SHORT PAPER

J. Chem. Research (S),
2000, 222–223

Amberlyst A-26 suppported peroxodisulfate. Part 1: an efficient reagent for selective carbon–nitrogen double bond cleavage of oximes†

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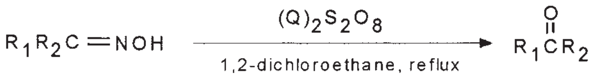
Convenient and efficient method for the selective deoximation reaction is described using amberlyst A-26 supported peroxodisulfate.

The carbon-nitrogen double bond cleavage of oximes to regenerate the original aldehydes and ketones has received much attention over the past decades.[1] As a result, several methods have been reported for this purpose. On the basis of their mechanism, three categories are involved: (i) acid catalysed hydrolysis,[2] (ii) oxidative deoximation,[3] (iii) reductive deoximation.[4] Recently, enzymatic hydrolysis of oximes has also been communicated.[5] Many of these procedures either do not describe the selective deoximation reaction or limit the scope of the reaction to exclude acid sensitive compounds. Furthermore, some of these methods suffer from overoxidation or reduction of the released aldehydes and ketones. In our laboratory we have investigated a heterogeneous system in order to immobilize the inorganic reagents producing a chemoselective reagent or catalyst.[6] We now report the selective oxidative regeneration of aldehydes and ketones from the corresponding oximes by amberlyst A-26 supported peroxodisulfate under non-aqueous conditions. This reagent is easily prepared by the simple exchange reaction of peroxodisulfate anion with the chloride form of amberlyst A-26 resin. This polymeric oxidant is stable and can be stored for months without appreciable loss of activity. The peroxodisulfate content of the reagent was determined by iodometric titration to be 0.9 mmole per gram of the reagent.



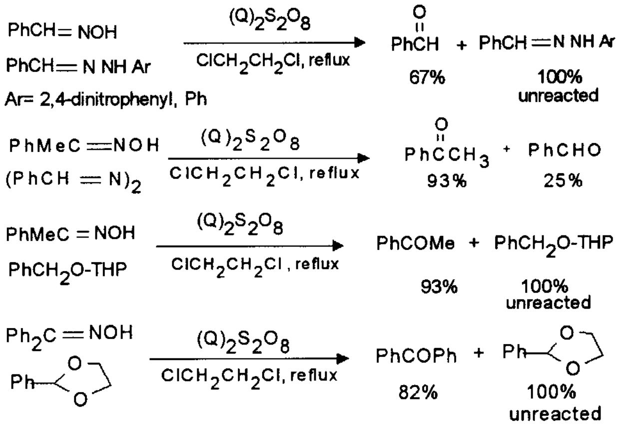
$$R_1R_2C{=}NOH \xrightarrow[\text{1,2-dichloroethane, reflux}]{(Q)_2S_2O_8} R_1\overset{O}{\overset{\|}{C}}R_2$$

$(Q)_2S_2O_8$ = Amberlyst A-26 supported peroxodisulfate

As shown in Table 1, oximes are efficiently converted to their corresponding aldehydes and ketones in 1,2-dichloroethane at 80°C. The reaction is most suitable for the conversion of ketoximes to ketones, and deoximation of aldoximes requires a longer reaction time. Two or three equivalents of oxidant are necessary to obtain good yields. However, further oxidation of the liberated carbonyls was not observed. As seen in Scheme 1, competitive reaction of oximes *vs* hydrazones or azenes shows selectivity of the reagent as a particular feature, since carbon-nitrogen double bond cleavage of hydrazones and azines occurred only at longer period of time and at very low yields; isolation and analysis of the reaction mixture clearly show the unreacted hydrazone or azine. In addition, under the same condition, 1,3-dioxolanes and tetrahydropyranyl ethers remained intact in reaction mixture (Scheme 1).

Experimental

All products were characterized by comparison of their spectral and physical data with those of known samples. IR spectra were obtained using a Shimadzu 470 instrument. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX 60 MHz NMR spectrometer with TMS as internal standard. Amberlyst A-26 (Cl^- form) was purchased from Merck.



Scheme 1

Preparation of amberlyst A-26 supported peroxodisulfate: To a solution of potassium peroxodisulfate (1.17 g, 4.3 mmol) in water (25 ml), amberlyst A-26 (Cl^- form, 5.13g) (the resin as supplied contains 61% of water) was added. The mixture was stirred magnetically at room temperature for 20 minutes and then filtered. The reagent was dried at 35°C in a vacuum desiccator.

General procedure for conversion of oximes to their corresponding carbonyl compounds: The oxime (0.41–0.82 mmol) was dissolved in 1,2-dichloroethane (5 ml). The oxidant (1.66–3.54 mmoles) was added and the reaction mixture was heated under nitrogen for (5.5–18) h. The progress of the reaction was monitored by TLC (eluent: carbon tetrachloride/methanol). The reaction mixture was left at room temperature for 10 minutes and filtered. The solid material was washed with 1,2-dichloroethane (5 ml). After evaporation of the solvent, the resulting crude material was purified on a short silica gel column which afforded pure product in 50–95% yields.

General procedure for competitive deoximation reactions: To an equivalent solution of oximes and azine or hydrazones or THP-ethers

Table 1 Regeneration of aldehydes and ketones from oximes[a]

Entry	R_1	R_2	Time (h)	Yield (%)[b]
a	Ph	Me	8	92
b	*p*-MeC$_6$H$_4$	Me	5.5	96
c	*p*-NO2C$_6$H$_4$	Me	14	86
d	*o*-MeO$_6$H$_4$	Me	5	92
e	*p*-ClC$_6$H$_4$	Me	9	93
f	*p*-BrC$_6$H$_4$	Me	9	90
g	Ph	Ph	14	84
h	-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$-		18	78
i	Ph	PhCO	18	68
j	Ph	H	18	67
k	*p*-MeC$_6$H$_4$	H	18	74
l	*p*-NO2C$_6$H$_4$	H	18	68
m	*p*-ClC$_6$H$_4$	H	18	68
n	CH$_3$(CH2)$_5$CH$_2$-	H	18	70

[a] Reactions are conducted in refluxing 1,2-dichloroethane with 4:1 molar ratio of oxidant to substrate.
[b] Isolated yields.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

in dichloroethane (10 ml), was added 3.0 g of polymeric reagent. The mixture was stirred under reflux for 20 h, and filtered. The resulting mixture was purified on silica-gel plate with an appropriate eluent.

We are thankful to Prof. B. Tamami and Dr. B. Movassagh for their help and encouragement and grateful to the Razi Council for partial support of this work.

Received 24 November 1999; accepted 22 May 2000
Paper 99/32

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