described in the literature.[18-23] Identification was by melting point, ir, and nmr.

The Kinetics of Reaction of β-Bromo-β-phenylpropionic Acid Anions.—Two analytical procedures were used to follow reactions of the β-bromo acid anions. (a) Reaction was initiated by adding a weighed amount of the bromo acid to a base solution (sodium bicarbonate in water or sodium hydroxide in ethanol–water mixtures) that had attained the temperature of the thermostated bath. The reaction was followed by potentiometric estimation of bromide ion released. Aliquot parts of the reaction mixture were titrated with silver nitrate at appropriate time intervals. The electrode assembly and titration procedure have been described previously.[9] It was confirmed that neither starting material or products interfered with the analytical method. (b) For those reactions leading to formation of the appropriate styrene in high yield it was convenient to follow the course of the reaction by observation of the increase in absorbance at 258 $m\mu$. The substrates also had absorbance maxima at this wavelength, but with lesser extinction coefficients.

Reaction was initiated by addition of 5 μl of a solution (0.03 M) of the bromo acid in acetone to the solvent (3 ml) contained in a cuvette of 1-cm path length. The reaction vessel and contents had previously been allowed to attain the temperature of the thermostated cell compartment. In ethanol–water solution the wavelength at which the absorbance change was a maximum during the course of reaction was chosen by inspection and found always to be in the range of 245–255 $m\mu$. All rate constants were evaluated by least-squares analysis of data recorded during a minimum time span of three reaction half-lives. The data were processed with the aid of a CDC 6400 computer at the Northwestern University Vogelback Computing Center.

Product Analysis.—The bromo acid (1 g) was stirred in a heterogeneous mixture of aqueous sodium bicarbonate (50 ml, 0.15 M) and chloroform (50 ml) at the appropriate temperature for 10 half-lives. The aqueous layer was saturated with sodium chloride and extracted with four 100-ml portions of chloroform. The combined chloroform extract was washed with water (50 ml), dried ($MgSO_4$), and evaporated to a volume of 1.5 ml by rotary evaporation at 25° (20 mm). DMSO (150 μl) was added and the nmr spectrum of the solution was recorded immediately. In every case the spectrum was that of a mixture of the appropriate lactone and styrene. The percentage composition of each product was evaluated from the integral and the overall recovery of products was evaluated with reference to the integral of the DMSO protons. The analyses were repeated in triplicate with good reproducibility as revealed in Table III.

Acknowledgment.—We are grateful to the National Science Foundation (GP 7065) for support of this investigation.

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Silicon-Functional 1,2,5-Oxadisilacyclopentane Heterocyclics

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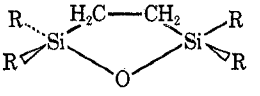
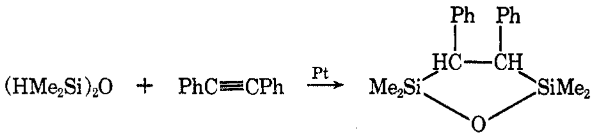
Ligand redistribution of appropriate alkoxy- or chlorosiloxane substrates at elevated temperatures afforded examples of the title heterocyclic system bearing easily solvolyzable substituents at one or both silicon sites. Also described are novel spirocyclic derivatives of the bidentate alkoxy ligand, $-OCMe_2CH_2CH_2CMe_2O-$.

The first examples of the strained 1,2,5-oxadisilacyclopentane heterocyclic system, 1 (R = all combinations of Ph and CH_3), were reported by Merker[1] and his coworkers who employed alkaline thermal siloxane rearrangement of appropriate polymeric substrates.



1

Other members of this interesting system (*e.g.*, 2) have been reported[2] to form directly from certain hydrosilation reactions.



2

The previous literature contained no examples of this heterocyclic system containing easily hydrolyzable silicon substituents. We describe herein the first examples of chloro- and alkoxy-substituted 1,2,5-dioxasilacyclopentanes.[3]

Results and Discussion

During an attempt to prepare a linear polymer (4) by the combined base-catalyzed partial hydrolysis and alkoxy exchange reaction of 3, overheating occurred and the novel spirocyclic 5 distilled from the reaction mixture. By a very similar approach, using $(MeO)_3SiCH_2CH_2Si(OMe)_3$ rather than 3, we were able to prepare very readily the related structure 6 containing *two* spiro sites. Although compounds 5 and 6 did indeed constitute representatives of the previously unknown alkoxy-functional 1,2,5-oxadisilacyclopentanes, it was of interest to attempt the synthesis of simpler examples bearing monodentate silicon ligands. With this objective, 3 was subjected to alkaline pyrolysis which did indeed afford good yields of 7 *via* alkoxy–siloxy redistribution as well as the expected by-product 8. This type of synthesis is fairly general if the alkoxy ligand is selected with due regard for favorable volatility relationships among the species to be expected at equilibrium. Thus, 9 can be prepared in good yield *via* the reaction shown since it is the most volatile species

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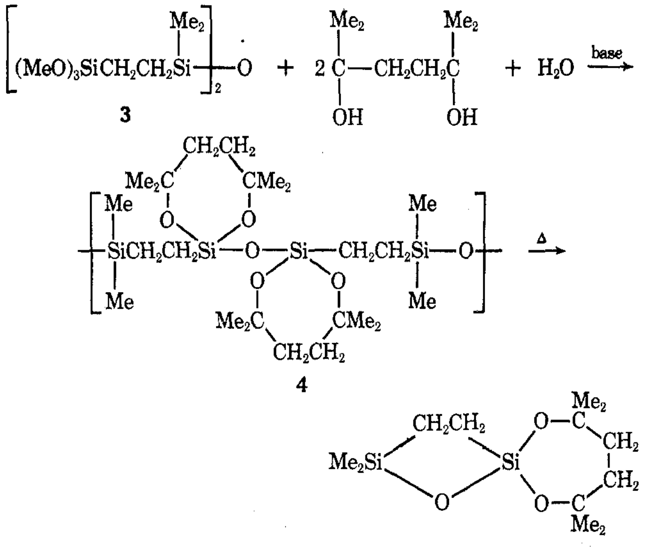
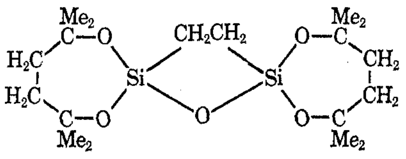
[1] (a) W. A. Piccoli, G. C. Haberland, and R. L. Merker, *J. Amer. Chem. Soc.*, **82**, 1883 (1960); (b) R. L. Merker and M. J. Scott, *J. Polym. Sci.*, **43**, 297 (1960).

[2] A. M. Polyakova, M. D. Suchkova, V. V. Korshak, and V. M. Vdovin, *Izv. Akad. Nauk. SSSR, Ser. Khim*, **7**, 1267 (1965).

[3] Information concerning the utility of such species may be found in U. S. Patent 3,427,338 (Feb 11, 1969) (C. L. Frye). Subsequent to the completion of our work, related acetoxy-substituted examples were disclosed in U. S. Patent 3,338,951 (Aug 29, 1967) (E. W. Khaub).



5



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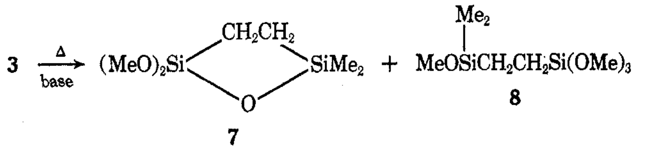
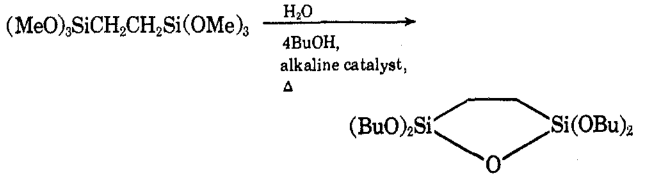
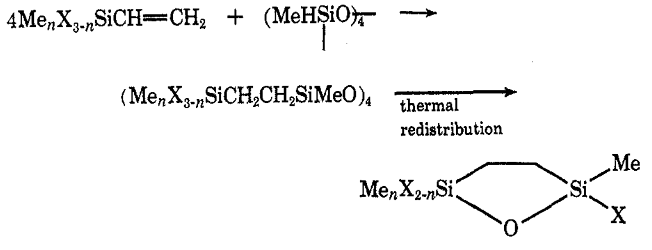




9

available from the simple redistribution of alkoxy and siloxy linkages and can consequently be preferentially removed from the higher boiling $(BuO)_3SiCH_2CH_2Si(OBu)_3$; with smaller alkoxy groups, the hexaalkoxydisilethane would be lower boiling than the tetraalkoxyheterocyclic, precluding this type of synthesis. At sufficiently high temperatures (*i.e.*, about 400°), the desired redistribution occurs even in the absence of any deliberately added catalyst; however, the addition of alkaline substances permitted a substantial decrease of the reaction temperature (250–350°).

This base-catalyzed 1,2,5-oxadisilacyclopentane synthesis is by no means free of complication. Since this heterocyclic system is strained, its formation presumably involves a rather large activation energy and is, therefore, favored by higher temperatures. The use of too much catalyst lowers the reaction temperature so drastically that other processes may predominate over strained-ring formation. Consequently, the choice of catalyst and its concentration can sometimes have a very marked effect on the nature of the resulting products. A particularly good example of the importance of catalyst concentration was provided by the redistribution of **3** to **7**. Relatively little catalyst (NaOMe) was employed the first time the reaction was run, resulting in an initial "cracking" temperature of approximately 285° and a fair yield (49%) of **7**. In a subsequent attempt, a much higher catalyst concentration was used, resulting in a much lower reaction temperature (200–250°) and volatile products which contained relatively little **7**. In this particular instance, base-catalyzed redistribution[4] of carbon–silicon bonds was sufficiently rapid at the higher catalyst levels to afford copious amounts of $Me_2Si(OMe)_2$ rather than the desired heterocyclic. Unwanted C–Si redistribution of this type is perhaps the most serious and common complication in the application of this method. To the extent that volatile "end-block-rich" species such as $Me_2Si(OMe)_2$ are distilled from the system the residue is depleted of end blocks resulting in ultimate gelation. Additional examples of this heterocyclic system bearing methoxy or chloro substituents were prepared by the following rather general procedure involving redistribution of appropriate hydrosilation adducts of vinylsilanes and $(MeHSiO)_4$.



10, X = MeO; $n = 2$
11, X = MeO; $n = 0$
12, X = Cl; $n = 2$
13, X = Cl; $n = 0$

Alkaline catalysis is of course precluded when chlorosilanes are involved; in these instances, catalysis with Lewis acids such as $FeCl_3$, $AlCl_3$, or $(BuO)_3B$ was attempted but no lowering of reaction temperature was observed.

Experimental Section

General.—The nmr data were obtained on a Varian Associates Model A-60 instrument using Me_4Si as an internal standard. The silane and siloxane reactants were obtained from a Dow Corning Corp. pilot plant and were checked for purity by vpc prior to use and distilled if necessary. The chloroplatinic acid catalyst solution used in the preparation of the hydrosilation adducts was prepared by dissolving 3.5 g of reagent grade $H_2PtCl_6 \cdot 2H_2O$ in 23.3 g of glacial acetic acid.

2,2,7,7,10,10-Hexamethyl-1,6,11-trioxa-2,5-disilaspiro[4.6]undecane (5).—Compound **3** was prepared *via* the chloroplatinic acid catalyzed hydrosilation reaction of 2 mol of vinyltrimethoxysilane with 1 mol of tetramethyldisiloxane. This adduct (43 g, 0.10 mol) was then combined with 2,5-dimethylhexane-2,5-diol (29.2 g, 0.20 mol), water (1.8 g, 0.10 mol), and a catalytic amount of NaOMe (0.05 g). Upon heating this mixture, hydrolysis and alcoholysis proceeded; after distilling 17.3 g of methanol from the system, the temperature was raised to 300–340°, whereupon cracking occurred. The fractions collected at a head temperature of 80–200° were combined and refractionated to yield product **5**: bp 55° (0.2 mm); ir (CCl_4) 10.7 μ (strained SiOSi). *Anal.* Calcd for $C_{12}H_{26}O_3Si_2$: C, 52.6; H, 9.5; Si, 20.5. Found: C, 52.3; H, 9.4; Si, 20.4.

2,2,5,5,11,11,14,14-Octamethyl-1,6,8,10,15-pentaoxa-7,9-disiladispiro[6.1.6.2]heptadecane (6).—1,2-Bis(trimethoxysilyl)ethane was prepared from the chloroplatinic acid catalyzed hydrosilation reaction of $CH_2{=}CHSi(OMe)_3$ and $HSi(OMe)_3$. This adduct (18.6 g, 0.069 mol) was then heated with 2,5-dimethylhexane-2,5-diol, H_2O, and a trace of NaOMe as in the preceeding example. Cracking at 300–360° (0.2 mm) produced 25 g of distillate which, upon fractionation, afforded 12.4 g of **6**

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[4] J. W. Ryan, *J. Amer. Chem. Soc.*, **84**, 4730 (1962).

(46% yield): bp 97° (0.05 mm); mp 78–80°; ir (CCl_4) 10.7 μ (strained SiOSi); nmr (CCl_4) τ 9.35 (s, 4, CH_2Si), 9.23 (s, 8, CH_2CMe_2), 8.78 and 8.70 (2 s, 24, C–CH_3); the C–CH_3 protons showed two singlets (12 protons in each) as a consequence of the two nonequivalent locations relative to the silethylene and siloxane adjacent ring elements. *Anal.* Calcd for $C_{18}H_{36}O_5Si_2$: C, 55.7; H, 9.28; Si, 14.47. Found: C, 55.9; H, 9.26; Si, 14.45.

2,2-Dimethoxy-5,5-dimethyl-1,2,5-oxadisilacyclopentane (7).—Compound **3** (98.5 g, 0.229 mol) containing NaOMe (0.05 g) underwent redistribution at a reaction temperature of 285–250° producing volatile products (88 g) which were distilled from the system. Careful refractionation afforded 21.7 g (49% yield) of pure **7**: bp 52° (15 mm); ir (CCl_4) 10.7 μ (strained SiOSi); nmr (CCl_4) τ 9.82 (s, 6, CH_3Si), 9.28 (m, 4, CH_2Si), 6.54 (s, 6, CH_2O). *Anal.* Calcd for $C_6H_{16}O_3Si_2$: C, 37.5; H, 8.34; Si, 29.24. Found: C, 37.6; H, 8.7; Si, 29.1.

An almost quantitative yield (55 g) of material believed to be the expected by-product $Me_2(MeO)SiCH_2CH_2Si(OMe)_3$ (**8**), was also obtained: bp 82° (7.5 mm). This material contains no strained siloxane moiety (as evidenced by the absence of absorbtion at 10.7 μ) and was identical (glc) with the hydrosilation adduct of $ViMe_2SiOMe$ and $HSi(OMe)_3$. When much larger amounts of NaOMe (*i.e.*, 0.8 g) were employed, redistribution occurred at somewhat lower temperatures (200–250°) and a major portion of the distillate was identified as $Me_2Si(OMe)_2$ by comparison with authentic material.

2,2,5,5-Tetra-*n*-butoxy-1,2,5-oxadisilacyclopentane (9).—1,2-Bis(trimethoxysilyl)ethane (54 g, 0.2 mol), 1-butanol (59 g, 0.8 mol), and isopropyl titanate (2 drops) were heated under a Nester–Faust spinning-band column. After collecting 25.5 g of methanol, water (3.6 g), additional 1-butanol (1.0 g), and KOH (0.25 g) were added to the reaction mixture. Heating was resumed and an additional 11.5 g of methanol was collected at 65°. A mixture of MeOH and *n*-BuOH (3.4 g) was collected over a range of 65–120°. The reaction mixture was then heated at 250–285°. The crude redistribution products (53.2 g) were collected at a head temperature of 175–185° (5 mm). Refractionation through the same band afforded 33.3 g (43% yield) of pure **9**: bp 119° (0.01 mm); ir (neat) 10.7 μ (strained SiOSi); nmr (neat) τ 6.27 (t, 8, CH_2O), 9.23 (s, 4, CH_2Si), 8.1–9.3 (m, 28, $CH_3CH_2CH_2CH_2O$). *Anal.* Calcd for $C_{18}H_{40}O_5Si_2$: C, 55.7; H, 10.3; Si, 14.45. Found: C, 55.7; H, 10.1; Si, 14.3.

1,2-Bis(tri-*n*-butoxysilyl)ethane (10.4 g) was also recovered from the fractionation: bp 150° (0.03 mm); ir (CCl_4) no line at 10.7 μ (*i.e.*, no strained SiOSi); nmr (neat) τ 6.31 (t, 12, CH_2O), 9.43 (s, 4, CH_2Si), 8.1–9.2 (m, 42, $CH_3CH_2CH_2CH_2O$). *Anal.* Calcd for $C_{26}H_{58}O_6Si_2$: C, 59.8; H, 11.1; Si, 10.8. Found: C, 59.8; H, 11.2; Si, 10.9.

2,2,5-Trimethoxy-5-methyl-1,2,5-oxadisilacyclopentane (11).—A suitable hydrosilation adduct was prepared by the gradual addition of $(MeHSiO)_4$ (360 g, 1.50 mol) to well-stirred, preheated (100°) $ViSi(OMe)_3$ (906 g, 6.1 mol) containing 12 drops of chloroplatinic acid solution; this caused the temperature to rise steadily to a maximum of 160°, whereupon the adduct was cooled to room temperature and stored in a polyethylene container. An aliquot of this adduct (108 g, 0.51 equiv of $SiCH_2CH_2Si$) was then heated with 0.1 g of BaO to a temperature of 380°, whereupon cracking commenced; a total of 80 g of volatile materials were distilled from the system. Glc analysis showed this material to contain approximately 36 g (34% yield) of compound **11** which was then isolated by fractional distillation: bp 61° (4.5 mm); ir (neat) 10.7 μ (strained SiOSi); nmr (CCl_4) τ 9.28 (m, 4, CH_2Si); 9.83 (s, 3, CH_3Si); 6.43, 6.48, 6.52 (3s, 9, CH_3O). *Anal.* Calcd for $C_6H_{16}O_4Si_2$: C, 34.6; H, 7.7; Si, 26.9. Found: C, 34.9; H, 7.6; Si, 27.0.

2-Methoxy-2,5,5-trimethyl-1,2,5-oxadisilacyclopentane (10).—The hydrosilation adduct for this redistribution reaction was prepared by gradually adding $(MeHSiO)_4$ (360 g, 1.50 mol) to refluxing $ViMe_2SiOMe$ (703 g, 6.06 mol) containing 4 drops of the chloroplatinic acid solution at such a rate as to avoid an excessive exotherm.

A 75-g (0.43 equiv of $SiCH_2CH_2Si$) aliquot of this adduct was then diluted with 75 ml of hydrogenated terphenyl (a commercially available heat transfer agent) and catalyzed with BuLi (1 ml of 1.6 *M* hexane solution.) Upon heating at a temperature of 300–355°, 69 g of volatile materials were distilled from the system and shown by glc analysis to contain 36 g (48% yield) of compound **10**, which was then isolated by fractional distillation: bp 30° (5.5 mm); ir (neat) 10.7 μ (strained SiOSi); nmr (CCl_4) τ 9.88 (2 poorly resolved singlets, 6, CH_3SiCH_3), 9.81 (s, 3, CH_3SiOCH_3), 9.26 (m, 4, CH_2Si), 6.57 (s, 3, CH_3O). *Anal.* Calcd for $C_6H_{16}O_2Si_2$: C, 40.9; H, 9.1; Si, 31.6. Found: C, 40.7; H, 8.7; Si, 31.2.

2,2,5-Trichloro-5-methyl-1,2,5-oxadisilacyclopentane (13).—The hydrosilation precursor for this preparation was obtained by slowly adding $ViSiCl_3$ (333 g, 2.05 mol) to refluxing $(MeHSiO)_4$ (120 g, 0.5 mol) containing 12 drops of chloroplatinic acid solution as catalyst. Heating was continued until consumption of Si–H functionality was complete (as evidenced by disappearance of the characteristic infrared absorption at 4.5 μ). This adduct was then heated at 410–420° where cracking occurred, yielding 140 g of distillate before the contents of the reaction flask gelled. Refractionation afforded a cut boiling at 50–60° (4–5 mm) and believed to be compound **13**, which exhibited the strong infrared absorption at 10.7 μ, characteristic of the strained siloxane believed to be present. Subsequent analysis showed the material to be somewhat impure. *Anal.* Calcd for $C_3H_7Cl_3OSi_2$: C, 16.3; H, 3.16; Si, 25.3; Cl, 48.1. Found: C, 17.5; H, 3.33; Si, 24.6; Cl, 48.5.

Infrared examination showed the 10.7 band to decrease sharply within a few days, presumably owing to the near impossibility of maintaining this material acid free and the extreme sensitivity of these strained heterocyclics to acid-catalyzed polymerization. Because of the extreme reactivity of this material, no further characterization was attempted.

2-Chloro-2,5,5-trimethyl-1,2,5-oxadisilacyclopentane (12).—The hydrosilation adduct was obtained by slowly adding $(MeHSiO)_4$ (240 g, 1.00 mol) to refluxing $ViMe_2SiCl$ (490 g, 4.06 mol) containing 6 drops of chloroplatinic acid catalyst solution; as the exothermic reaction proceeded, the temperature gradually increased to a final value of 240°. Thermal redistribution of 151 g (0.84 equiv of $SiCH_2CH_2Si$) of this material at 360–380° for 6 hr afforded 123 g of distillate which boiled at approximately 120°, had the expected intense ir absorption at 10.7 μ, and is believed to have been compound **12**: nmr (CCl_4) τ 9.84 (s, 3, CH_3SiCH_3), 9.75 (s, 3, CH_3SiCH_3), 9.47 (s, 3, $ClSiCH_3$), 9.0 (m, 4, $SiCH_2CH_2Si$). It was necessary to prevent contact of this material with atmospheric moisture since hydrolysis results in HCl and this highly strained system undergoes very facile acid catalyzed ring-opening reactions. If suitable precautions were taken, vpc analysis showed very little loss of product even after several days. *Anal.* Calcd for $C_5H_{13}OSi_2Cl$: C, 33.2; H, 7.2; Si, 31.1; Cl, 19.7. Found: C, 33.0; H, 7.5; Si, 31.5; Cl, 20.0.

Registry No.—**5**, 16881-69-9; **6**, 16930-89-5; **7**, 16881-66-6; **8**, 25383-60-2; **9**, 20325-53-5; **10**, 16881-67-7; **11**, 20238-72-6; **12**, 16881-68-8; **13**, 25383-65-7; 1,2-bis(tri-*n*-butoxysilyl)ethane, 18846-06-5.