

## Copper Nanoparticles as efficient catalyst for the transesterification of $\beta$ -ketoesters

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### ABSTRACT

Transesterification, one of the most effective methods for ester synthesis, is usually conducted under acid or basic conditions. Although quite a few methods have been reported for transesterification, they are not general as far as  $\beta$ -ketoesters are concerned. Some of these methods used toxic, expensive reagents and in relative large amount. In this research, transesterification reaction six types  $\beta$ -ketoesters achieved in presence of Cu powder and Cu nanoparticles as catalyst and  $\beta$ -ketoesters prepared using this method. Copper Nanoparticles is an efficient catalyst for the transesterification of  $\beta$ -ketoesters with several kinds of alcohols, leading to good yields with high selectivity.

**Keywords:** Toluene alkylation; 2-Propanol; H<sub>3</sub>PO<sub>4</sub>; Modified ZSM-5; Cymene; Xylene; Catalyst

### INTRODUCTION

Transesterification is an important reaction which has wide applications both in academic and industrial research [1, 2].  $\beta$ -ketoesters [3] are multicoupling reagents having electrophilic carbonyl and nucleophilic carbon which make them a valuable tool for the synthesis of complex molecules. They are one of the basic building blocks in the total synthesis of sex pheromones like serricornine [4] and other natural products like thiolactomycin [5], trichodiene [6], polyoximic acid [7], chokol [8], prostaglandin PGF<sub>2a</sub> [9], ar-pseudotsugonoxide [10], syncarpic acid [11], diplodialide [12] and podophyllotoxin [13].

In the literature, there are various alternative routes to obtain  $\beta$ -ketoesters [14, 15], but the transesterification of these compound has been recognized as a very important and useful process because, it's allows the preparation of more complex products from more easily accessible synthesis [16]. The transesterification of  $\beta$ -ketoesters (Scheme 1) is an equilibrium process [16] that can be catalyzed by many kinds of catalysts, such as Bronsted base [17], DMAP [17], distanoxanes [18], solid superacids [19], zeolites [20], titanium(IV) alkoxides

[21], indium triiodide [22], natural clays [23], transition metal complexes [24], Mo-ZrO<sub>2</sub> [25], nonionic superbases [26], yttria-zirconia Lewis acid [27], Mg-Al-O-t-butyl hydrotalcite [28], diphenylammonium triflate [29], montmorillonite [30], Copper dust [31], basic silica [32], amberlyst [27, 33], sodium perborate [34], lithium perchlorate [35], and NBS [36].

Many procedures for the synthesis of  $\beta$ -ketoesters have been reported over a long time, but there exist many drawbacks and disadvantages necessitating improved methods for their synthesis. Of the many models of bond formation that exist for  $\beta$ -ketoesters synthesis, two notable ones are C2-C3 bond formation and C1-O bond formation (Scheme 2) [37].

Some of results, i.e. synthesis of  $\beta$ -ketoesters by condensation of aldehydes with ethyl diazoacetate catalyzed by zeolites and by transesterification of  $\beta$ -ketoesters with different alcohols also catalyzed by zeolites [37] and Copper-bipyridine-catalyzed for

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enantioselective  $\alpha$ -amination of  $\beta$ -ketoesters [10] have been communicated recently.

We have successfully performed transesterification of 6  $\beta$ -ketoesters using Copper powder and Copper nanoparticles as catalyst. Comparison between the two catalysts in both yield and time of reaction were also done.

## EXPERIMENTAL

### General experimental procedure for transesterification

All solvents were distilled prior to use. Petroleum ether refers to the fraction collected in the boiling range 60-80°C (The IR spectra were recorded on Perkin-Elmer spectrophotometer model 683B. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AC-200 instruments using with tetramethylsilane as the internal standard using  $\text{CDCl}_3$  as solvent. The mass spectra were recorded on Finnegan MAT-1020-B-70eV mass spectrometer. Cu Powder from Merck Company and Cu nanoparticles prepared from Nanostructured & Amorphous Materials, Inc (99.9% (metal basis, APS 35 nm, SSA: 30 - 50  $\text{m}^2/\text{g}$ ).

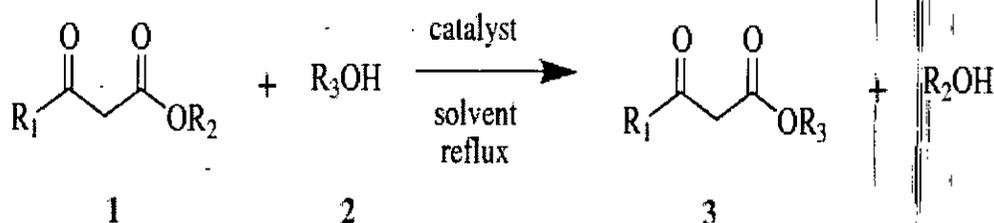
### General procedure for the synthesis transesterification of $\beta$ -ketoesters

A mixture of ketoesters (1 equiv), alcohol (1 equiv), and catalyst (15% by weight) in toluene (10 mL) was refluxed using Dean-Stark apparatus for the indicated length of time (Table 2). The reaction was monitored by T.L.C. After completion of the reaction, the catalyst was filtered and the filtrate were concentrated to get the crude product which was purified by silica gel column chromatography using petroleum ether/ethyl acetate as elutriation to effect the pure transistor product. All products were characterized by IR,  $^1\text{H}$ NMR and mass spectroscopic data.

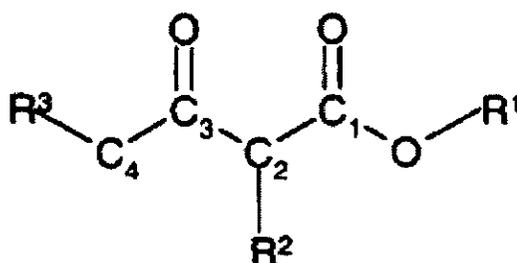
## RESULTS AND DISCUSSION

### Reaction between benzoyl ethyl acetate with 3-phenyl-1- propanol

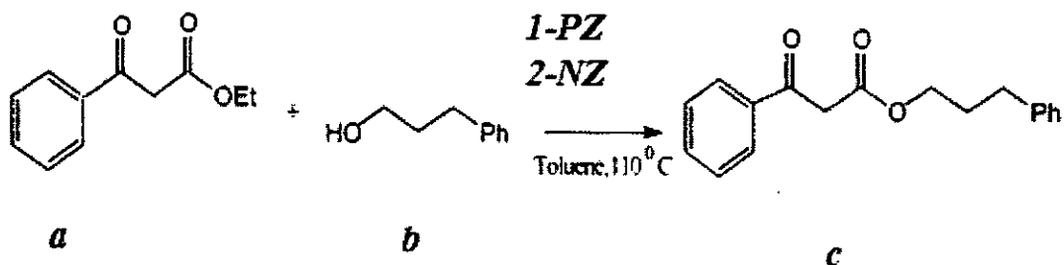
The reaction between benzoyl ethyl acetate molecules (compound a, scheme 3) and 3-phenyl -1- propanol (compound b, scheme 3) in toluene using copper powder and also nano copper particles in 110 °C gives 3-phenyl 1-propyl benzoyl acetate red liquid (compound c, scheme3).



Scheme 1. General Transesterification process for  $\beta$ -ketoesters.



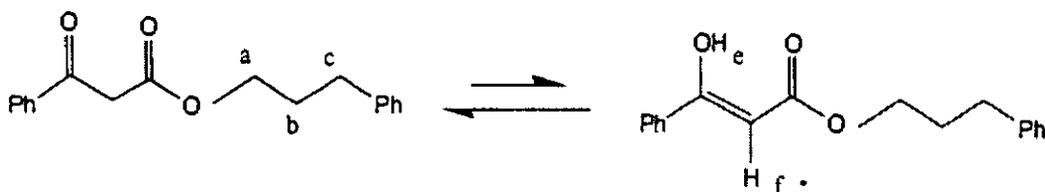
Scheme 2. Structure of  $\beta$ -ketoester.



**Scheme 3.** Reaction between benzoyl ethyl acetate(a) and 3-phenyl -1-propanol (b) to give 3-phenyl 1-propyl benzoyl (c)-[1-PZ: particle Copper powder and 2-NZ: nanoparticles Copper powder].

IR spectrum of compound c, strong peaks in 1680 and 1740  $\text{cm}^{-1}$  correspond to C=O and 1475-1620  $\text{cm}^{-1}$  are related to aromatic carbonyl groups. Bands appearing in 2950 and 3100  $\text{cm}^{-1}$  are related to aliphatic and aromatic C=O

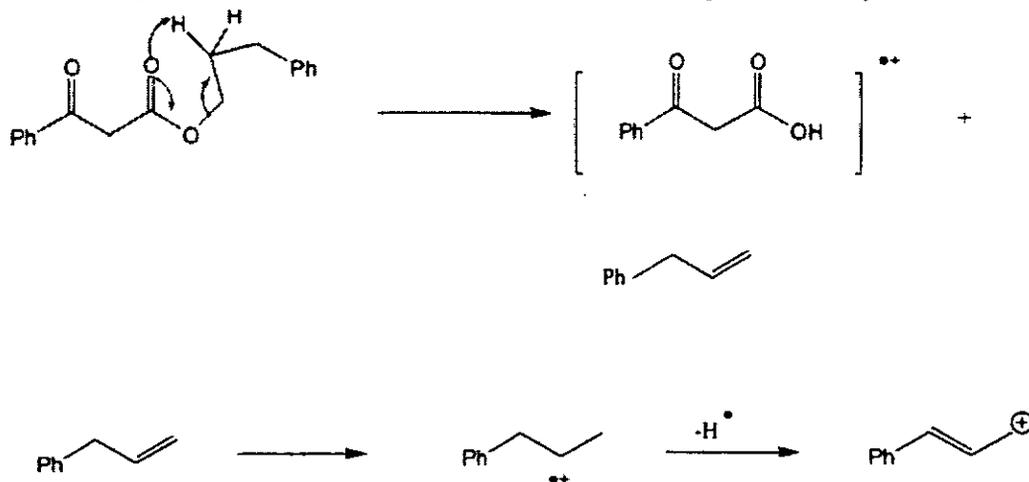
respectively. Combination of bending and stretching vibrations of PhCOC appears in 1200-1300  $\text{cm}^{-1}$ . Tautomerism compound of c in acetone is as scheme 4.



**Scheme 4.** Tautomerism of phenyl 1-propyl benzoyl acetate.

Multiple peaks appearing in 1.5 ppm is related to hydrogens b, triplet in 2.3 ppm corresponds to c hydrogens. Triplet of hydrogens, singlet of d and f (produced by tautomerism) and e hydrogens, are seen in 3.6, 3.6, 5.45, and 20 ppm respectively. Spread peak in 6.7-7.5 is appeared as the result of phenyl ring hydrogens splitting. The peak appearing in  $m/e=281.7$  in mass

spectrum give the molecular weight. McLafferti rearrangement gives  $[\text{PhCOCH}_2\text{COOH}^+]$  cation which is responsible for the peak appeared in  $m/e=147.1$ . During the rearrangement molecule first lose  $\text{PhCH}_2=\text{CH}_2$  which then lose hydrogen and produce a stable allylic and benzylic carbonium which correspond to the peak appears in 117. This procedure may be shown as:

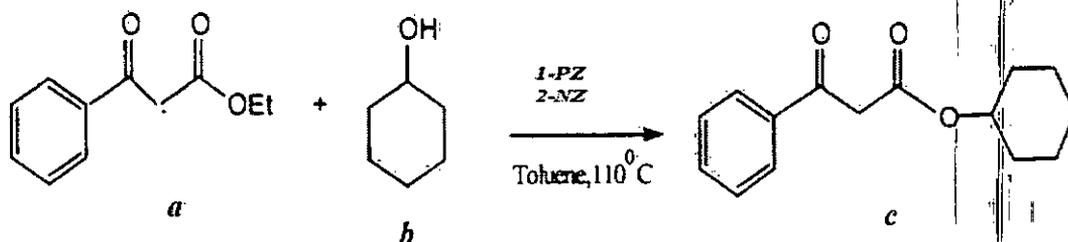


**Scheme 5.** McLafferti rearrangement which produce stable carbonium.

The peaks appeared in  $m/e=77.1$ ,  $147.1$ ,  $105$  and  $91.1$  are related to  $\text{PhCOCH}_2^+\text{CO}^+$ ,  $\text{PhC}^+\text{O}^+$ ,  $\text{PhCH}_2^+$  and  $\text{Ph}^+$  respectively.

Ethyl benzoyl acetate (compound a, scheme.6) in reaction with cyclohexanol (compound b, scheme 6) gives cyclohexyle benzoyl acetate (compound c, scheme 6). This reaction was carried out in toluene and Copper nanoparticles were used as catalyst.

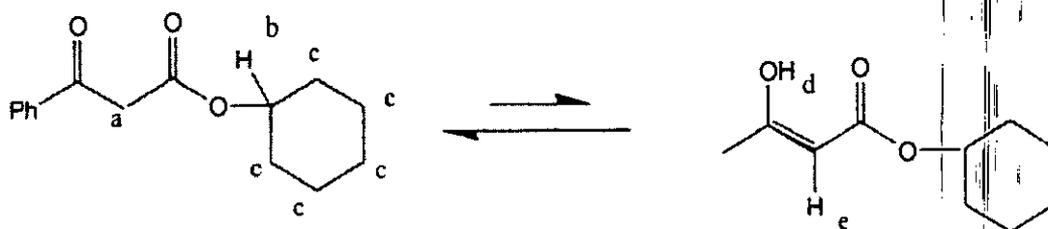
**Reaction of benzoyl ethyl acetate with cyclohexanol**



**Scheme 6.** Reaction of ethyl benzoyl acetate with cyclohexanol in toluene. Copper powder and Copper nanoparticles are used as catalyst. [1-PZ: particle Copper powder and 2-NZ: nanoparticles Copper powder].

IR spectrum of compound c scheme 6, shows strong peaks in  $1680$  and  $1740$  ( $\text{C}=\text{O}$ ) and also aromatic-carbonyl in  $1675$  and  $1600$   $\text{cm}^{-1}$ . The band appearing  $1100$   $\text{cm}^{-1}$  and  $1220-1300$   $\text{cm}^{-1}$

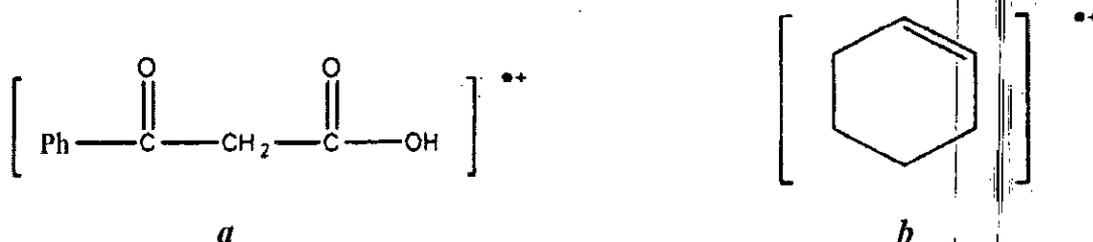
reveal bending and stretching vibrations of ketone carbonyl group.  $2950-3100$   $\text{cm}^{-1}$  appears aliphatic and aromatic  $\text{C}-\text{O}$  respectively, HNMR spectrum of this compound is as scheme 7.



**Scheme 7.** Tautomerism of cyclohexyle benzoyl acetate.

The peak appearing  $0.5-1.7$  ppm is related to c hydrogens of cyclohexane ring and sharp one in  $3.4$  ppm, is showing hydrogen a. Vinyl hydrogens appear in  $4.2-4.7$  and hydrogens d in

$20$  ppm. The peaks in  $82.1$  and  $163.9$  ppm in mass spectrum are related to cations a and b respectively produced by mlaferri rearrangement shown in scheme 8.

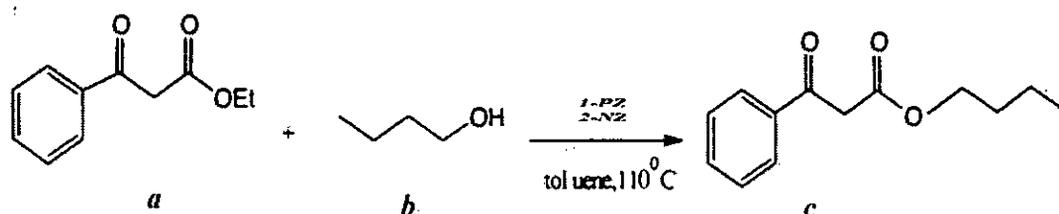


**Scheme 8.** mass spectrum of cation radical resulting from cyclohexyle benzoyl acetate.

The peaks of  $77.1$ ,  $104.2$  and  $147$  are show  $\text{PhCOCH}_2^+\text{CO}^+$ ,  $\text{PhC}^+\text{O}^+$  and  $\text{Ph}^+$  respectively.

Copper powder and Copper nano particles as catalyst reaction of ethyl benzoyl acetate and n-buthanol in toluene produce buthyl benzoyl acetate (compound c, scheme 9)

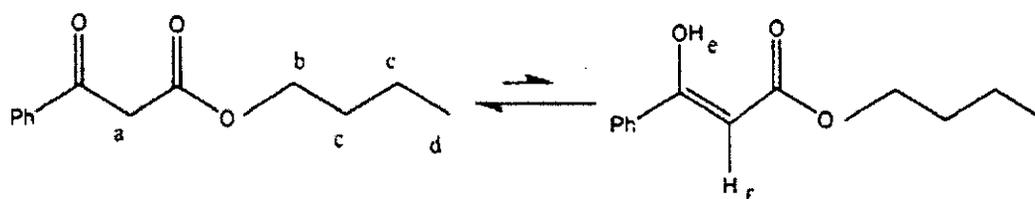
**Reaction of ethyl benzoyl acetate with buthanol**



**Scheme 9.** Reaction between ethyl benzoyl acetate and n-butanol. Butyl benzoyl acetate is produced. [1-PZ: particle Copper powder and 2-NZ: nanoparticles Copper powder].

IR spectrum of compound c absorption bands in  $1470\text{-}1600\text{ cm}^{-1}$  are related to aromatic C=C and the one in  $2950$  and  $3100\text{ cm}^{-1}$  are representative of aliphatic and aromatic C-H respectively. The

bands in  $1200\text{-}1300\text{ cm}^{-1}$  are the combinations of bending and stretching vibrations of ketone carbonyl group. Tautomerism of this compound is shown in scheme 10.

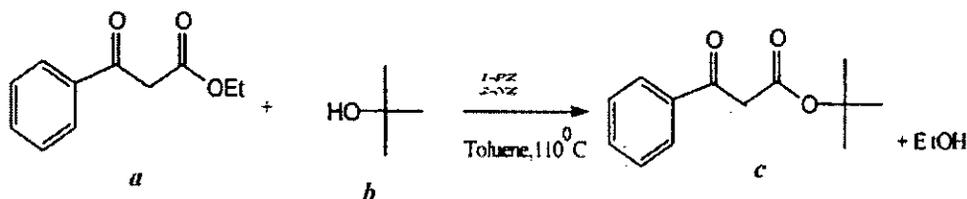


**Scheme 10.** Tautomerism of butyl benzoyl acetate.

Multiple peaks in 0.5 ppm are related to d, 0.5-1.2 ppm to c and triple in 3.7 ppm to b hydrogens. F Hydrogens appear in 3.5 and benzene ring hydrogens in 7-7.8 ppm. The singlet in 20 ppm is hydrogen e. since the tautomerism like to shift to left, the intensity of peaks corresponding to e and f hydrogen is low.

#### Ethyl benzoyl acetate reaction with tertio buthyl alcohol

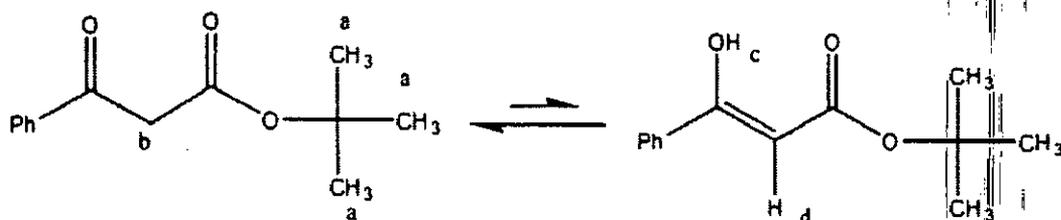
Tertio buthyl benzoyl acetate ( compound. c, scheme 10) as the product of reaction of ethyl benzoyl acetate with tertio buthyl alcohol, using Copper powder and Copper nano particles as catalyst.



**Scheme 11.** tertio buthyl benzoyl acetate as the product of reaction of ethyl benzoyl acetate with tertio buthyl alcohol, using Copper powder and Copper nanoparticles as catalyst. [1-PZ: Copper powder and 2-NZ: Copper nanoparticles].

The absorption bands in  $1475\text{-}1620\text{ cm}^{-1}$  and  $2950$  and  $3100\text{ cm}^{-1}$  are representative of aromatic C=C and aliphatic and aromatic C-H

respectively. HNMR spectrum of this compound is shown in scheme 11.

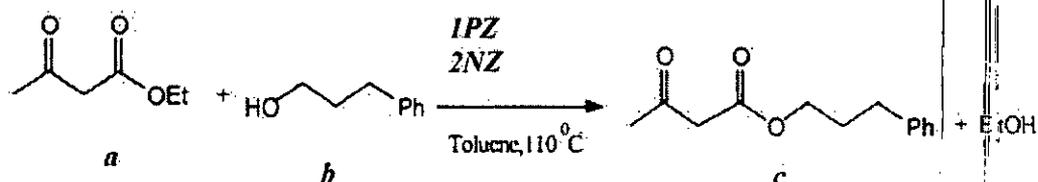


Scheme 12. Tautomerism equilibrium of tertio buthyl benzoyl acetate.

Singlet of hydrogens a and b appears in 0.8 and 3.4 respectively. Hydrogen e appears in 20ppm and the peaks seen in 7-7.6 ppm are related to phenyl ring hydrogen's.

Reaction between ethyl aceto acetate (compound a, scheme 12), with 3-phenyl -1- propanol (compound b, acheme12) in presence of Copper powder and Copper nanoparticles.

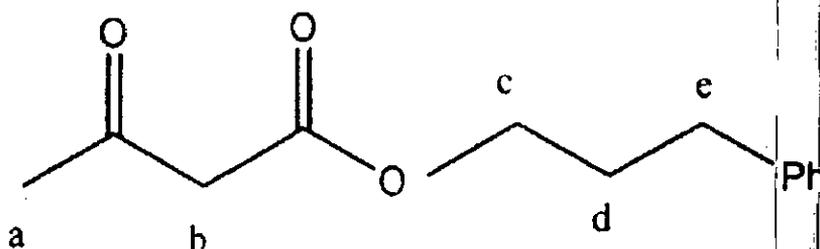
### Reaction of ethyl aceto acetate with 3-phenyl-1- propanol



Scheme 13. Reaction of ethyl aceto acetate with 3-phenyl -1- propanol in presence of Copper powder and Copper nanoparticles. [1-PZ: particle Copper powder and 2-NZ: nanoparticles Copper powder].

In IR spectrum of the compound c, there can be seen strong bands in 1680 and 1740  $\text{cm}^{-1}$ . Absorption bands in 1470 and 1600 and also

2950 and 3100  $\text{cm}^{-1}$  are representative of aromatic C=C, aromatic and aliphatic C-H respectively. HNMR spectrum is shown below.

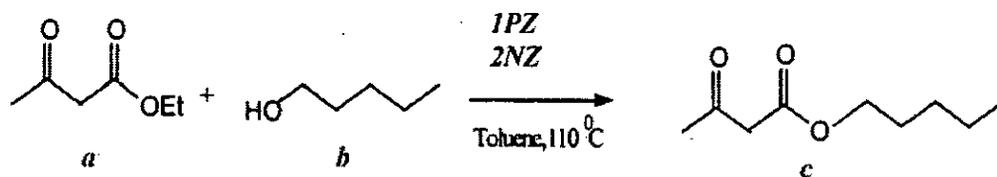


Scheme 14. Hydrogen's of 3-phenyl -1- propyl aceto acetate.

Multiple peaks in 1.4 ppm are corresponding to d hydrogens. In 1.6 ppm appear a hydrogens and triplet in 3.2 is representative of c ones. B, c and phenylic hydrogens appear in 3, 3.4 and 7.2 ppm respectively. Mass spectrum of this compound the peak appears in 221.3 is related to  $\text{M}^{+1}$  and the ones in 117, 105.1, 91 and 43.1 are corresponding to  $\text{PhC}^+\text{HCH}=\text{CH}_2$ ,  $\text{PhC}^+\text{O}$ ,  $\text{PhC}^+\text{H}_2$  and  $\text{CH}_3\text{C}^+\text{O}$  Respectively.

### Reaction of ethyl aceto acetate reaction with n-penthanol

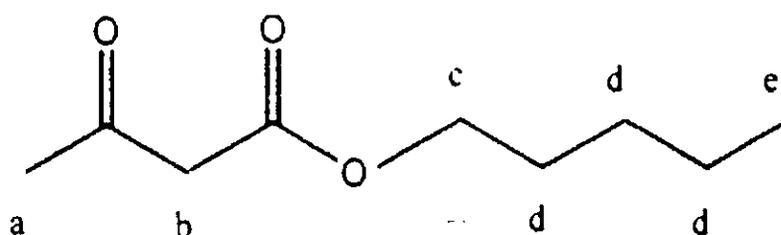
pentyl aceto acetate (compound c, scheme 14) is given in reaction of ethyl aceto acetate(compound a, scheme.14) with n-penthanol (compound b, scheme.14).



**Scheme 15.** penthyl aceto acetate is given in reaction of ethyl aceto acetate with n-penthanol. [1-PZ: particle Copper powder and 2-NZ: nanoparticles Copper powder].

IR spectra of compound c shows strong bands in 1680 and 1740  $\text{cm}^{-1}$  [C=O] and in 2970 and 2850  $\text{cm}^{-1}$  is related to aliphatic C-H bonds. NMR

spectrum of this compound in acetone is shown in scheme 15.



**Scheme 16.** hydrogen's of penthyl aceto acetate.

**Table 1.** Transesterification of  $\beta$ -ketoesters with different alcohols catalyzed by powder and nanoparticles Copper

Entry	$\beta$ -ketoesters	Alcohols	Catalyst (mg)	Reaction time (h)	Yield (%)
1			PZ <sup>c</sup> =400	3.0	84.0
			NZ <sup>d</sup> =400	2.5	95.2
2			PZ <sup>c</sup> =400	3.0	88.0
			NZ <sup>d</sup> =400	2.5	95.4
3			PZ <sup>c</sup> =400	2.0	91.1
			NZ <sup>d</sup> =400	1.7	96.5
4			PZ <sup>c</sup> =400	12.0	44.3
			NZ <sup>d</sup> =400	10.5	69.8
5			PZ <sup>c</sup> =400	2.5	91.4
			NZ <sup>d</sup> =400	2.0	92.3
6			PZ <sup>c</sup> =400	2.0	95.1
			NZ <sup>d</sup> =400	1.6	93.3

a. Yields refer to isolated pure products.

b. All products were characterized by IR, <sup>1</sup>HNMR and Mass spectroscopic data.

c. Powder Copper

d. Nanoparticles Copper

Triplet in 0.9 ppm shows hydrogens e, singlet peaks appear in 2.2 and 3.5 are related to a and b hydrogens and the peaks seen in 3.5 and 4 ppm are demonstrating hydrogens a and c respectively. The structure is also proven using mass spectrometry.

Apparently using nano size particles improved the yield of the reaction which can be related to the contact surface of the reactants and the catalyst species increase. It also decreases the time of reaction [38]. The results are shown in table 1.

## CONCLUSION

Transesterification of a variety of alcohols were carried out using Copper powder and Copper nanoparticles as catalyst. The results demonstrate

that nano-size catalyst is more efficient in both yield of the reaction and the time, reaction needs to be compound.

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