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Iodotrimethylsilane-Promoted Additions of Monoorganocopper Compounds to α,β-Unsaturated Ketones, Esters, and Lactones

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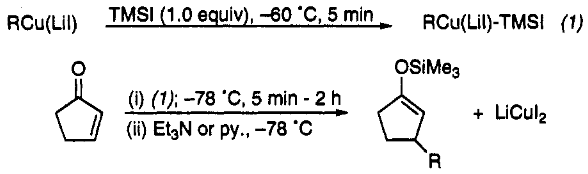
Conjugate additions with the efficient monoorganocopper–iodotrimethylsilane combination, exemplified mainly with methylcopper, butylcopper, and *tert*-butylcopper, proceed cleanly, smoothly, and rapidly to a variety of α,β-unsaturated carbonyl compounds; cyclic and acyclic enones, β-alkoxy enones, enoates and lactones in ether, THF, and dichloromethane, often at −78 °C. The RCu(LiI)–TMSI reagent gives a good economy of group transfer with good to excellent yields of conjugate adducts. Lithium iodide, present from preparation of the organocopper compounds, increases the rate of the reactions and is a favorable component. Additions are faster, but somewhat less selective, in THF than in ether. Careful workup after addition of triethylamine or pyridine at low temperature permits isolation of TMS enol ethers and TMS ketene acetals. Acyclic enones preferentially give the *Z*-silyl enol ethers. The RCu(LiI)–TMSI system is a most useful alternative to the conventional lithium diorganocuprates in conjugate additions.

Introduction

There are many types of copper-promoted conjugate additions to α,β-unsaturated carbonyl compounds.[1] The additions of lithium diorganocuprates dominate, often in the presence of chlorotrimethylsilane[2,3] (TMSCl) and sometimes with dummy ligands.[4] Other approaches are use of higher-order cuprates,[5] additions of RCu–LiI–BF$_3$,[6] additions of RCu–LiBr–HMPA–TMSCl[7] or RCu–LiI–TMEDA–TMSCl[8] and the additions of RCu–LiI, sometimes in the presence of phosphines, to reactive enones.[9,10] We have reported[11-13] the useful organocopper–iodotrimethylsilane combination, RCu/TMSI (with or without LiI), for a number of conjugate additions and for highly diastereoselective additions to chiral crotonates.[14] In our experience the RCu/TMSI combination is unusually efficient, mild and economical for most conjugate additions.

The present paper describes an extension of our work on conjugate addition of RCu(LiI)–TMSI to α,β-unsaturated ketones and esters giving the silyl enol ethers or silyl ketene acetals of the β-adducts. In the following we describe the practical handling of the reactions with representative monoorganocopper compounds and with representative substrates. We have mainly used butylcopper, *tert*-butylcopper and the less reactive methylcopper species. We describe below additions to cyclic and acyclic α,β-unsaturated carbonyl compounds. Most experiments have been done in THF and in ether.

Scheme I



Results

Addition of 1 molar equiv (or a slight excess) of iodotrimethylsilane (TMSI) at low temperature to a monoorganocopper compound, RCu(LiI), from copper(I) iodide and an appropriate organolithium reagent generally gives the reagent system RCu(LiI)–TMSI (1) as a heterogeneous mixture in THF, ether, or dichloromethane. However, the mixture is homogeneous for *tert*-butylcopper in THF. The mixtures are fairly stable and used below −40 °C. We add the α,β-unsaturated carbonyl compound to the mixture and often notice a transient yellowish color and then precipitation of CuI. When the reaction is complete we add triethylamine or pyridine, which "neutralizes" any excess of TMSI and let the mixture warm up to room temperature. In THF the solid copper(I) iodide will then dissolve as LiCuI$_2$. The products can then be isolated after a direct nonaqueous workup or after an aqueous workup for less sensitive products. For isolation of the adduct ketone the aqueous workup is done under desilylation conditions. The overall process for the conjugate addition reactions is summarized in Scheme I.

Table I shows representative results for additions to 2-cyclopentenone, 2-cyclohexenone, and 5-methyl-2-cyclohexenone. Additions of butyl-, *tert*-butyl-, and methylcopper to 2-cyclopentenone to give the silyl enol ethers proceed in good yields, but only in the presence of lithium

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[8] Johnson, C. R.; Marren, T. J. *Tetrahedron Lett.* **1987**, *28*, 27.

[9] House, H. O.; Fischer, W. F., Jr. *J. Org. Chem.* **1968**, *33*, 949.

[10] Suzuki, M.; Suzuki, T.; Kawagishi, T.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1247.

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[12] Bergdahl, M.; Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *Tetrahedron* **1989**, *45*, 535.

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[14] Bergdahl, M.; Nilsson, M.; Olsson, T.; Stern, K. *Tetrahedron* **1991**, *47*, 9691.

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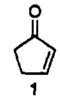
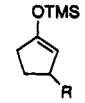
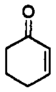
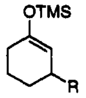
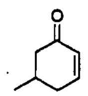
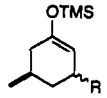
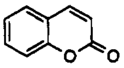
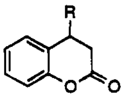
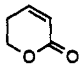
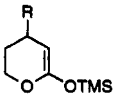
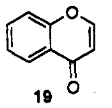
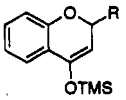
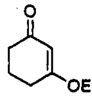
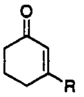
Table I. Conjugate Addition Reactions with Different Copper Reagents to α,β-Unsaturated Cyclic Enones and Enoates[a]

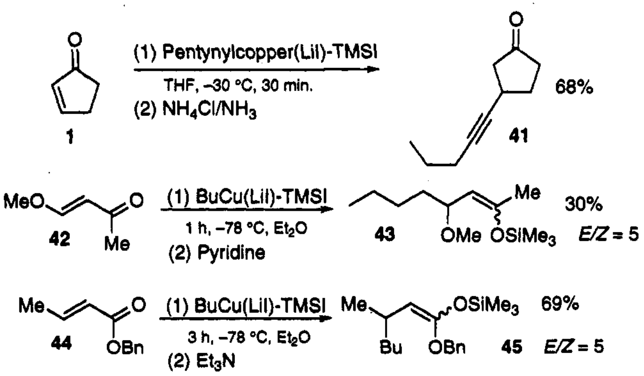
					product(s)			
entry	substrate	copper reagent[c]	solvent	conditions (°C, time)		R =	yield[b]	isomer ratio[d]
1	 1	BuCuTMSI	THF	(−78, 5 min)		Bu (2)	91[e]	
2		BuCuTMSI	THF	(−78, 15 min)		Bu (2)	80[f]	
3		BuCu(−LiI)TMSI	ether	(−78, 2 h)		Bu (2)	8	
4		t-BuCuTMSI	ether	(−78, 40 min)		t-Bu (3)	70	
5		MeCuTMSI	THF	(−78, 15 min)		Me (4)	72	
6		MeCuTMSI	ether	(−78, 2 h)		Me (4)	75	
7		MeCu(−LiI)TMSI	ether	(−78, 2 h)		Me (4)	9	
8		MeCu(3LiI)TMSI	ether	(−78, 2 h)		Me (4)	74	
9	 5	BuCuTMSI	THF	(−78, 10 min)		Bu (6)	94	
10		MeCuTMSI	THF	(−78, 15 min)		Me (7)	75	
11		MeCuTMSI	ether	(−78, 2 h)		Me (7)	75	
12	 8	BuCuTMSI	ether	(−78, 30 min)		Bu (9)	84	10:1
13		BuCuTMSI	THF	(−78, 10 min)		Bu (9)	84	2:1
14		t-BuCuTMSI	THF	(−78, 15 min)		t-Bu (10)	85	99:1
15		$\mathrm{Me_2CuLiTMSCl}$	ether	(−78, 1 h)[h]		Me (11)	87	99:1
16		$\mathrm{Me_2CuLiTMSI}$	ether	(−78, 15 min)[i]		Me (11)	69[i]	4:1
17		$\mathrm{Me_2CuLiTMSI}$	THF	(−78, 15 min)			0[j]	
18		MeCuTMSCl	ether	(0, 30 min)		Me (11)	95	5:1
19	 12	MeCuTMSI	$\mathrm{CH_2Cl_2}$	(−78 then 0)		Me (13)	93	
20		BuCuTMSI	$\mathrm{CH_2Cl_2}$	(−78 then 0)		Bu (14)	88	
21		BuCuTMSI	THF	(−78, 50 min)		Bu (14)	82	
22		t-BuCuTMSI	THF	(−60, 18 h)		t-Bu (15)	47	
23	 16	t-BuCuTMSI	THF	(−78, 2 h)		t-Bu (17)	91[g]	
24		t-BuCuTMSI	ether	(−78, 4 h)		t-Bu (18)	75	
25	 19	BuCuTMSI	THF	(−78, 20 min)		Bu (20)	79	
26		MeCuTMSI	THF	(−78, 2 h)		Me (21)	87[g]	
27		t-BuCuTMSI	ether	(−78, 3 h)		t-Bu (22)	81[g]	
28		MeCu(−LiI)TMSI	ether	(−78 then 0)		Me (21)	80[g]	
29		BuCuTMSI	THF	(−78, 20 min)		Bu (23)	98[g]	
30	 24	t-BuCuTMSI	THF	(−40, 10 h)		t-Bu (25)	30[k]	

[a] General Procedure. Substrate was added to the copper reagent, 1.25–1.50 equiv, maintained at −78 °C. Then base ($\mathrm{Et_3N}$ or pyridine), 1.5–2 equiv, or $\mathrm{NH_4Cl/NH_3}$ (buffer, pH 8) after time and temperature as indicated. [b] Isolated yields after chromatography or distillation. [c] Unless otherwise stated all the reactions contain LiI from the preparation of the copper reagents. [d] Determined with the help of GC and ^{1}H-NMR spectroscopy of the crude products. [e] $\mathrm{Et_3N}$ was used. Water after 5 min at −78 °C, afforded 87% of the adduct ketone. [f] Pyridine was used. [g] Isolated as the adduct ketone/ester. [h] The reaction is faster than indicated. [i] 0 °C after 15 min gave 30% adduct ketone. [j] 90% recovery of 8. [k] *ca.* 70% recovery of 24.

iodide. When lithium iodide had been removed by repeated washing of the alkylcopper with fresh solvent the rates and yields dropped strongly. Addition of extra lithium iodide to the RCu(LiI)–TMSI mixture did not improve the result. The reactions were faster in THF than in ether. The workup was very critical for isolation of the 3-alkyl-1-(silyloxy)cyclopent-1-enes (2 and 4). When triethylamine or pyridine was added at low temperature immediately after the conjugate addition was complete, the pure silyl enol ethers 2 and 4 could be isolated without problems. If we warmed the reaction mixture to room temperature and then added base we obtained mixtures of the two isomeric silyl enol ethers, often in ca. 1:1 ratio. Experiments with pure enol ether 4 and TMSI, kept at −40 °C, eventually gave a 1:1 mixture of the two ethers, indicating a separate isomerization process.

Addition of pentynylcopper–LiI and TMSI to 2-cyclopentenone was successful (Scheme II). Copper acetylides or acetylenic cuprates generally do not add to enones.[15] However, Kim and Lee reported recently the conjugate addition of alkynylzinc reagents to enones promoted by trimethylsilyl triflate.[16]

Scheme II



β-Alkoxy enones 19, 24, and 42 are interesting substrates as they could provide important mechanistic information.

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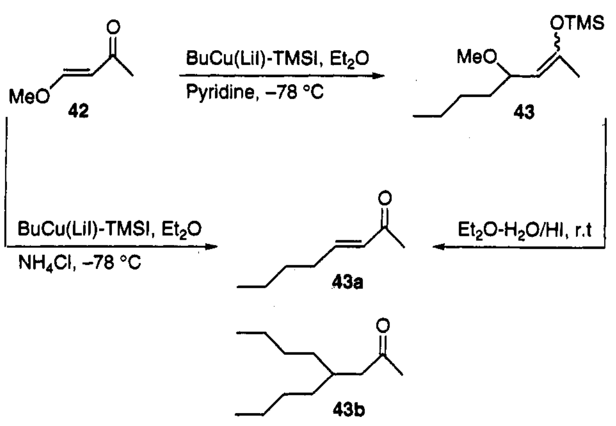
(15) House, H. O.; Fischer, W. F. *J. Org. Chem* **1969**, *34*, 3615.

(16) Kim, S.; Lee, J. M. *Tetrahedron Lett.* **1990**, *31*, 7627.

Scheme III



The chromone **19** gave high yields of ketone or of TMS enol ether. Removal of lithium iodide from methylcopper slowed the reaction considerably but did not affect the yield of **21**, entry 28. Enone **24** reacts slowly with *tert*-butylcopper, entry 30. The acyclic enone **42** exhibits a complex reaction pattern in contrast to the chromone **19**. The primary product from the conjugate addition is the silyl enol ether **43**, a rather sensitive product which can be isolated after addition of pyridine at −78 °C (Scheme II). It is however, stable enough to permit aqueous workup and distillation. If we instead add aqueous NH$_4$Cl at −78 °C, the α,β-unsaturated octenone is the major product (Scheme III). This octenone is also obtained if the silyl enol ether **43** is either hydrolyzed with dilute acid or subjected to flash chromatography. Another interesting feature of this reaction is the formation of the disubstituted ketone **43b**. The amount of this side product depends on the excess organocopper reagent used and the best result (virtually no **43b**) was obtained with 1.1 equiv of BuCu(LiI)–TMSI.

Conjugate addition of BuCu(LiI)–TMSI to benzyl crotonate (**44**) and addition of Et$_3$N followed by anhydrous workup gave silyl ketene acetal **45**.[17] Also α,β-unsaturated lactones give high yields of conjugate adducts in THF and in dichloromethane. Coumarin (**12**) reacts slowly with *t*-BuCu(LiI)–TMSI to give a moderate yield, entry 22, in contrast to reactions with MeCu(LiI)–TMSI or BuCu(LiI)–TMSI. We isolated the silyl ketene acetal or its hydrolysis product from lactone **16**.[17]

The conjugate addition to 5-methyl-2-cyclohexenone (**8**, Table I) provides a testing ground for stereoselectivity as shown already by House and Fischer.[9] Additions of MeCu(LiI)–TMSCl gave a low *trans/cis* ratio.[12] The selectivity increased with butylcopper but became adequate only with *tert*-butylcopper. This shows an important dependence on the size of the entering alkyl group. The reactions are much faster but less selective in THF than in ether and much less selective than early conjugate additions with methylcopper–LiI made at 0 °C.[9] The lithium diorganocuprates give high stereoselectivity in ether solution,[9] as also demonstrated in entry 15. On the other hand, in THF the cuprate is destroyed by TMSI,[18] entry 17, to give MeCu and Me$_4$Si.

To illustrate the reactivity, we investigated additions to acyclic enones using simple examples, 4-hexen-3-one (**26**) and 4-penten-3-one (**28**), and some with bulky substituents, mesityl oxide (**34**), benzalacetone (**37**), benzalpinacolone (**30**), and chalcone (**32**) (Table II). The conjugate additions with RCu(LiI)–TMSI gave the silylated conjugate adducts in moderate to excellent yields and preferentially as *Z*-silyl enol ethers.[19] The enones with small substituents (**26, 28**) gave moderate to high yields and lower *Z/E* ratios. Enones with bulky substituents at the carbonyl carbon (**30, 32**) gave the highest yields and the best *Z/E* selectivity. Substrates with crowded β positions (**34, 37**) give some 1,2-addition and this side reaction is more marked in THF than in ether. NOE measurement for silyl enol ether **27** confirmed the dominating *Z* form (*Z/E* = 2). A NOE of 6% was found for the *Z* form and virtually none for the *E* form. Silyl enol ether **29** afforded a surprising *Z/E* ratio of 0.6, which is the dominating *E* form. The assignment was confirmed with NOE measurements which gave a 7% NOE for the *Z* form and approximately 1% for the *E* form (Scheme IV). Compound **31** was a single isomer. The *Z* assignment is based on analogy with Heathcock's results where *n*-alkyl *tert*-butyl ketones give *Z*-enolates.[20]

Discussion

The results described above show that RCu(LiI)–TMSI is a practical and useful reagent system for the synthesis of silyl enol ethers and silyl ketene acetals (or of the corresponding carbonyl compounds) from α-ethylenic carbonyl compounds. In contrast to common lithium diorganocuprates, the RCu(LiI)–TMSI reagent transfers the group R (and silyl groups) to the substrate without wastage. The yields are good to excellent.

The intriguing question is the role of TMSI in these reactions. Conjugate additions of MeCu(LiI) or BuCu(LiI) with TMSCl to enones[11] are slow at −78 °C and reactions without TMSCl should be still slower. With TMSI the reaction is very fast and generally complete within a few minutes. We prefer to add TMSI to the RCu(LiI) mixture and then add the substrate. Premixing of substrate and TMSI gives no advantage.

A description of the reactions should consider (mutual) interactions between RCu, TMSI, substrate, LiI, and solvent. We assume a π complexation between copper and the carbon–carbon double bond[4,21–23] and observe a transient yellow color as an indication for this. Lithium iodide itself promotes addition of RCu to very reactive substrates, presumably by coordination of Li to the carbonyl oxygen and perhaps by iodide to the copper. There is little interaction between RCu and LiI, since lithium iodide stays in (ether) solution and can be removed easily, although this does not exclude a lithium organoiodocuprate, LiRCuI, as the reactive species.[24] TMSI promotes the additions of RCu to acyclic enones even in the absence of LiI. The combination RCu(LiI)–TMSI gives even faster additions, especially to cyclic enones and

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[17] When we isolated the silyl ketene acetals we used 6 equiv of Et$_3$N.

[18] Christenson, B.; Ullenius, C.; Håkansson, M.; Jagner, S. *Tetrahedron* **1992**, *48*, 3623.

[19] The resonance for the α-vinyl proton in *E*-silyl enol ethers generally appears downfield from the corresponding resonance in *Z*-silyl enol ethers. See: (a) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (b) Evans, D. A. In *Asymmetric synthesis*, Morrison, J. D., Ed.; Vol. 3; Academic Press: New York, 1984; pp 12–14.

[20] Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330.

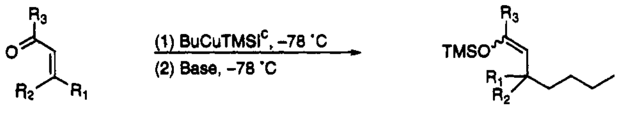
[21] Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1984**, *265*, C22.

[22] Christenson, B.; Olsson, T.; Ullenius, C. *Tetrahedron* **1989**, *45*, 523.

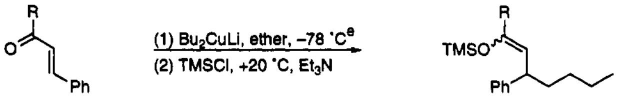
[23] Bertz, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8276.

[24] Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 5869.

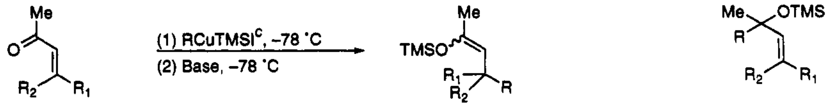
Table II. Conjugate Additions of Different Butylcoppers to Noncyclic α,β-Unsaturated Ketones[a]



entry	substrate	solvent, time (min)	product(s)	Z/E ratio[d]	yield[b]
31	**26**, R_1 = Me; R_2 = H; R_3 = Et	THF, 20	**27**	2	94
32	**28**, R_1 = R_2 = H; R_3 = Et	THF, 20	**29**	0.6	83
33	**30**, R_1 = Ph; R_2 = H; R_3 = *t*-Bu	THF, 50	**31**	>100	94
34	**32**, R_1 = R_3 = Ph; R_2 = H	THF, 10	**33**	70	91
35	**32**, R_1 = R_3 = Ph; R_2 = H	ether, 45	**33**	>100	80



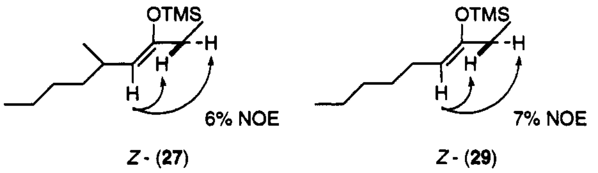
entry	substrate	product(s)	Z/E ratio[d]	yield[b]
36	**30**, R = *t*-Bu	**31**	>100	90
37	**32**, R = Ph	**33**	10	85



entry	substrate	solvent, time (min)	"1,4-product"	Z/E ratio[d]	yield[b]	"1,2-product"	1,2/1,4-ratio[d]
38	**34**, R_1 = R_2 = Me	ether, 25	**35**, R = Bu	>100	80	**36**, R = Bu	1/1.4
39	**34**, R_1 = R_2 = Me	THF, 45	**35**, R = Bu	>100	82	**36**, R = Bu	5/1
40	**37**, R_1 = Ph, R_2 = H	ether, 25	**38**, R = Bu	7	81	**39**, R = Bu	1/7
41	**37**, R_1 = Ph, R_2 = H	THF, 25	**38**, R = Bu	2	80	**39**, R = Bu	1/3
42	**37**, R_1 = Ph, R_2 = H	ether, 30	**40**, R = *t*-Bu	7	88		0

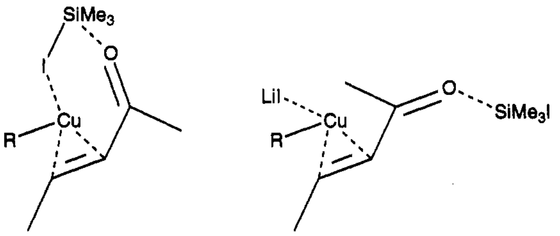
[a] General Procedure. The starting material was added to the copper reagent, 1.25 equiv, then Et_3N, 1.5–2 equiv, at −78 °C. [b] Isolated yields. [c] All reactions contain LiI from the preparation of the copper reagents. [d] Determined with the help of GC and ^{1}H-NMR spectroscopy of the crude products.

Scheme IV



Z-(**27**) Z-(**29**)

Scheme V



to enoates. There is no visible reaction when TMSI is added to RCu(LiI). One could speculate about a complex RCu–ISiMe$_3$. Such a complex with a hard silicon and a soft copper atom could be an intermediate in the reactions. TMSI could interact directly also with the substrate, acting as a *Lewis acid* toward the carbonyl oxygen. Such an adduct with a labile iodine could interact with an organocopper compound to provide a favorable (cyclic) intermediate or transition state, particularly for the acyclic substrates. However, additions to α,β-unsaturated esters proceed via an *s-trans* conformer.[13,14]

Conjugate addition of TMSI to the substrate[25] to give a β-iodo silyl enol ether could provide an additional pathway, since such an intermediate, an allylic iodide, could possibly react with RCu(LiI). Treatment of ethyl vinyl ketone with TMSI gives the β-iodo ketone after aqueous workup[25] and surprisingly this ketone couples with BuCu(LiI), though in moderate yield (45%). If the β-iodo silyl enol ether was directly transferred via cannula to BuCu(LiI), a similar yield (52%) was obtained. In order to check the possible formation of a β-iodo silyl ketene acetal from methyl crotonate and TMSI we mixed these in dichloromethane-d_2 and kept the solution at −40 °C for 1 h. The NMR spectrum recorded at room temperature showed that around 80% of the starting materials remained unchanged. We saw none of the expected signals from an iodo silyl ketene acetal but observed minor new signals at δ 4.45 (m), 2.95 (dd), and 1.92 (d). These signals increased very slowly at room temperature. We therefore conclude that initial formation of a β-iodo silyl ketene acetal from enoate and TMSI is not a likely pathway.

In some reactions we could safely assign the *Z* and *E* isomers of the silyl enol ethers and see high *Z*/*E* ratios. In other reactions the assignment of isomers is more tentative.[19] The preferential formation of *Z* silyl enol ethers could speak for favorable cyclic transition states/intermediates but also can reflect favorable *s-cis* conformations of starting materials.

The conclusions above can be summarized in the following formulas for plausible intermediates (transition states) for the additions to s-*cis* and s-*trans* conformers (Scheme V). The reactions are faster in THF than in ether. We have no definite clue to the favorable influence of THF on the rate of the conjugate addition but believe that the better solubility/solvation of the organocopper compounds in THF is at least part of the explanation. We have shown earlier that the tributylphosphine, which also helps dissolution, improves the rate.[12] The fast reactions

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(25) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1979**, 2305.

in THF are sometimes less stereoselective, as shown for 5-methyl-2-cyclohexenone, and less regioselective, giving more 1,2-addition to substrates with crowded β positions.

The use of THF as solvent in the presence of TMSI may seem surprising. There was little cleavage of THF as long as lithium iodide was present. Reactions without lithium iodide gave considerable cleavage of THF to 1-iodo-4-((trimethylsilyl)oxy)butane[26,27] and thus contamination of the products.[28] After the reaction is complete, THF also dissolves copper iodide as lithium diiodocuprate and thus gives a homogeneous solution, at least at higher temperature. We have not seen other side reactions and conclude that the reaction conditions are mild enough for many functionalities such as ethers, silyl ethers, and esters. We have found that different organocopper compounds and TMSI add fast and selectively to a variety of α,β-unsaturated carbonyl compounds. We recommend the RCu(LiI)–TMSI system as a most useful alternative to the conventional lithium diorganocuprates, with or without TMSCl, in conjugate additions.

Experimental Section

General. All reactions were performed under argon and in cooled oven-dried glassware (140 °C). NMR spectra were recorded on 400- or 500-MHz instruments having $CDCl_3$ as solvent with TMS as internal standard ($\delta = 0$). Coupling patterns are abbreviated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J, coupling constant given in hertz (Hz). Mass spectra were recorded on a GCMS (70 eV, capillary column, DB-1) with the structurally most important peaks (M^+, molecular peak) given as relative abundance. IR spectra were recorded on a FT-IR instrument. Elemental analyses were performed by Analytische Laboratorien in Engelskirchen, Germany.

Chemicals. Copper(I) iodide was purified *via* its dimethyl sulfide complex and crystallized in pentane; crystals were collected, pumped until constant weight, and stored, light-protected, in a desiccator. Lithium iodide was dried over P_2O_5 *in vacuo*. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium–benzophenone ketyl and were collected when the solution became deep blue. Triethylamine (Et_3N) and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under argon and used immediately. Pyridine was distilled from CaH_2 under nitrogen and stored septum-capped (Aldrich sealed) over argon and 4-Å molecular sieves. BuLi (1.6 M in hexane), *t*-BuLi (1.7 M in pentane), and MeLi (1.6 M in Et_2O) were purchased from Aldrich or Fluka and titrated prior to use. Iodotrimethylsilane (TMSI) was purchased from Janssen and was stored septum capped at −25 °C under argon with copper chips in a light-protected bottle. Chlorotrimethylsilane (TMSCl) was purchased from Fluka, septum capped, and stored at 8 °C under argon.

General Procedure for the Reactions. 1a. TMSI-Promoted *t*-BuCu and BuCu Additions. BuLi or *t*-BuLi (6.25 mmol, 1.25 equiv) was slowly added to a rapidly stirred slurry of copper(I) iodide (1.05–1.1 equiv) in dry solvent (15 mL) at −78 °C, and the heterogeneous mixture was stirred for 15 min at −78 °C and approximately 40 min at −60 °C. Then, at this temperature, iodotrimethylsilane (6.25 mmol) was added *via* syringe and the resulting heterogeneous mixture stirred an additional 5 min. The temperature was then lowered to −78 °C and the α,β-unsaturated compound (5 mmol) in dry solvent (5–10 mL) was slowly added *via* the flask wall as to maintain a temperature of −78 °C. The characteristic color of the copper reagents generally disappeared within a few minutes with the enones. After the time indicated in Tables I and II, respectively, dry triethylamine or pyridine (2.5 equiv) was added at −78 °C and the mixture stirred an additional *ca.* 4 h at this temperature. Then, under continous stirring, the temperature was slowly raised toward room temperature during *ca.* 6 h and the solvent was evaporated to give a syrup that was treated with pentane (5 × 50 mL). The pentane extracts were filtered through a 3-cm pad of Celite and the solvent was evaporated, affording the crude silyl enol ethers which were distilled.

1b. TMSI-Promoted MeCu Additions. MeLi (6.25 mmol, 1.25 equiv) was added dropwise to a rapidly stirred slurry of copper(I) iodide (1.3–1.4 equiv) in dry solvent (15 mL) at 0 °C. The resulting yellow suspension was stirred for 45 min at 0 °C, the temperature was lowered to −60 °C, TMSI (6.25 mmol) was added slowly, and the resulting mixture was stirred for 5 min. Then, at −78 °C the substrate (5 mmol) in dry solvent (5–10 mL) was added as described above. After identical treatment with base and working up as in **1a** the crude silyl enol ethers were obtained. For MeCu in CH_2Cl_2, however, the method described in **1a** is used.

3-Butyl-1-((trimethylsilyl)oxy)-1-cyclopentene (2):[8] colorless oil distilled bulb-to-bulb, 77–78 °C (10 mbar), 91% yield. ^{1}H NMR: δ 4.62 (d, $J = 1.5$, 1H), 2.57 (m, 1H), 2.24 (m, 2H), 2.01 (m, 1H), 1.40 (m, 1H), 1.26 (m, 6H), 0.89 (t, 3H), 0.20 (s, 9H). MS: $m/z = 212$ (M^+, 7), 197 ($M-CH_3$, 4), 155 ($M-C_4H_9$, 100), 73 (75). IR (neat): 2957, 1645, 1252, 845 cm^{-1}.

3-*tert*-Butyl-1-((trimethylsilyl)oxy)-1-cyclopentene (3):[8] colorless oil distilled bulb-to-bulb, 65–66 °C (10 mbar), 70% yield. ^{1}H NMR: δ 4.63 (d, $J = 1.2$, 1H), 2.44 (m, 1H), 2.22 (m, 2H), 1.83 (m, 1H), 1.58 (m, 1H), 0.82 (s, 9H), 0.21 (s, 9H). MS: $m/z = 212$ (M^+, 1), 197 ($M-CH_3$, 14), 155 ($M-C_4H_9$, 100), 73 (78). IR (neat): 2960, 1646, 1253, 846 cm^{-1}.

3-Methyl-1-((trimethylsilyl)oxy)-1-cyclopentene (4): colorless oil distilled bulb-to-bulb, 45–47 °C (13 mbar), 72% yield. ^{1}H NMR: δ 4.60 (d, $J = 2.0$, 1H), 2.75–1.30 (m, 5H), 1.00 (d, $J = 6.5$, 3H), 0.20 (s, 9H). MS: $m/z = 170$ (M^+, 15), 155 ($M-CH_3$, 95), 73 (100).

3-Butyl-1-((trimethylsilyl)oxy)-1-cyclohexene (6): colorless oil distilled bulb-to-bulb, 73–75 °C (1.5 mbar), 94% yield. ^{1}H NMR: δ 4.80 (m, 1H), 2.14–1.48 (m, 6H), 1.34–1.18 (m, 6H), 1.08 (m, 1H), 0.89 (t, $J = 7.0$, 3H), 0.18 (s, 9H). MS: $m/z = 226$ (M^+, 6), 211 ($M-CH_3$, 2), 169 ($M-C_4H_9$, 100), 73 (32). IR (neat): 2922, 1662, 1250, 844 cm^{-1}.

3-Methyl-1-((trimethylsilyl)oxy)-1-cyclohexene (7):[29] colorless oil, yield 75%. MS: $m/z = 184$ (M^+, 13), 169 ($M-CH_3$, 78), 73 (100).

5-Methyl-3-butyl-1-((trimethylsilyl)oxy)-1-cyclohexene (9) (*trans/cis* ratio = 10): colorless oil distilled bulb-to-bulb, 85–86 °C (8 mbar), 84% yield. ^{1}H NMR: δ 4.85 (d, $J = 4.0$, 1H), 2.14 (m, 1H), 2.05 (dd, $J = 17.0$, 6.0, 1H), 1.90 (m, 1H), 1.66 (m, 2H), 1.33–1.28 (m, 7H), 0.94 (d, J 7.0, 3H), 0.89 (t, 3H), 0.18 (s, 9H). MS: $m/z = 240$ (M^+, 2), 225 ($M-CH_3$, 2), 183 ($M-C_4H_9$, 80), 73 (100). IR (neat): 2956, 1664, 1251, 845 cm^{-1}.

5-Methyl-3-*tert*-butyl-1-((trimethylsilyl)oxy)-1-cyclohexene (10) (*trans* isomer): colorless oil distilled bulb-to-bulb, 78–80 °C (8 mbar), 85% yield. ^{1}H NMR: δ 4.91 (s, 1H), 2.15 (m, 1H), 2.08 (m, 1H), 1.95 (m, 1H), 1.61 (d, $J = 17.0$, 1H), 1.34 (m, 2H), 0.94 (d, $J = 7.0$, 3H), 0.85 (s, 9H), 0.18 (s, 9H). MS: $m/z = 240$ (M^+, 0.7), 225 ($M-CH_3$, 4), 183 ($M-C_4H_9$, 100), 73 (96). IR (neat): 2959, 1664, 1252, 845 cm^{-1}.

3,5-Dimethyl-1-((trimethylsilyl)oxy)-1-cyclohexene (11)[29] (>99% *trans* isomer): colorless oil, 87% yield. ^{1}H NMR: δ 4.79 (d, $J = 4.0$, 1H), 2.32 (m, 1H), 2.05 (dd, $J = 13.0$, 4.5, 1H), 1.93 (m, 1H), 1.64 (m, 1H), 1.32 (m, 1H), 1.27 (m, 1H), 0.97 and 0.92 (2t, 3H each), 0.16 (s, 9H). MS: $m/z = 198$ (M^+, 13), 183 ($M-CH_3$, 84), 141 (28), 73 (100).

4-Methyldihydrocoumarin (13):[30] obtained after flash chromatography (CH_2Cl_2, $R_f = 0.39$), 93% yield. ^{1}H NMR: δ 7.29–7.23 (m, 2H), 7.16–7.12 (m, 1H), 7.08–7.05 (m, 1H), 3.24–3.14 (m, 1H), 2.85 (dd, $J = 16.0$, 5.6, 1H), 2.59 (dd, $J = 16.0$, 7.4, 1H), 1.35 (d, J 7.2, 3H). MS: $m/z = 162$ (M^+, 41), 147 ($M-CH_3$, 32), 119 (29), 103 (23), 91 (100), 77 (45). IR (neat): 1773 cm^{-1}.

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(26) ^{1}H NMR for 4-iodo-1-butanol: 3.69 (t, $J = 7$ Hz, 2 H), 3.24 (t, $J = 7$ Hz, 2 H), 1.97–1.90 (m, 2 H), 1.72–1.65 (m, 2 H), 1.54 (s, 1 H).

(27) ^{1}H NMR for 4-iodo-1-((trimethylsilyl)oxy)butane: 3.60 (t, $J = 7$ Hz, 2 H), 3.22 (t, $J = 7$ Hz, 2 H), 1.94–1.84 (m, 2 H), 1.66–1.58 (m, 2H), 0.11 (s, 9 H).

(28) The silyl ethers and silyl ketene acetals are rather sensitive and generally decompose on chromatography. The NMR spectra often show the presence of small amounts of 4-iodo-1-((trimethylsilyl)oxy)butane or 4-iodo-1-butanol resulting from cleavage of THF and often the presence of both *E*- and *Z*-silyl enol ethers.

(29) Binkley, E. S.; Heathcock, C. H. *J. Org. Chem.* **1975**, *40*, 2156.

(30) Cannone, P.; Belanger. D.; Lemay. G. *Synthesis* **1980**, 301.

4-Butyldihydrocoumarin (14):[31] obtained after flash chromatography (30% ether in pentane, $R_f = 0.6$), 88% yield; bp 100 °C (0.2 mbar), colorless oil. ^{1}H NMR: δ 7.30–7.03 (m, 4H), 2.97 (m, 1H), 2.83 (dd, $J = 16.0, 6.0$, 1H), 2.75 (dd, $J = 16.0, 4.0$, 1H), 1.58 (m, 2H), 1.40–1.24 (m, 4H), 0.89 (t, $J = 7.0$, 3H). MS: m/z = 204 (M^+, 23), 147 ($M-C_4H_9$, 100), 91 (38). IR (neat): 2967, 1772, 1150 cm^{-1}.

4-*tert*-Butyldihydrocoumarin (15): white crystals, 47% yield. ^{1}H NMR: δ 7.31–7.05 (m, 4H), 3.05 (d, $J = 16.0$, 1H), 2.76–2.64 (m, 2H), 0.96 (s, 9H). MS : m/z = 204 (M^+, 5), 147 ($M-C_4H_9$, 60), 91 (20). IR (neat): 2967, 1772, 1150 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.32; H, 7.80.

4-*tert*-Butyl-δ-valerolactone (17): obtained after flash chromatography (EtOAc/hexane 50%, $R_f = 0.43$), 91% yield. ^{1}H NMR: δ 4.40 (ddd, $J = 11.1, 4.6, 4.0$, 1H), 4.22 (dt, $J = 11.1, 11.1, 3.6$, 1H), 2.63 (ddd, $J = 17.0, 6.2, 1.6$, 1H), 2.28 (dd, $J = 17.0, 11.1$, 1H), 1.90 (m, $J = 14.0, 5.2, 4.0, 3.6, 1.6$, 1H), 1.75 (ddt, $J = 11.1, 11.1, 6.2, 5.2$, 1H), 1.58 (ddt, $J = 14.0, 11.1, 11.1, 4.6$, 1H), 0.91 (s, 9H). MS: m/z = 141 ($M-CH_3$, 1.5), 100 (58), 69 (16), 57 (100). IR (neat): 2958, 2873, 1738 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.94; H, 10.15.

4,5-Dihydro-4-*tert*-butyl-2-((trimethylsilyl)oxy)-2*H*-pyran (18): colorless oil distilled bulb-to-bulb, 50–55 °C (0.7 mbar), 75% yield. ^{1}H NMR: δ 4.18 (ddd, $J = 10.4, 3.6, 3.6$, 1H), 3.92 (ddd, $J = 11.6, 10.4, 2.0$, 1H), 3.83 (dd, $J = 1.6, 1.6$, 1H), 2.12–2.06 (m, 1H), 1.74–1.65 (m, 1H), 1.61–1.50 (m, 1H), 0.85 (s, 9H), 0.22 (s, 9H). MS: m/z = 228 (M^+, 0.7), 213 ($M-CH_3$, 3.5), 171 ($M-C_4H_9$, 100), 103 (27), 73 (80). IR (neat): 2956, 2870, 1682 cm^{-1}.

2-Butyl-4-((trimethylsilyl)oxy)-3-chromene (20): colorless oil distilled bulb-to-bulb, 60–62.5 °C (0.06 mbar), 79% yield. ^{1}H NMR: δ 7.30–6.75 (4m, 1H each), 4.94–4.90 (m, 1H), 4.83 (d, $J = 3.6$, 1H), 1.84–1.23 (m, 6H), 0.92 (t, $J = 7.0$, 3H), 0.28 (s, 9H). MS: m/z = 276 (M^+, 1), 261 ($M-CH_3$, 3), 219 ($M-C_4H_9$, 100), 73 (71). IR (neat): 2957, 1649, 1253, 883 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75. Found: C, 69.65; H, 8.72.

2-Methyl-4-chromanone (21):[32] obtained after flash chromatography (10% ether in pentane, $R_f = 0.33$), 85% yield; mp 32 °C. ^{1}H NMR: δ 7.90–7.87 (m, 1H), 7.50–7.45 (m, 1H), 7.03–6.96 (m, 2H), 4.66–4.54 (m, 1H), 2.69 (d, $J = 7.2$, 2H), 1.52 (d, $J = 6.2$, 3H). MS: m/z = 162 (M^+, 50), 147 ($M-CH_3$, 13), 120 (100), 92 (70). IR (KBr): 1696 cm^{-1}.

2-*tert*-Butyl-4-chromanone (22): obtained after flash chromatography (CH_2Cl_2, $R_f = 0.43$), 81% yield; mp 63.5–64.5 °C. ^{1}H NMR: δ 7.88–7.45 (2m, 1H each), 7.01–6.98 (m, 2H), 4.06 (dd, $J = 13.0, 4.0$, 1H), 2.74–2.62 (m, 2H), 1.06 (s, 9H). MS: m/z = 204 (M^+, 24), 189 ($M-CH_3$, 13), 147 ($M-C_4H_9$, 100), 121 (83), 92 (40), 91 (19), 77 (7), 57 (41). IR (KBr): 1693 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.36; H, 7.84.

2-Butyl-4-chromanone (23): obtained after flash chromatography (CH_2Cl_2, $R_f = 0.48$), 98% yield; bp 57–60 °C (0.06 mbar). ^{1}H NMR: δ 7.89–7.86 (m, 1H), 7.50–7.45 (m, 1H), 7.02–6.96 (m, 2H), 4.48–4.40 (m, 1H), 2.69 (d, $J = 7.6$, 2H), 1.94–1.84 (m, 1H), 1.76–1.66 (m, 1H), 1.60–1.34 (m, 4H), 0.95 (t, $J = 7.0$, 3H). MS: m/z = 204 (M^+, 18), 147 ($M-C_4H_9$, 37), 121 (100), 120 (55), 92 (41). IR (neat): 1694 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.60; H, 7.89.

3-*tert*-Butyl-2-cyclohexenone (25):[33] obtained after flash chromatography (80% ether in pentane, $R_f = 0.55$), 30% yield. ^{1}H NMR: δ 5.95 (s, 1H), 2.40–2.30 (m, 4H), 2.00–1.94 (m, 2H), 1.12 (s, 9H). MS: m/z = 152 (M^+, 18), 137 ($M-CH_3$, 13), 124 (48), 109 (100), 96 (69). IR (neat): 2966, 2870, 1671, 1258 cm^{-1}.

5-Methyl-3-((trimethylsilyl)oxy)-3(*E,Z*)-nonene (27): colorless oil (Z/E ratio = 2) distilled bulb-to-bulb, 90–92 °C (13 mbar), 94% yield. ^{1}H NMR: [(*Z*)-**27**] δ 4.23 (dt, $J = 9.0, 1.0$, 1H), 2.41 (m, 1H), 2.01 (dq, $J = 6.5$, 3H), 1.30–1.20 (m, 6H), 1.02 (t, $J = 7.5$, 3H), 0.89 (d, $J = 6.5$, 3H), 0.87 (t, $J = 7.5$, 3H), 0.18 (s, 9H); [(*E*)-**27**] δ 4.36 (d, $J = 9.5$, 1H), 2.15 (m, 1H), 2.05 (m, partly hidden, 2H), 1.30–1.20 (m, 6H), 1.01 (t, $J = 7.5$, 3H), 0.93 (d, J 6.5, 3H), 0.88 (t, partly hidden, 3H), 0.18 (s, 9H). MS: [(*Z*)-**27**] m/z = 228 (M^+, 2), 213 ($M-CH_3$, 5), 171 ($M-C_4H_9$, 75), 73 (100); [(*E*)-**27**] m/z = 228 (M^+, 2), 213 (3), 171 (62), 73 (100).

3-((Trimethylsilyl)oxy)-3(*E,Z*)-nonene (29): colorless oil (Z/E ratio = 0.6) distilled bulb-to-bulb, 55–60 °C (1.3 mbar), 83% yield. ^{1}H NMR: [(*Z*)-**29**] δ 4.45 (t, $J = 7$, 1H), 2.01 (q, partly hidden, 2H), 1.97 (q, partly hidden, 2H), 1.36–1.20 (m, 6 H), 1.02 (t, $J = 7$, 3H), 0.88 (t, $J = 7$, 3H), 0.19 (s, 9H); [(*E*)-**29**] δ 4.58 (t, $J = 7$, 1H), 2.05 (q, $J = 7$, 2H), 1.91 (q, $J = 7$, 2H), 1.36–1.20 (m, 6H), 1.01 (t, $J = 7$, 3H), 0.88 (t, $J = 7$, 3H), 0.18 (s, 9H). MS: m/z = 214 (M^+, 4), 199 ($M-CH_3$, 3), 185 ($M-C_2H_5$, 6), 157 ($M-C_4H_9$, 100), 144 (38), 129 (6), 73 (93). IR (neat): 2964, 2924, 2874, 2854, 1665 cm^{-1}.

2,2-Dimethyl-5-phenyl-3-((trimethylsilyl)oxy)-3(*Z*)-nonene (31): colorless oil distilled bulb-to-bulb, 76–78 °C (0.1 mbar), 94% yield. ^{1}H NMR: δ 7.29–7.24 (m, 2H), 7.22–7.13 (m, 3H), 4.77 (d, $J = 10.0$, 1H), 3.48 (dt, $J = 10.0, 7.0$, 1H), 1.67–1.45 (2m, 1H each), 1.30–1.10 (m, 4H), 1.05 (s, 9H), 0.84 (t, $J = 7.0$, 3H), 0.18 (s, 9H). MS: m/z = 318 (M^+, 0.2), 303 ($M-CH_3$, 0.2), 261 ($M-C_4H_9$, 68), 171 ($M-C_{11}H_{15}$, 38), 73 (100). IR (neat): 2957, 1655, 1252, 846 cm^{-1}. Anal. Calcd for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.18; H, 10.60.

1,3-Diphenyl-1-((trimethylsilyl)oxy)-1(*E,Z*)-heptene (33): colorless oil (Z/E ratio = 70) distilled bulb-to-bulb, 95–96 °C (0.24 mbar), 91% yield. ^{1}H NMR: [(*Z*)-**33**] δ 7.48–7.44 (m, 2H), 7.32–7.14 (m, 8H), 5.38 (d, $J = 10.0$, 1H), 3.76 (dt, $J = 10.0, 7.0$, 1H), 1.78–1.61 (m, 2H), 1.37–1.17 (m, 4H), 0.86 (t, $J = 7.0$, 3H), 0.08 (s, 9H). The olefinic proton in the *E* form can be identified at 5.24 ppm (d, $J = 10.0$). MS: [(*Z*)-**33**] m/z = 338 (M^+, 6), 323 ($M-CH_3$, 5), 281 ($M-C_4H_9$, 90), 73 (100); [(*E*)-**33**] 338 (9), 323 (2), 281 (100), 73 (80). IR (neat): 2957, 1645, 1252, 846 cm^{-1}.

4,4-Dimethyl-2-((trimethylsilyl)oxy)-2(*Z*)-octene (35): colorless oil including the silylated 1,2-adduct (**36**), distilled bulb-to-bulb, 26–30 °C (0.37 mbar), yield 80% (Z/1,2 ratio = 5). ^{1}H NMR: (**35**) δ 4.18 (s, 1H), 1.77 (s, 3H), 1.35–1.17 (m, 6H), 1.02 (s, 6H), 0.88 (t, $J = 7.0$, 3H), 0.20 (s, 9H); (**36**) δ 5.16 (q, $J = 1.0$, 1H), 1.78 and 1.68 (2s, 3H each), 1.58–1.48 (m, 2H), 1.31 (s, 3H), 1.30–1.20 (m, 4H), 0.87 (t, $J = 7.0$, 3H), 0.08 (s, 9H). MS: [(*Z*)-**35**] m/z = 228 (M^+, 4), 213 ($M-CH_3$, 7), 171 ($M-C_4H_9$, 95), 73 (100); (**36**) m/z = 228 (M^+, 1), 213 (1), 171 (100), 73 (92). IR (neat): 2958, 1669, 1251, 842 cm^{-1}.

4-Phenyl-2-((trimethylsilyl)oxy)-2(*E,Z*)-octene (38): colorless oil (Z/E ratio = 7) distilled bulb-to-bulb, 64–66 °C (0.26 mbar), 81% yield. ^{1}H NMR: [(*Z*)-**38**] δ 7.20 (m, 5H), 4.61 (dq, $J = 9.0, 1.0$, 1H), 3.58 (m, 1H), 1.78 (d, $J = 1.0$, 3H), 1.60 (m, 2H), 1.30 (m, 4H), 0.88 (t, 3H), 0.18 (s, 9H); [(*E*)-**38**] δ 7.20 (m, 5H), 4.85 (dq, $J = 9.0, 1.0$, 1H), 3.28 (m, 1H), 1.74 (d, $J = 1.0$, 3H), 1.60 (m, 2H), 1.30 (m, 4H), 0.88 (t, 3H), 0.18 (s, 9H). MS: [(*Z*)-**38**] m/z = 276 (M^+, 2), 261 ($M-CH_3$, 4), 219 ($M-C_4H_9$, 100), 73 (71); [(E)-**38**] 276 (1), 261 (3), 219 (100), 73 (96). IR (neat): 2957, 1672, 1252, 846 cm^{-1}. According to GC analysis ca. 13% of 1,2-addition product (**39**) after distillation. MS (**39**): m/z = 276 (3), 219 (100), 73 (84).

5,5-Dimethyl-4-phenyl-2-((trimethylsilyl)oxy)-2(*E,Z*)-hexene (40): colorless oil (Z/E ratio = 7) distilled bulb-to-bulb, 53–54 °C (0.26 mbar), 88% yield. ^{1}H NMR: [(*Z*)-**40**] δ 7.28–7.10 (m, 5H), 4.93 (d, $J = 10.0$, 1H), 3.42 (d, $J = 10.0$, 1H), 1.81 (s, 3H), 0.86 (s, 9H), 0.04 (s, 9H); [(*E*)-**40**] δ 7.20 (m, 5H), 5.20 (d, $J = 10.0$, 1H), 3.05 (d, $J = 10.0$, 1H), 1.67 (s, 3H), 0.87 (s, 9H), 0.19 (s, 9H). MS: [(*Z*)-**40**] m/z = 276 (M^+, 0.2), 261 ($M-CH_3$, 10), 220 ($M-C_4H_9$, 100), 73 (64); [(*E*)-**40**] m/z = 276 (M^+, 0.1), 261 (4), 220 (100), 73 (88). IR (neat): 2960, 1670, 1252, 845 cm^{-1}.

3-(1-Pentynyl)cyclopentanone (41). To a solution of 1-pentyne (7.5 mmol, 0.74 mL) in 20 mL of dry THF was added *n*-BuLi (7.5 mmol) at −10 °C. The solution was stirred for 30 min at −10 °C and then CuI (8.25 mmol, 1.57 g) was added in one batch via a solid addition funnel. The resulting yellow heterogeneous suspension was stirred for 1 h at −10 °C and then the temperature was lowered to −60 °C. TMSI (7.5 mmol, 1.07 mL) was added dropwise and the mixture was stirred for 5 min at −60 °C followed by 5 min at −78 °C. A solution of cyclopentenone (5.0 mmol, 0.42 mL) in 5 mL of dry THF was added slowly via the flask wall. No apparent change in color of the copper reagent could be observed at −78 °C. The temperature was raised to −30 °C and the mixture stirred for 30 min. Saturated NH_4Cl (15 mL) was added and the mixture was allowed to reach room

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temperature. To affect complete hydrolysis, HCl (3 M, 3 mL) was added and the mixture stirred for 30 min. The mixture was diluted with 50 mL of Et_2O and 50 mL of H_2O and the phases were separated. The aqueous phase was extracted with 50 mL of Et_2O and the combined ethereal layer was washed once with 100 mL of 5% $Na_2S_2O_2$ and once with 100 mL of brine and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography on silica gel (20% ether in pentane, $R_f = 0.37$) afforded 0.51 g (68%) as a colorless oil. ^{1}H NMR: δ 3.03 (dt, J = 8.0, 2.0, 1H), 2.46 (dd, J = 18.0, 8.0, 1H), 2.38 (m, 1H), 2.28–2.17 (m, 2H), 2.14 (m, 1H), 2.13 (dt, J = 5.0, 2.0, 2H), 1.98 (m, 1H), 1.50 (m, 2H), 0.96 (t, J = 7.0, 3H). MS: m/z = 150 (M^+, 8), 135 (M–CH_3, 32), 93 (33), 79 (100). IR (neat): 1743 cm^{-1}. HRMS: Calcd 150.104, found 150.099.

4-Methoxy-2-((trimethylsilyl)oxy)-2(*E*,*Z*)-octene (43) was prepared according to the general procedure with the following exceptions: The substrate (5 mmol) was diluted with 30 mL of Et_2O to ensure solubility during addition via the flask wall. Only 1.1 equiv of BuCu(LiI)–TMSI was used. **43** was obtained after addition of pyridine (10 equiv) at –78 °C after 1 h: colorless oil (E/Z ratio = 5) distilled bulb-to-bulb, 29–32 °C (0.17 mbar), 30% yield. ^{1}H NMR: [(*E*)-**43**] δ 4.50 (dd, J = 10.0, 1.0, 1H), 3.71 (dt, J = 10.0, 7.0, 1H), 3.23 (s, 3H), 1.80 (d, J = 1.0, 3H), 1.24–1.34 (m, 6H), 0.89 (t, J = 7.0, 3H), 0.21 (s, 9H); [(*Z*)-**43**] 4.33 (dd, J = 9.0, 1.0, 1H), 4.02–3.96 (m, 1H), 3.25 (s, 3H), 1.84 (d, J = 1.0, 3H), 1.24–1.34 (m, 6H), 0.89 (t, 3H), 0.20 (s, 9H). MS: [(*E*)-**43**] m/z = 198 (M–CH_3O, 5), 173 (M–C_4H_9, 50), 141 (56), 73 (100); [(*Z*)-**43**] m/z = 198 (1), 173 (59), 141 (54), 73 (100). IR (neat): 2961, 1667, 1254, 845 cm^{-1}.

(*E*)-3-Octen-2-one (43a)[34] was obtained after addition of aqueous NH_4Cl (10 mL) after 1 h at –78 °C. Extraction with ether and drying over Na_2SO_4 followed by flash chromatography (20% ether in pentane, R_f =0.43) gave 71% isolated yield. Spectroscopic data were in agreement with those reported in the literature.[34]

3-Methyl-1-((trimethylsilyl)oxy)-1-(benzyloxy)-1(*E*,*Z*)-heptene (45): colorless oil (E/Z ratio = 5) distilled bulb-to-bulb, 61 °C (0.12–0.16 mbar), 69% yield. ^{1}H NMR: [(*E*)-**45**] ($CDCl_3$) δ 7.24–7.38 (m, 5H), 4.84–4.77 (2d, O-CH_2, 2H), 3.52 (d, $J_{\text{vinyl-methine}}$ = 9.8 Hz, 1H), 2.40–2.31 (m, 1H), 1.33–1.12 (m, 6H), 0.89–0.82 (d and t, 5H), 0.20 (s, 9H); [(*Z*)-**45**] benzylic protons at 4.70 (2d) and vinylic proton at 3.40 (d, J = 9.3 Hz). MS: [(*E*)-**45**] m/z = 306 (M^+, 0.4), 291 (M–CH_3, 0.7), 250 (M–C_4H_9, 2), 222 (3), 131 (7), 91 (C_7H_7, 100), 73 (37). MS: [(*Z*)-**45**] m/z = 306 (M^+, 2), 291 (3), 250 (5), 222 (11), 131 (13), 91 (100), 73 (40). IR (neat): 2957, 1678, 1254, 848 cm^{-1}.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **4**, **6**, **9**, **10**, **17**, **18**, **20**, **27**, **29**, **33**, **35**, **38**, **40**, **41**, **43**, and **45** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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