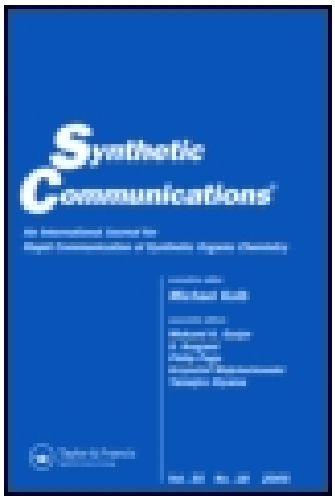

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 16 Aug 2006.

To cite this article: Mohammed M. Hashemi & Yousef A. Beni (2001) REGENERATION OF CARBONYL COMPOUNDS BY OXIDATIVE CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS WITH MOLECULAR OXYGEN IN THE PRESENCE OF COPPER(I) CHLORIDE/KIESELGHUR AS CATALYST, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:2, 295-299, DOI: 10.1081/SCC-100000213

To link to this article: http://dx.doi.org/10.1081/SCC-100000213

SYNTHETIC COMMUNICATIONS, 31(2), 295–299 (2001)

REGENERATION OF CARBONYL COMPOUNDS BY OXIDATIVE CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS WITH MOLECULAR OXYGEN IN THE PRESENCE OF COPPER(I) CHLORIDE/KIESELGHUR AS CATALYST

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ABSTRACT

Kieselghur-supported copper(I) chloride was found to be an efficient and convenient catalyst for the oxidative cleavage of oximes, phenylhydrazones, and *p*-nitrophenylhydrazones to the corresponding carbonyl compounds with molecular oxygen.

Oximes, phenylhydrazones, and *p*-nitrophenylhydrazones have been employed as ketone or aldehyde functional group equivalents in organic synthesis (1–3). The regeneration of carbonyl compounds from their derivatives provides an attractive method for the synthesis of aldehydes and ketones.

Many methods have been developed for the oxidative cleavage of oximes, phenylhydrazone, and *p*-nitrophenylhydrazones to the corresponding carbonyl

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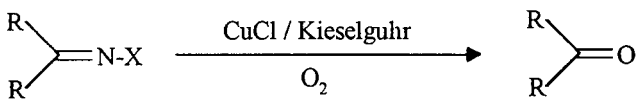
compounds (4–29), but some of them have limitations for oximes, and some, in spite of generality, have the drawback of using expensive oxidants, tedious work-up, low chemical yields, strong oxidative conditions (4–29), or side product formation.

During the course of our systematic study on catalytic oxidation of organic compounds with molecular oxygen, we have recently developed a heterogeneous catalytic method based on copper(I) chloride adsorbed on Kieselghur that is an efficient and convenient catalyst for the oxidation of alkyl halides and alkyl tosylates to the carbonyl compounds using molecular oxygen (30).

We report here a new and very convenient procedure for the oxidative cleavage of carbon-nitrogen double bonds using molecular oxygen and CuCl/Kieselghur. This catalyst is stable, reusable, and easily prepared by the addition of weighed amounts of Kieselghur to an aqueous solution of CuCl, followed by evaporation of solvent to dryness. The oxidative cleavage of carbon-nitrogen double bonds is carried out in DCM as solvent and work-up is simply by extraction and separation of the catalyst by filtration. After removal of the solvent and purification of products by chromatography, carbonyl compounds are obtained in high yields (Table 1).



X = OH, NHPh, $NHC_6H_4(NO_2\text{-}p)$

This catalyst is reusable and the reusability of the catalyst after 4 successive oxidations of benzaldehyde oxime to benzaldehyde is shown in Table 2. The catalyst was recovered quantitatively after each experiment.

EXPERIMENTAL

Chemicals were purchased from Merck, Aldrich, and Riedel de Haen AG chemical companies and were used without further purification. IR spectra were recorded (KBr) on a FT-IR Unicam Mattson 1000 Spectrophotometer. ^{1}H-NMR spectra were recorded on a Brucker AC-80 (80 MHz) spectrometer in $CDCl_3$ and chemical shifts are indicated in δ ppm. All products are known compounds and they were identified by their m.p.s, or b.p.s, IR and ^{1}H-NMR, spectroscopic properties. All yields refer to pure isolated products. Oximes, phenylhydrazones, and *p*-nitrophenylhydrazones were prepared by usual procedure.

Preparation of CuCl/Kieselghur Reagent

To a water solution of CuCl (10 mg in 100 mL of water) Kieselghur (50 g) was added and the mixture stirred for 30 min. Water was evaporated in vacuo and

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Table 1. Oxidative Cleavage of Carbon-Nitrogen Double Bonds Using Molecular Oxygen and CuCl/Kieselghur

Entry	Substrate[a]	Time (min)	Product[a]	Yield (%)[b]
1	benzaldoxime	20	benzaldehyde	96
2	acetophenone oxime	25	acetophenone	97
3	4-methylacetophenone oxime	30	4-methylacetophenone	96
4	cyclohexanone oxime	25	cyclohexanone	90
5	anthrone oxime	30	anthrone	85
6	cinnamaldoxime	30	cinnamaldehyde	92
7	2-thiophenaldoxime	30	2-thiophenaldehyde	88
8	4-nitrobenzaldoxime	30	4-nitrobenzaldehyde	91
9	4-methylbenzaldoxime	20	4-methybenzaldehyde	98
10	heptanal oxime	25	heptanal	89
11	benzophenone-PH[c]	25	benzophenone	97
12	4-pyridine carbaldehyde-PH[c]	30	4-pyridinecarbaldehyde	95
13	4-methylbenzaldyde-PH[c]	30	4-methybenzaldyde	94
14	benzaldehyde-PH[c]	25	benzaldyde	98
15	4-methylbenzaldyde-4-NPH[d]	30	4-methybenzaldyde	90
16	acetophenone-4-NPH[d]	30	acetophenone	92
17	4-chlorobenzaldehyde-4-NPH[d]	30	4-chlorobenzaldyde	86

[a]All compounds were fully characterized by their mps, IR and ^{1}H-NMR spectra.
[b]Yields refer to pure isolated products.
[c,d]PH represents 4-nitrophenylhydrazone and 4-NPH represents 4-nitrophenylhydrazone.

the residue dried in an oven at 110°C for 5 h to give 59 g of CuCl/Kieselghur reagent.

Regeneration of Carbonyl Compounds

To a stirring solution of benzaldehyde oxime (2 mmol) in DCM (25 mL) was added CuCl/Kieselghur reagent (5 g). The reaction mixture was stirred at room

Table 2. Reusability of Catalyst[a]

Experimental Trial	Starting Material	Product	Yield (%)
1st	benzaldehyde oxime	benzaldehyde	98
2nd	benzaldehyde oxime	benzaldehyde	95
3rd	benzaldehyde oxime	benzaldehyde	93
4th	benzaldehyde oxime	benzaldehyde	91

[a]All reactions are carried out under similar conditions as Table 1.

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temperature, during which time oxygen was bubbled at a rate of 10 mL min^{-1}. Progress of the reaction was monitored by TLC (hexane ethylacetate 5:1). When the reaction was completed, the reaction mixture was filtered through a sintered glass funnel. The residue was washed thoroughly with the solvent (25 mL). Removal of the solvent followed by column chromatography on silica gel (hexane ethylacetate 5:1) gave the pure product.

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

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Received in the UK November 24, 1999

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