Stable Silicon Heterocyclic Derivatives of Branched Alkanediols

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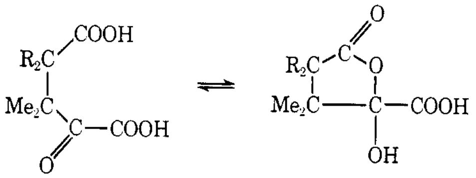
The cyclic stabilizing effect of alkyl substituents has been exploited for the preparation of a series of spirosilicates derived from 1,2-, 1,3-, and 1,4-diols. Vicinal 1,2 disubstitution and geminal 1,1 disubstitution are apparently more effective than geminal 2,2 disubstitution. A series of related heterocyclic organosilicon derivatives is also described.

The literature contains numerous examples of silicon heterocyclic derivatives of various diols,[1] but, with the exception of two papers,[1a,1h] there has been little apparent effort to relate heterocyclic stability[2] to diol structure. The paucity of such correlations is somewhat surprising, because dioxasila-heterocyclic substrates are well suited for studying the effect of structure upon ring-chain equilibria, since (1) structural variation is simple, (2) facile interconversion of ring and chain forms is easily catalyzed, and (3) the interconversion results in no new functional moieties. Regarding this last point, much of the earlier ring-chain work has dealt with systems such as the following[3] equilibrium in which any interpretation is necessarily complicated by changes in functionality.



The present paper reports the deliberate effort to exploit the well-known cyclic-stabilizing effect of alkyl substituents[4] for the preparation of a number of interesting silicon heterocyclic diol derivatives. Included are examples of 1,2-, 1,3-, and 1,4-diol spirosilicates (I–IX) as well as several related organosilicon heterocyclics (Table I). The relative effect of several types of dialkylation on cyclic stability is also illustrated.

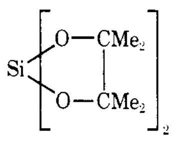
Table I

Organosilicon Modifications

Alkanedioxysilane[a,b] (G = $-\underset{n\text{-Pr}}{\mathrm{OCH}}-\underset{\mathrm{Et}}{\mathrm{CH}}\mathrm{CH_2O}-$)	Bp, °C (mm), uncorrected	Viscosity (centistokes) 25°	75°	125°	200°
$[\mathrm{Me(G)Si}]_2\mathrm{G}$	170 (0.5)	66.2	7.76	2.59	1.06
$[n\text{-}\mathrm{Pr(G)Si}]_2\mathrm{G}$	185 (0.3)	61.8	8.79	3.14	1.23
$[n\text{-}\mathrm{Pr(G)Si}]_2\mathrm{G}$	130 (0.01)	20.6	4.36	1.82	0.79
$[n\text{-}\mathrm{Pentyl(G)Si}]_2\mathrm{G}$	180 (0.05)	95.1	11.9	3.89	1.44
$[\mathrm{Ph(G)Si}]_2\mathrm{G}$	250 (0.01)	7.75	26.5	6.01	1.88
n-Pr(G)SiOMe	114 (10)				

[a] Prepared by reaction of the organomethoxysilanes with 2-ethylhexane-1,3-diol and, in the case of the disiloxane, the appropriate amount of water. [b] In all cases, an elemental analysis consistent with the assigned structure was obtained.

Diol Alcoholysis of Ethyl Silicate.—In this work, spirosilicates were prepared by catalyzed (NaOMe or isopropyl titanate) alcoholysis of ethyl silicate with appropriate diols under conditions whereby ethanol was removed from the system as it formed. The resulting spirosilicates were then isolated by distillation or crystallization. In appropriately decorated systems, monomeric spirosilicate species are so favored that the initial *neat* undistilled product is essentially free of higher oligomers, even in the presence of agents capable of catalyzing rapid redistribution of SiOC bonds (in this category fall I,[5] III,[5] IV, VI, VIII, and IX). In some systems, the decoration is less effective and, at equilibrium, the crude alcoholysis product contains much material of higher molecular weight. In such instances, distillation in the presence of a catalyst can,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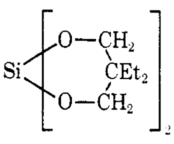
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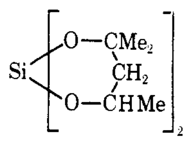
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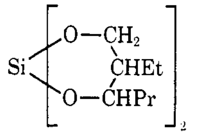
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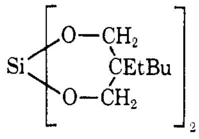
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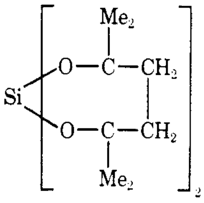
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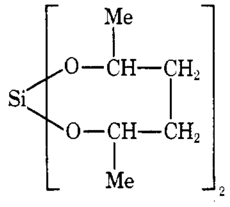
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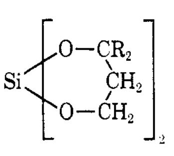
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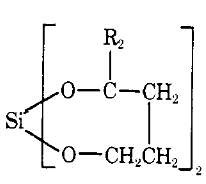
IX

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(1) (a) H. Staudinger and W. Hahn, *Makromol. Chem.*, **11**, 24 (1953); (b) W. Hahn, *ibid.*, **10**, 261 (1953); (c) W. Hahn, *ibid.*, **11**, 51 (1953); (d) R. Schwarz and W. Kuchen, *Z. Anorg. Allgem. Chem.*, **279**, 84 (1955); (e) F. S. Kipping and J. T. Abrams, *J. Chem. Soc.*, 81 (1944); (f) J. J. Zuckermann, *ibid.*, 873 (1962); (g) C. M. Silcox and J. J. Zuckerman, *J. Organometal. Chem.*, **5**, 483 (1966); (h) R. Calas and P. Nicon, *Compt. Rend.*, **249**, 1011 (1959); (i) R. C. Mehrotra and R. C. Pant, *J. Indian Chem. Soc.*, **41**, 563 (1964); (j) R. C. Mehrotra and R. C. Pant, *ibid.*, **1**, 380 (1963); (k) Yn. N. Vol'nov and B. N. Dolgov, *J. Gen. Chem. USSR* (Engl. Transl.), **10**, 550 (1940); (l) M. M. Koton, *et al.*, *Zh. Obshch. Khim.*, **36**, 87 (1966); (m) M. F. Shostakovskii, *et al.*, U.S.S.R. Patent 165,452; *Chem. Abstr.*, **62**, 6514*a* (1965); (n) R. H. Krieble and C. A. Burkhard, *J. Amer. Chem. Soc.*, **69**, 2689 (1947); (o) G. W. Pedlow, Jr., and C. S. Miner, Fr., U. S. Patent 2,566,365 (1946); (p) R. Müller and L. Heinrich, *Chem. Ber.*, **94**, 2225 (1961); (q) C. L. Frye, R. M. Salinger, and T. J. Patin, *J. Amer. Chem. Soc.*, **88**, 2343 (1966).

(2) Throughout this paper the terms "stable heterocyclic" and "cyclic stability" refer to the thermodynamic stability relative to acyclic alternatives. No inferences regarding solvolytic or oxidative stability are intended.

(3) E. Rothstein and C. W. Shoppee, *J. Chem. Soc.*, 531 (1927).

(4) (a) G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 468. (b) N. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960). (c) For other leading references, see F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *J. Amer. Chem. Soc.*, **81**, 2698 (1959).

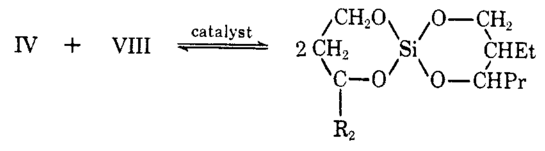
(5) Pinacol spirosilicate (I) has been prepared previously[1c,i] but not from alkyl orthosilicates. Likewise, compound III has also been previously described.[10]

by displacing the mobile equilibrium, be used to give high yields of the monomeric species (thus, II, V, and VII were prepared in this fashion). Finally, there are systems, *i.e.*, $[Si(OCH_2CH_2O)_2]_x$, which are so thoroughly polymeric at equilibrium as to completely frustrate all attempts to form and distil monomer from the *neat* system. The claim[11] that spirosilicates derived from ethylene, propylene, and butylene glycols had indeed been prepared is certainly unwarranted in view of the complete lack of volatility or solubility of the reported materials.

While examination of molecular models indicates the six- and seven-membered rings to be essentially strain-free, the five-membered ring species I appears to be appreciably strained. This strain is presumably related to the marked ease with which I is converted into stable pentacoordinate silicon derivatives.[6,7]

As will be seen below, geminal 1,1 dialkylation effectively stabilized the six-membered cyclics; however, this degree of substitution did not stabilize spirosilicates with five-membered rings; *i.e.*, the reaction of ethyl silicate and isobutylene glycol afforded only cross-linked gels from which we were unable to distil any spirosilicate. The fact that I does *not* undergo polymerization under equilibrating conditions despite its strained nature underscores the overriding importance of alkyl decoration upon ring-chain equilibria.

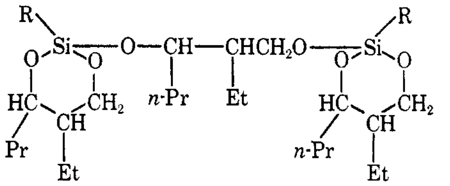
Vicinal Decoration and Heterocyclic Stability.—Some types of decoration appear to stabilize cyclics much more effectively than others. For instance, the vicinal 1,2 disubstitution in IV is apparently superior in this respect to the geminal 2,2 disubstitution of V. Upon heating these pure distilled spirosilicates briefly to 100° after the addition of catalytic KOH, IV (vicinal substitution) was unaffected, while V rearranged rapidly to an obviously cross-linked polymer. The greater stability of IV is possibly related to restriction of rotation about the vicinally substituted C-C bond; *i.e.*, constraint of rotation about this bond should diminish any loss of segmental rotational entropy which might result from cyclization. Although geminal 2,2 disubstitution did not confer much stability to the cyclic species (*i.e.*, V), very marked stability did accrue, however, from geminal 1,1 disubstitution (*e.g.*, VIII and IV); thus, under equilibrating conditions, VIII and IX afford no ring-opened oligomers. This stability is perhaps a consequence of the greater steric interactions to be expected in the hypothetical open-chain oligomers of VIII and IX; certainly decoration at the 1 site should produce more crowding about the silicon than should decoration at the 2 site. That these observations were indeed made under dynamic equilibrium conditions (*i.e.*, that cyclic stability was not merely the consequence of a slow and incomplete ring-opening reaction) was easily demonstrated. Thus, admixture of two stable cyclic species such as IV and VIII in the presence of a catalyst resulted in the rapid formation of an additional species of intermediate volatility (*i.e.*, the mixed spirosilicate).



Similar attempts to prepare a stable spirosilicate from the 1,5-diol, $HOCH_2CH_2CH_2CH_2C(Bu)_2OH$, led only to a viscous nonvolatile oil containing little, if any, of the desired monomer. Thus, this negative result would appear to indicate, at least qualitatively, a limit to the geminal 1,1 dialkyl "cyclic stabilizing" effect.

Although V did indeed gel, the number of cross links is apparently inversely proportional to the temperature, since upon heating to 200–220° the gel reverted to a mobile liquid. The catalyzed polymer thus behaves as a thermoplastic resin. The explanation for this thermal reversibility is believed to be similar to that advanced above to account for the stability of IV relative to polymeric forms. That is, certain motions (rotation of the geminal substituents, perhaps) more readily accommodated in the monomeric structure become increasingly important at higher temperature, thus favoring the spirosilicate species. Other motions also presumably facilitated in the lower molecular weight species, such as stretching vibrations and molecular translation, would become increasingly important at higher temperatures.

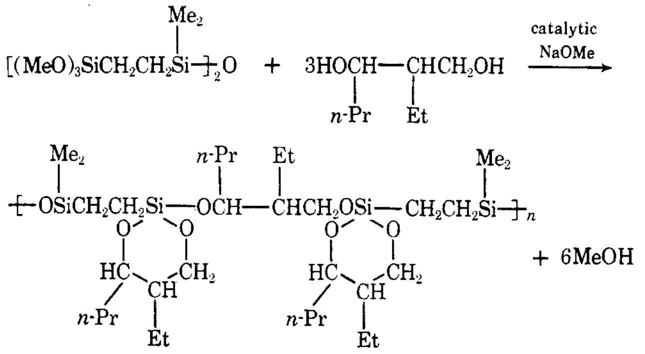
Organosilicon Modifications.—A number of related 2-ethylhexane-1,3-diol derivatives involving organo-substituted silicon (X, R = Me, *n*-Pr, *n*-pentyl, Ph)



X

were also prepared. Because of their possible utility as hydraulic fluids, viscosity data from 25–200° was obtained, and this information is also included in Table I.

The marked cyclization tendency engendered by this type of alkyl decoration was particularly well illustrated by the following reaction.



A *soluble* polymer was obtained, and this observation seemed immanently consistent with the presumed cyclic structure suggested, since any appreciable ring-opening would have certainly resulted in cross linking and consequent gelation.

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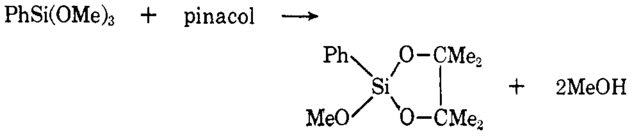
[6] R. Müller and L. Heinrich, *Chem. Ber.*, **94**, 1943 (1961).

[7] Unpublished work from this laboratory to be described in a forthcoming paper.

Of especial interest were the organosilicon heterocyclic species derived from pinacol, *e.g.*



XI

Like I, the analogous spirosilicate, XI, appears to be highly strained and, as a presumed consequence of this strain, undergoes a number of interesting transformations to stable isolable pentaccordinate silicon derivatives.[7]

Experimental Section

2,2,3,3,7,7,8,8-Octamethyl-1,4,6,9,5-tetraoxasilaspiro[4.4]-nonane (I, Pinacol Spirosilicate).—This material has been prepared before,[1a,i] but the following procedure utilizing alkoxy exchange is believed to be the most convenient method now available. To a 1-l. erlenmeyer flask were added 118 g (1.00 mol) of pinacol and 100 ml of benzene. After boiling this solution vigorously for about 5 min to azeotropically expel any moisture, 104 g (0.500 mol) of ethyl silicate was added. Upon heating to 135°, the absence of ethanol evolution suggested no reaction to be occurring. Therefore, tetraisopropyl titanate (0.5 ml) was added as a catalyst, resulting in the immediate commencement of ethanol evolution. The flask was then heated to a pot temperature of 190° and allowed to cool, whereupon crystallization occurred. Recrystallization from hexane yielded 70 g of pinacol spirosilicate; mp 112°. The filtrate was concentrated and taken up in pentane, and upon refrigeration deposited an additional 31 g of product. These two crops represent a 78% yield, and no further effort was expended with the filtrate, although it presumably contained additional spirosilicate. The infrared spectrum was consistent with the anticipated structure (absorption due to hydroxy and ethoxy being absent), and the anticipated molecular weight (260) was confirmed by mass spectroscopy.

2,2,4,8,8,10-Hexamethyl-1,5,7,11,6-tetraoxasilaspiro[5.5]-undecane (III, Hexylene Glycol Spirosilicate).—This material[1i,10] was prepared in similar fashion to that employed above for I, the only difference being that NaOMe was employed as catalyst rather than isopropyl titanate. The product was freed of catalyst by filtration of its hexane solution. The clear filtrate was then stripped of hexane to give a crystalline product (90% yield) which was recrystallized from methanol or pentane; mp 73–77°. The broad melting point is not unexpected in view of the diastereomeric possibilities.

2,2,5,5,9,9,12,12-Octamethyl-1,6,8,13,7-tetraoxasilaspiro[6.6]-tridecane (VI).—Ethyl silicate (16.0 g, 0.077 mol) and 2,5-dimethyl-2,5-hexanediol (22.0 g, 0.150 mol) were combined and heated to 140° with no indication of ethanol formation. The addition of a catalytic amount of powdered sodium methoxide resulted in the immediate commencement of boiling. Allowing ethanol to escape as it formed, the reaction mixture was heated to 220° and held at that temperature for 20 min. The low viscosity of this solvent-free melt attests to the absence of polymeric products. Recrystallization of the resulting solid product from methanol yielded 13.9 g (59% yield) of pure VI; mp 81–83°. An infrared spectrum showed this material to be completely free of hydroxyl content and to have a strong Si–O absorption at 9.5 μ.

Anal. Calcd for $SiC_{16}H_{32}O_4$: C, 60.8; H, 10.23; Si, 8.89; mol wt, 316. Found: C, 61.1; H, 10.23; Si, 8.83; mol wt, 359.

In an earlier attempt to prepare this material using tetraisopropyl titanate as catalyst, little or no reaction was observed.

3,9-Diethyl-3,9-dibutyl-1,5,7,11,6-tetraoxasilaspiro[5.5]undecane (V).—Into a 1-l. distillation flask were placed 320 g (2.00 mol) of 2-ethyl-2-butyl-1,3-propanediol and 100 ml of benzene. This material was then briefly heated to boiling under a 36 in. × 10 mm Nester–Faust spinning-band column to azeotropically remove any moisture from the system. A slurry of 0.1 g of NaOMe in 208 g (1.00 mol) of ethyl silicate was then added, and, upon further heating, benzene and ethanol was removed while the still temperature climbed to 255°. Fractionation at reduced pressure yielded 329 g (95%) of spirosilicate; bp 150–155° (0.5 mm), n^{25}_{D} 1.4631.

Anal. Calcd for $SiC_{18}H_{36}O_4$: C, 62.8; H, 10.46; Si, 8.16. Found: C, 62.7; H, 10.64; Si, 8.15.

A sample of this spirosilicate (16.8 g) was heated for several minutes at a temperature of 100–150° with a trace of KOH (0.04 g), resulting in gelation. Heating this gel at a temperature of 200–230° caused the obviously cross-linked material to revert to a mobile liquid which, of course, gelled again as the temperature was lowered. Another sample of the spirosilicate showed no discernible viscosity change upon heating at 100–150° for 2 hr in the absence of KOH.

3,9-Diethyl-2,8-dipropyl,1,5,7,11,6-tetraoxasilaspiro[5.5]-undecane (IV).—This material was prepared in the same manner as was V; bp 134–137° (0.8 mm), n^{25}_{D} 1.4536. Temperature and viscosity (in centistokes) follow: 0°, 425; 25°, 54.0; 100°, 3.41.

Anal. Calcd for $SiC_{16}H_{32}O_4$: C, 60.8; H, 10.12; Si, 8.88; mol wt, 316. Found: C, 61.3; H, 10.46; Si, 8.93; mol wt, 350.

When a sample of this material was heated with catalytic KOH for 2 hr at 100–150°, there was no discernible change, in striking contrast to the behavior of V noted in the preceding example.

3,3,9,9-Tetraethyl-1,5,7,11,6-tetraoxasilaspiro[5.5]undecane (II).—To a 250-ml distillation flask were added 20.8 g (0.100 mol) of ethyl silicate, 26.4 g (0.200 mol) of 2,2-diethyl-1,3-propanediol, and 0.1 g of powdered KOH. The flask was placed under a 36 in. × 10 mm Nester–Faust spinning-band column and heat was applied. Commencing at a pot temperature of 85–90°, ethanol formation was noted. During the next 30 min, 17 g (92% of theoretical) of ethanol was collected while the still temperature rose to 230°. Fractionation at reduced pressure then yielded 26.4 g (92% yield) of the spirosilicate; bp 130–133° (0.8 mm), n^{26}_{D} 1.4633. An infrared spectrum showed this material to be free of hydroxyl. Refrigeration of its pentane solution caused crystallization; mp 61–63°.

Anal. Calcd for $SiC_{14}H_{28}O_4$: C, 58.35; H, 9.72; Si, 9.75. Found: C, 58.24; H, 9.52; Si, 9.70.

2,5,9,11-Tetramethyl-1,6,8,13,7-tetraoxasilaspiro[6.6]tridecane (VII).—Ethyl silicate (62.4 g, 0.30 mol) of 2,5-hexanediol (71.5 g, 0.60 mol), and catalytic KOH (0.10 g) were heated to 210°, removing ethanol as it formed. Subsequent fractional distillation afforded the desired product in fair yield (29%); bp 110° (4.5 mm), $n^{26.5}_{\mathrm{D}}$ 1.4430. Infrared spectroscopy confirmed the absence of carbinol groups.

Anal. Calcd for $SiC_{12}H_{24}O_4$: C, 55.4; H, 9.29; Si, 10.78. Found: C, 55.6; H, 8.8; Si, 10.73.

2,2,8,8-Tetrabutyl-1,5,7,11,6-tetraoxasilaspiro[5.5]undecane (VIII, R = Bu).—3-Butylheptane-1,3-diol (9.0 g, 0.048 mol) was heated with ethyl silicate (5.0 g, 0.024 mol) after adding 80 μl of $(i\text{-PrO})_4Ti$ to catalyze the alcoholysis reaction. Ethanol was distilled from the reaction mixture, and distillation of the residue afforded a 62% yield (6 g) of the anticipated spirosilicate, VIII, which eluted as a single component from a gas chromatograph. Positive structural confirmation was provided by mass spectroscopy (a parent ion of the theoretically anticipated molecular weight of 400), as well as nmr spectroscopy which showed the following absorptions of the proper intensity ratios: A poorly resolved triplet at τ 9.07 ($C-CH_3$), a triplet at τ 6.01 (OCH_2), and a complex multiplet at τ 8.2–8.9 ppm ($-CH_2-CH_2CH_2-$).

The glycol needed for the above preparation (*i.e.*, 3-butylheptane-1,3-diol) was prepared as follows. A solution of β-propiolactone (29 g, 0.40 mol) in toluene (50 ml) was slowly added to a 1.6 *M* hexane solution of *n*-BuLi (containing 0.8 mol of the lithium reagent) while maintaining the temperature at 0°. The resulting product was washed well with water, dried (Na_2SO_4), and fractionally distilled to afford 20 g (27% yield) of the desired diol; bp 88–90° (0.15 mm). [Mol wt: calcd, 188; found (mass spectrum), 188.]

The nmr spectrum showed the following absorptions of the anticipated intensity ratios: A poorly resolved triplet at τ 9.08 ($C-CH_3$), a triplet at τ 6.29 ($O-CH_2$), a complex multiplet at τ 8.2–8.9 ($-CH_2CH_2CH_2-$), and a singlet at τ 5.92 ppm (OH).

2,2,8,8-Tetramethyl-1,5,7,11,6-tetraoxasilaspiro[5.5]undecane (VIII, R = Me).—This spirosilicate was prepared (75% yield) in the same fashion as was VIII; bp 67° (2.4 mm). [Mol wt: calcd, 232; found (mass spectrum), 232.] The nmr spectrum showed a singlet at τ 8.73 ($C-Me_2$), a triplet at τ 8.31 ($C-CH_2$), and a triplet at τ 5.99 ($O-CH_2$); and these absorptions were of the expected intensity ratios. The diol required for this preparation was obtained from the slow addition of β-propiolactone (29 g, 0.40 mol) to 550 ml of ethereal MeLi (containing 0.88 mol of lithium reagent) while maintaining the reaction temperature at −18°; the reaction product was then allowed to rise to room temperature and enough water (0.88 mol) was added to hydrolyze the lithium alkoxide, whereupon LiOH precipitated and was removed by filtration. Subsequent distillation of the filtrate afforded a 25% yield (10 g) of the desired diol,[8] 3-methylbutane-1,3-diol, which was characterized by mass and nmr spectroscopy. [Mol wt: calcd, 104; found (mass spectrum), 104].

The nmr spectrum showed the following absorptions of the expected intensity ratios: a singlet at τ 8.88 (C-Me_2), a triplet at τ 8.41 (C-CH_2), a triplet at 6.49 (OCH_2), and a broad unresolved band at τ 5.65 ppm (OH).

2,2,9,9-Tetrabutyl-1,6,8,13,7-tetraoxasilaspiro[6.6]tridecane (IX).—This spirosilicate was prepared in the same fashion as were the previous two examples; bp 153° (0.6 mm). The diol precursor to this derivative (*i.e.*, 4-butyloctane-1,4-diol) was prepared in 39% yield by the addition of *n*-BuLi to γ-butyrolactone, as in the above related examples; bp 119° (0.65 mm), $n^{25}D$ 1.4596. The diol was characterized by mass spectroscopy (the calculated molecular weight value of 202 was confirmed), and nmr spectroscopy (in dimethyl sulfoxide), which showed peaks at τ 5.63 (CH_2OH), τ 6.20 (R_2COH), τ 6.6 (CH_2O), and τ 8.7–9.1 ppm (aliphatic) in the expected intensity ratios of 1:1:2:22, respectively.

Attempted Polymerization of VIII and IX.—Neither VIII nor IX could be caused to polymerize when heated for long periods (*i.e.*, 48 hr) at 60° with catalytic amounts of KOH or $(i\text{-PrO})_4Ti$. To demonstrate that alkoxysilicon linkages were indeed undergoing exchange, VIII and IX were admixed with IV in the presence of such catalysts; glpc assay revealed in each case the almost immediate appearance of an additional peak attributable to the mixed spirosilicate.

Phenyl(tetramethylethylenedioxy)methoxysilane (XI).—Phenyltrimethoxysilane (1.00 mol) and pinacol (1.00 mol) were heated in the presence of an alkaline catalyst (0.1 g of NaOMe), distilling the methanol from the reaction zone as it formed. This required a time of 5–6 hr, with a maximum temperature of 215° being reached. "Methanol volatiles" in the amount of 64.7 g were collected; there was some indication of a small amount of Ph-Si cleavage in the latter part of the reaction; *i.e.*, the refractive index of the volatiles was somewhat higher, suggesting the presence of some benzene. The crude product was strip distilled and then carefully fractionated on a 36 in. × 10 mm Nester–Faust spinning-band column to afford a 63% yield (160 g) of IV, bp 85° (0.15 mm), $n^{25}D$ 1.4890.

Anal. Calcd for $SiC_{13}H_{29}O_3$: C, 61.9; H, 7.94; Si, 11.14. Found: C, 62.0; H, 6.9; Si, 11.08.

The nuclear magnetic resonance spectrum showed a doublet at τ 8.82 and 8.40 (*cis* and *trans* methyls of the pinacoloxy moiety) a singlet at τ 6.45 (OMe), and a complex multiplet at τ 2.1–2.8 ppm (C_6H_5); the integrated intensity ratios were consistent with the structure. This compound is *very* hygroscopic and must be protected from atmospheric exposure to avoid hydrolysis.

2-Ethylhexane-1,3-diol Derivatives of Organo-Substituted Silanes (X).—The preparation of the 2-ethylhexane-1,3-diol derivatives of $PrSi(OMe)_3$ described below illustrate the methods used to prepare related organosilicon species from other alkoxysilanes.

2-Ethyl-1,3-bis(2,4-dipropyl-5-ethyl-1,3,2-dioxasila-2-cyclohexoxy)hexane (X, R = Pr).—Propyltrimethoxysilane (67.6 g, 0.41 mol), 2-ethylhexane-1,3-diol (87.6 g, 0.60 mol), and sodium methoxide (0.05 g) were heated to 260° during a 2–3-hr period, and methanol was distilled from the system as it formed. Subsequent fractional distillation afforded 103 g (90% yield) of the desired product (X, R = Pr); bp 180–190° (0.3 mm), $n^{25}D$ 1.4525. An infrared spectrum confirmed the absence of residual OH groups.

Anal. Calcd for $Si_2C_{30}H_{62}O_6$: C, 62.7; H, 10.85; Si, 9.78. Found: C, 63.3; H, 11.05; Si, 9.77.

When glycol sufficient to react with only two-thirds of the methoxy groups was added, the monomeric species, $Pr(MeO)\underline{SiOCH_2CHEtCHPrO}$, was obtained in 50% yield; bp 114° (10 mm), $n^{25.8}D$ 1.4339. This monomethoxysilane (123 g, 0.5 mol) was heated to 150° for 3 hr with H_2O (4.5 g, 0.25 mol) after adding a small amount of powdered KOH to serve as catalyst; during this time 15 g (94% yield) of methanol distilled from the reaction. Subsequent distillation afforded 98 g (88% yield) of the expected disiloxane, bis-2,4-dipropyl-5-ethyl-1,3,2-dioxasila-2-cyclohexyl ether; bp 155° (0.5 mm), $n^{25.8}D$ 1.4475.

Anal. Calcd for $Si_2C_{22}H_{46}O_5$: C, 59.2; H, 10.3; Si, 12.59. Found: C, 59.5; H, 10.3; Si, 12.2.

Registry No.—I, 837-00-3; II, 20505-17-3; III, 887-37-6; IV, 20505-19-5; V, 20505-20-8; VI, 20483-232; VII, 20505-21-9; VIII, R = Bu, 20505-22-0; 3-butylheptane-1,3-diol, 20483-24-3; VIII, R = Me, 20505-23-1; IX, 20505-24-2; X, R = Pr, 20505-25-3; bis-2,4-dipropyl-5-ethyl-1, 20505-26-4; 3,2-dioxasila-2-cyanohexyl ether; $Pr(MeO)\underline{SiOCH_2CHEtCHPrO}$, 20505-27-5; X, R = Me, 20505-28-6; X, R = pentyl-*n*, 20505-29-7; X, R = PL, 20483-25-4; XI, 20505-30-0.

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[8] This preparative method is superior in terms of yield and convenience to those previously employed; see S. Searles, Jr., E. K. Ives, and S. Nukina, *J. Org. Chem.*, **24**, 1170 (1959), and references therein.