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Alpha-lithiosilanes, III. The Reaction of Vinylalkoxysilanes with Organolithium Reagents.

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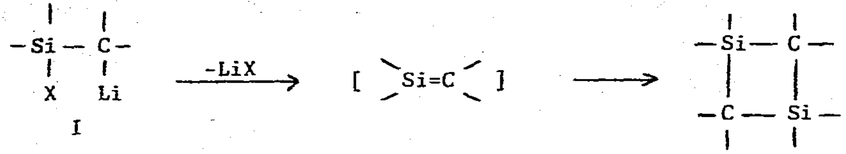
SUMMARY

The reaction of two equivalents of vinyldimethylethoxysilane or vinyldimethylmethoxysilane with hydrocarbon soluble alkyllithium reagents; t-BuLi, s-BuLi, or n-BuLi; in hexane at low temperature gives high yields of 1,1-dimethyl-2-alkyl-4-(dimethylalkoxysilyl)silacyclobutanes. With methyl- or phenyllithium substituted vinylsilanes are obtained. The stereochemistry of the silacyclobutanes is assigned on the basis of Si-29 and H-1 NMR. For vinyldimethylethoxysilane the ratio of cis to trans silacyclobutane is about 57/43, and is independent of the alkyllithium reagent used. In the reaction of vinyldimethylmethoxysilane with t-BuLi a 70/30 ratio of the cis and trans silacyclobutane is obtained. A pathway is proposed which is consistent with the stereochemical results and with the products isolated in the reaction run in THF.

INTRODUCTION

We recently reported that the reaction of t-butyllithium with vinyldimethylchlorosilane in hydrocarbon solvent at low temperature gives high yields of disilacyclobutanes as the major products [1]. Evidence from competition experiments with chlorosilanes and trapping experiments with 1,3-butadiene was obtained which indicated that silaethylene intermediates can be produced by the elimination of lithium choloride from α-lithiochlorosilanes under appropriate experimental conditions [2]. Disilacyclobutane formation under similar conditions had previously been observed by Seyferth and Lefferts in the reaction of bis(trimethylsilyl)bromomethyllithium with dimethyldichlorosilane at low temperatures in ether solvents [3]. Subsequent to both of these reports Wiberg and Preiner reported that α-lithiosilyl phosphates, phosphites or tosylates also give rise to disilacyclobutanes and suggested the intermediacy of a silaethylene [4].

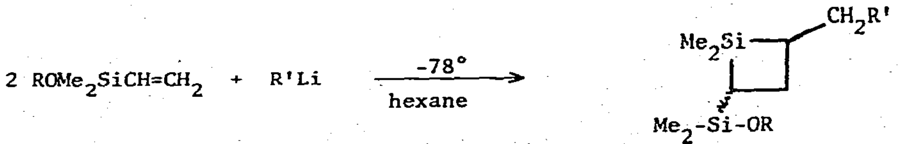


I

Intermediates similar to I can conceivably undergo three types of reactions: elimination of LiX to give silaethylene type intermediates, intermolecular coupling to give cyclic or polymeric products, or addition to another alkene. One might anticipate that the favored process in a given system should be a function of the leaving group, X, on silicon. These considerations lead us to investigate the reactions organolithium reagents with vinyldimethylalkoxysilanes. We report herein the results of that investigation.

RESULTS AND DISCUSSION

When vinyldimethylethoxysilane was added to an equimolar amount of t-butyllithium in hydrocarbon solvent cooled to -78° there was obtained, after warming and hydrolytic work-up, a 40% yield of a mixture of the cis- and trans-isomers of 1,1-dimethyl-2-neopentyl-4-(dimethylethoxysilyl)silacyclobutane, IIb. To our surprise, none of the disilacyclobutanes, the major products from the analogous reaction with vinyldimethylchlorosilane, could be detected in the reaction mixture.



II

II: a, R = Me, R' = t-Bu; b-d, R = Et, R' = t-Bu, s-Bu, or n-Bu.

Because the stoichiometry for the formation of II requires two moles of silane for every mole of organolithium reagent we repeated the reaction using this ratio of reactants. Under these conditions the yield of IIb was increased to 86%. An investigation of the reaction employing a variety of organolithium reagents showed that it is apparently general for those organolithium reagents which are soluble in hydrocarbon. The results are summarized in Table 1.

With those lithium reagents which are hydrocarbon insoluble the major products were those resulting from substitution at silicon rather than addition to the vinyl linkage. Thus methyllithium gave a 60% yield of vinyltrimethylsilane. Phenyllithium gave a 40% yield of phenyldimethylvinylsilane along with a trace of a material which was tentatively identified by mass spectrometry as

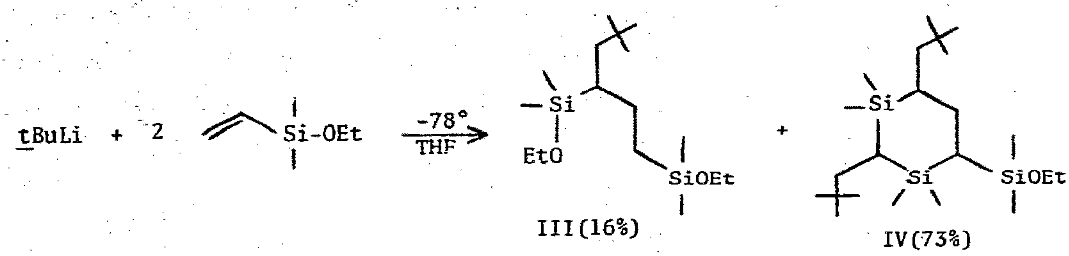
Table 1. Product Yields and isomer distributions for the reactions of vinyldimethylalkoxysilanes with organolithium reagents in hexane.

RO	R'Li		Silacyclobutane products			Substitution product
			Isomer ratio[a] cis-	trans-	% Yield	% Yield
MeO	t-BuLi	IIa	70	30	88	-
EtO	t-BuLi	IIb	59	41	40[b]	-
EtO	t-BuLi	IIb	57	43	86	-
EtO	s-BuLi	IIc	55	45	65	-
EtO	n-BuLi	IId	57	43	79	-
EtO	MeLi				-	60[c]
EtO	PhLi				5	40

[a] With the exception of IIb these ratios were estimated from the H-1 NMR spectra of the mixtures. For IIb the ratio is from GLC integration. On duplicate runs the ratios were reproducible to within ±2 %. [b] In this reaction a 1:1 ratio of vinyldimethylethoxysilane to t-BuLi was used. [c] In the reaction with methyllithium about 40% of unreacted vinyldimethylethoxysilane was recovered.

the silacyclobutane products. It can be seen in Table 1 that the yields of silacyclobutanes are consistently good for either vinyldimethylmethoxysilane or vinyldimethylethoxysilane in the reaction with a hydrocarbon soluble organolithium reagent.

When the reaction of t-butyllithium with two equivalents of vinyldimethylethoxy silane was carried out in THF rather than hexane as the solvent a complete change in the products resulted. Instead of the silacyclobutanes, IIb, compounds III and IV were obtained.



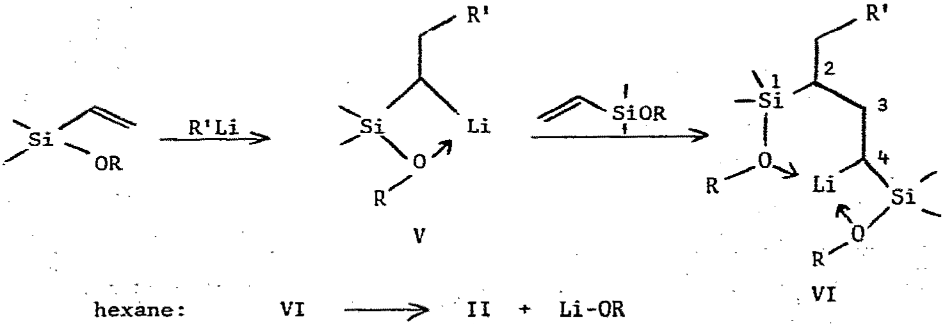
III(16%)

IV(73%)

For the 1,3-disilacyclohexane, IV, three of the four possible stereoisomers could be detected by GLC. The stereochemistry of these isomers has not been established.

The products obtained in these reactions are all consistent with the following Scheme, involving an intermediate, VI, resulting from the addition of the initially formed α-lithiosilane, V, to a second mole of vinylsilane.

Scheme



hexane: VI $\longrightarrow$ II + Li-OR

THF: VI + V $\longrightarrow$ IV + 2 Li-OR

In hydrocarbon solvents the intermediate VI undergoes intramolecular substitution to give the silacyclobutane products. In THF the additional solvation of the intermediate lithium compound VI permits intermolecular coupling reactions to occur leading to the 1,3-disilacyclohexanes, IV. Compound III produced in the THF reaction presumably arises from hydrolysis of the intermediate VI during work-up, although it could arise from ring cleavage of the silacyclobutane, IIb, by ethoxide, followed by hydrolysis.

It is interesting to note that the THF reaction mixture gave a negative Gilman color test II [5] prior to hydrolysis. This observation suggests that if, as is suggested by the detection of III among the products, the organolithium intermediate VI was indeed present in the mixture at this time it is not sufficiently reactive to undergo a rapid lithium-halogen exchange with p-bromo-N,N-dimethylaniline. In related studies we have observed that trimethylsilylmethyllithium does give a positive Gilman test I with Michler's ketone, but a negative Gilman test II [6]. Intramolecular coordination of the alkoxy groups with lithium in VI, or stabilization of the α-lithio compound by the adjacent silyl groups might provide an explanation for this observation.

It might be suggested that the silacyclobutanes formed in hydrocarbon solvents arise from a [2 + 2] cycloaddition of a silaethylene intermediate with another vinylsilane. There are at least two observations which seem to rule out this pathway. Firstly, in none of the reactions were any of the 3-(dimethylalkoxysilyl)-1-silacyclobutane adducts observed. We have observed that, under conditions where the silaethylene intermediates are produced by the elimination reaction, all possible cycloadducts are formed with a reactive olefin [2,6]. Secondly, the ratio of cis- to trans-silacyclobutanes obtained in the reactions with vinyldimethylethoxysilane is insensitive to the steric bulk of the organolithium reagent, Table 1. If these compounds were produced by a [2 + 2] cycloaddition, one would expect their stereochemistry to be affected by the steric requirements of the reacting silaethylene intermediate.

Stereochemistry of the Silacyclobutanes

The determination of the stereochemistry of the disubstituted silacyclobutanes produced in these reactions was a non-trivial problem. For each of the mixtures, IIa-d, it was possible to detect two peaks in the GLC. However, only in the case of the neopentyl compounds, IIb, was it possible to resolve

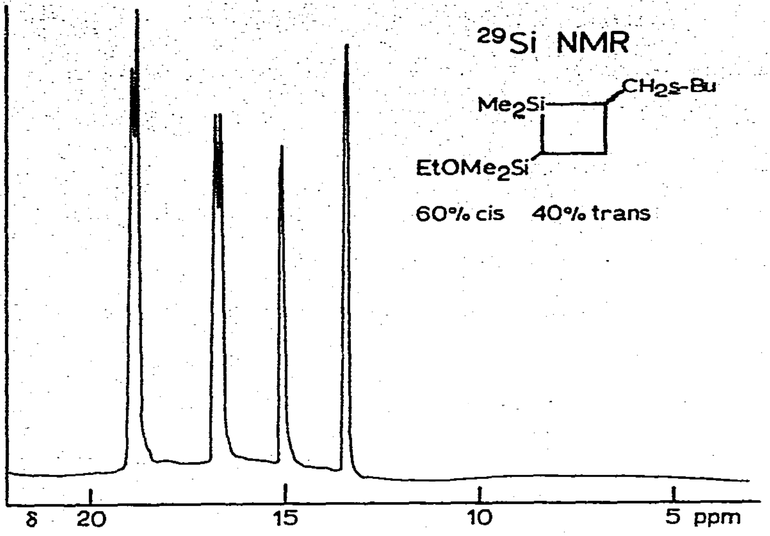
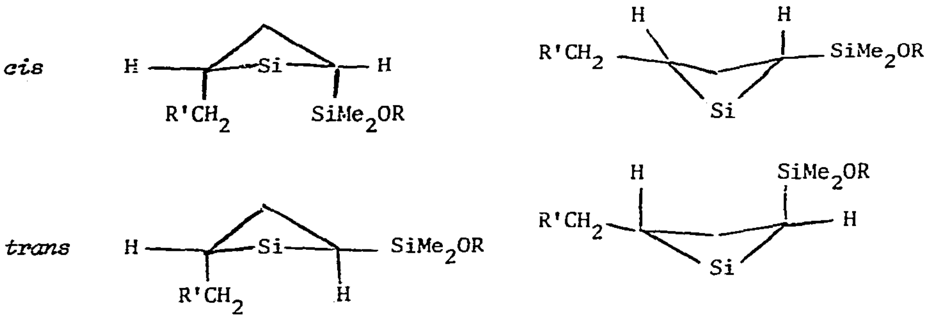


Figure. Si-29 FT NMR spectrum of a mixture of *cis*-, and *trans*-1,1-dimethyl-2-(2'-methylbutyl)-4-(dimethylethoxysilyl)silacyclobutane, IIc.

the two peaks sufficiently to permit intergration of the chromatogram and collection of the individual isomers. The H-1 NMR spectra of these two isomers showed only very subtle differences. The most distinguishing feature of these two spectra was in the chemical shift for the methyl protons of the dimethylethoxysilyl groups. For the major isomer these protons appeared at δ 0.08 while for the minor isomer they appeared at δ 0.14. For each of the other silacyclobutane mixtures two resolvable singlets appeared in this region of the spectrum. In each case the higher-field singlet was more intense and the intergrated ratio of these two peaks corresponded to the apparent ratio of the two isomers observed in the gas chromatograms of the mixtures. From the H-1 NMR spectra by themselves we could not differentiate between the cis and trans isomers.

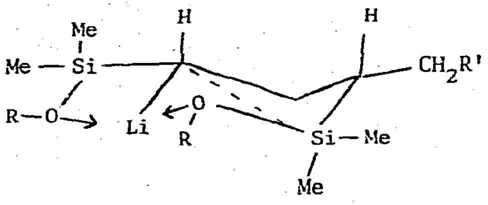
The Si-29 Fourier-transform NMR spectrum of the mixture of silacyclobutane isomers produced by the reaction of *sec*-butyl-lithium with vinyldimethylethoxysilane, Figure 1, provided a clue to the identity of the isomers. The spectrum shows two sets of peaks corresponding in intensity to the ratio of the two isomers in the mixture. The lower field peaks at δ 18.6 and 16.5 are due to the silicons in the dimethylethoxysilyl groups while the remaining peaks are due to the silicons in the rings. Each of the absorptions are partially split into two, indicating that each of the silicons are found in two slightly differing chemical environments. The differences are most apparent for the silicons of the dimethylethoxysilyl groups. These slight differences are consistent with the possible conformers which exist for the cis and trans isomers. These conformers are illustrated below.



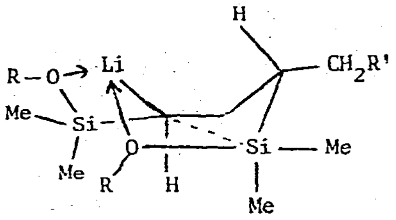
For the cis isomer one would anticipate that the conformer with the two bulky groups in pseudo equatorial positions should be favored over that in which the alkyl group and the dimethylethoxysilyl group occupy pseudo axial positions. On the other hand in the trans isomer both conformers have one bulky group in an axial orientation, and more nearly equal populations of each conformation should be observed. It is clear from the Si-29 NMR spectrum that the isomer present in higher concentration has one conformer favored over the other. The isomer present in lower concentration has approximately equal amounts of each conformer. On this basis we have assigned the cis stereochemistry to the major isomer in the mixture.

If this assignment is correct then the higher field resonance for the methyl protons of the dimethylalkoxysilyl group in the H-1 NMR spectra of the isomer mixtures corresponds to the cis silacyclobutane. The chemical shift difference is consistent with the observations of other workers that cis substitutents in silacyclobutane rings shield each other more than trans substituents [7]. The isomer distributions given in Table 1 are based on this assignment.

The stereochemical preference for the cis over the trans isomer in the silacyclobutanes produced in the cyclization reactions is consistent with the reaction scheme we proposed above. The stereochemistry of the 2,4-disubstituted silacyclobutane depends on the configuration at carbons 2 and 4 in intermediate VI when cyclization occurs. If both of these carbons have the same configuration the cis isomer will result. If the 2 and 4 carbons have opposite configurations the trans isomer will be produced in the cyclization.



VI; S,S → *cis*



VI; S,R → *trans*

In the initial addition of the alkyllithium reagent to the vinylsilane, two achiral molecules, equal amounts of the R and S enantiomers of the α-lithio intermediate, V, should be produced. However, in the addition of V to a second mole of vinylsilane, the stereochemistry of the adduct is affected by the configuration of the chiral carbon in V. Examination of models of the compounds reveals that more effective coordination of the lithium by the alkoxy groups and fewer steric interactions develop during the addition if it occurs in the manner which produces the same configuration at carbons 2 and 4 in the intermediate VI.

Simple, non-rigid secondary alkyllithium reagents are only configurationally stable at low temperatures and in the absence of electron donors [8]. It seems reasonable that the coordinating effects of the alkoxy groups in VI should be sufficient to permit inversion of configuration at carbon 4 in intermediate VI. If this inversion is competing with cyclization in our systems the stereochemical results may be explained. Intermediate VI; S,S or R,R; which leads to cis product is formed more rapidly than VI; S,R or R,S. With ethoxide as the leaving group interconversion of the stereoisomers procedes at a rate comparable to the cyclization leading to the 57/43 ratio of cis to trans product. It should be noted that steric interactions in VI; R,S or S,R which leads to trans product are greater than the steric interactions in VI; S,S or R.R. When ethoxide is replaced with the better leaving group, methoxide, cyclization occurs more rapidly than inversion and more of the cis product is obtained. Experiments aimed at determining the thermodynamic ratio of the cis and trans isomers of the 2,4-disubstituted silacylobutanes are presently in progress.

EXPERIMENTAL

All experiments were carried out under dry nitrogen or argon atmospheres. Apparatus was flame-dried or assembled hot from the drying oven. Reagents and solvents were transferred by standard syringe or double ended needle techniques [9]. Alkyllithium reagents were obtained from Lithium Corporation of America and were standardized using the method of Kofron and Baclawski [10].

Vinyldimethylmethoxysilane

The procedure of Weber and Childs was adapted for the preparation of this compound [11]. To 64.5 ml (0.500 mole) of vinyldimethylchlorosilane (Petrarch) in a 250 ml flask fitted with a reflux condensor, septum, and gas inlet was slowly added 51.5 ml (0.500 mole) of trimethylorthoformate (Aldrich). The mixture was allowed to react for 3 days and distilled to give 51 g (87% yield) of vinyldimethylmethoxysilane, b. 80-85°. The NMR; δ (CCl_4, $CHCl_3$ int. std.), 0.03 (s,6H), 3.2 (s, 3H), 5.76 (m, 3H) was consistent with the desired structure.

Reaction of lithium reagents with vinyldimethylalkoxysilanes in hexane.

The general procedure is illustrated by the reaction of t-butyllithium with vinyldimethylmethoxysilane. To a solution of 10 mmole of t-butyllithium in about 50 ml of hexanes cooled to -78° with an acetone/dry ice bath was slowly added 3.0 ml (20 mmole) of vinyldimethylmethoxysilane. The acetone/dry ice bath was allowed to evaporate slowly overnight (ca. 12-18h). The white precipitate which had formed dissolved when the reaction was quenched with 4.0 ml of sat'd ammonium chloride solution. The organic layer was separated, and the aqueous layer extracted three times with ether. After drying the combined organic layers with anhydrous magnesium sulfate the solvents were removed using a rotary evaporator. GLC analysis of the residue using internal standards showed an 88% yield of the cis and trans isomers of 1,1-dimethyl-2-neopentyl-4-(dimethylmethoxysilyl)silacyclobutane, Ia, in the ratio of 70:30. Analytical samples of the IIa isomer mixture were obtained by collection from the GLC.

The same procedure was used for all of the organolithium reagents. For methyllithium and phenyllithium hexane was used a the solvent and the heterogeneous mixtures were allowed to warm from -78 ° with stirring. Product yields and isomer distributions for the products from the reaction of the lithium reagents with the vinyldimethylalkoxysilanes are summarized in Table 1. Table 2 gives the analytical data for the cis-trans isomer mixtures of the new silacyclobutanes. NMR data for the purified compounds is as follows:

Cis-, and trans-1,1-dimethyl-2-neopentyl-4-(dimethylmethoxysilyl)silacyclobutane, IIa, 70% cis, 30% trans: δ -0.25 to -0.10 (m,1H), 0.1 (s, 6H), 0.31 (s, 3H), 0.36 (s, 3H), 0.89 (s, 9H), 0.66-1.66 (m, 5H), 3.38 (s, 3H).

Cis-1,1-dimethyl-2-neopentyl-4-(dimethylethoxysilyl)silacyclobutane, cis-IIb: δ-0.20 to -0.10 (m, 1H), 0.08 (s, 6H), 0.31 (s, 3H), 0.36 (s, 3H), 0.60 to 0.65 (m, 1H), 0.92 (s, 9H), 1.22 (t, 3H, *J* = 7 Hz), 1.41 to 2.58 (m, 4H), 3.59 (q, 2H, *J* = 7 Hz).

Table 2. Analytical Data for the Silacyclobutanes[a]

Compound	% C	% H	Mass (m/e,M$^+$)
IIa Calcd for $C_{12}H_{30}OSi_2$	60.39	11.70	258
Found	60.18	11.60	258
IIb-d Calcd for $C_{14}H_{32}OSi_2$	61.69	11.83	272
IIb Found	61.80	11.70	272
IIc Found	61.56	11.70	272
IId Found	61.40	11.89	272

[a] Elemental analyses performed by Galbraith Laboratories, Inc.

Trans-1,1-dimethyl-2-neopentyl-4-(dimethylethoxysilyl)silacyclobutane, trans-IIb: δ -0.25 to -0.10 (m, 1H), 0.14 (s, 6H), 0.31 (s, 3H), 0.37 (s, 3H), 0.70 to 0.75 (m, 1H), 0.90 (s, 9H), 1.22 (t, 3H, J = 7 Hz), 1.41-2.50 (m, 4H), 3.63 (q, 2H, J = 7 Hz).

Cis- and trans-1,1-dimethyl-2-(2'-methylbutyl)-4-(dimethylethoxysilyl)-silacyclobutane, IIc: δ -0.20 to -0.05 (m, 1H), 0.07 (s, 6H, cis-isomer), 0.13 (s, 6H, trans-isomer), 0.26 to 0.36 (overlapping singlets, 6H), 0.67 to 2.07 (multiplets, 14H) 1.17 (t, 3H, J = 7 Hz), 3.61 (q, 2H, J = 7 Hz). The ratio of the peaks assigned to the cis- and trans- isomer was 55:45.

Cis-, and trans- 1,1-dimethyl-2-pentyl-4-(dimethylethoxysilyl)-1-silacyclobutane, cis-, and trans- IId: δ -0.20 to -0.10 (s, 1H), 0.11 (s, 6H, cis-isomer), 0.14 (s, 6H, trans-isomer), 0.31 to 0.35 (overlapping singlets, 6H). 0.59 to 2.51 (overlapping multiplets, 17H), 3.64 (q, 2H, J = 7 Hz).

Silicon-29 nmr were of IIc recorded on a JEOL-PFT-100 Fourier transform pulsed nmr spectrometer. Chemical shifts were measured in $CDCl_3$ solution and are reported in ppm downfield from internal tetramethylsilane. cis-IIc: δ 13.5(ring Si), 18.6 (dimethylethoxysilyl Si). trans-IIc: δ 15.0 (ring Si), 16.5 (dimethylethoxysilyl Si). The spectrum is shown in Fig. 1.

Reaction of vinyldimethylethoxysilane with t-butyllithium in tetrahydrofuran.

To 50 ml of freshly distilled THF cooled to -78° was added 10 mmole of t-butyllithium in pentane and 3.3 ml (20 mmole) of vinyldimethylethoxysilane (Petrarch). The yellow-orange solution turned to a dark brown color with no visible precipitate after slow warming (24h) to room temperature. A Gilman color test II, [5], was negative indicating no active organolithium reagent remained. After hydrolysis with water and separation of the layers the aqueous layer was saturated with potassium carbonate and extracted three times with ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvents removed using a rotary evaporator. GLC analysis of the residue showed 4 major peaks; 2-ethoxy-2,7,7-trimethyl-5-(dimethylethoxysilyl)-2-silaoctane, III: 16.5% yield; NMR (CCl_4) δ, 0.12 (s, 12H), 0.48 to 0.88 (m, 7H), 0.92 (s, 9H), 1.19 (t, 6H, J = 7 Hz), 3.66 (q, 4H, J = 7 Hz); Mass spec, M^+ calcd. 318, found, 318.

1,1,3,3-tetramethyl-2,4-dineopentyl-6-(dimethylethoxysilyl)-1,3-disilacyclohexane, IV, mixture of three isomers, (CCl_4) δ −0.30 to 0.06 (m, 2H), 0.01 to 0.10 (singlets, 6H), 0.12 to 0.28 (singlets, 12H), 0.50 to 0.90 (m 3H), 0.91 to 0.98 (singlets, 18H), 1.21 (t, 3H, *J* = 7 Hz), 1.08 to 2.12 (m, 4H), 3.67 (q, 2H, *J* = 7 Hz). The mass spectra of each of the isomers gave essentially identical fragmentation patterns and showed a parent peak at M^+ 414 consistent with that calculated for the compound.

ACKNOWLEDGEMENT

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