

SYNTHESIS OF A NOVEL ORGANOCOPPER REAGENT AND ITS SYNTHETIC UTILITY AS A POTENTIAL REDUCING AGENT

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ABSTRACT

A new organocopper reagent has been synthesized in excellent yield using conventional synthetic method. The compound was characterized by IR, ¹H NMR and AAS spectroscopy. The synthetic use of the reagent as a powerful reducing agent has been reported. This reagent is quite stable and can be handled under normal temperature, and pressure conditions. The reagent is useful for reducing various aldehydes and ketones in excellent yields.

Key words: Organocopper, Reducing, Synthesis, Aldehyde, Ketone.

INTRODUCTION

Aldehydes and ketones can be effectively reduced by organolithium and organomagnesium reagents¹. Organocopper and organozinc reagents are also known to effect similar transformations². Gilman reagent is known to add in 1,4 fashion to conjugate ketones. Grignard-copper(I) reagents are also known to convert acid chlorides to ketones in quantitative yield³.

Reformatsky reaction is an excellent example of organozinc addition to carbonyl group of aldehydes or ketones⁴. Sodium borohydride and lithium borohydrides are also known for their property to reduce the aldehydes and ketones to corresponding alcohols⁵. Wolf-Kishner, and Clemmenson reductions are common in organic chemistry⁶. Ethanethiol esters can also be converted to aldehydes and ketones⁷. Indium and gallium mediated addition reactions are also known in the literature.

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In the present paper, a unique reducing agent has been reported derived from easily available organic substrates and copper acetate. The organocopper reagent thus formed is characterized by IR and ¹H NMR spectroscopy. The reagent is found to be useful for reducing variety of aldehydes and ketones quantitatively.

EXPERIMENTAL

Preparation of the reagent

1 g of o-aminophenol and copper acetate 1 g with 20 mL ethanol was taken in a 50 mL round bottom flask. The resultant reaction mixture was stirred for 10-15 min. The adduct, thus formed, was cooled, filtered and washed with ice-cold ethanol. The reagent was dried at 100°C for 1 hr and was subjected to IR and ¹H NMR spectroscopic characterization.

Reduction of carbonyl compounds

1 g of 4-chlorobenzaldehyde, and 100 mg of copper reagent in 20 mL ethylacetate was taken in a R. B. flask. The reaction mixture was boiled for 1 hr and the progress of reaction was monitored by TLC. Once the reaction is completed, the reaction mixture was filtered through Whatmann paper and the solvent was removed by evaporation. The crude product was crystalline in nature. The melting point and TLC were identical with the authentic 4-chlorobenzyl alcohol. Similarly, the numbers of carbonyl compounds were reduced in excellent yields. The results are summarized in Table 1.

Compound	Catalyst (mg)	Yield (%)	Physical constant
4-chloro benzaldehyde	100	90	70
Cyclohexanone	100	92	161
Acetophenone	100	90	204
Benzaldehyde	100	96	205
Benzophenone	100	86	67
Crotonaldehyde	100	85	121
Salicyladehyde	100	90	86
p-Methoxy benzaldehyde	100	89	259

Table 1: Reduction of aldehydes and ketones

IR and NMR data for organocopper catalyst.

IR (cm⁻¹) 2970-3000 (broad peak of bonded -NH), 3120-3260 (broad peak of bonded –OH))

¹H NMR (δ ppm) CDCl₃ 1.563 (bs, 1H), 6.581 (bs, 2H), 6.7-6.713 (m, 2H), 7.129-7.257 (m, 2H)

CONCLUSION

The organocopper reagent is unique and highly effective for reducing aldehydes and ketones. The reagent thus provides the best option as a reducing agent to the organic chemist.

REFERENCES

- 1. H. Zong, H. Huang, J. Liu, G. Bian and L. Song, J. Org. Chem., 77, 4645-4652 (2012).
- 2. S. H. Kim and R. D. Rieke, Molecules, 15, 8006-8038 (2010).
- 3. W. Bhanthumnavin, Organometallic Chemistry (2008).
- 4. R. K. Kloetzing, T. Thaler and P. Knochel, Org. Lett., 8(6), 1126-1128 (2006).
- H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and E. K. Hyde, J. Am. Chem. Soc., 75(1), 215-219 (1953).
- 6. H. Minlon, J. Am. Chem. Soc., **71**(10), 3301-3303 (1949).
- H. Tokuyama, S. Yokoshima, T. Yamashita, S. C. Lin, L. Li and T. Fukuyamaet, J. Braz. Chem. Soc., 9(4), 381-387 (1998).
- 8. P. H. Lee, Bull. Korean Chem. Soc., **28**(1), 17-28 (2007).

Revised : 11.08.2015

Accepted : 14.08.2015