Chemistry of Substituted (2-Butene-1,4-diyl)magnesium: A Facile Approach to Complex Carbocycles, Functionalized Ketones and Alcohols, and Silicon-Containing Heterocycles

Reuben D. Rieke* and Heping Xiong

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received December 27, 1990

Highly reactive magnesium reacts with a wide variety of substituted 1,3-dienes to give the corresponding substituted (2-butene-1,4-diyl)magnesium complexes. Reactions of symmetrical (2-butene-1,4-diyl)magnesium with α,ω-alkylene dihalides form three-, four-, five-, and six-membered carbocycles. Significantly, the cyclizations are always stereospecific and completely regioselective. Depending on the initial 1,3-diene and specific electrophiles, uncyclized products can be obtained. Stepwise reactions of (2,3-dimethyl-2-butene-1,4-diyl)magnesium with two different electrophiles afford polyfunctionalized ketones with the generation of a quaternary center. Formal 1,2-additions can be effected in this manner. Substituted five- and six-membered cyclic ketones can also be synthesized in one step by this approach. Treatment of unsymmetrical (2-butene-1,4-diyl)magnesium complexes with triorganosilyl chlorides followed by cyclohexanone results in additions across a terminal double bond with high regioselectivity. Silicon-containing heterocycles or spiro compounds can be readily synthesized by using the bis-Grignard reagents.

Introduction

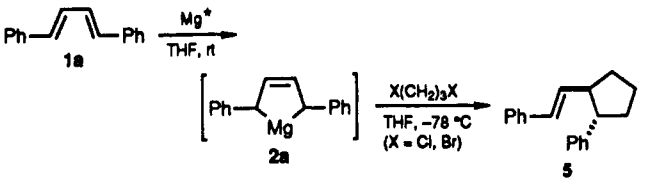
Metallic magnesium is known to react with certain 1,3-dienes yielding halide-free organomagnesium compounds.[1] However, there is a primary problem associated with the preparation of these reagents. The reaction of ordinary magnesium with 1,3-dienes such as 1,3-butadiene or isoprene is usually accompanied by dimerization, trimerization, and oligomerization. This reaction may be catalyzed by alkyl halides or transition-metal salts but is generally accompanied by a variety of byproducts. Consequently, the utilization of these reagents in organic synthesis has been quite limited,[2] except for 1,3-butadiene–magnesium, which has found considerable application in organometallic synthesis.[3]

We recently published a communication[4] demonstrating that substituted (2-butene-1,4-diyl)magnesium complexes can be conveniently prepared from the reaction of highly reactive magnesium with the corresponding 1,3-dienes. Significantly, these bis-Grignard reagents react with α,ω-alkylene dihalides to give complex carbocycles. Polyfunctionalized oragnic compounds can be obtained in this manner. Recently, we found that highly reactive calcium reacts also with 1,3-dienes to generate calcium metallocycles.[5] We now report the details of our studies on the chemistry of magnesium complexes of 1,3-dienes, including symmetrical and unsymmetrical (2-butene-1,4-diyl)magnesium complexes.

Results and Discussion

Highly reactive magnesium (Mg*) is readily prepared by the reduction of anhydrous magnesium chloride in THF with either preformed lithium naphthalenide[6] or lithium using naphthalene as an electron carrier.[7] The magnesium reacts with (*E,E*)-1,4-diphenyl-1,3-butadiene (**1a**), 2,3-dimethyl-1,3-butadiene (**1b**), isoprene (**1c**), myrcene (**1d**), or 2-phenyl-1,3-butadiene (**1e**) in THF at ambient temperature to give the corresponding substituted (2-butene-1,4-diyl)magnesium complexes. The structures of these complexes have not been determined to date except for (1,4-diphenyl-2-butene-1,4-diyl)magnesium, which has been shown to be a five-membered-ring metallocycle.[8] The most probable structure for the magnesium complex of 1,3-butadiene is an oligomer.[1a] Accordingly, the most likely structures for these complexes are five-membered metallocycles or oligomers. It is also possible that an equilibrium exists between these various forms.

Scheme I



Cyclizations of (1,4-Diphenyl-2-butene-1,4-diyl)-magnesium with α,ω-Alkylene Dihalides. Reaction of (*E,E*)-1,4-diphenyl-1,3-butadiene with newly generated magnesium in THF gave (1,4-diphenyl-2-butene-1,4-diyl)magnesium (**2a**). The resulting complex was deep red. This reagent acted as a dinucleophile when treated with α,ω-alkylene dichlorides, giving cyclic compounds (Scheme I). However, reactions of **2a** with α,ω-alkylene dibromides resulted in either cyclization or reduction of the electrophile, depending on the initial dibromides. The results are summarized in Table I. Significantly, these cyclizations are always stereospecific and completely regioselective. For example, cyclization proceeded rapidly at −78 °C in the reaction of **2a** with 1,3-dibromopropane and 1,3-dichloropropane, yielding a single product, *trans*-1-

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(2) (a) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Koeffer, D. P. J.; Ohst, H.; Soehnen, D. *Chem. Ber.* **1986**, *119*, 420. (b) Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293.

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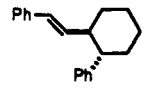
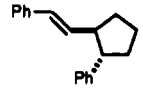
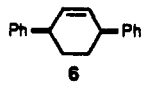
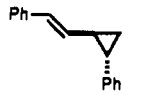
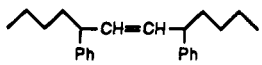
Table I. Cyclization of (1,4-Diphenyl-2-butene-1,4-diyl)magnesium with α,ω-Alkylene Dihalides[a]

entry	dihalide	product[b]	% iso. yield
1	$Br(CH_2)_4Br$	 **4**	40
2	$Cl(CH_2)_4Cl$	4	51
3	$Br(CH_2)_3Br$	 **5**	65
4	$Cl(CH_2)_3Cl$	5	81
5	$Br(CH_2)_2Br$		-
6	$Cl(CH_2)_2Cl$	 **6**	59
7	$BrCH_2Br$		-
8	$ClCH_2Cl$	 **7**	76
9	$CH_3(CH_2)_3Br$	 **8** (cis:trans = 56:44)[c]	93
10	$CH_3(CH_2)_3Cl$	8 (cis:trans = 28:72)[c]	87

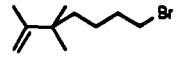
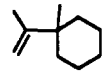
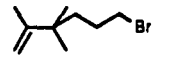
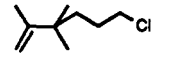
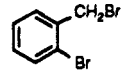
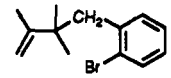
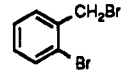
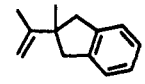
[a] Reactions were typically done at -78 °C and then the reaction mixtures warmed to room temperature prior to workup. [b] All compounds were fully characterized by ^1H NMR, ^{13}C NMR, IR, and mass spectra. [c] The ratio of cis to trans was based on the ^1H NMR spectra of the crude products. The individual isomers were separated by chromatography.

phenyl-2-((*E*)-2-phenylethenyl)cyclopentane (**5**) in 65% and 81% isolated yield, respectively (Table I, entries 3 and 4).

Similarly, the reaction of 1,4-dichlorobutane or 1,4-dibromobutane with **2a** gave *trans*-1-phenyl-2-((*E*)-2-phenylethenyl)cyclohexane (**4**) as the only cyclized product (Table I, entries 1 and 2).[9]

In contrast to the 1,2-cyclizations of **2a** with 1,3-dihalopropane and 1,4-dihalobutane, treatment of **2a** with 1,2-dichloroethane resulted in 1,4-addition, producing a cyclohexene derivative, *cis*-3,6-diphenylcyclohexene[5,10] (**6**). On the other hand, reaction of **2a** with 1,2-dibromoethane resulted in only recovered (*E,E*)-1,4-diphenyl-1,3-butadiene. Similar results were obtained in the reaction of **2a** with methylene dibromide. In these particular cases, **2a** is apparently acting as a two electron reducing agent. This mode of reaction has been observed for the magnesium–anthracene complex.[11]

Table II. Reactions of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium with Organodihalides

entry	dihalide[a]	product[b]	% iso. yield[c]
1	$Br(CH_2)_4Br$	 **9**	79
2	$Br(CH_2)_4Br$	 **10**	53[d] (69)
3	$Br(CH_2)_3Br$	 **11**	72[e]
4	$Br(CH_2)_3Br$	 **12**	- (75)
5	$Cl(CH_2)_3Cl$	 **13**	81
6	$Br(CH_2)_2Br$	 **14**	- (49)[f]
7	$Cl(CH_2)_2Cl$	14	- (61)[f]
8		 **15**	62[g]
9		 **16**	~30[h]

[a] Organodihalides were added to the THF solution of (2,3-dimethyl-2-butene-1,4-diyl)magnesium at -78 °C. The reaction mixture was stirred at -78 °C for 2 h and then typically warmed to room temperautre (unless specified) prior to workup. [b] All compounds have satisfactory spectral data including ^1H NMR, ^{13}C NMR, IR, and mass spectral data. [c] GC yields are given in parentheses. [d] Cyclization completed after the mixture was refluxed for 5 h. [e] Uncyclized product was obtained by controlling the reaction temperature below -35 °C. [f] Product was isolated by preparative gas chromatography. [g] Monoalkylated product was obtained by protonation at -78 °C. [h] Cyclization was achieved at reflux.

Surprisingly, **2a** cyclized with methylene dichloride to generate only a three-membered cyclic compound, *trans*-1-phenyl-2-((*E*)-2-phenylethenyl)cyclopropane[5,12] (**7**) in 76% isolated yield.

The initial attack of **2a** by the α,ω-alkylene dihalides is believed to occur at the 1,4-positions, followed by intramolecular alkylation to produce the cyclic product. Attempts to trap the initial adduct were unsuccessful. However, support for this mode of reaction comes from the treatments of **2a** with 1-bromobutane and 1-chlorobutane (Table I, entries 9 and 10), which yield exclusively 5,8-diphenyl-6-dodecene (**8**).

Reactions of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium with Organo Dihalides. It is particularly noteworthy that ordinary magnesium reacts with great difficulty with those 1,3-dienes that have more than one alkyl group about the double bonds. However, the use of highly reactive magnesium allows the facile preparation

(9) The stereochemistry on the ring for *trans*-1-phenyl-2-((*E*)-2-phenylethenyl)cyclohexane and *trans*-1-phenyl-2-((*E*)-2-phenylethenyl)-cyclopentane was determined by the ozonolysis of the double bond, followed by reduction with $NaBH_4$ (see experimental section for details), which gave (*trans*-2-phenylcyclohexyl)methanol and (*trans*-2-phenylcyclopentyl)methanol, respectively. (a) Baas, J. M. A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 285. (b) Brown, H. C.; Naik, R. G.; Singaram, B.; Pyun, C. *Organometallics* **1985**, *4*, 1925.

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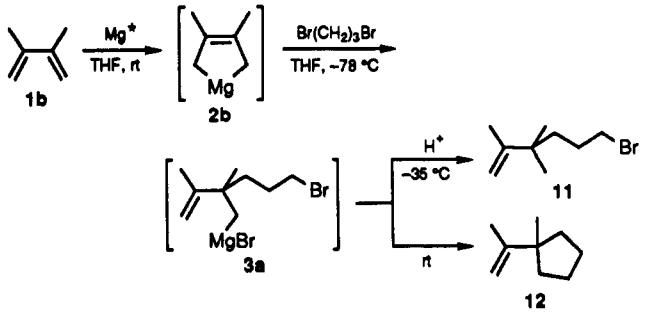
Scheme II



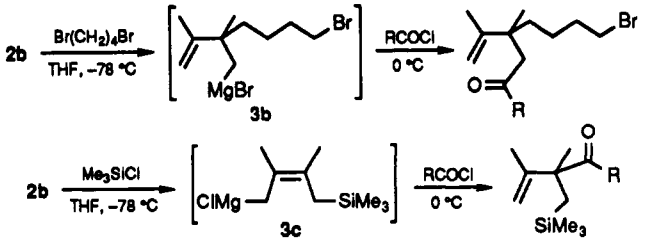
of (2,3-dimethyl-2-butene-1,4-diyl)magnesium complex (**2b**) under mild conditions. Freshly distilled 2,3-dimethyl-1,3-butadiene is simply added to the newly generated magnesium in THF. After the mixture is stirred for 5–10 h at ambient temperature, **2b** is formed as a soluble complex in THF. The color of the solution is pale orange.[13] The reactions of the resulting complex with α,ω-alkylene dihalides yield a number of highly useful transformations. For example, cyclizations of **2b** with a wide variety of organo dihalides generate four-, five- and six-membered carbocycles. In most cases, the initial adducts can be trapped by protonation, giving monoalkylated products. Some of these results are listed in Table II. For example, addition of 1,3-dibromopropane to **2b** at −78 °C formed an intermediate **3a**, which cyclized upon warming to room temperature to yield 1-methyl-1-(1-methylethenyl)cyclopentane (**12**) (Scheme II). On the other hand, an acidic workup of **3a** at −35 °C gave a single monoalkylated product, 6-bromo-2,3,3-trimethyl-1-hexene (**11**), in 72% isolated yield. Similar chemistry was observed with 1,4-dibromobutane, except that no cyclization would take place without refluxing. It is interesting to note that the cyclization of **3a** to **12** represents a cross coupling of a Grignard reagent with an alkyl bromide, which is normally only observed in the presence of certain transition-metal salts or complexes.[14]

Unlike 1,3-dibromopropane, treatment of **2b** with 1,3-dichloropropane at −78 °C followed by warming to room temperature only resulted in monoalkylation, giving 6-chloro-2,3,3-trimethyl-1-hexene (**13**). In this case, no significant cyclization was observed after the reaction mixture was stirred at room temperature for 48 h.

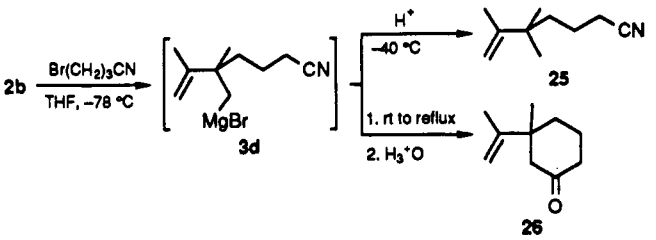
In sharp contrast to **2a**, treatment of **2b** with 1,2-dibromoethane generated a four-membered ring to give 1-methyl-1-(1-methylethenyl)cyclobutane (**14**) in fair yield. In this case, the cyclization proceeded rapidly even at −78 °C, preventing the trapping of the intermediate. Better yields were obtained with 1,2-dichloroethane (Table II, entry 7). This approach represents a facile new method for preparing highly substituted four-membered-ring hydrocarbons. In contrast, the traditional photochemical [2 + 2] cycloadditions[15] are mostly limited to intramolecular reactions. It is also unusual in that 1,2-dibromoethane rarely acts as a dielectrophile with organometallic reagents but instead is normally reduced to ethylene.

Interestingly, 2-bromobenzyl bromide reacted with **2b** at −78 °C selectively to produce a monoalkylated product,

Scheme III



Scheme IV



4-(2-bromophenyl)-2,3,3-trimethyl-1-butene (**15**), in 62% isolated yield. Warming up of the mixture to reflux resulted in cyclization to give 2-methyl-2-(1-methylethenyl)-2,3-dihydro-1*H*-indene (**16**) in modest yield. The cyclization from the initial adduct (refer to **3a**) to **16** involved an intramolecular cross coupling of a Grignard reagent with an aryl halide. Attempts to promote the cyclization by adding nickel or palladium complexes were fruitless. Considering the large number of well-established nickel- or palladium-catalyzed intermolecular cross-coupling reactions of Grignard reagents with sp^2-carbon halides,[16] the lack of catalytic cross coupling in this intramolecular reaction is difficult to understand.

Stepwise Reactions of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium with Two Different Electrophiles. One of the significant properties of **2b** lies in that it can react stepwise with two different electrophiles (Table III). For example, the intermediate derived from the initial attack at the 2-position in the reaction of **2b** with α,ω-alkylene dibromides (**3b**) or alkyl bromides can be reacted with other electrophiles. For example, addition of acid chlorides to **3b** afforded the corresponding ketones (Scheme III). The reactions worked equally well for both aliphatic and aromatic acid chlorides. The overall scheme provided a net "2,1-addition" to 2,3-dimethyl-1,3-butadiene, giving polyfunctionalized ketones with the generation of a quaternary center. The overall high isolated yields indicated that Grignard addition of the intermediate to the initially formed ketone was minimal.

Utilizing the reverse regioselectivity of harder electrophiles, one can effectively secure overall "1,2-addition". Treatment of **2b** with chlorotrimethylsilane at −78 °C resulted in initial attach at the 1-position, yielding an allylic Grignard reagent. Although there are two possible isomeric structures for the reagent, with the magnesium either on the secondary carbon or on the primary carbon, we consider that the latter is the predominate form (**3c**).[17] Reaction of **3c** with an acid chloride resulted in addition to the γ-carbon, producing a quaternary center. The overall

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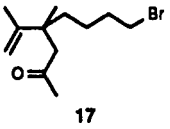
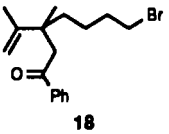
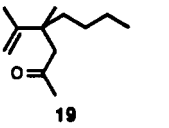
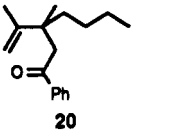
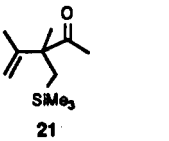
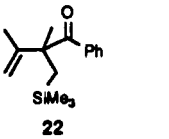
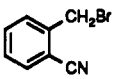
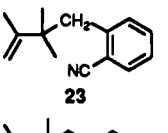
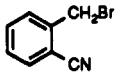
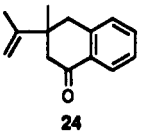
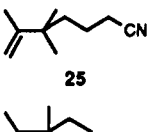
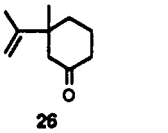
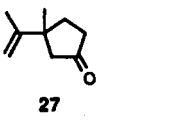
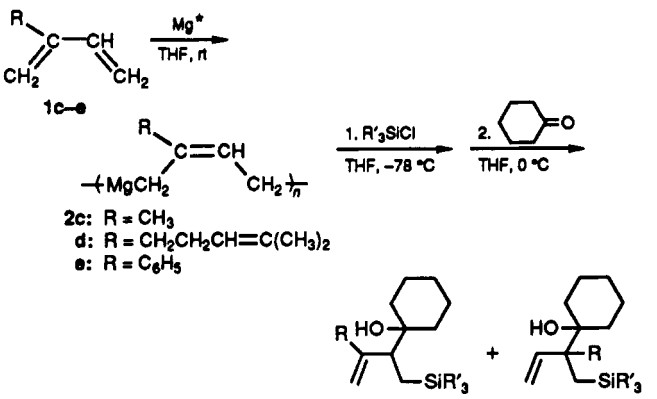
(16) For reviews on transition metal catalyzed intermolecular cross coupling of Grignard reagents with organic halides, see: (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333.
(17) Reports on ^1H NMR studies reveal that γ-substituted allylic Grignard reagents exist as a rapidly equilibrating mixture of *Z* and *E* primary stereoisomers. (a) Hutchison, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 1075. (b) Schlosser, M.; Stahle, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 487.

Table III. Stepwise Reactions of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium with Electrophiles

entry	first electrophile[a]	second electrophile[b]	product[c]	% iso. yield
1	$Br(CH_2)_4Br$	MeCOCl	 **17**	62
2	$Br(CH_2)_4Br$	PhCOCl	 **18**	60
3	$Me(CH_2)_3Br$	MeCOCl	 **19**	61
4	$Me(CH_2)_3Br$	PhCOCl	 **20**	82
5	Me_3SiCl	MeCOCl	 **21**	73
6	Me_3SiCl	PhCOCl	 **22**	79
7		$H^+{}_3O$	 **23**	35[d]
8			 **24**	30[e]
9	$Br(CH_2)_3CN$	$H^+{}_3O$	 **25**	58[f]
10	$Br(CH_2)_3CN$		 **26**	31[g]
11	$Br(CH_2)_2CN$		 **27**	42[h]

[a] The first electrophile was added to the THF solution of (2,3-dimethyl-2-butene-1,4-diyl)magnesium at −78 °C. The reaction mixture was then warmed to room temperature prior to the addition of the second electrophile. [b] The second electrophile was added at 0 °C. [c] All new compounds were completely characterized spectroscopically. [d] Protonation at −78 °C resulted in the survival of the cyano group. [e] Cyclization was achieved at reflux. [f] Acidic hydrolysis at −40 °C gave the nitrile. [g] The cyclic ketone was obtained at reflux followed by acidic hydrolysis. [h] Cyclization completed at room temperature.

Scheme V



reaction is a formal addition of Me_3SiCOR across a terminal double bond with the generation of a quaternary center and introduction of two functional groups.

Significantly, a molecule containing two different electrophilic centers can also react stepwise with **2b**. Treatment of α-bromo-2-toluonitrile with **2b** at −78 °C resulted in the survival of the cyano group (Table III, entry 7). Warming up of the mixture to reflux followed by acidic hydrolysis afforded a tetralone derivative (**24**) containing a quaternary center in the 3-position. This approach can also be extended to aliphatic bromonitriles. For example, addition of 4-bromobutyronitrile to **2b** at −78 °C formed a Grignard reagent containing a cyano group (**3d**), which cyclized upon warming to reflux. Workup gave 3-methyl-3-(1-methylethenyl)cyclohexanone (**26**) in modest yield (Scheme IV). Alternatively, protonation of **3d** at −40 °C gave 5,5,6-trimethyl-6-heptenenitrile (**25**).

A substituted five-membered cyclic ketone was also prepared from the corresponding reaction of **2b** with 3-bromopropionitrile (Table III, entry 11). In this case, the initial adduct cyclized rapidly even at −40 °C, preventing the trapping of the intermediate.

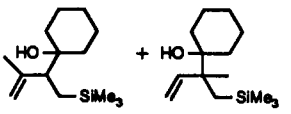
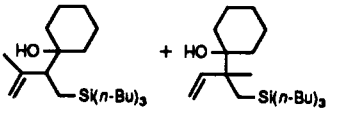
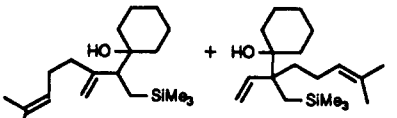
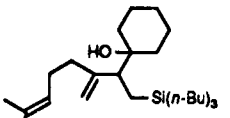
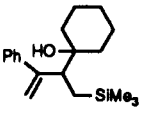
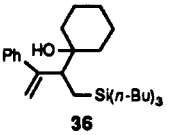
Regioselective Reactions of Unsymmetrical (2-Butene-1,4-diyl)magnesium Reagents with Two Different Electrophiles. It is particularly difficult to prepare unsymmetrical (2-butene-1,4-diyl)magnesium complexes from ordinary magnesium. The reaction is usually complicated by extensive polymerization. We have found that the use of highly reactive magnesium circumvents this problem. For example, an excess of newly generated active magnesium reacted with isoprene, myrcene, or 2-phenyl-1,3-butadiene in THF at room temperature in 2 h to give the corresponding unsymmetrical (2-butene-1,4-diyl)-magnesium complexes. The color of the resulting complexes varied with the diene: pale orange for isoprene,[1,13] light olive for myrcene,[18] and reddish brown for 2-phenyl-1,3-butadiene.[19]

The basic difference in chemistry between unsymmetrical and symmetrical (2-butene-1,4-diyl)magnesium originates from the fact that the former possesses four totally different reactive sites and the latter has only two nonidentical nucleophilic centers. Accordingly, the regiochemistry of electrophilic attack is one of the essential problems associated with the reactions of these unsymmetrical (2-butene-1,4-diyl)magnesium complexes. We have found that treatment of the magnesium complexes

(18) (a) Baker, R.; Cookson, R. C.; Saunders, A. D. *J. Chem. Soc., Perkin, Trans. 1* **1976**, 1815. (b) Akutagawa, S.; Otsuka, S. *J. Am. Chem. Soc.* **1976**, *98*, 7420.

(19) Acidic hydrolysis of the magnesium complex of 2-phenyl-1,3-butadiene at 0 °C gave a mixture of 2-phenyl-1-butene, 2-phenyl-2-butene, and 3-phenyl-1-butene in a ratio of 37:50:13.

Table IV. Regioselective Reactions of Unsymmetrical (2-Butene-1,4-diyl)magnesium Complexes with Two Different Electrophiles

entry	Mg diene[a]	R_3SiCl[b]	product(s)[c,d]	% yield
1	2c	$(CH_3)_3SiCl$	 **28** (77:23) **29**	91
2	2c	$(n\text{-Bu})_3SiCl$	 **30** (92:8) **31**	94
3	2d	$(CH_3)_3SiCl$	 **32** (94:6) **33**	82
4	2d	$(n\text{-Bu})_3SiCl$	 **34**	94
5	2e	$(CH_3)_3SiCl$	 **35**	95
6	2e	$(n\text{-Bu})_3SiCl$	 **36**	92

[a] **2c** = THF solution of (2-methyl-2-butene-1,4-diyl)magnesium; **2d** = THF solution of (2-(4-methyl-3-pentenyl)-2-butene-1,4-diyl)magnesium; **2e** = THF solution of (2-phenyl-2-butene-1,4-diyl)magnesium. [b] R_3SiCl was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and then warmed to 0 °C prior to the addition of cyclohexanone. [c] The compositions of all products (or major isomers) were determined by high-resolution mass spectroscopy and/or elemental analyses. The structures of all compounds were established by ^1H NMR, ^{13}C NMR, IR, and mass spectra. [d] Ratios of isomers are given in parentheses. Individual isomers were separated by chromatography.

with triorganosilyl chloride in THF at −78 °C, followed by cyclohexanone at 0 °C, afforded a stepwise addition across a terminal double bond with high regioselectivity (Scheme V). The results of the regioselective reactions are summarized in Table IV.

It is believed that the initial attack of the complex by the organosilicon reagent determined the selectivity, which was found to be dependent on both the diene substrate and the initial electrophile. The reaction of (2-methyl-2-butene-1,4-diyl)magnesium (**2c**) with trimethylsilyl chloride resulted in initial attack at the 4- or 1-position, producing two isomers of allylic Grignards (refer to **3c**).[17] Treatment of the allylic Grignards with cyclohexanone led to overall additions across a terminal double bond. Workup gave a 77:23 mixture of **28**/**29** in 91% total yield (Table IV, entry 1).

Increasing the size of the organosilicon reagent resulted in increased regioselectivity. This was demonstrated by using tri-*n*-butylsilyl chloride as the initial electrophile.

Larger substituents at the 2-position of the diene were also demonstrated to increase selectivity. The magnesium complex (**2d**) of myrcene reacted with trimethylsilyl chloride, followed by cyclohexanone, to yield compounds **32** and **33** in a 94:6 ratio (Table IV, entry 3). Furthermore, a single isomer was obtained in excellent yield by replacing the first electrophile with tri-*n*-butylsilyl chloride.

Remarkably, (2-phenyl-2-butene-1,4-diyl)magnesium (**2e**) reacted exclusively at the 4-position with either organosilicon electrophile. The resulting allylic Grignard added to cyclohexanone exclusively in the 3-position.

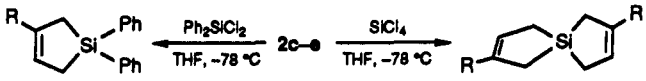
It is noteworthy to point out that reaction of unsymmetrical (2-butene-1,4-diyl)magnesium with α,ω-alkylene dihalides usually gives two isomeric products. For example, treatment of (2-phenyl-2-butene-1,4-diyl)magnesium with 1,3-dibromopropane at −78 °C followed by warming up to room temperature resulted in the generation of two five-membered carbocycles, 1-phenyl-1-ethenylcyclopentane and α-cyclopentylstyrene with a ratio of 77:23, in 76% isolated yield. The control of the regiochemistry is currently under study.

Preparation of Silicon-Containing Cyclic Compounds. One of the useful applications of substituted (2-butene-1,4-diyl)magnesium complexes is the facile synthesis of silicon-containing five-membered cyclic compounds. This reaction has been reported earlier for the magnesium complex of 1,3-butadiene.[20]

In contrast to the general 1,2-cyclizations of symmetrical (2-butene-1,4-diyl)magnesium complexes with α,ω-alkylene

(20) (a) Richter, W. J. *Synthesis* **1982**, 1102. (b) Richter, W. J. *J. Organomet. Chem.* **1985**, *289*, 45. (c) Salomon, R. G. *J. Org. Chem.* **1974**, *39*, 3602.

Scheme VI



dihalides, reactions of both symmetrical and unsymmetrical (2-butene-1,4-diyl)magnesium complexes with diorganosilyl dichlorides yield exclusively overall 1,4-additions, generating silicon-containing five-membered rings. Some of these results are summarized in Table V.

For example, dichlorodimethylsilane reacted with (1,4-diphenyl-2-butene-1,4-diyl)magnesium at −78 °C to give *cis*-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene (**37**) in 66% isolated yield. Unsymmetrically substituted silicon-containing heterocycles also can be prepared in this manner (Table V, entries 3–5) (Scheme VI).

Significantly, double annelation can be accomplished in one step by treating the magnesium complex with $SiCl_4$ to form spiroheterocycles (Scheme VI) (Table V, entries 6–8). Addition of $SiCl_4$ to the THF solution of (2-methyl-2-butene-1,4-diyl)magnesium at −78 °C caused an instantaneous disappearance of the pale orange color. Workup gave 2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene (**42**) in 75% isolated yield. This compound has been previously reported to be difficult to prepare.[21] Utilization of magnesium complexes of 1,3-dienes allows the preparation to be carried out under extremely mild conditions.

Conclusion

It has been demonstrated that substituted (2-butene-1,4-diyl)magnesium complexes can be readily prepared by using highly reactive magnesium. Significantly, these halide-free bis-Grignard reagents can be used for the convenient preparation of highly substituted three-, four-, five-, and six-membered carbocycles. Significantly, the cyclizations are always stereospecific and completely regioselective. Depending on the initial 1,3-diene and the specific electrophiles, uncyclized adducts can be trapped by protonation, producing complex halo olefins. In the case of (2,3-dimethyl-2-butene-1,4-diyl)magnesium, formal 1,2-additions can be effected by the proper choice of electrophiles. Polyfunctionalized organic molecules can be prepared in this manner. Substituted five- and six-membered cyclic ketones can also be synthesized in one step by this approach. The reactions of unsymmetrical (2-butene-1,4-diyl)magnesium complexes with two different electrophiles furnish stepwise additions across a terminal double bond in high regioselectivity with the introduction of two functional groups. Finally, silicon-containing heterocycles and spiro compounds can also be readily synthesized by this approach.

Experimental Section

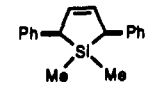
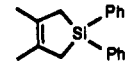
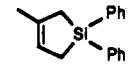
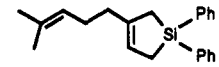
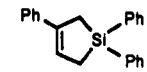
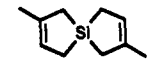
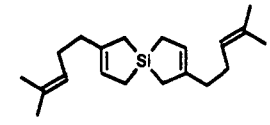
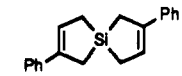
General Aspects. ^1H NMR (360 MHz) spectra were recorded in $CDCl_3$ solution unless specified. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Fully decoupled ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ solution. The center peak of $CDCl_3$ (77.0 ppm) was used as the internal reference. FTIR spectra are reported as cm^{-1}. Mass spectra were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln.

All manipulations were carried out under an atmosphere of argon on a dual manifold vacuum/argon system. The Linde prepurified grade argon was further purified by passage over a BASF R3-11 catalyst column at 150 °C, a phosphorus pentoxide column, and a column of granular potassium hydroxide. Lithium, naphthalene, and $MgCl_2$ were weighed out and charged into reaction flasks under argon in a Vacuum Atmospheres Company drybox. Tetrahydrofuran was distilled from Na/K alloy under an atmosphere of argon immediately before use.

Gas chromatographic analyses were done on a Hewlett-Packard 5890A chromatograph using stainless steel columns (12 ft × $^1/_8$ in.) packed with OV-17 (3%) on 100/120 Chromosorb G-AW or SE-30 (5%) on 100/120 Chromosorb G-NAW. Preparative gas chromatographic separations were obtained on a Varian Aerograph (model 920) chromatograph equipped with a stainless steel column (25 ft × $^1/_4$ in.) packed with GP 10% SP 2100 on 100–120 Supelcoport. Analytical thin-layer chromatography was performed by using Merck 5735 indicating plates precoated with silica gel 60 F_{254} (layer thickness 0.2 mm). Preparative thin-layer chromatographic separations were obtained by using Analtech silica gel GF (layer thickness 2 mm) preparative plates or Whatman PLKC 18F linear-K reversed-phase preparative plates (layer thickness 1 mm). Liquid chromatographic purifications were performed by flash column chromatography using glass columns packed with Merck silica gel 60 (230–400 mesh). Low-temperature conditions were obtained by utilizing a Neslab endocal ULT-80 refrigerated circulating bath or by utilizing dry ice/acetone baths.

Preparation of Activated Magnesium (Mg*). Activated magnesium was prepared by the reduction of anhydrous magnesium chloride with lithium using naphthalene as an electron carrier.[4,7] Highly reactive magnesium can also be prepared from the reduction of magnesium chloride by preformed lithium na-

Table V. Preparation of Silicon-Containing Heterocycles and Spiro Compounds from Substituted (2-Butene-1,4-diyl)magnesium

entry	Mg diene	electrophile[a]	product[b]	% yield
1	**2a**	Me_2SiCl_2	 **37**	66
2	**2b**	Ph_2SiCl_2	 **38**	65
3	**2c**	Ph_2SiCl_2	 **39**	96
4	**2d**	Ph_2SiCl_2	 **40**	91
5	**2e**	Ph_2SiCl_2	 **41**	93
6	**2c**	$SiCl_4$	 **42**	75
7	**2d**	$SiCl_4$	 **43**	62
8	**2e**	$SiCl_4$	 **44**	34

[a] Electrophiles were added to the THF solution of substituted (2-butene-1,4-diyl)magnesium complexes at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then warmed to 0 °C prior to workup. [b] All new compounds were completely characterized spectroscopically.

(21) Terumuna, D.; Hatta, S.; Araki, T.; Ueki, T.; Okazaki, T.; Suzuki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1545.

phthalenide. In a typical preparation, lithium (10.0 mmol) and naphthalene (10.8 mmol) in freshly distilled THF (15 mL) were stirred under argon until the lithium was completely consumed (ca. 2 h). The resulting dark green lithium naphthalenide was then transferred dropwise via a cannula into a THF solution (10 mL) of anhydrous magnesium chloride (4.8 mmol). The mixture was stirred at room temperature for 30 min. The newly formed magnesium slurry was allowed to settle for at least 3 h, and then the supernatant was drawn off via a cannula. Freshly distilled THF was added, followed by the appropriate 1,3-diene. (Note: The number of millimoles of Mg* cited in this paper refers to the theoretical amount possible, based on the original amount of magnesium chloride).

Typical Cyclization of (1,4-Diphenyl-2-butene-1,4-diyl)magnesium. (*E,E*)-1,4-Diphenyl-1,3-butadiene (0.825 g, 4.00 mmol) dissolved in 10 mL of THF was added via a cannula to the activated magnesium (4.80 mmol) in THF (20 mL) at room temperature. The reaction mixture turned purple immediately and then became red after the addition was completed. The mixture was stirred at room temperature for 2 h. The resulting dark red solution of **2a** was cooled to −78 °C. 1,3-Dichloropropane (0.507 g, 4.48 mmol) was added via a disposable syringe at −78 °C. Stirring was continued at −78 °C for 2 h. Then the reaction mixture was gradually warmed to room temperature and stirred for 30 min. An aqueous solution of 3 N HCl (10 mL) was added at 0 °C, giving a clear solution. The reaction mixture was washed with diethyl ether (30 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic portions were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and water (20 mL) and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was flash chromatographed on silica gel, eluting sequentially with hexanes and 100:1 hexanes/Et_2O. *trans*-1-Phenyl-2-((*E*)-2-phenylethenyl)cyclopentane (0.807 g) was obtained in 81% isolated yield. This compound was also prepared in 65% isolated yield from **2a** and 1,3-dibromopropane.

***trans*-1-Phenyl-2-((*E*)-2-phenylethenyl)cyclopentane[5] (5):** ^1H NMR δ 7.30–7.19 (m, 8 H), 7.18–7.11 (m, 2 H), 6.25–6.11 (m, 2 H), 2.85–2.75 (m, 1 H), 2.74–2.63 (m, 1 H), 2.22–2.02 (m, 2 H), 1.92–1.60 (m, 4 H); ^{13}C NMR δ 144.6, 137.8, 133.7, 129.3, 128.5, 128.3, 127.6, 126.8, 126.1, 126.0, 52.8, 51.7, 35.1, 33.3, 24.3; IR (neat) 3079, 3058, 3025, 2952, 2867, 1600, 1494, 1448, 964, 744, 698 cm^{-1}; EIMS *m/z* (relative intensity) 248 ($M^{\cdot+}$, 13), 157 (17), 144 (100), 129 (44), 117 (23), 91 (29).

***trans*-1-Phenyl-2-((*E*)-2-phenylethenyl)cyclohexane[5] (4):** 51% isolated yield from **2a** and 1,4-dichlorobutane; 40% isolated yield from **2a** and 1,4-dibromobutane; ^1H NMR δ 7.26–7.07 (m, 10 H), 6.12 (d, *J* = 16.0 Hz, 1 H), 5.95–5.86 (dd, *J* = 16.0, 7.1 Hz, 1 H), 2.42–2.32 (m, 2 H), 1.98–1.78 (m, 4 H), 1.60–1.30 (m, 4 H); ^{13}C NMR δ 146.0, 138.0, 135.0, 128.8, 128.3, 128.2, 127.7, 126.6, 125.9 (2 C), 50.6, 46.5, 35.5, 33.4, 26.7, 26.1; IR (neat) 3082, 3060, 3026, 2924, 2850, 1600, 1495, 1446, 962, 744, 698 cm^{-1}; EIMS *m/z* (relative intensity) 262 ($M^{\cdot+}$, 38), 171 (16), 158 (100), 143 (34), 129 (65), 117 (50), 115 (28), 91 (47).

5,8-Diphenyl-6-dodecene (8): 93% isolated yield as a 56:44 cis/trans mixture from **2a** and *n*-butyl bromide; 87% isolated yield as a 28:72 cis/trans mixture from **2a** and *n*-butyl chloride. Both isomers (cis and trans) were separated by preparative thin-layer chromatography as their diastereomers.

***cis*-5,8-Diphenyl-6-dodecene (8a):** mixture of diastereomers; ^1H NMR δ 7.33–7.00 (m, 10 H), 5.60–5.46 (m, 2 H), 3.67–3.54 (m, 2 H), 1.80–1.44 (m, 4 H), 1.42–0.97 (m, 8 H), 0.91 (t) and 0.76 (t) (6 H); ^{13}C NMR δ (145.8, 145.4), (133.6, 133.5), (128.4, 128.3), (127.4, 127.3), (125.9, 125.7), (43.8, 43.7), (36.9, 36.6), (29.9, 29.7), (22.8, 22.6), (14.1, 13.9); IR (neat) 3084, 3060, 3026, 3001, 2956, 2927, 2871, 2856, 1601, 1493, 1466, 1452, 1031, 741, 698 cm^{-1}; EIMS *m/z* (relative intensity) 320 ($M^{\cdot+}$, 1.3), 263 (20), 242 (4), 207 (4.0), 193 (7), 185 (12), 173 (10), 160 (12), 147 (12), 129 (16), 117 (40), 91 (100); HRMS calcd for $C_{24}H_{32}$ 320.2504, found 230.2502. Anal. Calcd: C, 89.94; H, 10.06. Found: C, 89.67; H, 10.26.

***trans*-5,8-Diphenyl-6-dodecene[22] (8b):** mixture of diastereomers; ^1H NMR δ 7.31–7.22 (m, 4 H), 7.20–7.12 (m, 6 H), 5.60–5.54 (m, 2 H), 3.24–3.12 (m, 2 H), 1.72–1.60 (m, 4 H), 1.35–1.05 (m, 8 H), 0.90–0.78 (m, 6 H); ^{13}C NMR δ (145.5, 145.4), (133.8, 133.6), 128.3 (2 C), (127.6, 127.5), 125.8 (2 C), (48.7, 48.6), (35.9, 35.8), (29.9, 29.8), (22.63, 22.60), (14.05, 14.00); IR (neat) 3081, 3060, 3025, 3001, 2954, 2925, 2869, 2856, 1601, 1493, 1466, 1452, 970, 755, 698 cm^{-1}.

***trans*-(2-Phenylcyclohexyl)methanol.** *trans*-1-Phenyl-2-((*E*)-2-phenylethenyl)cyclohexane (0.121 g, 0.46 mmol) mixed with 20 mL of CH_3OH/CH_2Cl_2 (3:1, v/v) was bubbled through by O_3 at −78 °C for 5 min. The solution was then immediately flushed with nitrogen for 3 min. Excess $NaBH_4$ was added at −78 °C, and then the reaction mixture was gradually warmed to room temperature and stirred for 1 h. Solvents were evaporated, and 15 mL of water was added. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phases were washed with brine (2 × 15 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent and flash column chromatography (eluted by hexanes/EtOAc, 5:1) afforded *trans*-(2-phenylcyclohexyl)methanol: 0.079 g, 91% yield; mp 50–51 °C (lit.[9a] mp 50–51 °C); ^1H NMR δ 7.31–7.24 (m, 2 H), 7.21–4.14 (m, 3 H), 3.35 (dd, *J* = 10.8, 3.8 Hz, 1 H), 3.20 (dd, *J* = 10.8, 6.2 Hz, 1 H), 2.32 (td, *J* = 11.6, 3.3 Hz, 1 H), 2.01–1.92 (m, 1 H), 1.90–1.02 (m, 8 H); ^{13}C NMR δ 145.8, 128.6, 127.4, 126.2, 66.5, 47.3, 45.2, 35.5, 29.9, 26.7, 26.1.

Typical Reaction of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium. An excess of freshly distilled 2,3-dimethyl-1,3-butadiene (1.5 mL) was added to activated magnesium (6.10 mmol) in THF (10 mL). The mixture was stirred at room temperature for 8 h, giving a pale orange solution.[4] The THF solution of newly formed **2b** was cooled to −78 °C, and 1,3-dibromopropane (1.079 g, 5.34 mmol) mixed with 10 mL of THF was added via a cannula. *n*-Undecane was added as an internal standard via a disposable syringe. The reaction was monitored by GC with an OV-17 column, and GC yield was based on the analyses of reaction quenches. The mixture was stirred at −78 °C for 2 h, then gradually warmed to room temperature, and stirred overnight. An aqueous solution of 3 N HCl (10 mL) was added at 0 °C. The reaction mixture was washed with diethyl ether (30 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL), and the combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and water (20 mL) and dried over anhydrous $MgSO_4$. Evaporation of solvents using a rotary evaporator at 0–5 °C and flash column chromatography (eluted by pentane only) gave **1-methyl-1-(1-methylethenyl)cyclopentane[5] (12):** 75% GC yield; ^1H NMR δ 4.71 (m, 1 H), 4.67 (m, 1 H), 1.76 (m, 3 H), 1.72–1.60 (m, 6 H), 1.48–1.37 (m, 2 H), 1.05 (s, 3 H); ^{13}C NMR δ 153.4, 107.7, 48.1, 37.8, 26.0, 23.8, 20.2; IR (neat) 3086, 2958, 2873, 1639, 1452, 1369, 889 cm^{-1}; EIMS *m/z* (relative intensity) 124 ($M^{\cdot+}$, 7), 109 (20), 95 (21), 84 (95), 83 (100), 69 (47); HRMS calcd for C_9H_{16} 124.1252, found 124.1250.

7-Bromo-2,3,3-trimethyl-1-heptene (9): 79% yield; ^1H NMR δ 4.76 (s, 1 H), 4.70 (s, 1 H), 3.40 (t, *J* = 6.9 Hz, 2 H), 1.82 (m, 2 H), 1.70 (s, 3 H), 1.38–1.20 (m, 4 H), 1.04 (s, 6 H); ^{13}C NMR δ 151.8, 109.7, 39.9, 38.7, 33.8, 33.6, 27.3, 23.4, 19.4; IR (neat) 3087, 2964, 2941, 2866, 1633, 1462, 1446, 1376, 890 cm^{-1}; EIMS *m/z* (relative intensity) 220 ($[M + 2]^{\cdot+}$, 0.8), 218 ($M^{\cdot+}$, 1.5), 206 (6.8), 204 (7.5), 137 (10), 135 (4), 128 (62), 109 (32), 83 (100), 69 (83). Anal. Calcd for $C_{10}H_{19}Br$: C, 54.80; H, 8.74. Found: C, 55.06; H, 8.69.

1-Methyl-1-(1-methylethenyl)cyclohexane (10):[5,23] 53% (69% GC) yield; ^1H NMR δ 4.79 (m, 1 H), 4.75 (m, 1 H), 1.71 (t, *J* = 0.5 Hz, 3 H), 1.71–1.63 (m, 2 H), 1.52–1.24 (m, 8 H), 0.98 (s, 3); ^{13}C NMR δ 152.7, 109.1, 38.8, 36.4, 27.1, 26.5, 22.6, 19.6; IR (neat) 3087, 2933, 2854, 1635, 1446, 1373, 891, 787 cm^{-1}; EIMS *m/z* (relative intensity) 138 ($M^{\cdot+}$, 4.4), 123 (9), 95 (15), 84 (100), 83 (86), 69 (22); HRMS calcd for $C_{10}H_{18}$ 138.1409, found 138.1411.

6-Bromo-2,3,3-trimethyl-1-hexene (11): 72% yield; ^1H NMR δ 4.77 (m, 1 H), 4.70 (m, 1 H), 3.38 (t, *J* = 6.7 Hz, 2 H), 1.70 (t, *J* = 0.6 Hz, 3 H), 1.74–1.65 (m, 2 H), 1.49–1.43 (m, 2 H), 1.05 (s, 6 H); ^{13}C NMR δ 151.4, 110.0, 39.3, 38.5, 34.7, 28.4, 27.3, 19.4; IR (neat) 3087, 2964, 2871, 1635, 1448, 1377, 1247, 893 cm^{-1}; EIMS *m/z* (relative intensity) 206 ($[M + 2]^{\cdot+}$, 0.2), 204 ($M^{\cdot+}$, 0.2), 191 (3.7), 189 (3.7), 125 (3.2), 109 (4.9), 84 (35), 83 (100), 69 (14); HRMS calcd for $C_9H_{17}{}^{79}Br$ and $C_9H_{17}{}^{81}Br$ 204.0513 and 206.0493, found 204.0508 and 206.0485.

(22) Forkner, M. W. Ph.D. Dissertation, University of Nebraska, Lincoln, NE, 1988.

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6-Chloro-2,3,3-trimethyl-1-hexene (13): 81% yield; ^{1}H NMR δ 4.77 (m, 1 H), 4.70 (m, 1 H), 3.50 (t, J = 6.5 Hz, 2 H), 1.70 (m, 3 H), 1.66–1.56 (m, 2 H), 1.49–1.42 (m, 2 H), 1.05 (s, 6 H); ^{13}C NMR δ 151.4, 110.0, 45.8, 38.5, 37.9, 28.1, 27.2, 19.3; IR (neat) 3089, 2965, 2871, 1637, 1446, 1377, 1307, 893 cm^{-1}; EIMS m/z (relative intensity) 162 ([M + 2]$^{\bullet+}$, 0.1), 160 (M$^{\bullet+}$, 0.3), 147 (1.2), 145 (3.5), 128 (1.4), 124 (1.4), 109 (2.1), 84 (25), 83 (100), 69 (12); HRMS calcd for $C_9H_{17}{}^{35}Cl$ and $C_9H_{17}{}^{37}Cl$ 160.1019 and 162.0989, found 160.1024 and 162.0992.

1-Methyl-1-(1-methylethenyl)cyclobutane (14): isolated by preparative GC, 49% GC yield from **2b** and 1,2-dibromoethane, 61% GC yield from **2b** and 1,2-dichloroethane; ^{1}H NMR δ 4.67 (m, 1 H), 4.61 (m, 1 H), 2.16–2.06 (m, 2 H), 2.00–1.66 (m, 4 H), 1.65 (t, J = 0.6 Hz, 3 H), 1.25 (s, 3 H); ^{13}C NMR δ 154.1, 106.7, 44.3, 32.6, 26.4, 17.9, 14.6; EIMS m/z (relative intensity) 110 (M$^{\bullet+}$, 1.6), 95 (36), 82 (92), 67 (100); HRMS calcd for C_8H_{14} 110.1096, found 110.1097.

4-(2-Bromophenyl)-2,3,3-trimethyl-1-butene (15): 62% yield; ^{1}H NMR δ 7.55 (m, 1 H), 7.22–7.10 (m, 2 H), 7.06–6.99 (m, 1 H), 4.80 (m, 1), 4.67 (m, 1 H), 2.89 (s, 2 H), 1.88 (t, J = 0.6 Hz, 3 H), 1.08 (s, 6 H); ^{13}C NMR δ 151.9, 138.9, 132.7, 131.9, 127.5, 126.5, 126.3, 110.4, 44.5, 40.8, 26.6, 20.0; IR (neat) 3089, 3064, 2968, 2931, 2873, 1635, 1591, 1566, 1469, 1437, 1377, 1026, 893, 754, 735 cm^{-1}; EIMS m/z (relative intensity) 254 ([M + 2]$^{\bullet+}$, 0.3), 252 (M$^{\bullet+}$, 0.3), 173 (27), 115 (4), 83 (100), 67 (7); HRMS calcd for $C_{13}H_{17}{}^{79}Br$ and $C_{13}H_{17}{}^{81}Br$ 252.0513 and 254.0494, found 252.0504 and 254.0499. Anal. Calcd: C, 61.67; H, 6.77. Found: C, 61.44; H, 6.59.

2-Methyl-2-(1-methylethenyl)-2,3-dihydro-1*H*-indene (16): ~30% yield; ^{1}H NMR δ 7.22–7.16 (m, 2 H), 7.15–7.11 (m, 2 H), 4.80 (d, J = 0.7 Hz, 1 H), 4.76 (d, J = 0.7 Hz, 1 H), 3.12 (d, J = 15.3 Hz, 2 H), 2.70 (d, J = 15.3 Hz, 2 H), 1.83 (s, 3 H), 1.16 (s, 3 H); ^{13}C NMR δ 152.2, 142.8, 126.1, 124.7, 108.6, 48.9, 44.8, 26.8, 20.2; IR (neat) 3082, 3022, 2962, 2927, 2843, 1639, 1481, 1458, 889, 750, 733 cm^{-1}; EIMS m/z (relative intensity) 172 (M$^{\bullet+}$, 44), 157 (M$^{\bullet+}$, 44), 157 (53), 143 (30), 142 (33), 129 (100), 115 (53), 91 (28), 83 (92), 69 (29); HRMS calcd for $C_{13}H_{16}$ 172.1252, found 172.1251.

Typical Stepwise Reaction of (2,3-Dimethyl-2-butene-1,4-diyl)magnesium. Freshly formed **2b**, prepared from freshly distilled 2,3-dimethyl-1,3-butadiene (2 mL) and activated magnesium (7.32 mmol), in 10 mL of THF was cooled to −78 °C. 1,4-Dibromobutane (1.299 g, 6.01 mmol) in 10 mL of THF was added dropwise via a cannula at −78 °C. After being stirred at −78 °C for 30 min, the reaction mixture was allowed to warm gradually to room temperature. Stirring was continued for 1 h at room temperature. The reaction flask was cooled to 0 °C with an ice bath, and an excess of benzoyl chloride (1.111 g, 7.90 mmol) was added via a disposable syringe. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature. An aqueous solution of HCl (1.5 N, 15 mL) was added at 0 °C. The mixture was washed with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL), and the combined organic portions were washed with brine (2 × 20 mL) and dried over $MgSO_4$. Evaporation of solvents and flash column chromatography (eluted by hexanes/Et_2O, 100:3) gave **7-bromo-2,3-dimethyl-3-((phenylcarbonyl)methyl)-1-heptene (18)**: 1.165 g, 60% yield; ^{1}H NMR δ 7.94–7.86 (m, 2 H), 7.56–7.48 (m, 1 H), 7.47–7.38 (m, 2 H), 4.87 (t, J = 1.2 Hz, 1 H), 4.74 (d, J = 0.7 Hz, 1 H), 3.38 (t, J = 6.8 Hz, 2 H), 3.11 (d, J = 15.3 Hz, 1 H), 3.00 (d, J = 15.3 Hz, 1 H), 1.86–1.77 (m, 2 H), 1.74 (d, J = 0.7 Hz, 3 H), 1.64–1.46 (m, 2 H), 1.40–1.22 (m, 2 H), 1.20 (s, 3 H); ^{13}C NMR δ 199.3, 149.3, 138.5, 132.6, 128.4, 127.9, 111.3, 46.6, 41.9, 38.4, 33.6, 33.2, 23.7, 22.7, 19.7; EIMS m/z (relative intensity) 324 ([M + 2]$^{\bullet+}$, 0.7), 322 (M$^{\bullet+}$, 0.6), 309 (1.6), 307 (1.4), 243 (18), 133 (5), 105 (100), 95 (17), 77 (94), 69 (31); HRMS calcd for $C_{17}H_{23}O^{79}Br$ and $C_{17}H_{23}O^{81}Br$ 322.0932 and 324.0912, found 322.0937 and 324.0906.

7-Bromo-2,3-dimethyl-3-((methylcarbonyl)methyl)-1-heptene (17): 62% yield; ^{1}H NMR δ 4.89 (s, 1 H), 4.73 (s, 1 H), 3.40 (t, J = 6.8 Hz, 2 H), 2.62 (d, J = 14.4 Hz, 1 H), 2.40 (d, J = 14.4 Hz, 1 H), 2.10 (s, 3 H), 1.87–1.77 (m, 2 H), 1.75 (s, 3 H), 1.56–1.46 (m, 1 H), 1.41–1.19 (m, 3 H), 1.16 (s, 3 H); ^{13}C NMR δ 207.9, 148.8, 111.8, 52.7, 41.6, 38.4, 33.6, 33.1, 32.1, 23.1, 22.5, 19.5, IR (neat) 3089, 2943, 2868, 1705, 1633, 1444, 1376, 1355, 895 cm^{-1}; EIMS m/z (relative intensity) 247 ([M + 2 − CH_3]$^{\bullet+}$, 2.5), 245 ([M − CH_3]$^{\bullet+}$, 2.7), 181 (18), 125 (100), 123 (53), 95 (34), 83 (72), 69 (65); HRMS calcd for $C_{12}H_{21}O^{79}Br$ and $C_{12}H_{21}O^{81}Br$ 260.0776 and 262.0756, found (HREI peak match) 260.0774 and 262.0756. Anal. Calcd: C, 55.18; H, 8.10. Found: C, 55.19; H, 8.00.

2,3-Dimethyl-3-((methylcarbonyl)methyl)-1-heptene (19): 61% yield; ^{1}H NMR δ 4.87 (m, 1 H), 4.72 (m, 1 H), 2.62 (d, J = 14.2 Hz, 1 H), 2.37 (d, J = 14.2 Hz, 1 H), 2.10 (s, 3 H), 1.74 (t, J = 0.6 Hz, 3 H), 1.53–1.43 (m, 1 H), 1.38–0.96 (m, 5 H), 1.14 (s, 3 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 208.0, 149.2, 111.5, 53.0, 41.7, 39.5, 32.0, 26.0, 23.2, 23.1, 19.5, 14.0; IR (neat) 3089, 2958, 2931, 2871, 2862, 1707, 1635, 1454, 1377, 1356, 893 cm^{-1}; EIMS m/z (relative intensity) 182 (M$^{\bullet+}$, 0.5), 167 (5.9), 149 (2.0), 125 (100), 111 (29), 109 (30), 95 (27), 83 (99), 69 (72); HRMS calcd for $C_{12}H_{22}O$ 182.1671, found 182.1677.

2,3-Dimethyl-3-((phenylcarbonyl)methyl)-1-heptene (20): 82% yield; ^{1}H NMR δ 7.94–7.88 (m, 2 H), 7.54–7.48 (m, 1 H), 7.45–7.38 (m, 2 H), 4.84 (s, 1 H), 4.72 (s, 1 H), 3.10 (d, J = 15.2 Hz, 1 H), 3.00 (d, J = 15.2 Hz, 1 H), 1.73 (s, 3 H), 1.61–1.42 (m, 2 H), 1.34–1.04 (m, 4 H), 1.19 (s, 3 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 199.4, 149.7, 138.6, 132.5, 128.3, 127.9, 110.9, 46.8, 41.9, 39.5, 26.1, 23.7, 23.2, 19.7, 14.0; IR (neat) 3087, 3060, 2956, 2931, 2871, 2860, 1691, 1676, 1635, 1597, 1448, 1213, 893, 752, 690 cm^{-1}; EIMS m/z (relative intensity) 244 (M$^{\bullet+}$, 0.1), 229 (1.1), 187 (17), 124 (8), 105 (100), 77 (52); HRMS calcd for $C_{17}H_{24}O$ 244.1827, found 244.1833. Anal. Calcd: C, 83.55; H, 9.90. Found: C, 83.32; H, 9.92.

3,4-Dimethyl-3-((trimethylsilyl)methyl)-4-penten-2-one[24] (21): 73% yield; ^{1}H NMR δ 5.01 (s, 1 H), 4.97 (s, 1 H), 2.01 (s, 3 H), 1.60 (s, 3 H), 1.26 (s, 3 H), 1.06 (s, 2 H), −0.01 (s, 9 H); ^{13}C NMR δ 211.7, 148.3, 112.2, 56.3, 24.2, 23.9, 22.5, 20.2, 0.4; IR (neat) 3089, 2952, 2898, 1710, 1637, 1450, 1419, 1379, 1352, 1250, 897, 850 cm^{-1}; EIMS m/z (relative intensity) 198 (M$^{\bullet+}$, 0.7), 183 (9), 155 (17), 125 (2.2), 109 (2.0), 73 (100); HRMS calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1449. Anal. Calcd: C, 66.60; H, 11.18. Found: C, 66.83; H, 10.93.

3-Benzoyl-2,3-dimethyl-4-(trimethylsilyl)-1-butene[25] (22): 73% yield; ^{1}H NMR δ 7.97–7.90 (m, 2 H), 7.47–7.40 (m, 1 H), 7.36–7.28 (m, 2 H), 5.17 (s, 1 H), 5.01 (s, 1 H), 1.71 (s, 3 H), 1.41 (s, 3 H), 1.40 (d, J = 14.4 Hz, 1 H), 1.21 (d, J = 14.7 Hz, 1 H), −0.06 (s, 9 H); ^{13}C NMR δ 204.2, 150.7, 137.4, 131.8, 129.0, 128.0, 110.8, 55.4, 27.2, 25.4, 20.5, 0.5; IR (neat) 3086, 3066, 2951, 2895, 1678, 1635, 1597, 1446, 1379, 1248, 1221, 899, 854 cm^{-1}; EIMS m/z (relative intensity) 260 (M$^{\bullet+}$, 1.2), 245 (20), 170 (4), 155 (22), 135 (4), 105 (32), 73 (100); HRMS calcd for $C_{16}H_{24}OSi$ 260.1596, found 260.1592.

4-(2-Cyanophenyl)-2,3,3-trimethyl-1-butene (23): 35% yield; ^{1}H NMR δ 7.62–7.57 (m, 1 H), 7.49–7.42 (m, 1 H), 7.32–7.25 (m, 1 H), 7.23–7.15 (m, 1 H), 4.82 (m, 1 H), 4.60 (m, 1 H), 2.91 (s, 2 H), 1.89 (t, J = 0.6 Hz, 3 H), 1.09 (s, 6 H); ^{13}C NMR δ 150.7, 143.1, 132.5, 131.7, 131.2, 126.5, 118.9, 114.0, 111.1, 44.2, 40.7, 26.5, 19.9; IR (neat) 3091, 3070, 2970, 2937, 2877, 2225, 1637, 1601, 1485, 1448, 1379, 895, 766 cm^{-1}; EIMS m/z (relative intensity) 199 (M$^{\bullet+}$, 4.5), 184 (7), 158 (12), 144 (15), 117 (61), 104 (39) 83 (100), 69 (21). Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.46; H, 8.73; N, 7.35.

3-Methyl-3-(1-methylethenyl)-1-tetralone (24): 30% yield, mp 49.5–50 °C; ^{1}H NMR δ 8.02–7.98 (m, 1 H), 7.50–7.42 (m, 1 H), 7.32–7.19 (m, 2 H), 4.78–4.73 (m, 2 H), 3.15 (dd, J = 16.3, 1.66 Hz, 1 H), 2.97–2.88 (m, 2 H), 2.60 (dd, J = 16.4, 0.6 Hz, 1 H), 1.71 (t, J = 0.5 Hz, 3 H), 1.20 (s, 3 H); ^{13}C NMR δ 198.0, 149.0, 142.2, 133.6, 132.0, 128.9, 126.7, 126.6, 111.7, 50.3, 41.9, 41.0, 26.5, 19.3; IR (neat) 3087, 3068, 2964, 2927, 2871, 1685, 1637, 1603, 1454, 1313, 1288, 897, 766, 748 cm^{-1}; EIMS m/z (relative intensity) 200 (M$^{\bullet+}$, 0.1), 185 (4), 158 (69), 143 (43), 128 (8), 118 (100), 90 (43), 77 (6); HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1197. Anal. Calcd: C, 83.96; H, 8.05. Found: C, 83.78; H, 8.09.

5,5,6-Trimethyl-6-heptenenitrile (25): 58% yield; ^{1}H NMR δ 4.77 (m, 1 H), 4.70 (d, J = 0.8 Hz, 1 H), 2.34–2.26 (m, 2 H), 1.70 (d, J = 0.7 Hz, 3 H), 1.51–1.45 (m, 4 H), 1.06 (s, 6 H); ^{13}C NMR δ 150.9, 119.7, 110.2, 39.6, 38.5, 27.1, 20.9, 19.3, 17.6; IR (neat) 3089, 2966, 2875, 2247, 1639, 1450, 1378, 893 cm^{-1}; EIMS m/z (relative intensity) 151 (M$^{\bullet+}$, 0.8), 150 (0.7), 136 (15), 108 (5), 83 (100), 69

(24) Calas, R.; Dunogues, J.; Pisciotti, F. *J. Organomet. Chem.* **1971**, *27*, C21.

(25) Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149.

(12); HRMS calcd for $C_{10}H_{17}N$ 151.1361, found 151.1363.

3-Methyl-3-(1-methylethenyl)cyclohexanone[26] (26): 31% yield; ^1H NMR δ 4.83 (s, 1 H), 4.74 (s, 1 H), 2.60 (d, J = 14.2 Hz, 1 H), 2.20 (d, J = 14.3 Hz, 1 H), 2.36–2.17 (m, 2 H), 1.96–1.54 (m, 4 H), 1.72 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR δ 211.5, 149.7, 111.7, 52.4, 43.7, 40.7, 34.7, 26.7, 21.8, 19.0; IR (neat) 3089, 2956, 2869, 1714, 1635, 1454, 1375, 1315, 1224, 900 cm^{-1}; EIMS m/z (relative intensity) 152 ($M^{\bullet+}$, 30), 137 (61), 123 (11), 109 (100), 95 (56), 83 (49), 82 (45), 81 (56), 67 (86); HRMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1201.

3-Methyl-3-(1-methylethenyl)cyclopentanone (27): 42% yield; ^1H NMR δ 4.80 (m, 1 H), 4.73 (d, J = 0.5 Hz, 1 H), 2.42 (d, J = 17.5 Hz, 1 H), 2.35–2.26 (m, 2 H), 2.13 (d, J = 17.1 Hz, 1 H), 2.10–2.02 (m, 1 H), 1.93–1.84 (m, 1 H), 1.79 (d, J = 0.5 Hz, 3 H), 1.20 (s, 3 H); ^{13}C NMR δ 218.8, 150.4, 109.4, 51.1, 44.8, 36.5, 33.7, 25.5, 19.4; IR (neat) 3084, 2960, 2873, 1745, 1639, 1454, 1406, 1375, 1163, 893 cm^{-1}; EIMS m/z (relative intensity) 138 ($M^{\bullet+}$, 8), 123 (9), 109 (4), 96 (100), 82 (80), 81 (74), 67 (59); HRMS calcd for $C_9H_{14}O$ 138.1044, found 138.1043.

General Procedure for the Preparation of Unsymmetrical (2-Butene-1,4-diyl)magnesium. Isoprene, myrcene, or 2-phenyl-1,3-butadiene was added to an excess of newly generated activated magnesium in 20 mL of THF (typical equivalent ratio of Mg*/diene = 1.5–1.8). After being stirred at room temperature for 2 h, the reaction mixture was allowed to stand until the solution became transparent (approximately 3 h). Then the upper clear solution of magnesium complex was transferred via a cannula to another flask under argon, followed by the appropriate electrophile.

Typical Regioselective Reaction of Unsymmetrical (2-Butene-1,4-diyl)magnesium. A THF solution of **2d** (20 mL), prepared from myrcene (0.281 g, 2.06 mmol, technical grade) and activated magnesium (3.44 mmol), was cooled to −78 °C, and Me_3SiCl (0.171 g, 1.57 mmol) was added via a disposable syringe. Stirring was continued at −78 °C for 1 h, and the reaction mixture was then gradually warmed to 0 °C. Excess cyclohexanone (0.278 g, 2.83 mmol) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. An aqueous solution of HCl (1.5 N, 10 mL) was added at 0 °C. The mixture was washed with diethyl ether (20 mL), and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (2 × 15 mL) and brine (20 mL) and dried over $MgSO_4$. Removal of solvents and flash column chromatography (eluted by hexanes/Et_2O, 98:2) gave **32** (0.372 g, 77%) and **33** (0.025 g, 5%) (compound **33** was eluted out before compound **32**) in 82% total yield.

1-(2-(4-Methyl-3-pentenyl)-1-((trimethylsilyl)methyl)-2-propenyl)cyclohexanol (32) and 1-(1-ethenyl-5-methyl-1-((trimethylsilyl)methyl)-4-hexenyl)cyclohexanol (33): 94:6. **32** (major): ^1H NMR δ 5.17–5.09 (m, 1 H), 4.89 (s, 1 H), 4.86 (s, 1 H), 2.20–2.00 (m, 5 H), 1.67 (s, 3 H), 1.60 (s, 3 H), 1.68–1.05 (m, 10 H), 0.84–0.69 (m, 2 H), 0.03 (s, 9 H); ^{13}C NMR δ 151.1, 131.5, 124.4, 111.4, 73.2, 53.0, 35.6, 35.5, 25.9, 25.8, 25.7, 22.3, 22.1, 17.6, 14.9, −0.9; IR (neat) 3485 (br), 3080, 2931, 2858, 1633, 1448, 1375, 1246, 972, 891, 860, 837 cm^{-1}; EIMS m/z (relative intensity) 290 ([M − H_2O]$^{\bullet+}$, 0.3), 275 (0.2), 210 (7), 171 (28), 141 (87), 99 (16), 73 (100); HRMS calcd for $C_{19}H_{38}OSi$ and $C_{18}{}^{13}CH_{38}OSi$ 308.2535 and 309.2563, found (HREI peak match) 308.2530 and 309.2559. Anal. Calcd: C, 73.96; H, 11.76. Found: C, 74.15; H, 11.80.

33 (minor): ^1H NMR δ 5.81 (dd, J = 17.6, 11.0 Hz, 1 H), 5.15–4.95 (m, 3 H), 2.10–0.95 (m, 14 H), 1.65 (s, 3 H), 1.59 (s, 3 H), 0.91 (d, J = 15.0 Hz, 1 H), 0.75 (d, J = 15.0 Hz, 1 H), 0.04 (s, 9 H); ^{13}C NMR δ 145.5, 131.0, 125.3, 114.1, 75.8, 50.6, 33.3, 31.6, 31.5, 25.7, 24.0, 22.0, 21.8, 19.8, 17.8, 1.6; IR (neat) 3566 (br), 3080, 2933, 2858, 1631, 1450, 1375, 1259, 1246, 1155, 958, 912, 860, 845 cm^{-1}.

1-(2-Methyl-1-((trimethylsilyl)methyl)-2-propenyl)cyclohexanol (28) and 1-(1-methyl-1-((trimethylsilyl)methyl)-2-propenyl)cyclohexanol (29): 77:23, 91% total yield.

28 (major): ^1H NMR δ 4.85 (m, 1 H), 4.76 (m, 1 H), 2.14 (dd, J = 11.7, 3.4 Hz, 1 H), 1.74 (dd, J = 1.2, 0.7 Hz, 3 H), 1.65–1.10 (m, 10 H), 0.82–0.68 (m, 2 H), −0.03 (s, 9 H); ^{13}C NMR δ 147.0, 114.1, 73.0, 52.6, 35.6, 35.5, 25.8, 22.3, 22.1, 14.0, −1.1; IR (neat) 3487 (br), 3068, 2933, 2858, 1639, 1448, 1373, 1246, 964, 889, 862, 841 cm^{-1}; HRMS (FAB) calcd for [$C_{14}H_{28}OSi$ + Li]$^+$ 247.2070, found 247.2075. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.46; H, 11.97.

29 (minor): ^1H NMR δ 5.91 (dd, J = 17.6, 10.8 Hz, 1 H), 5.13 (dd, J = 10.8, 1.6 Hz, 1 H), 5.01 (dd, J = 17.6, 1.6 Hz, 1 H), 1.67–1.20 (m, 10 H), 1.08 (d, J = 1.0 Hz, 3 H), 0.95 (dd, J = 14.2, 1.0 Hz, 1 H), 0.80 (d, J = 14.2 Hz, 1 H), −0.01 (s, 9 H); ^{13}C NMR δ 145.6, 114.0, 75.3, 46.8, 31.3, 30.5, 25.8, 24.2, 22.2, 22.0, 19.4, 1.00; IR (neat) 3492 (br), 3080, 2935, 2860, 1631, 1448, 1415, 1375, 1248, 1223, 910, 864, 839 cm^{-1}; EIMS m/z (relative intensity) 225 ([M − CH_3]$^+$, 0.7), 207 (0.6), 183 (0.3), 171 (5.3), 142 (12), 99 (27), 73 (100); HRMS calcd for $C_{14}H_{28}OSi$ and [M − CH_3] 240.1909 and 225.1675, found 240.1897 (EI peak match) and 225.1678.

1-(2-Methyl-1-((tri-*n*-butylsilyl)methyl)-2-propenyl)-cyclohexenol (30) and 1-(1-methyl-1-((tri-*n*-butylsilyl)-methyl)-2-propenyl)cyclohexanol (31): 92:8, 94% total yield.

30 (major): ^1H NMR δ 4.85 (m, 1 H), 4.77 (d, J = 1.9 Hz, 1 H), 2.12 (dd, J = 8.5, 6.1 Hz, 1 H), 1.76 (d, J = 0.4 Hz, 3 H), 1.68–1.10 (m, 22 H), 0.87 (t, J = 7.0 Hz, 9 H), 0.76–0.70 (m, 2 H), 0.52–4.44 (m, 6 H); ^{13}C NMR δ 147.2, 114.1, 73.2, 52.3, 35.6, 35.5, 26.9, 26.2, 25.9, 22.3, 22.2, 13.8, 12.4, 9.8; IR (neat) 3491 (br), 3068, 2954, 2924, 2870, 2856, 1636, 1456, 1375, 1196, 1082, 964, 887 cm^{-1}; EIMS m/z (relative intensity) 309 ([M − C_4H_9]$^+$, 0.5), 297 (4.3), 268 (7.8), 199 (100), 143 (67), 99 (19); HRMS calcd for $C_{23}H_{46}OSi$ and $C_{22}{}^{13}CH_{46}OSi$ 366.3318 and 367.3347, found (EI peak match) 366.3301 and 367.3338. Anal. Calcd: C, 75.33; H, 12.64. Found: C, 75.60; H, 12.77.

31 (minor, difficult to isolated): ^1H NMR δ 5.92 (dd, J = 17.6, 10.8 Hz, 1 H), 5.11 (dd, J = 10.8, 1.2 Hz, 1 H), 5.01 (dd, J = 17.6, 1.2 Hz, 1 H), 1.70–1.10 (m, 22 H), 1.07 (s, 3 H), 0.88 (t, J = 7.0 Hz, 9 H), 0.95–0.75 (m, 2 H), 0.53–0.45 (m, 6 H).

1-(2-(4-Methyl-3-pentenyl)-1-((tri-*n*-butylsilyl)methyl)-2-propenyl)cyclohexanol (34): 94% yield; ^1H NMR δ 5.17–5.09 (m, 1 H), 4.89 (s, 1 H), 4.88 (s, 1 H), 2.20–2.03 (m, 5 H), 1.67 (s, 3 H), 1.60 (s, 3 H), 1.70–1.10 (m, 22 H), 0.86 (t, J = 7.2 Hz, 9 H), 0.78–0.73 (m, 2 H), 0.50–0.43 (m, 6 H); ^{13}C NMR δ 151.2, 131.5, 124.3, 111.0, 73.4, 52.6, 35.6, 35.3, 26.9, 26.1, 25.9, 25.8, 25.7, 22.3, 22.1, 17.6, 13.8, 12.5, 10.5; IR (neat) 3491 (br), 3080, 2954, 2922, 2870, 2856, 1633, 1456, 1375, 1194, 964, 887 cm^{-1}; EIMS m/z (relative intensity) 336 ([M − $C_6H_{10}O$]$^{\bullet+}$, 2.3), 297 (1.9), 199 (100), 159 (39), 143 (53), 103 (18); HRMS calcd for $C_{28}H_{54}OSi$ and $C_{27}{}^{13}CH_{54}OSi$ 434.3944 and 435.3973, found (EI peak match) 434.3932 and 435.3961. Anal. Calcd: C, 77.34; H, 12.53. Found: C, 77.22; H, 12.42.

1-(2-Phenyl-1-((trimethylsilyl)methyl)-2-propenyl)cyclohexanol (35): 95% yield; ^1H NMR δ 7.43 (m, 2 H), 7.30 (m, 2 H), 7.23 (m, 1 H), 5.50 (s, 1 H), 5.16 (s, 1 H), 2.83 (t, J = 6.9 Hz, 1 H), 1.69–1.00 (m, 10 H), 0.97 (d, J = 6.9 Hz, 2 H), −0.03 (s, 9 H); ^{13}C NMR δ 150.5, 144.5, 128.3, 127.1, 126.6, 115.5, 74.1, 48.7, 35.6, 35.0, 25.7, 22.0, 21.9, 16.9, −0.5; IR (neat) 3483 (br), 3082, 3057, 3030, 2935, 2860, 1618, 1599, 1574, 1495, 1448, 1248, 966, 903, 862, 843, 704 cm^{-1}; EIMS m/z (relative intensity) 284 ([M − H_2O]$^{\bullet+}$, 0.3), 272 (0.3), 204 (30), 130 (8), 99 (13), 73 (100); HRMS (FAB) calcd for [$C_{19}H_{30}OSi$ + Li] 309.2226, found 309.2221.

1-(2-Phenyl-1-((tri-*n*-butylsilyl)methyl)-2-propenyl)-cyclohexanol (36): 92% yield; ^1H NMR δ 7.50–7.45 (m, 2 H), 7.35–7.28 (m, 2 H), 7.27–7.21 (m, 1 H), 5.53 (s, 1 H), 5.20 (s, 1 H), 2.83 (dd, J = 11.3, 3.5 Hz, 1 H), 1.75–0.89 (m, 24 H), 0.85 (t, J = 7.0 Hz, 9 H), 0.51–0.43 (m, 6 H); ^{13}C NMR δ 150.4, 144.2, 128.3, 127.1, 126.6, 115.0, 74.4, 48.6, 35.6, 34.9, 26.8, 26.1, 25.8, 22.0, 13.7, 12.7; IR (neat) 3487 (br), 3082, 3055, 3028, 2952, 2922, 2870, 2856, 1616, 1599, 1574, 1495, 1464, 1375, 1080, 964, 903, 706 cm^{-1}; EIMS m/z (relative intensity) 330 ([M − $C_6H_{10}O$]$^{\bullet+}$, 2.2), 273 (1.2), 199 (38), 143 (68), 101 (18), 69 (100); HRMS calcd for $C_{28}H_{48}OSi$ and $C_{27}{}^{13}CH_{48}OSi$ 428.3474 and 429.3504, found (EI peak match) 428.3467 and 429.3507.

Typical Reaction of Substituted (2-Butene-1,4-diyl)magnesium with Dichlorodiorganosilane. Newly formed **2a**, prepared from (*E*,*E*)-1,4-diphenyl-1,3-butadiene (0.932 g, 4.52 mmol) and activated magnesium (6.78 mmol), in THF (30 mL) was cooled to −78 °C, and Me_2SiCl_2 (1.105 g, 8.58 mmol) was added via a disposable syringe. After being stirred at −78 °C for 30 min, the mixture was gradually warmed to 0 °C for 30 min. Saturated aqueous NH_4Cl (10 mL) was added. Workup and flash column

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chromatography (eluted by hexanes only) gave ***cis*-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene**[5] **(37)** in 66% yield: ^{1}H NMR (200 MHz) δ 7.00–7.30 (m, 10 H), 6.11 (s, 2 H), 3.27 (s, 2 H), 0.39 (s, 3 H), −0.67 (s, 3 H); ^{13}C NMR δ 143.4, 135.0, 128.3, 126.4, 124.3, 39.9, −2.8, −6.8; IR (neat) 3078, 3059, 3020, 2956, 2850, 1599, 1493, 1248, 1061, 858, 802, 746, 698 cm^{-1}; EIMS *m/z* (relative intensity) 264 (M$^{\bullet+}$, 40), 249 (17), 205 (13), 173 (100), 145 (61), 121 (44), 105 (10), 91 (25), 77 (7); HRMS calcd for $C_{18}H_{20}Si$ and $C_{17}{}^{13}CH_{20}Si$ 264.1334 and 264.1368, found 264.1342 and 265.1365.

1,1-Diphenyl-3,4-dimethylsilacyclopent-3-ene[5,27] **(38)**: 65% yield; ^{1}H NMR δ 7.58–7.52 (m, 4 H), 7.42–7.32 (m, 6 H), 1.86 (s, 4 H), 1.77 (s, 6 H); ^{13}C NMR δ 136.4, 134.8, 130.8, 129.4, 127.9, 24.2, 19.4; IR (neat) 3064, 2978, 2895, 2868, 1645, 1587, 1427, 1167, 1115, 731, 698 cm^{-1}; EIMS *m/z* (relative intensity) 264 (M$^{\bullet+}$, 100), 262 (11), 186 (94), 181 (55), 145 (11), 105 (48).

1,1-Diphenyl-3-methylsilacyclopent-3-ene[27] **(39)**: 96% yield; ^{1}H NMR δ 7.64–7.58 (m, 4 H), 7.46–7.37 (m, 6 H), 5.70 (m, 1 H), 1.90 (m, 5 H), 1.83 (m, 2 H); ^{13}C NMR δ 140.1, 136.2, 134.7, 129.4, 127.9, 124.8, 22.6, 21.8, 17.6; IR (neat) 3066, 2999, 2908, 2879, 1637, 1587, 1427, 1155, 1115, 723, 698 cm^{-1}; EIMS *m/z* (relative intensity) 250 (M$^{\bullet+}$, 83), 208 (12), 181 (76), 172 (100), 145 (4), 105 (48).

1,1-Diphenyl-3-(4-methyl-3-pentenyl)silacyclopent-3-ene (40): 91% yield; ^{1}H NMR δ 7.66–7.61 (m, 4 H), 7.48–7.39 (m, 6 H), 5.78 (s, 1 H), 5.20 (s, 1 H), 2.26 (s, 4 H), 1.93 (s, 2 H), 1.86 (s, 2 H), 1.77 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR δ 144.0, 136.3, 134.7, 131.3, 129.4, 127.9, 124.4, 124.2, 36.7, 26.5, 25.7, 19.4, 17.7, 17.3; IR (neat) 3066, 3049, 2999, 2964, 2912, 2883, 1633, 1588, 1427, 1157, 1115, 727, 698, 623 cm^{-1}; EIMS *m/z* (relative intensity) 318 (M$^{\bullet+}$, 8), 275 (12), 249 (38), 240 (75), 207 (33), 171 (100), 145 (15), 105 (39), 69 (68); HRMS calcd for $C_{22}H_{26}Si$ 318.1804, found 318.1809. Anal. Calcd: C, 82.96; H, 8.23. Found: C, 83.16; H, 8.22.

1,1,3-Triphenylsilacyclopent-3-ene[28] **(41)**: 93% yield; ^{1}H NMR δ 7.62–7.15 (m, 15 H), 6.51 (m, 1 H), 2.25 (m, 2 H), 2.08 (m, 2 H); ^{13}C NMR δ 141.8, 140.2, 135.5, 134.7, 129.6, 128.2, 128.0, 127.0, 126.9, 125.7, 18.4, 18.1; IR (neat) 3066, 3049, 3018, 2914, 2879, 1606, 1493, 1427, 1153, 1117, 727, 696 cm^{-1}; EIMS *m/z* (relative intensity) 312 (M$^{\bullet+}$, 100), 234 (95), 156 (28), 105 (50).

Typical Reaction of Unsymmetrical (2-Butene-1,4-diyl)-magnesium with $SiCl_4$. Newly formed **2c**, prepared from isoprene (0.250 g, 3.67 mmol) and excess activated magnesium, in 20 mL of THF was cooled to −78 °C. $SiCl_4$ (0.256 g, 1.50 mmol) was added via a disposable syringe. After being stirred at −78 °C for 1 h, the mixture was gradually warmed to 0 °C and an aqueous solution of 1.5 N HCl (15 mL) was added. The reaction mixture was washed with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL), and the combined organic parts were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (15 mL) and dried over anhydrous Na_2SO_4. Evaporation of solvents and flash column chromatography afforded **2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene**[21] **(42)**: 0.185 g, 75%; ^{1}H NMR 5.53 (m, 2 H), 1.77 (t, *J* = 1.0 Hz, 6 H), 1.48 (d, *J* = 1.1 Hz, 4 H), 1.40 (s, 4 H); ^{13}C NMR δ 140.2, 124.9, 22.6, 21.8, 17.8; IR (neat) 3005, 2958, 2927, 2908, 2879, 2848, 1637, 1448, 1433, 1213, 1161, 1022, 756 cm^{-1}; EIMS *m/z* (relative intensity) 164 (M$^{\bullet+}$, 73), 149 (3), 136 (8), 122 (12), 109 (4), 96 (100).

2,7-Bis(4-methyl-3-pentenyl)-5-silaspiro[4.4]nona-2,7-diene (43): 62% yield; ^{1}H NMR δ 5.55 (s, 2 H), 5.09 (s, 2 H), 2.09 (s, 8 H), 1.67 (s, 6 H), 1.59 (s, 6 H), 1.47 (s, 4 H), 1.40 (s, 4 H); ^{13}C NMR δ 144.2, 131.3, 124.5, 124.1, 36.8, 26.4, 25.7, 19.4, 17.7, 17.3; IR (neat) 3001, 2966, 2912, 2879, 1631, 1448, 1375, 1161, 823, 760; EIMS *m/z* (relative intensity) 300 (M$^{\bullet+}$, 15), 257 (6), 231 (9), 203 (4), 175 (5), 163 (100), 135 (6), 121 (3), 109 (7), 95 (13), 69 (44); HRMS calcd for $C_{20}H_{32}Si$ 300.2273, found 300.2278. Anal. Calcd: C, 79.93; H, 10.73. Found: C, 80.24; H, 11.12.

2,7-Diphenyl-5-silaspiro[4.4]nona-2,7-diene (44): 34% yield; ^{1}H NMR δ 7.55–7.49 (m, 4), 7.36–7.20 (m, 6 H), 6.44 (s, 2 H), 1.96 (s, 4 H), 1.80 (s, 4 H); ^{13}C NMR δ 141.9, 140.4, 128.2, 127.1, 126.8, 125.6, 18.3, 18.2; IR (neat) 3080, 3057, 3020, 2916, 2879, 1604, 1493, 1444, 1159, 997, 767, 742, 694 cm^{-1}; EIMS *m/z* (relative intensity) 288 (M$^{\bullet+}$, 100), 158 (57), 105 (15), 71 (14); HRMS calcd for $C_{20}H_{20}Si$ 288.1334, found 288.1328.

Acknowledgment. The financial support of this work provided by the National Institutes of Health (Grant GM35153) is gratefully acknowledged.

Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra of **10–14, 16, 18, 19, 22, 25–33, 35, 36, 43,** and **44** (28 pages). Ordering information is given on any current masthead page.

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Synthesis of α-Ketols Mediated by Divalent Samarium Compounds

Jacqueline Collin, Jean-Louis Namy, Frédéric Dallemer, and Henri B. Kagan*

Laboratoire de Synthèse Asymétrique (URA CNRS 255), Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France

Received May 29, 1990

Coupling reactions of acid chlorides are mediated by SmI_2 and $SmCp_2$, leading to α-ketols **3**. Condensation reactions of acid chlorides on aldehydes similarly product α-ketols **5**; with ketones, best results are obtained with use of SmI_2. Reactivities of SmI_2 and $SmCp_2$ are compared and mechanisms of the reactions discussed. Formation of an acylsamarium species is shown.

Since our first report in 1977 on an easy preparation of diiodosamarium,[1] many applications of this reagent to organic synthesis have been developed by ourselves and different groups. These reactions are summarized in review articles.[2-5] Most of them are related to Barbier-type reactions[6-11] or to reductive properties of diiodosamarium, such as deoxygenation of epoxides,[6] reduction of alkyl halides,[7,12] or formation of pinacols.[13,14]

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0022-3263/91/1956-3118$02.50/0