SHORT PAPER

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Deoximation with hexamethylenetetramine-bromine supported on alumina in non-aqueous condition†

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Hexamethylenetetramine-bromine on alumina rapidly regenerates carbonyl compounds from their corresponding oximes in non-aqueous condition.

Keywords: hexamethylenetetramine-bromine, deoximation, alumina

Oximes are used not only to isolate and purify but also to protect[1] carbonyl compounds during multistep syntheses. The regeneration of carbonyl compounds from their oximes is an important reaction and it has assumed an added importance after the discovery of the Barton reaction in which oximes are produced from non-carbonyl compounds.[2]

Several methods for the regeneration of carbonyl compounds from their oximes such as pyridinium chlorochromate,[3] pyridinium chlorochromate–hydrogen peroxide,[4] triethylammoniumchlorochromate,[5] chromic-anhydride-chlorotrimethylsilane,[6] dinitrogen tetraoxide,[7] titanium silicate,[8] N-haloamide,[9] manganese triacetate,[10] Dess-Martin periodinane,[11] tetrabutylammonium peroxydisulfate,[12] clay supported ammonium chlorochromate[13] and clayfen[14] have been reported. Although some of these methods are carried out under mild reaction conditions most of them require strong acidic media, a strong oxidising agent, rare, poisonous reagents or sometimes long reaction times for the regeneration of carbonyl compounds from oximes. Thus there is still a need to develop a new and facile procedure for the regeneration of carbonyl compounds from oximes.

Hexamethylenetetramine-bromine is an inexpensive reagent which has been reported as an oxidizing agent.[15] Although there is a reference in the literature that indicates its application in other oxidative clevage reactions,[16] we found that in the absence of mineral supports the attempted cleavage of oximes is sluggish with hexamethylenetetramine-bromine even after prolonged reaction periods.

In recent years, the organic reactions on solid supports have attracted much attention because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation.[17] In continuation of our ongoing efforts in reagent supported reactions[18] and in view of the established beneficial effects of the reagents on solid supports we examined various mineral supports such as clays, silica and alumina with hexamethylenetetramine-bromine and soon discovered that alumina allows the clean regeneration of the correspounding carbonyl compounds from oximes. When this supported reagent was refluxed with oximes in CH_2Cl_2 the corresponding carbonyl compounds were regenerated almost quantitatively (Table 1).

In a typical reaction 2 equiv of hexamethylenetetramine-bromine supported onto alumina was added to a stirred and refluxed solution of an oxime in dry CH_2Cl_2. The reaction mixture was refluxed until the reaction was complete. It was then filtered and washed with dichloromethane. Evaporation of the solvent and column chromatography gave the corresponding carbonyl compounds in high yields (Table 1).

The formation of aluminium tribromide is possible in this reaction and deoximation can be carried out by the latter instead of hexamethylenetetramine-bromine. This possibility can be ruled out, because no trace of brominated products in aromatic rings were detected. The melting and boiling points of the products were compared with those of authentic samples (Table1).

In conclusion hexamethylenetetramine-bromine supported on alumina is a simple and inexpensive reagent for the regeneration of carbonyl compounds from oximes.

Experimental

All products were known and identified by comparison with authentic samples. Yields refer to isolated products. Hexamethylenetetramine-bromine supported on alumina was prepared by the reported procedure.[15b]

Deoximation of oximes(general procedure): Hexamethylenetetramine-bromine supported on alumina (2.5 mmol) was refluxed with the appropriate oxime (1.5 mmol) in CH_2Cl_2 (25ml) for indicated time (Table1). After completion of the reaction (monitored by TLC), the solvent was evaporated to the dryness and the crude was directly subjected to column chromatography using pet ether –AcOEt (80–20) as eluent to afford the corresponding carbonyl compound (Table 1).

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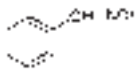
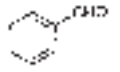
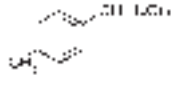
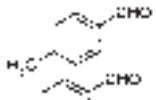
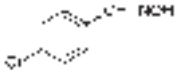
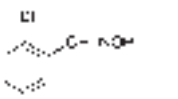
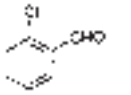
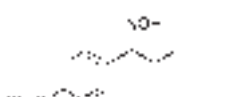
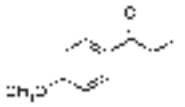
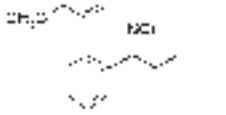
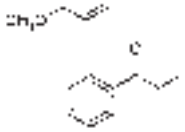
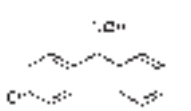
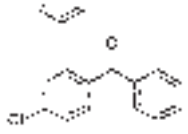
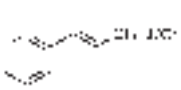
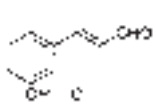
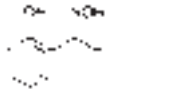
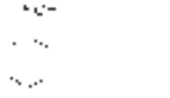
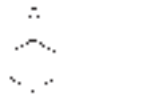
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Oxidative cleavage of oximes with hexamethylenetetramine bromine supported on alumina in non aqueous condition

Entry	Substrate	Carbonyl compound	Reaction time (min)	M.p./B.p./C/torr		Yield
				Found	Reported[19]	
1			40	178–179/760	174–176/760	92
2			40	201–203/760	204–205/760	90
3			45	48–51	47–50	88
4			45	206–213/760	209–215/760	83
5			55	28–30	27–29	81
6			50	215–219/760	218/760	82
7			60	73–77	75–77	78
8			45	198–200/200	199.3/200	85
9			40	194–196/760	197/760	90
10			45	152–155/760	155/760	82

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