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CHLORO- AND IODOTRIMETHYLSILANE-ACTIVATED ADDITIONS OF ORGANOCOPPER COMPOUNDS TO ENONES AND ENOATES

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Abstract - Organocopper compounds add to enones and enoates in the presence of chlorotrimethylsilane in ether giving the conjugate adducts in preparatively useful yields *via* the silyl enol ethers. Presence of lithium iodide is important and excess of chlorotrimethylsilane accelerates the reactions.

The combination of organocopper compound, iodotrimethylsilane and dimethyl sulfide gave faster reactions and very high yields, particularly in dichloromethane, where the reaction mixtures gradually became homogeneous.

This paper concerns conjugate addition of alkyl- and arylcopper compounds, activated by chlorotrimethylsilane (TMSCl), to some enones and enoates in ether. It also includes a study of additions with TMSI in ether, THF and dichloromethane and with TMSCl in the latter solvents.

Organocopper compounds (R-Cu) are interesting reagents for formation of carbon-carbon bonds. The low solubility has limited a more widespread use of alkyl-, alkenyl-, and arylcopper compounds in organic synthesis. The soluble lithium diorganocuprates dominate as reagents for conjugate addition. Organocopper compounds sometimes give conjugate addition in the presence of lithium iodide;[1] in our experience methylcopper/LiI adds to nitrostyrene[2] and 2-pyridylcopper-tributylphosphine/LiI adds to enones.[3]

Nakamura and co-workers[4] recently reported conjugate additions of chlorotrimethylsilane-activated butylcopper in THF in the presence of HMPA or 4-dimethylaminopyridine. They also described conjugate addition of lithium diorganocuprates activated by TMSCl/HMPA, utilising both groups in the cuprate. Johnson and Marren used the combination TMSCl/TMEDA in THF to promote addition of some organocopper compounds to enones.[5]

The use of TMSCl for trapping of the enolates from lithium organocuprate additions as silyl ethers has been popular for some years.[6] The report on the favourable influence of TMSCl on addition of lithium organocuprates and also of methylcopper to α,β-unsaturated aldehydes by Normant *et al.*[7] has been followed by good results for other α,β-unsaturated carbonyl compounds by Corey and Boaz[8] and by Alexakis, Berlan and Besace.[9] We have recently used chlorotrimethylsilane for activation of mixed lithium organo(2-thienyl)cuprates and then also observed new reagent species with NMR spectroscopy, as well as activation of 2-thienylcopper itself.[10]

RESULTS

Some organocopper compounds, namely butyl-, phenyl-, methyl- and 2-thienylcopper, were prepared from the corresponding organolithium compounds and copper(I) iodide in ether. They were reacted with benzalacetone, 2-cyclohexenone, methyl cinnamate or benzyl crotonate in the presence of TMSCl to give primarily the silyl enol ethers of the conjugate adducts, hydrolysed during work-up. Additional TMSCl increased the rates but not the yields.

Typically two equivalents of TMSCl were added to the cold organocopper reagent (containing lithium iodide). One equivalent of substrate was then added and the temperature allowed to rise gradually. The results are summarised in Table 1 which also contains some data for the TMSX/dimethyl sulfide/dichloromethane system described below.

Table 1. Typical yields (%) of conjugate adducts (after hydrolysis of silyl enol ethers) from addition of organocopper compounds to different substrates in ether in the presence of chlorotrimethylsilane. Yields (a) denote reactions with TMSCl/dichloromethane, and yields (b) TMSI/dichloromethane. Compare Table 2 for additions of methylcopper to methyl cinnamate.

Substrate	Organocopper			
	MeCu	PhCu	BuCu	2-ThCu
Benzalacetone	75, 97^a, 100^b	51	64	60
2-Cyclohexenone	38, 65^a	60	79	81
Methyl cinnamate	75, 92^b	95	33, 86^b	12
Benzyl crotonate	76^a	43	94^b	16, 62^a

The yields with TMSCl in ether are comparable to or better than those obtained in corresponding reactions with lithium organo(2-thienyl)cuprates (LiRThCu), which selectively transfer the group R.[11]

In some experiments methylcopper was washed with ether to remove most of the lithium iodide. The washed methylcopper added much slower to benzalacetone even in the presence of TMSCl. Thus the lithium iodide seems important for the reaction.

Since the presence of lithium iodide and chlorotrimethylsilane could lead to formation of iodotrimethylsilane we tested the influence of TMSI on the addition of methylcopper to methyl cinnamate in different solvents and soon found a remarkable acceleration. Encouraged by results in parallel NMR studies[12] we used methylcopper prepared from the dimethyl sulfide complex of copper iodide in dichloromethane, THF and ether in the conjugate additions. With dichloromethane or THF and TMSI the reaction mixtures then became practically homogeneous as the reaction proceeded.

Methylcopper/LiI in dichloromethane added fast and in very high yields, 80-90%, to methyl cinnamate both with TMSCl and TMSI. For comparison reactions in ether and THF were conducted at the same conditions of temperature and time, showing in all cases faster reactions with iodotrimethylsilane than with chlorotrimethylsilane (Table 2). Some values for these systems are included also in Table 1.

We also checked the primary formation of the enol ethers. In experiments with stoichiometric amounts of methylcopper/LiI, TMSX/dichloromethane and benzalacetone or methyl cinnamate the solvent was directly evaporated from the reaction mixture and the residues extracted with toluene-d_8. Gas chromatograms and mass and NMR spectra were recorded for the extracts showing the formation of comparable amounts of Z and E forms of the silyl enol ethers both from benzalacetone and from methyl cinnamate.

Table 2. Yields of conjugate adducts from additions of methylcopper/TMSX to methyl cinnamate at 0 °C for 2 h (determined from NMR spectra of chromatographed products, remaining methyl cinnamate in parenthesis). The reactions were interrupted before completion to permit a ranking of the rates. Details are given in the experimental part.

Solvent	TMSCl	TMSI
Dichloromethane	81 (12)	92 (0)
Ether	4 (88)	39 (56)
Ether, excl. LiI		53 (42)
Tetrahydrofuran (THF)	1 (92)	78 (21) (96 % after 6h)
THF, excl. LiI		62 (33)

DISCUSSION

The present results show that the TMSCl-promoted conjugate addition of organocopper compounds can be carried out in ether without addition of HMPA, 4-dimethylaminopyridine or TMEDA, provided lithium iodide is present in the medium. The use of organocopper compound and iodotrimethylsilane in dichloromethane (or THF) offers considerable improvements in rates and yields. Here the lithium iodide is less important for the reaction. Thus TMSI formed from TMSCl and lithium iodide may play an important role also in the TMSCl reactions.

The total stoichiometry of the addition of RCu/TMSX to enones/enoates (eqn *1*) is more favourable than that of lithium organocuprate additions (eqn *2*), since all the organometallic reagent is consumed. The driving force may also be more favourable and resembles that in the cross-coupling of organocopper compounds with organic halides (eqns *3* and *4*).

$$\mathrm{R{-}Cu + C{=}C{-}C{=}O + TMSX \longrightarrow R{-}C{-}C{=}C{-}O{-}TMS + CuX} \qquad (1)$$

$$\mathrm{LiR_2Cu + C{=}C{-}C{=}O \longrightarrow R{-}C{-}C{=}C{-}O{-}Li \;\; + RCu \xrightarrow{TMSX}}$$

$$\mathrm{R{-}C{-}C{=}C{-}O{-}TMS + LiX} \qquad (2)$$

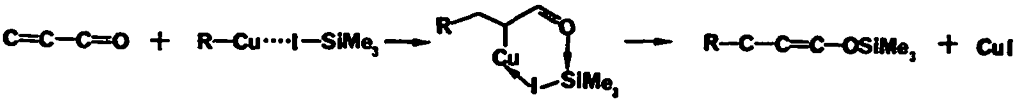
$$\mathrm{R{-}Cu + R^1X \longrightarrow R{-}R^1 + CuX} \qquad (3)$$

$$\mathrm{R{-}Cu + TMSX \longrightarrow R{-}TMS + CuX} \qquad (4)$$

The activations of organocopper compounds and of lithium diorganocuprates by halotrimethylsilanes may have some aspects in common. The addition of an organocopper compound to an enone stoichiometrically should produce a copper(I) enolate or an α-cuprio ketone (cf. Berlan *et al.*[13]). So far we have not seen any accumulation of copper enolate/α-cuprio ketone; the silyl enol ethers seem to be formed directly.

For a provisional mechanistic discussion we may consider interactions between the organocopper compound, the halosilane and the substrate. The three-component-reaction between enone, organocopper compound and halotrimethylsilane proceeds much faster than the direct coupling between organocopper and halosilane (eqn *4*) and only small amounts of R-TMS are observed. A closer examination could include interactions between copper and the halogen in TMSX, between copper and carbon-carbon double bond and between silicon and carbonyl oxygen. One may also consider such interactions in a ternary complex between organocopper compound, halosilane and substrate. The final result is the attachment of the organic group from the "soft copper" to the "soft" end of the enone system and of the "hard" silicon to the "hard" oxygen atom.

Our earlier NMR data indicated an interaction between lithium organo(2-thienyl)-cuprate and chlorotrimethylsilane.[10] It is therefore tempting to postulate the primary formation of a reactive complex between the organocopper compound and the iodosilane (eqn 5). A "3,4-addition" of such a reagent would give an α-cuprioketone/iodosilane complex favourable for *cis*-elimination of copper iodide and formation of silyl enol ether by a cyclic mechanism. The addition is probably preceeded by π-complex formation as established by recent NMR studies of lithium diorganocuprates and enoates.[14] X-Ray studies have demonstrated the structures of weak π-complexes between some enones and copper(I) chloride, with the copper almost equidistant from the α- and β-carbons.[15-17]



(5)

The interaction between halosilanes and enones has been considered weak.[4,8] Nevertheless the mild conjugate addition of TMSI itself to enones and enoates giving reactive allylic iodo-silyl enol ethers (or β-iodoketones)[18] could provide another pathway giving reactive silyl enol ethers of β-iodocarbonyl compounds, which might then react with the organocopper compound (eqn *6*).

$$\mathrm{Me_3Si{-}I} + \mathrm{C{=}C{-}C{=}O} \longrightarrow \mathrm{I{-}C{-}C{=}C{-}O{-}SiMe_3} \xrightarrow{\mathrm{RCu}} \mathrm{R{-}C{-}C{=}C{-}O{-}SiMe_3} + \mathrm{CuI} \qquad (6)$$

The use of halosilanes to activate the organocopper compounds provides new possibilities since the organocopper compounds have interesting advantages in low basicity and perhaps higher selectivity than the organocuprates. Lithium iodide seems less important in the TMSI-activated reactions than in those with TMSCl. The role of lithium salts should be considered further (cf. different preparations of lithium diorganocuprate described by Bertz *et al.*[19]), as should the importance of dimethyl sulfide and other soft ligands. We are exploiting the new possibilities and hope to report the parallel NMR study shortly.[12]

EXPERIMENTAL

All reactions were performed under argon and with dried equipment. Dichloromethane was distilled from calcium hydride. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. We used commercial butyllithium in hexane, methyllithium in ether, and phenyllithium in benzene (Aldrich). 2-Cyclohexenone was distilled and chromatographed immediately before use.

All products were checked or characterized by gas chromatography (HP 5880, OV 17), gas chromatography/mass spectrometry (Finnigan 1020, E.I. 70 eV, capillary column), ^{1}H-NMR (Bruker WH 270 or Varian XL 400) and IR (Perkin Elmer 197).

General procedure for conjugate addition: The organocopper compounds were prepared from copper(I) iodide (Fluka, 10 % excess), purified *via* potassium diiodocuprate, and the appropriate organolithium compound. The TMSX was added, the mixture stirred for some minutes and a solution of the substrate was added. The reactions were followed with GC or TLC. Generally the reaction mixtures were hydrolyzed by addition of aqueous ammonia/ammonium chloride at pH 8, extracted three times with ether and the extract dried over sodium sulphate. The organocopper-DMS reagents were prepared with 0.6 ml dimethyl sulfide per mmol CuI.

Methylcopper additions

4-Phenyl-2-pentanone. Chlorotrimethylsilane (12 mmol) was added to a yellow slurry of methylcopper (1.5 mmol) in ether (10 ml) at 0 °C. After 5 min. benzalacetone (1 mmol) in 5 ml ether was added. After 1 h. the mixture was allowed to reach room temperature and then quenched after 8 h. Flash chromatography (silica gel, ether/pentane, 1/9) gave 4-phenyl-2-pentanone (75 %) and starting material (18 %). The corresponding addition of methylcopper/DMS reagent in dichloromethane (prepared at -78 °C) with 4 eq. TMSCl or TMSI for 5 h. gave 97-100 % yield. Reaction with washed methylcopper/TMSCl in ether for 9 h. gave a 38 % yield, with most of the benzalacetone unchanged.

3-Methylcyclohexanone. Chlorotrimethylsilane (8 mmol) was added at 0 °C to methylcopper-DMS (2.5 mmol) in dichloromethane (10 ml) prepared at -78 °C. After 5 min. stirring at 0 °C freshly purified 2-cyclohexenone (2 mmol) in dichloromethane (5 ml) was added and the grey slurry was quenched after 100 min. Drying and flash chromatography (ether/pentane, 3/7) gave 3-methylcyclohexanone (65 %). NMR ($CDCl_3$): δ 2.45-2.17 (m, 3H), 2.14-1.80 (m, 4H), 1.78-1.61 (m, H), 1.43-1.26 (m, H), 1.05 (d, 3H). MS (*m/Z*): 112 (M^+, 31 %), 97, 69 (100 %), 56. IR (neat): 1700 cm^{-1}.

Methyl 3-phenylbutanoate (cf. Table 2). Halotrimethylsilane (5 mmol) was added to methylcopper-DMS (2.5 mmol), prepared at -78 °C with dry solvent (10 ml) and stirred for 20 min. Methyl cinnamate (2 mmol) in dry solvent (5 ml) was added at -78 °C, the temperature was raised to 0 °C and the mixture stirred for 2 h. and the reaction quenched. The best yield of methyl 3-phenylbutanoate (96%) was obtained with methylcopper/LiI and TMSI in THF at 0 °C after 6 h.

In parallel experiments we used methylcopper washed with ether or THF (4 x 10 ml) at 0 °C to remove lithium iodide. Flash chromatography did not separate the starting material and the conjugate adduct. Yields were therefore determined from NMR spectra of the chromatographed product and are given in Table 2. The highest reaction rates were observed in dichloromethane. The washings were treated with TMSI and methyl cinnamate but no addition product was detected. Thus only negligible amounts of methylcopper were lost in the washing.

In experiments with washed methylcopper in THF the TMSI attacked the solvent giving 1-iodo-4-trimethylsilyloxybutane; a considerable portion of the TMSI must have been consumed for ether cleavage. Very little iodo-trimethylsilyloxybutane was formed in the THF wash solution when substrate and TMSI were added. Obviously the lithium iodide slowed down the cleavage of THF.

Benzyl 3-methylbutanoate. Chlorotrimethylsilane (8 mmol) was added slowly to methylcopper-DMS (2.5 mmol) in dichloromethane (10 ml) at -78 °C. Benzyl crotonate (2 mmol) in dichloromethane (5 ml) was added. After 5 h. (4 h. at R.T.) the reaction was quenched and after flash chromatography (ether/pentane, 1/9) gave benzyl 3-methylbutanoate (76 %) and starting material (18 %). NMR ($CDCl_3$):

δ 7.35 (m, 5H), 5.10 (s, 2H), 2.25 (d, 2H), 2.12 (m, H), 0.95 (d, 6H). MS: 192 (M^+, 12%), 108, 91 (100 %), 85, 57. IR (neat): 1720 cm^{-1}.

Phenylcopper additions

4,4-Diphenyl-2-butanone. Chlorotrimethylsilane (4 mmol) was slowly added to a grey slurry of phenylcopper (2 mmol) prepared at 0 °C, in ether (10 ml). After 5 min. stirring at 0 °C benzalacetone (1.6 mmol), in 5 ml ether, was added. After 1 h. at 0 °C the mixture was allowed to reach room temperature and was then stirred for 5 h. Quenching and flash chromatography (ether/pentane, 1/9) gave 4,4-diphenyl-2-butanone (34 %) and its silyl enol ether. The silyl enol ether fraction was hydrolyzed with 2 M HCl and methanol bringing the total yield of 4,4-diphenyl-2-butanone to 51 %.

3-Phenylcyclohexanone. Chlorotrimethylsilane (5 mmol) was added slowly at -30 °C to phenylcopper (2.5 mmol) in ether (10 ml). Purified 2-cyclohexenone (2 mmol) in ether (3 ml) was added after 5 min. The temperature was raised to 0 °C and the reaction quenched after 3 h. Flash chromatography (ether/pentane, 3/7) gave 3-phenylcyclohexanone (60 %).

Methyl 3,3-diphenylpropanoate. Chlorotrimethylsilane (12 mmol) was added to a phenylcopper slurry (2 mmol) at 0 °C in ether (10 ml). Methyl cinnamate (1 mmol) in ether (5 ml) was added after 5 min. The mixture was quenched after 2 h. at 0 °C and 3 h. at R.T. Flash-chromatography (ether/pentane, 3/7) gave methyl 3,3-diphenylpropanoate (95 %), m.p. 143-145 °C.

Benzyl 3-phenylbutanoate. Chlorotrimethylsilane (30 mmol) was added to a phenylcopper-DMS slurry (3 mmol) in ether (10 ml) at 0 °C. After 5 min. benzyl crotonate (2.4 mmol) in ether (5 ml) was added and the mixture quenched after 12 h. at R.T. Flash chromatography (ether/pentane, 3/7) gave 3-phenyl-benzylbutanoate (43 %) and starting material (54 %). NMR ($CDCl_3$): δ 7.25 (m, 10H), 5.05 (s, 2H), 3.30 (m, H), 2.75 (dd dd, 2H), 1.30 (d, 3H). MS: 254 (M^+, 1 %), 163, 121 (100 %), 105, 91, 77 and 65. IR (neat): 1720 cm^{-1}.

Butylcopper additions

4-Phenyl-2-octanone. Chlorotrimethylsilane (2.5 mmol) was added to a slurry of butylcopper (1.25 mmol) in ether (5 ml) at -78 °C. Benzalacetone (1 mmol) in ether (5 ml) was added. After 35 min. the temperature had reached -35 °C. The temperature was then allowed to reach 0 °C. Quenching and workup gave 4-phenyl-2-octanone (64 %). NMR ($CDCl_3$): δ 7.29-7.14 (m, 5H), 3.10 (m, H), 2.70 (d, 2H), 1.99 (s, 3H), 1.58 (m, 2H), 1.2 (m, 4H), 0.82 (tr, 3H). MS: 204 (M^+, 6 %), 146, 117, 104, 91 (100 %), 77. IR (neat): 1700 cm^{-1}. Cf. ref. 20.

3-Butylcyclohexanone. Chlorotrimethylsilane (5 mmol) was added to a slurry of butylcopper (2.5 mmol) in ether (10 ml). 2-Cyclohexenone (2.5 mmol) in ether (5 ml) was added at -78 °C. The reaction was quenched after 3 h. and chromatographed (ether/pentane, 3/7) to give 3-butylcyclohexanone (79 %). NMR ($CDCl_3$): δ 2.5-1.6 (m, 6H), 1.30 (m, 8H), 0.9 (m, 4H). MS: 154 (M^+, 9 %), 111, 97 (100 %), 69, 55. IR (neat): 1705 cm^{-1}. Cf. ref. 21.

Methyl 3-phenylheptanoate. Chlorotrimethylsilane (4 mmol) was added to butylcopper (3 mmol) in ether (10 ml) at -78 °C. After 5 min. methyl cinnamate (2 mmol) in ether (5 ml) was added. The reaction was quenched after 4 h. at -78 °C and 6 h. at -35 °C. Flash chromatography (ether/pentane, 1/9) gave methyl 3-phenylheptanoate (33 %) and starting material (61 %). Several experiments with the TMSCl-ether system failed when the temperature was raised. Iodotrimethylsilane (3 mmol) and butylcopper-DMS (3 mmol) in dichloromethane for 1.5 H. at 0 °C gave 86 % yield; 6 % starting material remained. NMR ($CDCl_3$): δ 7.3-7.15 (m, 5H), 3.56 (s, 3H), 3.08 (m, H), 2.6 (dd dd, 2H), 1.74-1.55 (m, 2H), 1.40-1.02

(m, 4H), 0.82 (t, 3H). MS: 220 (M^+, 11 %), 160, 146, 121, 104, 91 (100 %), 77, 59. IR (neat): 1725 cm^{-1}.

Benzyl 3-methylheptanoate. Iodotrimethylsilane (3 mmol) was added to butylcopper-DMS (3 mmol) in dichloromethane (10 ml) at -78 °C. After 5 min. benzyl crotonate was added. The reaction was quenched after 1.5 h. at -78 °C and 20 min. at 0 °C. Flash chromatography (ether/pentane 1/9) gave benzyl 3-methylheptanoate (94 %) and starting material (4 %). NMR ($CDCl_3$): δ 7.38 (m, 5H), 5.12 (s, 2H), 2.30 (dd dd, 2H), 1.98 (m, H), 0.93 (d, 3H) and 0.87 (3H). MS: 234 (M^+, 2 %), 108, 91 (100 %). IR: 1725 cm^{-1}.

2-Thienylcopper additions

The thienylcopper-DMS reagent was prepared from thiophene (2.6 mmol) in ether (10 ml) and butyllithium (2.5 mmol) with stirring for 1 h. at 0 °C to give 2-thienyllithium. Copper(I) iodide (2.6 mmol) in dimethyl sulfide (2.2 ml) was added dropwise giving 2-thienylcopper as a yellow slurry.

4-Phenyl-4-(2-thienyl)-2-butanone. Chlorotrimethylsilane (10 mmol) was added to the slurry of thienylcopper-DMS (2.5 mmol) at 0 °C, followed by benzalacetone (2 mmol) in ether (5 ml). The reaction was quenched after totally 5 h. (1.5 h. at 0 °C). Flash chromatography (ether/pentane, 3/7) gave 4-phenyl-4-(2-thienyl)-2-butanone (60 %) and benzalacetone (12 %). NMR ($CDCl_3$): δ 7.25 (m, 5H), 7.11 (m, H), 6.90 (m, H), 6.80 (m, H), 4.83 (m, H), 3.19 (dd dd, 2H), 2.10 (s, 3H). MS: 230 (M^+, 22 %), 187, 173 (100 %), 129, 109, 103, 77. IR (neat): 1700 cm^{-1}.

3-(2-Thienyl)cyclohexanone. Chlorotrimethylsilane (6 mmol) was added to thienylcopper-DMS (3 mmol) at 0 °C, followed by 2-cyclohexanone (2 mmol) in ether (5 ml). The reaction was quenched after 8 h. at R.T. and on chromatography (ether/pentane, 3/7) gave 3-(2-thienyl)cyclohexanone (81 %) and 7 % of starting material. NMR ($CDCl_3$): δ 7.17 (m, H), 6.95 (m, H), 6.84 (m, H), 3.22 (m, H), 2.78 (m, H), 2.65-2.05 (m, 5H), 2.00-1.70 (m, 2H). MS: 180 (M^+, 42 %), 137, 123 (100 %), 110, 97. IR (neat): 1700 cm^{-1}. Cf. ref. 22.

Methyl 3-phenyl-3-(2-thienyl)propanoate. Chlorotrimethylsilane (10 mmol) was added to thienylcopper-DMS (3 mmol) at 0 °C followed by methyl cinnamate (2 mmol) in ether (5 ml). The reaction was quenched after 48 h. at room temperature and on flash chromatography (ether/pentane, 1/7) gave methyl 3-phenyl-3-(2-thienyl)-propanoate (12 %) and starting material (84 %). NMR ($CDCl_3$): δ 7.25 (m, 5H), 7.11 (m, H), 6.90 (m, H), 6.85 (m, H), 4.78 (m, H), 3.62 (s, 3H), 3.08 (dd dd, 2H). MS: 246 (M^+, 20 %), 186, 173 (100 %), 129, 103, 77. IR (neat): 1725 cm^{-1}.

Benzyl 3-(2-thienyl)-butanoate. Chlorotrimethylsilane (24 mmol) was added to a slurry of thienylcopper-DMS (2.5 mmol) in ether at 0 °C followed by benzyl crotonate (2 mmol) in ether (5 ml). Quenching after 12 h. at R.T. and after flash chromatography (ether/pentane, 1/9) gave a mixture of benzyl 3-(2-thienyl)-butanoate (16 %) and 71 % of starting material. The reaction with TMSCl in dichloromethane gave 62 % of the conjugate adduct (remaining starting material, 29 %, separated by short path distillation). NMR ($CDCl_3$): δ 7.31 (m, 5H), 7.10 (m, H), 6.88 (m, H), 6.81 (m, H), 5.08 (m, H), 3.62 (m, H), 2.79-2.57 (dd dd, 2H), 1.35 (d, 3H). MS: 260 (M^+, 2 %), 169, 127, 111, 91 (100 %). IR (neat): 1720 cm^{-1}.

Identification of silyl enol ethers

Methylcopper (0.67 mmol) was prepared in dichloromethane at -78 °C. An equivalent amount of TMSX (chloride or iodide, 0.67 mmol) was added followed by benzalacetone or methyl cinnamate (0.67 mmol) in dichloromethane (1.7 ml). The mixture was allowed to warm up, kept at room temperature for 7 h. and the solvent evaporated under argon. The residues were dissolved in toluene-d_8, the solutions filtered and the NMR spectra recorded; the spectral data will be reported separately.[12] Methyl cinnamate gave equal amounts of the Z and E forms of the silyl enol ether (1-methoxy-1-trimethylsilyloxy-3-phenyl-1-butene). Methyl additions to benzalacetone gave 2-silyloxy-4-phenyl-2-pentene with Z/E ratios of 1.6 and 1.2, on additions with TMSCl and TMSI, respectively.

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