Iodotrimethylsilane-Promoted 1,4-Addition of Copper Acetylides to α,*β*-Unsaturated Ketones and Aldehydes

Magnus Eriksson, Tommy Iliefski, Martin Nilsson,* and Thomas Olsson

Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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In the presence of iodotrimethylsilane (TMSI) and lithium iodide in tetrahydrofuran, the otherwise unreactive copper acetylides add to enones present as *s-trans* conformers to provide good yields of the silyl enol ethers of *β*-acetylido carbonyl compounds. Typically good substrates are 2-cyclopentenone, 2-cyclohexenone, α,*β*-unsaturated aldehydes, and *β*-alkoxy-α-enones. Copper acetylide reagents prepared from CuI and an alkynyllithium give considerably higher yields than those prepared from CuBr or CuCN. Iodotrimethylsilane is by far the most efficient silane, although trimethylsilyl triflate is useful in some cases.

Introduction

In this paper we demonstrate the conjugate addition of copper acetylides in THF together with iodotrimethylsilane (TMSI) and LiI to enones and to α,*β*-unsaturated aldehydes. This protocol gives good to excellent yields of silyl enol ethers of *γ*,*δ*-acetylenic carbonyl compounds. We have previously demonstrated that alkyl- and arylcopper reagents, RCu·LiI, in the presence of TMSI add to a variety of α,*β*-unsaturated enones and enoates.[1] We now report extensions of our previous observation that pentynylcopper(I)·LiI and TMSI add to 2-cyclopentenone.[2]

Conjugate addition of alkyl, alkenyl, and aryl groups via organocuprates and mono-organocopper compounds is a widely used synthetic method.[3] Activating agents like TMSI,[4] TMSCl,[5] and BF_3[6] have extended the scope, especially for the mono-organocopper compounds. Lithium iodide is often important in these reactions, and we therefore denote the copper reagents as RCu·LiI or RC≡CCu·LiI in the text. So far alkynyl ligands have been considered unreactive in copper-promoted conjugate additions and are often used as nontransferable groups in mixed lithium diorganocuprates.[7] Lithium bis(acetylido)cuprates on the other hand give 1,2-addition to α,*β*-unsaturated aldehydes.[5b] However, a recent report demonstrated conjugate addition of RC≡CCu·LiCN to α-enones in the presence of *tert*-butyldimethylsilyl triflate.[8]

Several of the existing methods for conjugate addition of alkynyl groups to α,*β*-unsaturated ketones involve organoaluminum or organoboron reagents. For example, alkynyldiethylalanes[9] add to enones capable of adopting an *s-cis* conformation, whereas cyclic enones give only 1,2-addition. Nickel-catalyzed addition[10] of organoaluminum acetylides is also effective for *s-trans* substrates. Alkynylboron reagents[11,12] add only to α,*β*-enones that assume an *s-cis* conformation, whereas lithium acetylidoaluminates[13] add both to *s-cis* and to *s-trans* enones. Trialkylsilyl triflates promote conjugate addition of alkynylzinc reagents.[14] Conjugate alkynylation with lithium acetylides alone is possible to both cyclic and acyclic α-enones if the carbonyl group is blocked by a bulky aluminum complex.[15]

Results

Treatment of an acetylene with butyllithium followed by copper(I) iodide, or addition of the lithium acetylide to a suspension of CuI, gives copper acetylide and lithium iodide. (Trimethylsilyl)acetylene and 5-(benzyloxy)pentyne give the copper acetylides as solutions in THF (ca. 0.35 M), whereas those from pentyne or phenylacetylene form suspensions. TMSI is added to the copper acetylide at −78 °C. In contrast to alkylcopper reagents, there is often a distinct change when TMSI is added to the alkynyl reagents; for example, [(trimethylsilyl)ethynyl]copper(I) goes from a greenish-yellow solution to a light-green suspension. This indicates the formation of a complex between the organocopper compound and TMSI. On adding 2-cyclohexenone (**1**) or 2-cyclopentenone (**2**) to the RC≡CCu·LiI−TMSI preparations, at −78 °C, we sometimes observe a color change toward yellow, which

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[1] (a) Bergdahl, M.; Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *Tetrahedron* **1988**, *44*, 2055. (b) Bergdahl, M.; Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *Tetrahedron* **1989**, *45*, 535. (c) Bergdahl, M.; Nilsson, M.; Olsson, T. *J. Organometal. Chem.* **1990**, *391*, C19. (d) Bergdahl, M.; Nilsson, M.; Olsson, T. Stern, K. *Tetrahedron* **1991**, *47*, 9691. (e) Eriksson, M.; Nilsson, M.; Olsson, T. *Synlett* **1994**, 271.

[2] Bergdahl, M.; Eriksson, M.; Nilsson, M.; Olsson, T. *J. Org. Chem.* **1993**, *58*, 7238.

[3] (a) Lipshutz, B. H.; Sengupta. S. *Org. React.* **1992**, *41*, 135. (b) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1992. (c) Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225.

[4] (a) Eriksson, M.; Hjelmencrantz, A.; Nilsson, M.; Olsson, T. *Tetrahedron* **1995**, *51*, 12631. (b) Bergdahl, M.; Iliefski, T.; Nilsson, M.; Olsson, T. *Tetrahedron Lett.* **1995**, *36*, 3227. (c) Nilsson, K.; Ullenius, C. *Tetrahedron* **1994**, *50*, 13173. (d) Eriksson, M.; Johansson, A.; Nilsson, M.; Olsson, T. *J. Am. Chem. Soc.* **1996**, *118*, 10904.

[5] (a) Chuit, C.; Foulon, J. P.; Normant, J. F. *Tetrahedron*, **1980**, *36*, 2305. (b) *Ibid.* **1981**, *37*, 1385. (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015. (d) *Ibid.* **1985**, *26*, 6019. (e) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. (f) Johnson, C. R.; Marren, T. J. *Tetrahedron Lett.* **1987**, *28*, 27.

[6] Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947.

[7] (a) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210. (b) Posner, G. H.; Chapdelaine, M. J.; Lentz, C. M. *J. Org. Chem.* **1979**, *44*, 3661.

[8] Kim, S.; Park, J. H.; Jon, S. Y. *Bull. Korean Chem. Soc.* **1995**, *16*, 783.

[9] Hooz, J.; Layton R. B. *J. Am. Chem. Soc.* **1971**, *93*, 7320.

[10] (a) Hansen, R. T.; Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2244. (b) Schwartz, J.; Carr, D. B.; Hansen, R. T.; Dayrit, F. M. *J. Org. Chem.* **1980**, *45*, 3053.

[11] (a) Sinclair, J. A.; Molander, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1977**, *99*, 954. (b) Molander, G. A.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 3106.

[12] Fujishima, H.; Takada, E.; Hara, S.; Suzuki, A. *Chem. Lett.* **1992**, 695.

[13] Kim, S.; Park, J. H. *Synlett* **1995**, 163.

[14] Kim, S.; Lee, J. M. *Tetrahedron Lett.* **1990**, *31*, 7627.

[15] Maruoka, K.; Shimada, I.; Imoto, H.; Yamamoto, H. *Synlett* **1994**, 519.

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Scheme 1

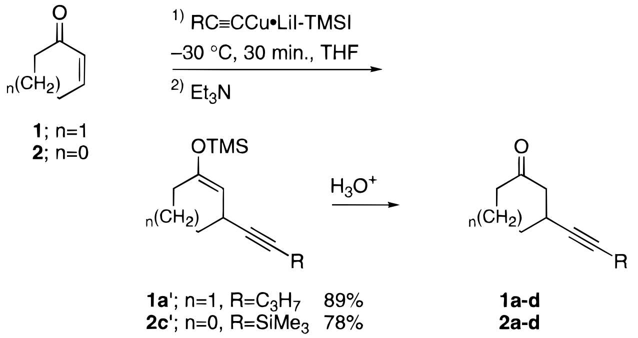


Table 1. Conjugate Addition of RC≡CCu(LiI)−TMSI[a] to 2-Cyclohexenone (1), 2-Cyclopentenone (2), 2-Methyl-2-cyclopentenone (3), and Chromone (5). The Yields Refer to Isolated Adduct Ketones

entry	enone	R	solvent	temp (°C), time	product	yield (%)
1	**1**	C_3H_7	THF	−30, 30 min	**1a**	89
2	**1**	C_3H_7	Et_2O	−30, 30 min	**1a**	32
3	**1**	C_3H_7	CH_2Cl_2	−30, 30 min	**1a**	33
4	**1**	C_3H_7(−LiI)	THF	−30, 1 h	**1a**	32
5	**1**	C_3H_7	THF	−30, 30 min	**1a**	52[b]
6	**1**	Ph	THF	−30, 30 min	**1b**	90
7	**1**	Me_3Si	THF	−30, 30 min	**1c**	88
8	**1**	*t*-Bu	THF	−78, 45 min	**1d**	97
9	**1**	*t*-Bu	Et_2O	−78, 45 min	**1d**	11
10	**2**	C_3H_7	THF	−30, 30 min	**2a**	68[e]
11	**2**	Ph	THF	−30, 1 h	**2b**	75
12	**2**	Ph	CH_2Cl_2	−40, 2 h	**2b**	41
13	**2**	Me_3Si	THF	−30, 30 min	**2c**	92
14	**2**	Me_3Si	THF	−30, 30 min	**2c**	70[b]
15	**2**	Me_3Si	THF	−30, 30 min	**2c**	68[c]
16	**2**	$BnO(CH_2)_3$	THF	−30, 1 h	**2d**	94
17	**3**	C_3H_7	THF	−50, 4 h	**3a**	45[d]
18	**3**	$BnO(CH_2)_3$	THF	−50, 4 h	**3b**	54[d]
19	**5**	Me_3Si	THF	−30, 70 min	**5a**	98
20	**5**	*t*-Bu	THF	−30, 70 min	**5b**	90

[a] All copper reagents contain LiI from the preparation unless otherwise noted. [b] Substrate:copper compound:TMSI = 1:1:1. [c] Substrate:copper compound:TMSI = 1:1:1.5. [d] Substrate:copper compound:TMSI = 1:1.5:3. [e] Taken from ref 2.

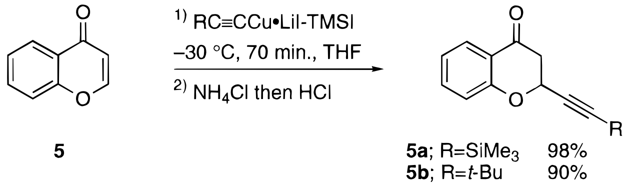
indicates formation of a π-complex.[16] In some cases the conjugate addition proceeds at −78 °C, but we generally observe the reaction leading to acetylenic silyl enol ethers around −30 °C. These can be isolated after addition of triethylamine at low temperature or hydrolyzed directly to the corresponding γ,δ-acetylenic ketones (Scheme 1).

Cycloalkenones. The scope of the reaction between some cyclic enones and alkynylcopper(I)•LiI−TMSI reagents is summarized in Table 1, where yields are given for the ketones obtained after hydrolysis.

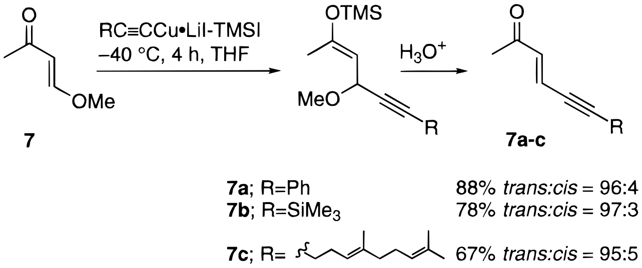
As seen from Table 1, the different alkynylcopper reagents add to 2-cyclopentenone and 2-cyclohexenone in good to excellent yields. Additions to 2-methyl-2-cyclopentenone (**3**) are slow and give lower yields. Here, cleavage of THF by TMSI competes to give 1-iodo-4-[(trimethylsilyl)oxy]butane, consuming TMSI. The reaction with RC≡CCu•LiI and trimethylsilyl triflate is slow but gives higher yields without significant THF cleavage (Table 2, entry 11). Addition of RC≡CCu•LiI-TMSOTf to 3-methyl-2-cyclopentenone (**4**) is slow, and the yield is poor (Table 2, entry 12).

Addition of (phenylethynyl)copper(I) to 3-ethoxy-2-cyclohexenone gives the substitution product, 3-(phenylethynyl)-2-cyclohexenone (30%). Additions of [(trimethylsilyl)ethynyl]copper(I) and (*tert*-butylethynyl)copper(I) to chromone[17] (**5**) give excellent yields of addition products (Table 1, entries 19 and 20).

Scheme 2



Scheme 3



Acyclic Enones. Additions of copper acetylide•LiI and TMSI to acyclic enones were less successful: (phenylethynyl)copper(I) and ethyl vinyl ketone (**6**) gave 37% of conjugate adduct **6a** and 4-hexen-3-one gave only 12% yield. For acyclic enones in general the *s-cis* conformation is favored.[18] Pentynylcopper(I)•LiI−TMSI added neither to 1-acetyl-1-cyclohexene nor to chalcone. Attempted additions of RC≡CCu•LiI−TMSI to methyl acrylate were unsuccessful.

To summarize so far, the cycloalkenones, which have *s-trans* geometry, give fast reactions and good yields, whereas acyclic alkenones, known to be present mainly as *s-cis* conformers, give rather poor results. We therefore predicted that acyclic substrates such as α,β-unsaturated aldehydes and (*E*)-4-methoxy-3-buten-2-one (**7**), known to prefer *s-trans* conformation,[2,5e,19] should react better. The prediction was valid and additions of (phenylethynyl)copper(I) and [(trimethylsilyl)ethynyl]copper(I) to (*E*)-4-methoxy-3-buten-2-one gave good yields of the substitution products after hydrolysis. Also a functionalized acetylene, prepared from geranylacetone,[20] added in good yield. The products are the result of initial conjugate addition to give the silyl enol ethers followed by elimination of MeOH during hydrolysis giving net substitution of the methoxy group (Scheme 3).[2,21]

(Phenylethynyl)copper(I)•LiI−TMSI also adds in reasonable yields both to acrylaldehyde (**8**) and to crotonaldehyde (**9**) to give predominantly *E*-silyl enol ethers. We presume that the reaction is general for α,β-unsaturated aldehydes (Scheme 4).

Reaction Conditions. In order to optimize the reactions we checked for suitable solvents and reagent proportions for the substrates 2-cyclopentenone and 2-cyclohexenone. The reactions in THF give considerably

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(16) Vellekoop, A. S.; Smith, R. A. J. *J. Am. Chem. Soc.* **1994**, *116*, 2902.

(17) Föhlisch, B. *Chem. Ber.* **1971**, *104*, 348.

(18) (a) Montaudo, G.; Librando, V.; Caccamese, S.; Maravigna, P. *J. Am. Chem. Soc.* **1973**, *95*, 6365. (b) Oelichmann, H.-J.; Bougeard, D.; Schrader, B. *Angew. Chem. Suppl.* **1982**, 1404. (c) Chamberlin, A. R.; Reich, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 1440.

(19) Gung, B. W.; Gerdeman, M. S.; Fouch, R. A.; Wolf, M. A. *J. Org. Chem.* **1994**, *59*, 4255.

(20) Bergström, G.; Johansson, A.; Olsson, T. *Tetrahedron Lett.* **1996**, *37*, 7127.

(21) Cahiez, G.; Alami, M. *Tetrahedron Lett.* **1989**, *30*, 3541.

Scheme 4

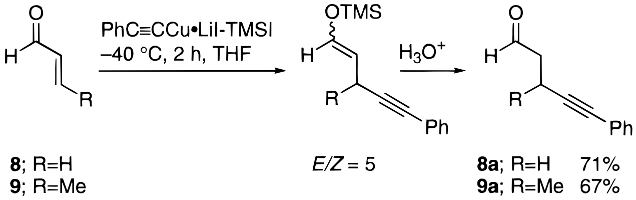

Table 2. The Influence of Different Additives. Conjugate Addition of RC≡CCu(LiI)−X in THF to 2-Cyclohexenone (1), 2-Cyclopentenone (2), 2-Methyl-2-cyclopentenone (3), and 3-Methyl-2-cyclopentenone (4). The Yields Refer to Isolated Adduct Ketones.

entry	enone	R	X	temp (°C), time	product	yield (%)
1	**1**	C_3H_7	TMSI	−30, 30 min	**1a**	89
2	**1**	C_3H_7	TMSBr	−30, 30 min	**1a**	<2
3	**1**	C_3H_7	TMSCl	−30, 30 min	**1a**	0
4	**2**	Ph	TMSI	−30, 1 h	**2b**	75
5	**2**	Ph	BF_3	−40, 2 h	**2b**	0
6	**2**	Ph	TMSCN	−40, 2 h	**2b**	0
7	**2**	C_3H_7	TMSI	−30, 30 min	**2a**	68
8	**2**	C_3H_7	TMSOTf	−30, 30 min	**2a**	25
9	**2**	C_3H_7	BF_3	−30, 30 min	**2a**	0
10	**2**	$SiMe_3$	BF_3	−30, 2 h	**2c**	0
11	**3**	$SiMe_3$	TMSOTf	−30, 1 h	**3c**	81
12	**4**	$SiMe_3$	TMSOTf	−40 to 0, 5 h	**4a**	16

higher yields and rates than those in diethyl ether or dichloromethane. A moderate excess of copper acetylide was beneficial and the best proportions of substrate: copper acetylide•LiI:TMSI were around 1:1.5:1.5.

Reagents. TMSI proved uniquely effective for the reactions as demonstrated in Table 2. TMSCl, TMSBr, TMSCN, and BF_3 are all ineffective. TMSI is clearly more effective than TMSOTf, and the latter requires the presence of LiI for reaction. Reaction of TMSOTf with LiI could give TMSI. A reagent from lithium (trimethylsilyl)acetylide and copper(I) triflate did not add to 2-cyclohexenone in the presence of TMSOTf; the THF polymerized instead.[22] On the other hand, this acetylide added to 2-cyclohexenone in the presence of TMSI, although only in trace amounts (Table 3, entry 4). Still TMSOTf can be useful in combination with copper acetylide•LiI for hindered enones (Table 2, entries 11 and 12).

The copper acetylide preparations obtained by treatment of an acetylene with butyllithium, followed by addition of solid copper iodide, are superior for the conjugate additions. They naturally contain lithium iodide. Removal of the dissolved lithium iodide gives a distinct drop in yield (Table 1, entry 4). Use of the complex CuI·0.75DMS (dimethyl sulfide), CuI purified via $KCuI_2$ or 99.999% CuI gave comparable results (see Experimental Section). Still the dimethyl sulfide complex is probably more soluble than the other preparations. Attempts to use CuBr•DMS complex or CuCN instead of CuI gave poor yields (Table 3). These findings are in line with the results of Bertz and Dabbagh for conjugate addition of BuCu•LiX reagents to 2-cyclohexenone in THF.[23]

Discussion

The present results further demonstrate the usefulness of TMSI in conjugate additions of mono-organocopper compounds to α,β-unsaturated carbonyl compounds. The conjugate addition of copper acetylide•LiI−TMSI requires a reactive substrate. Enoates do not react, and among enones only cycloalkenones and those that preferentially assume an *s-trans* conformation are good substrates. Other distinctive features are the importance of THF as solvent and the strong effect of LiI present.

Table 3. The Influence of Cu(I) Precursors. Conjugate Addition of RC≡CCu(LiX)−TMSI in THF to 2-Cyclohexenone (1) and 2-Cyclopentenone (2). The Yields Refer to Isolated Adduct Ketones.

entry	enone	R	X	temp, (°C), time	product	yield (%)
1	**1**	C_3H_7	I	−30, 0.5 h	**1a**	89
2	**1**	C_3H_7	Br	−30, 1 h	**1a**	7
3	**1**	$SiMe_3$	CN	−30, 1 h	**1c**	7
4	**1**	$SiMe_3$	OTf	−30, 1 h	**1c**	<1
5	**2**	Ph	I	−30, 1 h	**2b**	75
6	**2**	Ph	I	−30, 1 h	**2b**	73[a]
7	**2**	Ph	Br	−40, 2 h	**2b**	6
8	**2**	Ph	CN	−40, 2 h	**2b**	0

[a] CuI (Aldrich 99.999%) was used.

The preference for reactions with *s-trans* conformers parallels the reactions of reactive mono-organocopper compounds and TMSI with enoates, which are less reactive than enones. We have also seen this in additions to naphthylbornyl crotonates[1d] and allylic enoates.[1e] The present discussion therefore strongly connects to that in our recent paper on conjugate addition to allylic acrylates.[4a]

The results from all these investigations indicate a common mechanism for reactions of moderately reactive copper acetylides/TMSI with reactive substrates and of reactive mono-organocopper compounds/TMSI with the moderately reactive enoates.

NMR investigations of the reaction between organocuprates and α,β-unsaturated carbonyl compounds have shown that formation of a π-complex probably takes place prior to the transfer of the organic ligand.[16,24] A similar complexation seems probable also for the mono-organocopper reactions, including those of the copper acetylides, but remains to be proven. We have not yet been able to observe π-complexes between mono-organocopper compounds and enones by NMR methods, but we have seen color changes which indicate such complexes.[16]

There are important differences between the mono-organocopper and the organocuprate reactions. Mono-organocopper compounds in general require an additive, at least LiI from their preparation and preferably also TMSI. Such additives are not needed for the organocuprates, even though TMSCl often increases the reactivity of cuprates quite strongly and can affect the stereochemical outcome as well.[5] Coordination of the lithium of a diorganocuprate to the carbonyl oxygen of the substrate is crucial, however, and can be counteracted by THF, which slows down the reaction considerably.[25] For RC≡CCu•LiI−TMSI reactions, on the other hand, THF increases the rates. We believe that coordination of Li to the carbonyl oxygen is less important, whereas iodide from LiI and TMSI is important for the reactivity of the mono-organocopper compounds.

Organocuprates and monoorganocopper•LiI−TMSI reagents give different epimers when reacted with chiral

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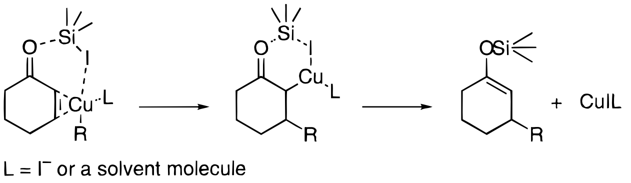
[22] Hrkach, J. S.; Matyjaszewski, K. *Macromolecules* **1990**, *23*, 4042.

[23] Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425.

[24] (a) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1985**, *282*, 133. (b) Christenson, B.; Olsson, T.; Ullenius, C. *Tetrahedron* **1989**, *45*, 523. (c) Bertz, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8276. (d) Krause, N. *J. Org. Chem.* **1992**, *57*, 3509.

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

Scheme 5



enoates.[1c,d] This difference indicates that the two types of reagents react with different conformations of the substrate. The organocuprate predominantly reacts with an enoate in the *s-cis* conformation, whereas the mono-organocopper·LiI–TMSI reactions prefer the *s-trans* conformation. On the other hand, TMSI can change the course of organocuprate additions as recently observed for allylic acrylates.[4a]

As also discussed in a recent paper, these observations have led us to propose the following common mechanism for additions of mono-organocopper compounds·LiI–TMSI to enones and enoates:

The first step is the formation of a π-complex, in which the enone can adopt either of the *s-cis* or *s-trans* conformations. Due to the strong interactions between the copper and the acetylide ligand,[26] we expect π-complexes between copper acetylides and enones to be weaker than those of alkylcopper compounds. Coordination of the silicon in TMSI to one of the electron pairs of the carbonyl oxygen then activates the substrate for the subsequent addition. For the *s-trans* conformer of the substrate, this arrangement is suitable for additional stabilization of the π-complex by interaction between copper and the iodine of TMSI. The arrangement also allows further reaction of the π-complex, either through direct decomposition yielding the silyl enol ether or formation of an α-cuprio ketone[27] with subsequent decomposition to product (Scheme 5). In this scheme an interaction between copper and TMSI is also possible, increasing the electrophilicity of silicon and also the reactivity of the copper acetylide.

For an *s-cis* conformer the stabilizations outlined above are not possible. For steric reasons the silicon must coordinate to the electron pair pointing away from the carbon–carbon double bond. Thus there is no good path for the decomposition of the intermediate π-complex to product.

The mechanism proposal given in Scheme 5 accounts for the *s-trans* selectivity in the mono-organocopper reactions and for the superiority of TMSI as an additive, since it can coordinate well to both the carbonyl oxygen and the copper. The solvation of Li^+ by THF leaves the carbonyl group open for interaction with TMSI and the iodide ion open for interaction with copper. In conjugate additions of reactive mono-organocopper compounds/TMSI to reactive substrates the selectivity is lower and formation of *Z* enol ethers often dominates, indicating a preferred path via *s-cis* conformers.

In conclusion, the activation of copper acetylides by TMSI has provided new synthetic possibilities and also some new aspects of the mechanism of conjugate additions of organocopper reagents.

Experimental Section

General. All reactions were performed under argon and in cooled oven-dried glassware (140 °C). NMR spectra were recorded at 400 MHz or 500 MHz with $CDCl_3$ as solvent and TMS as internal standard ($\delta = 0$). Coupling patterns are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constants are given in hertz (Hz). High resolution mass spectra (HRMS) were recorded at 70 eV, capillary column, DB-1. IR spectra were recorded on an FT-IR instrument. Elemental analyses were performed by Analytische Laboratorien in Engelskirchen, Germany.

Chemicals. All starting materials are commercially available from Aldrich, Merck, Fluka, or Janssen, unless otherwise noted. Copper(I) cyanide (99%) from Aldrich and CuBr·DMS complex prepared according to House *et al.*[28] were used. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine (Et_3N) and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under argon and used immediately. BuLi (1.6 M in hexane) was purchased from Aldrich and titrated prior to use. Iodotrimethylsilane (TMSI) was purchased from Janssen or Sigma and stored septum-capped at −25 °C under argon with copper chips in a light-protected bottle.

Purification of Copper Iodide.[28] Copper(I) iodide (Merck, 99%) was dissolved in an Et_2O/DMS mixture and filtered. Dilution with hexane precipitated the new CuI·1.5DMS complex[29] as white crystals. This complex was dried at room temperature under vacuum for 1–2 h to give CuI·0.75DMS as a white powder. The complex is stable at room temperature and does not spontaneously lose DMS on standing. Anal. Calcd for CuI·0.75DMS: C; 7.60. H; 1.91. Found: C; 7.42. H; 1.76. It should be pointed out that CuI (Aldrich 99.999%) or CuI purified *via* $KCuI_2$[30] are also useful precursors in these reactions.

Typical Procedure for the TMSI-Promoted Conjugate Addition of Alkynylcopper Reagents. BuLi (7.5 mmol) is added at −10 °C to a stirred solution of the acetylene (7.5 mmol) in 20 mL of dry THF. The solution is stirred for 20 min at −10 °C after which CuI·0.75DMS (8.25 mmol) is added in one batch. After stirring the copper acetylide suspension/solution for 45 min at −10 °C, the temperature is lowered to −78 °C and TMSI (7.5 mmol) added. The mixture is stirred at −78 °C another 5 min, and then the α,β-unsaturated substrate (5 mmol), dissolved in 5 mL of dry THF, is added slowly *via* the cold flask wall (this procedure cools down the substrate solution).

When the addition is complete the temperature is raised to the values indicated in the Tables 1–3, and the mixture is stirred for 0.5–5 h. Saturated NH_4Cl (10 mL) is added at low temperature, and the mixture is then stirred at room temperature for 30 min. To affect complete hydrolysis, 2 mL of 3 M HCl is added and the mixture stirred another 30 min at room temperature. The layers are separated, and the aqueous phase is extracted twice with ether. The combined ethereal layer is washed once with 5% $Na_2S_2O_3$, once with brine, and dried over Na_2SO_4. Evaporation of the solvent gives the crude product, generally as a slightly yellow oil, which is further purified by flash chromatography and bulb-to-bulb distillation.

Typical Procedure When Other Additives Are Used. The same procedure as above is used substituting TMSI for TMSCl, TMSCN, BF_3, etc.

Typical Procedure for Isolation of TMS Enol Ethers. When the reaction is complete, dry Et_3N is added at low temperature (ca. 3 mol equiv *versus* TMSI) instead of NH_4Cl. The reaction mixture is stirred at room temperature for 1 h and then diluted with Et_2O or pentane. The organic layer is washed once with saturated $NaHCO_3$ and once with brine and dried over Na_2SO_4. Evaporation of the solvent gives the crude product, generally as a slightly brown-yellow oil, which is

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(26) van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 4, Chapt 14.

(27) Berlan, J.; Battioni, J. P.; Koosha, K. *Bull. Soc. Chim. Fr.* **1979**, 183.

(28) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.

(29) Maelger, H.; Olbrich, F.; Kopf, J.; Abeln, D.; Weiss, E. *Zeit. Naturforsch. B* **1992**, *47(9)*, 1276.

(30) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

further purified by bulb-to-bulb distillation. Small amounts of the cleavage product of THF and TMSI, 4-iodo-1-[(trimethylsilyl)oxy]butane,[2] often remains in the product even after bulb-to-bulb distillation.

3-(1-Pentynyl)cyclohexanone (1a). Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.51) followed by bulb-to-bulb distillation (175−176 °C/3 mbar), 89% yield. ^{1}H NMR: δ 2.82−2.92 (m, 1H), 1.42−2.58 (m, 12H), 0.90 (t, J = 7.0, 3H). ^{13}C NMR: δ 209.7, 82.8, 81.4, 47.6, 41.3, 31.3, 30.3, 24.0, 22.4, 20.7, 13.5. IR (neat): 2254 (C≡C), 1715 (C═O) cm^{-1}. HRMS: Calculated for $C_{11}H_{16}O$: 164.120. Found: 164.120. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.21; H, 9.84.

1-[(Trimethylsilyl)oxy]-3-(1-pentynyl)cyclohexene (1a′). Obtained as a colorless oil after bulb-to-bulb distillation (70−72 °C/0.8 mbar), 89% yield. ^{1}H NMR: δ 4.86 (d, J = 4.0, 1H), 3.05−3.15 (m, 1H), 1.42−2.17 (m, 10H), 0.96 (t, J = 7.0, 3H), 0.19 (s, 9H). ^{13}C NMR: δ 151.0, 106.2, 83.9, 79.7, 29.8, 29.7, 27.0, 22.7, 21.2, 20.9, 13.6, 0.51. IR (neat): 1667 (C═C) cm^{-1}. HRMS: Calcd for $C_{14}H_{24}OSi$: 236.160. Found: 236.160.

3-(Phenylethynyl)cyclohexanone (1b).[31] Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.38) followed by bulb-to-bulb distillation (160−161 °C/0.4 mbar), 90% yield. ^{1}H NMR: δ 7.35−7.42 (m, 2H), 7.25−7.31 (m, 3H), 3.06−3.15 (m, 1H), 2.65 (dd, J = 14, 5, 1H), 2.52 (dd, J = 14, 9, 1H), 2.37 (t, J = 7, 2H), 2.04−2.24 (m, 2H), 1.74−1.96 (m, 2H). ^{13}C NMR: δ 209.3, 131.8, 128.4, 128.1, 123.4, 90.8, 82.9, 47.2, 41.4, 31.2, 30.9, 24.2. IR (neat): 2233 (C≡C), 1715 (C═O) cm^{-1}. HRMS: Calcd for $C_{14}H_{14}O$: 198.104. Found: 198.106.

3-[(Trimethylsilyl)ethynyl]cyclohexanone (1c).[10b] Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.51) followed by bulb-to-bulb distillation (123−125 °C/4 mbar), 88% yield. ^{1}H NMR: δ 2.85−2.92 (m, 1H), 2.29−2.60 (m, 4H), 1.96−2.15 (m, 2H), 1.68−1.86 (m, 2H), 0.14 (s, 9H). ^{13}C NMR: δ 209.1, 107.7, 86.7, 47.0, 41.2, 31.1, 31.0, 24.1, 0.2. IR (neat): 2171 (C≡C), 1715 (C═O) cm^{-1}. HRMS: Calcd for $C_{11}H_{18}OSi$: 194.113. Found: 194.113.

3-(*tert*-Butylethynyl)cyclohexanone (1d).[10b] Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.40) followed by bulb-to-bulb distillation (50−51 °C/0.3 mbar), 97% yield. ^{1}H NMR: δ 2.82−2.90 (m, 1H), 2.52 (dd, J = 14.4, 5.2, 1H), 2.37 (dd, J = 14.4, 8.4, 1H), 2.25−2.36 (m, 2H), 2.03−2.16 (m, 1H), 1.88−2.00 (m, 1H), 1.68-1.82 (m, 2H), 1.17 (s, 9H). ^{13}C NMR: δ 210.0, 91.8, 79.6, 47.8, 41.4, 31.5, 31.4, 30.2, 27.5, 24.0. IR (neat): 1719 (C═O) cm^{-1}. HRMS: Calcd for $C_{12}H_{18}O$: 178.136. Found: 178.136. Anal. Calcd for $C_{12}H_{15}O$: C, 80.85; H, 10.18. Found: C, 80.60; H, 10.11.

3-(Phenylethynyl)cyclopentanone (2b). Obtained as a colorless oil after flash chromatography (20% ether in pentane, R_f = 0.22) followed by bulb-to-bulb distillation (115−120 °C/1.5 mbar), 68% yield. ^{1}H NMR: δ 7.37−7.42 (m, 2H), 7.27−7.32 (m, 3H), 3.24−3.33 (m, 1H), 2.08−2.63 (m, 6H). ^{13}C NMR: δ 217.3, 131.8, 131.7, 128.5, 128.2, 123.3, 91.1, 82.0, 45.4, 37.7, 30.5, 28.4. IR (neat): 2228 (C≡C), 1744 (C═O) cm^{-1}. HRMS: Calcd for $C_{13}H_{12}O$: 184.089. Found: 184.089. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56. Found: C, 84.42; H, 6.58.

3-[(Trimethylsilyl)ethynyl]cyclopentanone (2c).[32] Obtained as a colorless oil after flash chromatography (20% ether in pentane, R_f = 0.35) followed by bulb-to-bulb distillation (42−45 °C/4 mbar), 92% yield. ^{1}H NMR: δ 3.03−3.12 (m, 1H), 1.98−2.54 (m, 6H), 0.15 (s, 9H). ^{13}C NMR: δ 217.3, 108.1, 86.1, 45.3, 37.6, 30.4, 28.6, 0.3. IR (neat): 2178 (C≡C), 1747 (C═O) cm^{-1}. HRMS: Calcd for $C_{10}H_{16}OSi$: 180.097. Found: 180.098.

1-[(Trimethylsilyl)oxy]-3-[(trimethylsilyl)ethynyl]cyclopentene (2c′).[32] Obtained as a colorless oil after bulb-to-bulb distillation (25−30 °C/0.08 mbar), 78% yield. ^{1}H NMR: δ 4.61 (d, J = 2.0, 1H), 3.44−3.52 (m, 1H), 1.83−2.42 (m, 4H), 0.22 (s, 9H), 0.14 (s, 9H). ^{13}C NMR: δ 156.3, 111.2, 103.5, 83.9, 33.6, 33.1, 29.9, 0.4, 0.2. IR (neat): 2170 (C≡C), 1643 (C═C) cm^{-1}. HRMS: Calcd for $C_{13}H_{24}OSi_2$: 252.136. Found: 252.137.

3-[5-(Benzyloxy)-1-pentynyl]cyclopentanone (2d). Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.27) followed by bulb-to-bulb distillation (125−130 °C/0.06 mbar), 94% yield. ^{1}H NMR: δ 7.22−7.38 (m, 5H), 4.51 (s, 2H), 3.54 (t, J = 6, 2H), 2.95−3.05 (m, 1H), 1.74−2.50 (m, 10H). ^{13}C NMR: δ 217.9, 138.7, 128.6, 127.8, 127.7, 82.0, 81.4, 73.1, 68.9, 45.7, 37.6, 30.7, 29.2, 27.8, 15.8. IR (neat): 1745 (C═O) cm^{-1}. HRMS: Calcd for $C_{17}H_{20}O_2$: 256.146. Found: 256.141. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.64; H, 7.75.

3-(1-Pentynyl)-2-methylcyclopentanone (3a). Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.52 and 0.62) followed by bulb-to-bulb distillation (54−56 °C/0.3 mbar), 45% yield. The presence of two diastereomers in comparable amounts is evident from gas chromatograms. ^{1}H NMR: δ 3.14−3.22 (m, 1H), 1.96−2.50 (m, 7H), 1.42−1.58 (m, 2H), 1.15 (d, J = 7.0, 3H), 0.97 (2t, J = 7.0, 3H). ^{13}C NMR: δ 219.6, 218.9, 84.6, 82.3, 81.2, 79.2, 51.4, 48.2, 37.1, 36.1, 35.7, 33.7, 28.6, 28.1, 22.6, 20.9, 13.6, 12.6, 11.2. IR (neat): 1745 (C═O) cm^{-1}. HRMS: Calcd for $C_{11}H_{16}O$: 164.120. Found: 164.120. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.18; H, 9.80.

3-[5-(Benzyloxy)-1-pentynyl]-2-methylcyclopentanone (3b). Obtained as a colorless oil (1:1 mixture of diastereomers) after flash chromatography (30% ether in pentane, R_f = 0.35) followed by bulb-to-bulb distillation (125−130 °C/0.05 mbar), 54% yield. The presence of two diastereomers in comparable amounts is evident from gas chromatograms. ^{1}H NMR: δ 7.24−7.40 (m, 5H), 4.50−4.52 (2s, 2H), 3.51−3.58 (2t, J = 6, 2H), 3.12−3.20 (m, 1H), 1.70−2.45 (m, 10H). ^{13}C NMR: δ 219.5, 218.9, 138.7, 128.7, 128.6, 128.0, 127.9, 127.8, 84.0, 81.7, 81.5, 79.4, 73.2, 69.0, 51.4, 48.1, 37.1, 36.0, 35.6, 33.7, 29.4, 29.3, 28.5, 28.0, 15.8, 15.7, 12.6, 11.3. IR (neat): 1742 (C═O) cm^{-1}. HRMS: Calcd for $C_{18}H_{22}O_2$: 270.162. Found: 270.160. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.84; H, 8.14.

3-[(Trimethylsilyl)ethynyl]-2-methylcyclopentanone (3c). Obtained as a colorless oil after flash chromatography (30% ether in pentane, R_f = 0.44 and 0.56) followed by bulb-to-bulb distillation (100°C/4 mbar), 82% yield. The presence of two diastereomers in comparable amounts is evident from gas chromatograms. ^{1}H NMR: δ 3.22 (m, 1H), 1.80−2.54 (m, 5H), 1.18 (d, 3H), 0.17 (s, 9H), 0.14 (s, 9H). ^{13}C NMR: δ 219.0, 218.3, 107.6, 105.7, 89.0, 86.5, 51.1, 47.7, 37.0, 36.7, 35.6, 34.4, 28.1, 27.7, 12.6, 11.2, 0.29, 0.23. IR (neat): 2173 (C≡C), 1744 (C═O) cm^{-1}. HRMS: Calcd for $C_{11}H_{18}OSi$: 194.115. Found: 194.113.

3-Methyl-3-[(trimethylsilyl)ethynyl]cyclopentanone (4a). Obtained as a yellow oil after flash chromatography (30% ether in pentane, R_f = 0.48), 16% yield. ^{1}H NMR: δ 2.68 (d, J =18, 1H), 2.43−2.70 (m, 1H), 2.22−2.36 (m, 2H), 2.14 (d, J =18, 1H), 1.84−1.94 (m, 1H), 1.40 (s, 3H), 0.14 (s, 9H). ^{13}C NMR: δ 217.7, 111.9, 85.2, 53.3, 37.7, 37.5, 36.2, 27.4, 0.3. IR (neat): 2160 (C≡C), 1748 (C═O) cm^{-1}. HRMS: Calcd for $C_{11}H_{18}OSi$: 194.113. Found: 194.112.

2-[(Trimethylsilyl)ethynyl]-4-chromanone (5a). Obtained as a white solid after flash chromatography (10% EtOAc in hexane, R_f = 0.31) followed by bulb-to-bulb distillation (80−82 °C/0.06 mbar), 98% yield, mp 56−58 °C. ^{1}H NMR: δ 7.88−7.91 (m, 1H), 7.48−7.53 (m, 1H), 7.02−7.08 (m, 2H), 5.20−5.26 (m, 1H), 2.92−3.04 (m, 2H), 0.17 (s, 9H). ^{13}C NMR: δ 190.7, 160.4, 136.4, 127.1, 122.2, 121.2, 118.4, 100.6, 93.4, 68.1, 43.6, −0.2. IR (neat): 2187 (C≡C), 1688 (C═O) cm^{-1}. HRMS: Calcd for $C_{14}H_{16}O_2Si$: 244.092. Found: 244.094. Anal. Calcd for $C_{14}H_{16}O_2Si$: C, 68.83; H, 6.61; Si, 11.46. Found: C, 68.69; H, 6.56; Si, 11.30.

2-(*tert*-Butylethynyl)-4-chromanone (5b). Obtained as a slightly yellow syrup after flash chromatography (10% ether in pentane, R_f = 0.29) followed by bulb-to-bulb distillation (90−92 °C/0.1 mbar), 90% yield. ^{1}H NMR: δ 7.86−7.92 (m, 1H), 7.46−7.53 (m, 1H), 7.01−7.07 (m, 2H), 5.17−5.28 (m, 1H), 2.88-2.98 (m, 2H), 1.20 (s, 9H). ^{13}C NMR: δ 191.2, 160.6, 136.3, 127.0, 122.0, 121.3, 118.5, 97.2, 74.8, 68.2, 44.2, 30.8, 27.6. IR

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[31] Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J.; Rubio, R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1657.

[32] Salaün, J.; Ollivier, J. *Nouv. J. Chim.* **1981**, *5(11)*, 587.

(neat): 2244 ($C\equiv C$), 1697 ($C=O$) cm^{-1}. HRMS: Calcd for $C_{15}H_{16}O_2$: 228.115. Found: 228.114. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 78.67; H, 7.02.

7-Phenyl-6-heptyn-3-one (6a). Obtained as a slightly orange oil after flash chromatography (10% ether in pentane, $R_f = 0.29$), 37% yield. ^{1}H NMR: δ 7.34−7.40 (m, 2H), 7.25−7.30 (m, 3H), 2.64−2.78 (2m, 2H each), 2.49 (q, $J = 7.2$, 2H), 1.09 (t, $J = 7.2$, 3H). ^{13}C NMR: δ 209.7, 131.7, 128.4, 127.9, 123.8, 88.9, 81.1, 41.4, 36.2, 14.3, 8.0. IR (neat): 2239 ($C\equiv C$), 1716 ($C=O$) cm^{-1}. HRMS: Calcd for $C_{13}H_{14}O$: 186.104. Found: 186.108.

(*E*)-6-Phenyl-3-hexen-5-yn-2-one (7a).[33] Obtained as a light-yellow solid (*trans:cis* = 96:4) after flash chromatography (20% ether in pentane, $R_f = 0.32$), 88% yield, mp 45−47 °C. ^{1}H NMR: δ 7.46−7.53 (m, 2H), 7.33−7.42 (m, 3H), 6.84 (d, $J = 16$, 1H), 6.58 (d, $J = 16$, 1H), 2.30 (s, 3H). ^{13}C NMR: δ 197.3, 138.0, 132.2, 129.6, 128.8, 128.7, 124.0, 122.3, 99.9, 86.9, 27.9. IR (neat): 2192 ($C\equiv C$), 1744 ($C=O$) cm^{-1}. HRMS: Calcd for $C_{12}H_{10}O$: 170.073. Found: 170.077. Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.79; H, 5.94.

(*E*)-6-(Trimethylsilyl)-3-hexen-5-yn-2-one (7b).[34] Obtained as a light-yellow oil (*trans:cis* = 97:3) after flash chromatography (5% ether in pentane, $R_f = 0.23$), 78% yield. ^{1}H NMR: δ 6.59 (d, $J = 16$, 1H), 6.51 (d, $J = 16$, 1H), 2.26 (s, 3H), 0.22 (s, 9H). ^{13}C NMR: δ 197.3, 138.9, 123.7, 106.6, 101.8, 27.8, 0.2. IR (neat): 2128 ($C\equiv C$), 1696, 1678 cm^{-1}. HRMS: Calcd for $C_9H_{14}OSi$: 166.081. Found: 166.080.

(*E*)-10,14-Dimethylpentadeca-3,9,13-trien-5-yn-2-one or (*E*)-7-Geranyl-3-hepten-5-yn-2-one (7c). Obtained as a slightly greenish oil (*trans:cis* = 95:5) after flash chromatography (10% ether in pentane, $R_f = 0.28$), 67% yield. ^{1}H NMR: δ 6.61 (dt, $J = 16.0, 2.4$, 1H), 6.41 (d, $J = 16.0$, 1H), 5.20−5.14 (m, 1H), 5.12−5.07 (m, 1H), 2.44−2.38 (m, 2H), 2.30−2.23 (m, 2H), 2.26 (s, 3H), 2.12−1.97 (m, 4H), 1.68 (s, 3H), 1.63 (s, 3H), 1.60 (s, 3H). ^{13}C NMR: δ 197.7, 137.7, 137.3, 131.7, 125.2, 124.3, 122.3, 102.6, 78.4, 39.9, 27.6, 27.1, 26.8, 25.9, 20.6, 17.9, 16.3. HRMS: Calcd for $C_{17}H_{24}O$: 244.183. Found: 244.185. In spite of the convincing spectral data the mixture gave a high carbon analysis. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 82.62; H, 10.20.

5-Phenyl-4-pentynal (8a). Obtained as a slightly yellow oil after flash chromatography (10% ether in pentane, $R_f = 0.17$), 71% yield. ^{1}H NMR: δ 9.85 (t, $J = 1$, 1H), 7.35−7.42 (m, 2H), 7.26−7.32 (m, 3H), 2.71−2.81 (m, 4H). ^{13}C NMR: δ 200.8, 131.8, 128.4, 128.1, 123.5, 87.9, 81.6, 42.8, 12.9. IR (neat): 2234 ($C\equiv C$), 1725 ($C=O$) cm^{-1}. HRMS: Calcd for $C_{11}H_{10}O$: 158.073. Found: 158.078.

3-Methyl-5-phenyl-4-pentynal (9a). Obtained after flash chromatography (30% ether in pentane , $R_f = 0.53$), followed by bulb-to-bulb distillation (54−55 °C/0.3 mbar), 67% yield. The product is a colorless oil which rapidly turns orange at room temperature. ^{1}H NMR: δ 9.85 (t, $J = 2.0$, 1H), 7.35−7.42 (m, 2H), 7.27−7.32 (m, 3H), 3.16−3.26 (m, 1H), 2.69 (ddd, $J = 2.0, 7.6, 16.6$, 1H), 2.59 (ddd, $J = 2.0, 6.4, 16.6$, 1H), 1.33 (d, $J = 6.8$, 3H). ^{13}C NMR: δ 201.2, 131.8, 128.4, 128.3, 128.2, 128.1, 123.5, 92.3, 81.9, 50.2, 21.4, 21.2. IR (neat): 2230 ($C\equiv C$), 1730 ($C=O$) cm^{-1}. HRMS: Calcd for $C_{12}H_{12}O$: 172.089. Found: 172.088.

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Supporting Information Available: NMR (^{1}H and ^{13}C) spectra for new substances which were not characterized by combustion analysis (14 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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[33] Jeffery, T. *Synthesis* **1987**, 70.

[34] Boronoeva, T. R.; Belyaev, N. N.; Stadnichuk, M. D.; Petrov, A. A. *Zh. Obshch. Khim.* **1974**, *44(9)*, 1949.