# Allylic Activation by Copper(I): Reactivity comparable with Catalysis by Palladium

**Jubaraj B. Baruah and Ashoka G. Samuelson***

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India*

Allylic chlorides and acetates accelerate the reaction between copper(II) perchlorate and copper metal powder to form copper(I) perchlorate which in turn is an extremely good catalyst for the activation of these substrates towards nucleophilic substitution.

Palladium has been the metal used for allylic activation for more than two decades. Recently it has been used for the conversion of xanthate esters to allyl sulphides,[1] allylation of ketones,[2] and coupling reactions.[3] We report here the use of a stoicheiometric mixture of copper(II) perchlorate and copper metal for carrying out nucleophilic substitutions on allylic chlorides and acetates at rates that are comparable with or even better than palladium-catalysed reactions.[4]

The reduction of copper(II) perchlorate by copper metal has been used to synthesize copper(I) alkene complexes.[5] However when a mixture of hydrated copper(II) perchlorate and copper(0) metal powder is treated with allyl chloride in the molar ratio 1:1:2 in methanol, a very rapid reaction occurs with precipitation of copper(I) chloride and quantitative formation of allyl methyl ether. The use of other alcohols as solvents instead of methanol leads to isolation of the corresponding allyl ethers. If diethyl ether is used as solvent diallyl ether is formed in excellent yield. The use of phenols as a substrate dissolved in ether leads to allylation of phenol in the *o*-position. Blocking both the *o*-positions led to allylation of the *p*-position. In the case of phenols this is not the result of a Claisen rearrangement of the allyl phenyl ethers since allyl phenyl ether itself remains unchanged under the reaction conditions. Allylation of the *o*-position may also be carried out on other activated aromatic compounds such as anisole.

When unsymmetrically substituted allyl halides are used the formation of products from allylic rearrangement is also observed. The ratio of the rearranged and unrearranged products from cinnamyl chloride is indicative of the intermediacy of an allyl cation.[6] However the formation of only *o*-substituted products suggests that it may be complexed to the copper.

Allyl acetates also give allyl ethers in the presence of copper(II)/copper(0). However the reaction proceeds at an appreciable rate only when carried out at 50 °C. In spite of the higher temperature used no rearrangement was observed in the case of cinnamyl acetate. An isolated yield of 75% was recorded for the cinnamyl ether.

Furthermore copper(I) chloride suspended in methanol is capable of converting 3 equiv. of allyl chloride into allyl methyl ether at room temperature. This conversion proceeds without allylic rearrangement. Both but-2-enyl and cinnamyl chlorides yield the unrearranged methyl ethers. Copper(I) chloride is converted into the tetrachlorocopper(I) trianion which is rapidly oxidised to give the copper(II) dianion. Addition of pyridine (py) precipitates the pyridinium complex $[pyH]_2[CuCl_4]$. However this reaction does not lead to the allylation of phenols or other activated aromatic rings. This suggests that the mechanisms of these processes are very different from the copper(II)/copper(0) reactions described earlier.

The role played by the counterion is quite significant and determines the rate of the reaction and the extent of rearrangement. The reduction of copper(II) perchlorate by copper metal is accelerated in a very similar way by the addition of sodium chloride. This suggests that the acceleration in the rate of copper(I) formation is due to the formation of chloride ions from allyl chloride.

Polarographic investigations have shown that copper(II) does not form complexes with alkenes.[7] This was confirmed spectroscopically also. Copper metal does not react with allyl chloride at room temperature although when refluxed with methanol allyl methyl ether is formed.[8] One-electron oxidation of copper by allyl chloride to give an allyl radical and copper(I) chloride was ruled out by carrying out the reaction in the presence of radical trapping agents such as 2,4-dinitrophenol and 2,6-di-t-butylphenol. It follows then that it is the stabilising interaction of $Cu^{I}ClO_4$ with the alkene that is responsible for the alkene complex formation and the subsequent labilisation of the substituted group (X) at the allylic position. Such a weakening could be the result of one of the filled orbitals of copper overlapping with the vacant C–X* orbital.[9] When X is benzoate the weakening is fairly insignificant and it is possible to trap the alkene complex as a phosphine adduct.

In conclusion, therefore, the combined use of copper(II) perchlorate and copper metal shows potential as an inexpensive substitute for the palladium-catalysed activation of allylic substrates. Furthermore, preliminary results suggest that homoallylic systems are also activated towards nucleophilic substitution by copper(I). Substitution at an allylic centre without rearrangement and under such mild conditions is thus a valuable reaction.

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