

**Preliminary communication**

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**Copper(I) promoted C–C bond forming reactions:  
direct activation of allyl alcohols**

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**Abstract**

Allylic alcohols, acetates, carbonates and chlorides can be activated by copper(I) salts towards nucleophilic substitution by carbon nucleophiles under relatively mild conditions.

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New and milder methods of activating allylic substrates toward C–C bond forming reactions have always attracted the attention of organic chemists [1–4]. Several metal complexes of the Ni group, primarily palladium, have been used to activate allylic substrates. Usually allylic alcohols have to be converted into the chloride or the acetate [5] before they can be activated, but there are a few examples of palladium-catalysed reactions in which the alcohols are directly activated towards nucleophilic substitution [6,7]. Another example of the direct use of allyl alcohols is provided by Felkin reaction, in which a Ni catalyst is used to promote C–C bond formation between allyl alcohols and Grignard reagents [8]. More recently it has been shown that a nickel(0) complex promotes allylation of the sodium salt of 1,3- $\beta$ -diketones [9] and this has prompted us to report some of our work involving the use of copper(I). We previously reported the use of copper(I) perchlorate in the conversion of allyl chlorides and acetates into allyl ethers under very mild, neutral and acidic conditions [10]. We report here C–C bond forming reactions at the allylic positions of several allylic substrates including allyl alcohol, thus providing the first example of allylic activation towards C–C bond formation under acidic conditions effected by copper(I).

Copper(I) perchlorate generated by the interaction of copper metal with copper(II) perchlorate in the reaction medium is very effective in promoting these nucleophilic substitutions. In a typical procedure, a suspension of copper powder (0.075 g, 1.18 mmol) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.371 g, 1 mmol) in THF (10 ml) containing allyl acetate (0.2 g, 2 mmol) and methyl acetoacetate (0.290 g, 2.5 mmol) is refluxed for 8 h under nitrogen. The THF is then removed under reduced pressure and 5 M aqueous HCl is added to dissolve the inorganic salts. After extraction with chloro-

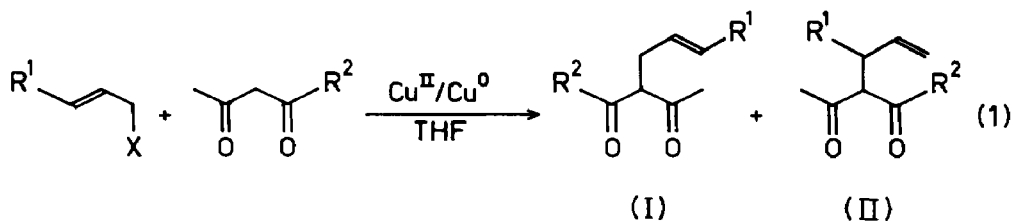
Table 1

Results of allylations with the substrates  $R^1CH=CHCH_2X^a$ 

$R^1$	X	$R^2$	Isolated yield (%)	Time (h)	Ratio I/II	Ratios of Pd <sup>0</sup> catalysed I/II	Ref.
H	Cl	CH <sub>3</sub>	79	1 <sup>b</sup>	—		
CH <sub>3</sub>	Cl	CH <sub>3</sub>	81	1 <sup>b</sup>	83/17		
H	Cl	Ph	48	1 <sup>b</sup>	—		
H	OCOCH <sub>3</sub>	OCH <sub>3</sub>	56	8	—		
CH <sub>3</sub>	OCO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	OCH <sub>3</sub>	55	6	74/26	71/29	3
CH <sub>3</sub>	OCOCF <sub>3</sub>	OCH <sub>3</sub>	55	6	74/26		
CH <sub>3</sub>	OCOCH <sub>3</sub>	OCH <sub>3</sub>	67	6	74/26		
H	OCOCH <sub>2</sub> COCH <sub>3</sub>	CH <sub>3</sub>	38	8	—		
CH <sub>3</sub>	OCOCH <sub>3</sub>	CH <sub>3</sub>	61	6	83/17	80/20	7
Ph	OCOCH <sub>3</sub>	OCH <sub>3</sub>	62	6	40/60	100/0	11
Ph	OCOCH <sub>3</sub>	CH <sub>3</sub>	52	6	34/66		
CH <sub>3</sub>	OCOCH <sub>3</sub>	OCH <sub>2</sub> CH <sub>3</sub>	67	6	74/26		
Ph	OCO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	OMe	61	6	40/60		

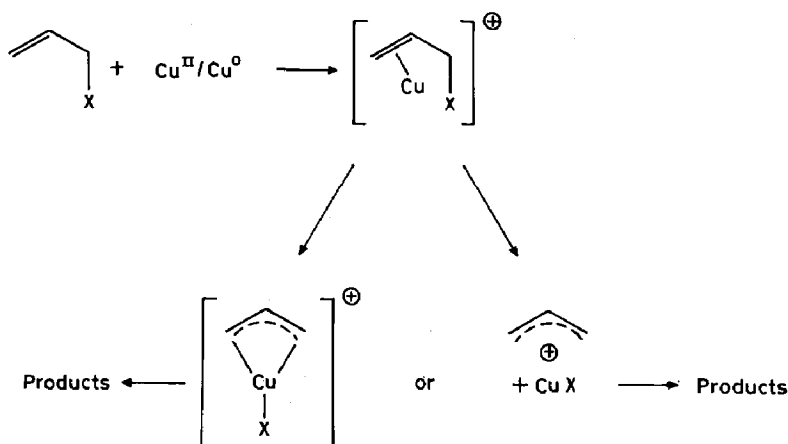
<sup>a</sup> For significance of  $R^2$ , I and II see eq. 1. <sup>b</sup> Reaction conditions described in the text were used, except in the case of allylic chlorides where the reaction was at room temperature and with ether as solvent.

form and the combined extract is concentrated, passed through a silica gel column to obtain the pure allylated product. Yields for the various reactions are shown in Table 1.



Unsymmetrical allyl substrates give rearranged products. The rate of the reaction depends on the leaving group and the metal complex used, but the ratio of rearranged to unrearranged products is independent of the leaving group. The reaction is fastest with chloride as the leaving group and perchlorate as the counter ion for the copper(II) cation. The most ionic copper(I) salts give the better yields and shorter reaction times; copper(I) acetate, for example, does not catalyse the transformation, whereas copper(I) tetrafluoroborate or triflate are very effective. Neither copper(II) or copper metal promotes the reactions. Allyl chloride alone can be activated by copper metal towards nucleophilic substitution at much higher temperatures [8].

The ratio of the rearranged to unrearranged products is markedly dependent on the incoming group. Larger nucleophiles tend to give the less substituted products. The ratios obtained with various nucleophiles are remarkably similar to those for the Pd-catalysed reactions. Experiments in the presence of copper carbonate confirmed that the acid liberated in the reaction was not involved in the isomerisation of the products formed, but in the presence of the carbonate or a tertiary amine the reaction was considerably slower.



Scheme 1.

The results indicate that a common intermediate is formed from the various allylic substrates in their interaction with  $\text{CuClO}_4$ . We have confirmed by NMR studies that an olefin complex is formed, and this is supported by the observation that the reaction between  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^0$  is much faster in the presence of the olefins. It is not clear, however, whether the olefin complex leads to the formation of a free cation or to a  $\pi$ -allyl complex of  $\text{Cu}^{\text{III}}$  through oxidative addition [15,16]. The similarity in the product ratios in the Pd-catalysed and Cu-promoted reactions suggests that it is probably a  $\pi$ -allyl complex.

Allylic alcohols can be activated if an esterifying agent such as ethyl acetate is present in the reaction medium. The yields obtained and the ratios of isomers formed during the reactions are listed in Table 2. This allows a one step functionalisation of allylic alcohols. No reaction occurs in the absence of ethyl acetate, indicating that transesterification precedes the activation. It is possible to activate alcohols in the absence of ethyl acetate if the water formed from the reaction of the alcohol and 1,3- $\beta$ -diketone is continuously removed as an azeotrope with benzene by use of a Dean and Stark apparatus. We expected this reaction to be catalytic, but found it did not occur with catalytic quantities of  $\text{Cu}^{\text{I}}$ .

Table 2

Direct activation of allylic alcohols

R <sup>1</sup>	X	R <sup>2</sup>	isolated yield	Time	Ratio I/II
H	OH	OCH <sub>2</sub> CH <sub>3</sub>	66	12	—
CH <sub>3</sub>	OH	OCH <sub>2</sub> CH <sub>3</sub>	58	12	74/26
CH <sub>3</sub>	OH <sup>a</sup>	OCH <sub>2</sub> CH <sub>3</sub>	78	12	74/26
CH <sub>3</sub>	OH <sup>b</sup>	OCH <sub>2</sub> CH <sub>3</sub>	58	12	74/26
Ph	OH	OCH <sub>3</sub>	57	8	40/60
Ph	OH	OCH <sub>2</sub> CH <sub>3</sub>	67	8	43/57
H	OH <sup>c</sup>	CH <sub>3</sub>	52	12	—
CH <sub>3</sub>	OH <sup>c</sup>	CH <sub>3</sub>	65	12	83/17
Ph	OH <sup>c</sup>	CH <sub>3</sub>	70	8	34/66

<sup>a</sup> Copper(II) tetrafluoroborate and copper metal powder used. <sup>b</sup> Copper(II) trifluoromethane sulphonate and copper metal powder used. <sup>c</sup> Ethyl acetate is used for esterification.

The observed copper(I)-promoted C–C bond forming reactions occur under mild and acidic conditions, and complements the much used Pd-catalysed reaction which occurs most effectively under neutral and basic conditions. The yields obtained from copper(I)-promoted reactions are comparable to those obtained from the Pd-catalysed reactions. The direct activation of alcohols is significant, since in this case the Pd-catalysed reactions require more vigorous conditions.

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