NOTA

# METAL CATALYSED OXIDATION: ALLYL ACETATES FROM MONOOLEFINS VIA A ONE COMPONENT OXIDATION SYSTEM

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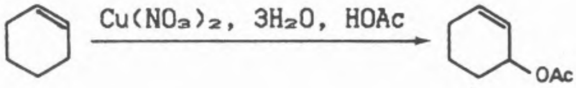
Due to the wide importance of allylic acetoxylation in the syntetic routes leading to complex organic molecules [1] and to the recent interest in methods originating acetoxylated intermediates through transition metal salts modulated reactions [2] we decided to disclose our results which lead to an allylic acetoxylation through a simpler and more accessible system than those previously known.

Both the $PdCl_2/CuCl_2$ and $Co(OAc)_3$ were known as oxidant systems for allylic acetoxylations. They lead to regioselective and sometimes to stereoselective reactions. However, the palladium salt containing system, which has catalytic activity in an oxygen consuming reaction, requires this expensive component, and the cobalt system which is also not cheap, has to be taken to the necessary cobalt oxidation state (III) prior to being used and is only operative when the cobalt salt is present in a quantity far greater than one equivalent.

We found that through the convenient choice of the anion, copper (II) is able to catalyse an allylic acetoxylation. While $CuCl_2$ does not show any activity over cyclohexene in acetic acid solution, $Cu(NO_3)_2$, when present in 1/3 eq. relative to the substrate, converts 87% of it after 7hrs at 75°C, yielding 68% of 3-acetoxycyclohexene.



The advantage of $Cu(NO_3)_2$ over $Co(AcO)_3$, which has to be used in a ratio of 2.5:1 eq. to originate solely 40% of the acetoxylated product [2e], is clear.

Regarding regioselectivity, we studied the $Cu(NO_3)_2$ catalytic activity on 1-methyl and 4-methyl-cyclohexene to conclude that, in the first case, the reaction is virtually nonregioselective since three allylic acetates are formed in 18.7, 17.9 and 15.3%: being the 6-acetoxyl-1-methyl-methylcyclohexene only slightly favored. However, with the 4-methyl-cyclohexene, the regioselectivity of the copper nitrate reaction is clear since the 3-acetoxy-5-