Microwave Promoted Regeneration of Carbonyl Compounds from Oximes Using *N, N*-Dichloro Poly(Styrene-co-divinylbenzene)Sulphonamide Resin

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Abstract: An efficient, economically viable and operationally simple method was developed for deoxygenation of oximes (of ketones and aldehydes) to their corresponding carbonyl compounds using polymer beads of *N, N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide resin. Polymeric reagent offered speedy conversion and substantial yields of products under mild condition and is recyclable. Deoxygenation was monitored by the use of ^{13}C NMR.

Keywords: Deoxygenation, *N, N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide, Solid phase reagent, Resin.

Introduction

Oximes play a significant role in the organic synthesis as carbonyl group protector and enable the isolation and purification of ketoximes and aldioximes by selectively protecting them¹⁻¹⁷. A plethora of papers in the literature reveals the interest of researchers towards the rapid development of novel techniques for regeneration of carbonyl compounds from oximes under the mild conditions.

A wide variety of deoxygenation reagents have been developed so far such as manganese triacetate¹⁸, dinitrogen tetroxide¹⁹, trimethylsilyl chlorochromate²⁰, titanium silicalite²¹, pyridinium chlorochromate²², bismuth trichloride²³, ammonium persulfate- silica gel²⁴, sodium periodate²⁵. Among them some require strong acidic condition; some takes long reaction time and give low product yield while some are poisonous and oxidative reagents posses serious isolation difficulties.

Heterogenised reagents²⁶⁻²⁸ has evinced the attention of researchers because of their handling ease, lower toxicity, non explosive and malodorous nature. Another important motive of supported reagents is facile isolation of the pure product than their solution phase equivalents. Few reports are available on the solid supported deoxygenating agents under mild condition^{29,30}.

N-halo reagents are widely used in fine organic synthesis because of its highly reactive N-X bond and various mode of its splitting. This polymeric resin proved to be a very strong chlorinating agent and found to be easily regenerable and reusable. In earlier work *N,N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide has been reported as decontaminant³¹ and as chlorinating reagent for synthesis of dialkyl chlorophosphates³². This development encouraged us to explore the utility of polymeric beads in multi-dimensions. Here we report an organic transformation: a conventional and microwave assisted clean, rapid and efficient method for the regeneration of carbonyl compounds with the help of beads.

Experimental

IR spectra were recorded on FT-IR spectrometer Perkin-Elmer model 1720 on KBr disk. (for solids) and neat for liquids. ¹³C{¹H}NMR spectra were recorded in CDCl₃ solvent on Bruker DPX Advance FT-NMR instrument at 400 MHz and 100 MHz respectively using trimethylsilane as an internal standard at 0.0 ppm. A house hold LG make oven was used for studies.

General procedure for deprotection of oximes

A mixture of oxime (2 mmol), carbon tetrachloride (8 mL) and *N,N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide resin (2 mmol) was refluxed or irradiated in the microwave oven at power 600 W for specific time period (Table 1). When all the oxime was converted, the intermediate was hydrolysed by adding water and washed with CCl₄. Before adding CCl₄ beads were separated out through filtration. The organic layer was dried with MgSO₄ after separation from aqueous layer. Carbon tetrachloride was evaporated to get desired product. The yield and ¹³C NMR chemical shift values are summarized in the Table 1 and 2 respectively.

Table 1. Deoxygenation with *N,N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide produced via Scheme 1

Entry	Product ^a	Time Reflux ^b / M.W. ^c	Yield, %	Entry	Product ^a	Time Reflux ^b / M.W. ^c	Yield %
1		55/60	96	9		65/120	81
2		50/60	92	10		75/90	89
3		75/90	89	11		75/120	85
4		65/90	90	12		55/90	82
5		90/120	91	13		65/90	88
6		65/90	91	14		70/120	76
7		50/90	85	15		70/90	79
8		60/90	90	16		50/60	86

M.W.=Microwave, ^aProducts were characterized by their physical properties, comparison with authentic samples and IR spectra. ^btime in minutes. ^ctime in seconds

Results and Discussion

The microwave energy has given a new dimension and vision to organic reactions²⁹. The reaction of oximes with polymeric reagent in CCl₄ provide carbonyl compound without any side product, under the microwave radiations (Scheme 1). The completion time of reaction was monitored by TLC and ¹³C{¹H} NMR spectroscopy.

Scheme 1

We obtained almost all quantitative yields in short reaction times. The microwave temperature for the reaction of various oximes with *N, N*-dichloro poly(styrene-co-divinylbenzene)sulphonamide polymeric beads afforded the corresponding carbonyl compounds in 55 to 90 sec. in excellent yields (Scheme 1, Table 1). The uniqueness of this method is its simplicity and time saving. The process of a typical reaction was monitored by appearance and disappearance of ¹³C NMR signal of carbonyl and oximino carbon respectively (Figure 1).

Figure 1. Progress of a typical reaction as monitored by ¹³C{¹H} NMR analysis at different time intervals for entry 2.

Reason behind the use of NMR is here, that it provides direct analysis of reaction mixture without the use of any tedious sample preparation method as it is required in GC-MS. The carbon chemical shift changes with significant difference ($\sim \Delta\delta = 35$ ppm) on conversion of oxime (δ range of C=N is 145-170 ppm) into carbonyl (δ range of C=O is 190-227 ppm). ¹³C{¹H} NMR chemical shifts of oximes and carbonyl compounds are presented in the Table 2. The results of conversion of oximes to their corresponding carbonyl compounds are presented in the Table 1. In order to evaluate the generality and applicability of this method a variety of oximes were deprotected to their parent carbonyl compounds. The product of reaction with polymeric reagent was isolated simply by filtering off the solid polymer and subsequently evaporation of the solvent from filtrate. The advantages of this method are good yield, mild condition, short reaction time and no side product. The recovered polymer was again chlorinated and reused up to several times without any loss in activity.

Table 2. $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of compounds

Entry	^{13}C NMR values of carbonyl carbon	^{13}C NMR values of oximino carbon	Entry	^{13}C NMR values of carbonyl carbon	^{13}C NMR values of oximino carbon
1	197.1	162.3	8	212.7	173.6
2	198.61	162.2	9	217.2	163.7
3	195.89	162	10	217.1	169.9
4	201.1	160.4	11	217.8 * 201.2	164.8 163.2
5	207.8	163.8	12	192	151.9
6	194.5	163.9	13	210.7	145.1
7	209.7	160.5	14	212.3	142.6
8	192.6	161.9	15	216.1	144.7

^a Chemical shift of carbonyl carbon in ppm, * acetyl group, ^b chemical shift of oximino carbon in ppm

Conclusion

In conclusion, *N, N*-dichloro poly(styrene-co- divinylbenzene)sulphonamide resin is a efficient reagent to fulfil different required objectives of organic synthesis. Here in this work it is proved to be an important and valuable reagent for the conversion of oximes to their corresponding carbonyl compounds. The conversion was very efficient, with excellent yield, and polymeric reagent can be recovered, activated and reused. The main advantage of the method is that reactions were very clean and operationally simple. Therefore method is attractive for organic chemist.

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