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Preliminary communication

NMR studies of TMS-halide activated organocopper compounds

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Abstract

Conjugate addition to methyl cinnamate in the reactions with methylcopper and lithium dimethylcuprate activated by either trimethylchlorosilane (TMSCl) or trimethyliodosilane (TMSI) has been studied by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. In the presence of TMSI, methylcopper adds to methyl cinnamate. In the reactions with TMSCl, the LiI usually present from the preparation of the methylcopper is necessary for the reaction to take place, and thus the iodine seems to play an important role in the process. The presence of LiI also influences the *E*/*Z* selectivity; reactions with MeCu/TMSI, in the absence of LiI give exclusively the *Z* isomer of the silyl ketene acetal.

Several groups have recently reported improved methods for conjugate addition or organocopper compounds by activation of the copper compound with trimethylchlorosilane and/or an extra ligand such as HMPA. Corey and Boaz [1] and Alexakis, Berlan, and Besace [2] have reported that TMSCl facilitates the addition of lithium diorganocuprates to enones. Nakamura and co-workers have carried out TMSCl/HMPA or dimethylaminopyridine-promoted additions of lithium diorganocuprates ($LiBu_2Cu$ and $LiPh_2Cu$) and butylcopper to enones [3]. Johnson and Marren have added alkyl- and phenylcopper activated by TMEDA in THF to different enones [4].

We have recently reported an NMR study of the effects of TMSCl on the reactions of lithium methyl(2-thienyl)cuprate [5] and also showed that organocopper compounds, RCu, activated with TMSCl or TMSI add to enones and enoates in the absence of HMPA, DMAP, or TMEDA [6,7]. We now present results from NMR studies (^{1}H, ^{13}C, and ^{29}Si) or organocopper/TMSX systems, and the investigation of the influence of lithium iodide on the *E*/*Z* selectivity of the formed ketene acetals.

The NMR studies were performed in CD_2Cl_2 with a small amount of dimethyl sulfide (Me_2S) added to improve the solubility of the copper compound. Methyl-

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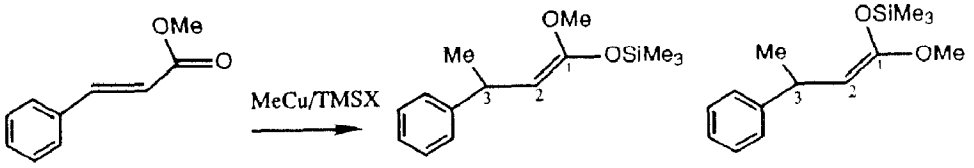
Table 1

Relevant NMR data for reagents and primary products in the reactions between MeCu/LiI/TMSX and methyl cinnamate



	1	2-*E*	2-*Z*
	^{1}H	^{13}C	^{29}Si
MeCu	-1.06	-7.7	-
TMSCl	0.42	3.27	31
TMSI	0.79	5.5	10.2
2-*E*[a]	2: 4.00	2: 92.2	
	3: 3.87	3: 37.1	
			ca 20
2-*Z*[a]	2: 3.64	2: 83.9	
	3: 3.94	3: 37.5	
			ca 20

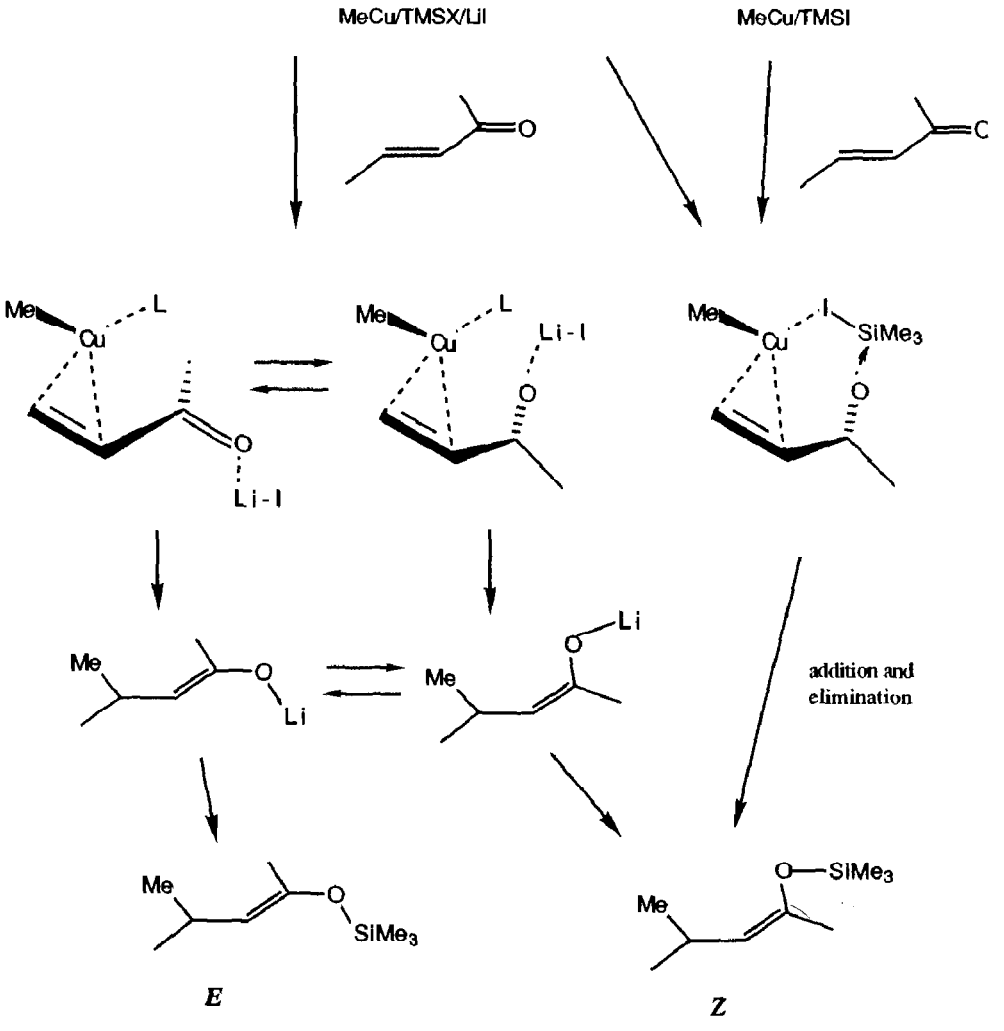
copper with one equivalent of lithium iodide remaining from the preparation, gives the ^{1}H NMR signal at -1.06 ppm and the ^{13}C signal at -7.7 ppm, both as a concentrated yellow suspension (1–2 *M*) and as a more dilute, homogeneous solution (ca. 0.1 *M*). Addition of TMSCl to a MeCu/LiI sample caused no significant change in the MeCu signals, but the signals (^{1}H, ^{13}C, and ^{29}Si) from the TMSCl decreased when the temperature was raised from -50 to $-10\,^{\circ}$C, and new ^{1}H, ^{13}C, and ^{29}Si signals at 0.75, 5.7, and 10.0 ppm, respectively, appeared. These new signals are practically identical to those from TMSI, which is evidently formed in the reaction mixture. In the absence of methylcopper, LiI and TMSCl form TMSI only extremely slowly. Addition of methyl cinnamate to the MeCu/LiI/TMSCl system caused a vigorous reaction even at $-78\,^{\circ}$C, and the silyl ketene acetals (both *E* and *Z* isomers) of methyl cinnamate were formed along with a white precipitate, probably copper(I) iodide or chloride. Significant peaks for the ketene acetals were seen at 92.2 and 83.9 ppm in the ^{13}C spectrum (C(2) of the two silyl ketene acetals) and a broad peak at ca. 20 ppm in the ^{29}Si spectrum (Me_3SiOC). See Table 1. Use of TMSI instead of TMSCl gave similar results, including a similar *E*/*Z* ratio, but the reaction was faster with TMSI than with TMSCl [6].

Similar results were obtained when MeCu/LiI/TMSCl was added to benzalacetone in ether.

Methylcopper free from LiI has a much lower solubility in CD_2Cl_2/Me_2S and no NMR signals could be detected. Addition of TMSCl gave rise to no signals other than those from TMSCl, and no reaction occurred when methyl cinnamate was

added. Addition of TMSI to a LiI-free sample of MeCu produced no NMR signals from MeCu, indicating that MeCu has a low solubility in this case also, but addition of methyl cinnamate resulted in a smooth conjugate addition to give exclusively the *Z*-isomer of the silyl ketene acetal. Hydrolysis of the reaction mixtures (MeCu/LiI/TMSX or MeCu/TMSI) with aqueous ammonia/ammonium chloride gave the product of conjugate adduct of a methyl group to methyl cinnamate (hydrolyzed silyl ketene acetals).

Lithium dimethylcuprate in CD_2Cl_2/Me_2S (1–2 *M*) reacts with TMSCl to form tetramethylsilane and methylcopper. At $-50\,^{\circ}C$ the reaction is very slow but at $-10\,^{\circ}C$ the coupling reaction is significant. The re-formed methylcopper adds to methyl cinnamate in the presence of an excess of TMSCl, but the reaction is much slower than the corresponding reaction with methylcopper formed directly from



(L = ligand; solvent, Li-I, or TMS halide)

Scheme 1

copper(I) iodide and methyllithium. Activation of re-formed butylcopper from $LiBu_2Cu$ by TMSCl/HMPA or DMAP has been observed by Nakamura and co-workers [3].

Our results indicate that the presence of lithium iodide or trimethyliodosilane, is important for the reaction. The presence of lithium iodide also influences the stereoselectivity of the formation of silyl ketene acetals. Without LiI, and with TMSI as the sole source of iodine, only the *Z* isomer of the silyl ketene acetal is formed. With LiI present, about equal amounts of *E* and *Z* isomers are formed independent of the identity of the activating agent (TMSCl or TMSI). This suggests that there may be two competing mechanisms for the conjugate addition reaction. When only MeCu and TMSI are present with the cinnamate, it seems plausible that coordination of the carbonyl oxygen to silicon activates the enone system. The iodine of TMSI could then coordinate to copper, thus leading the system into a cyclic intermediate in which copper might form a π-complex before the actual transfer of the methyl group to the β carbon. Simultaneous elimination of CuI from the most probable conformation of the π-complex would result in selective formation of the *Z* isomer of the silyl ketene acetal (Scheme 1). Another possible pathway involves the formation of an α-cuprioketone. *Syn* elimination of CuI from the α-cuprioketone intermediate would, however, give the *E* silyl ketene acetal. With LiI present, the lithium ion could coordinate to the carbonyl oxygen, and, possibly via a π-complex, give a lithium enolate, which would be subsequently silylated. This pathway would not require a cyclic intermediate and, thus not be stereoselective. An alternative explanation fo the loss of stereoselectivity when LiI is present is that the Li-enolates may not be configurationally stable.

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