CMe}_2\text{O})$. In the presence of suitable bases it underwent rapid ligand redistribution to

yield a pentacoordinate siliconate anion bearing two of the bidentate pinacolatoxy moieties (*i.e.*, $\text{PhSi}(\text{OCMe}_2\text{CMe}_2\text{O})_2$). However, with alkanolamine bases possessing the requisite structural features, intermediates bearing only one pinacolatoxy moiety were obtained. These intermediates are believed to be spirocyclic pentacoordinate structures in which a strategically appended donor moiety (*i.e.*, a dangling aminoalkoxy group) has become intramolecularly σ -bonded to the nearby electrophilic silicon center. The extent to which anchimeric coordination of this type occurs was shown to be dependent upon both the length of the aminoalkoxy group and the degree of N-alkylation.

Stable, easily isolable, extracoordinate silicon derivatives of *aromatic* 1,2-diols have been described in considerable detail;² however, the literature contains very little information concerning related derivatives of *aliphatic* 1,2-diols. The presence of such species in solution was inferred by Meerwein³ and convincingly demonstrated by Müller and Heinrich;⁴ the latter

authors also presented evidence for the isolation of two alkali metal pentacoordinate siliconate salts (I and II). Reported herein are facile preparative routes to a related



series of easily isolable crystalline alkylammonium

(4) R. Müller and L. Heinrich, *Chem. Ber.*, **94**, (8) 1943 (1961).

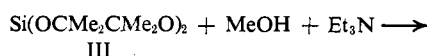
(1) Paper III: C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *J. Amer. Chem. Soc.*, **88**, 2727 (1966).

(2) (a) C. L. Frye, *ibid.*, **86**, 3170 (1964); (b) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, **90**, 6973 (1968); (c) C. L. Frye, U. S. Patents 3,355,477 and 3,360,525 (1967).

(3) H. Meerwein, *Justus Liebigs Ann. Chem.*, **476**, 113 (1929); *Angew. Chem.*, **63**, 489 (1951).

siliconate salts derived from various 1,2-diols including ethylene glycol, pinacol, and perfluoropinacol. As will be seen, it is also possible to prepare related siliconate salts containing a direct carbon to silicon linkage. In this *organosilicon* series it was found possible to isolate not only derivatives of the above diols, but, in addition, to obtain related species derived from α -hydroxycarboxylic acids.

In their study of the alkoxide titration of various silicate esters,⁴ Müller and Heinrich observed that 1,2-diol spiro-silicates interacted more strongly with the alkoxide than did all other silicate substrates. Their work⁴ was confined to alkali metal bases; however, in the present study simple amines were found to be sufficiently basic to afford similar alkoxide derivatives. Although pinacol spiro-silicate (III) may be recrystallized unscathed from dry Et_3N , recrystallization from Et_3N containing methanol afforded a low melting crystalline adduct (IV) believed to be of the "Müller-Heinrich" type. Alkanolamines react rapidly and exothermally

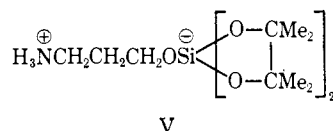
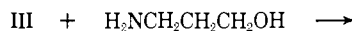


III



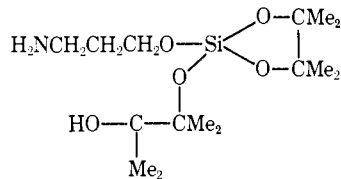
IV

with III to yield stable crystalline zwitterion structures characterized by high melting points and very low solubility in nonpolar solvents, *e.g.*, V, mp 190°. These



V

characteristics would certainly not be anticipated for unsymmetrical, nonpolar, merely tetracoordinate silicon structural alternatives such as VI. Similar zwitterion

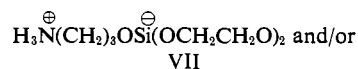
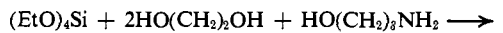


VI

structures were prepared from the reaction of III with *N,N*-dimethylaminoethanol and ethanolamine.

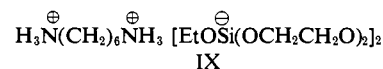
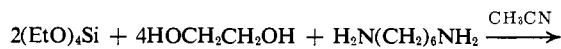
Because of the strain believed to be present in tetracoordinate 1,3,2-dioxasilolane heterocyclic systems, such as III, spiro-silicates derived from less highly alkyl-substituted 1,2-diols such as ethylene glycol cannot be prepared.⁵ It was therefore of interest to determine whether pentacoordinate silicon salts of the above type could be prepared without prior synthesis of the spiro-silicate. The necessity of such prior synthesis was implicit in earlier work. When 3-aminopropanol, ethyl silicate, and pinacol were refluxed together in acetonitrile solution, the desired salt (V) was indeed obtained in good yield. The generality of this method was then confirmed by preparing the analogous derivative (VII) of ethylene glycol, a 1,2-diol which does not yield an isolable spiro-silicate.⁵ The amine content of the resulting crystalline solid was intermediate between those values calculated for VII and VIII. In similar

(5) C. L. Frye, *J. Org. Chem.*, **34**, 2496 (1969).



VIII

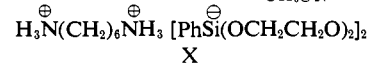
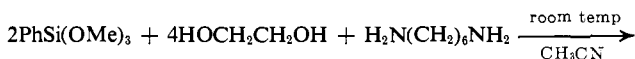
fashion, an ethylene glycol derivative (IX) employing hexamethylenediamine rather than an alkanolamine was also prepared, showing that alkanolamine components are not essential to these transformations.



IX

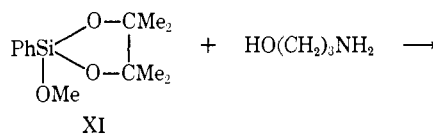
Similar attempts to isolate crystalline salts using ethylenediamine, propane-1,3-diamine, propane-1,2-diamine, triethylenetetramine, aniline, and 4,4'-methylenedianiline were unsuccessful. This may merely reflect the importance of symmetry and lattice energy in determining whether an equilibrating solution of tetra- and pentacoordinate species will form a solid crystalline deposit of the pentacoordinate salt.

In similar fashion, *organotrialkoxysilanes* also react directly with 1,2-diols and amines to yield pentacoordinate siliconates, *e.g.*, X. The novel strained hetero-

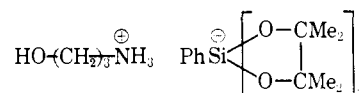


X

cyclic pinacol derivative XI provides still another route to organosiliconate salts of this type *via* an interesting ligand redistribution which occurs in the presence of amines as illustrated by the following example.



XI



XII

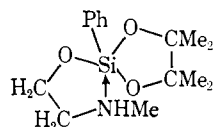
The rate of the above transformation is extremely solvent-dependent, requiring 1 to 2 weeks in heptane but proceeding to completion within only a few minutes in acetonitrile. Based on the amount of the bidentate pinacoloxo ligand available, the yield of XII was high (greater than 80% theoretical in the first crop); the liquors supernatant to the above crystalline deposit (XII) presumably contained various soluble alkoxy-silanes (*i.e.*, $\text{PhSi}(\text{OMe})_3$, $\text{PhSi}(\text{OMe})_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, etc.). The above redistribution does not require the presence of an alkanolamine as evidenced by the successful preparation of analogous salts using butylamine (mp 167–169°) and hexamethylenediamine (mp 217–218°).

At least part of the driving force for the above transformation from XI to XII (or III to V) is presumably associated with loss of ring strain accompanying the rehybridization of the silicon valences from sp^3 to dsp^3 . The 90° bond angles afforded by the rehybridized sys-

tem are much more compatible with the needs of the 1,3,2-dioxasilolane ring system (of XI or III) than were the sp^3 angles of 109° . This cannot, of course, be the only factor responsible for the formation of these salts, else they could not be prepared so easily from unstrained reactants as illustrated in some of our earlier examples. Formation of an additional σ bond to silicon appears to be energetically favorable, but in many systems this asset is more than offset by various liabilities such as loss of ligand translational entropy, loss of ligand segmental rotational entropy, increased steric interactions of the several ligands, etc. Many of these items are of minimal importance in the 1,2-diol derivatives, and consequently the inherent electrophilicity of the silicon center is manifested.

The methoxy substituent of heterocyclic XI is exceedingly susceptible to displacement, presumably as a consequence of the ring strain, although the ring itself emerges intact. Strain-induced enhancement of displacement processes at silicon with retention of the cyclic structure appears anomalous; however, parallel observations have been made on related phosphorus⁶ and sulfur⁷ systems, and a so-called "pseudo rotation" rationale has been evolved.⁸

Displacement reactions on such substrates are believed to involve initial attack on the hetero center (*i.e.*, S, P, Si, etc.) to form a pentacoordinate intermediate in which the incoming nucleophile occupies an apical site. Pseudorotation exchanges certain of the equatorial and apical ligands, and ultimately the ligand to be displaced departs from an apical site. As a consequence of rehybridization, and the resulting 90° bond angles, strain originally present is alleviated or eliminated in the pentacoordinate intermediate, and ring cleavage is therefore not particularly favored with respect to loss of some other ligand. Processes of the type described by Westheimer⁸ may very well be involved in the various transformations noted in the present paper. As will be seen below, there is good evidence that the presence of certain structural features interferes with the transformation of XI to phenyl-bis-pinacoloxysilicate salts, and indeed that precursory pentacoordinate *intermediates* can be isolated. Thus, when N-methylethanolamine was used with a nonpolar solvent (heptane), a simple alcohol exchange product (XIII) crystallized and was easily isolated and identified. Although XIII can be recrystallized under



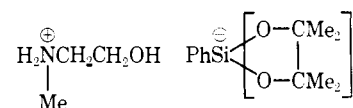
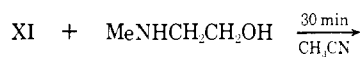
XIII

mild conditions from acetonitrile, it tends to undergo rather facile redistribution; thus, after refluxing the above reagents for 30 min in acetonitrile, the bis-pinacoloxysilicate salt (XIV) was the only crystalline product observed. The infrared spectrum of a CCl_4 solution of XIII differed so profoundly from that of its mineral oil mull as to suggest the following structural change

(6) P. C. Haake and F. H. Westheimer, *J. Amer. Chem. Soc.*, **83**, 1102 (1961); F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

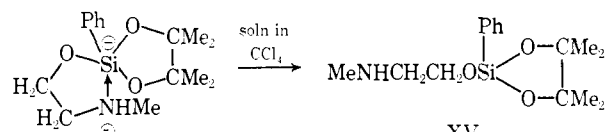
(7) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *ibid.*, **87**, 3781 (1965).

(8) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).



XIV

from pentacoordination to tetracoordination upon solution in a nonpolar medium.

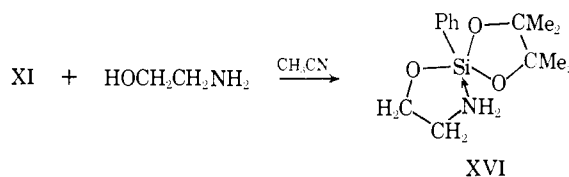


XIII

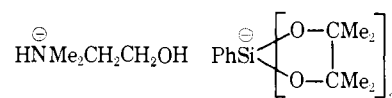
XV

The tetracoordinate nonpolar species XV should be more stable in the nonpolar CCl_4 environment, whereas the pentacoordinate species XIII, which possesses a dative bond, ought to be relatively stable in the bulk as a consequence of more favorable intermolecular dipolar interactions.

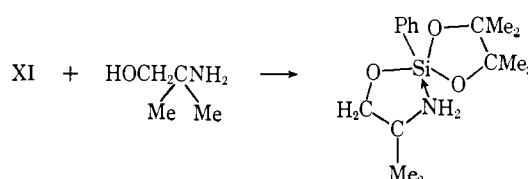
Structural features in the alkanolamine ligand appear to be extremely important in determining whether intermediates such as XIII can be observed. As illustrated above, β -amino alcohols are superior to γ -amino alcohols; *i.e.*, formation of a five-membered ring appears to provide more effective stabilization than formation of a six-membered ring. Moreover, as would be expected, alkylation of the donor nitrogen site was also shown to have an adverse effect upon the stability of such intermediates. Thus, ethanolamine itself yields an isolable intermediate (XVI) even when the polar acetonitrile is used as solvent, in contrast to the above example involving the related N-methyl derivative, which readily rearranges in this solvent. Going one step further, the use of N,N-dimethylethanolamine appears to completely preclude the formation of an isolable intermediate, affording only the bis-pinacoloxysilicate salt (XVII). The increased steric requirements of the N-alkylated species apparently lower the stability of structures involving dative bonding between nitrogen and silicon. As one would expect, alkylation more distant from the donor atom has no adverse effect; thus, 2-methyl-2-aminopropanol-1 readily yielded the



XVI



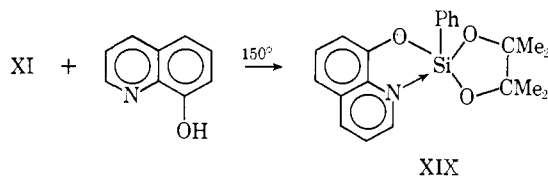
XVII



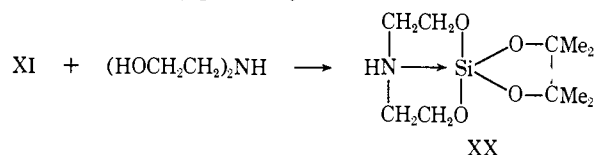
XVIII

expected intermediate, XVIII, which was stable even in acetonitrile. The above alkanolamine derivatives of XI bearing only one pinacol moiety presumably arise because of kinetic considerations; *i.e.*, not necessarily because they are more stable than the related bispinacolatoxy salts. Thus, attempts to prepare XVI and XVIII directly from $\text{PhSi}(\text{OMe})_3$, pinacol, and alkanolamine have thus far led only to the bispinacolatoxy salt structures.

In related reactions, 8-hydroxyquinoline was treated with XI to yield a crystalline oxinate, XIX. When XI

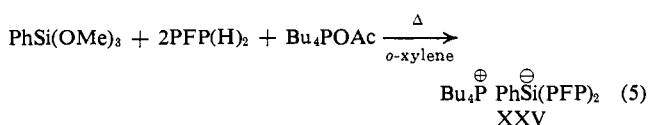
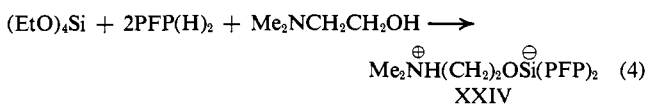
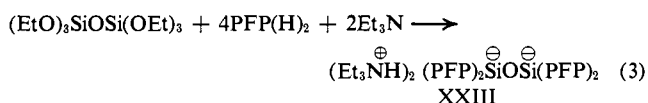
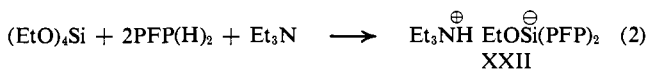
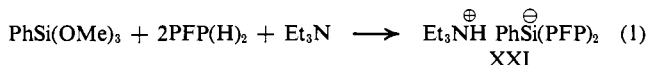


was heated with diethanolamine, phenyl cleavage led to the formation of the interesting derivative XX, in which there is very probably a transannular dative bond.



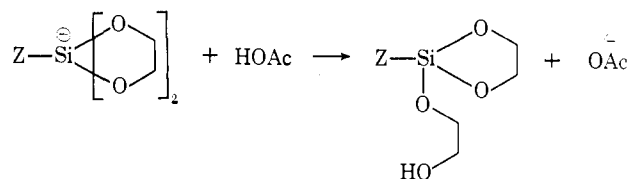
An independent synthesis of XX from the reaction of ethyl silicate, pinacol, and diethanolamine was achieved. These last two products are under investigation and will be described more fully at a later date.

Examination of the above anionic silicate structures suggests that increased stability might result from the presence of strongly electron withdrawing substituents in the glycol as a consequence of inductive delocalization of electronic charge from the silicon. Accordingly, a series of perfluoropinacol silicates was prepared as shown in eq 1-5 representing perfluoropinacol and the dibasic perfluoropinacolate ligand as PFP(H)₂ and PFP, respectively. These perfluoro-



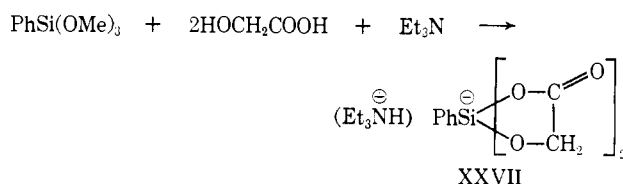
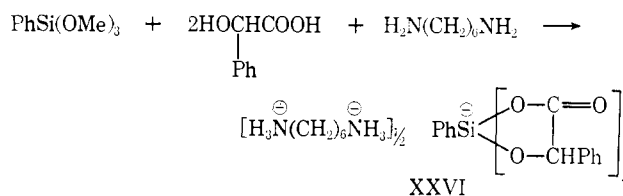
pinacolates were prepared by heating the appropriate reactants for about an hour at 150°. No reaction occurred even after 1 week when the reactants (in acetonitrile) were allowed to stand at room temperature. As anticipated, the resultant salts were appreciably stabilized by the trifluoromethyl substituents. Unlike the silicates hitherto prepared, they do not immediately disintegrate to tetracoordinate silicon species

when dissolved in a glacial acetic acid solution of perchloric acid. Catechol-, ethylene glycol-, or pinacol-silicate salts are "immediately titratable" as bases under such conditions. Evidently, in these examples an Si-OC bond rapidly undergoes protonation, forming acetate anion, which is the ultimate base in this medium.



In contrast, the perfluoropinacol-silicates neutralize added perchloric acid only upon heating or after lengthy periods (several hours) at room temperature. The exceptional solvolytic stability of the perfluoropinacol-silicate anions suggests their future use for solution studies uncomplicated by equilibria involving tetra-coordinate derivatives.

α -Hydroxy acids also constitute a family of 1,2-diols, and a few crystalline silicates of this somewhat different type have been prepared (*e.g.*, XXVI, XXVII).



Attempts to prepare similar derivatives of ethyl silicate have thus far been unsuccessful. Perhaps the structures form but are not sufficiently insoluble to deposit from the reaction mixture. Also unsuccessful have been attempts to prepare related derivatives of oxalic acid.

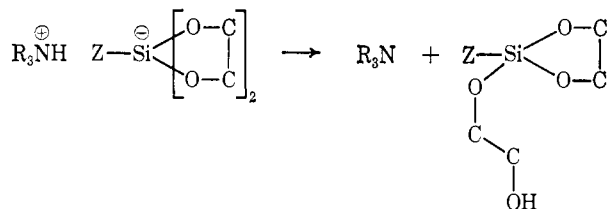
Comparison with Catechol Silicates

Although the chemistry of the silicates derived from aliphatic 1,2-diols is in many respects similar to that of the catechol derivatives, there are nevertheless several important differences.

(1) Silicon appears to exhibit a maximum coordination number of five in the aliphatic diol series; in the catechol series, however, only the organosilanes showed pentacoordination, while ethyl silicate yielded hexacoordinate structures.

(2) The catechol derivatives are much more resistant to hydrolytic decomposition. It is possible to prepare the catechol silicates in aqueous media, whereas the glycol derivatives must be carefully protected against even atmospheric moisture to prevent their decomposition. The perfluoropinacolates are an apparent exception to this generalization.

(3) Thermogravimetric analysis (tga) showed the glycol derivatives to revert to amine and tetracoordinate silicon structures much more readily than did comparable catechol derivatives; *i.e.*



Glycol derivatives undergo this type of decomposition at temperatures (100–200°) approximately 100° lower than those required for comparable catechol siliconates (200–300°). The increased stability of the catechol derivatives is presumably related to the ability of the aromatic rings to more effectively delocalize the negative charge otherwise residing on the central silicon atom.

Experimental Section

Triethylammonium Methoxybis(tetramethylethylenedioxy)siliconate (IV). The addition of 0.64 g (0.02 mol) of methanol to 2.60 g (0.01 mol) of III and 2.02 g (0.02 mol) of Et_3N caused the crystalline spiro-silicate to exothermally dissolve. Upon cooling in the refrigerator, crystallization occurred. The supernatant liquid was decanted and the crystalline solid was quickly washed with pentane and evacuated free of residual volatile solvent; the neutralization equivalent value of 416 accords fairly well with the value of 393 calculated for the anticipated product. In a separate experiment it was demonstrated that III could be recrystallized unscathed from Et_3N (*i.e.*, in the absence of an alcohol). Further analysis was not performed on this product since it was not very stable, tending to undergo loss of amine under rather mild conditions. More robust products resulted when primary amines were used. Thus, the analogous combination of methanol, pinacol spiro-silicate, and *n*-butylamine afforded a good yield of the anticipated salt, $n\text{-BuNH}_3^+\text{MeOSi}^-(\text{Pin})_2$, mp 107°.

Anal. Calcd for $\text{SiC}_{17}\text{H}_{30}\text{O}_5\text{N}$: C, 55.9; H, 10.7; Si, 7.7; neut equiv, 365. Found: C, 55.3; H, 10.6; Si, 7.7; neut equiv, 373.

Zwitterionic Salt V, *i.e.*, $\text{H}_2\text{N}(\text{CH}_2)_2\text{OSi}(\text{OCMe}_2\text{CMe}_2\text{O})_2$.

A. Direct Preparation from $(\text{EtO})_4\text{Si}$. A solution of 20.8 g (0.10 mol) of $(\text{EtO})_4\text{Si}$, 23.6 g (0.20 mol) of pinacol, and 7.5 g (0.10 mol) of 3-aminopropanol-1 in 50 g of acetonitrile was heated at reflux for 50 hr. After cooling to room temperature, the crystalline product V was removed by filtration, washed with a little acetonitrile, and vacuum dried to afford a 64% yield.

Anal. Calcd for $\text{SiC}_{13}\text{H}_{30}\text{O}_5\text{N}$: C, 53.7; H, 9.85; neut equiv, 335. Found: C, 53.4; H, 9.9; neut equiv, 339.

B. Preparation from Pinacol Spirosilicate. The addition of 0.75 g (0.01 mol) of 3-aminopropanol-1 to a solution of 2.6 g (0.01 mol) of III in 10 ml of benzene resulted in the immediate and exothermal deposition of a crystalline solid which was isolated by filtration, washed well with hexane, and vacuum dried to give a quantitative yield (3.3 g) of the expected zwitterionic product V, mp 190–195°, neut equiv 336 (calcd, 335). The infrared spectrum of this material was identical with that of the product prepared directly from ethyl silicate (part A, above).

Hexamethylenediammonium Di[phenylbis(ethylenedioxy)siliconate] (X). Combination of $\text{PhSi}(\text{OMe})_3$ (79.2 g, 0.40 mol), ethylene glycol (49.6 g, 0.80 mol), and melted hexamethylenediamine (23.2 g, 0.20 mol) resulted in a substantial exotherm (final temperature approximately 60°) and the initially immiscible reactants became completely miscible. Upon cooling to room temperature, crystallization ensued. The resulting crystalline deposit was slurried with acetonitrile, filtered, and then evacuated to dryness, affording 89 g (78% yield) of the desired siliconate salt, mp 130–140°.

Anal. Calcd for $\text{Si}_2\text{C}_{26}\text{H}_{44}\text{O}_8\text{N}_2$: C, 54.9; H, 7.74; Si, 9.88; neut equiv, 284. Found: C, 54.1; H, 7.9; Si, 9.52; neut equiv, 285.

A comparable structure bearing an alkyl rather than an aryl substituent on the silicon was also prepared. Thus a solution of $\text{MeSi}(\text{OMe})_3$ (13.6 g, 0.10 mol), ethylene glycol (12.4 g, 0.20 mol), and hexamethylenediamine (11.6 g, 0.10 mol) in 50 ml of tetrahydrofuran was allowed to stand at room temperature for several days, during which time very large crystals of $\text{H}_3\text{N}^+(\text{CH}_2)_6\text{N}^+\text{H}_3^+[\text{MeSi}^-(\text{OCH}_2\text{CH}_2\text{O})_2]$ formed, mp 92°.

Anal. Calcd for $\text{Si}_2\text{C}_{16}\text{H}_{40}\text{O}_8\text{N}_2$: C, 43.2; H, 9.0; Si, 12.6; neut equiv, 222. Found: C, 41.6; H, 9.5; Si, 12.6; neut equiv, 223.

Hexamethylenediammonium Di[ethoxybis(ethylenedioxy)siliconate] (IX). To a 250-ml suction flask was added 20.8 g (0.10 mol) of $(\text{EtO})_4\text{Si}$, 15.5 g (0.25 mol) of ethylene glycol, 5.9 g (0.05 mol) of hexamethylenediamine, and 35 ml of acetonitrile. A white crystalline solid formed immediately as the reactants were swirled together. After boiling the resulting slurry for 1 hr, the solid was removed by filtration, washed with fresh acetonitrile, and vacuum dried to give 15 g (63% yield) of a crystalline product; neut equiv 252 (calcd, 251).

Reaction of XI³ with Alkanolamines. A. Reaction with 3-Aminopropanol to Produce 3-Hydroxypropylammonium Phenylbis(tetramethylethylenedioxy)siliconate (XII). The addition of 5.04 g (0.02 mol) of XI and 1.50 g (0.02 mol) of 3-aminopropanol-1 to 10 g of acetonitrile led to the almost immediate formation of a needle-like crystalline solid believed to be XII. This material was filtered out, washed with additional acetonitrile, and vacuum dried; yield, 3.38 g (82%); mp, 140–143°.

Anal. Calcd for $\text{SiC}_{21}\text{H}_{30}\text{O}_5\text{N}$: C, 61.0; H, 9.44; Si, 6.79; neut equiv, 413. Found: C, 60.0; H, 8.90; Si, 6.75; neut equiv, 412.

In a similar preparation employing no solvent or using heptane in place of acetonitrile, periods of 1–2 weeks at room temperature were required for comparable conversions to this product. The above compound was also prepared by boiling a solution of $\text{PhSi}(\text{OMe})_3$ (0.1 mol) and pinacol (0.2 mol) in 50 ml of acetonitrile for 16 hr.

B. Reaction with *N*-Methylethanolamine to Produce XIII. To a 1-oz, screw-cap vial were added 15.0 g of heptane, 5.04 g (0.20 mol) of XI, and 1.50 g (0.02 mol) of $\text{MeNHCH}_2\text{CH}_2\text{OH}$. It should be noted that although this alkanolamine is immiscible with heptane, it dissolves immediately as the silane XI is added. The capped vial was placed in the refrigerator for 1 hr, during which time a large amount of crystalline product deposited. The supernatant solution was decanted and the solid washed with hexane and vacuum dried; the neutralization equivalent of this material was determined to be 292. Recrystallization from heptane produced little change (*i.e.*, neut equiv, 296). These results accord well with the value of 295 calculated for XIII. Infrared spectra of a mineral oil mull and of a CCl_4 solution of this material were obtained. As previously noted herein, these spectra differ so profoundly as to suggest extensive structural alteration (*i.e.*, rehybridization of the silicon from a penta-coordinate to a tetra-coordinate species).

C. Reaction with *N*-Methylethanolamine to Produce 2-Hydroxyethylmethylammonium Phenylbis(tetramethylethylenedioxy)siliconate (XIV). If the above reactants are heated for 30 min in acetonitrile, then the product which crystallizes has a neutralization equivalent of 414, which agrees well with the value of 413 calculated for the structure bearing two pinacol residues (XIV). The melting point of this material is 112–114°, and its infrared spectrum is readily distinguishable from those of both XIII and XV.

D. Reaction with *N,N*-Dimethylethanolamine to Produce 2-Hydroxyethyl dimethylammonium Phenylbis(tetramethylethylenedioxy)siliconate (XVII). A solution of 1.8 g (0.02 mol) of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$ and 5.04 g (0.02 mol) of XI in 15 g of heptane did not appear to react upon standing for several hours at room temperature. However, when inspected almost 5 months later, a deposit of crystalline material believed to be XVII had formed and 2.1 g was isolated (49% yield); neut equiv 432 (calcd, 427); mp 83–84°.

E. Reaction with 2-Amino-2-methylpropanol-1 to Produce XVIII. A crystalline solid deposited immediately when 0.9 g (0.01 mol) of 2-amino-2-methyl-1-propanol was added to a solution of 2.5 g (0.01 mol) of XI in 15 ml of hexane. This solid dissolved when its hexane suspension was heated to boiling and redeposited upon cooling to room temperature, affording a 71% yield (2.21 g) of XVIII; melting point nondescript over the range 50–120°.

Anal. Calcd for $\text{SiC}_{18}\text{H}_{27}\text{O}_5\text{N}$: C, 62.6; H, 8.74; Si, 9.1; neut equiv, 309. Found: C, 61.8; H, 9.2; Si, 8.5; neut equiv, 308.

F. Reaction with Ethanolamine to Produce XVI. Ethanolamine (0.61 g, 0.01 mol) was added to a solution of XI (2.5 g, 0.01 mol) in 5 ml of acetonitrile resulting in the immediate formation of a crystalline solid. The supernatant solution was carefully decanted and the residue was washed twice with fresh acetonitrile and then evacuated free of any volatiles to afford 1.44 g (51% yield) of the desired product, XVI; melting point nondescript over a broad range (50–130°).

Anal. Calcd for $\text{SiC}_{14}\text{H}_{23}\text{O}_5\text{N}$: C, 59.8; H, 8.2; Si, 10.0; neut equiv, 281. Found: C, 59.0; H, 8.6; Si, 9.65; neut equiv, 282.

Triethylammonium Ethoxybis(perfluorotetramethylethylenedioxy)siliconate (XXII). Triethylammonium perfluoropinacolate was prepared from the reaction of equivalent amounts of the amine and perfluoropinacol. A mixture of 10.0 g (0.023 mol) of this salt and ethyl silicate (2.1 g, 0.01 mol) was then heated for 1 hr at 140–150°. Recrystallization of the resulting dark colored product three times from toluene yielded 4 g (48% yield) of the desired perfluoropinacol siliconate salt, XXII. This material was very soluble in oxygenated solvents such as tetrahydrofuran, acetic acid, alcohols, acetone, etc., but poorly soluble in aliphatic hydrocarbons. Although initially neutral in glacial acetic acid, this product was titratable as a base upon long standing or upon heating at reflux.

Anal. Calcd for $\text{SiC}_{20}\text{H}_{21}\text{O}_3\text{NF}_{24}$: C, 28.6; H, 2.5; F, 54.3; Si, 3.35; neut equiv, 839. Found: C, 28.9; H, 2.6; F, 53.8; Si, 3.28; neut equiv, 859.

¹H nmr data [τ value (multiplicity)/relative intensity] obtained in deuterated DMSO: N-CH₂ [6.88 (4)/6]; O-CH₂ [6.32 (4)/2]; N-CH₂CH₃ [8.78 (3)/9]; O-CH₂CH₃ [8.95 (3)/3]. The infrared spectra of this and the other perfluoropinacol siliconates contain a fairly strong absorption at 11.4 μ ; triethylammonium perfluoropinacolate itself has a line at 11.5 μ .

Triethylammonium Phenylbis(perfluorotetramethylethylenedioxy)siliconate (XXI). Triethylamine (2.1 g, 0.02 mol), phenyltrimethoxysilane (2.0 g, 0.01 mol), and perfluoropinacol (6.7 g, 0.02 mol) were placed in an open 1-oz vial and heated at 150° on a hot plate for 30 min, whereupon the contents solidified to a crystalline mass. After extracting several times with boiling hexane, the solid was evacuated to a constant weight of 6.0 g (69% yield).

Anal. Calcd for $\text{SiC}_{24}\text{H}_{21}\text{O}_4\text{NF}_{24}$: C, 33.1; H, 2.41; neut equiv, 871. Found: C, 33.5; H, 2.73; neut equiv, 860.

This compound, like the other perfluoropinacol siliconates, is very soluble in oxygenated solvents and can be recrystallized from a toluene-THF mixture. It was qualitatively demonstrated that strong mineral acid accelerates the rate of the neutralization reaction which occurs when the perfluoropinacol siliconate anion is dissolved in glacial acetic acid. Thus, a solution of the above salt XXI in glacial acetic acid was divided into two equal aliquots and to one of them was added a small amount of perchloric acid (0.50 ml of a 0.1 N solution in glacial acetic acid). Both solutions slowly became less acidic, as evidenced by the gradual change of the methyl violet indicator from yellow-green to purple. After 9 hr at room temperature, titration back to neutrality (methyl violet \rightarrow blue-green) with additional 0.1 N HClO₄ revealed that the aliquot containing no initial mineral acid had produced base equivalent to only 0.08 ml of 0.1 N acid in this period. The other aliquot had produced base slightly in excess of that equivalent to the initially added HClO₄ during that same period (*i.e.*, 0.51 ml of 0.1 N acid was consumed). This observation seems to suggest a rate-determining step involving ring opening of a protonated species.

Bistriethylammonium Oxyl[bis(perfluorotetramethylethylenedioxy)siliconate] (XXIII). The addition of Et₃N (1.10 g, 0.011 mol) to a solution of perfluoropinacol (6.70 g, 0.02 mol) and hexaethoxydisiloxane (1.8 g, 0.005 mol) in 6 g of toluene resulted in the immediate exothermic formation of the simple triethylammonium perfluoropinacolate salt, which sometimes deposits from solution but redissolves upon further heating. After boiling for 1 hr, the solution was cooled to room temperature, whereupon a crystalline solid deposited, which was washed well with toluene and then with hexane before evacuating to a constant weight of 1.7 g (21% yield). This product is virtually insoluble in boiling heptane but does dissolve in hot toluene, from which it may be recrystallized.

Anal. Calcd for $\text{Si}_2\text{C}_{36}\text{H}_{16}\text{O}_9\text{N}_2\text{F}_{48}$: C, 26.9; H, 2.0; F, 56.8; neut equiv, 802. Found: C, 27.6; H, 2.41; F, 55.3; neut equiv, 806.

¹H nmr data [τ value (multiplicity)/relative intensity] obtained in acetone solution: N-CH₂ [6.65 (4)/6]; C-CH₃ [8.62 (3)/9]; the N-H is apparently broad and lost in the background; the absence of EtO content was confirmed by these data.

2-(N,N-Dimethylamino)ethoxybis(perfluorotetramethylethylenedioxy)silicon Zwitterion (XXIV). N,N-Dimethylaminoethanol (1.0 g, 0.011 mol) was added to a solution of ethyl silicate (2.1 g, 0.010 mol) and perfluoropinacol (6.7 g, 0.020 mol) in 10 g of *o*-xylene. The initially formed salt dissolves upon further heating and a second dense crystalline solid gradually deposits from the boiling solution. Titration of this crude product (about 6.5 g) revealed the presence of considerable amounts of "immediately titratable" base in addition to the latent basicity characteristic of

the perfluoropinacol siliconates. The immediately titratable amine content was removed by triturating three times with boiling *o*-xylene, whereupon the remaining solid was washed free of *o*-xylene with hexane and evacuated to a constant weight of 5.5 g (70% yield). This zwitterionic product is soluble in xylene-THF combinations and may be recrystallized therefrom.

Anal. Calcd for $\text{SiC}_{16}\text{H}_{11}\text{O}_3\text{NF}_{24}$: C, 24.6; Si, 3.6; neut equiv, 781. Found: C, 24.7; Si, 3.8; neut equiv, 782.

Although soluble in oxygenated organic solvents, XXIV is not soluble in water. When a sample was covered with water and heated to about 70°, little or no solution occurred. After evacuating the sample to free it of moisture, a mineral oil mull infrared spectrum showed no evidence of hydrolysis.

Tetrabutylphosphonium Phenylbis(perfluorotetramethylethylenedioxy)siliconate (XXV). The following materials were combined in a 1-oz vial and heated at the boiling point for 30 min on a hot plate: tetrabutylphosphonium acetate (3.82 g, 0.012 mol), phenyltrimethoxysilane (2.2 g, 0.011 mol), perfluoropinacol (6.7 g, 0.02 mol), and 5 g of *o*-xylene. After evacuation at an aspirator to remove most of the *o*-xylene, the residue was extracted with hexane, whereupon the hexane-immiscible product crystallized. The appearance of the crystalline solid was much improved by leaching with 2-propanol. Evacuation of the residue to constant weight afforded 5.7 g (55% yield) of XXV. An additional 1.6 g of XXV was obtained by diluting the 2-propanol washes with five volumes of hexane and chilling to induce crystallization. An infrared spectrum (mineral oil mull) was consistent with the anticipated structure (*i.e.*, no carbonyl or hydroxyl and a strong line at 11.4 rather than 11.5 μ , indicative of a perfluoropinacol siliconate rather than a simple salt of perfluoropinacol). The observed neutralization equivalent of 1043 was in excellent accord with the calculated value of 1028. The ¹H nmr data were also consistent with the above composition in that the typical aliphatic protons and aromatic protons were present in the expected amounts, *i.e.*, P-CH₂CH₂CH₂CH₃/Si-C₆H₅, 28/5.

α -Hydroxycarboxylic Acid Derivatives. A. Et₃NH⁺PhSi⁻(OCH₂C=OO)₂ (XXVII). To a 1-oz vial were added 4.0 g (0.02 mol) of PhSi(OMe)₃, 3.04 g (0.04 mol) of glycolic acid, 7 g of MeOH, and 2.1 g (0.02 mol) of Et₃N. The resulting solution was heated to boiling on the hot plate, *o*-xylene was added to displace the methanol, and as the methanol was allowed to distil from the vial, a heavy immiscible product layer formed. Dilution with about 10 ml of THF restored miscibility and upon chilling the resulting solution deposited a 77% yield of the desired product, which was then recrystallized from THF and evacuated free of volatiles, mp 111–113°.

Anal. Calcd for $\text{SiC}_{16}\text{H}_{25}\text{O}_6\text{N}$: C, 54.1; H, 7.04; neut equiv, 355. Found: C, 53.8; H, 7.11; neut equiv, 355.

B. H₃N⁺(CH₂)₆NH₃⁺[PhSi⁻(OCH₂COO)₂]₂. Phenyltrimethoxysilane (4.0 g, 0.02 mol), glycolic acid (3.04 g, 0.04 mol), and hexamethylenediamine (1.2 g, 0.01 mol) were combined in a 1-oz vial with 6.5 g of acetonitrile and 10 ml of methanol. After heating briefly to the boiling point on a hot plate and then cooling to room temperature, the large amount of crystalline product which formed was filtered, washed well with methanol, and evacuated to constant weight to give 3.8 g (61% yield) of the siliconate salt, mp 202–205°; a second crop of 1.5 g of the same material was collected from the filtrate, bringing the yield to 85%.

Anal. Calcd for $\text{Si}_2\text{C}_{26}\text{H}_{36}\text{O}_{12}\text{N}_2$: C, 50.0; H, 5.77; Si, 9.0; neut equiv, 312. Found: C, 49.1; H, 5.70; Si, 8.7; neut equiv, 317.

The infrared spectrum, consistent with the structure assigned, shows a well-defined ester type carbonyl absorption at 5.94 μ . In related fashion an analogous HMDA mandelic acid derivative XXVI was prepared in 84% yield; the observed neutralization equivalent of 463 was in excellent agreement with the calculated value of 464.

When half the starting mandelic acid was replaced by an equivalent of ethylene glycol, the resulting crystalline derivative (isolated in 70% yield) had a neutralization equivalent of 370, which accords well with the value of 374 calculated for the salt having mixed bidentate ligands, *i.e.*, H₃N⁺(CH₂)₆NH₃⁺[PhSi⁻(OCH₂CH₂O)(OCH-PhC=OO)]₂.

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