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Effects of Dimethyl Sulfide on the Reaction of Dibutylcopper Reagents with α,β-Unsaturated Ketones.

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Abstract:

Addition of Me_2S to a 1:2 CuI/BuLi mixture in toluene promotes 1,4- over 1,2-addition in reactions with a representative selection of α,β-unsaturated ketones. Unlike similar reactions studied with dialkyl ethers, the effect of Me_2S is not related to the amount of lithium salts in the reaction medium. The results are related to current mechanistic theories of organocuprate reactions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copper and compounds; Addition reactions; Enones

Introduction

The 1,4- (conjugate) addition reaction of lithium diorganocuprates (R_2CuLi)† with α,β-unsaturated ketones is a well established organic synthetic process for carbon-carbon bond formation.[1-4] In spite of the many applications of this reaction to organic synthesis, the mechanistic aspects remain uncertain.[5] Based on reaction studies, including some activation parameter determinations,[6] and direct spectroscopic observations[7-12] the currently accepted mechanistic scheme that has evolved entails initial lithium coordination of the substrate, followed by formation of a cuprate-alkene complex, then conversion to an enolate. The last component of this sequence has been the subject of much discussion and lead to the consideration of formally organocopper(III) intermediates (R_2Cu-C)†.[13-15] Although direct observations of this intermediate have not been reported, theoretical calculations on trimethylcopper(III)[16] and a trialkyl copper species containing a pendant enolate group[17] have supported the viability of copper(III) organometallics with the proviso that stabilization by heteroatom (O or N) coordination is necessary. Pyridine and triethylamine have been observed to enhance organocuprate 1,4-additions[18] which is in concert with these calculations. In addition, ingeneous considerations of other ways to stabilize the transition state has lead to the development of β-silylcuprates as stable, but nonetheless reactive, reagents.[19] The reactive silane, iodotrimethylsilane, facilitates reactions of organocopper compounds (RCu)† with

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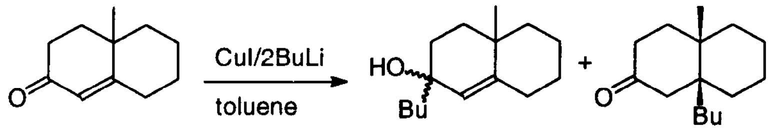
unsaturated systems,[20] but it appears that, in this situation, the enhanced reactivity is a consequence of preferential attack of the silane at oxygen.

Recently, a substantial and detailed theoretical analysis of the total 1,4-addition reaction mechanism manifold in the gas phase has appeared[21] which includes consideration of organometallic clusters and suggests that "open" and "closed" cluster intermediates may need to be considered. Other theoretical work has addressed the stereochemical aspects.[22,23] In addition, an elegant combination of experimentally determined ^{13}C kinetic isotope effects in the reaction of Bu$_2$CuLi/THF and 2-cyclohexenone with theoretical calculations on simple model systems has indicated that reductive elimination from the coordinated copper(III) intermediate complex is rate determining.[24]

In relation to our continuing interest in the mechanism of the reaction of diorganocuprates with α,β-unsaturated carbonyl compounds we have previously described the significant effects of ethers on the 1,4-/1,2- addition product ratios from reactions with butylcoppers prepared in toluene solvent.[25,26] These experiments are exemplified by the effect of diethyl ether (Et$_2$O) on the reaction of the organometallic mixture with 4,4a,5,6,7,8-hexahydro-4a-methyl-2(3H)-naphthalenone (**1**) to give various amounts of the 1,2- and 1,4-addition products **2** and **3**† (Scheme).[25]



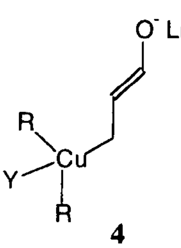
1 **2** **3**

98 : 2

+ 2 Et$_2$O 3 : 97

Scheme

The results were interpreted to be in accordance with the aforementioned calculations[16,17] in that Et$_2$O is a suitable ligand to facilitate the stabilization of the copper(III) reaction intermediate **4** (Y = Et$_2$O) and also may assist in the formation of the cuprate reagent.



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Various copper(I) salts have been used as source materials in organocuprate reactions.[27] Copper iodide (CuI) has been the traditional reagent for organocopper preparations, however copper bromide-dimethyl sulfide complex (CuBr·Me$_2$S)[28] has been promoted as an alternative copper source.[29] In some cases it has been found crucial to use CuBr·Me$_2$S rather than CuI to achieve successful reaction.[23] Reactivity differences between organocuprates derived from copper bromide (CuBr) and CuBr·Me$_2$S were noted and an "annealing period" in the reaction protocol was also found to be important in some cases.[27] This was the first indicator that even 1 equiv of Me$_2$S can have a profound influence on reactivity. In certain applications, a sulfur-coordinated copper salt precursor is essential *e.g.* access to the reactive α-alkoxyalkylcopper (RCu)† reagents can only be achieved by using CuBr·Me$_2$S.[30] Reports have also appeared that the product stereochemistry from reactions using diorganocuprates can be influenced by the type of copper salt employed[31] and precautions in handling diorganocuprates derived from CuBr·Me_2S have been advised.[32] Examples of organocopper reactions involving more complex alkyl thioether ligands have appeared[33] and the well-established use of copper thiophenoxide for organometallic reactions[34] has recently been revisited.[35]

The utilization of Me_2S as a reaction solvent for organocuprate reactions has been promulgated[36] and the effectiveness of this protocol in asymmetric applications of organocuprate reactions has been demonstrated.[37] Structural studies of copper(I) halides complexed with alkyl sulfides are well represented in the literature[38-41] and the incorporation of Me_2S into reaction systems has allowed definitive structural and spectroscopic analyses of various types of organocopper compounds.[42-46]

In the light of these features, a study of CuBr·Me_2S with respect to our butylcopper toluene system[25,26] was undertaken together with studies using Me_2S as a reaction addend. We found that the addition of Me_2S to the 1:2 CuI/BuLi mixture in toluene does indeed alter the 1,4-/1,2-addition ratio but, unlike similar reactions studied with ethers, the effect of Me_2S does not seem to be related to the amount of lithium salt in the reaction medium.

Results and Discussion

The results of the initial phase of this study are summarized in Table 1. As in previous studies, the reactions were carried out with slight excesses of copper salt and BuLi to compensate for any thermal decomposition. Equivalents of additive were based on half the amount of BuLi used in each experiment. Unreacted **1** was not detected in the reaction products from any of the experiments listed in Table 1 and the only ketone isolated was the *cis* compound (**3**).

Table 1
Reaction of Various 1:2 CuX/BuLi Mixtures with 1

$$\{\text{Cu}\} + 2\text{BuLi} \xrightarrow[-78^{0}\text{(1 min)}]{\text{solvent}} \xrightarrow[\substack{-78^{0}\text{(30 min),}\\ \text{temp A (time A)}}]{\text{additive A}} \xrightarrow[\text{temp B (10 min)}]{\text{additive B}} \xrightarrow[\substack{-78^{0}\text{(1 min),}\\ -40^{0}\text{(30 min)}}]{\mathbf{1}} \text{products}$$

entry	{Cu}	solvent[a]	additive A[b]	temp A[c] (*time*[d])	additive B[b]	temp B[c]	products (/%)[e]	
							2	**3**
1	CuBr·Me_2S	Et_2O	-	-40(*10*)	-	-	5	95
2[f]	CuI	Et_2O	-	-40(*5*)	-	-	5	95
3	CuBr· Me_2S	tol	-	-40(*30*)	-	-	3	97
4	CuI	tol	-	-20(*15*)	Et_2O (2)	-40	3	97
5[f]	CuI	tol	-	-20(*15*)	-	-40	98	2
6[g]	CuI	tol	Me_2S (1)	0(*20*)	-	-	8	92
7	CuI	tol	-	-20(*15*)	Me_2S (1)	-40	94	6
8	CuI	tol	Me_2S (1)	0(*20*)	-	-	4	96
9	CuI	tol	Et_2O (2)	-40(*25*)	-	-	3	97

[a] tol=toluene [b] ( )equiv to 0.5 x BuLi [c] degrees Celsius [d] min [e] determined by GC analysis [f] ref 25
[g] Me_2S added to CuI before BuLi

Reaction of the dibutylcopper reagent, derived from CuBr·Me_2S, in Et_2O with **1** showed high preference for the 1,4-addition product (**3**) (entry 1).This result was comparable to that obtained from the system derived from CuI under similar reaction conditions (entry 2)[25]. Repetition of the reaction with CuBr·Me_2S using toluene as the solvent required a longer time for reagent formation at -40°C, as judged by colour changes in the organometallic system, but gave a comparable result to the previous experiments (entry 3). The amount of **3** isolated in each of these reactions was closely aligned with that found with the 1:2:2 CuI/BuLi/Et_2O system in toluene[25] (entry 4) and contrasts significantly with the product distribution from the reaction of 1:2 CuI/BuLi mixture in straight toluene (entry 5). Further experiments were then undertaken to investigate whether this reactivity difference was related to the halide (CuBr *vs.* CuI) or to the sulfur ligand (Me_2S).

Addition of 1 mole equivalent of Me_2S to a toluene suspension of CuI followed by BuLi all at -78°C, in a similar manner to that described by Bertz *et al.*,[27] gave an off-white suspension which was visually unchanged even after 30 min at -40°C. Warming to 0°C for 10 min gave a grey/black mixture which, on recooling to -78°C, was exposed to **1**. After 30 min at -40°C the product mixture was found to comprise of **1**(14%), **2**(3%) and **3**(83%). It was surprising to find significant butyl activity from a butylcopper reaction system which had been exposed to temperatures in excess of the usual limits (*ca* -20°C). A mixture of CuI, BuLi and Me_2S prepared in toluene at -78°C then simply held at 0°C for 20 min, to ensure complete reagent formation, gave high 1,4-addition (entry 6) confirming a high temperature operational window was available. Although there were (necessarily) some differences between the reagent formation/annealing temperatures of the CuI/Me_2S and the CuBr·Me_2S systems, a dark reaction mixture was always obtained prior to the addition of **1**. In our previous studies with ethers,[25,26] the additive was introduced after the 1:2 CuI/BuLi mixture had changed color following a heating/cooling protocol (*e.g.* entry 4). Therefore, for true comparison, experiments where Me_2S was added to the pre-formed 1:2 CuI/BuLi mixture in toluene were undertaken. Analysis of this reaction product showed mainly **2** (entry 7). However 1,4-addition proclivity was maintained in reactions where the Me_2S was added after the BuLi (entry 8) - provided the mix was assembled at -78°C. A similar reaction occurred with Et_2O (entry 9). These results indicate that 1,4-addition promotion by Et_2O can be achieved by incorporation of the addend at any stage of the reagent preparation sequence. However it appears that Me_2S is unable to integrate into the organocopper cluster once it is formed in toluene by appropriate temperature manipulation and does not influence the reactivity of intermediates in these situations. A comparable reduction of the influence of LiI on pre-formed 1:2:2 CuI/BuLi/Et_2O mixtures has been noted.[25]

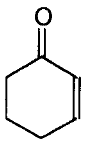
A series of experiments were then run with **1** and varying amounts of Me_2S, in order to evaluate the 1,4-addition reactivity profile (Table 2). The period required for reagent formation was found to be dependent on the amount of Me_2S used and it proved difficult to obtain highly reproducible data with small equivalent amounts of Me_2S. The use of very extended reagent formation times only partly resolved these difficulties as some unreacted **1** was often then recovered which indicated thermal decomposition of the organometallic. Notwithstanding this experimental uncertainty (+/- 5-10%) the results with using **1** as substrate clearly showed that between 0 and 1 equiv of Me_2S there was an increase in the amount of **3** produced and a corresponding decrease in the amount of **2** obtained. This effect was evident even when using small amounts of Me_2S, and contrasts with the results obtained with Et_2O where the 1,2-/1,4-addition ratio was unaffected until an excess of 1 equiv of Et_2O was involved.

Table 2
Reaction of 1:2 CuI/BuLi Containing Variable Amounts (*w*) of Me_2S with α,β-Unsaturated Ketones.

$$\mathrm{CuI + 2BuLi +}\ w\mathrm{Me_2S} \xrightarrow[-78^{o},\ 30\ \mathrm{min}]{\mathrm{toluene}} \xrightarrow[20-360\ \mathrm{min}]{0^{o}} \xrightarrow[-78^{o},1\ \mathrm{min}]{\mathrm{enone}} \xrightarrow[30\ \mathrm{min}]{-40^{o}} \mathrm{products}$$

enone	*w*	products (/%)[a]	
	Me_2S (/equiv)	1,2-	1,4-
1	0[b]	98	2
	0.1	70	30
	0.2	60	40
	0.5	40	60
	0.7	25	75
	0.9	15	85
	1.0	4	96
5	0[b]	66	34
	0.25	23	77
	0.5	3	97
	1.0	2	98
6	0[b]	95	5
	0.25	60	40
	0.5	5	95
	0.75	0	100
	1.0	0	100
	2.0	0	100
7	0[b]	90	10
	0.5	73	27
	1.0	5	95

[a] determined by GC analysis [b] ref 25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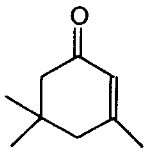
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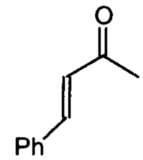

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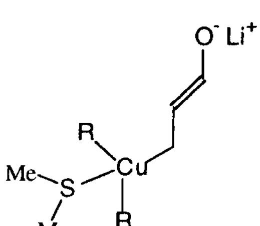
In order to ascertain if this was a general effect, a series of reactions were carried out with enones **5**, **6** and **7** as representatives of the various reactivity classes identified from studies with methylcuprates in Et_2O.[12] The results, summarised in Table 2, show a similar spectrum of 1,4-reactivity as seen in the original studies together with a consistent increase in the amount of 1,4-addition with increasing Me_2S. These data clearly show that even modest amounts of the sulfide are very influential on the regioselectivity of the reaction.

Conclusion

In concert with the conclusions from the previous work with ethers, it seems that Me_2S may provide an environment conducive for cuprate formation and/or facilitate 1,4-addition by sulfur stabilization of the trialkylcopper intermediate species (*i.e.* **8**). We have noted[25] that the addition of 1 equiv of LiI to a 1:2:2: CuI/BuLi/Et_2O mixture in toluene increases the amount of 1,2-addition, however with 3 equiv of Et_2O predominance of the 1,4- reaction is regained. These results were interpreted in terms of the free, unencumbered LiI preferentially coordinating with some of the Et_2O, which is therefore unavailable for the necessary coordination to copper. From this work it is evident that LiI is not competing with copper for the Me_2S and this is consistent with HSAB considerations.[47] Although thiophenes seem not to provide notable reactivity enhancement,[48] the findings in this paper confirm the effectiveness of dialkyl sulfides in promoting organocuprate 1,4-addition reactions and invite further studies with other ligands based on sulfur. A particular interest will be discovering if chiral alkyl sulfides influence the stereochemical outcome of the reaction.



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Experimental

General experimental details have been described previously.[25] The CuBr·Me_2S was purchased from Aldrich and recrystallized from Me_2S and hexane.[28] All organometallic reactions were carried out as detailed previously.[25]

Solvent Studies with 1:2 CuBr·Me_2S/BuLi and 1. A sample of CuBr·Me_2S (0.247 g, 1.2 mmol) was weighed into a dry Schlenk tube, then flushed with argon. Dry, degassed Et_2O or toluene (10 mL) was added and the resulting white suspension was cooled to -78 °C, with stirring. BuLi (2.2 mmol) was added and the mixture was stirred for 30 min at -78 °C, then 10 min (Et_2O) or 30 min (toluene) at -40 °C. Over this time period the suspension darkened from off white to black. The mixture was then cooled to -78 °C then **1** (155 μL, 1.0 mmol) and GC internal standard [*n*-C_{12} (227 μL, 1.0 mmol)] were added by syringe over 5 to 10 seconds. The mixture was stirred for 30 min at -40 °C then quenched at -40 °C with an aqueous mixture of saturated ammonium chloride/ammonia (NH_4^+/NH_3). The resulting biphasic mixture was allowed to warm to room temperature then two aliquots (≈ 0.5 mL) were removed from the organic phase and were added to separate sample tubes, each containing NH_4^+/NH_3 (≈ 0.5 mL), and diluted with hexane (2 mL). The mixtures were shaken until all the solids had dissolved, then allowed to settle, and the organic phase analyzed by GC. The results are given in the Table.

Reactions with 1:2 CuI/BuLi and 1 in Toluene. The reaction procedure as described above was followed except that CuI (0.228 g, 1.2 mmol) was weighed into a dry Schlenk tube, and evacuated for 5 min then filled with argon. Dry, degassed toluene (10 mL) was added and the resulting white suspension was cooled to -78 °C with stirring. BuLi (2.2 mmol) and any additive were added sequentially, and the mixture was stirred for 30 min at -78 °C. The white suspension was then warmed to various temperatures for specified times (*cf* Table). The resulting black mixture was then cooled to –78°C, reacted with **1**, and after 30 min at –40°C quenched and worked up as described previously.

Reactions (Table, entries 6-8) were carried out with Me_2S (81 μL, 1 equiv) as additive. For entry 6, the Me_2S was added before the BuLi to the CuI suspension in toluene and, for entry 7, the Me_2S was added after the CuI/BuLi reaction mixture had been held at –20°C for 15 min.

Reactions (Table, entries 4,9) with Et_2O (230 μL, 2 equiv) were carried out in the same manner as with Me_2S (entries 7,8).

Reaction of the 1:2:*w* CuI/BuLi/Me_2S mixtures with 1.

CuI (0.228 g, 1.2 mmol) was weighed into a dried Schlenk tube, evacuated for 5 min then filled with argon. Dry, degassed toluene (10 mL) was added and the resulting suspension was cooled to -78°C with stirring. BuLi (2.2 mmol) and Me_2S (*w* equiv) were added and the mixture stirred at -78°C for 30 min. The white suspension was then warmed to 0°C and stirred until a black mixture was obtained. The black material was cooled to -78°C and a mixture of **1** (155 μL, 1.0 mmol) and n-C_{12} (227 μL, 1.0 mmol) were added by syringe over 5 to 10 seconds. The reaction was then stirred at -40°C for 30 min then worked up as described above. The product distributions were analysed by GC and the results are listed in Table 2.

Reaction of the 1:2:*w* CuI/BuLi/Me_2S mixtures with 5, 6 and 7.

Reactions were carried out as described above for **1**. The reaction products, which have been identified previously,[25] were analysed by GC. Internal standard n-C_{12} was used for **7** and n-C_{14} was used for **5** and **6**.

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References and Notes

* FAX: +64 3 479 7906, email: rajsmith@alkali.otago.ac.nz. † This formula depicts the simplest stoichiometry and does not imply any particular molecular state. ‡ All compounds used were racemic, only one enantiomer is depicted in the diagrams.

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