with ten 50-ml portions of ether gave 3.0 g of an oil which was fractionated. Vpc on a 30% Carbowax 6000 column indicated that this product was 99% pure: bp 107–108° (7 mm), ν_{max} (neat) 1752 and 1242 cm^{-1}; nmr, $\tau \sim 5.25$ (broad, 1 H) and 8.04 (singlet, 3 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.10; H, 10.51.

The acetate obtained was reduced by lithium aluminum hydride and the product was fractionated, and 2.1 g of the pure material (42% yield based on I) was obtained, bp 101–102° (5 mm). The mixture melting point of the product with authentic spiro[5.5]undecan-2-ol was undepressed (52–53°), and the infrared and nmr spectra were identical with those of authentic spiro[5.5]undecan-2-ol.

1-(Δ^4-Pentenyl)cyclohexene (III) was isolated from the reaction mixture by the reaction of I in the presence of *p*-toluenesulfonic acid at 75.0° for 30 min. III was found to isomerize with chromatography over silica gel to spiro[5.5]undecene and other compounds. Pure 1-(Δ^4-pentenyl)cyclohexene (III) was obtained by repeated fractional distillation in 45% yield and was confirmed to be 98% pure by vpc, bp 105–106° (25 mm). The infrared and nmr spectra were identical with those of authentic 1-(Δ^4-pentenyl)cyclohexene (III).

1-(Δ^4-Pentenyl)cyclohexyl acetate (II) and spiro[5.5]undecene (IV) were not isolated.

Registry No.—I, 16133-73-6; II, 16133-74-7; III, 16133-75-8; VI, 16133-76-9; VII, 16133-77-0; VIII, 16133-78-1; IX, 16133-79-2; XII, 697-28-9.

Acknowledgment.—We wish to thank Dr. Yasuhiko Kondo for his helpful comments.

The Disilylation of Conjugated Dienes. The Configuration of Diene Anion Radicals and Dianions

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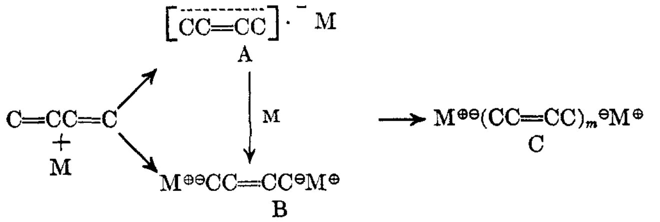
Butadiene, isoprene, and 2,3-dimethylbutadiene react rapidly with an alkali metal and trimethylchlorosilane in tetrahydrofuran (THF) at 25° to give bis(trimethylsilyl)butenes. A *cis*-1,4 addition of silyl groups is favored with sodium in THF (over 90% *cis*-1,4 addition), lithium naphthalenide in THF (65–80% *cis*), and lithium in diethyl ether (60% *cis*). A *trans*-1,4 addition of silyl groups is favored with lithium in THF. Dimethylchloromethoxysilane gave silacyclopentenes and disilylbutenes with the stereochemistry of the reaction determined by the choice of metal and solvent. Conversion of the *cis*-1,4-bis(dimethylmethoxysilyl)-2-butenes into cyclosiloxanes and the corresponding *trans* isomer to a linear polymer confirmed the structure assignments for the *cis*- and *trans*-1,4-disilyl-2-butenes. These data support the previously suggested scheme for the disilylation reaction which involves the trapping *via* reaction with a chlorosilane of short-lived organometallic reagents from the alkali metal and olefin. The stereochemistry of the reaction is apparently determined by the type of organometallic reagent being trapped by the chlorosilane. The anion radical, which in nonionizing solvents should exist in a *cis* configuration, leads to a *cis*-1,4 addition of silyl groups, whereas the organodimetallic reagent leads to a *trans*-1,4 addition of silyl groups.

Many conjugated dienes interact with alkali metals to give a variety of organoalkali reagents.[1] Butadiene and the simple alkyl-substituted butadienes in aprotic solvents give polymeric organoalkali reagents (C)[2] as shown in Scheme I.

SCHEME I



These polymerizations are similar to those observed with styrene and α-methylstyrene with the added complication provided by the choice of 1,2- and *cis*- or *trans*-1,4 addition to the diene in the initiating and propagating step. Although the stereochemistry of the propagation step has been shown to be dependent on the choice of metal and solvent, little is known about the geometry of the monomeric organoalkali reagents.

By the use of sodium dispersions at low temperatures in tetrahydrofuran (THF) solvent, Frank and Foster[3] have obtained high yields of the dimeric organodimetallic reagent, which upon carbonation gave a complex mixture of isomeric decadiendioic acids.

As in the polymerization of aryl olefins, the dimeric and polymeric organodialkali reagents are presumably reaction products of transitory and nonisolable monomeric organoalkali reagents; either the anion radical A or the dianion B in the above scheme. The trapping of these monomeric organoalkali reagents *via* protonation by some protic solvent forms the basis of the chemical reduction of dienes to give *cis*- and *trans*-alkenes.

The current study deals with the disilylation of 1,3-dienes; a reaction which involves trapping, *via* reaction with a chlorosilane, of organoalkali reagents formed from an alkali metal and a diene.[4] This reaction has provided a convenient synthesis for a variety of *cis*- and *trans*-1,4-disilyl-2-butenes and has given additional information on the factors governing the geometry of the monomeric organoalkali reagents from 1,3-dienes and an alkali metal.

Results

Butadiene, isoprene, and 2,3-dimethylbutadiene react with an alkali metal and trimethylchlorosilane in THF at 25° to yield the disilylated derivatives of the diene (Scheme II).

As in the disilylation of styrene,[4] both monomolecular derivatives containing one reduced olefin unit (I and II)

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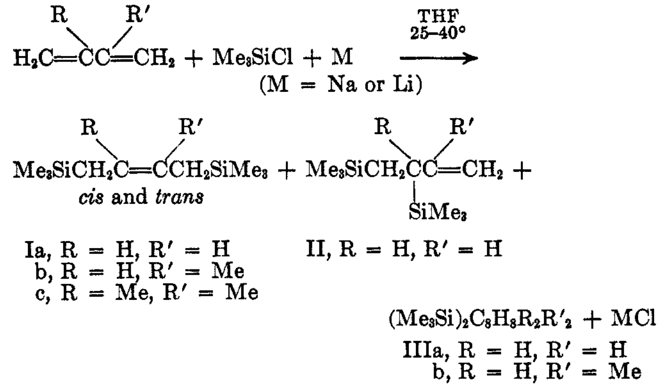
(1) K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

(2) M. Szwarc, *J. Polym. Sci.*, **40**, 585 (1959).

(3) C. E. Frank and W. E. Foster, *J. Org. Chem.*, **26**, 303 (1961).

(4) For a summary of studies on the disilylation reaction, see D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *ibid.*, **30**, 4096 (1965).

Scheme II



and bimolecular products containing two reduced olefin units (III) were formed. Up to 95% of the initial olefin was found in these two products with little or no higher boiling residues. The yield of the monomolecular derivative increased with increasing alkyl substitution on the diene with 2,3-dimethylbutadiene giving no bimolecular product.

The bimolecular products (III) were mixtures of at least three isomers with sodium and lithium giving quite different isomer ratios. No attempt was made to isolate and characterize the individual isomers. The monomeric products, which in all cases accounted for the major portion of the starting diene, were mainly 1,4-disilyl-2-butenes (I). The 3,4-disilyl-1-butene (II) was obtained in appreciable amount (18% of the disilylbutenes) only with lithium and butadiene. Less than 2% of a lower boiling isomer, assumed to be the 2-methyl-3,4-disilyl-1-butene, was obtained from isoprene and no 3,4 isomer was obtained from 2,3-dimethylbutadiene.

The above structures were assigned from the elemental analyses and the relatively simple H^1 nmr patterns. The assignments of the *cis* and *trans* configurations of the butadiene and isoprene derivatives were based on their infrared spectra and were confirmed by the chemical transformation involving ring closure of the *cis* isomer discussed later in this paper.

The most striking difference between the alkali metals in this synthesis was the stereochemistry of the 1,4-disilyl-2-butenes. As shown in Table I, sodium in THF gave over 95% *cis*-1,4-disilyl-2-butenes, whereas lithium gave mainly *trans*-1,4-disilyl-2-butenes with the three dienes included in this study.

Table I

The Disilylation of 1,3-Dienes

Olefin	Metal	Solvent	Ratio of addition products *cis*-1,4	*trans*-1,4
Isoprene	Na	THF	95	5
Isoprene	Li	THF	15	85
Isoprene	Li^+Nap^-	THF	81	19
2,3-Dimethylbutadiene	Na	THF	96	4
2,3-Dimethylbutadiene	Li	THF	4	96
2,3-Dimethylbutadiene	Li	Et_2O	60	40
2,3-Dimethylbutadiene	Li^+Nap^-	THF	66	33
Butadiene	Na	THF	>90[a]	<10[a]
Butadiene	Li	THF	<10	>90

[a] These isomers could not be separated by vpc. The above values are the estimated limits of detection from the infrared spectra.

The stereochemistry of the disilylation was also sensitive to solvent and to the form of the alkali metal. All conditions other than lithium metal in THF gave a *cis*-1,4 addition. Thus, substitution of ether for THF in the disilylation of 2,3-dimethylbutadiene with lithium changed the *cis/trans* ratio from 4:96 to 60:40. Also, the use of lithium naphthalenide in THF as the source of alkali metal gave a *cis*-1,4 addition of silyl groups. The absence of any isomerization of *cis*-Ic during the disilylation of 2,3-dimethylbutadiene with lithium and trimethylchlorosilane eliminated the possibility of *cis–trans* isomerization of the products either during or after the disilylation reaction.

The above factors also determined the stereochemistry of the disilylation with dimethylchloromethoxysilane and with dimethyldichlorosilane. Dimethylmethoxychlorosilane, 1,3-dienes, and sodium gave the following products from a *cis*-1,4 addition of silyl groups (Scheme III).

The disilylbutene fractions were over 80% *cis* IV. Although a chlorine is normally displaced from silicon in preference to a methoxy group by an organometallic reagent, the *intramolecular* displacement of an alkoxy group to form the silacyclopentene V competes with the intermolecular displacement of a halogen. As expected, the ratio of the cyclics V to open-chain dimer IV increased with increasing alkyl substitution on the diene. Whereas IVa and Va were obtained in 11 and 15% yields, respectively, from butadiene, IVc and Vc were obtained in 2.1 and 46% yields, respectively, from 2,3-dimethylbutadiene. The use of lithium in the above synthesis gave very low yields of V and correspondingly higher yields of disilylbutenes which were over 80% *trans* IV. The yield and isomer distribution of the various products from isoprene and 2,3-dimethylbutadiene are summarized in Table II. No attempt was made to optimize the yields or conversions.

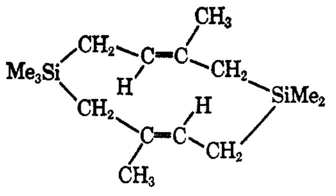
Table II

Isomer Distribution in the Disilylation of 1,3-Dienes with $Me_2Si(OMe)Cl$ in THF

Reactants Diene	Metal	Product yields, mole %[a] IV	*cis/trans* ratio	V	Dimer
Isoprene	Li	45	9:91	10	13
Isoprene	Na	10	85:15	40	7
2,3-Dimethylbutadiene	Li	30	2:98	10	
2,3-Dimethylbutadiene	Na	2.1	90:10	46	

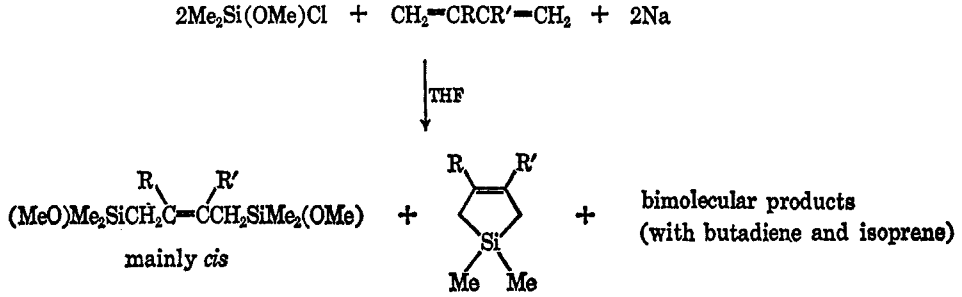
[a] Based on the diene.

Isoprene and dimethyldichlorosilane with sodium in THF gave a 25% yield of the silacyclopentene Vb, whereas the use of lithium in this reaction gave no silacyclopentene. The latter reaction gave a low yield of a disilacyclodecadiene VI, *trans,trans*-1,1,3,6,6,8-hexamethyl-1,6-disilacyclodecadiene-3,8 shown below. The simple H^1 nmr spectrum of the crystalline isomer of



VI

SCHEME III

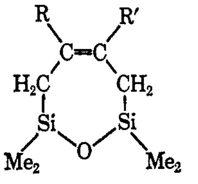


IVa, R = H, R′ = H
b, R = H, R′ = Me
c, R = Me, R′ = Me

Va, R = H, R′ = H
b, R = H, R′ = Me
c, R = Me, R′ = Me

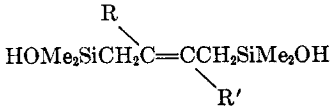
VI is consistent only with 1,1,3,6,8,8- or 1,1,3,6,6,9-hexamethyl-1,6-disilacyclodecadiene-3,8. From the method of preparation we assume that both double bonds are in the *trans* configuration. 1,1-Dimethyldivinylsilacyclopentenes have been reported by Nefedov,[5] *et al.*, from the reaction of butadiene, dimethyldichlorosilane, and lithium in THF.

Hydrolysis of the 1,4-bis(dimethylmethoxysilyl)-2-butenes confirmed the assignment of the *cis* and *trans* configurations for the 1,4-disilyl-2-butenes. Hydrolysis of *cis*-IVa and *cis*-IVb gave 50% yields of the cyclosiloxanes, VIIa and VIIb, whereas the corresponding



VIIa, R = H, R′ = H
b, R = H, R′ = Me
c, R = Me, R′ = Me

trans isomers gave only linear polymers. The intermediate crystalline *trans*-silanediols (VIIIb and VIIIc)

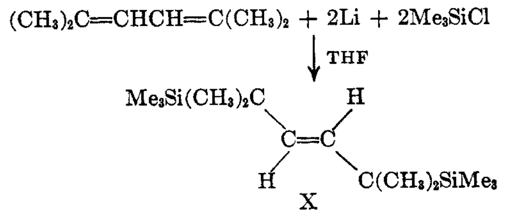


$HOMe_2SiCH_2C(R){=}C(R')CH_2SiMe_2OH$

VIIIb, R = H, R′ = Me
c, R = Me, R′ = Me

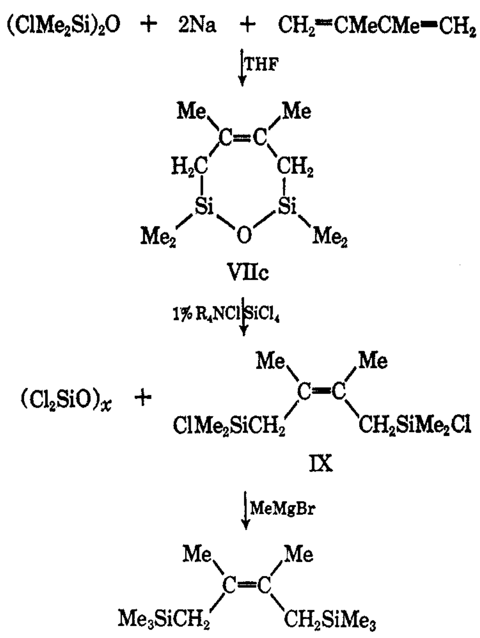
were isolated from the hydrolysis of *trans*-IVb and -IVc. Further proof of the isomer assignment for the 2,3-dimethylbutadiene derivatives was provided by the synthesis of *cis*-Ic (Scheme IV). This method of converting a hexaalkyldisiloxane to the corresponding chlorosilane, which is an extension of the chlorosilane–siloxane exchange described by Brown and Hyde,[6] has proved to be very useful for structures containing acid or base sensitive carbon–silicon bonds.

The disilylation of 2,5-dimethyl-2,4-hexadiene shows the strong preference for the 1,4 addition of silyl groups. A 1,2 addition of silyl groups would have placed the silyl groups on a secondary and tertiary carbon, whereas the 1,4 addition places both silyl groups on tertiary carbons.



X

SCHEME IV



cis-Ic

The physical properties of the compounds prepared in this study are reported in Table III.

Discussion

The preparation of disilylbutenes and disilyloctadienes from 1,3-dienes, an alkali metal, and a chlorosilane is consistent with the proposed scheme for the disilylation reaction which involves the trapping, *via* reaction with a chlorosilane, of short-lived organometallic reagents from the metal and olefin.[4,7,8] The species which is trapped by the chlorosilane can be either the anion radical XI or the dianion XII as shown in Scheme III. The path is determined by the relative rates of reactions 2 and 3.

It is instructive to consider the stereochemistry of this reaction in terms of the expected structures of these intermediates, XI and XII. The anion radical from a

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[5] O. M. Nefedov and M. N. Manakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 840 (1964); *Chem. Abstr.*, **61**, 438*gg* (1961).

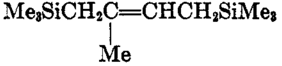
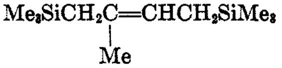
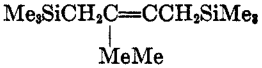
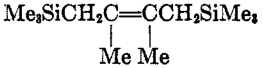
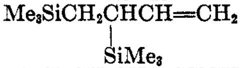
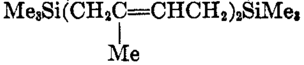
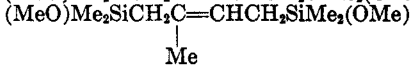
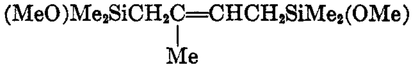
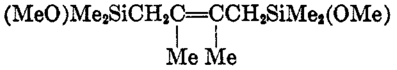
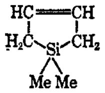
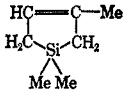
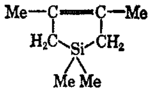
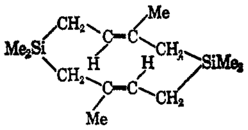
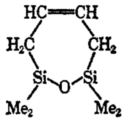
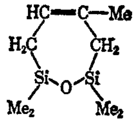
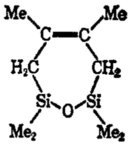
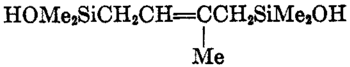
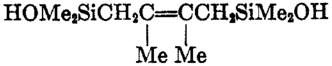
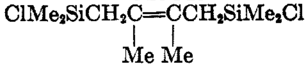
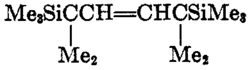
[6] P. Brown and J. F. Hyde, U. S. Patent 3,101,361 (Aug 20, 1963).

[7] D. R. Weyenberg and L. H. Toporcer, *J. Amer. Chem. Soc.*, **84**, 2843 (1962).

[8] D. R. Weyenberg and L. H. Toporcer, *J. Org. Chem.*, **30**, 943 (1965).

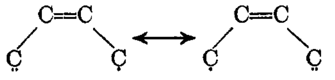
TABLE III

TABLE OF NEW COMPOUNDS

No.	Formula	Physical properties		Comments[a]
		Bp, °C (mm)	$n^{25}D$	
cis-Ia[b]	$Me_3SiCH_2CH{=}CHCH_2SiMe_3$	102 (48)	1.4406	
trans-Ia	$Me_3SiCH_2CH{=}CHCH_2SiMe_3$	. . .	1.4388	
cis-Ib	 $Me_3SiCH_2\underset{Me}{C}{=}CHCH_2SiMe_3$	104–106 (40)	1.4458	
trans-Ib	 $Me_3SiCH_2\underset{Me}{C}{=}CHCH_2SiMe_3$	102–103 (30)	1.4472	
cis-Ic	 $Me_3SiCH_2\underset{Me}{C}{=}\underset{Me}{C}CH_2SiMe_3$	112–113 (38)	1.4519	
trans-Ic	 $Me_3SiCH_2\underset{Me}{C}{=}\underset{Me}{C}CH_2SiMe_3$	127 (40)	1.4570	
II	 $Me_3SiCH_2\underset{SiMe_3}{CH}CH{=}CH_2$	. . .	1.4400	
IIIa	$Me_3Si(CH_2CH{=}CHCH_2)_2SiMe_3$	158–161 (48)	1.4584	Mixture of two isomers
IIIb	 $Me_3Si(CH_2\underset{Me}{C}{=}CHCH_2)_2SiMe_3$	146–148 (20)	1.4648	
cis-IVa	$(MeO)Me_2SiCH_2CH{=}CHCH_2SiMe_2(OMe)$	109–112 (25)	1.4396	
trans-IVa	$(MeO)Me_2SiCH_2CH{=}CHCH_2SiMe_2(OMe)$	110–115 (19)	1.4582	87% *trans* isomer
cis-IVb	 $(MeO)Me_2SiCH_2\underset{Me}{C}{=}CHCH_2SiMe_2(OMe)$	120 (27)	1.4441	Contains 15% *trans*
trans-IVb	 $(MeO)Me_2SiCH_2\underset{Me}{C}{=}CHCH_2SiMe_2(OMe)$	139–141 (53)	1.4441	
trans-IVc	 $(MeO)Me_2SiCH_2\underset{Me}{C}{=}\underset{Me}{C}CH_2SiMe_2(OMe)$	140–143 (36)	1.4550	
Va[c]		99–100	1.4443	
Vb		123	1.4467	
Vc		65 (41)	1.4574	
trans,trans-VI		92 (106)	1.5038	
VIIa		160–163	1.4438	
VIIb		84–87 (42)	1.4482	
VIIc		67–70 (60)	1.4558	
trans-VIIIb	 $HOMe_2SiCH_2CH{=}\underset{Me}{C}CH_2SiMe_2OH$	Mp 62–63		
trans-VIIIc	 $HOMe_2SiCH_2\underset{Me}{C}{=}\underset{Me}{C}CH_2SiMe_2OH$	Mp 109–111		
cis-IX	 $ClMe_2SiCH_2\underset{Me}{C}{=}\underset{Me}{C}CH_2SiMe_2Cl$	124 (15)	. . .	
trans-X	 $Me_3Si\underset{Me_2}{C}CH{=}CH\underset{Me_2}{C}SiMe_3$	121 (22)	1.4576	

[a] Compounds were over 98% purity by vpc analysis unless otherwise stated. [b] Ref 17. [c] Ref 19.

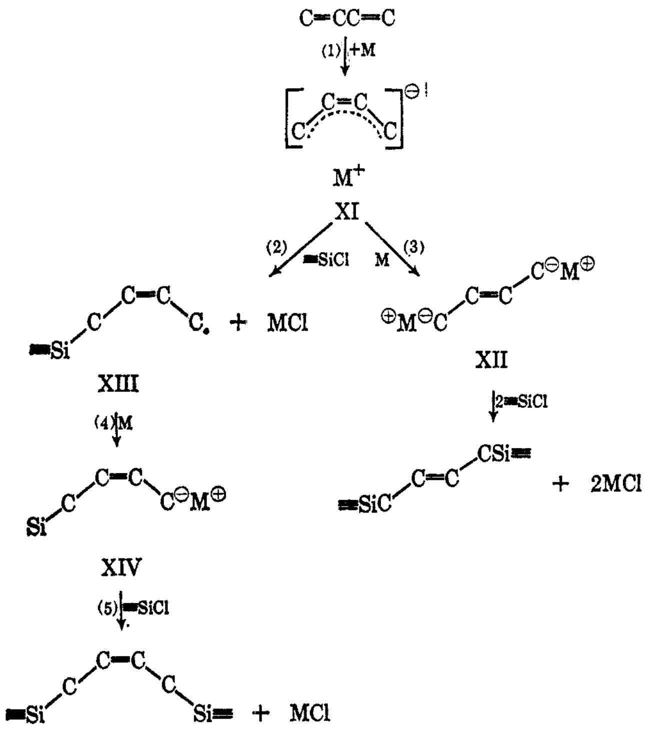
1,3-diene derives its stability from the resonance contributions which distribute the negative charge between the C-1 and C-4 position. In aprotic solvents where the



organometallic species are at least tight ion pairs, if not highly covalent structures, the *1,3-diene anion radical should prefer a cis configuration* as this structure would allow the gegenion to neutralize the partial charge on both the C-1 and C-4 atoms. The *cis*-1,4 disilylation which is observed under a variety of conditions presumably reflects this *cis* configuration of the anion radical being retained through the subsequent steps leading to the disilylbutene. Although the majority of the data involve a heterogeneous system where the reaction is occurring at or very near a metal surface, the preferred *cis*-1,4 addition is not a phenomenon associated only with a heterogeneous reaction. The generation of XI *via* electron transfer from a soluble species, lithium naphthalenide, also gave a predominantly *cis*-1,4 disilylation. This latter experiment adds convincing support to the above scheme.

The retention of configuration about the double bond in this sequence of reactions (Scheme V) is quite consistent with the recent demonstration of the configurational stability of both allylic free radicals[9a] and allylic anions.[9b]

SCHEME V



Although the *trans*-1,4 addition with lithium in THF could reflect a loss of configuration about the double bond either during step 5 or by isomerization of XIII or XIV, this explanation is not entirely consistent with several experimental facts. First, the expected similarity between lithium metal and lithium naphthalenide, which both proceed *via* XI, is not observed. If a *cis–trans* isomerization of XIV is rapid relative to reaction 5, silacyclopentenes would be formed from the difunctional silanes through facile ring closure from the *cis* configuration. However, these heterocyclics were obtained in only very low yields with lithium and THF. These considerations suggest that the 1,4-*trans* disilylation does not involve the trapping of the anion radical, but rather the trapping of the dianion XII which, because of the repulsion of the two negative charges, should prefer the *trans* configuration. Thus, the stereochemistry of this reaction would depend on the relative rates of reactions 2 and 3 as shown in Scheme III. The one alternative to this scheme would be an isomerization during reaction 4 which occurs only with lithium in THF.

The dramatic effects of solvent and metal on the course of this reaction are consistent with this proposed scheme (Scheme V). The equilibria between dianions, anion radicals, and olefins are quite sensitive to solvent polarity with the more highly charged species being favored in the more polar solvents.[10] It is therefore not surprising that reaction 3 can compete with 2 only in the more polar aprotic solvents such as THF. Substituting sodium for lithium should affect the rates of both reactions in the direction of increasing k_2/k_3. It is generally assumed that organosodium reagents, because of their more ionic carbon–metal bond, react more rapidly than an organolithium reagent with chlorosilanes.[11] Possibly the most important consideration is that lithium is often a better reducing agent than sodium. The Birch reduction of benzene in liquid ammonia is approximately 100 times faster with lithium than with sodium.[12] Although lithium has a lower ionization potential than sodium it is a better reducing agent (higher oxidation potential) than sodium in many media due to the greater solvation energy of the lithium cation in these media.[13] Lithium has, in fact, been recently shown to reduce naphthalene to the dianion in THF whereas sodium will convert it only to the anion radical.[14] Lithium naphthalenide should also be a much poorer reducing agent than lithium metal. All of these above factors would favor the route *via* the dianion XII for the reactions involving lithium metal in the more polar aprotic solvents.

A related scheme has been proposed by Bauld[15] to explain the preferred *cis*-1,4 addition of hydrogen in the reduction of butadiene with alkali metals in liquid NH_3. A preferred *cis* configuration of the diene anion radical was also assumed for relatively nonpolar aprotic solvents, and this preference for the *cis* configuration was assumed to decrease with increasing polarity of the media. The further assumption made in their earlier work,[15] that "the configuration of the dianion will necessarily be the same as the anion-radical precursor," is inconsistent with the current study.

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[9] (a) W. A. Thaler, A. A. Oswald, and B. E. Hudson, Jr., *J. Amer. Chem. Soc.*, **87**, 311 (1965); (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 193.

[10] G. E. Coates, "Organo-Metallic Compounds," 2nd ed, Methuen and Co. Ltd., London, 1960, p 33.

[11] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Publishers, Ltd., London, 1960, p 25.

[12] A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

[13] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 296.

[14] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

[15] N. L. Bauld, *ibid.*, **84**, 4345 (1962); **84**, 4747 (1962).

Experimental Section

All experiments involving alkali metals or organoalkali reagents were conducted under nitrogen atmosphere in flasks fitted with reflux condensers (water or Dry Ice), stirrer, thermometer, addition funnel or gas dispersion tubes, and external cooling bath. The melting points are uncorrected. The vpc analyses were obtained on F & M Model 300 instrument with a column packed with a mixture of Dow Corning FS 60 fluid and Dow Corning 200 fluid on Chromosorb W unless otherwise noted. The H^1 nmr spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The dimethylmethoxychlorosilane was the equilibrium mixture obtained from an equal molar ratio of dimethyldichlorosilane and dimethyldimethoxysilane at 25°.[16]

Butadiene with Trimethylchlorosilane and Sodium (*cis*-Ia).—Butadiene, 60 g (1.1 mol), was added during 2.5 hr to 46 g (2 g-atoms) of sodium (0.25-in. cubes) and 217 g (2 mol) of trimethylchlorosilane in 300 ml of THF. An exothermic reaction occurred after 6 hr of stirring at 25° which required external cooling to maintain a temperature below 45°. Filtration after an additional 4 days of stirring at 25° gave 22 g (0.95 g-atom) of recovered sodium. Fractional distillation gave 48.3 g (0.24 mol) of *cis*-1,4-bis(trimethylsilyl)-2-butene (*cis*-Ia) (bp 102° (48 mm); $n^{25.5}\mathrm{D}$ 1.4406[17]), 24.5 g of bis(trimethylsilyl)octadiene (IIIa) (bp 158–161° (48 mm); $n^{25}\mathrm{D}$ 1.4584), and 2 g of residue. Compound IIIa was a mixture of two compounds in a ratio of 13:87 by vpc ($(\mathrm{Me_2SiC_6H_4SiMe_2O})_x$ column).

Anal. Calcd for *cis*-Ia, $C_{10}H_{24}Si$: Si, 28.0; C, 59.9; H, 12.1; mol wt, 200.5. Found: Si, 27.6; C, 60.4; H, 12.5; mol wt, 181.

The infrared spectrum did not contain a band at 10.45 μ. The H^1 nmr spectrum showed a singlet for $SiCH_3$ (τ 9.98), an unresolved multiplet for $-CH_2-$ (τ 8.60) and unresolved multiplet for $-CH{=}$ (τ ~4.75) in ratio of 9:2:1, respectively.

Anal. Calcd for IIIa, $C_{14}H_{30}Si_2$: Si, 22.1; C, 66.1; H, 11.9; mol wt, 254.6; hydrogen no.,[18] 127.3. Found: Si, 22.2; C, 66.3; H, 12.2; mol wt, 240; hydrogen no., 134.

Butadiene with Trimethylchlorosilane and Lithium.—Butadiene, 62 g (1.15 mol), was added during 3.5 hr to 24 g (2.75 g-atoms) of 80% lithium sand (Foote Mineral Co.) and 259 g (2.4 mol) of trimethylchlorosilane in 350 ml of THF. The reaction was quite exothermic and was maintained at 15–25° by external cooling. After stirring for an additional 2 days at 25°, the reaction mixture was filtered. Fractional distillation gave 180 g (0.9 mol) of bis(trimethylsilyl)butene (bp 92–94° (35 mm); $n^{25.5}\mathrm{D}$ 1.4386–1.4388), and 18 g (0.07 mol) of bis(trimethylsilyl)octadiene (IIIa) (bp 142–148° (35 mm); $n^{25.4}\mathrm{D}$ 1.4550–1.4566), and 8 g of residue. The bis(trimethylsilyl)butene fraction contained 18% 3,4-bis(trimethylsilyl)-1-butene (II) and 82% *trans*-1,4-bis(trimethylsilyl)-2-butene (*trans*-Ia) by vpc analysis. Analytical samples were purified by preparative vpc: II, $n^{25}\mathrm{D}$ 1.4400, and *trans*-Ia, $n^{25}\mathrm{D}$ 1.4388.

Anal. Calcd for II, $C_{10}H_{24}Si_2$: Si, 28.0; C, 59.9; H, 12.1. Found: Si, 28.1; C, 60.0; H, 12.2.

The H^1 nmr spectrum contained two singlets for $SiCH_3$ (τ 10.2, 10.05), a doublet (τ 9.35), and a complex pattern (τ 8.35) for aliphatic CH, and two complex patterns (τ 3.9–5.3) for the olefinic CH in a ratio of 18:3:3, respectively.

Anal. Calcd for *trans*-Ia, $C_{10}H_{24}Si_2$: Si, 28.0; C, 59.9; H, 12.1. Found: Si, 27.8; C, 59.9; H, 12.3.

The infrared spectrum shows the characteristic band at 10.45 μ for *trans* double bond. The H^1 nmr spectrum contains a sharp singlet for CH_3Si (τ 10.0), a broad multiplet for $-CH_2-$ (τ 8.60), and a broad multiplet for the $-CH{=}$ (τ ~4.75) in a ratio of 9:2:1, respectively.

Anal. Calcd for IIIa, $C_{14}H_{30}Si_2$: Si, 22.1; C, 66.1; H, 11.9. Found: Si, 22.0; C, 66.9; H, 12.2.

Compound IIIa was a mixture of three compounds by vpc [$(\mathrm{Me_2SiC_6H_4SiMe_2O})_x$ column].

Butadiene with Dimethylmethoxychlorosilane and Sodium.—Butadiene, 55 g (1 mol), was added during 2.5 hr to 92 g (2 g-atoms) of 50% sodium dispersion (in isooctane) and 280 g (2.29 mol) of dimethylmethoxychlorosilane in 400 ml of THF. Approximately 2 hr after the addition was complete, an exothermic reaction occurred and external cooling was required to maintain the temperature below 40°. Filtration and fractional distillation after stirring for an additional 16 hr at 25° gave 13 g (0.12 mol) of 1,1-dimethyl-1-silacyclo-3-pentene (Va) (bp 99–100°; $n^{25}\mathrm{D}$ 1.4443; lit.[19] bp 100.5–101°; $n^{20}\mathrm{D}$ 1.4433), 24.1 g (0.10 mol) of *cis*-1,4-bis(dimethylmethoxysilyl)-2-butene (*cis*-IVa) (bp 109–112° (25 mm); $n^{25.4}\mathrm{D}$ 1.4396), 55 g (0.19 mol) of bis(dimethylmethoxysilyl)octadiene (bp 154–160° (25 mm); $n^{25.4}\mathrm{D}$ 1.4568–1.4605), and 16 g of residue.

Anal. Calcd for Va, $C_6H_{12}Si$: Si, 25.0; C, 64.2; H, 10.8. Found: Si, 24.4; C, 61.3;[20] H, 10.7.

The H^1 nmr spectrum showed a singlet (τ 9.84) for $SiCH_3$, a multiplet (τ 8.72) for aliphatic CH, and a mulitplet (τ 4.02) for olefinic CH in a ratio of 3:2:1, respectively.

Anal. Calcd for *cis*-IVa, $C_{10}H_{24}O_2Si_2$: Si, 24.2; C, 51.7; H, 10.4. Found: Si, 23.8; C, 50.7; H, 10.4.

Vpc analysis showed approximately 9% of a contaminant, presumably a 3,4-disilyl-1-butene.

Butadiene with Dimethylmethoxychlorosilane and Lithium.—Butadiene, 56 g (1.0 mol), was added during 1.5 hr to 25 g of 80% lithium sand in mineral oil (Foote Mineral Co.) and 249 g (2 mol) of dimethylmethoxychlorosilane in 300 ml of THF. External cooling was necessary to maintain the temperature between 15 and 25°. The exothermic reaction, which started immediately upon the addition of the butadiene, subsided within 1 hour after the addition was complete. After 1.5 days at room temperature, filtration and fractional distillation gave 152.5 g of impure *trans*-1,4-bis(dimethylmethoxysilyl)-2-butene (*trans*-IVa) (bp 110–115° (19 mm); $n^{25.4}\mathrm{D}$ 1.4582) and 14 g of residue.

Anal. Calcd for *trans*-IVa, $C_{10}H_{24}O_2Si_2$: Si, 24.1; C, 51.7; H, 10.4. Found: Si, 24.0; C, 52.2; H, 10.5.

Vapor phase chromatography shows approximately 13% of a contaminant, presumably the 3,4-disilyl-1-butene.

Isoprene with Trimethylchlorosilane and Sodium.—Isoprene (68 g, 1 mol) in 50 ml of THF was added to 46 g (2 g-atoms) of sodium (*ca.* 1-cm^3 pieces) and 217 g (2 mol) of trimethylchlorosilane in 300 ml of THF. Rapid stirring and the addition of rock salt (to abrade the sodium surface during the reaction) were used to initiate the reaction. External cooling was necessary to maintain the temperature at 25–30°. The reaction was complete within 5 hr. After stirring overnight, filtration and fractional distillation gave 93 g (0.44 mol) of *cis*-1,4-bis(trimethylsilyl)-2-methyl-2-butene (*cis*-Ib) (bp 104–106° (40 mm); $n^{25.2}\mathrm{D}$ 1.4458), 6.5 g (5%) of bis(trimethylsilyl)decadiene (IIIb) (bp 160–165° (40 mm); $n^{25.2}\mathrm{D}$ 1.4640–1.4656) and 3 g of residue.

Anal. Calcd for *cis*-Ib, $C_{11}H_{26}Si_2$: Si, 26.2; C, 61.6; H, 12.2. Found: Si, 26.1; C, 61.7; H, 12.3.

The H^1 nmr spectrum in CCl_4 showed two singlets (τ 10.02, 9.98) for $SiCH_3$, a narrow multiplet (τ 8.33) for CCH_3, a singlet (τ 8.55) for $SiCH_2(CH_3)C{=}$, a doublet (τ 8.73, J = 8 cps) for $SiCH_2CH{=}$, and a triplet (τ 5.0, J = 8 cps) for $C{=}CH$.

Anal. Calcd for IIIb, $C_{16}H_{34}Si_2$: Si, 19.9; C, 68.0; H, 12.3. Found: Si, 20.1; C, 67.4; H, 11.9.

When the above reaction was repeated using a sodium dispersion, a 69% yield of *cis*-Ib was obtained.

Isoprene with Trimethylchlorosilane and Lithium.—Isoprene, 68 g (1 mol), was added during 2.5 hr at 15–25° (external cooling) to 20 g (*ca.* 2.3 g-atoms of Li) of lithium sand (Foote Mineral Co. – 80% Li in mineral oil), 217 g (2 mol) of trimethylchlorosilane, and 300 ml of THF. Filtration and fractional distillation gave 148.5 g (6.70 mol) of mainly *trans*-1,4-bis(trimethylsilyl)-2-methyl-2-butene, *trans*-Ib (bp 102–103° (30 mm); $n^{25}\mathrm{D}$ 1.4468; contains 15% *cis* isomer by vpc) and 34.5 g (0.12 mol) of bis(trimethylsilyl)decadiene (IIIb) (bp 146–148° (20 mm); $n^{25}\mathrm{D}$ 1.4648). Redistillation of the butene fraction gave 98% pure *trans*-1,4-bis(trimethylsilyl)-2-methyl-2-butene ($n^{25}\mathrm{D}$ 1.4472).

Anal. Calcd for *trans*-Ib, $C_{11}H_{26}Si_2$: Si, 26.2; C, 61.6; H, 12.2. Found: Si, 25.8; C, 61.9; H, 12.0.

The H^1 nmr spectrum showed a singlet for $SiCH_3$ (τ 9.97), a narrow multiplet for CCH_3 (τ 8.43), a singlet for $\mathbf{CH_2C(CH_3){=}}$ (τ 8.53), a doublet for $CH_2CH{=}$ (τ 8.54, J = 8.5 cps), and a triplet for $C{=}CH$ (τ 5.0, J = 8.5 cps).

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(16) J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

(17) Literature reference for unspecified isomer of Ia (bp 190°, $n^{20}\mathrm{D}$ 1.4385); A. D. Petrov, G. I. Nikishin, and N. P. Smetankina, *J. Gen. Chem. USSR*, **28**, 2122 (1958).

(18) Grams of compound which react with 1 mol of hydrogen with a platinum catalyst 50° and 50 psi.

(19) A. D. Petrov, G. I. Nikishin, N. P. Smetankina, and Y. P. Egorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 947 (1955).

(20) Accurate and reproducible carbon analyses could not be obtained on the more volatile heterocyclics. Vpc analyses indicated purities of greater than 96%.

Isoprene with Trimethylchlorosilane and Lithium Naphthalenide.—A solution of lithium naphthalenide which was prepared from 1.4 g (0.2 g-atom) of lithium wire and 30 g (0.24 mol) of naphthalene in 200 ml of THF was added during 15 min at −15 to −20° to 6.8 g (0.1 mol) of isoprene and 23.7 g (0.22 mol) of trimethylchlorosilane in 100 ml of THF. A vpc analysis showed approximately equal amounts of 1,4-bis(trimethylsilyl)-2-methyl-2-butene (81.5% *cis*-Ib and 18.5% *trans*-Ib) and disilyldihydronaphthalenes. Distillation gave 5.3 g of *cis*-Ib containing 10% *trans*-Ib isomer by vpc.

Isoprene with Dimethyldichlorosilane and Sodium.—A mixture of 68 g (1 mol) of isoprene and 129 g (1 mol) of dimethyldichlorosilane was added during 2 hr at 25–35° (external cooling) to 46 g (2 g-atoms) of sodium (*ca.* 1-cm^3 pieces) and 50 g of rock salt in 300 ml of THF. The mildly exothermic reaction continued for several hours after the addition was complete. Filtration and fractional distillation gave 25.1 g (0.20 mol) of 1,1,3-trimethyl-1-sila-3-cyclopentene (Vb) (bp 123°; $n^{25.4}\mathrm{D}$ 1.4467), 15 g of unidentified product (bp 55–69° (0.05 mm); $n^{25.4}\mathrm{D}$ 1.4668–1.4889), and 37 g of residue.

Anal. Calcd for Vb, $C_7H_{14}Si$: Si, 22.3; C, 66.6; H, 11.2; mol wt, 126.3. Found: Si, 22.3; C, 65.6; H, 11.2; mol wt, 140.

The H^1 nmr pattern showed a singlet (τ 9.92) for $SiCH_3$ and unresolved multiplets for $SiCH_2$ (τ 8.87), for $=CCH_3$ (τ 8.34), and for olefinic CH (τ 4.65), in the ratio of 6:4:3:1.

Isoprene with Dimethyldichlorosilane and Lithium.—A mixture of 68 g (1 mol) of isoprene and 129 g (1 mol) of Me_2SiCl_2 was added during 1.25 hr at 5–10° to 15 g (2.2 g-atoms) of lithium wire and 300 ml of THF. Since only part of the lithium was consumed at the end of the addition period, rock salt was added and the stirring was continued at 25°. Titration of a reaction mixture sample with 0.1 *N* alkali indicated that the reaction was essentially complete after 20 hr. After filtration and washing of the filtrate with Na_2CO_3 solution, distillation gave 12 f of VI (bp 92° (10.6 mm) $n^{25.4}\mathrm{D}$ 1.5038) and 82 g of residue (viscous polymer of $(Me_2SiCH_2CH{=}CMeCH_2)[SiMe_2$ structure). No silacyclopentene was noted during the distillation. Compound VI was recrystallized from absolute ethanol to give mp 89–91°.

Anal. Calcd for VI, $C_{14}H_{28}Si_2$: Si, 22.25; C, 66.6; H, 11.2. Found: Si, 22.5; C, 65.9; H, 11.2.

The H^1 nmr pattern (CCl_4) showed a singlet for $SiCH_3$ (τ 9.90), a singlet for $\mathbf{CH_2}{-}C(CH_2){=}$ (τ 8.53), a narrow multiplet for $C(CH_3){=}$ (τ 8.35), a doublet for $CH_2CH{=}$ (τ 8.53, J = 8.5 cps), and a doublet for $=CH$ (τ 5.02, J = 8.5 cps).

Anal. Calcd for $(C_7H_{14}Si)_x$: Si, 22.25; C, 66.6; H, 11.2. Found: Si, 21.7; C, 66.0; H, 11.0.

Isoprene with Dimethylmethoxychlorosilane and Lithium.—Isoprene, 136 g (2 mol), was added during 2 hr at 15–35° to 496 g (4 mol) of $Me_2Si(OMe)Cl$, 50 g (*ca.* 5.7 g-atoms) of 80% lithium sand in mineral oil, and 600 ml of THF. The reaction was essentially complete at the end of the addition. However, the mixture was stirred for 24 hr at 25°. Filtration and removal of solvent and low-boiling material by distillation gave 369 g of liquid residue which was over 90% bis(dimethylmethoxysilyl)-methylbutene (vpc) in the following isomer ratio: (2%) isomer A; (8–10%) *cis*-1,4-bis(dimethylmethoxysilyl)-2-methyl-2-butene (*cis*-IVb); (90%) *trans*-1,4-bis(dimethylmethoxysilyl)-2-methyl-2-butene (*trans*-IVb). Careful fractional distillation through a 36-in. spinning-band column gave 110 g of pure *trans*-IVb (bp 139–141° (53 mm); $n^{25}\mathrm{D}$ 1.4441).

Anal. Calcd for *trans*-IVb, $C_{11}H_{26}O_2Si_2$: Si, 22.8; C, 53.6; H, 10.6. Found: Si, 22.7; C, 53.4; H, 10.8.

Isomer A was concentrated to 62% in one of the forecuts (bp 145–146° (99 mm); $n^{25}\mathrm{D}$ 1.4416, contained 16% *cis*-IVb and 22% *trans*-IVb).

Anal. Calcd for $C_{11}H_{26}O_2Si_2$: Si, 22.8; C, 53.6; H, 10.6. Found: Si, 22.2; C, 53.2; H, 10.6.

The infrared spectrum showed a medium intensity band at 6.15 μ characteristic of terminal unsaturation.

Isoprene with Dimethylmethoxychlorosilane and Sodium.—Isoprene, 68 g (1 mol), was added to 46 g (2 g-atoms) of sodium, 248 g (2 mol) of $Me_2Si(OMe)Cl$, and 50 g of rock salt in 300 ml of THF. The exothermic reaction, which started 3 hr after the addition was complete, was maintained at 25–30° by external cooling. After stirring for 2 days at 25°, filtration and fractional distillation gave 50.5 g (40%) of Vb (bp 123°; $n^{25.2}\mathrm{D}$ 1.4446; 98% pure by vpc), 25 g (10%) of impure *cis*-IVb (bp 120° (27 mm); $n^{25.2}\mathrm{D}$ 1.4441; contains 15% *trans*-IVb by vpc), 10 g of presumably dimeric material (bp 140–150° (5 mm); $n^{25.2}\mathrm{D}$ 1.4621–1.4663), and 5.0 g of residue.

2,3-Dimethylbutadiene with Trimethylchlorosilane and Sodium.—A solution of 20.5 g (0.25 mol) of 2,3-dimethylbutadiene in 50 ml of THF was added during 6 hr to 54.3 g (0.5 mol) of Me_3SiCl, 11.5 g (0.5 g-atom) of sodium, and 200 ml of THF. The reaction was mildly exothermic. After 17 hr, vpc analysis indicated that the reaction was 75% complete. Filtration and fractional distillation gave 18.4 g (0.8 mol) of *cis*-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene (*cis*-Ic) (*ca.* 4% *trans* isomer present) and 3.8 g of residue. *cis*-Ic was further purified (99% pure) by distillation (bp 112–113° (38 mm); $n^{25}\mathrm{D}$ 1.4519).

Anal. Calcd for *cis*-Ic, $C_{12}H_{28}Si_2$: Si, 24.6; C, 63.1; H, 12.3. Found: Si, 24.4; C, 63.4; H, 12.6.

The H^1 nmr spectrum indicated the expected three singlets (CH_3Si, τ 10.0; $-CH_2C$, τ 8.57 and CH_3C, τ 8.4).

2,3-Dimethylbutadiene with Trimethylchlorosilane and Lithium.—A solution of 20.5 g (0.25 mol) of 2,3-dimethylbutadiene in 50 ml of THF was added to 54.3 g (0.5 mol) of Me_3SiCl, 3.5 g (0.5 g-atom) of lithium wire, and 200 ml of THF. A more rapid and exothermic reaction was evident. Analysis by vpc on the reaction mixture after 20 hr at 25° showed that the reaction was essentially complete. After dilution with pentane and filtration, distillation gave 37.8 g (0.17 mol) of *trans*-1,4-bis-(trimethylsilyl)-2,3-dimethyl-2-butene (*trans*-Ic) (contains *ca.* 4% *cis* isomer) and 3 g of residue. A careful distillation gave a 99% pure yield of the *trans* isomer (bp 127° (40 mm); $n^{25}\mathrm{D}$ 1.4570).

Anal. Calcd for *trans*-Ic, $C_{12}H_{28}Si_2$: Si, 24.6; C, 63.1; H, 12.3. Found: Si, 24.5; C, 63.4; H, 16.4.

The H^1 nmr spectrum showed the three expected singlets with no olefinic C–H (CH_3Si, τ 10.0; CH_2C, τ 8.52; and CH_3C, τ 8.47).

2,3-Dimethylbutadiene with Trimethylchlorosilane and Lithium in the Presence of *cis*-Ic.—A solution of 8.2 g (0.1 mol) of 2,3-dimethylbutadiene in 18.3 g of THF was added during 2.5 hr to 21.7 g (0.2 mol) of Me_3SiCl, 1.4 g (0.2 g-atom) of lithium wire, 2.8 g of *cis*-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene, and 75 g of THF. The temperature rose to 36° during the addition. Analysis by vpc during the addition showed a steady increase in the concentration of the *trans*-Ic isomer, while the concentration of the *cis*-Ic isomer remained constant. Filtration after the addition of pentane and removal of the solvent by distillation gave 35.4 g of residue which gave the following area percentages on vpc: (THF, 57%, *cis*-Ic, 9.1%; *trans*-Ic, 30.5%).

2,3-Dimethylbutadiene with Trimethylchlorosilane and Lithium in Diethyl Ether.—2,3-Dimethylbutadiene (20 g, 0.25 mol) was added during 1 hr to 65.1 g (0.6 mol) of Me_3SiCl, 7 g (1.0 g-atom) of lithium wire, and 200 ml of diethyl ether. No exotherm was noticed during the addition or within 4 hr after the addition was complete. After 20 hr of stirring at room temperature, vpc analysis indicated only solvent, excess Me_3SiCl, and *cis*- and *trans*-disilylbutenes. Filtration and removal of solvent by distillation gave 49 g of residue which by vpc analysis was over 95% 1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene (55% *cis*-Ic and 45% *trans*-Ic, identified by internal standards, approximately 80% yield).

2,3-Dimethylbutadiene with Trimethylchlorosilane and Lithium Naphthalenide.—A 1 *N* solution of lithium naphthalenide in THF (60 ml, 0.06 equiv) was added during 15 min at 5–15° to 3 g (0.037 mol) of 2,3-dimethylbutadiene and 7.0 g (0.065 mol) of Me_3SiCl in 50 ml of THF. Vapor phase chromatography analysis showed a small amount (approximately 20%) of 1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene (67% *cis*-Ic and 33% *trans*-Ic, identified by internal standard) and a correspondingly greater amount of disilyldihydronaphthalenes.

2,3-Dimethylbutadiene with Dimethylmethoxychlorosilane and Sodium.—A solution of 20.5 g (0.25 mol) of 2,3-dimethylbutadiene in 50 ml of THF was added during 2.5 hr to 11.5 g (0.5 g-atom) of lump sodium, 62.3 g (0.5 mol) of $Me_2Si(OMe)Cl$, and 300 ml of THF. No exotherm was noted during the addition. After stirring for 3 days at room temperature, filtration and fractional distillation gave 16.1 g (0.012 mol) of 1,1,3,4-tetramethyl-1-sila-3-cyclopentene (Vc) (bp 65° (41 mm), $n^{25}\mathrm{D}$ 1.4574), 1.4 g of 1,4-bis(dimethylmethoxysilyl)-2,3-dimethyl-2-butene (IVc) (90% *cis*-IVc, 10% *trans*-IVc by vpc, bp *ca.* 100° (41 mm); $n^{25}\mathrm{D}$ 1.4130; identified by nmr), and 5 g of residue.

Anal. Calcd for Vc, $C_8H_{16}Si$: Si, 20.0; C, 68.5; H, 11.5. Found: Si, 19.8; C, 66.8; H, 11.5.

The H_1 nmr pattern showed a singlet for $SiCH_3$ (τ 9.87), a multiplet for $SiCH_2$– (τ 8.72), and a multiplet for C–CH_3 (τ 8.35) and gave an integration ratio of 3:2:3, respectively.

2,3-Dimethylbutadiene with Dimethylmethoxychlorosilane and Lithium.—A solution of 20.5 g (0.25 mol) of 2,3-dimethylbutadiene in 50 ml of THF was added to 3.5 g (0.5 g-atom) of lithium wire, 62.3 g (0.5 mol) of $Me_2Si(OMe)Cl$, and 300 ml of THF. After stirring at room temperature for 22 hr, filtration and distillation gave 3 g of Vc, 10 g of *trans*-IVc (bp 140–143° (35–37 mm); n^{25}D 1.4550), and 23 g of residue.

Anal. Calcd for *trans*-IVc, $C_{12}H_{28}Si_2O_2$: Si, 21.6; C, 55.3; H, 10.8. Found: Si, 22.7; C, 53.2; H, 11.7.

2,3-Dimethylbutadiene with Tetramethyl-1,3-dichlorodisiloxane and Sodium.—A mixture of 40.6 g (0.2 mol) of tetramethyl-1,3-dichlorodisiloxane and 16.4 g (0.2 mol) of 2,3-dimethylbutadiene was added during 2 hr to 27 g (0.6 g-atom of Na) of a 50% sodium dispersion in paraffin in 200 ml of THF. The exothermic reaction was maintained at 25–30° by external cooling. After an additional 2 hr of stirring at room temperature, filtration and fractional distillation gave 5.6 g (0.04 mol, 20% yield based on diene) of Vc (bp 67–70° (60 mm); n^{25}D 1.4558) and 21 g of residue.

Anal. Calcd for VIIc, $C_{10}H_{22}Si_2O$: Si, 26.2; C, 56.0; H, 10.4. Found: Si, 26.0; C, 55.3; H, 10.3.

The H^1 nmr spectrum indicated a singlet for $SiCH_3$ (τ 9.95), a singlet for $SiCH_2$– (τ 8.52), and a singlet for C–CH_2 (τ 8.31) in the ratio of 6:2:3.

2,5-Dimethyl-2,4-hexadiene with Trimethylchlorosilane and Lithium.—A solution of 5 g (0.045 mol) of 2,5-dimethyl-2,4-hexadiene in 25 ml of THF was added during 1.5 hr to 21.7 g (0.2 mol) of Me_3SiCl, 1.4 g (0.2 g-atom) of lithium wire, and 50 ml of THF. A slight exotherm was noted during the reaction. After stirring for 2 days at room temperature, vpc analysis showed complete consumption of the diene. Filtration and fractional distillation gave 7.5 g (0.3 mol) of *trans*-2,5-bis(trimethylsilyl)-2,5-dimethyl-3-hexene (*trans*-X) (bp 121° (22 mm); n^{25}D 1.4576; mp *ca.* 25°) and 0.8 g of residue.

Anal. Calcd for *trans*-X, $C_{14}H_{32}Si_2$: Si, 21.9; C, 65.5; H, 12.6. Found: Si, 21.9; C, 65.3; H, 12.7.

The H^1 nmr spectrum showed singlets for CH_3Si (τ 10.06), CH_3C (τ 9.03), and H—C=C (τ 4.85) in the ratio of 9:6:1, respectively. The infrared spectrum gave a strong absorption at 10.3 μ which indicated the *trans* double bond.

Preparation of *cis*-1,4-Bis(trimethylsilyl)-2,3-dimethyl-2-butene.—A mixture of 10.7 g (0.05 mol) of VIIc, 40 g (0.24 mol) of tetrachlorosilane, and 0.2 g of Arquad 2HT (R_2NMe_2Cl) was heated at reflux for a total of 3 days. Analysis by vpc showed a complete conversion of cyclosiloxane within 4 hr to presumably $Cl_3SiOMe_2SiCH_2CMe{=}CMeCH_2SiMe_2Cl$ which was converted into the *cis*-1,4-bis(dimethylchlorosilyl)-2,3-dimethyl-2-butene during 24 hr. Distillation gave 12.6 g (0.05 mol), *cis*-1,4-bis(dimethylchlorosilyl)-2,3-dimethyl-2-butene (*cis*-IX) (bp 124° (15 mm)).

Anal. Calcd for *cis*-IX, $C_{10}H_{22}Si_2Cl_2$: Si, 20.8; Cl, 26.3. Found: Si, 20.6; Cl, 27.0.

The H^1 nmr spectrum consisted of singlets for CH_3Si (τ 9.58), CH_3C (τ 8.28), and CH_2C (τ 8.16). Compound IX, 10.9 g (0.04 mol), was heated at reflux with 0.2 mol of MeMgBr in 100 ml of THF for 1 hr. Distillation after removal of magnesium salt and MeMgBr (by precipitation with aqueous NH_4Cl solution) gave 7.5 g (0.03 mol, 81% yield) of *cis*-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene (*cis*-Ic) (bp 116–120° (33 mm); n^{25}D, 1.4520).

Hydrolysis and Condensation of 1,4-Bis(dimethylmethoxysilyl)-2-butene.—Compound *cis*-IVa, 10 g (0.04 mol), was hydrolyzed with a mixture of 100 ml of H_2O, 25 ml of ether, and 0.5 ml of glacial acetic acid. After stirring overnight, the ether layer was separated, washed with H_2O, and dried over anhydrous sodium sulfate. Distillation gave 4.2 g (0.02 mol, 51% yield) of 4,4,6,6-tetramethyl-4,6-disila-5-oxacycloheptene (VIIa) (bp 160–163°; n^{25}D 1.4438) and 2.4 g of residue.

Anal. Calcd for VIIa, $C_8H_{18}OSi_2$: Si, 30.1; C, 51.6; H, 9.7. Found: Si, 30.7; C, 51.6; H, 10.0.

Treatment of the *trans*-IVa compound containing approximately 15% of the 1,4 isomer under the above conditions gave a maximum of 19% yield of VIIa and a correspondingly greater amount of residue.

Hydrolysis and Condensation of *cis*-1,4-Bis(dimethylmethoxysilyl)-2-methyl-2-butene.—Compound *cis*-IVb, 10 g (0.04 mol) (contained 14% *trans*-IVb isomer by vpc), when hydrolyzed as previously described, gave 4.1 g (0.02 mol) of 1,4,4,6,6-pentamethyl-4,6-disila-5-oxacycloheptene (VIIb) (bp 84–87° (42 mm); n^{25}D 1.4482).

Anal. Calcd for VIIb, $C_9H_{20}OSi_2$: Si, 28.0; C, 53.9; H, 10.1. Found: Si, 27.9; C, 54.3; H, 10.5.

The H^1 nmr pattern (CCl_4) showed singlets for $Si\mathit{CH}_3$ (τ 9.94, 9.97), for $C\mathit{CH}_3$ (τ 8.27) and for $\mathit{CH}_2C(CH_3){=}$ (τ 8.52); a doublet for $\mathit{CH}_2CH{=}$ (τ 8.60, J = ~7 cps) and a triplet for olefinic CH (τ 4.64, J = 8 cps).

Hydrolysis and Condensation of *trans*-1,4-Bis(dimethylmethoxysilyl)-2-methyl-2-butene.—Treatment of 50 g (0.2 mol) of *trans*-IVb (contained *ca.* 5% *cis*-IVb) with 75 ml of ether, 250 ml of water, and 1.5 ml of glacial acetic acid gave only a polymeric residue upon distillation.

In a duplication of the above experiment, the removal of the ether solvent at reduced pressure before the distillation step gave a crystalline solid. Two recrystallizations from pentane gave 21.7 g (0.1 mol), 49% yield, of *trans*-1,4-bis(dimethylhydroxysilyl)-2-methyl-2-butene (*trans*-VIIIb), mp 62–63.

Anal. Calcd for VIIIb, $C_9H_{22}Si_2O_2$: Si, 25.7; C, 49.5; H, 10.2. Found: Si, 25.6; C, 49.6; H, 10.4.

Hydrolysis and Condensation of *trans*-1,4-Bis(dimethylmethoxysilyl)-2,3-dimethyl-2-butene.—Treatment of 5.8 g of *trans*-IVc in 50 ml of diethyl ether for 40 hr with 100 ml of water and approximately 0.25 ml of glacial acetic acid followed by evaporation of the solvent and recrystallization from benzene gave 3.5 g (68% yield) of *trans*-1,4-bis(dimethylhydroxysilyl)-2,3-dimethyl-2-butene (*trans*-VIIIc), mp 109–111°.

Anal. Calcd for *trans*-VIIIc, $C_{10}H_{24}Si_2O_2$: Si, 24.2; C, 51.7; H, 10.4. Found: Si, 24.1; C, 52.1; H, 10.6.

Registry No.—*cis*-Ia, 16054-34-5; *trans*-Ia, 16054-35-6; *cis*-Ib, 16054-36-7; *trans*-Ib, 16109-36-7; *cis*-Ic, 16109-37-8; *trans*-Ic, 16054-38-9; II, 16054-37-8; IIIa, 3528-13-0; IIIb, 16054-07-2; *cis*-IVa, 16054-08-3; *trans*-IVa, 16054-09-4; *cis*-IVb, 16054-10-7; *trans*-IVb, 16054-11-8; *trans*-IVc, 16109-38-9; Va, 16054-12-9; Vb, 3528-14-1; Vc, 16109-39-0; *trans,trans*-VI, 16109-40-3; VIIa, 16054-14-1; VIIb, 16054-15-2; VIIc, 16054-16-3; *trans*-VIIIb, 16054-17-4; *trans*-VIIIc, 16054-18-5; *cis*-IX, 16054-19-6; *trans*-X, 16054-20-9.