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ORGANOCOPPER-IODOSILANE COMBINATIONS IN CONJUGATE ADDITIONS

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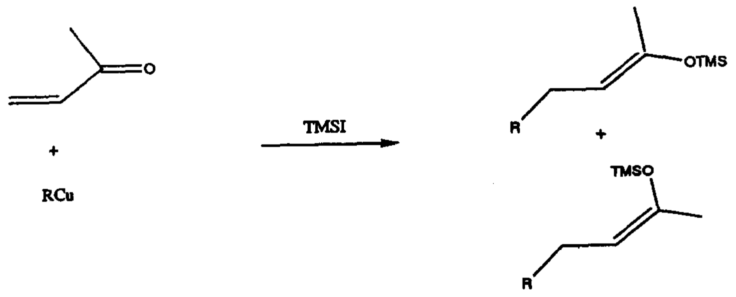
Abstract - This paper concerns new possibilities opened by the addition of (mono)organocopper compounds and iodotrimethylsilane (TMSI) to α,β-unsaturated ketones and esters giving the silyl enol ethers and ketene acetals, respectively. We demonstrate the homogeneous addition of methylcopper-tributylphosphine-iodotrimethylsilane to methyl cinnamate, the use of organocopper-bromotrimethylsilane combinations, the dominating formation of Z-silyl enol ethers on conjugate addition of methyl- and butylcopper/TMSI to benzalacetone, and the formation of silyl enol ethers in other additions of organocopper compounds and TMSX to conjugated ketones. The Z-selectivity for addition to benzalacetone corresponds to *s-cis* conformations in π-complexes between copper(I) chloride and 1-penten-3-one or 3-buten-2-one. The stereoselectivity could support a reaction path via π-complexes between organocopper-iodotrimethylsilane complexes and *s-cis* conformers of the substrates.

Very recently we reported that organocopper compounds and iodotrimethylsilane add to unsaturated ketones and esters giving silyl enol ethers/ketene acetals of the conjugate adducts in high yields.[1] We now briefly describe some additional possibilities in this field: utilisation of the methylcopper/tributylphosphine/iodotrimethylsilane combination, the use of bromotrimethylsilane, the Z selectivity in the addition of methyl- and butylcopper/TMSI to benzalacetone as well as halosilane-promoted organocopper additions to 2-cyclopentenone and 5-methyl-2-cyclohexenone. The work was done in the perspective of recent reports on conjugate addition of organocopper compounds with chlorotrimethylsilane/LiI alone[2] and with additives such as HMPA, 4-dimethylaminopyridine[3] or TMEDA.[4]



RESULTS

We have tested some variations of the methylcopper addition to cinnamates under conditions chosen for the *ranking of rates*, namely for 2 h at 0°C (cf. ref. 1, Table 2). Methylcopper is soluble in tributylphosphine and the conjugate addition of methylcopper/iodotrimethylsilane/LiI to methyl cinnamate could be performed in homogeneous ether solution with three molar equivalents of tributylphosphine giving 85 % yield, in comparison with 39 % yield without phosphine. The solution turned yellow on addition of the substrate; the colour, which might be due to a π-complex, gradually faded as the conjugate addition proceeded.

NMR spectra of reaction mixtures from methylcopper/TMSI additions to methyl cinnamate in the absence of lithium iodide and without tributylphosphine showed a strong dominance of the Z-trimethylsilyl ketal. Reaction in the presence of lithium iodide gave comparable amounts of E- and Z-isomers. The assignments are based on ^{13}C - ^{1}H-correlated 2D-spectra and literature analogies.[5]

The use of bromotrimethylsilane in the addition of methylcopper - dimethyl sulfide (DMS) reagent to benzyl cinnamate gave a 19 % yield, whereas iodotrimethylsilane gave 32 % yield under the same standard conditions. In these reactions the primary methyl trimethylsilyl ketene acetals were hydrolysed during work-up.

Table 1. Yields of conjugate adducts from additions of methylcopper to methyl cinnamate (or benzyl cinnamate) in ether at 0°C interrupted after 2 h as determined from NMR spectra of chromatographed products after hydrolysis. Compare Ref. 1, Table 2.

Reagents	Yields
TMSI, Bu_3P, LiI	85
TMSI, LiI[1]	39
TMSI, LiI, DMS; benzyl cinnamate	32
TMSBr, LiI, DMS; benzyl cinnamate	19

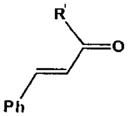
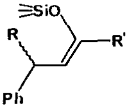
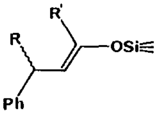
We have also checked the formation of silyl enol ethers in the conjugate addition of methylcopper/TMSI to benzalacetone, where excess TMSI was destroyed with pyridine or 4-dimethylaminopyridine to minimize hydrolysis of the silyl enol ethers. The configurations of the enol ethers were checked by NOE experiments. In all experiments, the Z-form of the silyl enol ether dominated. The best ratio, ca 5/1, was obtained in dichloromethane at -78 °C with lithium iodide-free methyl copper. However, here the change in the presence of lithium iodide was moderate. The addition of butylcopper-iodotrimethylsilane to benzalacetone also gave predominantly the Z isomer (ratio 7/1), whereas phenylcopper gave comparable amounts of E- and Z-isomers. The formation of silyl enol ethers is summarised in Table 2.

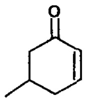
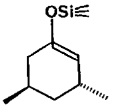
We have also checked addition of methylcopper to 5-methyl-2-cyclohexenone and of butylcopper to 2-cyclopentenone. The additions were fast, the yields good and often bromotrimethylsilane or chlorotrimethylsilane/lithium iodide provided sufficient activation. We observed some formation of 1,2-adducts and sometimes isomerisation of the primary silyl enol ethers during work-up. The *trans* adduct was favoured in the addition to 5-methyl-2-cyclohexenone (*trans/cis*-ratio ca 5/1).

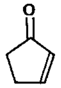
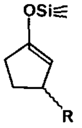
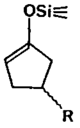
DISCUSSION

The direct iodosilane-promoted conjugate addition of organocopper compounds opens some new synthetic possibilities since the reagents should be less basic than the lithium diorganocuprates. The direct reaction between organocopper

Table 2. Typical isolated yields of *Z*- and *E*- silyl enol ethers from addition of organocopper compounds to different ketones in ether or dichloromethane* in the presence of halotrimethylsilane (TMSX).

	**RCu + TMSX**	 **Z**	**:**	 **E**	
R' = Me	MeCu, (X = I, 2 eq.) 0° C (4.5 h)	5	:	1	(68 %)
R' = Me	MeCu* (-LiI), (X = I, 2 eq.) -78° C (4.5 h)	5.1	:	1	(62 %)
R' = Me	PhCu, (X = I, 2 eq.) -78° C (5 min)→0° C (2 h)	1	:	1	(91 %)
R' = Me	BuCu, (X = I, 2 eq.) -78° C (45 min)→0° C (2 h)	7	:	1	(90 %)
R' = Ph	MeCu*DMS, (X = I, 1.7 eq.) -78° C→-30° C (4.5 h)	5	:	1	(49 %)

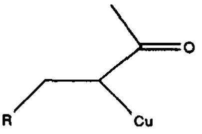
	MeCu, (X = Cl, 2.5 eq.) 0°C (30 min)	 *trans/cis:* 5/1	(95 %)

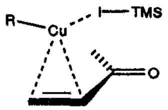
				
	BuCu, (X = Br, 2.0 eq.) -78° C (5 min)→0° C (25 min)	2.0	(92 %)	1.0
	BuCu, (X = I, 1.5 eq.) -78° C (1 h 40 min)	8.1	(68 %)	1.0
	BuCu, (X = I, 2.0 eq.) -78° C (1 h 40 min)	8.0	(70 %)	1.0
	BuCu, (X = I, 1.25 eq.) -78° C (1 min)→+4° C (2.5 h)	1.0	(87 %)	1.0
	BuCu, (X = I, 1.25 eq.) -78° C (2.5 h)	5.7	(86 %)	1.0

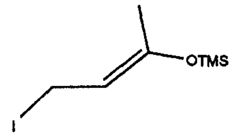
compound, iodosilane (or bromosilane and perhaps chlorosilane) and unsaturated compound also without lithium halide raises new mechanistic questions.

The net result is the attachment of the carbon from the soft copper to the soft β-position of the enone/enoate, the attachment of the hard silicon to oxygen and the favourable elimination of copper iodide. The activating effect of the halosilane is stronger than that of lithium iodide. The organocopper compound may be "activated" by complex formation with the halosilane, strongest by the iodosilane, presumably via the halogen. We have observed an analogous complexation between lithium methyl(2-thienyl)cuprate and TMSCl by NMR spectroscopy.[2] The complexation may increase the nucleophilic character of the carbon attached to copper, it may also affect the interaction between copper and the carbon-carbon double bond in π-complex formation. The organocopper-TMSI interaction could also lead to increased electrophilicity of the silicon.

As discussed earlier, a carbocupration reaction could lead to an α-cuprioketone, which could eliminate copper halide with formation of a silyl enol ether.[1] One could also consider a more or less concerted (and stereoselective) formation of product directly from the π-complexes. π-Complexes between lithium organocuprates and unsaturated esters have been observed with NMR-spectroscopy.[2,6] At the other extreme, one could depict activation of the unsaturated carbonyl compounds via conjugate addition of iodotrimethylsilane to give the silyl enol ether of a β-iodoketone.[7] This is essentially an allylic iodide, which should react readily with organocopper compounds.





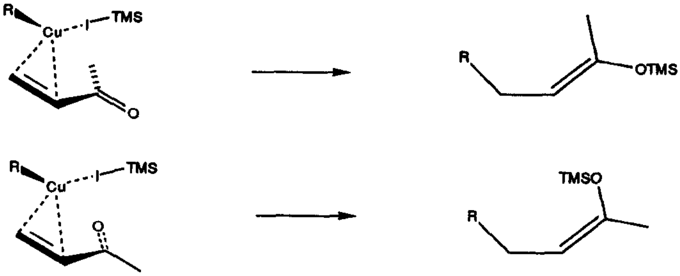


The Z-selectivity in the addition of methylcopper/TMSI to methyl cinnamate in the absence of lithium iodide is reported separately.[8] The dominance of the Z form of silyl enol ethers from benzalacetone with methylcopper/TMSI and with butylcopper/TMSI could be interpreted to proceed via a conjugate addition of iodotrimethylsilane to an *s-cis* form of the enone, followed by reaction of the allylic iodide with the organocopper. However, little is known about the stereoselectivity in conjugate addition of iodosilane.[7]

A third, and perhaps more important consideration is that π-complexes may derive from the *s-cis* or *s-trans* conformers of enones and enoates as shown by X-ray investigations of crystalline copper(I) chloride complexes of simple substrates: acrylaldehyde gives an *s-trans* complex,[9] 3-buten-2-one occurs both as *s-cis* and *s-trans* ligand[10] and 1-penten-3-one only as the *s-cis* conformer,[11] whereas the methyl acrylate in the polymeric complex is bound as the *s-trans* conformer.[12] The dominance of the Z-silyl enol ether from benzalacetone thus corresponds to the *s-cis* form in the π-complex of 1-pentene-3-one. Nakamura similarly has observed dominating formation of the Z-silyl enol ethers from methyl vinyl ketone with butylcopper/TMSCl/HMPA, whereas the unsaturated aldehydes gave the E-forms.[3] Some dominance of the Z-silyl enol ethers from ketones is evident also for the TMSCl/TMEDA-reaction.[4]

The Z-ketene acetal from methyl cinnamate, however, contrasts to the preferred conformation of methyl acrylate in the π-complex with CuCl. One could speculate that an interaction between silicon and the carbonyl oxygen could favour an *s-cis* conformation in a ternary complex between organocopper compound, TMSI and substrate.

Organocuprates have been considered to attack crowded esters in their *s-trans* conformation, whereas silylcuprates preferably attack similar substrates in their *s-cis* conformation.[13]



In our experiments, it seems probable that all three components - organocopper, halosilane and substrate - interact simultaneously in the critical steps. The possibility to study the homogeneous reaction in the presence of a phosphine gives hope for the further elucidation of the reaction and also for a closer study of the π-complexes and the stereoselectivity. It is also important to consider the role of lithium halide as well as the competition between the lithium halide- and halosilane-promoted reaction, the former possibly proceeding via the lithium enolates. Similarly, one should compare the present reactions with those involving HMPA, DMAP and TMEDA. Naturally, the new results should be compared with those in chlorotrimethylsilane-promoted conjugate addition with organocuprates,[14-17] and conjugate addition of organocopper compounds in the presence of lithium iodide.[18-20] The importance of lithium iodide in Gilman reagents has recently been demonstrated with NMR spectroscopy.[21] Copper iodide is a good leaving group as shown also in cross-couplings of arylcopper compounds with iodoarenes,[22] and formation of copper iodide may be important in the lithium iodide-promoted conjugate additions of organocopper compounds (and of organocuprates).

The present results can be explained by a complexation between iodotrimethylsilane and organocopper reagent leading to an activation of the organocopper compound. At the same time, formation of π-complexes is probable in view of the yellow colour in the methylcopper/phosphine addition. In our reactions, the halosilane seems to take the place of lithium in the lithium halide-promoted additions.

CONCLUSION

Our practical conclusion is that iodotrimethylsilane provides a good activation of organocopper compounds for conjugate addition. Bromotrimethylsilane and chlorotrimethylsilane/lithium iodide can be useful alternatives in reactive systems. Thus, the organocopper/halosilane combinations themselves provide good synthetic reagents, which may be less basic than the lithium organocuprates. Solubilisation of the organocopper compounds by tributylphosphine offers homogeneous reactions. The Z-selectivities in the formation of silyl enol ethers from ketones and esters may also open other possibilities for stereoselective synthesis, and may depend on a favoured π-complexation between substrate and reagent.

More work is needed to establish the roles of organocopper, halosilane and substrate and additives like phosphines, lithium halide etc. and the role of the π-complexes. Such work may provide a better understanding of organocopper reactions in general and also the relations between cross-coupling[22] and conjugate addition.

The present results are also relevant in connection with earlier observations on the favourable influence of lithium iodide on organocopper conjugate additions, particularly on reactive substrates. Previous hypotheses have been that the lithium iodide could solubilise the methyl copper.[18-20] Presumably iodide-copper interactions are important also in these systems.

EXPERIMENTAL

All reactions were performed under argon and with dried equipment. Ether was distilled from sodium benzophenone ketyl, and dichloromethane distilled from calcium hydride. Pyridine and tributylphosphine were distilled under nitrogen. We used commercial butyllithium in hexane, methyllithium in ether and phenyllithium in cyclohexane/ether (Aldrich). Copper iodide (Fluka) was purified via potassium diiodocuprate. Iodotrimethylsilane, bromotrimethylsilane (Janssen) and chlorotrimethylsilane (Fluka) were used as purchased. The products were checked with ^{1}H-NMR spectra ($CDCl_3$) on Bruker WH 270 or Varian XL 400 instruments.

General procedure for conjugate addition: The organocopper compounds were prepared from copper iodide, used in 10 % excess, and the appropriate organolithium compounds. In some reactions the organocopper compounds were allowed to settle, the supernatant was siphoned off and the solid organocopper compounds washed with some portions of ether to provide the "lithium iodide-free" organocopper compounds. The organocopper-dimethyl sulfide reagents were prepared with 0.6 ml of dimethyl sulfide per mmol copper iodide. The halotrimethylsilane was added to the organocopper compound followed by the unsaturated substrate. The reactions were followed by TLC. For isolation of silyl enol ethers we added pyridine (or 4-dimethylaminopyridine) to the reaction mixture to destroy excess of halotrimethylsilane. After treatment with water and drying the silyl enol ethers were isolated by flash chromatography or short path distillation. For direct preparation of the adduct ketones we quenched the reaction mixtures by adding concentrated aqueous ammonia-ammonium chloride at pH 8 and stirred until the enol ethers were hydrolysed.

Methylcopper additions

Methyl 3-phenylbutanoate. Tributylphosphine (7.5 mmol) was added to a slurry of methylcopper (2.5 mmol) in ether (10 ml) at 0 °C. When a homogeneous solution had formed, the temperature was lowered to -78 °C. Iodotrimethylsilane (5 mmol) was added, followed after 5 min. by methyl cinnamate (2 mmol) in ether (5 ml). The temperature was raised to 0 °C and the mixture stirred for 2 h. Quenching, drying and flash chromatography (ether/pentane, 7/3) gave methyl 3-phenylbutanoate (85 %) and unchanged methyl cinnamate (10 %). Reaction without tributylphosphine under the same conditions gave 3-phenylbutanoate (39 %) and starting material (56 %).

(*E*,*Z*)-1-Methoxy-1-trimethylsilyloxy-3-phenyl-butene. Iodotrimethylsilane (0.67 mmol) was added to a methylcopper slurry (0.67 mmol) in dichloromethane (3.3 ml) at -78 °C. After 5 min. methyl cinnamate (0.67 mmol) in dichloromethane (1.67 ml) was added and after another 5 min the temperature was raised to 0 °C. After 4 h at room temperature the solvent was evaporated under argon and the grey residue was extracted with dichloromethane-d_2. The NMR spectrum showed nearly equal amounts of the *Z*- and *E*-silyl ketene acetals. ^{1}H-NMR (CD_2Cl_2): (*E*)-1-Methoxy-1-trimethylsilyloxy-3-phenyl-1-butene δ 7.10(m, 5H, aromatic), 4.00(d, 1H, olefinic), 3.87(m, 1H, methine), 3.10(s, 3H, OMe), 1.40(d, 3H, Me), 0.15(s, 9H, TMS); (*Z*)-1-methoxy-1-trimethylsilyloxy-3-phenyl-1-butene δ 7.10(m, 5H, aromatic), 3.94(m, 1H, methine), 3.64(d, 1H, olefinic), 3.30(s, 3H, OMe), 1.38(d, 3H, Me), 0.12(s, 9H, TMS).

Benzyl 3-phenylbutanoate. Iodotrimethylsilane (5.0 mmol) was added to methylcopper-DMS (2.5 mmol) in ether (10 ml) at -78 °C. Benzyl cinnamate (2.0 mmol) in ether (10 ml) was added and after 5 min. the temperature raised to 0 °C and the mixture stirred for 2 h. Hydrolytic work-up and flash chromatography (ether/-pentane, 15/85) gave benzyl 3-phenylbutanoate (32 %) and starting material (60 %). Bromotrimethylsilane under the same conditions gave the conjugate adduct (19 %) and starting material (76 %). ^{1}H-NMR: δ 7.35(m, 10H), 5.03(s, 2H), 3.27(m, 1H), 2.69(dd, 1H), 2.65(dd, 1H), 1.30(d, 3H).

4-Phenyl-(*E*,*Z*)-2-trimethylsilyloxy-2-pentene. Iodotrimethylsilane (4.0 mmol) was added to methylcopper (2.5 mmol) in ether (10 ml) at 0 °C. After 5 min. benzalacetone (2 mmol) in ether (10 ml) was added. After 4.5 h. the reaction was complete and pyridine (or 4-dimethylaminopyridine, 2 mmol) was added and the mixture stirred overnight. Treatment with water, drying and flash chromatography (ether/pentane, 5/95) gave 0.320 g (68 %) of a 83:17 mixture of *Z*- and *E*-silyl enol ethers and silyl ether of the 1,2-adduct (0.066 g, 14 %). The *Z*- and *E*-silyl enol ethers were confirmed with NOE-experiments. Reaction in ether at 0 °C gave a ratio *Z*/*E*/1,2-adduct 5/1/1. Reaction in dichloromethane at -78 °C without lithium iodide gave a ratio *Z*/*E*/1,2-adduct 5.1/1/0.5. ^{1}H-NMR: 4-Phenyl-(*Z*)-2-trimethylsilyloxy-2-pentene δ 7.20(m, 5H), 4.61(dq, 1H, olefinic, J = 9, 1 Hz), 3.79(m, 1H), 1.79(d, 3H, J = 1 Hz), 1.30(d, 3H, CH$_3$), 0.18(s, 9H); (4-phenyl-(*E*)-2-trimethylsilyloxy-2-pentene) δ 7.20(m, 5H), 4.84(dq, 1H, olefinic, J = 9, 1 Hz), 3.49(m, 1H), 1.77(d, 3H, J = 1 Hz), 1.34(d, 3H, CH$_3$), 0.18(s, 9H).

1,3-Diphenyl-(*E*,*Z*)-1-trimethylsilyloxy-1-butene. Iodotrimethylsilane (4.0 mmol) was added to a slurry of methylcopper-dimethyl sulfide reagent (2.5 mmol) prepared at -78 °C in dichloromethane (10 ml). After 5 min. 1,3-diphenyl-2-propenone (2.3 mmol) in dichloromethane (10 ml) was added. The temperature was slowly raised to -30 °C and after 4.5 h. pyridine (2 mmol) was added. The temperature was raised and the mixture stirred for another 2 h. at room temperature. Work-up with water and flash chromatography (ether/pentane, 2/98) gave 0.330 g (total yield 49 %) of a 5/1 mixture of *Z*- and *E*-silyl enol ethers (80 %), silyl ether of 1,2-adduct (15 %) and hydrolysed silyl enol ether (5 %). ^{1}H-NMR: 1,3-Diphenyl-(*Z*)-1-trimethylsilyloxy-1-butene δ 7.90-7.20(m, 10H, aromatic), 5.39(d, 1H, olefinic, J = 9 Hz), 3.98(m, 1H, methine), 1.45(d, 3H, Me), 0.10(s, 9H, TMS); 1,3-diphenyl-(*E*)-1-trimethylsilyloxy-1-butene δ 7.90-7.20(m, 10H, aromatic), 5.23(d, 1H, olefinic, J = 9 Hz), 3.50(m, 1H, methine), 1.38(d, 3H, Me), 0.10(s, 9H, TMS). Quenching of the crude reaction mixture from the preparation above and flash chromatography (ether/pentane, 5/95) gave 1,3-diphenyl-1-butanone (82 %) m.p. 71.5-73.0 °C. ^{1}H-NMR: δ 7.90-7.10(m, 10H, aromatic), 3.50(m, 1H), 3.28(dd, 1H), 3.18(dd, 1H), 1.35(d, 3H). IR(KBr): 1670 cm^{-1}.

3,5-Dimethyl-1-trimethylsilyloxy-1-cyclohexene. Chlorotrimethylsilane (5.0 mmol) was added to methylcopper (2.5 mmol) prepared at 0 °C in ether (10 ml). After 5 min. freshly distilled 5-methyl-2-cyclohexene-1-one (2.0 mmol) in ether (10 ml) was added. After 30 min. pyridine (5 mmol) was added and the reaction mixture stirred over night. Treatment with water (5 ml), drying and flash chromatography (pentane) gave 3,5-dimethyl-1-trimethylsilyloxy-1-cyclohexene (95 %) as a 5/1 *trans*/*cis* mixture as determined from NMR spectra. ^{1}H-NMR: δ 4.77(d, H, olefinic in *trans*, J = 4 Hz), 4.70(broad s, 1H, olefinic in *cis*), 2.30(broad, 1H), 2.10-1.85(m, 2H), 1.67(m, 2H), 1.30(m, 2H), 0.97(d, 3H), 0.95 (d, 3H), 0.16(s, 9H). Acidic hydrolysis and flash chromatography (ether/pentane, 2/8) gave 3,5-dimethylcyclohexanone with a *cis*/*trans* ratio 5/1.

Butylcopper additions

4-Phenyl-(*E*,*Z*)-2-trimethylsilyloxy-2-octene. Iodotrimethylsilane (10.0 mmol) was added to a butylcopper slurry (6.25 mmol) in ether (20 ml) at -78 °C. After 5 min. benzalacetone (5.0 mmol) in ether (10 ml) was added and the mixture was stirred for 45 min. Pyridine (6 mmol) was added and the temperature was raised to 0 °C and the mixture stirred for another 2 h. Water (5 ml) was added and after drying and flash chromatography (ether/pentane, 5/95) gave 1.24 g (90 %) of *Z*- and *E*-silyl enol ethers (in a ratio 7/1) and silyl ether of the 1,2-adduct (1 %). ^{1}H-NMR: 4-Phenyl-(*Z*)-2-trimethylsilyloxy-2-octene δ 7.20(m, 5H, aromatic), 4.60(dq, 1H, olefinic, J = 9, 1 Hz), 3.60(m, 1H), 1.78(d, 3H, J = 1 Hz), 1.60(m, 2H), 1.30(m, 4H), 0.88(t, 3H), 0.18(s, 9H); 4-phenyl-(*E*)-2-trimethylsilyloxy-2-octene δ 7.20(m, 5H, aromatic), 4.85(dq, 1H, olefinic, J =9, 1 Hz), 3.28(m, 1H), 1.74(d, 3H, J = 1 Hz), 1.60(m, 2H), 1.30(m, 4H), 0.88(t, 3H), 0.18(s, 9H). Quenching of the crude reaction mixture from the preparation above and flash chromatography (ether/pentane, 15/85) gave 4-phenyl-2-octanone (93 %). ^{1}H-NMR: δ 7.29-7.13(m, 5H), 3.11(m, 1H), 2.70(d, 2H), 1.99(s, 3H), 1.58(m, 2H), 1.2(m, 4H), 0.82(t, 3H).

3-Butyl-1-trimethylsilyloxy-1-cyclopentene. Bromotrimethylsilane (10.0 mmol) was added to butylcopper (6.25 mmol) in ether (20 ml) at -78 °C. After 5 min. 2-cyclopentenone (5.0 mmol) in ether (10 ml) was added and the temperature raised to 0 °C. After 25 min. pyridine was added and the reaction mixture stirred over night. Work-up with water (5 ml), drying and flash chromatography (pentane) gave 3-butyl-1-trimethylsilyloxy-1-cyclopentene (62 %) and 4-butyl-1-trimethylsilyloxy-1-cyclopentene (30 %). ^{1}H-NMR: δ 4.63(d, 1H, olefinic, J = 1.5 Hz), 2.65-1.80(m, 5H, ring protons), 1.50-1.15(m, 6H, side chain-CH_2-), 0.90(t, 3H), 0.20(s, 9H). The olefinic proton in 4-butyl-1-trimethylsilyloxy-1-cyclopentene can be identified as a triplet at 4,57 ppm. Acidic hydrolysis of the silyl enol ether mixture gave after flash chromatography (ether/pentane, 1/9) 3-butyl-1-cyclopentanone (96 %). ^{1}H-NMR: δ 2.50-2.10(m, 5H), 1.80(m, 1H), 1.60-1.20(m, 7H), 0.90(t, 3H).

Phenylcopper addition

4,4-Diphenyl-(*E*,*Z*)-1-trimethylsilyloxy-2-butene. Iodotrimethylsilane (10.0 mmol) was added to a phenylcopper slurry (6.25 mmol) in ether (20 ml) at -78 °C. After 5 min. benzalacetone (5.0 mmol) in ether (10 ml) was added and after another 5 min. the temperature was raised to 0 °C. When the starting material was totally consumed (2 h.) pyridine was added and the reaction mixture stirred over night. Treatment with water (5 ml) drying and flash chromatography (pentane) gave *E*- and *Z*-silyl enol ethers (91 %) (ratio 1/1) and silyl ether of the 1,2-adduct (1 %). ^{1}H-NMR: 4,4-Diphenyl-(*E*)-1-trimethylsilyloxy-2-butene δ 7.20(m, 10H, aromatic), 5.16(d, 1H, methine, J = 9 Hz), 4.72(d, 1H, olefinic, J = 9 Hz), 1.82(s, 3H), 0.18(s, 9H); 4,4-diphenyl-(*Z*)-1-trimethylsilyloxy-2-butene δ 7.20 (m, 10H, aromatic), 4.98(d, 2H, J = 9 Hz), 5.06(d, 2H, J = 9 Hz), 1.87(s, 3H), 0.12(s, 9H). Acidic hydrolysis of the silyl enol ether mixture gave after flash chromatography (ether/pentane, 1/9) 4,4-diphenyl-2-butanone (98 %).

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