

# Synthesis, characterisation, and applications of a copper-based novel reducing agent

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**Abstract:** A novel organocopper reagent is synthesised from o-phenylene diamine and copper acetate. This reagent is highly stable at room temperature and easy to handle and use. This reagent is found to reduce various functional group compounds namely acids, aldehydes, ketones, nitriles and nitro aromatics.

**Keywords:** Organocopper reagent, reduction, o-phenylene diamine, nitro compounds.

## INTRODUCTION:

Reduction of various functional groups is an important chemical reaction in organic chemistry. The redox reactions are involved in the synthesis of numerous organic compounds. Selection of a reducing agent for the reduction of a particular functional group can be troublesome, if the selectivity of a reagent has not been evidenced before. A drive for the synthesis of a selective reducing agent is a continuous process. Some common reducing agents used in a day to day chemical laboratories are lithium aluminium hydride<sup>1</sup>, Lithium borohydride<sup>2</sup>, Yellow ammonium sulphide<sup>3</sup> and metal mediated hydrogenation<sup>4</sup>. Diisobutyl aluminium hydride is known for the conversion of nitrile to formyl group and hindered trialkyl borane like trisimyl borohydride are selective reagents for the chiral reduction of ketones. At low temperature, DIBAL-H reduces esters to the corresponding aldehydes and lactones to lactols<sup>5</sup>. Nitriles can be reduced to primary amines employing lithium aluminium hydride<sup>6</sup>. During this reaction, the hydride nucleophile attacks the electrophilic carbon in the nitrile to form an imine anion which forms dianion and eventually accepts protons to form an amine group. Acid chlorides can be selectively reduced to aldehydes using Rosenmund reduction<sup>7</sup>. A novel one pot procedure for a direct reductive conversion of the carbonyl function of esters to the corresponding ethers<sup>8</sup> is reported. Ketones can be reduced to asymmetric alcohols with Corey-Bakshi-sibata reaction<sup>9</sup>. The enantioselective reduction of ketones using borane and chiral oxazolidines as a catalyst. Silylative reduction of nitriles was studied under transition metal free condition by using B(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> as a catalyst with hydrosilanes as a reductant<sup>10</sup>. Alkyl and heteroalkyl nitriles were effectively converted to primary amines or imines under mild conditions. The choice of a silane determines the selectivity. A complete reduction of nitrile is feasible with bulky silanes. Selective reduction of one nitro group in a m- dinitrobenzene is executed by yellow ammonium sulphide<sup>11</sup>. Amide to amine functional group is accomplished by silylhydride derived reagent. In combination with an alkali metal base, it was found to catalyse reduction of all three types of amides classes under mild conditions<sup>12</sup>. Use of copper for Aza-Michael addition has been reported. Microwave assisted and copper catalysed Ullmann type coupling for the synthesis of aminoanthraquinone is reported<sup>13</sup>. Copper catalysed aryl amination for 1,2- disubstituted benzimidazole has been achieved. copper is used as a catalyst for the synthesis of benzoxazole derivatives under microwave conditions<sup>14</sup>. A cross coupling reaction between 2-haloanilines with isothiocyanates has been accomplished employing ligand-free copper (I) catalyst<sup>15</sup>. Fluorination of aromatic substrates has been done with copper fluoride<sup>16</sup>. An aerobic oxybromination is effected by the use copper catalyst in aqueous medium<sup>17</sup>. Oxidation of alkanes and alkenes in presence aldehydes is known to catalysed by the copper based catalyst<sup>18</sup>. Copper (II) triflate catalysed reduction of acids to alcohols and reductive etherification of carbonyl compounds have been reported recently<sup>19</sup>. Copper catalysed amide bond formation from formamide and carboxylic acid has been achieved in excellent yield<sup>20</sup>. Considering the multiple applications of copper and copper based derived reagents, we have synthesised a novel organocopper reagent from o-phenylene diamine and copper acetate. This reagent is characterised by IR and PMR spectroscopy. This reagent is stable at room temperature and can be stored and handled easily. This reagent is found to reduce acids, aldehydes, ketones, nitriles and nitro compounds in excellent yield. Development of improved method for the synthesis of organocopper reagent is very useful for the advancement of fundamental research in the field of chemistry .

## Materials and methods:

The chemicals were procured and purified prior to the use. The catalyst was stored in a stoppered bottle and can be used as per the requirement. The catalyst was found to be effective in reduction of different functional groups. The reaction is carried out at 75 °C for few minutes so chances of by products are less.

## Preparation of a reagent:

1gm of o-phenylene diamine and 1gm copper acetate was taken in round bottom flask. Methanol (20 mL) was introduced to it and the reaction mixture was stirred for 10 minutes. The adduct thus formed was cooled and filtered through Whatmann paper, washed with ethanol and was dried at 100 °C for 1 hr. The reagent was obtained as a blackish brown solid. Its m.p. was found to be 194 °C (dec.). The organocopper reagent is stored in a stoppered bottle. The reagent was subjected to the characterisation by IR and <sup>1</sup>H NMR spectroscopic techniques.

IR (cm<sup>-1</sup>): 3600, 3250, 1500, 1600, 500

$^1\text{H}$  NMR (DMSO) ppm: 3.5, 6.2–8.0, 13  
 EDAX: C = 70.33%, N = 18.80%, O = 9.49%, Cu = 1.38%  
 Matrix Correction ZAF

#### Reduction of various functional groups:

**General procedure:** In a round bottom flask 1 gm of 4-chloro benzaldehyde was charged. Catalyst (100 mg) and 20 mL of ethyl acetate was added to it and the reaction mixture was boiled for 15-20 min and the progress of reaction was monitored by T.L.C. Once the reaction is completed, the contents were filtered through Whatman filter paper and solvent was removed to furnish crude product. The crude product was given a charcoal treatment so as to remove any traces of the catalyst remained with it.

#### Results and Discussion:

The catalyst was employed for the reduction of different compounds. The findings are given in the following Table 1.

**Table 1.**

S.No.	Substrate	Catalyst mg	Time Min.	% Yield	Physical constant °C
1	4-Chloro benzaldehyde	100	15	92	70
2	3-Nitro benzaldehyde	100	20	87	178
3	2- Hydroxy Benzaldehyde	100	15	88	84
4	Benzaldehyde	100	15	94	205
5	Benzophenone	100	15	86	68
6	M-Dinitro benzene	100	15	89	114
7	4-chloro benzoic acid	100	30	90	70
8	Benzyl cyanide	100	30	88	194

The organocopper reagent was found to highly selective for the partial reduction of M-dinitro benzene to m-nitro aniline. It also reduces the nitrile group into a primary amine. The sterically hindered carbonyl group of benzophenone was also reduced to its secondary alcohol. It is powerful to reduce the carboxylic acid functional group to a primary alcohol. This reagent was found to be very useful reducing agent for the researchers in the discipline of chemistry.

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