of 2-propanol was titrated with aqueous 1 N sodium hydroxide to a stable phenolphthalein end point, diluted with water, and extracted with ether. Evaporation of the ether and distillation gave 1.17 g. (76%) of pure styrene oxide (**11**): b.p. 79–80° (17 mm.); $[\alpha]^{17}_D$ +3.36°, $[\alpha]^{17}_{436}$ +6.61° (c 10.05, benzene).

The styrene oxide obtained in the last reaction had a rotation which was 66% of that of the starting material; this corresponds to 17% inversion and, assuming that the transformation of **14** to **11** takes place with complete inversion, **14** should be formed from **11** with 83% inversion. Furthermore, on the basis of the optical purity of the starting **11**, optically pure (+)-(S)-2-chloro-2-phenylethanol (**18**) should have at least α^{22}_D +162.4°, α^{22}_{436} +341.1° (1 dm., neat); $[\alpha]^{20}_D$ +135.1°, $[\alpha]^{20}_{436}$ +279.1° (chloroform).

The results of all reactions carried out with **11** and hydrogen chloride, in a manner similar to that described above, are summarized in Table II. The percentage of inversion in the reaction carried out in 95:5 tetrahydrofuran-water is somewhat less accurate than the other ones, as the chlorohydrin was contaminated with some 1,4-butanediol and 4-chloro-1-butanol, which were formed by cleavage of solvent molecules and could not be completely eliminated by distillation.

The Disilylation of Styrene and α-Methylstyrene. The Trapping of Short-Lived Intermediates from Alkali Metals and Aryl Olefins[1]

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Monochlorosilanes, an alkali metal, and styrene or α-methylstyrene in aprotic solvents give disilylalkanes containing one (A) or two (B) reduced olefin units, phenyl-1,2-disilylethanes, and 1,4-diphenyl-1,4-disilylbutanes from styrene or 2-phenyl-1,2-disilylpropanes and 2,5-diphenyl-2,5-disilylhexanes from α-methylstyrene. Lithium naphthalenide also serves as a source of alkali metal in this synthesis to give the above products and naphthalene. The ratio of A and B with lithium in tetrahydrofuran (THF) can be altered by varying the ratio of chlorosilane to olefin: 2:1 or higher ratios give high yields of A and equal molar amounts of chlorosilane and olefin give high yields of B. Dimethyldichlorosilane and styrene with lithium in THF give 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane and 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane at chlorosilane to olefin ratios of 1:1 and 2:1, respectively. All structural assignments are confirmed by the H^1 n.m.r. spectra and conversion to known derivatives by alkaline cleavage of benzylic carbon–silicon bonds. These data support a reaction sequence involving the trapping, *via* reaction with a chlorosilane, of organoalkali intermediates from the alkali metal and aryl olefin. In the proposed reaction scheme the monomolecular derivatives (A) and bimolecular derivatives (B) result from the trapping of monomeric and dimeric organoalkali derivatives, respectively.

The preparation of organoalkali reagents *via* the interaction of alkali metals with olefins has been the subject of many excellent reviews[2–4] since its discovery by Schlenk and Bergmann.[5] This reaction provides a convenient source of dimeric organodialkali reagents from 1,1-diaryl olefins and polymeric organodialkali

$$Ph_2C{=}CH_2 + M \xrightarrow{THF} M^{+-}Ph_2CCH_2CH_2CPh_2{}^-M^+$$

reagents from the more polymerizable monoaryl olefins, styrene and α-methylstyrene.[6,7] Even with these latter olefins, high yields of the dimeric organodialkali reagents have been obtained at low temperatures with sodium dispersions.[8]

$$PhMeC{=}CH_2 + M \xrightarrow{THF} M^{+-}(PhMeCCH_2)_x(CH_2CPhMe)_y{}^-M^+$$

In all cases the organodialkali reagents represent the reaction products of short-lived monomeric organoalkali reagents, anion radicals, formed *via* electron transfer from the alkali metal to the aryl olefin.[9]

$$M + PhCH{=}CH_2 \longrightarrow [PhCH{=}CH_2]^-M^+ \longrightarrow M^{+-}PhCHCH_2CH_2CHPh^-M^+$$

Owing to their reactivity, any synthetic procedure utilizing these monomeric or dimeric organoalkali reagents from monoaryl olefins must be based on trapping them as they are formed from the alkali metal and olefin. The chemical reduction of olefins and aromatic compounds[10] represents such a trapping system where these intermediate reagents are protonated by some protic solvent to give either monomolecular or bimolecular products.[11] Trialkylchlorosilanes

$$PhMeC{=}CH_2 + EtOH + Li \xrightarrow{THF} PhCHMe_2 + (PhMeCHCH_2)_2$$

and dialkylalkoxychlorosilanes have a high reactivity toward organoalkali reagents and a low reactivity toward alkali metals which are the main requirements for a successful trapping agent. Their utility in the trapping of a minutely low equilibrium concentration of anion radicals has been demonstrated by the synthesis of 3,6-disilyl-1,4-cyclohexadienes from benzene, trimethylchlorosilane, and lithium in THF.[12] The current study demonstrates the utility of these chlorosilanes for the trapping of anionic species from alkali metals and aryl olefins which, in the absence of trapping

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[1] Presented in part before the Organic Section at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

[2] G. E. Coates, "Organometallic Compounds," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 32–43.

[3] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

[4] K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

[5] W. Schlenk and E. Bergmann, *Ann. Chem.*, **463**, 1 (1928); *Chem. Abstr.*, **22**, 4493 (1928).

[6] M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

[7] M. Szwarc, *Macromol. Chem.*, **35**, 132 (1960).

[8] C. E. Frank, J. R. Leebrick, L. F. Moormeier, J. A. Scheben, and O. Homberg, *J. Org. Chem.*, **26**, 307 (1961).

[9] For an excellent review of the reactions of anion radicals, see B. J. McClelland, *Chem. Rev.*, **64**, 301 (1964).

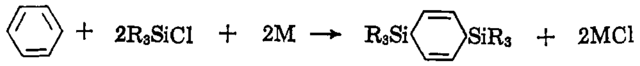
[10] For an excellent review of chemical reduction, see H. Smith, "Organic Reactions in Liquid Ammonia," Vol. I, part 2, Interscience Publishers, New York, N. Y., 1963, pp. 151–280.

[11] A 65% yield of the bimolecular reduction product, 2,5-diphenylhexane, is obtained from an equal molar mixture of α-methylstyrene and ethanol with lithium in THF: D. R. Weyenberg, *J. Org. Chem.*, **30**, 3236 (1965).

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

agent, would be present in minutely low concentration owing to rapid reaction with the olefin. A second paper in this series will describe the trapping of anionic species from 1,3-dienes.[13] The synthesis of silacyclopentanes from styrene or α-methylstyrene, dimethyldichlorosilane, and alkali metal which has been reported by Nefedov, Manakov, and Petrov[14] probably involves a similar reaction path.

This general reaction of a carbon–carbon unsaturated compound with an alkali metal in the presence of a chlorosilane to yield the alkali metal halide and products derived by the addition of two silyl groups across the carbon–carbon double bond or conjugated double-bond system will be referred to as the "disilylation reaction." Monomolecular and bimolecular disilylation will refer to reactions yielding silanes containing one and two reduced olefin units.



$$\mathrm{CH_2{=}CH{-}CH{=}CH_2 + R_3SiCl + M \longrightarrow R_3SiCH_2CH{=}CHCH_2SiR_3 + 2MCl}$$

$$\mathrm{PhCH{=}CH_2 + R_3SiCl + M \longrightarrow \begin{matrix} R_3SiCHPhCH_2SiR_3 \\ or \\ (R_3SiCHPhCH_2)_2 \end{matrix} + MCl}$$

Results

The addition of styrene or α-methylstyrene to trimethylchlorosilane and sodium or lithium in tetrahydrofuran gives, in a rapid and exothermic reaction, the alkali metal chloride and the disilylated derivatives of the olefins, 1-phenyl-1,2-bis(trimethylsilyl)ethane (I) and *dl*- and *meso*-1,4-diphenyl-1,4-bis(trimethylsilyl)butane (III) from styrene and 2-phenyl-1,2-bis(trimethylsilyl)propane (II) and *dl*- and *meso*-2,5-diphenyl-2,5-bis(trimethylsilyl)hexane (IV) from α-methylstyrene. No higher molecular weight products are obtained with either olefin. The yields of I and III normally account for 65–90% of the styrene, and v.p.c. analyses show only trace amounts of other volatile by-products in this reaction. The disilylation of α-methylstyrene produced a minor amount of 2,5-diphenyl-2-trimethylsilylhexane (V).

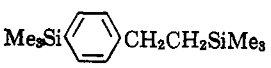
$$\mathrm{Me_3SiCl + PhRC{=}CH_2 + M \xrightarrow{THF} \underset{\begin{matrix} I,\ R \equiv H \\ II,\ R \equiv Me \end{matrix}}{Me_3SiCPhRCH_2SiMe_3} + \underset{\begin{matrix} III,\ R \equiv H \\ IV,\ R \equiv Me \end{matrix}}{[Me_3SiCPhRCH_2]_2} + MCl}$$
$$\mathrm{M \equiv Na\ or\ Li}$$

Structures I to V were assigned from their very simple H^1 n.m.r. spectra which in all cases showed the expected singlets for *Me₃Si* and multiplets for the remaining aliphatic hydrogens. These structural assignments were confirmed by the nearly quantitative conversion of I, III, and IV to known structures by the base-catalyzed cleavage of the benzylic carbon–silicon bonds in these compounds. The α-arylalkyl group is cleaved from silicon by alcoholic alkali, whereas other alkyl and aryl groups are unaffected by this reagent.[15] Partial desilylation of IV provided an authentic sample of V.

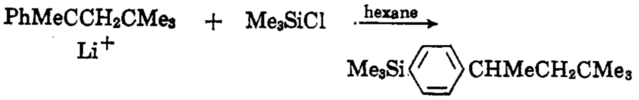
$$\mathrm{\underset{I}{Me_3SiCHPhCH_2SiMe_3} \xrightarrow[ROH]{KOH} Me_3SiCH_2CH_2Ph}$$

$$\mathrm{III\ or\ IV \xrightarrow[ROH]{KOH} RPhCHCH_2CH_2CHRPh}$$
$$\mathrm{R \equiv H\ or\ Me}$$

Although lithium naphthalenide reacts rapidly with chlorosilanes to give disilyldihydronaphthalenes,[16] it serves as a source of alkali metal in the disilylation of styrene. Thus, the addition of lithium naphthalenide to styrene and trimethylchlorosilane in tetrahydrofuran gave I and III and recovered naphthalene. The disilylation of styrene with trimethylchlorosilane proceeds slowly with bulk sodium in ether at 25° and rapidly with a sodium dispersion in benzene at 70° to give over 50% yields of III and minor quantities of I. In the latter reaction, v.p.c. analyses showed several by-products which were not present when THF was used as the solvent. The major by-product, which accounted for approximately 10% of the initial styrene, was 1-(4-trimethylsilylphenyl)-2-trimethylsilylethane (VI). This structure was assigned from its H^1 n.m.r. spectrum showing an AB pattern for the four aromatic hydrogens and separate multiplets for the two different sets of methylene hydrogens. A similar abnormal coupling of a benzylic organoalkali reagent with trimethylchlorosilane to give the *para* rather than the expected α-silyl derivative was noted recently in our laboratory.[17]



VI



The ratio of monomolecular to bimolecular disilylation varies greatly with the conditions under which these syntheses are conducted. The variation of product ratio with ratio of silane to olefin with lithium in tetrahydrofuran was particularly dramatic and provides a simple means of directing the course of these reactions to nearly quantitative yields of either monomolecular or bimolecular derivative. As shown in Table I, a 1:1 ratio of silane to olefin greatly favored bimolecular disilylation, whereas a 2:1 or higher ratio of silane to olefin favors monomolecular disilylation.

The disilylation reaction appears to be general for monochlorosilanes with dimethylchlorosilane or dimethylmethoxychlorosilane, sodium, and styrene giving the expected dimethylsilyl (VII) and dimethylmethoxysilyl derivatives (VIII and IX). Bimolecular products

$$\mathrm{Me_2HSiCl + PhCH{=}CH_2 + Na \xrightarrow{THF} \underset{VII}{HMe_2SiCHPhCH_2SiMe_2H} + NaCl}$$

$$\mathrm{Me_2Si(OMe)Cl + PhCH{=}CH_2 + Na \xrightarrow{THF} \underset{VIII}{(MeO)Me_2SiCHPhCH_2SiMe_2(OMe)} + \underset{IX}{[(MeO)Me_2SiCHPhCH_2]_2}}$$

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[13] D. R. Weyenberg, L. H. Toporcer, and L. E. Nelson, to be published.

[14] O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1717 (1961); *Chem. Abstr.*, **56**, 3504*a* (1962). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1228 (1962); *Chem. Abstr.*, **58**, 5713*d* (1963); *Dokl. Akad. Nauk SSSR*, **154**, 395 (1964); *Chem. Abstr.*, **60**, 9304*g* (1964).

[15] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, Chapter 4.

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

[17] A. E. Bey and D. R. Weyenberg, *ibid.*, **30**, 2436 (1965).

TABLE I

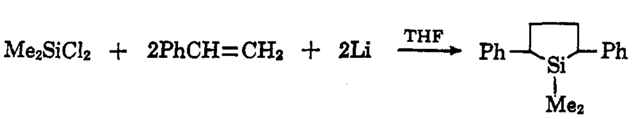
DISILYLATION OF STYRENE AND α-METHYLSTYRENE WITH TRIMETHYLCHLOROSILANE AND LITHIUM IN THF[a]

Olefin	Reagent ratio		Product ratio[b]	
	Olefin	Chlorosilane	Monomolecular	Bimolecular
Styrene	1	4	30 (76)	1
	1	2	8	1
	1	1	1	30 (81)
α-Methylstyrene	1	4	(75)	0
	1	1	1	7 (50)

[a] Procedure is described in bimolecular disilylation of styrene with trimethylchlorosilane in the experimental section. [b] Product ratios are v.p.c. area ratios with thermal conductivity detectors. Yields based on olefins which were isolated from preparative scale experiments are given in parentheses.

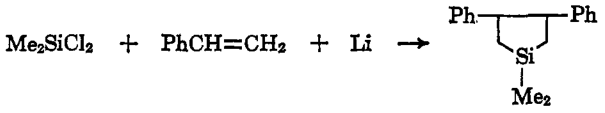
were present in the former reaction but were not isolated and characterized. The latter reaction gave a 20% yield of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X). Although chlorine is normally displaced from silicon in preference to an alkoxyl group by an organoalkali reagent, these data suggest that the intramolecular displacement of alkoxyl competes with the intermolecular displacement of chlorine when the silicon atom is separated from the organoalkali center by four atoms.

High yields of X were obtained under the conditions (1:1 ratio of styrene to equivalent of halosilane) which favored bimolecular disilylation with trimethylchlorosilane. A 40% yield was obtained with sodium in THF. The three singlets for *MeSi* in the H^1 n.m.r. spectrum of X have been interpreted as arising from *cis* (two *MeSi* absorptions) and *trans* (one *MeSi* absorption) isomers.[18] This assignment was confirmed by partial separation of these isomers. These structural assignments were confirmed by conversion of a mixture of the *cis* and *trans* isomers, in 88% yield, to 1,4-diphenylbutane by treatment with alcoholic alkali. The recent conversion of X to 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene[18] provides further confirmation of these assignments. It is apparent upon comparison of physical properties that the silacyclopentane prepared by Nefedov, Manakov, and Petrov[14] by nearly identical procedures is also the 2,5-diphenyl derivative.



X (71%)

Changing the ratio of dimethyldichlorosilane and styrene toward that favoring a monomolecular disilylation gave a complex mixture of products containing no X. The major volatile product was 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane (XI). The assignment of the phenyl groups to the 3 and 4 positions was confirmed by the complete recovery of this compound after treatment under alkaline conditions which gave quantitative desilylation of X.



XI

Discussion

The simplest and most general reaction scheme which correlates all of the data on the disilylation reaction involves the trapping, *via* reaction with a chlorosilane, of anionic species formed from the carbon-carbon unsaturated organic compound and alkali metal. The similarity between the products of this reaction and those of the chemical reduction of aryl olefins[10] is in complete accord with this reaction path. Particularly, the structures from the bimolecular disilylation of styrene and α-methylstyrene which involve exclusive coupling of the two terminal carbon atoms of the olefin are in accord with the known structure of the dimeric anionic species from these olefins.[8,10,11] The complete absence of products containing more than two reduced olefin units is consistent with a recent study of the relative reactivity of organolithium reagents with trimethylchlorosilane and styrene.[19] Also, the absence of polymeric structures shows that the reduction of any intermediate radicals under these conditions by electron transfer from the alkali metal or an anion radical is rapid relative to the radical-catalyzed polymerization of the olefins.

This synthesis normally involves reaction at a metal surface. The use of lithium naphthalenide as a "soluble alkali metal" shows, however, that the above conclusions are not limited to reactions at a metal interface. This example again demonstrates the speed of the electron-transfer reactions relative to the other reactions occurring in these systems.

An alternative scheme, involving initial reaction between the chlorosilane and alkali metal, would lead

$$\mathrm{Me_3SiCl + M \longrightarrow \underset{A}{Me_3SiM} + MCl}$$

$$\mathrm{A + PhCH{=}CH_2 \longrightarrow \underset{B}{Me_3SiCH_2CHPhM}}$$

$$\mathrm{B + PhCH{=}CH_2 \longrightarrow I}$$

to the monomolecular disilylation products but not to the bimolecular disilylation products. Furthermore, the nonreactivity of trimethylchlorosilane toward lithium or sodium under the conditions of these reactions is not in accord with such a scheme. The applicability of this scheme with dimethyldichlorosilane,[20] which reacts rapidly with lithium in tetrahydrofuran at 25°, is also open to question.

Scheme I summarizes some of the possible routes to monomolecular and bimolecular products *via* the

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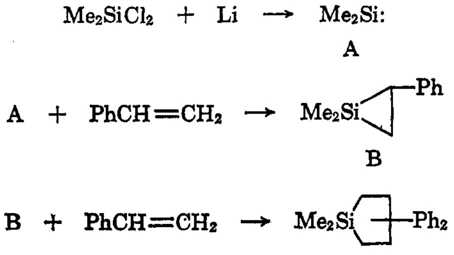
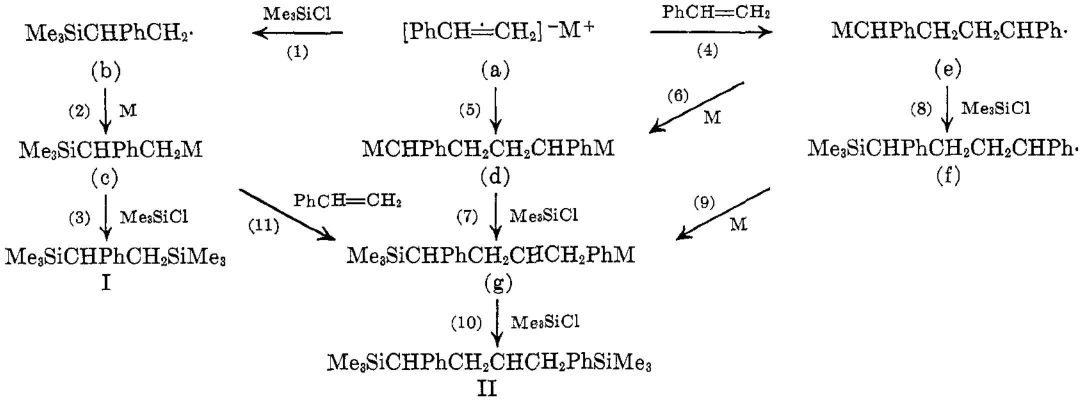
[18] H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 291 (1964).

[19] Although primary alkyllithium reagents react more rapidly with styrene than with trimethylchlorosilane, benzylic organolithium reagents react exclusively with the trimethylchlorosilane.[17]

[20] Nefedov, Manakov, and Petrov[14] suggested an initial reaction between chlorosilane and alkali metal to explain their synthesis of silacyclopentane.



SCHEME I



trapping of organoalkali species for styrene and trimethylchlorosilane. The monomeric organodimetallic reagent,[21] MCH_2CHPhM, is not included in this scheme, nor are the possible reactions of the silylalkyl radical (b) other than reduction (step 2) included for reasons given above.

The reaction sequence proposed for the monomolecular disilylation (steps 1, 2, and 3) is thus the sequence of reaction with a chlorosilane, reduction of the resulting radical, and a second reaction with the chlorosilane which has been suggested for the disilylation of benzene[12] and naphthalene[16] and which is completely analogous to the currently accepted general scheme for the chemical reduction of olefins.[10] The choice of the carbon α to the aryl group for the initial attachment of the silyl group is quite arbitrary for the alternative would also lead to I.

Two general routes to the bimolecular derivatives are possible. The first route, *via* the trapping of a monomeric organoalkali reagent and subsequent reaction of the silylalkyl alkali with olefin (step 11), is a possibility only if the first silicon is attached to the carbon α to the phenyl group. The second route involves the trapping of a dimeric organoalkali reagent (d or e). The former route is quite possible for styrene which is more reactive than trimethylchlorosilane toward primary alkyllithium reagents, but this route cannot explain the bimolecular derivatives from α-methylstyrene which is much less reactive than trimethylchlorosilane toward alkyllithium reagents.[17] Thus, because of the similar behavior of styrene and α-methylstyrene in this synthesis, we favor the latter reaction path where the ratio of monomolecular to bimolecular disilylation is determined by whether a monomeric or dimeric organoalkali reagent is intercepted by the chlorosilane. The dimeric species could be the dimeric radical anion (e) or dianion (d). The large effect of the olefin to silane ratio in directing the course of this reaction toward monomolecular or bimolecular disilylation may be the result of some kinetic scheme controlled by diffusion of reactants and intermediate species to and from the lithium surface.

The disilylation with dimethyldichlorosilane again emphasizes the effect of reagent concentration on the course of this reaction and adds convincing support to the above argument that monomolecular and bimolecular derivatives are not derived from a common silyl intermediate. The high yield of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X) under conditions which gave bimolecular disilylation with monochlorosilanes shows the similarity of the reactions with the mono- and dichlorosilanes. As these are the conditions used by Nefedov, Manakov, and Petrov for the preparation of silacyclopentanes, their original proposal that this synthesis represents the trapping of dimethylsilane *via* silacyclopropanes is quite unlikely.[20] However, under slightly modified reaction conditions the situation becomes more complex. The absence of X and formation of the 3,4-diphenylsilacyclopentane (XI) at higher ratios of chlorosilane to styrene indicate a complete change in reaction path. Although this latter reaction would now be more consistent with an initial reaction between chlorosilane and lithium,[20] it would be equally consistent with the above path for the monomolecular disilylation which could also lead to anomalous products *via* silacyclopropanes.[23] Although further investigation is necessary to establish the nature of the intermediates in these reactions, these data show that isolation of sila- and disilacycloalkanes from the reaction of olefins, alkali metals, and dichlorosilanes is of limited value in establishing the intermediacy of divalent silicon intermediates.[24]

Experimental Section

All reactions involving alkali metals or organometallic reagents were conducted under nitrogen in flasks fitted with stirrer, reflux condenser, and external cooling baths. Melting points and boiling points are uncorrected. V.p.c. traces were obtained on an F and M Model 300 instrument with an 8 ft × 0.25 in. column packed with a mixture of Dow Corning FS 60® and Dow Corning 200 Fluid® on Chromosorb W. The H^1 n.m.r. spectra were obtained with a Varian Associates A-60 spectrometer with tetramethylsilane as an internal standard.

Disilylation of Styrene with Trimethylchlorosilane. Monomolecular Disilylation. Compound I.—A mixture of 86.7 g. (0.8 mole) of trimethylchlorosilane, 20.8 g. (0.2 mole) of styrene, 3.47 g. (0.50 g.-atom) of lithium, and 200 ml. of THF was stirred for 4 days at 20–30°. Filtration and fractional distillation gave 38 g. (76%) of phenyl-1,2-bis(trimethylsilyl)ethane (I), b.p. 93–97° (4–5 mm.), $n^{26.5}D$ 1.4882, and 11 g. of residue.

Anal. Calcd. for $C_{14}H_{26}Si_2$: C, 67.1; H, 10.5; Si, 22.4. Found: C, 67.1; H, 10.5; Si, 22.8.

Bimolecular Disilylation. Compound III.—A mixture of 10.9 g. (0.1 mole) of trimethylchlorosilane, 10.4 g. (0.1 mole) of

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[21] The data of Lee, Smid, and Szwarc[22] showing the dimeric anion radical (e) as an intermediate in the reaction of sodium and α-methylstyrene in THF provides some experimental evidence for eliminating this reagent from consideration.

[22] C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **66**, 904 (1962).

[23] Silacyclopropanes have been shown to be unstable: P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

[24] O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, **76**, 270 (1964).

styrene, 1.4 g. (0.2 g.-atom) of lithium wire, and 150 ml. of THF was stirred for 5 hr. at 0–10° and at 25° overnight. Analysis by v.p.c. showed a 1:30 ratio of I to III. Filtration and distillation gave 14.3 g. (81%) of *dl*- and *meso*-1,4-diphenyl-1,4-bis(trimethylsilyl)butane (III), b.p. 160–170° (1.5 mm.), crystalline solid. The *dl* and *meso* isomers (IIIA and IIIB) were separated by fractional crystallization from methanol.

IIIA had m.p. 50.5–52.0°.

Anal. Calcd. for $C_{22}H_{34}Si_2$: C, 74.5; H, 9.7; Si, 15.8. Found: C, 73.9; H, 9.7; Si, 16.0.

IIIB had m.p. 106.5–108°.

Anal. Found: C, 73.9; H, 9.8; Si, 15.9.

The H^1 n.m.r. patterns showed singlets for SiCH_3 at τ 10.15 for IIIA and 10.19 for IIIB, complex patterns for CH_2 and CH at 8.0–8.3, and C_{ar}–H at 2.8–2.9 in ratios of 18:6:10.

With Sodium in THF. Compounds I and III. A mixture of 104 g. (1 mole) of styrene and 217 g. (2 moles) of trimethylchlorosilane was added during 45 min. to 46 g. (2 g.-atom) of sodium (approximately 1-cm.^{3} pieces) and 50 g. of rock salt (to abrade the sodium surface during the reaction) in 300 ml. of THF. The exothermic reaction was maintained at 30–40° by external cooling. After stirring for an additional 4 days, filtration, extraction with water, and fractional distillation gave 86 g. (34%) of I, 80 g. (45%) of III, and 6 g. of residue.

With Sodium in Benzene. Compounds I, III, and VI.—The addition of a mixture of 26 g. (0.25 mole) of styrene and 54.3 g. (0.5 mole) of trimethylchlorosilane during 11 min. to 12.5 g. (0.53 g.-atom) of sodium (added as a dispersion in paraffin wax) in 110 ml. of benzene at 65–75° resulted in an exothermic reaction. A v.p.c. analysis after 15 min. showed an approximately 1:1:7 ratio of I to 1-trimethylsilyl-2(4-trimethylsilylphenyl)ethane (VI) to III. Filtration and distillation gave 24 g. (54%) of III.

Compound VI, separated by v.p.c., was identified from its H^1 n.m.r. pattern showing SiCH_3 singlets at τ 10.0 and 9.86, a SiCH_2 multiplet at 9.15, a PhCH_2 multiplet at 7.42, and an AB pattern for C_{ar}–H at 2.82 in a ratio of 18:2:2:4.

With Lithium Naphthalenide. Compounds I and III.—A freshly prepared 1.0 *M* solution of lithium naphthalenide in THF (80 ml., 0.08 equiv., prepared from lithium wire and 10% excess naphthalene) was added during 45 min. at 0–10° to 10.4 g. (0.1 mole) of styrene and 10.9 g. (0.1 mole) of trimethylchlorosilane. The green color of the naphthalenide solution disappeared immediately upon contact with the other reagents. A v.p.c. analysis showed unreacted styrene, naphthalene, a 1:3 mole ratio of I to III, and traces of bis(trimethylsilyl)dihydronaphthalene.[16] Distillation of the products from similar experiments confirmed the absence of nonvolatile products.

Doubling the amount of trimethylchlorosilane in the above procedure (2:1 molar ratio of chlorosilane to styrene) gave a 3:1 ratio of I to III.

Disilylation of Styrene with Dimethylchlorosilane. Compound VII.—A mixture of 199 g. (2 moles) of dimethylchlorosilane and 104 g. (1.0 mole) of styrene was added during 5 hr. to 46 g. (2 g.-atom) of sodium (approximately 1-cm.^{3} pieces) and 50 g. of rock salt in 300 ml. of THF. An exothermic reaction occurred on completion of the addition, which required extensive cooling to maintain a temperature of 40–50°. Filtration and fractional distillation after 24 hr. gave 56 g. (25%) of 1-phenyl-1,2-bis(dimethylsilyl)ethane (VII), b.p. 88–90° (4–5 mm.), n^{26}D 1.5000, and 26 g. of residue.

Anal. Calcd. for $C_{12}H_{22}Si_2$: C, 64.7; H, 10.0; Si, 25.3. Found: C, 64.3; H, 10.1; Si, 25.0.

The H^1 n.m.r. spectrum showed a 12:2:1:2:5 ratio of SiCH_3:CH_2:CH:SiH:C_{ar}–H.

Disilylation of Styrene with Dimethylmethoxychlorosilane. Compounds VIII, IX, and X.—Styrene (2 moles) was added during 2 hr. to 506 g. (4 moles) of dimethylmethoxychlorosilane and 92 g. (4 g.-atom) of sodium (1-cm.^{3} pieces) in 750 ml. of THF at 20–30°. Filtration and fractional distillation after 48 hr. gave 114 g. (20%) of 1-phenyl-1,2-bis(dimethylmethoxysilyl)ethane (VIII), b.p. 124–126° (6–7 mm.), n^{25}D 1.4950–4958 (*Anal.* Calcd. for $C_{14}H_{26}O_2Si_2$: Si, 19.9. Found: Si, 19.8.) 63.6 g. (24%) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X), and 69.5 g. (18%) of 1,4-bis(dimethylsilyl)-1,4-diphenylbutane, b.p. 145–148° (0.3 mm.), crystalline solid (*Anal.* Calcd. for $C_{22}H_{34}O_2Si_2$: C, 68.3; H, 8.9; Si, 14.5. Found: C, 68.3; H, 8.8; Si, 15.0.).

Disilylation of Styrene with Dimethyldichlorosilane. 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentane (X).—A solution of 10.4 g. (0.1 mole) of styrene and 6.45 g. (0.05 mole) of dimethyldichlorosilane in 50 ml. of THF was added during 3 hr. to 1.4 g. (0.20 g.-atom) of lithium in 100 ml. of THF at 0–10°. Analysis by v.p.c. showed a single product, X. Distillation after an additional 18 hr. gave 9 g. (68%) of X, b.p. 137-150° (0.3-0.4 mm.), n^{25}D 1.5740, single peak by v.p.c. on silicone gum, 2 peaks on toluene adduct of bis(chloromethyl)diphenyl oxide.

Anal. Calcd. for $C_{18}H_{22}Si$: C, 81.2; H, 8.3; Si, 10.5. Found: C, 80.7, 80.4; H, 8.2, 8.7; Si, 10.4, 10.6.

The H^1 n.m.r. spectrum showed SiCH_3 singlets at τ 10.64 and 9.71 for the *cis* isomer and 10.14 for the *trans* isomer, a complex multiplet for CH_2 and CH at *ca.* 7.7, and C_{ar}–H at 2.9. These assignments of the SiCH_3 absorptions were confirmed by partial separation of the isomers by chromatography on 60-80-mesh charcoal with hexane–benzene mixtures.

A 71% yield of X was obtained by rapid mixing of the above reagents and stirring at 0–10° for 24 hr.

A 41% yield of X was obtained by the slow addition of a 2:1 molar ratio of styrene and dimethyldichlorosilane to sodium in THF.

1,1-Dimethyl-3,4-diphenyl-1-silacyclopentane (XI).—A solution of 10.4 g. (0.1 mole) of styrene and 12.9 g. (0.1 mole) of dimethyldichlorosilane in 50 ml. of THF was added during 4.5 hours to 1.4 g. (0.2 g.-atom) of lithium in 100 ml. of THF at 0–10°. A v.p.c. analysis after 24 hr. showed one major volatile product, XI, and no X. Filtration, rapid distillation to 200° at 0.2 mm., and recrystallization of the approximately 10 g. of crystalline distillate (75% XI by v.p.c.) from methanol gave 1.4 g. (10.6%) of XI, m.p. 92–95°.

Anal. Calcd. for $C_{18}H_{22}Si$: C, 81.2; H, 8.3; Si, 10.5. Found: C, 80.5; H, 8.2; Si, 10.7.

The H^1 n.m.r. spectrum showed a SiCH_3 singlet at τ 9.73, a SiCH_2 multiplet at 8.8, a PhCH multiplet at 7.1, and C_{ar}–H at 2.9 in a ratio of 6:4:2:10.

A duplication of the above experiment with molar quantities of silane and olefin gave 40 g. (30%) of crude XI.

Disilylation of α-Methylstyrene. Monomolecular Disilylation. Compound II.—A mixture of 11.8 g. (0.1 mole) of α-methylstyrene and 43.4 g. (0.4 mole) of trimethylchlorosilane was added rapidly to 2.8 g. (0.4 g.-atom) of lithium in 120 ml. of THF. After stirring for 15 min. at 0–10°, analysis by v.p.c. showed no unreacted olefin and a single product, II. Filtration and fractional distillation gave 19.7 g. (75% yield) of 2-phenyl-1,2-bis(trimethylsilyl)propane (II), b.p. 123° (9 mm.), n^{26}D 1.5011, and less than 1 g. of residue.

Anal. Calcd. for $C_{15}H_{28}Si_2$: C, 68.2; H, 10.65; Si, 21.2. Found: C, 67.8; H, 11.08; Si, 21.3.

The H^1 n.m.r. spectrum shows the expected singlets for SiCH_3 at τ 10.13 and 10.22, a singlet for C–CH_3 at 8.59, C_{ar}–H at 2.85, and an AB pattern for CH_2 at τ_A 8.49 and τ_B 9.16 ($J_{AB} = 15$ c.p.s.).

A 50% yield of XI was obtained from the above ratio of silane and olefin with sodium (1-cm.^{3} pieces) in THF after stirring for 24 hr. at 20–35°.

Bimolecular Disilylation. Compounds IV and V.—The rapid addition of a mixture of 21.7 g. (0.2 mole) of trimethylchlorosilane and 23.6 g. (0.2 mole) of α-methylstyrene to 4.2 g. (0.6 g.-atom) of lithium in 225 ml. of THF gave a mildly exothermic reaction. After 30 min. and approximately 80% consumption of olefin (by v.p.c.) the solution became deep red, indicating complete consumption of chlorosilane. The color disappeared upon addition of an additional 20 g. of trimethylchlorosilane. A v.p.c. analysis showed a 0:1:1:6 ratio of olefin to II to V to IV. Filtration and fractional distillation gave 22.5 g. (50%) of *dl*- and *meso*-2,5-diphenyl-2,5-bis(trimethylsilyl)hexane (IV), b.p. 190° (*ca.* 1 mm.), crystalline solid (contains *ca.* 15% V by v.p.c.), and 9.2 g. of residue. The two isomers of IV were separated by fractional crystallization from hexane and methanol

IVA had m.p. 181–182.5°.

Anal. Calcd. for $C_{24}H_{38}Si_2$: C, 75.3; H, 10.0; Si, 14.7. Found: C, 75.9; H, 10.2; Si, 14.7.

IVB had m.p. 86–89°.

Anal. Found: C, 75.1; H, 10.1; Si, 14.9.

The n.m.r. spectra of IVA and B showed the expected singlets for SiCH_3 and C–CH_3 at τ 10.23 and 8.65 and multiplets for C_{ar}–H at 2.6–3.2. The spectra differed only in the splitting patterns for the CH_2 protons at τ 7.3–8.3.

A sample of 2,5-diphenyl-2-trimethylsilylhexane (V) was isolated by v.p.c. The H^1 n.m.r. spectrum showed a singlet for SiCH_3 at τ 10.20, a complex pattern for CH_2 and CCH_3 at 8.4–8.9, a multiplet for CH at 7.5, and C_{ar}–H at 2.96 in a ratio of 9:10:1:10. The spectrum was identical with that of an authentic sample separated by v.p.c. from the partial alkaline desilylation of IV.

Alkaline Desilylations. Phenyl-1,2-bis(trimethylsilyl)ethane (I).—Heating 27 g. of I, 90 ml. of ethanol, 6 ml. of water, and 60 g. of potassium hydroxide at reflux (115°) for 24 hr., dilution with water, extraction with ether, and fractional distillation gave 17 g. (88.5%) of 1-phenyl-2-trimethylsilylethane: b.p. 117° (40 mm.), $n^{25}D$ 1.4840; lit.[25] b.p. 117° (40 mm.), $n^{25}D$ 1.4840. The infrared and H^1 n.m.r. spectra were identical with that of an authentic sample.[25]

1,4-Diphenyl-1,4-bis(trimethylsilyl)butane (III).—Heating 5 g. of III, 60 ml. of ethanol, 4 ml. of water, and 40 g. of potassium hydroxide at reflux for 5 days, dilution with water, and recrystallization from methanol gave 2.2 g. (74%) and 2.3 g. (78%) of 1,4-diphenylbutane, m.p. 53°, lit.[26] 52.3° (infrared spectrum identical with reported spectrum[27]), from IIIA and IIIB, respectively.

2,5-Diphenyl-2,5-bis(trimethylsilyl)hexane (IV).—A 0.6-g. sample of IV, 6 g. of ethanol, 1 g. of water, and 1 g. of potassium hydroxide were heated in a Parr bomb at 200° for 16 hr. The cleavage product was isolated by preparative v.p.c. after diluting with pentane and extraction with water. Isomers IVA and IVB gave 0.290 (78%) and 0.340 g. (92%), respectively, of 2,5-diphenylhexane, $n^{25}D$ 1.5392. The infrared and H^1 n.m.r. spectra were identical with those of an authentic mixture of *dl* and *meso* isomers.[11] The H^1 n.m.r. spectrum shows a doublet for CH_3 at τ 8.86, a multiplet for CH_2 at 8.55, a multiplet for CH at 7.46, and C_{ar}–H at 2.95 in a ratio of 3:2:1:5.

Heating the above samples for 16 hr. at 150° gave partial desilylation of IV to a mixture of V and 2,5-diphenylhexane.

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentane (X).—Heating 2.0 g. of X, 6 g. of ethanol, 1 g. of water, and 2 g. of potassium hydroxide in a Parr bomb at 100° for 24 hr., dilution with water, and recrystallization from methanol gave 1.38 g. (88%) of 1,4-diphenylbutane.

1,1-Dimethyl-3,4-diphenyl-1-silacyclopentane (XI).—Treatment of 2 g. of XI by the above procedure gave 1.7 g. of recovered XI. A v.p.c. analysis prior to work-up showed no trace of cleavage products.

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Synthesis of Substituted β- and γ-Lactams

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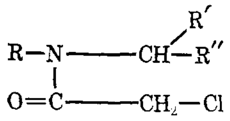
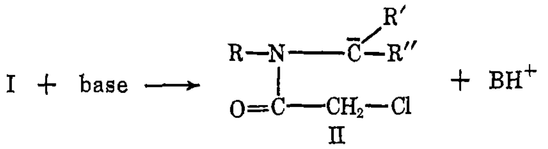
The cyclization of N-substituted diethyl chloroacetamidomalonates, ethyl α-chloroacetamidophenylacetates, and diethyl ω-bromopropionamidomalonates to the corresponding substituted β- and γ-lactams has been achieved in high yields using a quaternary ammonium hydroxide type of anion-exchange resin, Amberlite IRA-400 (OH^-), as catalyst.

Interest in the synthesis and chemistry of β-lactams has been greatly accelerated since the discovery of penicillin in 1929. Several[1] special and unique methods were developed to build up this cyclic amide which is very susceptible to reactions involving the carbonyl group. Among these, the Sheehan and Bose[2] synthesis appears to be most general in nature, as the yields reported were very high in all the cases. The method depends on a base-catalyzed ring closure of N-substituted diethyl chloroacetamidomalonates. It was shown that this intramolecular alkylation could be carried out in presence of such a weak base as triethylamine. The method, though novel, suffers from the fact that all the β-lactams possess one or two carbethoxy groups in position 4. The work carried out in this laboratory (to be published later) has shown the effectiveness of alcoholic potassium hydroxide in the intramolecular alkylation of compounds (I) in which the methine hydrogen is activated by groups other than two carbethoxy functions. A carbanion (II) is formed as an intermediate in all the cases, which undergoes cyclization with the elimination of halide ion.



Ia, R′ = H; R″ = COC_6H_5
b, R′ = C_6H_5; R″ = $COOC_2H_5$



II

Ion-exchange resins are finding increasing importance in a wide variety of organic reactions.[3] Resins have been shown to be excellent catalysts in reactions such as cyanohydrin formation; aldol, Knoevenagel, and Michael condensations[4,5]; the preparation of heterocyclic ketols[6]; the synthesis of nitriles[7] from appropriate benzylhalides; and C-acylation of phenols.[8]

Shimo and Wakamatsu[9] have reported the alkylation of various active methylene group containing compounds like ethyl malonate, cyanoacetic ester, and cyanoacetamide with various alkyl halides in the presence of an anion-exchange resin, Amberlite IRA-400 (OH^-). However, utilization of an anion-exchange resin for the intramolecular alkylation leading to a ring closure has not been reported so far. The success achieved with anion-exchange resin in various alkylations encouraged us to synthesize β-lactams and γ-lactams according to Scheme I.

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