bromo-4-methylpentane, 7694-01-1; 2,3-dibromo-2,3-dimethylbutane, 594-81-0; 2-bromo-3-chloro-2,3-dimethylbutane, 22690-18-2; 2,3-dichloro-2,3-dimethylbutane, 594-85-4; *trans*-1,2-dibromocyclohexane, 7429-37-0; *trans*-1-bromo-2-chlorocyclohexane, 13898-96-9; *trans*-1,2-dichlorocyclohexane, 822-86-6; (*dl*)-2,3-dibromobutane, 598-71-0; (*dl*)-2,3-dichlorobutane, 2211-67-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1,2-ditosyloxyethane, 6315-52-2; *erythro*-2,3-dihydroxy-4-methylpentane, 6702-10-9; *trans*-1-bromo-2-hydroxycyclohexane, 2425-33-4; *erythro*-2-bromo-3-formyloxybutane, 71911-92-7; *threo*-2-bromo-3-formyloxybutane, 71911-92-7; 1-bromo-2-methoxyethane, 6482-24-2; 1-bromo-2-methoxy-2-methylpropane, 19752-21-7; 2-bromo-3-methoxybutane, 24618-36-8; 2-bromo-3-methoxy-3-methylbutane, 67133-53-3; 2-bromo-3-methoxy-2,3-dimethylbutane, 17678-92-1; *threo*-2-bromo-3-methoxybutane, 29842-03-3; *erythro*-2-bromo-3-methoxybutane, 29842-02-2; *threo*-2-bromo-3-(trimethylstannyl)butane, 71911-93-8; *erythro*-2-bromo-3-(trimethylstannyl)butane, 71911-94-9; 4-methyl-2-pentene, 1809-26-3; cyclohexene, 110-83-8; 2-(trimethylstannyl)-3-methoxybutane, 71911-95-0; 1-(trimethylstannyl)-2-methyl-2-methoxypropane, 71911-96-1; 2-(trimethylstannyl)-3-methyl-3-methoxybutane, 71911-97-2; trimethylstannylsodium, 16643-09-7; *erythro*-2-(trimethylstannyl)-3-methoxybutane, 71911-98-3; *threo*-2-(trimethylstannyl)-3-methoxybutane, 71911-99-4; 2-methoxybutane, 6795-87-5; 2,3-dimethyl-2-butene, 563-79-1; *trans*-4-methyl-2-pentene, 674-76-0.

Chemistry of Diorganocuprates Containing Functionalized Ligands. 2. Methodology for Conjugate Addition of Synthetic Equivalents of Enolates and Acyl Anions

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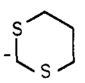
Received June 11, 1979

Methodology is described by which several classes of masked synthons, the synthetic equivalents of acyl anions and enolates, can be rendered reactive as ligands in the corresponding diorganocuprate complexes. Vinyl ethers and vinylsilanes were studied, and a comparison of their reactivities, stabilities and unmasking characteristics is given. The two classes of reagents prove nicely complementary in terms of their spectrum of reactivity, selectivity, and ease in unmasking.

Diorganocuprate reagents have assumed a prominent place in the arsenal of organometallic reagents which are available to the synthetic organic chemist. Two excellent reviews have documented the utility of these reagents for a variety of carbon–carbon bond-forming reactions.[2] Furthermore, significant strides have been made toward the understanding of the mechanism, the scope of reactivity, and the stereochemistry of the interaction of these reagents with a variety of organic substrates.[3] One area which has received somewhat less attention until relatively recently is the extension of the scope of the preparation and use of these reagents to functionalized ligands. Most of the studies have involved unfunctionalized hydrocarbon or olefinic groups in part due to the ease of preparation and handling of the prerequisite lithium reagents. Several examples of functionalized systems have been reported, including the work of Eaton,[4] the Syntex group (among several),[5] Marino,[6] Grieco,[6] and ourselves.[7] Among the more useful types of carbanion ligands whose cuprate complexes have not been reported when this work was begun were those of protected acyl anions such as **1** and **2** and enolates of esters and ketones such as **3** and **4**. These masked synthetic equivalents would be valuable additions to the available synthetic methodology if reactive complexes could be prepared. Direct formation of either reactive homogeneous diorganocuprate complexes or mixed-ligand complexes (**5**) does not appear feasible particularly in the case of the latter two types of ligands. A rough correlation of copper–ligand bond strength vs. reactivity suggests that **3** and **4** would function as nontransferable ligands in the manner of –SR, –OR, and –C≡CR. Ligands such as **3** and **4** would tend to behave as metal enolates and not undergo conjugate addition and other reactions characteristic of standard cuprate reagents, if indeed such complexes could be formed at all.



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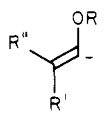

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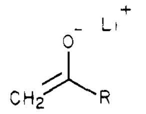

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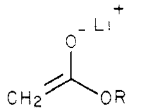

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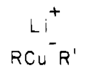
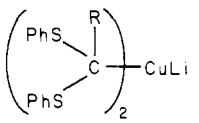

$$Li^+ \; RCu^-R'$$

5



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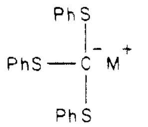

7

R = alkyl, H, vinyl; R′ = *t*-BuO, RC≡C, PhS

Consequently, we embarked upon a program to explore the potential of masked equivalents of these species (**1**–**4**) which could function as transferable ligands in mixed or homogeneous cuprate reagents.[8] Only a single example of an acyl anion equivalent functioning as a reactive ligand had been reported at that time. Mukaiyama had established the use of diphenyl dithioacetals (**6**) as ligands for conjugate addition to certain simple unsaturated ketones,[9]

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[1] (a) Fellow of the Alfred P. Sloan Foundation (1976–1980). (b) Recipient of a Research Career Development Award (CA-00273) from the National Cancer Institute of the National Institutes of Health (1976–1981).

[2] (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) *Ibid.* **1975**, *22*, 253.

[3] House, H. O.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 5495.

[4] Eaton, P. E.; Cooper, P. E.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947.

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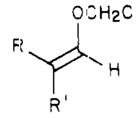
[8] Preliminary accounts of this work have appeared: Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron Lett.* **1974**, 3365; Boeckman, R. K., Jr.; Bruza, K. J.; Baldwin, J. E.; Lever, O. W. *J. Chem. Soc., Chem. Commun.* **1975**, 519.

0022-3263/79/1944-4781$01.00/0

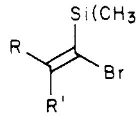
but the reactivity characteristics of these reagents led one to question whether these species should be formulated as true cuprates. Subsequently, it has been shown that the related trithio ortho ester anions (**7**) also are species which are capable of conjugate addition and other reactions typical of diorganocuprates.[10] Alternatively, direct non-copper-mediated conjugate addition of acyl anion equivalents has also been reported in those instances where, by virtue of manipulation of the reaction conditions and solvent or the nature of the carbanion and/or substrate, the kinetic 1,2-addition can be rendered reversible, and the thermodynamically favored 1,4-addition process takes precedence.[11]

Acyl Anion Equivalents

We were attracted to two types of vinyl carbanions which seemed to satisfy the requirements of a potential ligand: (1) easy preparation of the lithium reagent, (2) the resulting carbanion be unstabilized, and (3) the masking group be removable under specific conditions. These two systems are the vinyl ethers **8** and vinyl silanes **9**. Baldwin[12] and Schölkopf[13] had established that certain vinyl ethers undergo ready transformation to the α-vinyl anion upon treatment with *t*-BuLi in THF. This reaction has subsequently been extended to cyclic systems[14] and to alkoxymethyl vinyl ethers.[15] The products resulting from reactions with electrophiles are easily unmasked upon mild acid treatment, and the anion exhibits the spectrum of reactivity characteristic of unstabilized anions, such as irreversible 1,2-addition to α,β-unsaturated ketones.[12] Alternatively, in some instances, it would be desirable to have a transferable ligand whose masking group exhibits a greater degree of stability if a number of subsequent transformations are contemplated prior to unmasking. The (α-halovinyl)silanes seemed to satisfy this requirement since Stork had shown that vinylsilanes, while quite stable, are transformable to carbonyl groups by epoxidation followed by acid or Lewis acid treatment[16] (eq 1). Subsequently Hudrlik and others have further developed the rich transformation chemistry of vinylsilanes and epoxysilanes, permitting the preparation of a variety of functional groups.[17]



8



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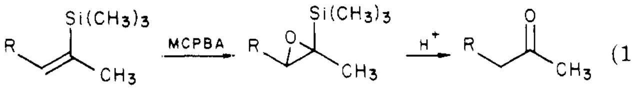


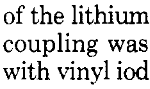
(1)

Preparation of the homogeneous diorganocuprate derived from α-lithioethyl vinyl ether was accomplished after some experimentation by rapid addition of a THF solution containing 2 equiv of the vinyl anion to a suspension of freshly purified cuprous iodide in dry THF at −78 °C and warming the mixture to $\sim$−25 °C for 1 h to afford a deep red solution of the cuprate. Slow addition of the anion apparently induces formation of the insoluble mono copper species which results in reductive coupling. The corresponding mixed cuprate with *n*-pentynylcopper was obtained as a yellow solution in THF by a similar procedure. A comparable procedure for the diorganocuprate was reported simultaneously by Heathcock using dimethyl sulfide as a solubilizing reagent.[18]

We screened a representative group of unsaturated ketones as substrates for conjugate addition. The results are given in Table I. Our results indicate that the cuprate derived from **8** is moderately reactive but somewhat sensitive to the enone substitution even when employed in excess. In our studies and in those of Heathcock, it was observed that β substitution severely retarded 1,4-addition and that essentially no useful yields of addition products were obtained.[8,18] Furthermore, we have observed that an example of an α,β-unsaturated aldehyde (**10**) underwent 1,2-addition exclusively, which is commonly observed for systems of this type. Acyclic enones suffered from the same limitations on β substitution, as shown by recovery of 75–80% of enone **11** together with about 20–25% of the 1,4-adduct as estimated by NMR.

The relatively low thermal stability of this cuprate results in low reactivity with hindered substrates even in the presence of excess reagent. The temperatures required for addition to the β-substituted enones (≥−10 °C) are in excess of the decomposition temperature of the reagent which is estimated to begin between −35 and −25 °C.

The reagents behave as true cuprates as is shown by their spectrum of reactivity with halides. Treatment of 3-bromo-1-cyclohexene with an excess of the reagent (entry 5, Table I) as is usually employed[1] provided the expected coupling product, diene **12**, in 93% yield. Analogous reactivity was observed by Heathcock for benzyl bromide.[18] Attempted coupling with saturated halides, both primary and secondary bromides, or epoxides afforded only products resulting from the self-coupling of the reagent, e.g., **13**. These alkylations can, however, be accomplished, at least in the case of the primary halides, by resorting to use of the lithium reagent.[12] Somewhat surprisingly, no crossed coupling was observed in the case of vinyl halides; even with vinyl iodides only **13** was obtained. The apparent lack of reactivity obviates a nice route to alkoxy-substituted 1,3-butadienes and is unexpected on the basis of literature precedents.[1] Further work along these lines is in progress. This high selectivity for benzylic and allylic systems is noteworthy and may prove useful in multifunctional cases.



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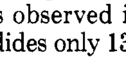

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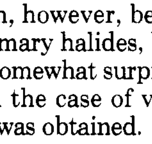

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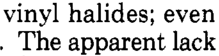

13

The vinyl ethers generated in the above described manner are exceedingly easily hydrolyzed to the derived carbonyl compound. In some cases purification of the intermediate vinyl ether is tedious and results in substantial losses. The crude products are in most cases of

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(9) Mukaiyama, T.; Narasaka, K.; Furosato, M. *J. Am. Chem. Soc.* **1972**, *94*, 8641.

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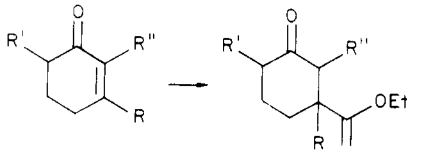
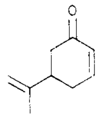
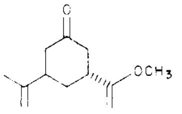
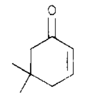
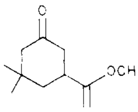
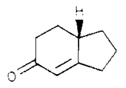
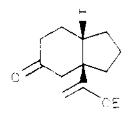
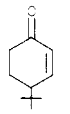
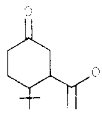
Table I.



entry no.	substrate	reagent[a]	product	yield,[b] %
1	R = R′ = R″ = H	A		84
		B		83
2	R = R″ = H; R′ = CH_3	A		91
3	R = R′ = H; R″ = CH_3	A[c]		80
4	R = R″ = H; R′ = n-C_3H_7	A[c]		82
5	R = CH_3; R′ = R″ = H	A		*d*
6	R′ = H; R = R″ = CH_3	A		*e*
7				50[f]
8				67[f]
9		A		*e*
10		A		*e*

[a] Reagents: A = $[CH_2{=}C(OC_2H_5)CuLi]_2$; B = $CH_2{=}C(OC_2H_5)CuC{\equiv}C$-$n$-PrLi. [b] Isolated yields of products. [c] Stoichiometry of 2:1 cuprate/enone utilized. [d] Starting material (80%) and 1,2-adduct recovered. [e] Starting enone recovered (>90%). [f] Cf. ref 18.

sufficient purity for direct conversion to the derived carbonyl compound.

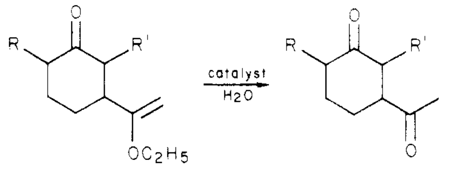
We developed mild conditions for hydrolysis of the vinyl ether adducts which provided the hydrolysis products in high yields with no double bond rearrangements or byproduct formation. The major limiting factor in the isolated yields is the water solubility of some of the substances. A selection of cases is given in Table II. A mild general procedure consists of exposure of the vinyl ether in ether (1 mmol/10 mL) to 0.1 N HCl (1 mmol/5 mL) at room temperature until hydrolysis is complete (~1 h). In cases where the products are sensitive to even these mildly acidic conditions (cf. Table II, entries 3 and 4), exposure to 0.1 N oxalic acid in methanol or SiO_2 in wet benzene is preferred. A selection of other hydrolysis conditions has been employed previously.[12]

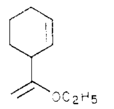
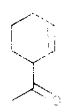
In view of the relatively high sensitivity of the cuprate reagents derived from 8 and related systems to steric congestion in the substrate and to temperature, we examined the preparation of the analogous reagent from an (α-halovinyl)trimethylsilane. We hoped this reagent would possess enhanced thermal stability and possibly be somewhat less sterically demanding due to the longer C–Si bond. Thus the silane reagent, which would provide more stable adducts and undergo unmasking under entirely different conditions, would provide a nice complement to the reagent described above.

The required halide, silane **9** (R = H), is readily available,[19] and exchange can be efficiently conducted by transmetalation at −78 °C with 2 equiv of *t*-BuLi in ether.[20,21] The diorganocuprate **14** is obtained by treatment of purified cuprous iodide (1 equiv) in THF at −78 °C with 2 equiv of the lithium reagent and warming to −20 °C to afford a deep green-black homogeneous solution of the cuprate. Mixed-ligand cuprates are also available by an analogous procedure.

The temperature at which significant decomposition of the bis(silylvinyl) cuprate reagent occurs is significantly

Table II



entry no.	substrate	product	yield,[a] %
1	R = H; R′ = H		95 (74)
2	R = CH_3; R′ = H		90 (58)
3	R = $CH(CH_3)_2$; R′ = H		99 (57)
4			91 (70)[b]

[a] Isolated yields of essentially pure products; chromatographed or distilled yields are in parentheses. [b] 0.1 N oxalic acid in CH_3OH/H_2O (~10:1).

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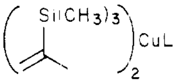

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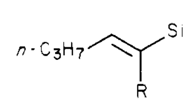
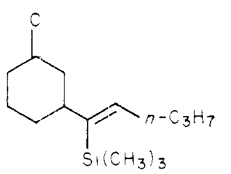


15, R = Br
16, R = H



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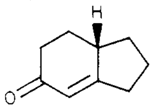


18

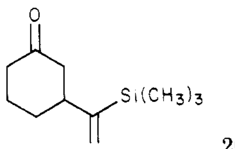
higher (−20 to 0 °C) than that of the bis(ethoxyvinyl) reagent, as judged by deposition of elemental copper. This observation suggested that this reagent may be applicable to more hindered systems since higher reaction temperatures can be utilized.

The cuprate **14**, indeed, proved more reactive with a variety of α,β-unsaturated ketones, including β,β-disubstituted types. However, the reactions with the more highly substituted ketones required extended reaction periods and the use of excess reagent (4 equiv) as shown in Table III. Nevertheless, acceptable yields were obtained in most cases. A further increase in reactivity may be realizable by employing less coordinating solvent mixtures in unreactive cases.[22]

The reagent **14** provides a vehicle for nucleophilic addition of the equivalent of an acetyl group. We felt it would be of interest to explore extension of this concept to somewhat more complex acyl anion equivalents. Halosilane **15** was prepared by a general route applicable to most terminal acetylenes. Platinum-catalyzed hydrosilylation of 1-pentyne with $SiHCl_3$ according to Benkeser[23] followed by exhaustive methylation with CH_3MgBr afforded vinylsilane **16** in 72% yield. Bromination–dehydrobromination as previously described affords the desired halide in 63% overall yield from **16**.[24]

Halogen–metal exchange of **15** with *t*-BuLi in ether proceeded in the same manner as with **9**, and cuprate formation occurred smoothly as described for **14**. Conjugate addition to unhindered enones proceeds normally; for example, 2-cyclohexen-1-one affords the expected vinyl silane **17** in 82% yield. The cuprate prepared from **15** does, however, show substantially lower reactivity with hindered enones such as **18**. Only low yields of conjugate addition products were obtained under the usual conditions.

Unmasking of the latent carbonyl in these silane adducts was then attempted in the manner previously described for simple vinylsilanes.[16] However, upon attempted epoxidation of **19** with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2, the primary products obtained in good yield were the lactones (**20**) resulting from Baeyer–Villager oxidation. This pathway is presumably preferred due to the fact that the π system of vinylsilanes is relatively electron poor due to back-donation into the empty silicon d orbitals in spite of the dipole being reversed in the σ system. Consequently, the ketone was blocked by ketalization to preclude Baeyer–Villager oxidation. Treatment with MCPBA then afforded the epoxy ketal **21** in good yield (76% overall for two steps). Methanolic sulfuric acid proved too harsh, as was demonstrated by exposure of independently synthesized diketone **22** to these conditions, resulting in decomposition.[25] A catalytic amount of perchloric acid in CH_3OH did provide **22** in 40% yield from **21**; however, these conditions did not prove to be general.



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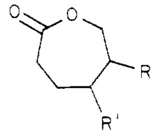
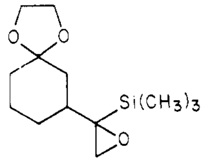
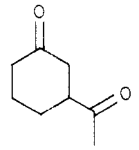


20a, R = CH_2=C—Si$(CH_3)_3$; R′ = H
b, R = H; R′ = CH_2=C—Si$(CH_3)_3$

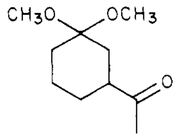


21

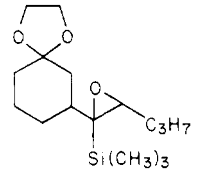


22

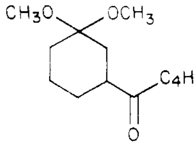
We then screened several Lewis acids and discovered the most satisfactory to be $BF_3\cdot Et_2O$ in aqueous methanol which afforded 77% of the ketal ketone **23**. The usual aqueous acetic acid hydrolysis provided **22**. The structure of **23** was confirmed by preparation from known materials.[25] This exchange/hydrolysis provides an unexpected bonus in serving to differentiate the two carbonyl groups during the unmasking operation. This result may also prove useful in multifunctional systems where it is desired to operate selectively on one of the two carbonyl groups. The use of nonalcoholic solvents proved unsatisfactory in our hands, with only small amounts of the desired dione **22** being obtained. Recent studies of silyl epoxides by Hudrlik suggest that further improvement of the unmasking procedure is possible.[17] The analogous silane **24** (60% from **17**) afforded the monoketal **25** in ~75% yield upon treatment with $BF_3\cdot Et_2O$ in CH_3OH/H_2O.



23



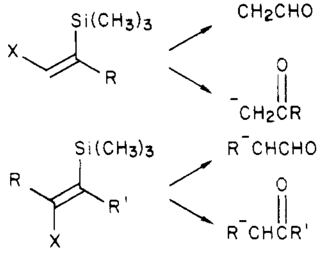
24



25

Enolate Anion Equivalents

The successful utilization of (α-halovinyl)silanes as acyl anion equivalents suggested that the other isomeric (halovinyl)silanes could be employed in a similar fashion. These isomers and their latent functional equivalents are shown in eq 2. These systems are of particular interest because they constitute the equivalents of a class of carbanions whose copper-mediated transfer does not occur.



(2)

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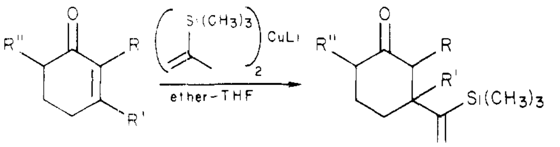
[22] House, H. O.; Wilkins, J. M. *J. Org. Chem.* **1978**, *43*, 2443.

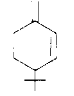
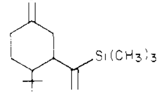
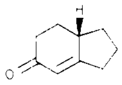
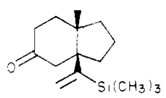
[23] Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Am. Chem. Soc.* **1961**, *83*, 4385.

[24] The procedure utilized was adapted from that of ref 19.

[25] Compound **38** was prepared by ozonolysis of 3-allylcyclohexanone followed by reductive (DMS) workup. Compound **22** was synthesized by conjugate addition of isopropenylmagnesium bromide to 2-cyclohexen-1-one under copper catalysis and ozonolysis followed by reductive workup. An authentic sample of **23** was prepared from 3-isopropenylcyclohexanone by ketalization [$HC(OCH_3)_3$/*p*-TsOH], ozonolysis (O_3/CH_2Cl_2/−78 °C), and workup with dimethyl sulfide.

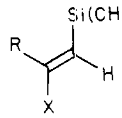
Table III



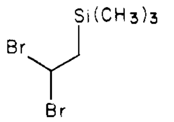
entry no.	substrate	product	yield,[a] %
1	R = R' = R'' = H		71
2	R = CH_3; R' = R'' = H		40[b]
3	R = R'' = H; R' = CH_3		56[b]
4	R = R' = H; R'' = CH_3		67
5	R = R' = H; R'' = $CH(CH_3)_2$		34
6	R = R' = CH_3; R'' = H		c
7			25[d]
8			61[b]

[a] Yield of products purified by distillation or chromatography. [b] Stoichiometry of cuprate/enone was 4:1. [c] ~90% starting material recovered. [d] 75% starting material recovered; yield determined by NMR.

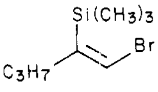
The synthetic route to (β-halovinyl)silanes of general structure **26** involves controlled treatment of a 1-silylalkyne with HBr in pentane.[26] In this way **27** and **28** were prepared in yields of 62% in each case. Interestingly, rapid treatment of (trimethylsilyl)acetylene with excess HBr afforded a 60% yield of dibromo silane **29**, which is the final intermediate proposed in the radical addition of HBr to 1-(trimethylsilyl)alkynes and confirms the published mechanism fully.[26b]



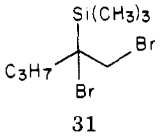
26, R = H, alkyl; X = Br
27, X = Br; R = H
28, X = Br; R = C_3H_7



29



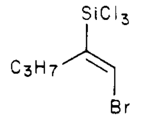
30



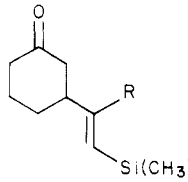
31

We were unable to develop a satisfactory synthesis of **30** although two routes were investigated. We prepared dibromide **31** in two steps from 2-bromo-1-pentene but were unable to effect satisfactory dehydrohalogenation.[27] Low yields of **30** were obtained from 1-pentyne in three steps via trichlorosilane **32**.[28] A variation of the latter route may result in a viable synthesis. No effort was made to investigate the chemistry of **30** or to prepare the tetrasubstituted isomer shown in eq 2.

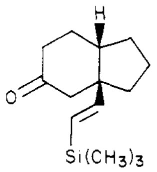
Halogen-metal exchange and cuprate formation from **27** proceeded as previously described for **9**, affording a deep green-black solution of the derived cuprate. Treatment of this solution with unsaturated ketones provided the expected conjugate addition products. A more limited selection of substrates was studied, but no marked differences in behavior from the α-substituted system were noted. For example, treatment with 2-cyclohexen-1-one afforded adduct **33** in 82% yield. Use of the more hindered enone **18** provided silane **34** in 64% yield. The slightly higher yield in this case may stem from the expected lower steric bulk of the incoming group.



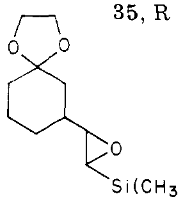
32



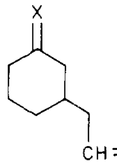
33, R = H
35, R = C_3H_7



34



36



37, X = $(OCH_3)_2$
38, X = O

The homologous halide **28** behaved similarly to **27** and afforded adduct **35** with 2-cyclohexenone in 70% yield. The addition of the reagent derived from **28** to **18** was not investigated; however, it may well succeed where that derived from **17** failed due to the lower steric requirements.

In view of the experience gained previously, unmasking of the above adducts was conducted by prior protection of the carbonyl group. For example, **33** was converted to epoxy ketal **36** in 76% overall yield. Hydrolysis with $BF_3 \cdot Et_2O$ in methanol afforded the bis protected system **37** in 53% yield, reflecting the greater stability of acetals vs. ketals. Aqueous acetic acid treatment then provided **38** identical with an independently synthesized sample.[25] Selective hydrolysis of ketals such as **37** is sometimes possible, providing a differentiated dicarbonyl system.[29] In general, hydrolysis of systems like **36** is more difficult due to the ready aldol condensation of the products.

Summary

We have described methodology whereby several important classes of latent carbonyl functional groups can be utilized as ligands in diorganocuprate complexes. These ligands behave normally, undergoing the usual range of coupling and conjugate-addition reactions. The ligands differ in several important ways: (1) the thermal stability of the resulting cuprate complexes, (2) the sensitivity of the derived reagents to steric hindrance in the substrate, and (3) the conditions required for unmasking the latent carbonyl function. The reagents derived from lithio vinyl ethers and silanes are nicely complementary and permit hitherto unavailable modes of carbon-carbon bond construction.

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(26) (a) Komarov, N. V.; Yarosh, O. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1583. (b) Boeckman, R. K., Jr.; Blum, D. M. *J. Org. Chem.* **1974**, *39*, 3307.

(27) Exposure to a variety of bases afforded either recovered starting dihalide or 2-bromo-1-pentene resulting from elimination of $(CH_3)_3SiBr$.

(28) 1-Pentyne was brominated to afford 1-bromopentyne; addition of $SiCl_3H$ afforded **32**. Methylation with excess CH_3MgBr afforded low yields of the desired **30**.

(29) The ketone carbonyl is usually liberated at a greater rate upon exposure to buffered aqueous acetic acid: Boeckman, R. K., Jr., unpublished results.

Experimental Section

Boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 137 or 251 spectrophotometers, and maxima are reported in reciprocal centimeters (cm^{-1}). Spectra of solid samples were obtained in $CHCl_3$ and spectra of liquids were obtained as neat films unless otherwise noted. NMR spectra were obtained in $CDCl_3$ on a Varian T-60 spectrometer, and chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (Me_4Si) or chloroform. Gas chromatography was performed on the Hewlett-Packard 5750 chromatograph with a flame-ionization detector. Columns utilized were $^1/_4$ in. × 6 ft in length and were packed with 20% SE-30 on Chromosorb W or 20% Carbowax 20-M on Chromosorb P. Mass spectra were obtained on an AEI MS-902. Elemental analyses were performed by Midwest Microlab Inc., Indianapolis, IN.

(2-Bromo-1-vinyl)trimethylsilane (27).[26] (Trimethylsilyl)acetylene[26] (20 g, 204 mmol) and dibenzoyl peroxide (120 mg) were treated at 0 °C with gaseous HBr for approximately 40 min. The reaction was monitored by gas chromatography and terminated when polybrominated materials began to be observed (~70% conversion). The crude reaction mixture was taken up in ether (100 mL) and washed with saturated $NaHCO_3$, water, and saturated aqueous NaCl solution. The organic layer was dried over magnesium sulfate and concentrated carefully and the residue fractionated affording **27**: 22.8 g, 62%; bp 42–44 °C (26 mm); IR 2910, 1560, 1250, 950, 850 cm^{-1}; NMR δ 6.4 (s, 2), 0.1 (s, 9).

1-Bromo-1-(trimethylsilyl)-1-pentene (15). 1-(Trimethylsilyl)-1-pentene[23] (5.8 g, 41 mmol) was cooled to −78 °C and treated dropwise with bromine (8.0 g, 50 mmol). After completion of the addition, the mixture was warmed slowly to 0 °C, and 30 mL (150 mmol) of anhydrous diethylamine was cautiously added. After any initial exothermic reaction subsided, the mixture was heated at reflux for 12 h. Ether (100 mL) was added after cooling of the mixture, the precipitated salts were removed by filtration, and the precipitate was washed well with ether. The combined filtrates were washed with 5% HCl solution till the washes were acidic, saturated $NaHCO_3$ solution, and saturated brine. After being dried ($MgSO_4$) and concentrated in vacuo, the residue was fractionally distilled to afford **15**: 5.6 g, 63%; bp 55–57 °C (1 mm); IR 2920, 1610, 1450, 1250, 1160, 980, 850 cm^{-1}; NMR δ 6.15 (t, J = 6 Hz, 1), 2.2 (q, 2), 1.7–1.15 (m, 2), 0.85 (t, 3), 0.08 (s, 9).

Exact mass calcd for $C_8H_{17}Br^{79}Si$: 220.0252. Found: 220.0283.

2-Bromo-1-(trimethylsilyl)-1-pentene (28).[26,30] A solution of 1-(trimethylsilyl)-1-pentyne[31] (4.2 g, 30 mmol) was treated with gaseous HBr at 0 °C and the progress monitored by VPC (5% SE-30 at 45 °C). Addition was discontinued when the monoaddition product was maximized. The pentane solution was washed with water, dried over $MgSO_4$, and concentrated. Fractional distillation of the residue afforded **28**: 4.11 g, 62%; bp 82–84 °C (20 mm); IR 2960, 1450, 1250, 850 cm^{-1}; NMR δ 5.85 (s, 1), 2.40 (t, 2), 1.85–1.15 (m, 2), 0.9 (t, 3), 0.1 (s, 9); mass spectrum, m/e 220, 222 (p^+, $p^+ + 2$).

General Procedures for Preparation and Reaction of Lithium Bis(α-Ethoxyvinyl)cuprate. Preparation of 3-(1-Ethoxyvinyl)cyclohexanone. A solution of 2.16 g (30 mmol) of purified ethyl vinyl ether in 20 mL of THF under Ar at −78 °C was treated with a solution of 26.4 mL (20 mmol of a 0.75 M solution) of *tert*-butyllithium in pentane dropwise. The resulting mixture was allowed to warm slowly to ~+5 °C (40 min) and then recooled to −78 °C. This solution was added rapidly by syringe or cannula to a stirred suspension of 1.9 g (10 mmol) of CuI in 50 mL of THF under Ar at −78 °C. The mixture, which rapidly became deep red, was warmed to −30 °C and held there for 1 h. To the resulting solution at −78 °C was added dropwise a solution of 2-cyclohexen-1-one (960 mg, 10 mmol) in 20 mL of THF and the mixture warmed slowly to 0 °C. The reaction was quenched with 100 mL of NH_4Cl/NH_4OH solution (pH 8) and ether (100 mL). The organic layer was washed with 10% NH_4Cl/NH_4OH (pH 8), water, and saturated brine. After the organic layer was dried ($MgSO_4$), concentration afforded 1.42 g (84%) of nearly pure ketone: IR 2900, 1715, 1655, 1450, 1070, 975 cm^{-1}; NMR δ 4.2–3.5 (m, 4), 2.6–1.0 (m, 12), 1.25 (t, 3); mass spectrum, m/e 168 (p^+).

Preparation and Reaction of Lithium (α-Ethoxyvinyl)-1-pentynylcuprate. A solution of (α-ethoxyvinyl)lithium was prepared as described above from 1.1 g (15 mmol) of ethyl vinyl ether and *t*-BuLi (10 mmol). The anion solution was rapidly added to a stirred suspension of cuprous pentyne[21] (653 mg, 5 mmol) in 40 mL of THF at −78 °C under Ar. The mixture was warmed to −20 °C and held there for 1 h. Addition of 2-cyclohexen-1-one (480 mg, 5.0 mmol) in 20 mL of THF to the resulting homogeneous yellow solution of the cuprate, warming to 0 °C, and workup as above afforded ketone (700 mg, 83%) identical spectrally with that obtained above.

3-(1-Ethoxy-1-vinyl)-6-methylcyclohexanone. The general procedure outlined for the lithium bis(α-ethoxyvinyl)cuprate was utilized. Treatment of the cuprate solution with 6-methyl-2-cyclohexen-1-one (528 mg, 4.8 mmol) afforded 790 mg (91%) of the title compound: IR 2900, 1710, 1660, 1450, 1350, 1070, 975 cm^{-1}; NMR δ 3.9–3.4 (m, 4), 2.55–1.0 (m, 15), 1.25 (t, 3).

2-Methyl-3-(1-ethoxyvinyl)cyclohexanone. By the general procedure previously described, utilizing 1.5 equiv of cuprate to 1 equiv of unsaturated ketone, treatment of 220 mg (2 mmol) of 2-methyl-2-cyclohexen-1-one afforded the title compound: 292 mg, 80%; IR 2900, 1715, 1660, 1450, 1370, 1070, 975 cm^{-1}; NMR δ 4.0–3.5 (m, 4), 2.6–1.0 (m, 15).

3-(1-Ethoxyvinyl)-6-isopropylcyclohexanone. By the general procedure previously described utilizing 2 equiv of cuprate to 1 equiv of enone, treatment of 633 mg (4.8 mmol) of 6-isopropyl-2-cyclohexen-1-one afforded the title compound: 823 mg, 82%; IR 2900, 1710, 1450, 1375, 1060, 970 cm^{-1}; NMR δ 4.0–3.5 (m, 4), 2.5–0.8 (m, 9), 1.25 (t, 3), 0.9 (m, 6).

3-(1-Ethoxyvinyl)-1-cyclohexene (12). To a solution of the bis(α-ethoxyvinyl) cuprate prepared as previously described (12.5 mmol) was added 403 mg (2.5 mmol) of 3-bromocyclohexene at −78 °C. Warming to 0 °C followed by the usual $NH_4Cl/NH_4OH/Et_2O$ workup afforded a crude product which upon short-path distillation gave 357 mg (93%) of **12**: IR 2910, 1660, 1475, 1450, 1210, 1070, 975 cm^{-1}; NMR δ 5.7 (br s, 2), 4.0–3.45 (m, 4), 2.25–1.05 (m, 7), 1.25 (t, 3).

Hydrolysis of the Ethyl Vinyl Ether Adducts. Preparation of 3-Acetylcyclohexanone.[32] A solution of 84 mg (0.5 mmol) of 3-(1-ethoxyvinyl)cyclohexanone in 10 mL of ether was combined with 0.1 N HCl (5 mL) and stirred for 1 h. The mixture was saturated with salt and extracted with ether three times. The combined extracts were dried over $MgSO_4$ and concentrated to afford nearly pure 3-acetylcyclohexanone (68 mg, 95%). Further purification by column chromatography on SiO_2 in 15% acetone/benzene gave 52 mg (74%) of the dione: IR 2900, 1710, 1450, 1350, 1260, 1225, 1160 cm^{-1}; NMR δ 2.4–1.0 (m, 12), 2.1 (s, 3). The structure of the product was verified by comparison with an authentic sample prepared by ozonolysis of 3-isopropenylcyclohexanone.[33]

3-Acetyl-6-methylcyclohexanone. A solution of 364 mg (2 mmol) of 3-(1-ethoxyvinyl)-6-methylcyclohexanone in 20 mL of ether and 10 mL of 0.1 N HCl was stirred at 0 °C for ~2 h. Workup as above afforded nearly quanitatively the crude dione (300 mg). Purification by short-path distillation (Kugelrohr) afforded the title compound (176 mg, 58%) with some losses: IR 2890, 1715, 1450, 1370 cm^{-1}; NMR δ 2.5–1.3 (m, 8), 2.08 (s, 3), 1.2 (d, 3); mass spectrum, m/e 154 (p^+).

Exact mass calcd for $C_9H_{14}O_2$: 154.0994. Found: 154.1021.

3-Acetyl-6-isopropylcyclohexanone. A solution of 3-(1-ethoxyvinyl)-6-isopropylcyclohexanone (210 mg, 1.0 mmol) in 5 mL of CH_3OH and 2.5 mL of 0.1 N HCl was stirred for 0.5 h at room temperature. Saturated brine (20 mL) was added and the product isolated by ether extraction (three times). The extracts were dried over $MgSO_4$ and concentrated to afford 171 mg of crude dione (~60% pure by NMR). Purification by short-path distillation afforded 104 mg (57%) of the title dione: IR 2890, 1705, 1440, 1375, 920 cm^{-1}; NMR δ 2.8–1.4 (m, 9), 2.18 (s, 3), 1.35–0.9 (m, 6); mass spectrum, m/e 182 (p^+).

Exact mass calcd for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1299.

3-Acetyl-1-cyclohexene.[34] 3-(1-Ethoxyvinyl)-1-cyclohexene

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(30) This experiment was performed by D. M. Blum.

(31) For a general preparation cf. ref 26b.

(32) McCoubrey, A. *J. Chem. Soc.* **1951**, 2931.

(33) House, H. O.; Latham, R. A.; Slater, C. D. *J. Org. Chem.* **1966**, *31*, 2667.

(34) Gillois-Doucet, J. *Ann. Chim. (Paris)* **1955**, *10*, 497.

(**12**; 226 mg, 1.47 mmol) was dissolved in 50 mL of a mixture of 2.5 g of oxalic acid dihydrate, 15 mL of water, and 200 mL of CH_3OH and stirred at room temperature for 1.5 h. The reaction mixture was extracted with 40 mL of ether (four times), and the ether extracts were washed with 10% $NaHCO_3$, water, and saturated brine. After the extracts were dried over magnesium sulfate, concentration afforded the crude ketone 167 mg (91%). Further purification by chromatography on silica gel afforded 117 mg (70%) of the title ketone: IR 2900, 1710, 1445, 1350, 1160 cm^{-1}; NMR δ 5.8 (br s, 2), 2.15 (s, 3), 2.3–1.0 (m, 7).

General Procedures for Conjugate Addition of (Trimethylsilyl)vinyl Cuprates. 3-[1-(Trimethylsilyl)-1-vinyl]cyclohexanone (19). Procedure A. A solution of *t*-BuLi/*n*-pentane (80 mL of a 0.75 M solution, 60 mmol) was added to anhydrous ether (100 mL) and the mixture cooled to −78 °C under Ar. To this mixture was added dropwise a solution of 5.37 g (30 mmol) of **9** in 40 mL of ether. After addition, the mixture was warmed to −20 °C, held there for 0.5 h, and then recooled to −78 °C. The solution of the anion is transferred by syringe or cannula to a stirred suspension of cuprous iodide (2.85 g, 15 mmol) in 150 mL of dry ether at −78 °C. To the homogeneous deep green-black solution of the cuprate was added dropwise 2-cyclohexen-1-one (1.44 g, 15 mmol) in 25 mL of ether. The mixture was allowed to warm to ~0 °C over 1 h and quenched with 100 mL of aqueous NH_4Cl/NH_4OH solution (pH 8). The organic layer was washed with 10% NH_4Cl/NH_4OH, water, and saturated NaCl and dried over $MgSO_4$. Short-path distillation afforded 2.04 g of the ketone **19** (71%): bp 67–68 °C (0.7 mm); IR 3000, 2880, 1710, 1250, 935, 840 cm^{-1}; NMR δ 5.6 (dd, J_1 = 2 Hz, J_2 = 1 Hz, 1), 5.4 (d, J = 2 Hz, 1), 3.0–0.8 (m, 9), 0.05 (s, 9); mass spectrum, *m/e* 196 (p^+). Anal. ($C_{11}H_{20}OSi$): C, H.

3-Methyl-3-[1-(trimethylsilyl)-1-vinyl]cyclohexanone. Procedure B. A solution of [1-(trimethylsilyl)vinyl]lithium (~40 mL) was prepared as previously described (procedure A) from **9** (1.40 g, 8.0 mmol). This solution was added to cuprous iodide (760 mg, 4.0 mmol) in ether (40 mL) and the temperature raised to −25 °C for 1 h. The resulting solution of the cuprate at −78 °C was treated with 3-methyl-2-cyclohexen-1-one (110 mg, 1.0 mmol) in 5 mL of ether. The mixture was warmed over 1 h to −20 °C and held at −20 °C (freezer) for 10 h. Workup as described previously (procedure A) and purification of the crude product by chromatography on silica gel in benzene gave the title ketone: 120 mg (56%); IR 3000, 2920, 1715, 1450, 1380, 1250, 1060, 850 cm^{-1}; NMR δ 5.60 (d, 1), 5.4 (d, 1), 2.6–1.1 (m, 8), 0.95 (s, 3), 0.08 (s, 9); mass spectrum, *m/e* 210 (p^+).

Exact mass calcd for $C_{11}H_{20}OSi$ ($p^+ - 15$): 195.1205. Found: 195.1246.

3-[2-(Trimethylsilyl)-1-vinyl]cyclohexanone (33). By use of procedure A above, 2-cyclohexen-1-one (960 mg, 10 mmol) afforded 1.26 g of **33**: 64%; bp 93–98 °C (0.8 mm); IR 2920, 1720, 1250, 842 cm^{-1}; NMR δ 5.9 (m, 1), 5.73 (d, J = 18 Hz, 1), 2.8–0.9 (m, 9), 0.05 (s, 9); mass spectrum, *m/e* 196 (p^+).

3-[1-(Trimethylsilyl)-1-pentenyl]cyclohexanone (17). Treatment of 2-cyclohexen-1-one (288 mg, 3.0 mmol) with the cuprate derived from **15** according to procedure A afforded ketone **17**: 585 mg, 82%; IR 2900, 1715, 1450, 1250, 850 cm^{-1}; NMR δ 5.65 (t, J = 6 Hz, 1), 2.4–1.1 (m, 13), 0.85 (t, 3), 0.05 (s, 9); mass spectrum, *m/e* 238 (p^+).

3-[1-(Trimethylsilyl)-1-vinyl]-6-isopropylcyclohexanone. Treatment of 6-isopropyl-2-cyclohexen-1-one (140 mg, 1.0 mmol) according to procedure B afforded 176 mg of the title compound: 74%; IR 2980, 2890, 1705, 1445, 1360, 1250, 935, 845 cm^{-1}; NMR δ 5.60 (d, 1), 5.40 (d, 1), 2.8–0.9 (m, 9), 1.00 (dd, 6), 0.08 (s, 9); mass spectrum, *m/e* 238 (p^+).

Exact mass calcd for $C_{14}H_{26}OSi$: 238.1753. Found: 238.1755.

3-[1-(Trimethylsilyl)-1-vinyl]-2-methylcyclohexanone. Treatment of 2-methyl-2-cyclohexen-1-one (165 mg, 1.5 mmol) according to procedure B afforded the title compound: 126 mg, 40%; IR 3000, 2900, 1710, 1450, 1250, 930, 840 cm^{-1}; NMR δ 5.6 (d, 1), 5.45 (d, 1), 3.0–1.2 (m, 8), 1.02 (t, 3), 0.01 (s, 9); mass spectrum, *m/e* 210 (p^+).

Exact mass calcd for $C_{12}H_{22}OSi$: 210.1440. Found: 210.1430.

1-[1-(Trimethylsilyl)-1-vinyl]bicyclo[4.3.0]nonan-3-one. Treatment of enone **18** (136 mg, 1.0 mmol) according to procedure B above afforded, after purification by column chromatography on SiO_2 in benzene, 143 mg (61%) of the title ketone: IR 3000, 2920, 1720, 1450, 1250, 935, 840 cm^{-1}; NMR δ 5.67 (d, 1), 5.45 (d, 1), 2.9–1.1 (m, 13), 0.1 (s, 9); mass spectrum, *m/e* 236 (p^+), 221 ($p^+ - 15$).

Exact mass calcd for $C_{14}H_{24}OSi$: 236.1596. Found: 236.1598. Exact mass calcd for $C_{13}H_{21}OSi$ ($p^+ - 15$): 221.1361. Found: 221.1356.

3-[1-(Trimethylsilyl)-1-vinyl]-6-methylcyclohexanone. The general procedure for A was utilized except the ratio of cuprate to enone was 1.5, and the reaction was kept 1 h at −78 °C and 2 h at 0 °C. Treatment of 6-methyl-2-cyclohexen-1-one (165 mg, 1.5 mmol) as described afforded, after chromatographic purification, 213 mg of the title ketone: 67%; IR 3000, 2910, 2830, 1720, 1450, 1250, 930, 840 cm^{-1}; NMR δ 5.65 (m, 1), 5.40 (d, 1), 2.8–1.1 (m, 8), 1.0 (t, 3), 0.08 (s, 9); mass spectrum, *m/e* 210 (p^+).

Exact mass calcd for $C_{12}H_{22}OSi$: 210.1440. Found: 210.1412.

1-[2-(Trimethylsilyl)-1-vinyl]bicyclo[4.3.0]nonan-3-one (34). By use of the general procedure A above, treatment of enone **18** (136 mg, 1.0 mmol) afforded ketone **34** (150 mg, 64%) after chromatographic purification (EtOAc/benzene, 1:19, v/v): IR 2980, 1715, 1450, 1250, 930, 850 cm^{-1}; NMR δ 5.8 (s, 1), 5.68 (s, 1), 217–1.1 (m, 13), 0.1 (s, 9); mass spectrum, *m/e* 236 (p^+).

Exact mass calcd for $C_{14}H_{24}OSi$: 236.1596. Found: 236.1591.

General Procedures for Unmasking Keto Vinyl Silanes: Ketalization and Epoxidation. Preparation of Epoxy Ketal 21. A mixture of 3-[1-(trimethylsilyl)-1-vinyl]cyclohexanone (3.7 g, 19 mmol), ethylene glycol (2.45 g, 38 mmol), and 50 mg of *p*-toluenesulfonic acid in 150 mL of benzene was heated at reflux with water separation by use of a Dean–Stark trap. After 12 h at reflux, the mixture was washed several times with water, dried ($MgSO_4$), and concentrated to afford 4.3 g of the ethylene ketal (~95%) of sufficient purity to be used directly.

To a 1.33-g (5.12-mmol) portion of the above ketal in 100 mL of CH_2Cl_2 at room temperature under Ar was added 1.04 g (6 mmol) of *m*-chloroperbenzoic acid. After 18 h the solution was washed successively with 5% aqueous sodium hydroxide and water and dried ($MgSO_4$). Concentration followed by column chromatography on silica gel [benzene/ethyl acetate (9:1)] afforded 1.12 g (79%) of ketal epoxide **21**: IR 2900, 1440, 1250, 1090, 850 cm^{-1}; NMR δ 3.94 (s, 4), 2.62–2.38 (q, J_{AB} = 5 Hz, 2), 1.9–0.7 (m, 9), 0.1 (s, 9); mass spectrum, *m/e* 256 (p^+).

Exact mass calcd for $C_{13}H_{24}O_3Si$: 256.1545. Found: 256.1544.

Epoxy Ketal 24. The above general procedure beginning with **17** (74 mg, 0.31 mmol) afforded epoxy ketal **24** (60 mg) after the usual purification: 53% overall; IR 2900, 1450, 1250, 1090, 854 cm^{-1}; NMR δ 3.9 (s, 4), 2.6 (m, 1), 1.8–0.8 (m, 16), 0.1 (s, 9); mass spectrum, *m/e* 298 (p^+).

Epxoy Ketal 36. By use of the above procedure, 3-[2-(trimethylsilyl)-1-vinyl]cyclohexanone (82 mg, 0.42 mmol) was converted to ketal **36**: 88 mg, 73% overall; IR 2920, 1450, 1375, 1250, 1080, 845 cm^{-1}; NMR δ 3.92 (s, 4), 2.55 (br s, 1), 1.97 (d, J = 4 Hz, 1), 1.97–1.1 (m, 9), 0.15 (s, 9); mass spectrum, *m/e* 256 (p^+).

Exact mass calcd for $C_{13}H_{24}O_3Si$: 256.1544. Found: 256.1519.

Rearrangement of Ketal Epoxides: 3-Acetylcyclohexanone (22) and 3-Acetylcyclohexanone Dimethyl Ketal (23). (a) Perchloric Acid. A solution of ketal **21** (44 mg, 0.17 mmol) in 2 mL of CH_3OH containing enough water to cause slight turbidity was treated with 2 drops of concentrated perchloric acid and warmed at 50–60 °C for 0.5 h. After isolation of the product by ether extraction, Kugelrohr distillation (short path) afforded 10 mg (41%) of 3-acetylcyclohexanone[31] identical with an authentic sample. The crude material seems to contain a larger amount of material and may be pure enough for use.

(b) Boron Trifluoride Etherate. Boron trifluoride etherate (568 mg, 4.0 mmol) was dissolved in CH_3OH (5 mL) containing 4 drops of water. To this stirred solution was added dropwise a solution of ketal **21** (128 mg, 0.5 mmol) in 2 mL of CH_3OH. After 2 h at room temperature, 10 mL of ether and 5.0 mL of aqueous of $NaHCO_3$ were added, and the mixture was stirred an additional 10 min. The organic layer was washed successively with 5% aqueous $NaHCO_3$ and saturated NaCl and dried ($MgSO_4$). Concentration afforded 72 mg (77%) nearly pure **23**: IR 2900, 1715, 1450, 1360, 1080 cm^{-1}; NMR δ 3.13 (s, 3), 3.07 (s, 3), 2.5–1.1 (m, 8), 2.1 (s, 3). This compound was identical with a sample prepared from 3-isopropenylcyclohexanone.[25,33]

3-(2,2-Dimethoxyethyl)-1,1-dimethoxycyclohexane (37). By use of the above procedure b, ketal **36** (75 mg, 0.293 mmol) was hydrolyzed to afford 36 mg (53%) of **37**: IR 2900, 1450, 1100 cm^{-1}; NMR δ 4.4 (t, J = 6.3 Hz, 1), 3.3 (s, 6), 3.15 (s, 3), 3.05 (s, 3), 2.1–1.0 (m, 11); mass spectrum, m/e 232 (p^+), 217 ($p^+ - 15$). The structure of **37** was further verified by comparison with authentic material synthesized independently.[25]

1,1-Dimethoxy-3-(1-oxobutyl)cyclohexane (25). By use of the above procedure b, ketal **24** (60 mg; 0.2 mmol) was converted to **25** (35 mg; 77%) of good purity. Further purification by column chromatography resulted in some loss, affording 20 mg (44%) of **25**: IR 2890, 1710, 1450, 1160, 1050 cm^{-1}; NMR δ 3.15 (s, 3), 3.05 (s, 3), 2.6–0.8 (m, 20); mass spectrum, m/e 228 (p^+).

Exact mass calcd for $C_{13}H_{24}O_3$: 228.1725. Found: 228.1738.

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Registry No. 9, 13683-41-5; **12**, 71785-71-2; **15**, 55339-30-5; **17**, 71785-72-3; 18, 1489-28-7; **19**, 55339-32-7; **21**, 55339-38-3; **22**, 15040-97-8; **23**, 71785-73-4; **24**, 71785-74-5; **25**, 71785-75-6; **27**, 41309-43-7; **28**, 71785-76-7; **33**, 55339-33-8; **34**, 55339-34-9; **36**, 55339-39-4; **37**, 71785-77-8; 3-(1-ethoxyvinyl)cyclohexanone, 71785-78-9; 3-(1-ethoxy-1-vinyl)-6-methylcyclohexanone, 71785-79-0; 2-methyl-3-(1-ethoxyvinyl)cyclohexanone, 71785-80-3; 3-(1-ethoxyvinyl)-6-isopropylcyclohexanone, 71785-81-4; 3-acetyl-6-methylcyclohexanone, 56893-77-7; 3-acetyl-6-isopropylcyclohexanone, 56893-78-8; 3-acetyl-1-cyclohexene, 29372-98-3; 3-methyl-3-[1-(trimethylsilyl)-1-vinyl]cyclohexanone, 71785-82-5; 3-[1-(trimethylsilyl)-1-vinyl]-6-isopropylcyclohexanone, 71785-83-6; 3-[1-(trimethylsilyl)-1-vinyl]-2-methylcyclohexanone, 71785-84-7; 1-[1-(trimethylsilyl)-1-vinyl]bicyclo[4.3.0]nonan-3-one, 55339-35-0; 3-[1-(trimethylsilyl)-1-vinyl]-6-methylcyclohexanone, 71785-85-8; 2-cyclohexen-1-one, 930-68-7; 6-methyl-2-cyclohexen-1-one, 6610-21-5; 2-methyl-2-cyclohexen-1-one, 1121-18-2; 6-isopropyl-2-cyclohexen-1-one, 43209-90-1; 3-methyl-2-cyclohexen-1-one, 1193-18-6; 3-bromocyclohexene, 1521-51-3; (trimethylsilyl)acetylene, 1066-54-2; 1-(trimethylsilyl)-1-pentene, 56183-56-3; 1-(trimethylsilyl)-1-pentyne, 18270-17-2; ethyl vinyl ether, 109-92-2; 4-*tert*-butyl-2-cyclohexen-1-one, 937-07-5; 3-[1-(trimethylsilyl)-1-vinyl]-4-*tert*-butylcyclohexanone, 71785-86-9.

Reaction of 2-(1,3-Butadienyl)magnesium Chloride with Carbonyl Compounds and Epoxides. A Regioselectivity Study

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The reaction of 2-(1,3-butadienyl)magnesium chloride (**1**) with carbonyl compounds and epoxides afforded a mixture of the "normal" addition product 1,3-dienyl alcohol and the "rearranged" allenic alcohol. The formation of the "rearranged" allenic alcohol was favored by lower basicity of solvent, by more covalent carbon–metal bonding, and by increased steric hindrance in ketones. The regioselectivity of the reaction was consistent with the six-membered cyclic transition state **10**.

The Grignard reagent 2-(1,3-butadienyl)magnesium chloride (**1**) was first prepared by Aufdermarsh[1] from 4-chloro-1,2-butadiene (**9**), and, later, Sultanov et al.[2] reported the synthesis of **1** from easily accessible 2-chloro-1,3-butadiene (chloroprene) (**8**) in the presence of zinc chloride catalyst (Scheme I).

Aufdermarsh showed that **1** was the 2-(1,3-butadienyl)magnesium chloride compound rather than the allenic one.

Kondo et al.[3] recently studied the reaction of **1** with carbonyl compounds and epoxides and found that a mixture of 1,3-dienyl alcohol and allenic alcohol was formed in the reaction shown in Scheme II.

We have studied the reaction in detail and found the ratios of **3** to **4** and **6** to **7** (regioselectivity of the reaction) could be influenced very much by the reaction conditions and we report the results.

Results and Discussion

Effect of Solvents. The reactions were generally carried out in tetrahydrofuran (THF) solution. The effects of adding the basic solvents hexamethylphosphoric triamide (HMPA), diglyme, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to reactions with carbonyl compounds are shown in Table I. Diglyme tends to increase the product yield but has little effect on the regioselectivity (the ratio of **3** to **4**). TMEDA has a tendency to decrease the yield, but it alters the selectivity between **3** and **4**. The reactions in the presence of TMEDA increase the ratio of **3** to **4** compared to the ratio in the presence of THF. HMPA has a great effect on the selectivity. In the reactions with acetone and methyl ethyl ketone, dienyl alcohol **3** was exclusively formed in the presence of HMPA. The effects of basic solvents on acetaldehyde and acetophenone are minor.

It is known that the solvation of a Grignard reagent by a basic solvent increases the ionic character between a carbon–magnesium bond.[4-7] The formation of dienyl alcohol **3** seems to be favored by the solvation with a basic solvent.

Effects of Alkyl Groups of Carbonyl Compounds. The effects of the bulkiness of the alkyl groups of carbonyl

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