clopropylacetophenone 2,4-DNPH, 58502-92-4; 3-methyl-4-cyclopropyl-α-methylstyrene, 58502-93-5; 2,6-dimethylphenylcyclopropane, 36825-29-3; 2,6-dimethylstyrene, 2039-90-9; 2,4-dimethyl-3-cyclopropylacetophenone, 58502-94-6; 2,4-dimethyl-3-cyclopropylacetophenone 2,4-DNPH, 58502-95-7; 3,5-dimethyl-4-cyclopropylacetophenone, 58502-96-8; 3,5-dimethyl-4-cyclopropylacetophenone 2,4-DNPH, 58502-97-9.

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Copyrolysis of *sym*-Tetramethoxydimethyldisilane and 2,5-Dimethylfuran

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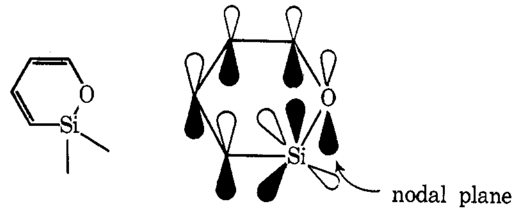
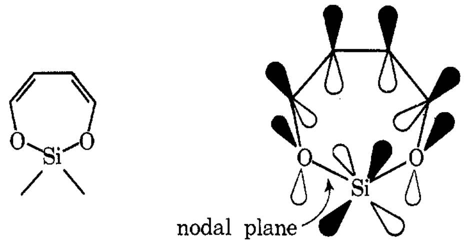
The reaction of methoxymethylsilylene (generated by pyrolysis of *sym*-tetramethoxydimethyldisilane) with 2,5-dimethylfuran yields 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene and 2-methoxy-2,4,7-trimethyl-1,3-dioxo-2-silacyclohepta-4,6-diene.

The synthesis of unsaturated organosilicon heterocycles whose spectral properties might permit elucidation of the extent and nature of the interaction between vacant 3d orbitals on silicon and an adjacent π electron system has attracted considerable interest.[1,2]

The 1-oxo-2-silacyclohexa-3,5-diene (I) system has been a goal of our efforts. Interaction of a lone pair of electrons on oxygen with an empty 3d orbital on silicon and with the diene system would yield a 6π electron system possessing a nodal plane. Such a system is antiaromatic by the Mobius concept.[3,4]

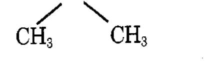


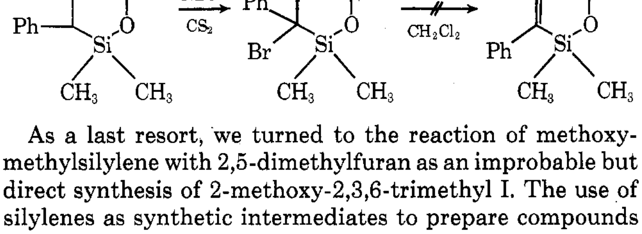
A related goal has been the 1,3-dioxo-2-silacyclohepta-4,6-diene (II) system. Interaction of two lone pairs of electrons from the two oxygens with an empty 3d orbital on silicon and with the diene system yields an 8π electron system possessing a nodal plane. Such a system is aromatic by the Mobius concept.[3,4]



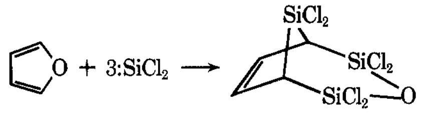
The overlap of pairs of electrons with adjacent empty 3d orbitals on silicon has often been used to explain the properties of compounds possessing adjacent silicon and oxygen atoms.[5,6] Thus the properties of I and II appeared to present an interesting test of this often proposed interaction.

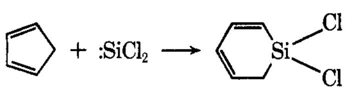
Rational synthetic approaches to both I and II resulted in failure. An attempt to prepare 2,2,4,7-tetramethyl II by reaction of dimethyldichlorosilane with 2,5-hexanedione in the presence of triethylamine,[7] conditions which have been successfully used to prepare the bis(trimethylsilyl)enol ether of 2,5-hexanedione, resulted only in polymer. Attempts to prepare 2,2-dimethyl I by cyclization of suitable alicyclic precursors also failed. While benzylic bromination of 2,2-dimethyl-1-oxo-3-phenyl-2-silacyclohex-5-ene with NBS was easily accomplished,[8] dehydrohalogenation with tertiary amine bases failed to yield the desired 2,2-dimethyl-3-phenyl I.





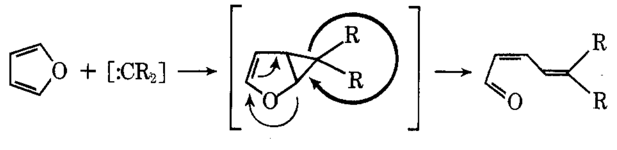
As a last resort, we turned to the reaction of methoxymethylsilylene with 2,5-dimethylfuran as an improbable but direct synthesis of 2-methoxy-2,3,6-trimethyl I. The use of silylenes as synthetic intermediates to prepare compounds which are inaccessible in other ways has been previously reported.[9–14] Nevertheless this approach seemed unlikely for several reasons. Thus although furan is known to react as a 1,3-diene in Diels–Alder reactions[15] it is an aromatic heterocycle and therefore might be expected to be less reactive than most 1,3-dienes as a trapping reagent for silylenes. The reaction of methoxymethylsilylene generated by pyrolysis of *sym*-tetramethoxydimethyldisilane with 1,3-dienes is always a competition between reaction of the silylene with the 1,3-diene, insertion of the silylene into the silicon–oxygen single bonds of *sym*-tetramethoxydimethyldisilane to yield $[CH_3(CH_3O)_2Si]_3SiCH_3$, and finally polymerization of the methoxymethylsilylene.[16–19] In addition, the reaction of dichlorosilylene with furan has been reported to yield an adduct formed from one molecule of furan and three reactive dichlorosilylenes.[20] On the other hand, dichlorosilylene has been reported to react with cyclopentadiene to yield 1,1-dichloro-1-silacyclohexa-2,4-diene.[20,21] If methoxymethylsilylene reacted with 2,5-dimethylfuran in an analogous manner it would constitute a direct synthesis of 2-methoxy-2,3,6-trimethyl I.



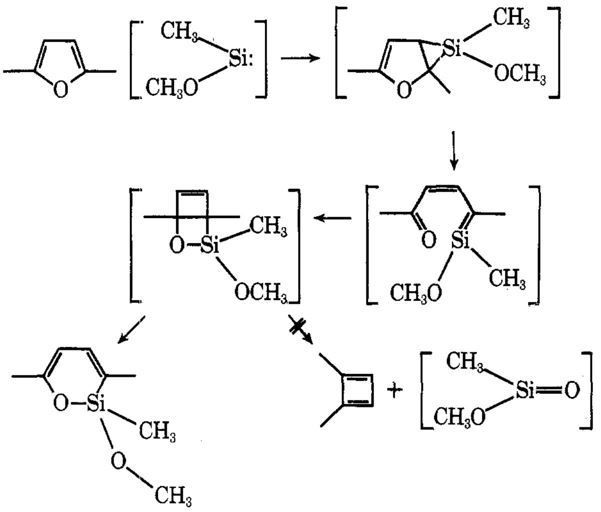


The following experimental conditions were used. *sym*-Tetramethoxydimethyldisilane was used since it undergoes α-elimination to yield methoxymethylsilylene and trimethoxymethylsilane at relatively low temperature.[14,16–19] A flow pyrolysis system was used.[14] The products were rapidly cooled after formation in the hot zone. Experience has shown that prolonged heating of products is undesirable. 2,5-Dimethylfuran was chosen since the methyl groups would be expected to retard further condensation reactions.

2-Methoxy-2,3,6-trimethyl I was isolated from the copyrolysis reaction of *sym*-tetramethoxydimethyldisilane and 2,5-dimethylfuran. However, the yield of 2-methoxy-2,3,6-trimethyl I was never better than a few percent based on methoxymethylsilylene generated, despite numerous attempts at modification of experimental parameters. A possible mechanism for the formation of 2-methoxy-2,3,6-trimethyl I may be formulated on the basis of analogous carbene chemistry. Carbenes add to furan to yield 2,4-dien-1-one systems. This result has been explained in terms of initial addition of the carbene to one of the carbon–carbon double bonds of the furan to form an unstable vinyl cyclopropane which undergoes ring opening.[22,23] By analogy, addition of methoxymethylsilylene to one of the carbon–carbon double bonds of 2,5-dimethylfuran yields an unstable vinyl silacyclopropane intermediate.[17,24,25] Ring opening in an analogous manner yields an intermediate possessing a reactive silicon–carbon double bond. A [2 + 2] intramolecular cycloaddition reaction between the silicon–carbon double bond and the carbonyl group yields a 1,2-silaoxetane. Intermolecular [2 + 2] cycloaddition reactions of silicon–carbon doubly bonded intermediates and ketones have been proposed.[8,26–28] Ring opening of the 1,2-silaoxetane yields 2-methoxy-2,3,6-trimethyl I. This is *not* the usual fragmentation pathway of a 1,2-silaoxetane intermediate which would be expected to yield methoxymethylsilanone and 1,2-dimethylcyclobutadiene. The strain and instability of 1,2-dimethylcyclobutadiene may disfavor the usual fragmentation pathway.



However, an additional unexpected product was also isolated from the reaction, namely, 2-methoxy-2,4,7-trimethyl



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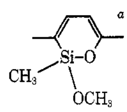
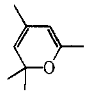
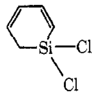
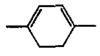
II. Pathways for its formation are purely speculation at this time. It is formed in 1.5% yield based on methoxymethylsilylene generated. Certainly, 2,5-dimethylfuran is not a reactive trapping agent for methoxymethylsilylene.[16–19]

Finally, what are the properties of 2-methoxy-2,3,6-trimethyl I and 2-methoxy-2,4,7-trimethyl II? Is 2-methoxy-2,3,6-trimethyl I an antiaromatic system and 2-methoxy-2,4,7-trimethyl II an aromatic system as predicted by the Mobius concept? The answer to this question may test the assumption underlying the prediction, namely that empty 3d orbitals on silicon interact appreciably with filled 2p orbitals on adjacent carbon or oxygen atoms.

A problem in attempting to answer this question is a shortage of material owing to the low yields of both 2-methoxy-2,3,6-trimethyl I and 2-methoxy-2,4,7-trimethyl II obtained. Thus we will rely on comparison of their spectroscopic properties with those of model compounds. On the basis of ultraviolet spectra both 2-methoxy-2,3,6-trimethyl I and 2-methoxy-2,4,7-trimethyl II seem quite ordinary. (See Tables I and II for data.) Thus we would conclude that overlap of empty 3d orbitals on silicon with adjacent 2p orbitals on oxygen or carbon is unimportant even in cyclic systems where symmetry and theory predict that stabilization will result from such overlap. Study of the effect of silyl substitution on the inversion barriers of amines and phosphines has resulted in similar conclusions.[29–31]

Table I. Ultraviolet Spectra of 2-Methoxy-2,3,6-trimethyl I and Model Compounds

Compd	λ_{max}, Å	ϵ	Solvent	Ref
 [a]	2730	8500	Cyclohexane	This work
	2820	3900	Ethanol	32
	2650	Extinction coefficient and solvent not specified		33
	2640	7420	Solvent not specified	34

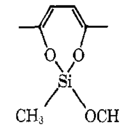
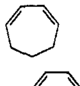
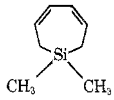
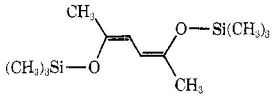
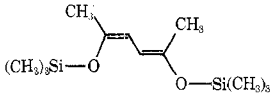
[a] Registry no., 58449-10-8.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian T-60 or XL-100 spectrometer. Spectra were taken using 10% solutions in carbon tetrachloride with benzene or acetone as internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing voltage of 70 eV. High-resolution mass spectra were obtained on a AEI-MS-9. Exact mass determinations of the compositions of ions were carried out at a resolution of at least 15 000 by peak matching with peaks of known mass of perfluorokerosene at 70 eV. Vapor phase chromatography was carried out on a Hewlett Packard F & M 700. Microanalysis was performed by Elek Microanalytical Laboratories, Torrance, Calif. Boiling points are not corrected.

Copyrolysis of 2,5-Dimethylfuran and *sym*-Tetramethoxydimethyldisilane. The pyrolysis apparatus has been described previously.[14] The oven was heated to 410 °C. A mixture of 5.1 g (0.024 mol) of *sym*-tetramethoxydimethyldisilane and 14.9 g (0.155 mol) of freshly distilled 2,5-dimethylfuran was placed in an addition funnel. The nitrogen flow rate was adjusted to 1 ml/s. The mixture was added to the pyrolysis tube at a rate of 1 drop every 10 s. A flow of nitrogen gas was continued through the column for 30 min after completion of the addition. The material from the two cold traps was combined (19.0 g). One gram of material was lost on the column. Recovered 2,5-dimethylfuran (14.1 g, 0.147 mol) and trimethoxymethylsilane (2.4 g, 0.018 mol) were removed by distillation through a 15-cm Vigreux column. A single fraction, bp 90–100 °C (760 mm), was collected. Its composition was determined by NMR integration and GLC on a 15 ft × 0.25 in., 10% polyphenyl ether on Chromosorb P column at 110 °C. Thus 75% of the starting *sym*-tetramethoxydimethyldisilane has

Table II. Ultraviolet Spectra of 2-Methoxy-2,4,7-trimethyl-II and Model Compounds

Compd	Registry no.	λ_{max}, Å	ϵ	Solvent	Ref
	58449-11-9	2480	10500	Cyclohexane	This work
		2480	7500	Not specified	35
		2470	3000	Cyclohexane	36
	58449-12-0	2520	21000	Cyclohexane	This work
	58449-13-1	2520	12200	Cyclohexane	This work

reacted to yield methoxymethylsilylene and trimethoxymethylsilane. The pot residue (2.4 g) was bulb to bulb distilled at 0.5 mm. In this manner 1.2 g of clear, slightly yellow liquid was obtained. The pot residue (1.2 g) was a thick, yellow, nonvolatile oil whose NMR indicated only CH_3Si and CH_3OSi signals in a 1:1 ratio by integration. Thus the pot residue must be polymers of methoxymethylsilylene. The pot residue (1.2 g) amounts to 0.0176 mol of methoxymethylsilylene. Thus of the methoxymethylsilylene produced greater than 90% undergoes polymerization. Separation of the volatile yellow liquid (1.2 g) by preparative GLC, on the same column as above, at 140 °C gave 2-methoxy-2,3,6-trimethyl I (0.1 g, 0.59 mmol) in 3.3% yield and 2-methoxy-2,4,7-trimethyl II (0.05 g, 0.27 mmol) in 1.5% based on the amount of methoxymethylsilylene produced. In addition unreacted *sym*-tetramethoxydimethyldisilane (0.24 g, 1.2 mmol) as well as higher molecular weight products of insertion of methoxymethylsilylene into the Si–O bond of *sym*-tetramethoxydimethyldisilane were observed.[16–19]

2-Methoxy-2,3,6-trimethyl-I. Samples were purified by preparative GLC on a 6 ft × 0.25 in., 10% β,β-ODPN on Chromosorb P column at 80 °C from material which had been collected from the polyphenyl ether column above. It had the following spectral properties: NMR, s (3 H) δ 0.25, s (3 H) 1.84, s (3 H) 1.88, s (3 H) 3.30, d (1 H) 4.93, J = 6 Hz, and d (1 H) 6.43, J = 6 Hz; ir (CCl_4) Si–CH_3 1220 and 830 cm^{-1}, Si–O and C–O 1100, 1080, and 1016 cm^{-1}, and C═C 1630 cm^{-1}; mass spectrum (70 eV) parent ion at m/e 170 (100%), P − CH_3 at m/e 155 (90.4%), and P − OCH_3 at m/e 139 (66.7%); uv (cyclohexane) λ_{max} 2730 Å, ϵ 8500. Anal. Calcd for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29. Found: C, 56.29; H, 8.22.

2-Methoxy-2,4,7-trimethyl-II. Samples were purified by preparative GLC on a 10 ft × 0.25 in., 20% Ucon Polar on Chromosorb P column at 135 °C from material which had been collected from the polyphenyl ether column above. It had the following spectral properties: NMR, s (3 H) δ 0.20, s (6 H) 1.90, s (3 H) 3.65, s (2 H) 4.70; ir (CCl_4) Si–CH_3 1265 cm^{-1}, Si–O and C–O 1100 and 1185 cm^{-1}, and C═C 1650 cm^{-1}; uv (cyclohexane) λ_{max} 2480 Å, ϵ 10 500; mass spectrum (70 eV) parent ion at m/e 186 (100%), P − CH_3 at m/e 171 (20%); high-resolution mass spectrum, the exact mass of the parent ion (calcd for $C_8H_{14}O_3Si$, 186.07122; found, 186.0713).

Preparation of *cis*- and *trans*-2,5-Bis(trimethylsiloxy)-2,4-hexadiene. In a dry three-neck 500-ml round-bottom flask equipped with a reflux condenser, a Teflon-covered magnetic stirring bar, and a nitrogen inlet was placed 100 ml of dimethylformamide (freshly distilled from CaH_2), trimethylchlorosilane (27.0 g, 0.25 mol), and triethylamine (47.0 g, 0.43 mol).[7] 2,5-Hexanedione (10.0 g, 0.095 mol) was added through the top of the reflux condenser. White fumes and a yellow solid rapidly formed. The mixture was refluxed for 72 h. It was cooled and 200 ml of pentane was added. The solution was placed in a separatory funnel and extracted three times with 200-ml portions of aqueous $NaHCO_3$. The organic layer was dried over anhydrous $MgSO_4$, filtered, and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 12-cm vacuum-jacketed Vigreux column. A fraction bp 125–126 °C (25 mm) was collected (13.0 g, 53%). The mixture of isomers was separated by GLC on a 20% polyphenyl ether on Chromosorb P, 25 ft × 0.25 in. column at 140 °C. The more symmetrical trans isomers eluted first.

***trans*-2,5-Bis(trimethylsiloxy)-2,4-hexadiene** had the following spectral properties: NMR s (18 H) δ 0.1, s (6 H) 1.65, s (2 H) 5.18; ir Si–CH_3 1250 and 850 cm^{-1}, Si–O and C–O at 1160 cm^{-1}, and C═C conjugated at 1615 cm^{-1}. High-resolution mass spectrum, the exact mass of the parent ion (calcd for $C_{12}H_{26}Si_2O_2$, 258.1464; found, 258.1471). Anal. Calcd for $C_{12}H_{26}Si_2O_2$: C, 55.74; H, 10.14. Found: C, 55.11; H, 9.74.

***cis*-2,5-Bis(trimethylsiloxy)-2,4-hexadiene** had the following spectral properties: NMR s (18 H) δ 0.1, s (3 H) 1.62, s (3 H) 1.67, d (1 H) 4.98, J = 12 Hz, d (1 H) 5.38, J = 12 Hz; ir Si–CH_3 1250 and 850 cm^{-1}, Si–O and C–O 1212 and 1175 cm^{-1}, and C═C conjugated at 1615 cm^{-1}. Anal. Calcd for $C_{12}H_{26}O_2Si_2$: C, 55.74; H, 10.14. Found: C, 55.36; H, 9.89.

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Registry No.—2,5-Dimethylfuran, 625-86-5; *sym*-tetramethoxydimethyldisilane, 18107-32-9.

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