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Formation of a New Bis-Organocopper Reagent from the Reaction of 2,3-Dichloropropene and Highly Active Zero Valent Copper Derived from a CuCN·2LiCl Complex

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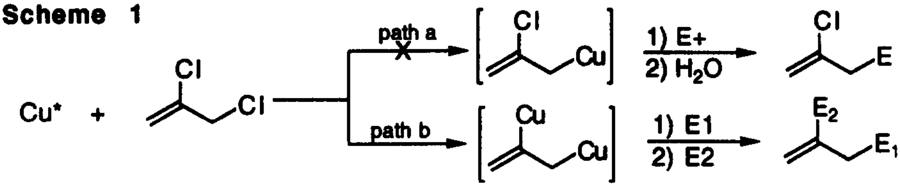
Abstract: Highly reactive zero valent copper derived from a CuCN•2LiCl complex reacts directly with 2,3-dichloropropene to yield a new bis-organocopper species containing both a nucleophilic allylic and vinylic moiety. This new bis-ograncopper reagent undergoes selective one-pot addition to two different electrophiles in good to excellent yields.

Allyl copper reagents have seen renewed interest recently due in part to major improvements in their preparation[1]. The use of a highly reactive form of zero valent copper[2], Cu*, derived from CuCN•2LiCl complexes[3], not only allows for facile formation of allyl organocopper reagents directly from allyl chlorides, but also allows for a wide, diverse range of functional groups to be present in the resulting organocopper species[3b]. The highly functionalized allylic organocopper reagents have been shown to undergo reactions with various electrophiles in high yield. In the course of examining different allyl chloride precursors, we were surprised to find that the reaction of 2,3-dichloropropene with Cu* resulted in oxidative addition of Cu* to both carbon-chlorine bonds (path b, Scheme 1). The replacement of the vinyl chloride with a proton (from aqueous work-up) inferred the proposed bis-organocopper structure 1. Moreover, it was thought that addition of other electrophiles to the vinylic site would allow for a one-pot selective addition of two different electrophiles to the 2,3 position of the 1-propene unit.

Scheme 1

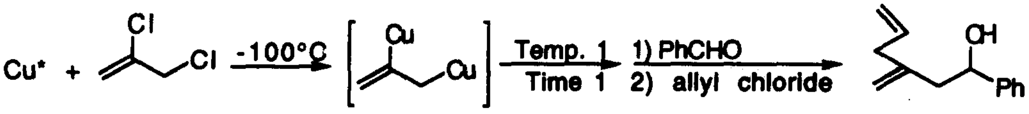


The reaction of one equivalent 2,3-dichloropropene with four equivalents of Cu* (Cu* is a one electron reagent) occurs rapidly in minutes at -100°C. Trapping 1 with an excess of phenylacetaldehyde shows that oxidative addition occurs in c.a. 40 to 50% yield with total consumption of the dichloride. Presumably the formation of allene is responsible for the cut in yield[4]. Once formed, the bis-organocopper reagent selectively reacts with two different electrophiles. The more reactive allyl carbon-copper bond adds to the first electrophile (E1) followed by incorporation of the second electrophile (E2) to the vinyl carbon-copper bond.

Table 1 shows the one pot reaction of 1 with various electrophile combinations. Aldehydes, ketones and imines are suitable electrophiles for reaction with the allylic terminus while allyl chlorides, allyl bromides, alkyl iodides and iodine add to the vinyl copper bond. Entry 2 shows that a 3-iodohomoallyl alcohol can be easily prepared by this one-step procedure. 3-Halohomoallyl alcohols are valuable synthetic intermediates in the formation of alpha-methylene-lactones[5]. Entry 7 illustrates that the addition 1 is chemoselective towards a carbonyl group in the presence of a nitrile.

In order to investigate the thermal stability of 1, a set of reactions were carried out whereby the bis-organocopper reagent was allowed to stand overnight at various temperatures before the addition of E1 and E2. The results shown in Scheme 2 indicate that 1 decomposes between -20 and 0°C.

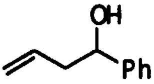
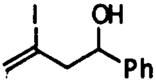
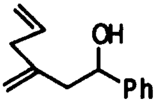
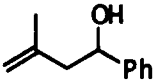
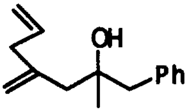
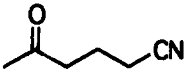
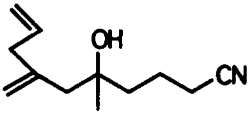
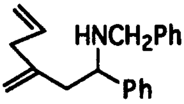
Scheme 2



Temp. 1	Time 1	%Yield
-78°C	15 min.	83
-20°C	16 hrs.	68
0°C	16 hrs.	0
R.T.	16 hrs.	0

Procedure. All reactions were conducted under an argon atmosphere using air exculsion techniques. THF was freshly distilled under argon over a Na/K alloy. All reported temperatures are bath temperature readings. CuCN (12 mmol) and

Table 1. Reaction of 1 with two successive electrophiles

entry	E1	E2	Product[a]	%Yield[b,c]
1	PhCHO	H^+		88
2	PhCHO	I_2		69
3	PhCHO			71
4	PhCHO		"	83
5	PhCHO	MeI		63
6	$PhCH_2COCH_3$			22
7				54
8	$PhCH=NCH_2Ph$			79

a) All products gave consistent ^1H NMR, ^{13}C NMR, FTIR and HRMS spectra e.g. entry 3: ^1H (360 MHz) ppm 7.21-7.34(m, 5H), 5.73-5.85(m,1H), 5.07-5.09(m, 1H), 4.93(s, 1H), 4.91(s, 1H), 4.76(dd, J=8.5Hz, J=4.92Hz, 1H) 2.77(d, J=6.7Hz, 2H), 2.39-2.43(m, 2H), 2.32(bs, 1H). ^{13}C (50MHz) ppm 144.5, 144.0, 135.8, 128.3, 127.4, 125.7, 116.6, 113.9, 71.7, 46.2, 40.5.

b) Isolated yields. c) Yields based on equivalents of E1.

LiCl (24 mmol) were dissolved in 12ml of THF. Lithium (13 mmol) and naphthalene (14.5 mmol) were dissolved in 20 ml THF until all the lithuium was consumed (c.a. 2 to 3 hrs.). The CuCN•2LiCl was cooled to 0°C then transfered via cannula to the LiNp solution which was held at -100°C (4:1 hexane:Et_2O in liq. N_2); the solution was allowed to stir at -100°C for 10 min. 2,3-Dichloropropene (3 mmol) was weighed into an 8ml vial, covered with a septa and the air was replaced with argon via a freeze-pump-thaw technique. THF (2 ml) was added to the vial and its contents were cooled to -78°C. The solution was transferred via cannula to the Cu* solution which was held at -100°C. The solution was allowed to warm to -78°C when benzaldehyde (1 mmol), in a speta covered vial admixed with 2 ml THF, was added via cannula. The solution was warmed to -20°C over the course of an hour and was held at -20°C for an additional 3 hours. Allyl chloride (4.5 mmol) was added neat via syringe at -20°C. The solution was allowed to warm to 0°C over 2 hrs and then quenched with $NH_4Cl_{(sat.)}$. The crude mixture was washed with brine, back extracted with Et_2O and dried over $MgSO_4$. The product was separated via flash silca gel chromatography using hexane, ethyl acetate mixtures.

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References and Notes

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