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CHLOROSILANE-ACCELERATED CONJUGATE ADDITION OF CATALYTIC AND STOICHIOMETRIC ORGANOCOPPER REAGENTS

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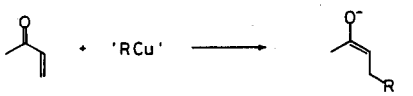
Abstract-- Trialkylsilyl chlorides, particularly in combination with hexamethylphosphoramide or 4-dimethylaminopyridine, dramatically accelerates the conjugate addition of catalytic and stoichiometric organocopper reagents onto enones, enals, and enoates, in which very high degrees of stereo- and chemoselectivities were observed.

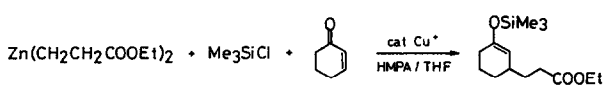
Conjugate addition of organocopper reagents represents a valuable synthetic procedure in modern organic chemistry (eq. 1).[1] The original catalytic reaction developed in the 1940's[2] has a merit of simplicity, while it suffers from the lack of selectivity (i.e., 1,2- vs. 1,4-addition) and from the sensitivity to structural variation of the substrate.[1a] Studies on the stoichiometric copper species[1b] demonstrated the merit of the well-defined cuprate reagent and evolved into development of an array of related, more selective reagents.[1c] A common demerit of the stoichiometric species however involves the need of excess alkylating agents (e.g., lithium alkyls). This stems from the inherent stoichiometry of the reagent itself (i.e., R_2CuLi-stoichiometry), as well as from the fact that the temperature needed to effect the reaction with electrophile is similar to that sufficient to cause decomposition of the reagent.[1d] Thus the reaction requires careful temperature control around -40 to 0 °C.



(1)

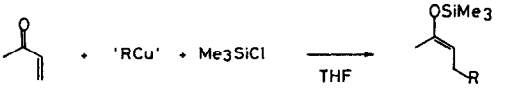
'RCu' = RMgX/cat Cu, RCu, R_2CuLi etc.*

In 1984, we reported an observation that conjugate addition of the zinc homoenolate of propionate **1** is tremendously accelerated by Me_3SiCl and HMPA (eq 2).[3] Such rate enhancement by Me_3SiCl was unknown at that time. Me_3SiCl was also found to accelerate a 1,2-addition reaction.[4]



(2)

We therefore decided to examine the nature of such effects in a broader framework to confirm its generality.[5] Indeed, various chlorosilanes besides Me_3SiCl have been found to strongly accelerate the conjugate addition reaction of both catalytic and stoichiometric organocopper reagents (eq 3),[6] significantly changing the nature of the reaction. Most important is that, in addition to the acceleration effect, the use of Me_3SiCl opened a new dimension in the stereo- and chemoselectivity of the conjugate addition reactions. Concomitant with our findings, two other groups[7] also noted the same aspect of the rate enhancement of the stoichiometric reactions. We describe here details of our studies about the effects of R_3SiCl in the conjugate addition of the organocopper reagents.



(3)

Table 1. Conjugate Addition of the o-Tolyl Grignard Reagent to 3-Methylcyclohexenone (eq 4)a

entry	solv	Me_3SiCl (equiv)	HMPA[b] (equiv)	temp (°C)	time (min)	adduct (%yield) 1,4	1,2	ratio	recovery (%)
1	ether	0	0	-70	30	11	12	47:53	6
2	THF	0	0	0	180	73	17	81:19	0
3	THF	0	0	-70	30	2	11	18:82	46
4	THF	2.4	0	-70	30	31	4	89:11	0
5	THF	6	0	-70	30	33	4	90:10	0
6	THF	2.4	2.4	-70	30	99.8	0.2	500:1	0
7	THF	2.4	2.4	-70	5	61	1	98:2	24
8	THF	2.4	2.4	-30	30	98	2	98:2	0
9	THF	2.4	2.4	0	120	58	4	94:6	29
10	THF	0	6	-70	5	0	0	-	87
11	THF	2.4	H	-70	30	28	6	84:16	17
12	THF	2.4	TEA	-70	30	25	7	79:21	
13	THF	2.4	TMEDA	-70	30	6	10	36:64	57
14	THF	2.4	DMI	-70	30	52	2	96:4	

[a]Five mol% of CuBr·Me_2S complex was used. [b]H: diisopropylethylamine. TEA: triethylamine. TMEDA: tetramethylethylenediamine. DMI: dimethylimidazolidinone. Two equiv each of these additives instead of HMPA were used.

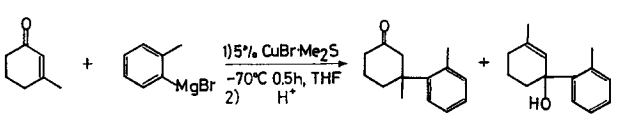
Table 2. Conjugate Addition of the n-Butyl Grignard Reagent to 3-Methylcyclohexenone (eq 5)

entry	solv	Me_3SiCl (equiv)	HMPA[a] (equiv)	temp (°C)	time (h)	adduct (%yield) 1, 4	1, 2	ratio	recovery (%)
1	THF	0	0	-70	0.5	1	8	11:89	82
2	THF	0	2.4	-70	2.0	2	0.2	91:9	75
3	THF	2.0	0	-70	2.0	40	15	73:27	45
4	THF	2.4	2.4	-70	2.5	93	0.7	130:1	29
5	THF	1.2	1.2	-70	4.0	91	0	100:0	0
6	ether	2.0	2.4	-70	2.0	44	8	85:15	30

[a]Five mol% of CuBr·Me_2S complex was used.

(A) Copper Catalyzed Reaction of the Grignard Reagent.

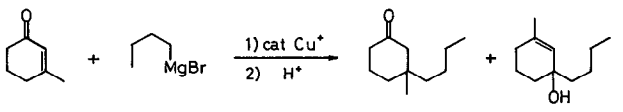
Copper-catalyzed conjugate addition of the Grignard reagent onto an α,β-unsaturated carbonyl compound has conventionally been conducted in such a manner that a small amount of a reactive organocopper species generated in situ is allowed to react with the carbonyl compound. 1,2-Addition reaction tends to compete with the desired 1,4-addition, and this side reaction has rendered the catalytic procedure an unfavorable synthetic choice. However, since such a catalytic reaction is so simple and convenient to perform, it is indeed worthy of revival, if it could be made as selective as the stoichiometric counterpart.



(4)

Initial studies were conducted for the combination of nearly equimolar amounts of relatively unreactive reactants. (In the optimization studies, the reactions were normally terminated after 5 or 30 min by addition of acetic acid in THF in order to obtain semi-quantitative information on the reaction rate.) The case we studied extensively was the reaction between 3-methylcyclohexenone and o-tolylmagnesium bromide in ether or THF (eq 4). Being unreactive due to reduction-potential[8] and steric problems, they gave the best 1,4:1,2-ratio of only 4:1 in 90% total yield (Table I, entry 2) under conventional conditions. The reactions at low temperatures either in ether or in THF (entries 1, 3) gave considerable amount of the 1,2-adduct. When the reaction was conducted in the presence of of 2 equiv Me_3SiCl in THF, the yield and the ratio improved to 30-40% and 9:1, respectively. As observed in most of the latter cases, use of a large excess of Me_3SiCl did not result in further improvement (entries 4, 5). The presence of 2.4 equiv each of the chlorosilane and HMPA produced a dramatic effect, affording the 1,4-adduct in quantitative yield with 500:1 selectivity (entry 6). The reaction becoming very rapid, about 70% of the reactants was already consumed after 5 min at -70 °C (entry 7). While the selectivity still remained very high

even at -30 °C (entry 8), it dropped to 94:6 at 0 °C (entry 9). It is noteworthy that, as reported by House,[9] HMPA by itself greatly retarded the reaction (entry 10). Excess HMPA even adversely affected the effect of Me_3SiCl (entry 10). Both selectivity and yield dropped drastically (e.g., to 9:1 in 30% yield after 5 min) when the amount of Me_3SiCl and/or HMPA was reduced to 1.2 equiv. Effects of basic additives other than HMPA are summarized in entries 11-14. Comparison with the standard Me_3SiCl/HMPA-acceleration (entry 4) reveals the adverse effect of a simple tertiary amine (entry 12). We found in the reaction of butylmagnesium bromide (vide infra) that dimethylaminopyridine (DMAP), which is as effective as HMPA in the stoichiometric reactions (vide infra), does not assist the effect of the chlorosilane. Tetramethylethylenediamine (TMEDA) was not an effective additive in this reaction.[7c] Me_3SiF was totally devoid of the ability to accelerate the reaction.



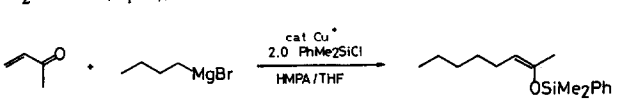
(5)

The reaction of butylmagnesium bromide with 3-methylcyclohexenone was also examined to obtain essentially the same conclusion (Table 2). This reaction was very slow in the absence of Me_3SiCl at -70 °C in THF or in HMPA/THF (entries 1,2), and considerable acceleration occurred in the presence of Me_3SiCl alone (entry 3). Important finding in this set of experiments was that only one equiv each of the chlorosilane and HMPA was necessary for this combination of reactants to obtain the optimum result (cf. entries 4 and 5). As observed by us[6] and others[7] in the stoichiometric reactions, Me_3SiCl show marginal effects in ether (entry 6). When the Grignard reagent was replaced by butyllithium under otherwise the same conditions as in entry 4, a 4:1:32 mixture of 1,2-, 1,4-adducts, and the starting enone was obtained in an >80% combined yield.

These studies defined the "fail-safe" conditions being the use of 2 equiv each of Me_3SiCl and HMPA in THF at -70 °C. The workup procedure described in the Experimental Section allowed isolation of the adduct as an enol silyl ether free from hydrolysis product. Examples in Table 3 illustrates several important points: (1) High yield obtained with nearly a stoichiometric amount of the Grignard reagent of diverse structural variety. (2) Very high chemoselectivity. (3) Successful reaction with enal and enoates that give poor results even with conventional stoichiometric reagents.[1a,c] The reaction in entry 9 was studied extensively during the course of our recent synthesis of (±)-cortisone,[10] and the Me_3SiCl-accelerated reaction has proven superior to various other Grignard-based conjugate additions.

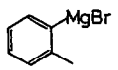
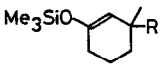
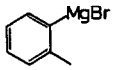
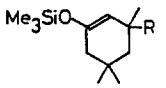
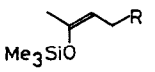
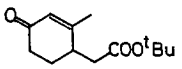
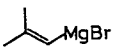
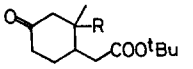
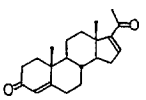
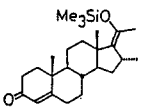
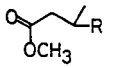
The stereoselectivity of conjugate addition onto cyclohexenone derivatives is of considerable synthetic interests.[11] The selectivity of the reaction for two typical substrates, 4-methyl- and 5-methylcyclohexenone was however found unaffected by the presence of Me_3SiCl/HMPA (Scheme I). In contrast to this result, we recently found a case where additives (Me_3SiCl/HMPA and $BF_3{\cdot}Et_2O$) alter the stereochemistry of the copper-catalyzed conjugate addition of $Zn(CH_2CH_2COOR)$.[10]

The Me_3SiCl/HMPA assisted addition revealed its highest potentiality in the reaction with enals (Table 4), where considerable trouble has been encountered even with the stoichiometric reagents.[12] The reaction of the Grignard reagents (1.2-1.5 equiv) with an enal under conditions defined above gave the conjugate adduct in quantitative yield as an E-enol silyl ether. The stereoselectivity was found considerably temperature dependent (Table 5). The selectivity showed good reproducibility, and was independent of the amount of Me_3SiCl used. The substituent on the silicon however exercised some effects on the stereochemistry of the enol silyl ether. For instance, the 28:72 E/Z ratio in the reaction of methyl vinyl ketone obtained with Me_3SiCl changed to 19:81 with $Me_2PhSiCl$ (eq 6).



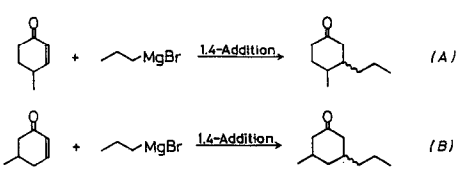
(6)

Table 3. Me_3SiCl/HMPA Accelerated Conjugate Addition of Catalytic Copper Reagents[a]

entry	Enone	RMgBr	Enol silyl ether	% yield [E: Z]
1				77% (100%)
2		$n\text{-}C_3H_7MgBr$		85
3				80
4		$n\text{-}C_4H_9MgBr$		89
5		$CH_2{=}CHMgBr$		97
6		$n\text{-}C_4H_9MgBr$		(96) [28:72]
7		$n\text{-}C_6H_{13}MgBr$		91 [23:77]
8		C_6H_5MgBr		78 [46:54]
9				71[b,c]
10		CH_3MgBr		94[d] [2:98]
11		C_6H_5MgBr		76[b]

[a]All reactions were carried out for 2--4 h at -78 °C according to the procedure described in the Experimental Section using either 1.2 equivalent of a standardized Grignard reagent or the reagent prepared in situ from 1.5 equivalent of an organic bromide. Unless stated otherwise, yields refer to the enol silyl ether of at least 95% purity obtained by distillation. Quantitative GLC yields are in parentheses, and E:Z ratios are in brackets. The E/Z-ratio was determined capillary GLC analysis and was supported by ^1H NMR analysis. [b]Isolated as carbonyl compounds. [c]The reaction was performed with 4 equiv of Me_3SiCl (without HMPA). [d]Performed at -50 °C for 15 h.

Scheme I.



	cat.Cu: Me_3SiCl, HMPA		cat.Cu[a]	
	Yield (%)	trans:cis	Yield (%)	trans:cis
(A)	79	79:21	78	(80:20)
(B)	80	97:3	81	97:3 (93:7)

[a]The ratios in parentheses have been taken from ref 11.

Table 4. Conjugate Addition onto Unsaturated Aldehyde[a]

Entry	Enal	RMgBr (R =)	Temp(°C)	Enol Silyl Ether %yield	E:Z
1		n-hexyl	-78	83 (95)[b]	94: 6
2		n-butyl	-78	86	97: 3
3		phenyl	-78	89	86: 14
4			-100	90	91: 9
5		n-hexyl	-78	89	96: 4
6		phenyl	-78	(91)[b]	96:4
7		phenyl	-78	89	87: 13
8		n-butyl	-78	76	92: 8
9		n-hexyl	-100	(78)[b]	93: 7
10		c-hexyl	-100	80	98. 6: 1. 4
11		phenyl	-78	90	97: 3

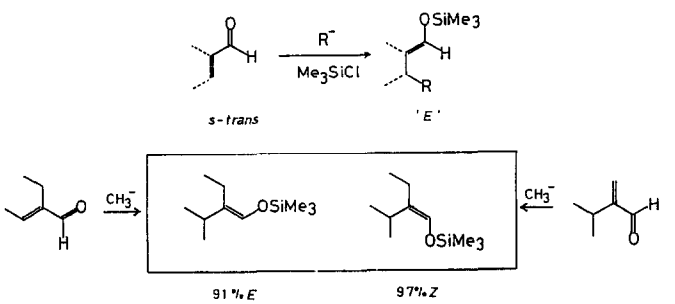
[a]See Table I. [b]Quantitative GLC yields in parentheses.

Table 5. Temperature Effect on the Stereoselectivity

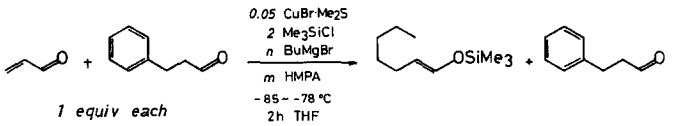
Me_3SiCl equiv	temp °C	E : Z R = butyl	R = phenyl
2	-50 to -30	84: 16	
2	-78	97: 3	86: 14
2	-100	98: 2	91: 9
6	-100	98: 2	90: 10

Although the precise origin of the E-selectivity in the reaction of enals is obscure, it formally arises from the addition of the nucleophile onto the most stable s-trans conformer of aldehyde.[13] Use of such protocol realized synthesis of both E- and Z-isomers of α,α-disubstituted aldehydes (Scheme II). The current lack of methods for the stereoselective synthesis of this type of aldehydes would render the conjugate-addition approach a useful new tool in enolate chemistry.

Scheme II.



We then examined the most demanding test of chemoselectivity (eq 7). When 1 equiv of butylmagnesium bromide in THF was added to a mixture of acrolein, 3-phenylpropionaldehyde, Me_3SiCl, and HMPA at -85 °C, the enol silyl ether **2** due to conjugate addition and the starting saturated aldehyde was obtained. The acceptable material balance compares favorably with the very poor result of the reaction conducted with dibutylcuprate in the absence of additives.

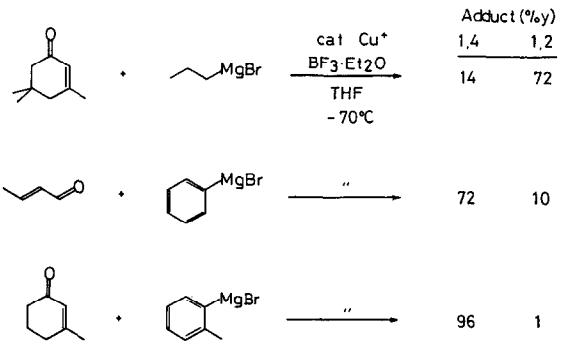


(7)

n = 1.2, *m* = 2.4	82%	63%
n = 1.0, *m* = 2.0	55%	84%

Finally, attempts for the extension of the Me_3SiCl-acceleration to Ni-Catalyzed addition,[14] and CuH addition[15] proved unfruitful. $BF_3{\cdot}Et_2O$ which directs the reaction of stoichiometric copper reagents to 1,4-addition pathway[16] was found to promote some catalytic reactions; however, the effect was not general (Scheme III).

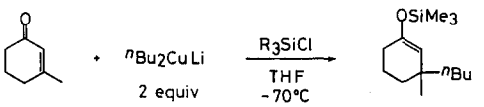
Scheme III.



(B) Conjugate Addition of Stoichiometric Reagents.

A variety of effective yet elaborate procedures have been developed to overcome the problems associated with the stoichiometric reagents.[1] The observations made for the catalytic copper reagents suggested that Me_3SiCl would also provide a simple solution in the stoichiometric case.

The protocol was essentially the same as the one used above (eq 8). A colorless clear solution of Bu_2CuLi prepared in THF from butyllithium and $CuBr{\cdot}Me_2S$ at -70 to -40 °C was cooled to -70 °C, an additive added, and a mixture of 3-methylcyclohexenone and a chlorosilane in THF added dropwise. The reaction was quenched with acetic acid in THF generally before completion, to obtain information on the reaction rate. Under these conditions contribution of 1,2-addition pathway was negligible.



(8)

Whereas the uncatalyzed conjugate addition below -70 °C was very slow and ca. 30% conversion occurred after 1 h (Table 6, entry 1), the Me_3SiCl-assisted reaction completed in 5 min to give quantitative yield of the 1,4-adduct. As in the catalytic reaction, ether was not a suitable solvent.[7] We then examined the effect of tert-butyldimethylsilyl chloride to find that this reagent does not accelerate the reaction (entry 3). There has been reported a observation contrary ours.[7a] The significant acceleration occurred however (entry 4) when $^tBuMe_2SiCl$ was used with HMPA, which by itself retarded the addition (entry 8).

In light of a recent report that HMPA complexes with silyl trifluoromethane sulfonate as strongly as DMAP,[17] it was felt that HMPA might be replaced by DMAP. In fact, this reagent exhibited the same level of acceleration (entry 5) as found with HMPA. Less powerful activator of R_3SiX (e.g., DMI or DMF) proved less effective (entries 6, 7).

Table 6. Acceleration of Conjugate Addition of Dibutylcuprate[a]

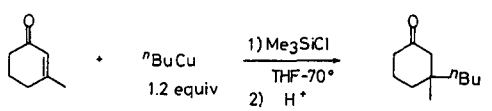
entry	R_3SiCl (2 equiv)	additive (2 equiv)	time (min)	1,4-adduct enolsilane	1,4-adduct ketone	recovery (%yield)
1	-	-	60	0	28	70
2	Me_3SiCl	-	5	99	0	0
3	$^tBuMe_2SiCl$	-	60	0	31	63
4	$^tBuMe_2SiCl$	HMPA	60	85	5	9
5	$^tBuMe_2SiCl$	DMAP	60	86	4	10
6	$^tBuMe_2SiCl$	DMI	60	0	65	35
7	$^tBuMe_2SiCl$	DMF	60	9	31	59
8	-	HMPA	60	12	0	88
9	-	DMI	60	0	15	85

[a]Product was isolated either as an enol silyl ether or as a ketone.

Table 7. Conjugate Addition of Butylcopper Reagents onto 3-Methylcyclohexenone

entry	reagent (equiv)	Me_3SiCl (2.0 equiv)	additive (2.0 equiv)	time	GLCyield (%) 1,4-adduct	recovery
1	BuCu (1.2)	-	-	1 h	0	95
2		+	-	20 min	24	65
3		+	-	3 h	56	42
4		+	HMPA	20 min	53	33
5		+	DMAP	20 min	57	34
6		+	HMPA	1 h	89	8
7	Bu_2CuLi (0.6)	+	HMPA	3 h	87	13

Me_3SiCl also facilitates addition of (otherwise very unreactive) butylcopper (eq 9; Table 7, entries 1, 2). The effect was further enhanced by the use of HMPA or DMAP (entries 4, 5) to obtain the 1,4-adduct in nearly quantitative yield after 1 h. Johnson et al. reported a similar effect of TMEDA.[7c] Under conventional conditions, only one of the R groups in an R_2CuLi reagent reacts with the substrate to leave RCu unreacted. The above results imply that Me_3SiCl/HMPA might enable the full use of the Rs in the cuprate. In fact, conjugate addition conducted with 0.6 equiv of Bu_2CuLi proceeded expectantly to give the adduct in high yield (entry 7).

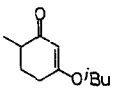


(9)

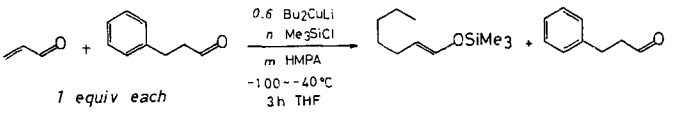
Table 8 summarizes the examples of the stoichiometric conjugate addition in the presence of Me_3SiCl. All reactions were performed with reagents prepared from 1.2 equiv of organolithium reagents.

The selectivity as to the double bond geometry in the product (Table 8) was found almost identical with that in the catalytic reaction. In contrast to the high E-selectivity found in our cases, the reaction of enals under conventional conditions has been reported[12] to produce a nearly 1:1 mixture of stereoisomers. Our own experiments performed for methyl vinyl ketone also revealed the reversal of the stereochemistry due to the presence of Me_3SiCl (compare entry 1 with 2 and 3). This is a straightforward demonstration of fundamental mechanistic distinction between the present reaction and the common "enolate trapping".

Table 8. Me_3SiCl/HMPA-Assisted Conjugate Addition of Organocopper Reagents (-70 to -40 °C) Prepared from 1.2 Equiv of Organolithium Reagents

entry	substrate	reagent (equiv)	Me_3SiCl (2.0 equiv)	HMPA	% yield	E:Z
1		Bu_2CuLi (1.2)	-	-	82	67:33
2			+	-	85	38:62
3		(0.6)	+	+	84	28:72
4		BuCu (1.2)	+	+	82	15:85
5		Bu_2CuLi (1.2)	+	-	88	89:11
6		(0.6)	+	+	80	98: 2
7		BuCu (1.2)	+	+	71	95: 5
8		Ph_2CuLi (0.6)	+	+	84	92: 8
9		Ph_2CuLi (0.6)	+	+	99	97: 3
10		Bu_2CuLi (0.6)	+	+	92	1,4:1,2 = 3:2--2:3

Chemoselectivity of the reaction was also examined (eq 10). The poor performance of the reaction in the absence of Me_3SiCl was greatly improved by the chlorosilane. Since Me_3SiCl also accelerates 1,2-addition reaction,[19] careful control of reagent stoichiometry may be necessary to optimized the result.



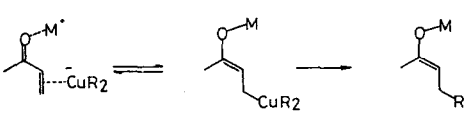
(10)

$n = 0$ $m = 0$*	31%	40%
$n = 1.1$, $m = 1.2$	86%	81%

*The reaction mixture was quenched with Me_3SiCl after completion of the reaction.

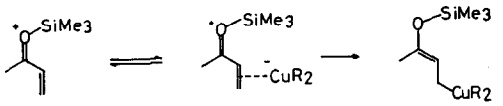
Discussion

The mechanism of the conjugate addition of organocopper reagents has been the subject of debate for a long time. In a broader framework, the mechanism (eq 11)[20] involves the initial interaction of the organocopper with the π-systems of the substrate (**A**) followed by formation and reductive elimination of an intermediate having C-Cu bond (**B**). House has established a good correlation between the reduction potential and the reactivity of the substrate,[8] which has been accepted as a guideline for predicting the reactivity of a given substrate. The presence of Lewis acid metals (e.g., Li, Mg) has been known essential for the conjugate addition.[21] Such function of the Lewis acid is consistent with the view that the Lewis acidic coordination (**A**) lowers LUMO level of the substrate, consequently facilitating flow of electron(s) from the organocopper species to the substrate. There is still much controversy whether the stage which follows the first is the single electron transfer from the metal or the nucleophilic attack of the copper itself.



(11)

A B



(12)

C

There can be at least two types of rationales to account for the observed tremendous rate enhancement by chlorosilanes. One relates such acceleration to the very first stage of the reaction, where coordination of the chlorosilane with the substrate (**C** in eq 12) and the resultant lowering of the enone LUMO are assumed. Another postulates[7a] that chlorosilane simply traps the enolate intermediate **B** to drive the equilibrium in eq 11 to product formation.

Physical support of the former hypothesis is lacking; namely, ^{1}H NMR measurement for a mixture of cyclohexenone and Me_3SiCl either in $CDCl_3$ or in HMPA/THF-d_8 revealed no sign of a Lewis acid/Lewis base complex.[22] However, there have been at least two reported cases in which activation of carbonyl groups by Me_3SiCl has been chemically implicated. One is the Me_3SiCl-promoted conjugate addition of ketene silyl acetal[23] and the other the 1,2-addition of zinc homoenolate.[4]

The Me_3SiCl-assisted addition onto 3-alkoxycyclohexenone (Table 8, entry 10) provides us with mechanistic information. This substrate, being very much less reactive than normal enones, is inert to BuCu or MeCu even at 0 °C for an extended period. House ascribed the poor reactivity to the very low reduction potential,[8] assuming that the initial crucial interaction between the reactants does not occur due to the unfavorable energetic factor.[8] On the basis of such argument, smooth reaction observed under Me_3SiCl(/HMPA) assistance gives a positive support to the Lewis-acidic activation by the chlorosilane (cf. **C**). Formation of a nearly 1:1 mixture of the 1,2- and 1,4-adducts and the observed lack of reproducibility of this ratio imply that the reaction proceeds through a nearly symmetrical intermediate (**E**), which undergoes rapid allylic rearrangement before collapsing to the product.

(13)

E

In summary, the present studies have demonstrated that Me_3SiCl strongly accelerates the conjugate addition of organocuprates. These as well as the works by others[7] indicate that a broad spectrum of conjugated carbonyl compounds and congeners such as α,β-unsaturated aldehydes, ketones, esters, amide,[7b] and nitriles[7b] of diverse structural varieties serve as the substrate of conjugate addition under assistance of Me_3SiCl. The use of Me_3SiCl has thus already become a standard protocol for enhancing the efficiency of the conjugate addition.[24] Besides the obvious merit that the intermediary enolate can be isolated as an enol silyl ether, very mild reactivity of Me_3SiCl makes this method complementary to the well-established $BF_3{\cdot}Et_2O$ activation.[16] The ability of Me_3SiCl to promote 1,2- and 1,4-addition of other organometallics[3,4,19,23] indicates the generality of strategy to use Me_3SiCl as a very mild promoter of nucleophilic reactions.

Experimental

General. All the reactions dealing with air and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen. Liquid samples were introduced either neat via a micro syringe or in a organic solvent via a hypodermic syringe. Solid samples were weighed into a vessel in a nitrogen filled bag. Routine flash chromatographic purification was achieved with purified (by sedimentation) Wako C-300 silica gel using hexane/AcOEt as eluent.

^{1}H NMR spectra taken at 200 MHz on a JEOL FX-200 instrument, which was also used for ^{13}C NMR spectra at 50 MHz. Spectra are reported in part per million from internal tetramethylsilane. IR spectra were recorded on a Hitachi 260-10 instrument; absorptions are reported in cm^{-1}. Gas chromatographic analysis was performed on a Hitachi 063 or on a Shimazu 4BM machine equipped with

glass capillary column (0.25 mm x 25 m). GC-MS analysis was performed on a Shimazu 9020-DF equipped with a OV-1 (7 m) capillary column.

Material. Ethereal solvents were distilled from benzophenone ketyl immediately before use. Hexane was distilled from $LiAlH_4$ under nitrogen and stored over potassium mirror. HMPA was distilled in vacuo from CaH_2 and stored under molecular sieves. CuBr·Me_2S complex was prepared as described and handled with caution as recently reported.[24] All commercially available reagents were either distilled or recrystallized before use.

General Procedure for Optimization of Conditions: Workup A. To a weighed amount of CuBr·Me_2S (2 mg, 0.001 mmol) in 0.4 ml of THF at -70 °C was added 0.40 ml (0.211 mmol) of a 0.53 M solution of o-tolylmagnesium bromide (prepared from o-tolyl bromide; concentration estimated from the NMR yield of the reaction with benzaldehyde). A solution of 3-methylcyclohexenone (20 micro L, 0.176 mmol), Me_3SiCl (56 micro L, 0.422 mmol), and HMPA (77 micro L, 0.422 mmol) in 0.2 ml of THF was then added dropwise. After the yellow mixture being stirred at -70 °C, a solution of acetic acid (25 micro L, 0.422 mmol) in 0.2 mL of THF was added, and the cooling bath was removed. An internal standard (ethyl laurate, 15 micro L) was added, and an aliquot was analyzed for the content of the starting enone and the addition products by capillary GLC (OV-1, 60-130 °C). The 1,2-adduct flows faster than the 1,4-adduct.

Typical Procedure of Catalytic Conjugate Addition: 1-Trimethylsiloxy-1-nonene. To a solution of n-hexylmagnesium bromide prepared from hexyl bromide (5.78 g, 35.0 mmol) and magnesium (912 mg, 37.5 mmol) in 80 mL of THF was added - 70 °C CuBr·Me_2S (257 mg, 1.25 mmol) and HMPA (10.8 g, 60 mmol). After stirring for several minutes, a mixture of acrolein (1.40 g, 25.0 mmol) and Me_3SiCl (5.43 g, 50 mmol) in 20 mL of THF was added 30 min (slow addition is essential to realize high geometrical purity of the enol silyl ether). After 2 h, triethylamine (7 mL, 50 mmol) was added and the mixture was diluted with dry hexane. A small amount of water (or pH 7.4 phosphate buffer) was added, and the mixture was filtered through Celite. The filtrate was washed 5-10 times with 5-mL portions of water (to remove HMPA), and the water layer was extracted one with hexane. The organic layer was washed one with sat. NaCl, dried over $MgSO_4$, and concentrated. Distillation of the residue gave the title ether of high purity (3.86 g, 83%). GLC (OV-1) analysis indicated an E/Z ratio of 94:6, and the identity of the minor Z-isomer was confirmed by equilibration of the major isomer in the presence of p-toluenesulfonic acid: Bp 74-78 °C, 1 mm Hg; IR (neat) 1660 (s): ^1H NMR (200 MHz, $CDCl_3$) 0.18 (s, 9 H), 0.88 (t, 3 H, J = 6 Hz), 1.27 (br s, 10 H), 1.88 (m, 2 H), 4.99 (dt, 1 H, J = 7.6, 12.0 Hz), 6.19 (dt, 1 H, J = 12.0, 1.2 Hz). The J value and NOE (16% enhancement between C^1H and C^3H_2) indicated the E-geometry of the major product.

Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.21; H, 12.22. Found: C, 67.27; H, 12.14.

Workup B. After the reaction period, 2 equiv of triethylamine and silica gel (about 4 times the weight of the product) was added. After stirring for for several minutes at room temperature, dry hexane (about twice the total volume of the reaction mixture) was added and the slurry was filtered. The filtrate was distilled to remove HMPA. A small amount of desilylated material invariably occurred by this procedure.

The details of the conditions for each combination of reactants are summarized in Table 9, and the physical properties of the products are list below.

General Procedure for the Optimization of Stoichiometric Reaction. 1-tert-Butyldimethylsiloxy-3-butyl-3-methyl-1-cyclohexene. To a stirred suspension of CuBr·Me_2S (82.2 mg, 0.4 mmol) in 1 mL of THF at -70 °C was added dropwise butyllithium in hexane (0.80 mmol). The mixture was stirred to -40 °C for 30 min, and then cooled to -70 °C (butylcopper and lithium diphenylcuprate were prepared in the same manner). HMPA (70 micro L, 0.40 mmol) was added, and after a while a mixture of tert-butyldimethylsilyl chloride (60 mg, 0.40 mmol) and 3-methyl-2-cyclohexenone (23 micro L, 0.20 mL) and an internal standard (undecane or tetradecane) in 0.2 ml of THF was added. After 1 h, 0.05 mL of phosphate buffer (pH 7.4) and the organic portion was analyzed by GLC (OV-1). The yield was 95% with 5% recovery of the enone; ^1H NMR (60 MHz, CCl_4) 0.10 (s, 6 H), 0.64-1.13 (m, involving 0.90, s), 4.51 (br s, 1 H).

General Procedure for Conjugate Addition of Stoichiometric Reagent. To a cooled (-70 °C) solution of Bu_2CuLi (0.3 mmol prepared as above) was added HMPA (174 micro L, 1.0 mmol). After several minutes, a mixture of acrolein (33.4 micro L, 0.50 mmol), chlorotrimethylsilane (120 micro L, 1.0 mmol) and decane (internal standard) in 0.3 ml of THF was added dropwise. After 2.5 h at -70 °C, 80 micro L of triethylamine and pH 7.4 phosphate buffer was added. GLC analysis of the resulting mixture indicated 80% yield and an E:Z ratio of 98:2.

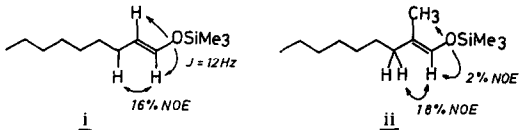
Chemoselective Conjugate Addition. To a solution of Bu_2CuLi (0.12 mmol) and HMPA (42 micro L, 0.24 mmol) in THF at -100 °C was added a solution of acrolein (13.4 micro L, 0.20 mmol), 3-phenylpropanal (26.3 micro L, 0.20 mmol), chlorotrimethylsilane (28 micro L, 0.22 mmol) and decane (internal standard) in 0.3 ml of THF. After 30 min the temperature was raised to -70 °C, then after 1 h to -40 °c. Triethylamine (15 micro L) was added. Phosphate buffer (pH 7.4, 0.03 mL) was added and the mixture was analyzed by GLC (OV-1, 110 °C) which indicated the presence of 1-trimethylsiloxy-1-heptene (86%, E:Z = 89:11, 8.2, and 6.8 min, respectively) and 3-phenylpropanal (81%, 9.5 min).

Physical Properties of Conjugate Adducts (Enol Silyl Ethers).

Geometry of the Enol Silyl Ethers. The well-established ^1H NMR protocol on the coupling constant was applied for assigning the E-stereochemistry of the disubstituted double bond in the aldehyde enolates such as i, the H^a-H^b-coupling constants of which fell in a narrow range of values around 12 Hz. In the case of the compound i, nuclear Overhauser effect (NOE, 16%) between H^a and H^c confirmed this assignment. The minor Z-isomer showed a coupling constant of ca. 6 Hz. The successful generalization proposed by House[26] that an olefinic proton cis to the siloxy group resonates down field than that trans to it has been applied to trisubstituted ketone enolates.

The assignment of the tetrasubstituted ketone enolates and trisubstituted aldehyde enolates was more problematic. There have been observed for enol silyl ethers of aldehydes and ketones that

the aliphatic protons of a substituent cis to the siloxy group resonates at a lower field than the trans ones,[25] and we relied on such a physical protocol to make the assignment, although the basis of such a "rule" has been rather circumstantial. For the compound ii, we could obtain strong support of the E-geometry from an NOE experiment as indicated below. Except in a few special cases, the Z-isomers move faster than the E-isomer in GLC glass capillary columns coated with OV-101 or OV-1.



i ii

3-Methyl-3-(2-methylphenyl)-1-trimethylsiloxy-1-cyclohexene. Bp 125-140 °C, 5 mm Hg; IR (neat) 1660, 1254, 1198, 843: ^{1}H NMR ($CDCl_3$) 0.22 (s, 9 H), 1.50 (s, 3 H), 1.98-2.12 (m, 2 H), 2.50 (s, 3 H), 4.93 (s, 1 H), 7.07-7.18 (m), 7.38-7.47 (m); ^{13}C NMR ($CDCl_3$) 0.7 (q), 20.2 (t), 22.6 (q), 29.6 (q), 29.8 (t), 35.2 (t), 41.0 (s), 115.4 (d), 125.4 (d), 126.0 (d), 128.1 (d), 132.8 (d), 136.2 (s), 147.0 (s), 148.9 (s).

The ketone obtained by hydrolysis of the enol silyl ether afforded correct analytical data.

Anal. Calcd for $C_{14}H_{18}OSi$: C, 83.12; C, 8.97. Found: C, 83.19; H, 8.99.

1-Trimethylsiloxy-3-methyl-3-propyl-1-cyclohexene. Bp 87-91 °C, 7.6 mm Hg; ^{1}H NMR ($CDCl_3$) 0.18 (s, 9 H), 0.88 (br t, 3 H), 0.93 (s, 3 H), 1.12-1.46 (m), 1.57-1.73 (m), 1.93 (br t, 2 H); ^{13}C NMR ($CDCl_3$) 0.4 (q), 15.1 (q), 17.5 (t), 19.8 (t), 28.2 (q), 30.0 (t), 34.7 (s), 34.9 (t), 46.2 (t), 114.8 (d), 149.1 (s).

3,5,5-Trimethyl-1-trimethylsiloxy-3-(2-methylphenyl)-1-cyclohexene. Bp 99-102 °C, 5.6 mm Hg; ^{1}H NMR ($CDCl_3$) 0.65 (s, 3 H), 1.00 (s, 3 H), 1.48 (s, 3 H), 1.86 (br s, 3 H), 2.52 (s, 3 H), 5.06 (s, 1 H), 7.1 (m), 7.45 (m).

Anal. Calcd for $C_{19}H_{30}OSi$: C, 75.43; H, 10.00. Found: C, 75.15; H, 9.95.

3-Butyl-3,5,5-trimethyl-1-trimethylsiloxy-1-cyclohexene. Bp 95-98 °C, 2.2 mm Hg; IR (neat) 1660, 1246, 1212, 1144, 850; ^{1}H NMR ($CDCl_3$) 0.18 (s, 9 H), 0.88 (br t, J = 6 Hz, 3 H), 0.97 (s, 3 H), 0.99 (s, 3 H), 1.00 (s, 3 H), 1.06-1.38 (m, 8 H), 1.70 (d, J = 16 Hz, 1 H), 1.82 (d, J = 16 Hz, 1 H), 4.64 (br s, 1 H); ^{13}C NMR ($CDCl_3$) 0.6 (q), 14.4 (q), 23.7 (t), 26.6 (t), 28.9 (q), 29.3 (q), 31.6 (q), 31.8 (s), 35.4 (s), 47.3 (s), 113.5 (d), 147.7 (s).

Anal. Calcd for $C_{16}H_{31}OSi$: C, 71.57; H, 12.01. Found: C, 71.77; H, 11.92.

3-Ethenyl-3,5,5-trimethyl-1-trimethylsiloxy-1-cyclohexene. IR (neat) 1662, 1357, 1254, 1150, 842; ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 0.91 (s, 3 H), 0.96 (s, 3 H), 1.05 (s, 3 H), 1.27 (d, J = 13.4 Hz, 1 H), 1.46 (d, J = 13.4 Hz, 1 H), 1.72 (d, J = 16.8 Hz), 1.86 (d, J = 16.8 Hz, 1 H), 4.79 (s, 1 H), 4.83 (dd, J = 10.5, 1.2 Hz), 4.95 (dd, J = 17.3, 1.2 Hz), 5.83 (dd, J = 10.5, 17.3 Hz); ^{13}C NMR ($CDCl_3$) 0.6 (q), 28.8 (q), 31.4 (q), 31.7 (q), 32.0 (s), 39.0 (s), 44.1 (t), 48.9 (t), 110.0 (t), 110.5 (d), 148.8 (s), 149.5 (d).

Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.38; H, 11.00.

(Z)-2-Trimethylsiloxy-4-phenyl-2-butene. Bp 115-117 °C, 5.5 mm Hg; IR (neat) 1666, 1254, 1162, 840; ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 1.82 (d, J = 1.0 Hz, 3 H), 3.34 (d, J = 7.1 Hz, 2 H), 4.65 (tq, J = 7.1, 1.0 Hz, 1 H), 7.10-7.33 (m, 5 H); with additional resonances due to the E-isomer at 0.19 (s), 3.30 (d, J= 7.8 Hz), 4.86 (tq, J = 7.8, 1.0 Hz).

Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 71.01; H, 9.15.

(Z)-2-Trimethylsiloxy-2-decene. Bp 81-83 °C, 2.4 mm Hg; IR (neat) 1675, 1378, 1252, 844; ^{1}H NMR ($CDCl_3$) 0.18 (s, 9 H), 0.88 (t, J = 7 Hz, 3 H), 1.27 (br s, 10 H), 1.76 (s, 3 H), 1.94 (m, 2 H), 4.42 (t, J = 7 Hz, 1 H); with additional resonances due to the E-isomer at 1.72 (s), 4.64 (t).

Upon GLC analysis (OV-101), the Z isomer eluted faster than the E-isomer.

Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.34; H, 12.41.

(E)-1-Trimethylsiloxy-3-phenyl-1-propene. Bp 104-105 °C, 6.5 mm Hg; IR (neat) 1654, 1250, 1155, 862, 840; ^{1}H NMR ($CDCl_3$) 0.20 (s, 9 H), 3.24 (d, J = 7.3 Hz, 2 H), 5.16 (dt, J = 12.0, 7.3 Hz, 1 H), 6.31 (d, J = 12.0 Hz, 1 H), 7.09-7.34 (m, 5 H); with additional resonances due to the Z-isomer at 3.43 (d, J = 7.3 Hz), 4.71 (dt, J = 5.9, 7.3 Hz).

GLC (OV 101, 130 °C) retention times for E, and Z-isomers were 21.2 and 18.4 min, respectively.

Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.61; H, 8.73.

(E)-1-Trimethylsiloxy-1-nonene. Bp 74-78 °C, 1.0 mm Hg; IR (neat) 1658, 1250, 1160, 842; ^{1}H NMR ($CDCl_3$) 0.18 (s, 9 H), 0.88 (t, J = 6 Hz, 3 H), 1.27 (br s, 10 H), 1.88 (m, 2 H), 4.99 (dt, J = 12.0, 7.6 Hz, 1 H), 6.19 (dt, J = 12.0, 1.2 Hz, 1 H); 16% NOE was observed between protons at C^1 and C^3; ^{13}C NMR ($CDCl_3$) -0.29 (q), 22.8 (q), 27.5 (t), 29.2 (t), 29.3 (t), 30.6 (t), 32.1 (t), 112.3 (d), 139.4 (d).

GLC (OV 101, 140 °C) retention times for E, and Z-isomers were 11.7 and 10.1 min, respectively.

Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.21; H, 12.22. Found: C, 67.27; H, 12.14.

(E)-1-Trimethylsiloxy-1-heptene. IR (neat) 1660, 1253, 1161, 872, 843; ^{1}H NMR ($CDCl_3$) 0.18 (s, 9 H), 0.88 (br t, J = 6.8 Hz, 3 H), 1.13-1.41 (m, 6 H), 1.88 (br q, J = 7.3 Hz, 2 H), 4.99 (dt, J = 12.0, 7.3 Hz, 1 H), 6.19 (dt, J = 12.0, 1.5 Hz, 1 H); with additional peaks due to Z-isomer at 0.17 (s), 2.05 (br q, J = 7.3 Hz), 4.49 (dt, J = 5.9, 7.3 Hz), 6.14 (dt, J = 5.9, 1.5 Hz).

GLC (OV 1, 110 °C) retention times for E and Z-isomers were 8.2 and 6.9 min, respectively.

Table 9. Me_3SiCl/HMPA Assisted Conjugated Addition of Catalytic Copper Reagents.[a]

substrate g mmol	Mg mg mmol	RBr g mmol	CuBr·Me_2S mg mmol	Me_3SiCl g mmol	HMPA g mmol	temp (time) °C (h)	product g %yield[c], g
3-methyl-cyclohexenone		o-$CH_3C_6H_5$-					
1.49	493	3.23	138	3.52	3.35	-70 (1.5)	2.88
13.5	20.3	18.9	0.675	32.4	30.9	0 (1.5)	77, C
3-methyl-cyclohexenone		n-C_3H_7-					
0.971	321	1.69	90.7	1.91	3.80	-70 (2)	1.69
8.81	13.2	13.7	0.441	17.6	21.2	-30 (0.25)	85, C
isophorone		o-$CH_3C_6H_5$-					
2.00	528	3.47	149	3.14	6.22	-70 (1.5)	3.37
14.5	21.7	20.3	0.725	28.9	34.7	25 (1.5)	80, B
isophorone		n-C_4H_9MgBr					
0.967	b	b	72.0	3.01	1.52	-70 (1.5)	1.68
7.00		8.40	0.35	16.8	14.0	30 (1.5)	89, B
isophorone		CH_2=$CHMgBr$					
1.25	b	b	93.4	1.97	3.90	-70 (1.5)	2.10
9.08		10.9	0.453	18.2	21.8	25 (1)	97[d], B
methyl vinyl ketone		n-C_4H_9-					
0.140	b	b	20.6	0.44	0.86	-70 (2)	0.325
2.00		2.40	0.100	4.00	4.80		80, B
methyl vinyl ketone		n-C_6H_{13}-					
1.98	1040	6.58	294	5.22	12.3	-70 (2)	5.00
28.2	42.8	39.9	1.43	48.1	68.5	25 (1)	91, B
methyl vinyl ketone		C_6H_5-					
2.00	1040	6.26	294	5.31	12.3	-70 (4)	4.91
28.5	42.8	39.9	1.43	48.9	68.5		78, C
methyl crotonate		C_6H_5MgBr					
0.114	b	b	206	0.217	0.538	-70 (2)	0.149
1.00		1.50	0.100	2.00	3.00		78, A
acrolein		n-C_4H_9MgBr					
0.959	519	2.81	177	3.72	7.35	-100 (4)	3.00
17.1	21.4	20.5	0.855	34.2	41.0		94, B
acrolein		C_6H_5-					
1.91	1040	6.26	294	5.31	12.3	-70 (4)	5.20
28.5	42.8	39.9	1.43	48.9	68.5		89, B
acrolein		nC_6H_{13}-					
1.40	912	5.78	257	5.43	10.8	-70 (2)	3.86
25.0	37.5	35.0	1.25	50.0	60.0		83, B
methacrolein		CH_3-					
3.51	b	b	1000	10.7	17.9	-70 (15)	5.2
50.0		60.0	5.0	100	100		60
methacrolein		n-C_6H_{13}-					
0.701	182	1.16	103	2.17	4.30	-70 (2)	2.03
10.0	7.50	7.00	0.50	24.0	24.0	25 (1)	89, B
methacrolein		C_6H_5-					
1.40	b	b	206	4.34	8.60	-70 (1.5)	3.26
20.0		24.0	1.00	40.0	48.0		79, B
crotonaldehyde		C_6H_5-					
1.05	b	b	247	3.26	6.45	-70 (2)	2.96
15.0		18.0	1.20	30.0	36.0		89, B
crotonaldehyde		n-C_4H_9MgBr					
0.0701	b	b	10.3	0.543	0.430	-70 (1)	e
1.00		1.20	0.05	5.00	2.40		76, B
2-ethylcroton-aldehyde		n-C_6H_{13}-					
1.96	608	3.96	206	4.35	7.88	-100 (3.5)	3.89
20.0	25.0	24.0	1.00	40.0	44.0		76, B

Table 9 (continued).

2-ethylcroton-aldehyde		$C_6H_{11}MgBr$					
1.38	b	b	145	3.07	5.57	-100 (2)	2.88
14.1		15.6	0.707	28.3	31.1		80, B
2-ethylcroton-aldehyde		MeMgBr					
0.0207	b	b	1.9	0.040	0.99	-70 (36)	f
0.211		0.380	0.009	0.368	0.552		97, B
2-isopropyl-acrolein		MeMgBr					
0.0157		b	1.9	0.040	0.99	-70 (36)	f
0.160	b	0.380	0.009	0.368	0.552		89, B
methyl crotonate		C_6H_5MgBr					
0.114	b	b	20.6	0.217	0.538	-70 (2)	0.149,
1.00		1.50	0.100	2.00	3.00		78, A

[a]The reaction was run in THF (0.3-0.5 M to the substrate). [b]Preformed and titrated Grignard reagent was used. MeMgBr was prepared in ether and others in THF. [c]Distilled yield unless otherwise noted. [d] Yield after chromatographic purification. [e]Quantitative NMR yield. [f]Quantitative GLC yield. [g]For workup methods A and B, see the Experimental Section.

(E)-2-Methyl-1-trimethylsiloxy-1-butene. Bp 120 °C; IR (neat) 1665, 1225, 1168, 878, 842; ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.97 (t, J 2.1 Hz, 3 H), 1.59 (s, 3 H), 1.89 (q, J 2.1 Hz, 3 H), 6.01 (s, 1 H).

GLC (OV-1, 90 °C) retention times for E- and Z-isomers were 5.2 and 4.9 min, respectively.

(E)-1-Trimethylsiloxy-2-methyl-1-nonene. Bp 96-98 °C, 5.8 mm Hg; IR (neat) 1670, 1252, 1160, 880, 825; ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.88 (t, J = 6.9 Hz, 3 H), 1.23 (br s, 10 H), 1.56 (d, J = 1.3 Hz, 3 H), 1.84 (t, J = 7 Hz, 2 H), 6.00 (q, J = 1.3 Hz, 1 H).

GLC (OV 101, 140 °C) for E and Z-isomers were 13.7 and 12.1 min, respectively.

Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.62; H, 12.39.

(E)-Trimethylsiloxy-2-methyl-3-phenyl-1-propene. Bp 87-90 °C, 0.8 mm Hg; IR (neat) 1673, 1260, 1160, 880, 852, 700; ^1H NMR ($CDCl_3$) 0.18 (s, 9 H), 1.48 (d, J = 1.4 Hz, 3 H), 3.15 (s, 2 H), 6.14 (q, J = 1.4 Hz, 1 H), 7.03-7.36 (m, 5 H).

GLC (OV-101, 150 °) retention times for E and Z isomers were 9.7 and 7.6 min, respectively.

(E)-1-Trimethylsiloxy-3-phenyl-1-butene. IR (neat) 1644, 1248, 840; ^1H NMR ($CDCl_3$) 0.18 (s, 9 H), 1.34 (d, J = 7.1 Hz, 3 H), 3.38 (dq, J = 7.8, 7.1 Hz, 1 H), 5.21 (dd, J = 12.0, 7.8 Hz, 1 H), 6.26 (br d, J = 12.0 Hz, 1 H), 7.09-7.37 (m, 5 H); with additional peaks due to Z-isomer at 0.16 (s), 1.32 (d, J = 7.1 Hz), 3.99 (dq, J = 9.5, 7.1 Hz), 4.67 (dd, J = 9.5, 5.9 Hz), 6.15 (d, J = 5.9 Hz).

GLC (OV-101, 170 °C) retention times for E and Z-isomers were 7 and 8.9 min, respectively.

(E)-2-Ethyl-1-trimethylsiloxy-3-methyl-1-nonene. Bp 75-91 °C, 0.75 mm Hg; IR (neat) 1655, 1252, 1162, 842; ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.87 (t, J = 6.7 Hz, 3 H), 0.97 (t, J = 7.5 Hz, 3 H), 0.97 (d, J = 7.1 Hz, 3 H), 1.24 (br s, 10 H), 1.88-2.09 (m, 3 H), 5.99 (s, 1 H); ^{13}C NMR ($CDCl_3$) -0.34 (q), 13.8 (q), 14.2 (q), 18.7 (t), 20.8 (q), 22.9 (t), 27.8 (t), 29.6 (t), 32.1 (t), 35.8 (t), 36.7 (d), 128.5 (s), 133.4 (d).

GLC (OV-1, 160 °C) retention times for E and Z-isomers were 8.9 and 8.3 min, respectively.

Anal. Calcd for $C_{15}H_{32}OSi$: C, 70.23; H, 12.58. Found: C, 70.23; H, 12.61.

(E)-2-Ethyl-1-trimethylsiloxy-3-phenyl-1-butene. ^1H NMR ($CDCl_3$) 0.19 (s, 9 H), 0.83 (t, J = 7.6 Hz, 3 H), 1.33 (d, J = 7.1 Hz, 3 H), 1.71 (dq, J = 13.4, 7.6 Hz, 1 H), 2.11 (dq, J = 13.4, 7.6 Hz, 1 H), 3.39 (d, J = 7.1 Hz, 1 H), 6.17 (br s, 1 H), 7.07-7.32 (m, 5 H).

GLC (OV-1, 180 °C) retention times for E- and Z-isomers were 6.7 and 5.8 min, respectively.

Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.79; H, 9.72.

(E)-2-Ethyl-3-cyclohexyl-1-trimethylsiloxy-1-butene. Bp 96 °C, 1.6 mm Hg; IR (neat) 1655, 1455, 1252, 1166, 872, 842, ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.64-1.32 (m, involving 0.96, d, J = 7.1 Hz, 0.98 (t, J = 7.6 Hz), 1.48-1.85 (m), 1.97 (q, J = 7.6 Hz, 2 H), 5.95 (s, 1 H).

GLC (OV-1, 165 °C) retention times for E- and Z-isomers were 8.9 and 8.1 min, respectively.

Anal. Calcd for $C_{15}H_{30}OSi$: C, 69.93; H, 11.74. Found: C, 70.02; H, 11.73.

(E)-2-Ethyl-1-trimethylsiloxy-3-methyl-1-butene. IR (neat) 1658, 1255, 1178, 847; ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.97 (t, J = 7.6 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 6 H), 2.05 (q, J = 7.6 Hz, 2 H), 2.22 (dqq, J = 0.95, 6.8, 6.8 Hz, 1 H), 6.02 (br s, 1 H).

Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.42; H, 11.79.

(Z)-2-Ethyl-1-trimethylsiloxy-3-methyl-1-butene. IR (neat) 1660, 1255, 1168, 876, 846; ^1H NMR ($CDCl_3$) 0.16 (s, 9 H), 0.987 (t, J = 7.3 Hz, 3 H), 0.991 (d, J = 7.1 Hz, 6 H), 1.89 (dq, J = 1.5, 7.3 Hz, 2 H), 2.91 (qq, J = 7.1, 7.1 Hz, 1 H), 5.93 (br s, 1 H).

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