Enzymatic Deoximation of Oximes by Ultrasonically Stimulated Baker's Yeast

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The enzymatic conversion of oximes by ultrasonically stimulated baker's yeast yields the corresponding aldehydes and ketones in high yields.

Because of the use of oximes as protecting groups and selective activating groups, the regeneration of ketones from them is of importance.[1,2] This is particularly so now that the Barton reaction, in which oximes are produced at non-activated hydrocarbon sites, has potential for the preparation of carbonyl compounds.[4] Since acid catalysed hydrolysis[5,6] of oximes to carbonyl compounds and hydroxy amines is non-selective, particularly in the presence of acid-sensitive functions in the molecule, a number of oxidative[7,8] and reductive[9,10] deoximation methods have been developed. In spite of this, most of them are quite non-selective and unsatisfactory.

Although baker's yeast (*Saccharomyces cerevisiae*) mediated reduction of carbonyl compounds has been investigated[11] extensively, while the reduction or oxidation of other functional groups has not much been studied. We have recently explored the use of baker's yeast for the enzymatic hydrolysis of hydrazones to their corresponding carbonyl compounds.[12] In continuation of this finding as well as our interest on the application of enzymes as biocatalysts[13–15] in organic synthesis, we herein report an exceptionally mild, convenient and facile deoximation reaction employing baker's yeast. This study also demonstrates the effect of ultrasonic pretreatment of baker's yeast in these reactions.

A wide variety of oximes (**a–j**) were hydrolysed by baker's yeast to afford the corresponding aldehydes and ketones. It is interesting to note that the ultrasonic pretreatment of baker's yeast not only enhanced the yields by *ca.* 35% but accelerated these transformations as well (Table 1). The reactions were monitored by HPLC on TSK Si-150 column (250 × 4.6 mm), 5 μm, chloroform–hexane (65:35) at 254 nm and 0.9 ml/min flow rate. A control incubation using a boiled yeast preparation afforded 98% of the recovered oxime.

All the compounds were characterized on the basis of elemental analysis, spectroscopic data and by comparison with the standard samples.

Thus, this biocatalytic method with almost quantitative yields employing ultrasonically stimulated baker's yeast is a simple, mild and convenient procedure for the regeneration of carbonyl compounds from their oximes, Further applications and the mechanistic aspects of this bio-oxidative transformation of oximes to carbonyl compounds are in progress.

Table 1 Enzymatic regeneration of aldehydes and ketones from oximes

	Aldehydes and ketones **2**	Yield (%) Unsonicated[a]	Sonicated[b]
a	Benzaldehyde	68	96
b	*p*-Methoxybenzaldehyde	72	98
c	Caproaldehyde	75	95
d	Acetophenone	56	63[c]
e	Benzophenone	51	62[c]
f	Cyclohexanone	65	87
g	Pinacolone	68	92
h	Camphor	76	97
i	ε-Caprolactone	63	94
j	Butan-2-one	58	93

[a] After 3 days of incubation. [b] After 2 days of incubation. [c] Lower yield in these cases is probably due to the relative less solubility of oximes.

Experimental

To ultrasonically pretreated baker's yeast,[13] Sigma type I (15 g) in 0.1 mol dm^{-3} phosphate buffer, pH 7.2 (150 ml) was added the oxime (700 mg) in ethanol (15 ml). The mixture was incubated at 37 °C and after oxime conversion had ceased (2–3 days), it was filtered through Celite. The filtrate was extracted twice with ethyl acetate and the Celite layer was also washed three times with ethyl acetate. The combined organic phase was dried and evaporated under reduced pressure. The residue obtained was purified by column chromatography to yield the aldehydes or ketones.

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