Conclusion

In this paper we have reported the synthetic, spectroscopic, and structural investigations of several Pt(II)-substituted indole derivatives. These species were obtained by intramolecular cyclization reactions of an electrophilic isocyanide carbon with the adjacent carbanion of an ylide group generated by nucleophilic attack of a base on the acidic methylene protons of either the free or metal-coordinated isocyanides o-($BF_4^-R_3P^+$–CH_2)C_6H_4NC. When such ligands are coordinated to Pt(II), these reactions are also metal-promoted since Pt acts as an activating agent for the isocyano function, thus making possible the subsequent action of the otherwise uneffective mild base NEt_3. Furthermore, the Pt(II) fragment can be selectively placed in the 1- or 2-position of the indole ring depending on whether the nucleophilic attack of the base on the $-CH_2PR_3^+$ group precedes or follows, respectively, the coordination of the isocyano function to the metal. The heterodifunctional ligands o-(XCH_2)C_6H_4NC (X = organic or organometallic functionality) are being currently investigated with the aim of effecting intramolecular attack at the coordinated isocyanide by changing X or the isocyanide-bound metal. In particular, when X is a metal fragment,[9] such reactions should lead to novel homo- or heterobinuclear systems with the two metal centers lying in close proximity via base-promoted generation of the metal-substituted carbanion $X\ddot{C}H^-$–, which subsequently attacks the appropriately activated metal-coordinated isocyanide. The possibility of generating a transition-metal-substituted carbanion has been recently demonstrated.[49]

Acknowledgment. R.A.M. thanks CNR (Rome) for an operating grant based on a U.S.–Italy Cooperative Science Program and Prof. R. J. Angelici (Department of Chemistry, Iowa State University) for helpful discussions during a visit to I.S.U. related to this program. R.A.M. is grateful to Dr. L. Weber (Universität Essen-GHS, Chemie) for correspondence regarding *P*-ylide–isocyanide transition-metal chemistry. Technical assistance by Mr. A. Berton (CNR, Padua) is also acknowledged.

Registry No. **1**, 104241-66-9; **2**, 103925-31-1; **3**, 104241-68-1; **4**, 104241-70-5; **5**, 104241-72-7; **6**, 104267-45-0; **7**, 104267-47-2; **8**, 104241-74-9; **9**, 104267-49-4; **10**, 103925-21-9; **11**, 104241-76-1; **12**, 104241-78-3; **13**, 104241-80-7; **14**, 104241-82-9; **15**, 104241-84-1; L^1, 104292-21-9; L^2, 103925-27-5; L^3, 104292-23-1; L^4, 104292-25-3; L^5, 104292-28-6; AFA, 2258-42-6; *trans*-[$(PCy_3)_2Pt(CNC_6H_4$-o-$CH_3)$]BF_4, 104292-27-5; *cis*-{$(PPh_3)_2Pt[N(o\text{-}C_6H_4)C(PPh_3)C(H)]Cl$}$BF_4$, 104321-47-3; *trans*-$(PPh_3)Pt[N(o\text{-}C_6H_4)C(PPh_3)C(H)]Cl_2$, 104241-85-2; *cis*-$(PPh_3)_2PtCl_2$, 15604-36-1; *trans*-[$(PMePh_2)_2Pt(CH_3)Cl$], 24833-61-2; *cis*-$(Ph_2PCH{=}CHPPh_2)PtCl_2$, 37410-35-8; *cis*-$[(PPh_3)_2PtCl]_2(BF_4)_2$, 19394-83-3; *cis*-$[(PPh_3)PtCl_2]_2$, 15349-80-1; *trans*-$[(PMe_2Ph)_2Pt(CH_3)Cl]$, 24833-58-7; *trans*-$[(PCy_3)_2Pt(CH_3)Cl]$, 98839-59-9; o-$(HOCH_2)C_6H_4NHCHO$, 104292-17-3; o-$(ClCH_2)C_6H_4NHCHO$, 104292-18-4; o-$(ClCH_2)C_6H_4NC$, 88644-59-1; o-$(Cl^-Me_3P^+CH_2)C_6H_4NC$, 104322-35-2; o-$(Cl^-Me_2PhP^+CH_2)C_6H_4NC$, 103697-57-0; o-$(Br^-Ph_3P^+CH_2)C_6H_4NC$, 104322-36-3; o-$(Br^-Ph_2MeP^+CH_2)C_6H_4NC$, 104292-19-5; o-aminobenzyl alcohol, 5344-90-1.

Supplementary Material Available: Listings of hydrogen atom coordinates, bond distances and angles, and thermal parameters (17 pages); a list of observed and calculated structural factors (23 pages). Ordering information is given on any current masthead page.

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Preparation and Reactions of (*E*)-α-Lithio-α-(methyldiphenylsilyl)alkenes†

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Received January 28, 1986

Alkylation of (dibromomethyl)methyldiphenylsilane and thermolysis of the resulting (α,α-dibromoalkyl)silanes in DMF provides the (*Z*)-1-bromo-1-(methyldiphenylsilyl)alkenes in good yield. These have been converted to their corresponding lithium reagents by metal–halogen exchange. The stereointegrity of these vinyllithium reagents was found to be excellent at temperatures below 0 °C. These lithium reagents were reacted with alkyl halides, group IV (14) chlorides, aldehydes, benzoyl chloride, and acetic anhydride. The synthetic potential of these systems was demonstrated by the preparation of (*Z*)-heneicosene, the pheromone of the house fly (musca domestica), and of 1-phenyl-1,2-butadiene. The Grignard reagents of the vinyl bromides were also studied, but to a lesser extent.

Introduction

In conjuction with an interest in investigating the potential of organosilicons optically active at silicon in enantioselective synthesis, studies which currently involve the 1-naphthylphenylmethylsilyl group,[2] we have been carrying out several studies with the diphenylmethylsilyl group, which serves as a reasonable, readily available model for the 1-naphthylphenylmethylsilyl group. We wish to report herein on the preparation of and some of the

† Dedicated to Dr. George Zweifel on the occasion of his 60th birthday.

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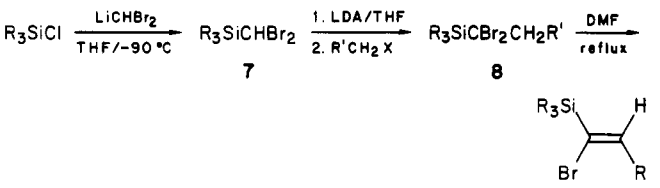
0276-7333/86/2305-2274$01.50/0

Table I. Preparation of 7, 1, and 2

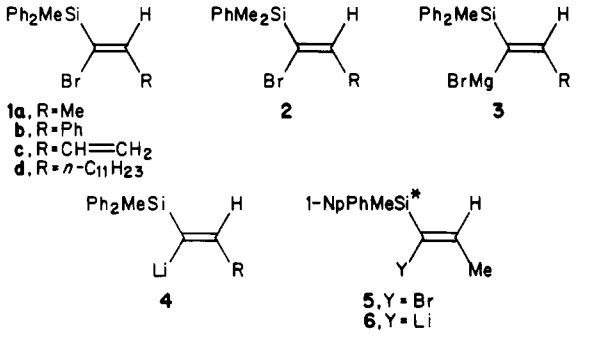
entry	R_3Si	R^1CH_2X	% yield 7[a]	% yield 1 or 2[a]	Z:E ratio[b]
1	Ph_2MeSi	C_2H_5I	84	86	98:2
2	Ph_2MeSi	n-C_4H_9I	82	71	98:2
3	Ph_2MeSi	n-$C_{12}H_{23}I$	79	78[c]	95:5
4	Ph_2MeSi	C_3H_5Br	78	41	95:5
5	$PhMe_2Si$	C_2H_5I	77	54	91:9
6	$PhMe_2Si$	C_3H_5Br	81	95	66:34
7	$PhMe_2Si$	$PhCH_2Br$	58	81	98:2

[a] Isolated yields. Products purified by silica gel chromatography or crystallization. [b] Ratio determined by capillary GLC on a 25-m FFAP or 25-m SE-30 column (1%) or by ^1H NMR spectroscopy (5%). [c] Product prepared from crude alkylated product. Yield calculated based on starting (dibromomethyl)diphenylmethylsilane.

Scheme I



chemistry derived from the (Z)-(α-bromovinyl)silanes 1 and to a lesser extent the dimethylphenylsilyl analogue 2.



The principle questions that we wanted to address in these studies are (1) how to best prepare compounds of the type 1 in a regiospecific manner, (2) what would be the stereointegrity of their Grignard and lithium reagents, 3 and 4, respectively, (3) what would be the reactivity of 3 and 4 toward alkyl halides and other electrophiles, and finally (4) what would be the results of applying the Grignard and lithium reagents of 5 toward asymmetric syntheses.[3]

Preparation of 1 and 2. Although a variety of methods have been employed in the preparation of compounds of the general type 1 as well as for their E counterparts,[4] we chose to prepare them via the convergent route outlined in Scheme I. (Dibromomethyl)lithium is readily silylated at low temperature in good yield to provide the corresponding (dibromomethyl)silane 7 which can in turn be deprotonated and alkylated with alkyl halides to give 8 in good to excellent yield.[5,6] These (α,α-dibromoalkyl)silanes tend to lose hydrogen bromide upon standing, and best results are obtained when they are directly converted in crude form to the (α-bromovinyl)silanes 1, 2, or 5 in refluxing dimethylformamide.[7] This procedure gives predominantly the Z product in all cases with the more sterically demanding methyldiphenylsilyl group providing the greatest stereoselectivity as can be seen by comparison of entries 1 and 5 and 4 and 6 in Table I. If this reaction is allowed to proceed for an extended period of time, considerable amounts of the ethynylsilane are formed presumably due to the trans arrangement of the vinyl proton and the bromine in the initial elimination product. Considering a trans elimination of hydrogen bromide, it can be argued that the observed product is derived from conformer 9 as opposed to 10. In addition to being the predicted lower energy conformer, 9 holds 2:1 statistical advantage over 10. These results are consistent with those found for the elimination of hydrogen chloride from (α,α-dichloroalkyl)silanes in refluxing DMF.[7] This sequence was carried out successfully with ethyl iodide, benzyl bromide, allyl bromide, and dodecyl iodide but was not successful with benzyl chloride, allyl chloride, alkyl brom-

Table II. Stereointegrity of Lithium Reagents 4a[a] and Grignard 3a[b] as a Function of Temperature

vinylmetallic	temp, °C	E:Z ratio
Li	−78	95:5
Li	−40	91:9
Li	−20	91:9
Li	0	91:9
Li	30	87:13
MgBr	−78	95:5
MgBr	−40	95:5
MgBr	−20	95:5
MgBr	0	95:5
MgBr	30	95:5

[a] Prepared from a 95:5 Z:E ratio of 1a and *sec*-butyllithium in THF as a 0.5 M solution. [b] Prepared from 4a and $MgBr_2$ initially at −78 °C.

(3) Results on this aspect of the work will be reported in due course.
(4) For (α-bromovinyl)silanes consult: (a) Ottolenghi, A.; Fridkin, M.; Zikha, A. *Can. J. Chem.* **1963**, *41*, 2977. (b) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. Miller, R. B.; McGarvey, G. *Ibid.* **1978**, *44*, 4623. (c) Zweifel, G.; Lewis, W. *Ibid.* **1978** *44*, 2739. (d) Grobel, B.-Th.; Seebach, D. *Chem. Ber.* **1977**, *110*, 867. (e) Seyferth, D.; Lefferts, J. L.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1977**, *142*, 39. For an erratum on this paper consult: *Ibid.* **1979**, *168*, C32. (f) Yamaguchi, R., Kawasaki, H.; Kawanisi, M. *Synth. Commun.* **1982**, *12*, 1027. (g) Yarosh, O. G.; Voronof, V. K.; Komarov, N. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 875. (h) Komarov, N. V.; Yarosh, O. G. *Ibid.* **1971**, *1573*. (i) Boeckman, R. K.; Jr.; Bruza, K. J. *Tetrahedron Lett.* **1974**, 3365. (j) Miller, R. B.; Al-Hassan, M. I. *J. Org. Chem.* **1983**, 4113. (k) Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* **1976**, *121*, 293. (l) Chan. T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 171. (m) Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 2024. (n) Villieras, J.; Rambaud, M.; Kirschleger, B.; Tarhouni, R. *J. Organomet. Chem.* **1980**, *190*, C31. (o) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem. Chem.* **1978**, *43*, 1526. For (α-iodovinyl)silanes consult: (p) Zweifel, G.; Murray, R. E. *Ibid.* **1981**, *46*, 1292. (q) Hasan, I.; Kishi, Y. *Tetrahedron Lett.* **1980**, *22*, 4229.

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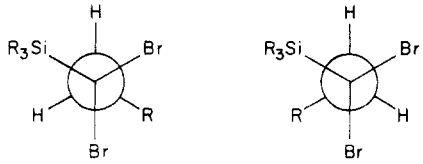
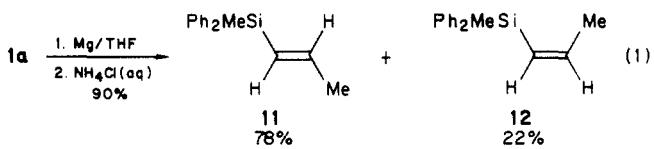
(6) For a comparable procedure in the preparation of α,α-diidosilanes consult: Seyferth, D.; Lambert, R. L.; Jr. *J. Organomet. Chem.* **1973**, *54*, 123.
(7) Larson, G. L.; Rosario, O. *J. Organomet. Chem.* **1979**, *168*, 13.
(8) For spectral data on similar systems but containing the trimethylsilyl group consult ref 4b,c,e.
(9) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1979**, *9*, 831.
(10) For examples of other useful α-silylvinylmetallics consult: (a) Sato, F.; Ishikawa, H.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 85. (b) Westmijze, H.; Meijer, J.; Vermeer, P. *Ibid.* **1977**, 1824. (c) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. (d) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215. (e) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2941.



ides, isopropyl iodide, and neopentylmethane sulfonate. The results of the alkylation of the (dibromomethyl)silanes and their elimination to 1 are given in Table I.

The assigned *Z* geometry to the principle isomers of the (α-bromovinyl)silanes formed is based on the results of the elimination of hydrogen chloride from the α,α-dichloroalkyl)silanes[7] and the ^{1}H NMR spectrum of the vinyl region, which in all cases shows a major resonance at ca. 6.3 ppm for the *Z* isomer and a small resonance at ca. 6.9 ppm for the minor *E* isomer.[8] It is interesting to note that the vinyl proton in the dimethylphenylsilyl and methyldiphenylsilyl systems resonate at essentially the same place as their trimethylsilyl counterparts. In the butadienes and styrene systems this key proton resonates at ca. 6.9 ppm and in the aromatic region for the *Z* and *E* isomers, respectively. Further confirmation of the assigned geometry comes from the attempted isomerization of (*Z*)-**1a** under conditions employed by Zweifel and Lewis[4c] to successfully prepare (*Z*)-(α-bromovinyl)trimethylsilanes in high isomeric purity from their *E* isomers.[4c] This attempted isomerization provided only starting (*Z*)-**1a**. The final isomeric ratios of all systems were determined by capillary GLC on a 30-m SE-30 or a 25-m FFAP column.

Preparation and Reactions of 3 and 4. It was of interest to study both the generation and the stereointegrity of **3** and **4**. Treatment of **1a** with magnesium turnings in THF followed by protonation gave **11** and **12** in excellent yield, but as a 78:22 *E*:*Z* mixture. On the basis of this result, the Grignard reagent was not further studied. It is worthwhile noting, however, that the bromomagnesium reagent **3a** prepared by treatment of **4a** with magnesium bromide at 0 °C maintained its stereointegrity providing **11** and **12** in a 95:5 *E*:*Z* ratio, the same ratio as the starting vinyl bromide implying that the loss of stereochemistry in **3a** occurs during the direct formation of the Grignard reagent and is not a result of the stability of the vinyl Grignard reagent itself.

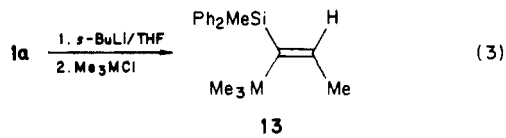


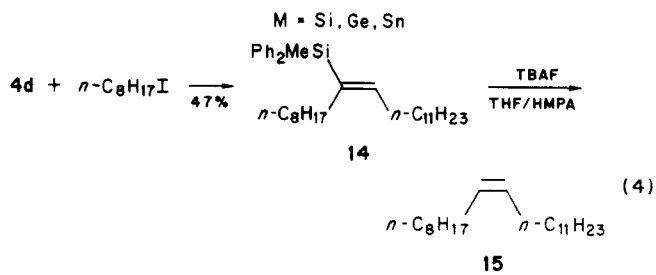
The formation of the lithium reagent was readily accomplished with *n*-, *sec*-, or *tert*-butyllithium in THF at −78 °C.[9] The use of *n*-butyllithium, however, led to the formation of butylated material via reaction of the **1a** with the 1-bromobutane produced from the metal–halogen exchange as had been found by Miller and McGarvey in similar studies.[4b] The use of a single equivalent of *sec*-butyllithium or 2 equiv of *tert*-butyllithium provided excellent entries into the (*E*)-(α-lithio-α-silyl)alkenes **4**. The stereointegrity of these useful reagents[10] was studied as a function of temperature via **3a** and **4a**. The results of this study are given in Table III. As can be seen these lithium reagents maintain their stereochemistry over a wide temperature range, noteworthy being the conversion of a 95:5 *Z*:*E* mixture of **1a** to a 91:9 *E*:*Z* mixture of 1-(methyldiphenylsilyl)propene. This is to be compared to the results found with [α-(trimethylsilyl)vinyl]lithium reagents which provide an equilibrium *E*:*Z* mixture of about 86:14 at 0 °C starting from greater than 99% pure (*E*)-α-(trimethylsilyl)vinyl iodide.[4p] It thus appears that the use of the methyldiphenylsilyl group leads to greater stereointegrity of the vinyllithium reagent.

Table III. Group IV (14) Metalation and Alkylation of Lithium Reagent 4a

entry	RX	% yield	*E*:*Z* ratio
1	Me_2SO_4	50	96:4
2	C_2H_5I	51	95:5
3	n-C_4H_9I	47	95:5
4	n-$C_8H_{17}I$	79	95:5
5	n-$C_{10}H_{21}I$	76	95:5
6	Me_3SiCl	42	90:10
7	Me_3GeCl	92	2:98
8	Me_3SnCl	85	2:98

Reaction of 4a with Trimethylchlorosilane, -germane, and -stannane. The metalation of **4a** with group IV (14[21]) chlorides proceeds in good yield with high stereospecificity according to eq 3. The assignment of the stereochemistry is based on the stereochemistry of the starting lithium reagent as described above.





Alkylation of 4. Generation of **4d** from the reaction of **1d** with a slight excess of *sec*-butyllithium followed by reaction with methanol gave a 99% yield of 1-(methyldiphenylsilyl)-1-tridecene, indicating excellent formation of the lithium reagent. A similar result was observed for the two-step conversion of **1c** to 1-(methyldiphenylsilyl)-1,3-butadiene, although the yield was a lower 70%. Lithium reagent **4a** was successfully alkylated with ethyl, *n*-butyl, *n*-octyl, and *n*-decyl iodide and with dimethyl sulfate as shown in Table III. However, it did not react with methyl iodide, allyl chloride, allyl bromide, or benzyl bromide even in the presence of hexamethylphosphoramide or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

The stereochemical assignments are again based on ^{1}H NMR data, which showed essentially a single resonance at 5.85 ppm for the vinyl proton consistent with the results of Zweifel and Lewis,[4c] Miller and McGarvey,[4b] and Seyferth and co-workers[4e]. This alkylation procedure was applied to the synthesis of (*Z*)-heneicosene, the major component of the sex pheromone for the house fly (*Musca domestica*). Thus, lithium reagent **4d** was treated with *n*-octyl iodide to give vinylsilane **14** in 47% yield and greater than 95% stereochemical purity. Protiodesilylation of this material gave 58% of the desired pheromone component, whose isomeric ratio was determined to be greater than 98:2 *Z*:*E* by ^{1}H NMR analysis of its epoxide.[12]

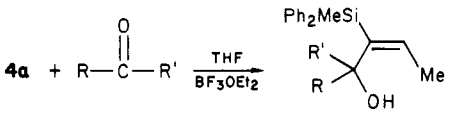
(11) Carlson, D. A.; Mayer, M. S.; Silhacek, D. L.; James, J. D.; Beroza, M.; Bierl, B. A. *Science (Washington, D.C.)* **1971**, *174*, 76.

Table IV. Reaction of 4a with Aldehydes and Cyclohexanone with BF_3OEt_2 Catalysis

entry	carbonyl compd	% yield[a] 16	% yield[a] 17
1	PhCHO	81	81
2	*i*-PrCHO	79	56[b]
3	*t*-BuCHO	*c*	
4	cyclohexanone	72	64

[a] Isolated yield. All products are greater than 98% *Z* isomer. [b] Product very volatile analyzed by ^1H NMR. [c] Product unstable analyzed by ^1H NMR.

Reaction of 4a with Aldehydes and Ketones. On the basis of the excellent results of the reaction of several [α-(trimethylsilyl)vinyl]lithium reagents, with and without β-substituents, with aldehydes and ketones[4j,l,13] we were somewhat surprised to find that lithium reagent **4a** reacted very poorly (<5%) with aldehydes in THF at temperatures up to 0 °C. The bulkier methyldiphenylsilyl group must exhibit a considerable steric effect on the reaction. This lack of reactivity can be overcome by the addition of boron trifluoride etherate to the reaction mixture immediately after the mixing of **4a** and the aldehyde or ketone.[14] In this way the benzaldehyde adduct can be prepared in 81% yield and cyclohexanone reacts in 72% yield. Isobutyraldehyde and pivaldehyde also react, with the product of the pivaldehyde reaction being rather unstable. Other conditions employed in the reaction of **4a** with benzaldehyde were the addition of HMPA as cosolvent, the addition of potassium *tert*-butoxide, the addition of zinc chloride or magnesium bromide, and the use of titanium tetraisopropoxide as a Lewis acid catalyst. Improvements on the original, uncatalyzed reaction were realized with potassium *tert*-butoxide (30%) and titanium tetraisopropoxide (55%). In a different approach to the same end **1a** was reacted with benzaldehyde in the presence of chromium(II) chloride in DMF as reported by Takai and co-workers.[15] This, however, failed to give any of the desired product, resulting in recovery of the starting vinyl bromide **1a**.



(5)

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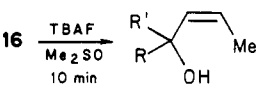
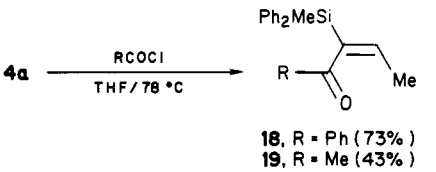


(6)

17

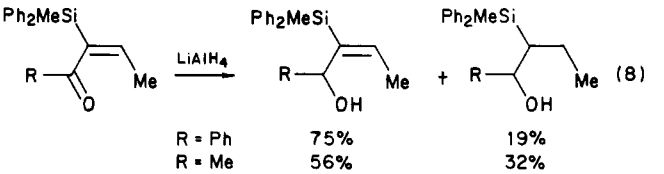
These vinylsilanes are readily protiodesilylated to the corresponding (*Z*)-allyl alcohols via treatment with tetra-*n*-butylammonium fluoride in Me_2SO for 10 min.[16] These results are included in Table IV.

Reaction of 4a with Benzoyl Chloride and Acetic Anhydride. The lithium reagent **4a** was also reacted with benzoyl chloride and acetic anhydride to prepare the α-silyl α,β-unsaturated ketones, which were desired in order to study their conversion to systems such as **16**[4m] (eq 7). The addition of benzoyl chloride to a solution of **4a** in THF gave none of the desired material. However, when inverse addition was employed the desired ketone was obtained in 73% yield, but as a mixture of *Z* and *E* diastereoisomers apparently as a result of warming of the lithium reagent during the addition. The reaction with acetic anhydride carried out with maintenance of the temperature of the lithium reagent below about −20 °C provided a 95:5 *E*:*Z* mixture of **19** in 43% yield. Interestingly, but unfortunately, lithium aluminum hydride reduction of **18** and **19** led to a mixture of totally reduced material and the allyl alcohols (eq 8). Apparently 1,4 addition of hydride occurs



(7)

18, R = Ph (73%)
19, R = Me (43%)

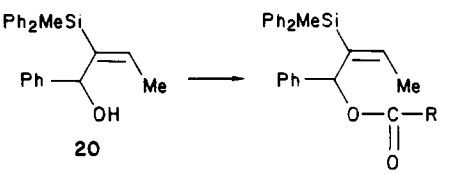


(8)

R = Ph	75%	19%
R = Me	56%	32%

quite readily in these systems as a result of the previously indicated steric congestion engendered by the methyldiphenylsilyl group coupled with the greater propensity for these systems to undergo Michael addition.[17]

Preparation of 1-Phenyl-1,2-butadiene. In conjunction with our eventual desire to attempt to prepare chiral allenes starting from **5**,[3] we next turned our attention to the conversion of **20** to 1-phenyl-1,2-butadiene. It has been shown by Chan and co-workers that direct Peterson-type elimination of β-hydroxysilanes to allenes results in protiodesilylation and that the hydroxyl group must be first converted to a better leaving group.[4o] Conversion of **20** to its acetate **21** and trifluoroacetate **22** proceeded without problem. Treatment of the acetate **21** with anhydrous potassium fluoride, tetra-*n*-butylammonium fluoride (TBAF), and tris(dimethylamino)sulfur (trimethylsilyl)-difluoride (TAS-F) in Me_2SO/THF gave only traces of the allene and principally starting acetate. The trifluoroacetate **22** was somewhat more cooperative providing 28% of the allene with potassium fluoride in Me_2SO/THF at 120 °C along with recovered allyl alcohol. Best results were obtained with TAS-F and **22**, which gave the allene in 40% yield (59% based on recovered allyl alcohol). Although



(9)

20

21, R = Me
22, R = CF_3

these results are somewhat disappointing, they are consistent with other results on this same general conversion employing the acetate or trifluoroacetate. In keeping with our ultimate goal of the asymmetric synthesis of allenes, the chloride leaving group was not investigated due to its reported isomerization.[18]

Experimental Section

General Considerations. All reactions were carried out in

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(16) (a) Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 3479. (b) Fristad, W. A.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3028.
(17) (a) Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152. (b) Boeckman, R. K. *Ibid.* **1973**, 95, 6867.
(18) Chan, T. H.; Mychajlowski, W. Ong, B. S.; Harpp, D. N. *J. Am. Chem. Soc.* **1978**, *43*, 1526.

flame-dried glassware under an atmosphere of dry nitrogen. The standard apparatus used consisted of a three-necked, round-bottomed flask of appropriate size which was equipped with a magnetic spin bar, pressure-equalizing dropping funnel, condenser with a nitrogen inlet, and a rubber septum. IR data are for neat liquid films, except where otherwise noted, and are reported in inverse centimeters. ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR data were recorded with a JEOL FX90Q spectrophotometer in $CDCl_3$ and are recorded with reference to tetramethylsilane for ^{1}H and ^{29}Si and to $CDCl_3$ for ^{13}C. Mass spectral data were obtained at 70 eV and are reported as m/e (relative abundance). Lithium diisopropylamide was prepared by the treatment of diisopropylamine with an equivalent of n-butyllithium in THF initially at −78 °C and then 15 min at room temperature. The isomeric ratios of Z:E mixtures of olefins was determined by capillary GC using a 25-m FFAP column or by ^{1}H NMR. The GC ratios are accurate to within 1%, and the NMR ratios to about 5%.

Silylation of Dibromomethane. Following the procedure of Villieras, Bacquet, and Normant,[5a] the standard apparatus was charged with the diisopropylamine, tetrahydrofuran, and ether. The system was then cooled to −78 °C by means of a dry ice–acetone bath, and n-butyllithium in hexane was added dropwise. The low-temperature bath was removed, and the reaction mixture was stirred for 15–20 min. After this period the temperature was lowered to −90 °C by means of a liquid nitrogen–ether bath, and the dibromomethane, diluted in tetrahydrofuran, was added dropwise. The solution was allowed to stir for 35 min for the complete formation of the anion. The anion was then quenched with the corresponding chlorosilane at −90 °C, and the solution was allowed to stir for 2 h at that same temperature. The reaction mixture was then allowed to warm to room temperature and was hydrolyzed with 1.5 N hydrochloric acid. The two layers were separated, and the aqueous layer was extracted with pentane. The combined organic layers were dried over anhydrous magnesium sulfate. The solution was filtered and the product concentrated under reduced pressure and purified by distillation at reduced pressure.

Preparation of (Dibromomethyl)methyldiphenylsilane. Following the general procedure above, 21.73 g (125 mmol) of dibromomethane in 150 mL of tetrahydrofuran was reacted with 125 mmol of LDA in 150 mL of tetrahydrofuran and 200 mL of ether. The anion was quenched with 23.28 g (100 mmol) of chloromethyldiphenylsilane affording, after workup and reduced pressure distillation, 31.89 g (86%) of the desired product: bp 131–134 °C (0.15); n^{23}_D 1.6023; ^{1}H NMR δ 7.7–7.31 (m, 10 H), 5.49 (s, 1 H), 0.83 (s, 3 H); ^{13}C NMR δ 135.24, 132.47, 130.30, 128.03, 32.68, −5.72; ^{29}Si NMR δ −5.40; MS, m/e (relative abundance) 53 (8), 105 (4), 165 (10), 197 (100), 198 (17). Anal. Calcd for $C_{14}H_{14}SiBr_2$: C, 45.40; H, 3.80. Found: C, 45.51; H, 3.83.

Preparation of (Dibromomethyl)dimethylphenylsilane. Following the general procedure above, 52.14 g (300 mmol) of dibromomethane in 150 mL of tetrahydrofuran was reacted with 375 mmol of LDA in 450 mL of THF and 600 mL of ether. The anion was quenched with 51.2 g (300 mmol) of chlorodimethylphenylsilane affording, after workup and reduced pressure distillation, 66.14 g (72%) of the desired product: bp 85–90 ° (0.5); n^{20}_D 1.5703; ^{1}H NMR δ 7.67–7.21 (m, 5 H), 5.23 (s, 1 H), 0.56 (s, 6 H); ^{13}C NMR δ 134.42, 133.83, 130.20, 127.9, 35.3, −4.8; ^{29}Si NMR δ 2.66; MS, m/e (relative abundance) 136 (14), 135 (100). Anal. Calcd for $C_9H_{12}Br_2Si$: C, 35.10; H, 3.89. Found: C, 35.31; H, 3.91.

Preparation of 1,1-Dibromo-1-(methyldiphenylsilyl)alkanes. Following the procedure of Larson and Rosario,[7] the standard apparatus was charged with diisopropylamine and tetrahydrofuran. The system was then cooled to −78 °C by means of a dry ice–acetone bath and n-butyllithium in hexane was added dropwise. The dry ice–acetone bath was removed, and the mixture was stirred for 20–30 min. After this period the temperature was again lowered to −78 °C, and the (dibromomethyl)methyldiphenylsilane diluted in tetrahydrofuran was added dropwise. The solution was allowed to stir for 1.5 h. The anion was then quenched with an excess of alkyl halide and the solution allowed to stir for 1.5 h at that same temperature. The reaction mixture was then allowed to slowly warm to room temperature where it was hydrolyzed with 1.5 N hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate. The solution was filtered, the solvent was removed under reduced pressure, and the crude product was purified by using silica gel column chromatography eluting with hexane. This reaction was unsuccessful with 2-bromopropane, 2-iodopropane, and 2,3-dimethyl-1-mesyloxypropane. The (α,α-dibromoalkyl)silanes were analyzed for carbon and hydrogen as their dehydrobrominated materials since they tend to lose hydrogen bromide.

Preparation of 1,1-Dibromo-1-(methyldiphenylsilyl)propane. Following the general procedure above, 7.40 g (20 mmol) of (dibromomethyl)methyldiphenylsilane in 25 mL of tetrahydrofuran was reacted with 21 mmol of LDA. The anion was quenched with 8.73 g (56 mmol) of iodoethane affording, after silica gel filtration, 6.7 g (84%) of the desired product: n^{22}_D 1.6077; ^{1}H NMR δ 7.86–7.32 (m, 10 H), 3.34 (q, 2 H, J = 6.8 Hz), 1.25 (t, 3 H, J = 6.8 Hz), 0.90 (s, 3 H); ^{13}C NMR δ 136.05, 132.9, 130.09, 127.82, 69.58, 38.54, 11.62, −3.88; ^{29}Si NMR δ −4.58; 8; MS, m/e (relative abundance) 197 (100).

Preparation of 4,4-Dibromo-4-(methyldiphenylsilyl)-1-butene. Following the general procedure above 19.9 g (53 mmol) of (dibromomethyl)methyldiphenylsilane in 25 mL of tetrahydrofuran was reacted with 55 mmol of LDA in 180 mL of tetrahydrofuran. The anion was quenched with 18.15 g (150 mmol) of 3-bromopropene affording, after rapid silica gel chromatography, 16.9 g (78%) of the title compound: n^{23}_D 1.6142; IR 1640 cm^{-1}; ^{1}H NMR δ 7.87–7.24 (m, 10 H), 6.07 (ddt, 1 H, CH=, J_{cis} = 10.32 Hz, J_{trans} = 16.70 Hz, J_{vic} = 6.4 Hz), 5.23 (dt, 1 H, J_{cis} = 10.32 Hz, $J_{allylic}$ = 1.09 Hz), 5.09 (dd, 1 H, J_{trans} = 16.7 Hz, J_{gem} = 1.76), 3.12 (dt, 2 H, J = 6.37 Hz, $J_{allylic}$ = 1.09 Hz), 0.91 (s, 3 H); ^{13}C NMR δ 135.99, 133.5, 132.59, 130.10, 127.81, 119.71, 64.4, 49.5, −3.70, ^{29}Si NMR δ −4.03; MS, 263 (8), 197 (100).

Preparation of 1,1-Dibromo-1-(methyldiphenylsilyl)pentane. Following the general procedure above, 3.70 g (10 mmol) of (dibromomethyl)methyldiphenylsilane in 10 mL of tetrahydrofuran was reacted with 11.27 mmol of LDA in 25 mL of tetrahydrofuran. The anion was quenched with 5.5 g (30 mmol) of 1-iodobutane affording, after rapid silica gel chromatography, 4.26 g (82%) of the title compound: n^{19}_D 1.5970; ^{1}H NMR δ 7.86–7.28 (m, 10 H), 2.31 (b t, 2 H), 1.74 (m, 2 H), 1.27 (m, 2 H), 0.87, (t, 3 H, J = 6.7 Hz), 0.90 (s, 3 H); ^{13}C NMR δ 135.94, 132.85, 129.98, 127.71, 68.12, 45.10, 29.27, 22.06, 13.99, −3.77; ^{29}Si NMR δ −4.72; MS, m/e (relative abundance) 263 (9), 197 (100).

Preparation of 1,1-Dibromo-1-(methyldiphenylsilyl)tridecane. Following the general procedure above 3.7 g (10 mmol) of (dibromomethyl)methyldiphenylsilane in 10 mL of tetrahydrofuran was reacted with 11.27 mmol of LDA in hexane in 25 mL of tetrahydrofuran. The anion was quenched with 5.92 g (20 mmol) of 1-iodododecane affording, after rapid silica gel chromatography, 4.25 g (79%) of the desired product: n^{18}_D 1.5504; ^{1}H NMR δ 7.86–7.22 (m, 10 H), 2.39 (m, 2 H), 1.25 (b s, 20 H), 0.91 (s, 3 H), 0.88 (b t, 3 H); ^{13}C NMR δ 136.05, 132.96, 129.98, 127.76, 67.98, 45.53, 31.98, 29.70, 29.54, 29.43, 29.05, 27.21, 22.77, 14.21, −3.67; ^{29}Si NMR δ −4.80; MS, m/e (relative abundance) 278 (15), 197 (100).

Preparation of 1,1-Dibromo-1-(dimethylphenylsilyl)alkanes. The procedure for these preparations is the same as that above for the methyldiphenylsilyl system with the exception that the anion generated was that of [(dimethylphenylsilyl)dibromomethyl]lithium.

Preparation of 1,1-Dibromo-1-(dimethylphenylsilyl)propane. Following a procedure analogous to that above 301.8 g (100 mmol) of (dibromomethyl)dimethylphenylsilane in 25 mL of tetrahydrofuran was treated with 110 mmol of LDA in 150 mL of tetrahydrofuran. The anion was quenched with 31.2 g (200 mmol) of iodoethane affording, after rapid silica gel chromatography, 25.9 g (77%) of the title product: n^{25}_D 1.5637; ^{1}H NMR δ 7.75–7.33 (m, 5 H), 2.20 (q, 2 H, J = 6.6 Hz), 1.23 (t, 3 H, J = 6.6 Hz), 0.63 (s, 6 H); ^{13}C NMR δ 135.29, 133.72, 130.04, 127.71, 72.23, 38.00, 11.72, 0.02; ^{29}Si NMR δ 4.75; MS, m/e (relative abundance) 254 (10), 135 (100).

Preparation of 1,1-Dibromo-1-(dimethylphenylsilyl)-2-phenylethane. Following the general procedure above 4.6 g (15 mmol) of (dibromomethyl)dimethylphenylsilane in 10 mL of tetrahydrofuran was treated with 16.5 mmol of LDA in 40 mL of tetrahydrofuran. The anion was quenched with 5.13 g (30 mmol) of benzyl bromide affording a white solid which was crystallized twice from methanol to give 3.45 g (58%) of the desired

product: mp 68.7–69.2 °C; ^{1}H NMR δ 7.81–7.22 (m, 10 H), 3.49 (s, 2 H), 0.64 (s, 6 H); ^{13}C NMR δ 135.24, 133.34, 131.45, 130.04, 127.65, 127.38, 67.57, 49.42, –3.99; ^{29}Si NMR δ 5.57; MS, *m/e* (relative abundance) 51 (8), 53 (6), 77 (14), 91 (13), 103 (25), 105 (11), 107 (9), 135 (100), 136 (14), 137 (8), 154 (9). Anal. Calcd for $C_{16}H_8Br_2Si$: C, 48.27; H, 4.52. Found: C, 48.23; H, 4.57.

Preparation of 4,4-Dibromo-4-(dimethylphenylsilyl)-1-butene. Following the general procedure above 4.62 g (15 mmol) of (dibromomethyl)dimethylphenylsilane in 10 mL of tetrahydrofuran was reacted with 16.5 mmol of LDA in 40 mL of tetrahydrofuran. The anion was quenched with 3.63 g (30 mmol) of 3-bromopropene affording, after rapid silica gel chromatography, 4.24 g (81%) of the desired product: n^{25}_D 1.5662; IR 1648 cm^{-1}; ^{1}H NMR δ 7.84–7.19 (m, 5 H), 6.04 (ddt, 1 H, J_{cis} = 10.3 Hz, J_{trans} = 16.7 Hz, J = 6.4 Hz), 5.25 (d, 1 H, J = 9.44 Hz), 5.13 (d, 1 H, J = 16.7 Hz), 2.98 (dt, 2 H, J = 6.6 Hz, $J_{allylic}$ = 1.1 Hz); ^{13}C NMR δ 135.29, 133.94, 133.83, 130.15, 127.76, 119.37, 66.86, 49.20, -3.99; ^{29}Si NMR δ 5.49; MS, *m/e* (relative abundance) 137 (6), 135 (100).

Preparation of (Z)-1-Bromo-1-(methyldiphenylsilyl)alkenes. Following the procedure of Larson and Rosario,[7] the standard apparatus was charged with *N,N*-dimethylformamide and 1,1-dibromo-1-(methyldiphenylsilyl)alkane at a concentration of 0.3 M. The reaction mixture was heated to reflux for 40–60 min. The reaction mixture was allowed to cool to room temperature and was diluted with pentane before being washed with 10% hydrochloric acid. The initial aqueous layer was extracted three times with small portions of pentane. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solution was filtered, and the product was concentrated under reduced pressure and purified by crystallization or silica gel column chromatography. The isomeric purity was checked by capillary GLC on an FFAP 25-m or SE-30 30-m column.

Preparation of (Z)-1-Bromo-1-(methyldiphenylsilyl)-1-propene. Following the general procedure above, 25.0 g (68 mmol) of (dibromomethyl)methyldiphenylsilane was reacted with the corresponding amount of LDA and quenched with iodoethane to give, after rapid silica gel chromatography, 1,1-dibromo-1-(methyldiphenylsilyl)propane which was heated to reflux in 250 mL of *N,N*-dimethylformamide for 60 min. After workup, the solvent was removed at reduced pressure affording a white solid, which was recrystallized from methanol, to provide 18.46 g (86%) of the desired product: mp 71.5–72 °C; IR ($CHCl_3$) 1613 cm^{-1}; ^{1}H NMR δ 7.67–7.29 (m, 10 H), 6.33 (q, 1 H, J = 6.35 Hz), 1.86 (d, 3 H, J = 6.35), 0.76 (s, 3 H); ^{13}C NMR δ 141.75, 135.12, 134.19, 129.76, 128.39, 127.90, 18.54, –4.08; ^{29}Si NMR δ –10.59; MS, *m/e* (relative abundance) 264 (17), 197 (100). Anal. Calcd for $C_{16}H_{17}BrSi$: C, 60.56; H, 5.39. Found: C, 60.74; H, 5.48. GLC analysis (25-m FFAP capillary column) of this product indicated a *Z:E* ratio of 98:2.

Preparation of (Z)-1-Bromo-1-(methyldiphenylsilyl)-1-pentene. Following the general procedure above, 3.7 g (10 mmol) of (dibromomethyl)methyldiphenylsilane was reacted with the corresponding amount of LDA and quenched with 1-iodobutane to give, after silica gel filtration, 1,1-dibromo-1-(methyldiphenylsilyl)pentane. This material was then heated to reflux in 27 mL of *N,N*-dimethylformamide for 60 min. After workup, the solvent was removed at reduced pressure. Silica gel column chromatography afforded 2.44 g (71%) of the desired product: n^{20}_D 1.5785; IR 1617 cm^{-1}; ^{1}H NMR δ 7.60–7.31 (m, 10 H), 6.26 (t, 1 H, J = 6.6 Hz), 2.30 (q, 2 H, J = 7.1 Hz), 1.42 (sextet, 2 H, J = 6.8 Hz), 0.90 (t, 3 H, J = 6.6 Hz), 0.75 (s, 3 H); ^{13} C NMR δ 146.99, 135.08, 134.21, 129.66, 127.87, 126.95, 34.64, 21.31, 13.73, –3.99; ^{29}Si NMR δ –10.70; MS, *m/e* (relative abundance) 265 (18), 197 (100). Anal. Calcd for $C_{18}H_{21}BrSi$: C, 62.61; H, 6.09. Found: C, 62.64; H, 6.13. GLC analysis (25-m FFAP capillary column) of this product indicated an isomeric *Z:E* ratio of 98.2.

Preparation of (Z)-1-Bromo-1-(methyldiphenylsilyl)-1,3-butadiene. Following the general procedure above, 19.9 g (53 mmol) of (dibromomethyl)methyldiphenylsilane was reacted with the corresponding amount of LDA and quenched with 3-bromopropene to give, after silica gel filtration, 4,4-dibromo-4-(methyldiphenylsilyl)-1-butene. This material was then heated to reflux in 127 mL of *N,N*-dimethylformamide for 60 min. After workup, the solvent was removed under reduced pressure affording a white solid, which was recyrstallized from methanol, to give 5.13 g (41%) of the desired product: mp 66.0–66.5 °C; IR (CCl_4) 1619 cm^{-1}; ^{1}H NMR δ 7.62–7.21 (m, 10 H), 6.98–6.67 (m, 2 H), 5.45–5.26 (m, 2 H), 0.78 (s, 3 H); ^{13}C NMR δ 143.36, 135.17, 134.54, 133.80, 129.90, 128.44, 128.00, 122.4, –4.08; ^{29}Si NMR δ –9.79; MS, *m/e* (relative abundance) 264 (6), 128 (100). Anal. Calcd for $C_{17}H_{17}BrSi$: C, 62.02; H, 5.16. Found: C, 61.80; H, 5.21. GLC analysis (25-m FFAP capillary column) of this product indicated an isomeric *Z:E* ratio of 95:5. This material proved to be rather unstable decomposing in the referigerator in 2 days.

Preparation of (Z)-1-Bromo-1-(methyldiphenylsilyl)-1-tridecene. Following the general procedure above, 14.81 g (40 mmol) of (dibromomethyl)methyldiphenylsilane was reacted with the corresponding amount of LDA and quenched with 1-iodododecane to obtain after silica gel filtration 1,1-dibromo-1-(methyldiphenylsilyl)tridecane. This material was then heated to reflux in 130 mL of *N,N*-dimethylformamide for 60 min. After workup and purification by silica gel column chromatography 14.35 g (78%) of the title compound was obtained: n^{24}_D 1.5424; IR 1615 cm^{-1}; ^{1}H NMR δ 7.60–7.33 (m, 10 H), 6.25 (t, 1 H, J = 6.6 Hz), 2.32 (m, 2 H), 1.26 (b s, 18 H), 0.88 (b t, 3 H), 0.75 (s, 3 H); ^{13}C NMR δ 147.37, 135.13, 134.32, 129.71, 127.92, 126.73, 32.74, 29.65, 31.93, 29.38, 29.27, 29.00, 28.03, 22.72, 14.11, –3.99; ^{29}Si NMR δ –10.64; MS, *m/e* (relative abundance) 378 (10), 197 (100). Anal. Calcd for $C_{26}H_{37}BrSi$: C, 68.29; H, 8.10. Found: C, 68.39; H, 8.17. ^{1}H NMR (90 MHz) analysis indicated an isomeric *Z:E* ratio of 95:5.

Preparation of 1-Bromo-1-(dimethylphenylsilyl)-1-propene. Following the general procedure above, 12.34 g (36.7 mmol) of 1,1-dibromo-1-(dimethylphenylsilyl)propane was heated to reflux in 123 mL of *N,N*-dimethylformamide for 1 h. After workup, the crude product was purified by reduced pressure distillation to afford 6.7 g (54%) of the desired product: bp 88–90 ° (2.7); IR 1610 cm^{-1}; ^{1}H NMR δ 7.59–7.27 (m, 5.8 H), 6.88 (q, 0.14 H, J = 6.9 Hz, *E* isomer =CH), 6.27 (q, 1 H, J = 6.4 Hz, *Z* isomer =CH), 1.79 (d, 3.2 H, J = 6.4 Hz, *Z* isomer =CCH_3), 1.46 (d, 0.32 Hz, J = 7.2 Hz, *E* isomer =CCH_3), 0.52 (s, *E* isomer), 0.45 (s, *Z* isomer); ^{13}C NMR δ 143.99, 138.63, 137.07, 135.90, 134.10, 133.76, 130.83, 129.51, 128.51, 127.85, 18.30 (=CCH_3, *Z* isomer), –0.86 (s, $SiCH_3$, *E* isomer), –3.16 (s, $SiCH_3$, *Z* isomer); ^{19} Si NMR δ –6.31 (*Z* isomer); MS for the *Z* isomer, *m/e* (relative abundance) 256 (9), 201 (100). Anal. Calcd for $C_{11}H_{15}BrSi$: C, 51.76; H, 5.89. Found: C, 51.52; H, 5.90. GLC analysis (25-m FFAP capillary column) of this product showed an isomeric *Z:E* ratio of 91:9.

Preparation of 1-Bromo-1-(dimethylphenylsilyl)-1,3-butadiene. Following the general procedure above, 3.9 g (11 mmol) of 4,4-dibromo-4-(dimethylphenylsilyl)-1-butene was heated to reflux in 48 mL of *N,N*-dimethylformamide for 1 h. After workup the product was purified by reduced pressure distillation to afford 2.81 g (95%) of the desired product: bp 83–86 °C (0.25); IR 1575, 1595 cm^{-1}; ^{1}H NMR δ 7.63–7.23 (m, 10 H), 6.69–6.58 (m, 2 H), 5.53–5.04 (m, 2 H), 0.56 (s, $SiCH_3$, *E* isomer), 0.50 (s, $SiCH_3$, *Z* isomer); ^{13}C NMR δ 148.46, 140.93, 135.40, 134.70, 134.16, 133.89, 132.96, 130.80, 129.65, 127.98, 121.69, 120.40, –0.85 ($SiCH_3$, *E* isomer), –3.17 ($SiCH_3$, *Z* isomer); ^{29}Si NMR δ –5.32; MS for the *Z* isomer *m/e* (relative abundance) 202 (6), 129 (100). GLC analysis (25-m FFAP capillary column) of this product indicated a *Z:E* isomer ratio of 66:34. This material proved to be rather unstable decomposing even in the referigerator in 2 days.

Preparation of (Z)-1-Bromo-1-(dimethylphenylsilyl)-2-phenylethene. Following the general procedure above, 2.0 g (5.0 mmol) of 1,1-dibromo-1-(dimethylphenylsilyl)-2-phenylethane was heated to reflux in 17 mL of *N,N*-dimethylformamide for 1 h. After workup the product was purified by silica gel column chromatography to afford 1.3 g (81%) of the desired product: IR 1605 cm^{-1}; ^{1}H NMR δ 7.71–7.23 (m, 11 H), 0.56 (s, 6 H); ^{13}C NMR δ 140.17, 136.21, 135.46, 134.10, 129.61, 129.17, 128.58, 128.25, 127.93, –3.07; ^{29}Si NMR δ –4.09; MS, *m/e* (relative abundance) 318 (21), 201 (100). Anal. Calcd for $C_{16}H_{17}BrSi$: C, 60.54; H, 5.36. Found: C, 60.66; H, 5.41. GLC analysis (25-m FFAP capillary column) of this product indicated it to be greater than 98% of the *Z* isomer.

Attempted Isomerization of (Z)-1-Bromo-1-(methyldiphenylsilyl)-1-propene. Following the procedure of Zweifel and Lewis,[4c] 0.04 g (0.13 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was placed into an NMR tube under nitrogen

along with 1 mL of ether, 6.3 μL of pyridine, and 12.6 μL of a 1.0 M solution of bromine in dichloromethane. The tube was irradiated with a 250 mW/cm² Xe lamp for 0.5 h and an additional 12.6 L of the bromine solution added in two portions over a period of 2 h. The ^{1}H NMR spectrum of the material after treatment was identical with that of the starting *Z* isomer, indicating the no isomerization had taken place.

Preparation of the 1-Lithio-1-(methyldiphenylsilyl)-1-alkenes. The standard apparatus was charged with 0.32 g (1.0 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-alkene in 2 mL of tetrahydrofuran. The reaction mixture was cooled to −78 °C by means of a dry ice–acetone bath, and 1.17 mL (1.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane was added dropwise. The reaction mixture was stirred for 10 min. At this time this reagent is ready for use.

Alkylation of 1-Bromo-1-(methyldiphenylsilyl)-1-alkenes. Following the general procedure above, the lithium reagent was treated with an excess of alkylating agent. The reaction mixture was allowed to stir for 6–8 h at −78 °C and was then allowed to warm to room temperature where it was hydrolyzed by addition of a saturated solution of ammonium chloride. The aqueous layer was washed with hexane (2 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate. The solution was filtered, and the solvent was removed at reduced pressure. The product was purified either by flash chromatography or preparative gas chromatography.

Preparation of (*E*)-1-(Methyldiphenylsilyl)-1-propene. Following the general procedure above, 0.32 g (1 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 1.17 mL (1.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane in 1.5 mL tetrahydrofuran. The anion was quenched with 1 mL of methanol. After workup, the crude product was purified by silica gel column chromatography affording 0.22 g (91%) of the desired product: n_D^{17} 1.5654; IR 1613 cm^{-1}; ^{1}H NMR δ 7.49–7.08 (m, 10 H), 6.25–5.74 (m, 2 H, CH=CH), 1.79 (d, 3 H, *J* = 4.9 Hz), 0.57 (s, 3 H); ^{13}C NMR δ 146.14, 136.97, 134.78, 129.07, 127.70, 127.17, 22.73, −3.69; ^{29}Si NMR δ −15.44; MS, *m/e* (relative abundance) 238 (65), 223 (100). Anal. Calcd for $C_{16}H_{18}Si$: C, 80.67; H, 7.56. Found: C, 80.78; H, 7.65. ^{1}H NMR analysis (90 MHz) of this product showed an isomeric purity of 95%.

Preparation of (*E*)-2-(Methyldiphenylsilyl)-2-butene. Following the general procedure above, 0.32 g (1 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 1.17 mL (1.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane in 1.5 mL of tetrahydrofuran and 0.5 mL of *N,N,N',N'*-tetramethylethylenediamine. The anion was quenched with 0.63 g (5 mmol) of dimethyl sulfate. After workup, the crude product was analyzed by gas chromatography (6 ft, 10% SE-30) indicating a 50% yield of the desired product. A small amount was purified by preparative GLC (5 ft $^3/_8$ in., 20% SE-30, 250 °C): IR (CCl_4) 3070 (CH, arom, vinylic), 1619 cm^{-1}; ^{1}H NMR δ 7.56–7.22 (m, 10 H), 5.90 (qq, 1 H, *J* = 1.95 Hz, *J* = 7.14 Hz), 1.73 (m, 6 H), 0.60 (s, 3 H); ^{13}C NMR δ 138.60, 136.59, 135.30, 135.13, 129.06, 127.78, 14.97, 14.43, −4.37; MS, *m/e* (relative abundance) 253 (9), 197 (100). Anal. Calcd for $C_{17}H_{20}Si$: C, 80.95; H, 7.94. Found: C, 80.76; H, 8.01. GLC analysis (25-m FFAP capillary column) of this product indicated an isomeric *E*:*Z* ratio of 96:4.

Reaction of 1-Lithio-1-(methyldiphenylsilyl)propene with Benzoyl Chloride. To a solution of 0.33 g (2.4 mmol) of benzoyl chloride in 13.2 mL of THF at −78 °C was added 1.0 mmol of the title lithium reagent, prepared from 1 mmol of bromide and 2 mmol of *tert*-butyllithium in THF at −78 °C. The resulting reaction mixture was stirred at that temperature for 2 h and quenched with 1 mL of methanol. This reaction mixture was allowed to reach room temperature and was washed with saturated sodium bicarbonate (2 × 5 mL). The organic layer was then washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. After removal of the solvent at reduced pressure, silica gel chromatography eluting with 5% ethyl acetate–hexane gave 0.251 g (73%) of 1-(methyldiphenylsilyl)-1-benzoylpropene as a 31:69 mixture of *E* and *Z* isomers, which were not separated. This mixture showed: IR 1655 cm^{-1}; ^{1}H NMR δ 7.82–7.25 (m, 15 H), 6.80 (q, vinyl proton of *Z* isomer, *J* = 7.02 Hz), 6.25 (q, vinyl proton of *E* isomer, *J* = 6.68 Hz), 1.72 (d, methyl of *Z* isomer, *J* = 7.03 Hz), 1.65 (d, methyl of *Z* isomer, *J* = 6.75 Hz), 0.69 (s, Si methyl of *E* isomer), 0.60 (s, Si methyl of *Z* isomer); ^{13}C NMR δ 201.40, 143.32, 135.12, 134.88, 134.74, 132.93, 129.47, 129.07, 128.40, 127.88, 127.76, 18.37, 18.29, −3.66; MS, *m/e* (relative abundance) 342 (100). Anal. Calcd for $C_{23}H_{22}SiO$: C 80.65; H, 6.47. Found: C, 80.56; H 6.51.

Preparation of (*E*)-1-(Methyldiphenylsilyl)-2-pentene. In an analogous procedure to that above, 0.95 g (3 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 3.5 mL (4.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane in 3 mL of tetrahydrofuran and 3 mL of TMEDA. The anion was quenched with 2.34 g (15 mmol) of iodoethane. After workup, the crude product was purified by flash chromatography eluting with hexane to obtain 0.41 g (51%) of the desired product. A small amount was purified by preparative GC (5 ft $^3/_8$ in., 20% SE-30, 250 °C): n^{24}_D 1.5634; IR 1610 cm^{-1}; ^{1}H NMR δ 7.56–7.24 (m, 10 H), 5.92 (q, 1 H, *J* = 6.6 Hz), 2.22 (q, 2 H, *J* = 7.6 Hz), 1.74 (d, 3 H, *J* = 6.6 Hz), 0.83 (t, 3 H, *J* = 7.3 Hz), 0.62 (s, 3 H); ^{13}C NMR δ 139.73, 138.92, 136.97, 135.13, 129.01, 127.65, 22.66, 14.38, 14.26; ^{29}Si NMR δ −10.97; MS, *m/e* (relative abundance), *E* isomer, 266 (100), 197 (85), *Z* isomer, 266 (47), 197 (100). Anal. Calcd for $C_{18}H_{22}Si$: C, 81.20; H, 8.27. Found: C, 81.22; H, 8.33. GLC analysis (25-m FFAP capillary column) of this product indicated an *E*:*Z* ratio of 95:5.

Preparation of (*E*)-3-(Methyldiphenylsilyl)-2-heptene. In an analogous procedure to that above, 0.95 g (3 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 3.5 mL (4.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane in 3 mL of tetrahydrofuran and 3 mL of TMEDA. The anion was quenched with 2.76 g (15 mmol) of 1-iodobutane. After workup, the product was purified by flash chromatography eluting with hexane to give 0.42 g (47%) of the desired product. A small amount was purified by preparative GC (5 ft $^3/_8$ in., 20% SE-30, 250 °C): n_D^{24} 1.5508; IR 1605 cm^{-1}; ^{1}H NMR δ 7.56–7.19 (m, 10 H), 5.89 (q, 1 H, *J* = 6.6 Hz), 2.18 (b t, 2 H), 1.73 (d, 3 H, *J* = 6.6 Hz), 1.16 (m, 4 H), 0.77 (b t, 3 H), 0.62 (s, 3 H); ^{13} C NMR δ 139.14, 138.38, 137.03, 135.13, 128.95, 127.00, 31.87, 29.54, 22.99, 14.59, 13.84, −3.61; ^{29}Si NMR δ −10.89; MS, *m/e* (relative abundance) *E* isomer, 294 (54), 197 (100), *Z* isomer, 294 (26), 197 (100). Anal. Calcd for $C_{20}H_{26}Si$: C, 81.63; H, 8.84. Found: C, 81.68; H, 8.90. GLC analysis (25-m FFAP capillary column) of this product indicated an *E*:*Z* ratio of 95:5.

Preparation of (*E*)-3-(Methyldiphenylsilyl)-2-tridecene. In an analogous procedure to that above, 0.66 g (2.1 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 1.68 mL (2.5 mmol) of a 1.49 M solution of *n*-butyllithium in hexane. The anion was quenched with 1.61 g (6 mmol) of 1-iododecane. After workup, the crude product was purified by flash chromatography eluting with hexane to obtain 0.59 g (76%) of the desired product: n^{25}_D 1.5231; IR 1613 cm^{-1}; ^{1}H NMR δ 7.55–7.26 (m, 10 H), 5.91 (q, 1 H, *J* = 6.6 Hz), 2.19 (b t, 2 H), 1.73 (d, 3 H, *J* = 6.6 Hz), 1.16 (b s, 16 H), 0.88 (b t, 3 H), 0.61 (s, 3 H); ^{13}C NMR δ 139.07, 138.53, 137.02, 135.22, 129.03, 127.66, 32.05, 30.05, 29.46, 29.70, 22.78, 14.64, 14.15, −3.55; ^{29}Si NMR δ −10.81; MS, *m/e* (relative intensity) 197 (100). Anal. Calcd for $C_{26}H_{38}Si$: C, 82.54; H, 10.05. Found: C, 82.59, H, 10.15. ^{1}H NMR analysis showed an isomeric purity *E*:*Z* ratio of greater than 95%.

Preparation of (*E*)-1-(Methyldiphenylsilyl)-1-(trimethylsilyl)-1-propene. In an analogous procedure to that above, 1.5 g (5 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 5.86 mL (7.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane in 10 mL of tetrahydrofuran. The anion was quenched with 2.7 g (25 mmol) of chlorotrimethylsilane. After workup, the crude product was purified by flash chromatography eluting with hexane to obtain 0.66 g (42%) of the desired product. A small amount was purified by preparative GC (5 ft $^3/_8$ in., 20% SE-30, 250 °C): n^{23}_D 1.5545; IR 1565 cm^{-1}; ^{1}H NMR δ 7.35–7.13 (m, 10 H), 6.50 (q, 1 H, *J* = 6.6 Hz), 1.79 (d, 3 H, *J* = 6.6 Hz), 0.51 (s, 3 H), −0.09, −0.13 (singlets for the *E* and *Z* isomers); ^{13}C NMR δ 157.55, 137.90, 135.00, 134.43, 128.84, 127.60, 21.96, 1.38, −2.20; ^{29}Si NMR δ −7.93, −8.67, less intensity −7.77, −8.99; MS, *m/e* (relative abundance) E isomer 310 (24), 197 (100), *Z* isomer, 310 (15), 197 (100). Anal. Calcd for $C_{19}H_{26}Si_2$: C, 73.55; H, 8.39. Found: C, 73.51; H, 8.44. GLC analysis (30-m OV 1701 capillary column) of this product showed it to be 90% of the *E* isomer.

Preparation of (*Z*)-1-(Trimethylgermyl)-1-(methyldiphenylsilyl)-1-propene. In an analogous procedure to that

above, 0.64 g (2.0 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene in 4 mL of tetrahydrofuran was treated with 2.3 mL (3 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane. The anion was quenched with 0.53 g (10 mmol) of chlorotrimethylgermanium. The low-temperature bath was removed, and the system was allowed to warm to room temperature. The reaction mixture was heated to reflux gently for 1 h. After this period the system was allowed to cool to room temperature and the workup was done. The crude product was analyzed by GC and ^{1}H NMR indicating the formation of the desired product in greater than 85% yield. A small amount was purified by preparative GC (5 ft $^3/_8$ in., 20% SE-30, 250 °C): IR ($CHCl_3$) 1577; ^{1}H NMR δ 7.52–7.12 (m, 10 H), 6.6 (q, 1 H, J = 6.6 Hz), 1.90 (d, 3 H, J = 6.3 Hz), 0.62 (s, 3 H), 0.16 (s, 9 H); ^{13}C NMR δ 154.31, 140.11, 137.68, 135.13, 128.90, 127.65, 21.69, 1.27, −2.52; MS, m/e (relative abundance) 342 (16), 181 (100). Anal. Calcd for $C_{19}H_{26}SiGe$: C, 64.30; H, 7.33. Found: C, 64.23; H, 7.42. GLC analysis (25-m FFAP capillary column) of this product showed it to be 98% the Z isomer.

Preparation of (Z)-1-(Methyldiphenylsilyl)-1-(trimethylstannyl)-1-propene. In a procedure analogous to that above, 0.32 g (1.0 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene in 2 mL of tetrahydrofuran was treated with 1.17 mL (1.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane. The anion was quenched with 1 g (5 mmol) of chlorotrimethyltin. The low-temperature bath was removed, and the system was allowed to warm to room temperature. The reaction mixture was heated to reflux for 1 h. After this period the system was allowed to cool to room temperature and the workup was done. The crude product was analyzed by GC and ^{1}H NMR indicating the formation of the desired product in greater than 85% yield. A small amount was purified by preparative GC: IR 1570 cm^{-1}; ^{1}H NMR δ 7.50–7.34 (m, 10 H), 6.76 (q, 1 H, J = 6.1 Hz), 1.98 (d, 3 H, J = 6.3 Hz), 0.66 (s, 3 H), 0.07 (s, 9 H); ^{13}C NMR δ 154.79, 141.31, 137.35, 135.02, 128.90, 127.65, 24.29, −2.85, −7.24; MS, m/e (relative abundance) 389 (10), 197 (100). Anal. Calcd for $C_{19}H_{26}SiSn$: C, 56.90; H, 6.49. Found: C, 56.81; H, 6.53. ^{1}H NMR analysis showed the product to be 98% isomerically pure.

Preparation of (E)-1-(Methyldiphenylsilyl)-1-tridecene. In a procedure analogous to that above, 0.46 g (1 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-tridecene in 2 mL of tetrahydrofuran was treated with 1.2 mL (1.5 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane. The anion was quenched with 1 mL of methanol. After workup, the crude product was purified by using flash chromatography eluting with hexane to obtain 0.24 g (64%) of the desired product: n^{24}_D 1.5267; IR 1612 cm^{-1}; ^{1}H NMR δ 7.58–7.29 (m, 10 H), 6.16–6.00 (m, 2 H), 2.31–2.04 (m, 2 H), 1.26 (b s, 18 H), 0.88 (b t, 3 H), 0.59 (s, 3 H); ^{13}C NMR δ 151.54, 137.13, 134.80, 129.06, 127.76, 125.38, 36.97, 32.04, 29.60, 29.44, 29.27, 28.67, 29.76, 22.77, 14.16, −3.50; ^{29}Si NMR δ −15.28; MS, m/e (relative abundance) 363 (15), 121 (100). Anal. Calcd for $C_{26}H_{38}Si$: C, 82.54; H, 10.05. Found: C, 82.55; H, 10.16. ^{1}H NMR analysis showed the product to be 95% isomerically pure.

Preparation of (E)-9-(Methyldiphenylsilyl)-9-heneicosene. In a procedure analogous to that above, 0.9 g (2 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-tridecene in 4 mL of tetrahydrofuran was treated with 2.3 mL (3 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane. The anion was quenched with 2.4 g (10 mmol) of 1-iodooctane. The low-temperature bath was removed, and the system was allowed to reach room temperature. The reaction mixture was heated to reflux gently for 1 h. After this period the system was cooled to room temperature and the workup was done. The crude product was purified by flash chromatography eluting with hexane to give 0.46 g (47%) of the desired product: IR 1605 cm^{-1}; ^{1}H NMR δ 7.56–7.22 (m, 10 H), 5.79 (t, 1 H, J = 6.9 Hz), 2.10 (m, 4 H), 1.26 and 1.14 (both are b s, 30 H), 0.88 (m, 6 H), 0.61 (s, 3 H); ^{13}C NMR δ 145.48, 137.13, 136.92, 135.18, 128.95, 127.59, 31.87, 29.70, 30.25, 30.14, 29.98, 29.49, 29.38, 29.22, 28.84, 22.66, 14.12, −3.50; MS, m/e (relative abundance) 197 (100). Anal. Calcd for $C_{34}H_{54}Si$: C, 83.27; H, 11.02. Found: C, 83.31; H, 11.11. ^{1}H NMR analysis showed the product to be 95% isomerically pure.

Preparation of *cis*-9-Heneicosene. In an analogous procedure to that above 3.02 g (6.6 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-tridecene in 12 mL of THF was treated with 7.75 mL (9.9 mmol) of a 1.28 M *sec*-butyllithium solution in cyclohexane. The anion was quenched with 7.9 g (33 mmol) of 1-iodooctane. The low temperature bath was removed, and the system was allowed to warm to room temperature. The reaction mixture was heated to reflux for 1 h. After this period the system was allowed to cool to room temperature where the workup was done. The excess 1-iodooctane was distilled at reduced pressure. The remaining crude product was heated to reflux in 33 mL (33 mmol) of a 1.0 M tetra-*n*-butylammonium fluoride solution in tetrahydrofuran and 50 mL of HMPA. The solution was then stirred for 1.5 h at 90–100 °C. After this period, the system was allowed to cool to room temperature where it was diluted in 300 mL of ethyl acetate and was washed with water (4 × 125 mL). The solution was dried over anhydrous sodium sulfate. The solution was filtered, and the solvent was distilled at reduced pressure. The crude product was filtered through a short column of silica gel to provide 1.13 g (58%) of the desired product. A small amount was further purified by preparative GC: n^{25}_D 1.4482 (lit.[19] n^{23}_D 1.4493); IR 1650 cm^{-1}; ^{1}H NMR δ 5.34 (b t, 2 H), 1.98 (m, 4 H), 1.26 (b s, 30 H), 0.87 (b t, 6 H), ^{13}C NMR δ 129.93, 31.98, 29.81, 29.71, 29.38, 27.27, 22.72, 14.05; Determination of the Z:E ratio: Following the procedure of Chan et al.,[18] the standard apparatus was charged with 0.38 g (1.3 mmol) of the 9-heneicosene obtained above was dissolved in 13 mL of dichloromethane, and then 0.3 g (1.56 mmol) of 3-chloroperoxybenzoic acid in 20 mL of dichloromethane was added dropwise at 0 °C. The solution was stirred for 6 h at room temperature. The solution was washed with a saturated solution of sodium bicarbonate, and the organic layer was dried over anhydrous magnesium sulfate. This solution was filtered, and the solvent was distilled at reduced pressure to affording the desired product in 95% yield as adjudged by ^{1}H NMR. The crude product was filtered through a short plug of silica gel eluting with hexane: ^{1}H NMR δ 2.89 (s, 2 H, cis, methines), 1.27 (b s, 34 H), 0.88 (b t, 6 H). The Z:E ratio was shown to be greater than 98:2 as calculated by ^{1}H NMR since no resonance at δ 2.59 for the trans epoxide protons could be seen.

Preparation of 1-(Methyldiphenylsilyl)-1-propene via the Grignard Reagent. The standard apparatus was charged with 0.13 g (5.4 mol) of magnesium turnings, 0.5 mL of tetrahydrofuran, and 0.11 g (0.36 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene. After the initiation of the reaction, an additional 1.0 g (3.2 mmol) of the bromide was added and the reaction was heated to reflux for 15 h. The Grignard reagent was hydrolyzed with 7 mL of a saturated solution of ammonium chloride. The aqueous layer was washed with hexane (2 × 7 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solution was filtered, and the solvent was distilled under reduced pressure. The crude product was analyzed by ^{1}H NMR showing a (78:22) E:Z ratio of the title product.

Preparation of 3-(Methyldiphenylsilyl)-2-pentene via the Grignard Reagent. Following the procedure of Sato et al.,[20] the Grignard reagent was treated with a catalytic amount of copper(I) iodide followed by 1.05 g (6.7 mmol) of iodoethane at 0 °C. The reaction mixture was stirred 2 h at room temperature and was hydrolyzed with 15 mL of a saturated solution of ammonium chloride. The aqueous layer was extracted with ether (2 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solution was filtered, and the solvent was distilled at reduced pressure. The crude product was analyzed by GC (6 ft × $^1/_8$ in., 10% SE-30) indicating the formation of an equimolar ratio of the desired product and 1-(methyldiphenylsilyl)-1-propene.

Preparation of [(Z)-1-(Methyldiphenylsilyl)-2-methyl-1-propenyl]magnesium Bromide via Lithium Reagent. Equilibration at Different Temperatures. Following preparation of the lithium reagent as above, 0.64 g (2.1 mmol) of 1-bromo-1-(methyldiphenylsilyl)-1-propene was treated with 2.35

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(21) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is elminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

mL (3.0 mmol) of a 1.28 M solution of *sec*-butyllithium solution in cyclohexane in 6 mL of tetrahydrofuran. The solution was warmed to −60 °C, and 3.1 mL (2.2 mmol) of a 0.71 M solution of magnesium bromide in tetrahydrofuran was added followed by stirring for 20 min at that same temperature. An aliquot was hydrolyzed with a saturated solution of ammonium chloride and analyzed by ^{1}H NMR (60 MHz) to observe the *E*:*Z* ratio. Aliquots were also removed at −40, −20, and 0 °C. In all cases the *E*:*Z* ratio was 95:5.

Preparation of 1-(Methyldiphenylsilyl)-1-propene via the Lithium Reagent: Equilibration at Different Temperatures. The lithium reagent was prepared as described above at −78 °C. Aliquots were taken at −60, −40, −20, and 0 °C, each was hydrolyzed with 10% ammonium chloride, and the *E*:*Z* ratio of the vinylsilanes formed analyzed by ^{1}H NMR and GC analyses. At all temperatures the *E*:*Z* ratio was 95:5. This ratio changed to 87:13 at room temperature, however.

(*E*)-3-(Methyldiphenylsilyl)-3-penten-2-one. In a reaction analogous to that above 1 mmol of lithium reagent was reacted with 2.4 mmol of acetic anhydride at −78 °C. Silica gel chromatography of the crude product gave 0.108 g (43%) of the title product, which was greater than 95% the *E* isomer: IR 1684, 1604 cm^{-1}; ^{1}H NMR δ 7.60–7.25 (m, 10 H), 5.95 (q, 1 H, J = 6.79 Hz), 2.05 (s, 3 H), 1.80 (d, 3 H, J = 6.80 Hz), 0.70 (s, 3 H); ^{13}C NMR δ 151.70, 142.37, 135.03, 134.59, 129.61, 129.13, 127.91, 32.14, 17.51, −3.71; MS, *m*/*e* (relative abundance) 280 (15), 265 (97), 203 (100). Anal. Calcd for $C_{18}H_{20}SiO$: C, 77.09; H, 7.19. Found: C, 77.14; H, 7.22.

(*E*)-1-Phenyl-2-(methyldiphenylsilyl)-2-buten-1-ol. The standard apparatus was charged with 11.4 mL (16.8 mmol) of a 1.5 M solution of *tert*-butyllithium in hexane at −78 °C and 8 mL of THF. To this solution was then added 2.5 g (2.89 mmol) of **1a** in 2.2 mL of THF via syringe over a 5-min period. The resulting reaction mixture was stirred for 1 h at −78 °C, and 0.93 g (8.8 mmol) of benzaldehyde in 3.2 mL of THF was rapidly added followed by the immediate addition of 1.3 g (8.8 mmol) of boron fluoride etherate. This reaction mixture was stirred at −78 °C for 2 h and quenched by the addition of aqueous sodium acetate. After room temperature was reached, the aqueous layer was removed and the organic layer washed with 10% ammonium chloride. The combined aqueous layers were extracted with ether (3 × 15 mL). The combined organic layers were washed with saturated sodium chloride and dried over anhydrous potassium carbonate. The solvents were removed at reduced pressure, and the crude product was purified via silica gel chromatography eluting with 5% ethyl acetate–hexane to give 2.19 g (81%) of the title compound as a single isomer: IR 1615 cm^{-1}; ^{1}H NMR δ 7.6–7.2 (m, 15 H), 6.07 (dq, 1 H, J = 1.47, 6.83 Hz), 5.84 (b s, 1 H), 1.72 (d, 3 H, J = 6.83 Hz), 0.49 (s, 3 H); ^{13}C NMR δ 143.09, 142.17, 140.98, 137.35, 135.13, 134.86, 129.06, 128.84, 128.09, 127.82, 127.54, 126.84, 126.14, 73.10, 15.89, −2.52; ^{29}Si NMR δ −11.00; MS, *m*/*e* (relative abundance) 344 (0.3), 137 (100). This somewhat unstable material was analyzed for C and H as its acetate—see below.

(*E*)-3-(Methyldiphenylsilyl)-5-methyl-2-hexen-4-ol. Following the procedure above on a 3-mmol scale reaction with isobutyraldehyde provided 0.74 g (79%) of the title compound as a single isomer: IR 1611 cm^{-1}; ^{1}H NMR δ 7.60–7.29 (m, 10 H), 5.95 (dq, 1 H, J = 0.49, 6.82 Hz), 4.40 (d, J = 8.40 Hz), 1.75 (d, J = 6.83 Hz), 0.95 (d, J = 6.52 Hz), 0.82 (d, J = 6.85 Hz), 0.73 (s, 3 H); ^{13}C NMR δ 140.67, 135.13, 134.82, 129.01, 128.84, 127.80, 127.58, 77.81, 34.05, 19.25, 19.00, 16.07, −1.66; MS, *m*/*e* 309 (M − 1 from chemical ionization). Anal. Calcd for $C_{20}H_{20}SiO$: C, 77.36; H, 8.44. Found: C, 77.12; H, 8.44.

(*E*)-1-[1-(Methyldiphenylsilyl)-1-propenyl]cyclohexanol. Following the procedure above on a 1-mmol scale reaction with cyclohexanone provided 0.25 g (72%) of the title compound as a single isomer: IR 1631 cm^{-1}; ^{1}H NMR δ 7.60–7.30 (m, 10 H), 5.68 (q, 1 H, J = 7.21 Hz), 1.82 (d, 3 H, J = 7.25 Hz), 1.84–1.0 (m, 10 H), 0.80 (s, 3 H); ^{13}C NMR δ 149.29, 138.93, 134.80, 128.65, 127.71, 76.71, 36.62, 25.35, 21.72, 17.46, −1.51; MS, *m*/*e* 335 (M − 1 from chemical ionization). Anal. Calcd for $C_{22}H_{28}SiO$: C, 78.51; H, 8.39. Found: C, 78.36; H, 8.43.

(*Z*)-1-Phenyl-2-buten-1-ol. A standard apparatus was charged with 0.52 g (1.5 mmol) of **20**, and 9.4 mL of anhydrous Me_2SO, and then 7.5 mL (7.5 mmol) of a 1 M solution of tetra-*n*-butylammonium fluoride in THF. The reaction mixture was stirred for 1 h at room temperature and diluted with ethyl acetate (75 mL) and the resulting solution washed with water (4 × 30 mL). The organic phase was dried over anhydrous potassium carbonate, the solvents were removed at reduced pressure, and the crude product was purified by silica gel chromatography eluting with 10% ethyl acetate–hexane to give 0.18 g (81%) of the title compound as a 96.5:3.5 Z:E mixture: IR 1665 cm^{-1}; ^{1}H NMR δ 7.6–7.2 (m, 5 H), 5.6 (m, 3 H, vinyl and CHO hydrogens), 2.0 (b s, 1 H), 1.87 (d, 3 H, J = 4.98 Hz); ^{13}C NMR δ 143.61, 132.84, 128.43, 127.34, 126.29, 125.77, 69.36, 13.30; MS, *m*/*e* 149 (M + 1 from chemical ionization). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.17; H, 8.21.

(*Z*)-1-(1-Propenyl)cyclohexanol. Following the procedure above on a 1.5-mmol scale reaction, **16** (R, R′ = $-(CH_2)_5-$) provided 0.135 g (64%) of the title compound as a single isomer: IR 1651 cm^{-1}; ^{1}H NMR δ 5.50 (m, 2 H), 1.85 (d, 3 H, J = 5.48 Hz), 1.85 (b s, 1 H), 1.62 and 1.40 (two multiplets, 10 H); ^{13}C NMR δ 136.77, 126.77, 126.25, 72.48, 39.01, 25.44, 22.43, 14.43; MS, *m*/*e* 141 (M + 1 from chemical ionization). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.92; H, 11.54.

(*E*)-1-Phenyl-1-acetoxy-2-(methyldiphenylsilyl)-2-butene. A mixture of 0.76 g (2.2 mmol) of **20**, 0.33 g (3.3 mmol) of triethylamine, 0.34 g (3.3 mmol) of acetic anhydride, and 0.005 g (0.04 mmol) of 4-(dimethylamino)pyridine in 4 mL of dichloromethane was stirred for 15 h at room temperature. The reaction mixture was washed with saturated sodium bicarbonate, and the organic layer was dried over potassium carbonate. The solvent was removed at reduced pressure to give 0.77 g (91%) of the title compound: IR 1771, 1625 cm^{-1}; ^{1}H NMR δ 7.6–7.2 (m, 15 H), 7.0 (s, 1 H), 6.02 (dq, 1 H, J = 1.18, 6.78 Hz), 1.79 (d, J = 6.77 Hz), 1.40 (s, 3 H), 0.44 (s, 3 H); ^{13}C NMR δ 170.20, 143.03, 135.11, 134.66, 129.00, 128.95, 128.23, 127.70, 127.60, 127.38, 126.61, 74.63, 20.25, 16.04, −2.94; MS, *m*/*e* 385. Anal. Calcd for $C_{25}H_{26}SiO_2$: C, 77.68; H, 6.78. Found: C, 77.79; H, 6.81.

(*E*)-1-(Trifluoroacetoxy)-1-phenyl-2-(methyldiphenylsilyl)-2-butene. A mixture of 0.615 g (1.8 mmol) of **20**, 0.27 g (2.7 mmol) of triethylamine, and a small amount of 4-(dimethylamino)pyridine in 3.1 mL of dichloromethane was added to 0.57 g (2.7 mmol) of trifluoroacetic anhydride and the reaction mixture stirred at 0 °C for 1 h to give 0.55 g (96%) of the title compound: IR 1816, 1641 cm^{-1}; ^{1}H NMR δ 7.45–7.20 (m, 15 H), 7.10 (s, 1 H), 6.20 (dq, J = 6.84 Hz, allylic coupling very small), 1.84 (d, J = 6.84 Hz), 0.05 (s, 3 H); ^{13}C NMR δ 144.95, 137.35, 135.02, 134.73, 129.34, 129.18, 128.53, 128.18, 127.78, 127.69, 126.34, 79.44, 16.11, −3.08; MS, *m*/*e* 440.

1-Phenyl-1,2-butadiene. Several procedures were attempted for this transformation. That reported here represents the best results obtained. A standard apparatus was charged with 4.3 g (15.7 mmol) of tris(dimethylamino)sulfur (trimethylsilyl)difluoride (TAS-F), and then 1.67 g (3.8 mmol) of **22** in 22 mL of dry Me_2SO was added. The reaction, as monitored by TLC, was complete in 15 min after which time it was diluted with pentane (50 mL). The reaction mixture was then washed with saturated sodium chloride (1 × 50 mL) and dried over anhydrous potassium carbonate. The solvent was removed by distillation at atmospheric pressure through a glass packed column. Bulb to bulb distillation of the residue afforded 0.20 g (40%) of the allene as a yellowish green oil: IR 1960 cm^{-1}; ^{1}H NMR δ 7.40–7.18 (m, 5 H), 6.08 (dq, 1 H, J = 3.19, 6.39 Hz), 5.52 (pentet, 1 H, J = 7.0 Hz), 1.76 (dd, 3 H, J = 3.20, 7.05 Hz).

Acknowledgment. We wish to thank the NIH-MBRS program (RR-8102-14), the UPR, Pfizer, Inc., and Squibb Manufacturing, Inc., for their support of our efforts. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank the NSF for funds to purchase the JEOL FX90Q NMR spectrophotometer. Dr. Osvaldo Rosario is thanked for the GC–mass spectra data. Professor J. A. Soderquist is thanked for several helpful discussions. E.T. thanks the NSF for a predoctoral fellowship.

Registry No. 1 (R = $Ch_2CH_2CH_3$), 102979-12-4; **1a**, 102979-11-3; **1c**, 102979-13-5; **1d**, 102979-14-6; (*E*)-**2a**, 102979-15-7; (*Z*)-**2a**, 102979-18-0; (*Z*)-**2b**, 102979-17-9; (*E*)-**2c**, 102979-16-8; (*Z*)-**2c**,

102979-19-1; **11**, 102979-20-4; **12**, 102979-32-8; (*E*)-**13** (M = Si), 102979-27-1; (*Z*)-**13** (M = Ge), 102979-28-2; (*Z*)-**13** (M = Sn), 102979-29-3; **14**, 102979-31-7; **15**, 39836-21-0; **16** (R = Pr-i, R′ = H), 102979-36-2; **17**, 52755-38-1; (*E*)-**18**, 102979-22-6; (*Z*)-**18**, 102979-23-7; **19**, 102979-41-9; **20**, 102979-35-1; **21**, 102979-39-5; **22**, 102979-40-8; CH_2Br, 74-95-3; $Ph_2MeSiCl$, 144-79-6; $Ph_2MeSiCH_2Br$, 102979-03-3; $PhMe_2SiCH_2Br$, 102979-04-4; $PhMe_2SiCl$, 768-33-2; $PhCH_2Br$, 100-39-0; n-$C_8H_{17}I$, 629-27-6; 1,1-dibromo-1-(methyldiphenylsilyl)propane, 102979-05-5; 4,4-dibromo-4-(methyldiphenylsilyl)-1-butene, 102979-06-6; 1,1-dibromo-1-(methyldiphenylsilyl)pentane, 102979-07-7; 1,1-dibromo-1-(methyldiphenylsilyl)tridecane, 102979-08-8; iodoethane, 75-03-6; 3-bromopropene, 106-95-6; 1-iodobutane, 542-69-8; 1-iodododecane, 4292-19-7; 1,1-dibromo-1-(dimethylphenylsilyl)-propane, 102979-09-9; 1,1-dibromo-1-(dimethylphenylsilyl)-2-phenylethane, 103002-63-7; (*E*)-1-(methyldiphenylsilyl)-2-pentene, 102979-24-8; (*E*)-3-(methyldiphenylsilyl)-2-heptene, 102979-25-9; (*E*)-3-(methyldiphenylsilyl)-2-tridecene, 102979-26-0; (*E*)-1-(methyldiphenylsilyl)-1-tridecene, 102979-30-6; 1-iododecane, 2050-77-3; 3-(methyldiphenylsilyl)-2-pentene, 102979-33-9; [(*Z*)-1-(methyldiphenylsilyl)-2-methyl-1-propenyl]magnesium bromide, 102979-34-0; (*Z*)-1-(1-propenyl)cyclohexanol, 102979-38-5; 1-phenyl-1,2-butadiene, 2327-98-2; (*E*)-2-(methyldiphenylsilyl)-2-butene, 102979-21-5; 4,4-dibromo-4-(dimethylphenylsilyl)-1-butene, 102979-10-2; (*E*)-1-[1-(methyldiphenylsilyl)-1-propenyl]cyclohexanol, 102979-37-3.

Metal–Metal Multiple Bonds. 18. Addition Reactions of Diazoalkanes with the Mo≡Mo Triple Bond in $R_2Mo_2(CO)_4$ (R = C_5H_5, C_5H_4Me, C_5Me_5)

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Received May 30, 1986

The Mo≡Mo triple bond in $R_2Mo_2(CO)_4$ (R = C_5H_5, C_5H_4Me, C_5Me_5) (**1**) reacts with diazoalkanes to give 1:1 adducts whose bonding modes depend markedly on the substituents, R, as well as on the diazoalkane. Diaryldiazomethanes form an adduct in which the terminal N atom asymmetrically bridges a Mo–Mo single bond. Bond distances suggest the N atom is doubly bonded to one Mo atom and singly bonded to the other. These adducts (R = Cp) lose N_2 upon photolysis or thermolysis via an intramolecular 1,3-dipolar cycloadduct to give μ-diarylmethylene complexes. Me_2CN_2 reacts to give a mixture of isomers, one similar to the diaryldiazomethane adducts and the other contains a μ-η^1,η^2-diazoalkane bridge with the terminal nitrogen bonded to both Mo atoms and the central N atom bonded to only one. Ethyl diazoacetate forms an adduct with the latter structure when R = C_5Me_5. Diethyl diazomalonate or α-keto diazoalkanes react with **1** to give adducts in which the carboxyl or ketone oxygen forms a chelate ring to one Mo atom and the metal–metal bond is broken entirely. ^1H and ^{13}C NMR spectra for these complexes are reported. The crystal structures of $Cp_2Mo_2(CO)_4(\mu$-$N_2CPh_2)$ (**2**), $Cp_2Mo_2(CO)_4[N_2C(CO_2Et)_2]$ (**4A**), and $(C_5Me_5)_2Mo_2(CO)_4(N_2CHCO_2Et)$ (**6**) were determined. For **2**: a = 11.847 (4) Å, b = 10.407 (3) Å, c = 20.572 (6) Å; β = 97.81 (2)°; V = 2513 (1) Å^3; Z = 4, ρ = 1.64 g/mL; space group $P2_1/n$ (no. 14); R_1 = 0.048, R_2 = 0.059. Some pertinent bond distances (Å): Mo1–Mo2 = 2.987 (4), Mo1–N1 = 1.914 (8), Mo2–N1 = 2.083 (8), N1–N2 = 1.35 (1), N2–C15 = 1.28 (1). For **4A**: a = 11.144 (2) Å, b = 7.497 (1) Å, c = 28.939 (7); β = 95.13 (2)°; V = 2408.2 (9) Å^3; Z = 4; ρ_{calcd} = 1.71 g/mL; space group $P2_1/c$ (no. 14); R_1 = 0.048, R_2 = 0.061. Selected distances (Å): Mo1–N1 = 1.86 (1), N1–N2 = 1.24 (1), N2–C15 = 1.42 (1), C15–C16 = 1.41 (2), C16–O5 = 1.26 (1), O5–Mo2 = 2.14 (1), Mo2–N2 = 2.21 (1). For **6**: a = 10.515 (3) Å, b = 18.868 (6) Å, c = 15.334 (4) Å; β = 104.43 (2)°; V = 2946 (1) Å^3; Z = 4, ρ_{calcd} = 1.55 g/mL; space group $P2_1/n$ (no. 14); R_1 = 0.034, R_2 = 0.035. Selected distances (Å): Mo1–Mo2 = 3.040 (1), Mo1–N1 = 2.105 (4), Mo2–N1 = 2.109 (4), Mo2–N2 = 2.108 (5), N1–N2 = 1.336 (6), N2–C5 = 1.288 (7).

Introduction

Diazoalkanes, R_2CN_2, are reactive carbenoid synthons with wide applications in preparative organic chemistry,[3] particularly in the conversion of olefinic functional groups to cyclopropanes. Carbenoid transfer to unsaturated organic substrates is usually catalyzed by small amounts of transition-metal salts such as those of copper. The intermediate in carbenoid transfer is presumed to be a metal alkylidene derived from attack of the metal salt on the diazoalkane α-carbon and loss of dinitrogen.

The fact that transition-metal compounds are effective catalysts for diazoalkane decomposition has limited study of the coordination chemistry of these molecules. In principle, diazoalkanes should exhibit a variety of coordination modes in mononuclear and dinuclear complexes because of the possibilities for C- or N-terminal coordination, C=N or N=N side-on coordination, or even metallacyclic structures with both diazoalkane ends coordinated. Examples of several of these have been synthesized,[4] either by direct addition of the diazoalkane to an organometallic reactant or by condensation reactions of ketones or dihalomethanes with transition-metal hydrazide or dinitrogen complexes. In general, the interest in the

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