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Copper(I) Chloride/Kieselguhr: a Versatile Catalyst for Oxidation of Alkyl Halides and Alkyl Tosylates to the Carbonyl Compounds†

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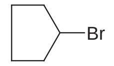
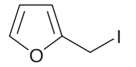
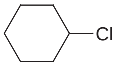
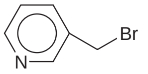
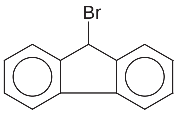
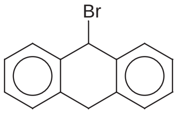
Copper(I) Chloride adsorbed on Kieselguhr in the presence of oxygen catalyses oxidation of alkyl halides and alkyl tosylates to the aldehydes and ketones in high yields.

The introduction of supported reagents for bringing about various organic reactions of synthetic significance has recently been accomplished.[1] These reagents not only modify the activities but also may impart product selectivities. For example oxidation of alkyl halides and alkyl tosylates to carbonyl compounds using supported reagents is an important method for preparation of aldehydes and ketones. In this regard various reagents have been developed: dimethyl sulfoxide,[2] *N,N*-dimethyl-4-nitrosoaniline[3] (Krohnke oxidation), nitronate anion and $Pd(PPh_3)_4$,[4] pyridine *N*-oxides[5] and other amine oxides,[6] chromate and dichromate systems,[8] silver nitrate,[9] hexamethylene tetraamine,[10] pyrazinyl sulfoxides[11] and pyridine *N*-oxide with microwave irradiation.[12]

Table 1 Oxidation of alkyl halides and tosylates to carbonyl compounds

$$R^1R^2CHX \xrightarrow[O_2]{CuCl/Kieselguhr} R^1R^2C{=}O$$

Entry	Substrate	Solvent	Reaction time/h	Yield(%)
1	CH_3CH_2Cl	CH_2Cl_2	1.5	94
2	$CH_3CH_2CH_2Cl$	CH_2Cl_2	1.5	91
3		Hexane	2.5	99
4	$C_6H_5CH_2Cl$	Hexane	2.5	90
5	*p*-$CH_3C_6H_4CH_2Br$	Hexane	4	87
6		Hexane	2	93
7		Hexane	3	88
8		Hexane	2.5	84
9		Toluene	4	86
10		Toluene	4	81[a]
11	CH_3CH_2OTs	Hexane	0.75	89
12	$CH_3(CH_2)_5CH_2OTs$	Hexane	1	85
13	$C_6H_5CH_2OTs$	Hexane	3	87
14	*p*-$CH_3C_6H_4CH_2OTs$	Toluene	3.75	85
15	$C_6H_5CH{=}CHCH_2OTs$	Hexane	4	91[b]

[a] The product is anthrone. [b] Yield of 2,4-dintrophenylhydrazone derivative.

Table 2 Reusability of catalyst[a]

Experimental trial	Yield(%)
1st	90
2nd	88
3rd	87
4th	87
5th	86

[a] All reactions are carried out under similar conditions, time 2.5 h.

Some of these reagents or catalysts have low yields,[2,5,6,10] others using high temperature,[2,10] long reaction times,[3,4,11] bulk requirement of the solid bed[7,8] and pyridine *N*-oxides with microwave irradiation only oxidize benzylic halides to aldehydes.[12]

In recent works we have reported a mixture of cobalt and manganese salts of *p*-aminobenzoic acid supported on silica gel as a catalyst in the presence of oxygen as a mild and efficient oxidizing agent for different functional groups such as benzylic and allylic alcohols to their corresponding carbonyl compounds,[13] aromatization of 1,4-dihydropyridines to pyridine derivatives,[14] conversion of xylenes into toluic acids[15] and oxidation of phenols to quinones.[16] However, this procedure did not work satisfactorily for oxidation of alkyl halides and tosylates to corresponding carbonyl compounds.

Now, we report a very simple and convenient procedure for oxidation of primary and secondary alkyl halides and tosylates to carbonyl compounds using molecular oxygen and CuCl/Kieselguhr as catalyst. The catalyst is prepared by addition of weighed amounts of Kieselguhr to a water solution of CuCl followed by evaporation of solvent to dryness. The oxidation conditions are shown in Table 1.

Table 2 shows the reusability of the catalyst after 5 replicate oxidations of benzyl chloride to benzaldehyde. The catalyst was recovered quantitatively after each experiment.

In conclusion, mild reaction conditions, good yields, ease of work-up, stability and reusability of the catalyst are the most significant aspects of this method.

Experimental

Alkyl halides were purchased from Fluka, Merck and Aldrich. Alkyl tosylates were prepared by treatment of corresponding alcohols with tosyl chloride in acetonitrile. All products are known compounds and were identified by their FT-IR spectra and mps of their 2,4-dinitrophenylhydrazone derivatives. Yields reported refer to isolated products.

Preparation of CuCl/*Kieselguhr Reagent*.—To a water solution of CuCl (10 mg in 100 ml of water), Kieselguhr (50 g) was added and the mixture stirred for 30 min. Water was evaporated *in vacuo* and the residue dried in an oven at 110 °C for 5 h to give 59 g of CuCl/Kieselguhr reagent.

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Oxidation of Alkyl Halides and Tosylates to Carbonyl Compounds: Typical Procedure.—To a stirring solution of benzyl chloride (8 mmol) in hexane (30 ml) was added CuCl/Kieselguhr reagent (5 g). The reaction mixture was refluxed for 2.5 h during which time oxygen was bubbled at a rate of 10 ml min^{-1}. The mixture was then cooled to room temperature and filtered through a sintered glass funnel. The residue was washed thoroughly with the solvent (20 ml). Removal of the solvent followed by distillation of the residue gave 0.22 g (90%) of benzaldehyde.

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