

Microwave Assisted Facile Cleavage of Oximes by Poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide]

Ardeshir Khazaei^{1(*)}, Shadpour Mallakpour² and Ramin Ghorbani Vaghei¹

(1) Department of Chemistry, Faculty of Science, Bu-Ali Sina University,
P.O. Box: 65174-4119, Hamadan, I.R. Iran

(2) College of Chemistry, Isfahan University of Technology, Isfahan-84156, I.R. Iran

Received 26 June 2002; accepted 19 October 2002

ABSTRACT

The main objective of this research was preparation of polymeric compound that to be able to deoximate the ketone and aldehyde oximes to their corresponding carbonyl compounds. In this work poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide] (I) was prepared and used as reagent for deoximation of keto and aldoximes. The first step of this work involved the preparation of polymeric reagent. Poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide] was prepared by the reaction of sodium *p*-styrenesulphonate with PCl_5 and ammonia, polymerization with AIBN, and then chlorination with $\text{Cl}_2(\text{g})$ to yield the corresponding chlorinating polymer in excellent yield as a semi-solid, which was identified by ^1H NMR and IR spectroscopy. This material proved to be a very powerful chlorinating agent and was found to be easily recovered, regenerated and reused. This polymeric reagent was used for oxidation of aldehyde and ketone oximes to their corresponding carbonyl compounds under microwave irradiation. For this purpose a mixture of oximes, CCl_4 and poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide] were used and then irradiated in a domestic microwave oven at a power output of 700 W for the appropriate time. Since this polymer reagent (I) contains two chlorine atoms which are attached to nitrogen atom it is very possible that this reagent upon heating or under microwave irradiation releases in situ Cl^+ which could act as an electrophilic species.

Iranian Polymer Journal, **12** (2), 2003, 115-118

Key Words:

microwave;
polymeric reagents;
cleavage; synthesis;
ketones; aldehydes.

INTRODUCTION

Oximes are used not only to isolate and purify, but also to protect carbonyl compounds in synthesis and intermediates for many reactions such as the preparation of amides by Beckmann rearrangement [1-3]. Readily prepared and highly stable ketoximes are particularly useful

both as protecting groups and selective activating groups. Thus, regeneration of the parent carbonyl compounds from oximes is a necessary and important step in the above mentioned applications of oximes. Since oximes can be prepared from non-carbonyl compounds [4], the regen-

(*)To whom correspondence should be addressed.
E-mail: a_khazaei@basu.ac.ir

Table 1. Deoximation with poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide] (I) under microwave irradiation.

Entry	R ₁	R ₂	Product ^a	Reaction time (s)	Yield (%)
1	CH ₃	C ₆ H ₅	Acetophenone	50	90
2	CH ₃	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -Methoxyacetophenone	50	91
3	C ₆ H ₅	C ₆ H ₅	Benzophenone	60	89
4	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	<i>p</i> -Chlorobenzophenone	40	90
5	H	C ₆ H ₅	Benzaldehyde	50	91
6	H	<i>o</i> -ClC ₆ H ₄	<i>o</i> -Chlorobenzaldehyde	60	88
7	H	<i>o</i> -OHC ₆ H ₄	<i>o</i> -Hydroxybenzaldehyde	60	89
8	H	<i>p</i> -ClC ₆ H ₄	<i>p</i> -Chlorobenzaldehyde	40	91
9	C ₆ H ₅	C ₆ H ₄ CH(OH)	Benzoin	55	92
10	C ₆ H ₅	C ₂ H ₅	Propiophenone	60	89
11	CH ₃	C ₆ H ₁₃	2-Octanone	60	90

(a) Products were characterized by their physical constants, in comparison with authentic samples and IR spectra.

eration of carbonyl compounds from oximes provides an alternative method for preparation of aldehydes and ketones. Some of the reagents reported for deoximation [5-18] are carried out under mild conditions, most of those for the regeneration of carbonyl compounds from oximes require strong acid media, strong oxidizing agents, rare reagents, poisonous reagents, or sometimes long reaction times. Thus, there has been considerable interest in the development of novel techniques for the conversion of oximes back into carbonyl compounds, which work under mild conditions.

EXPERIMENTAL

General

IR Spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets). A domestic microwave oven (Shivaki Co., input 220V-50Hz, RF output 2450 MHz 700 W) was used for irradiation. The oximes were prepared by a standard procedure. The purity of compounds were checked by TLC (silica gel 60 F₂₅₄/CHCl₃ and CCl₄/UV). All chemicals were purchased from Fluka and Merck. Polymeric reagent (I) was prepared according to our previous report [19].

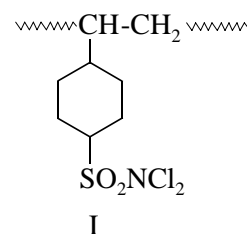
General Procedure for Facile Cleavage of Oximes with Polymer Reagent I

A mixture of oxime (5 mmol), carbon tetrachloride (15 mL) and (I) (5 mmol) were introduced in a flask and then it was irradiated in the microwave oven at power 700 W for an appropriate time indicated in Table 1. After irra-

diation, cold water was added to hydrolyze the intermediate, and the insoluble polymer II was removed by filtration and washed with cold carbon tetrachloride (10 mL). The organic layer was separated from aqueous layer and dried with MgSO₄. Carbon tetrachloride was removed under reduced pressure to give the crude product. Solid products were recrystallized from diethyl ether. Oily products were dissolved in ether and the ether solutions were washed with water, dried and concentrated.

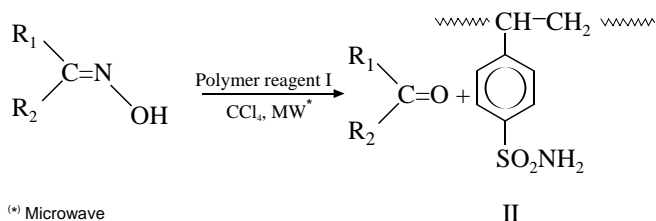
RESULTS AND DISCUSSION

We have previously reported a convenient method for deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds by *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluenesulphonamide) [20] and polymeric reagent I under solution conditions [21].



Here, we wish to report a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds using a new reagent under microwave radiation for accelerating the rate of chemical processes (Scheme I).

The results of the conversion of various ketoximes



(*) Microwave

Scheme I

and aldoximes to ketones and aldehydes are presented in Table 1. The products of the reactions with poly[4-vinyl-*N,N'*-dichlorobenzene-sulphonamide] were isolated simply by filtering off the solid polymer **II** and subsequent evaporation of the solvents from the filtrates. This method has advantages in terms of yields, simplicity of reaction conditions, short reaction times and no side-products. The recovered starting polymer **II** was chlorinated and used many times without any reduction in its efficiency.

Since this polymer reagent **I** contains two chlorine atoms which are attached to a nitrogen atom, it is very possible that the reagent upon heating or under microwave irradiation releases in situ Cl^+ which could act as electrophilic species. An evidence for this claim has been reported in our previous work [22] in which Cl^+ was generated in situ from *N,N'*-2,3,4,5,6-heptachloroaniline. Therefore, we wish to propose a possible mechanism for the deoxygenation reaction with this polymer reagent **I** under microwave irradiation (Scheme II). This Cl^+ first reacts with nitrogen atom of

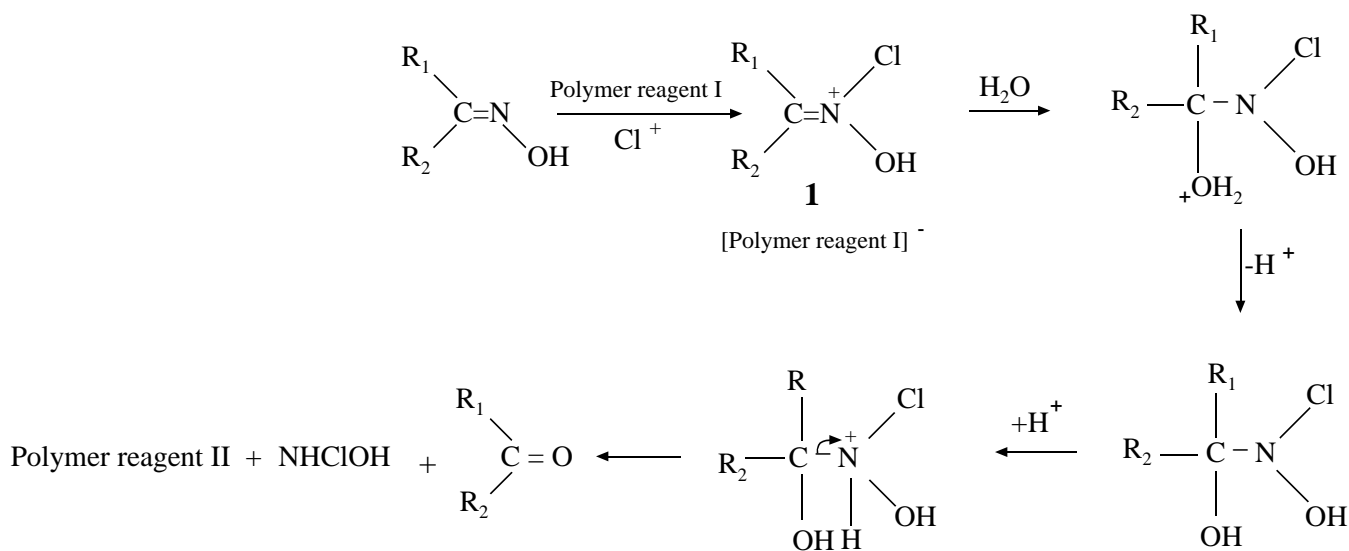
oximes and produces structure 1. The intermediate 1 upon hydrolysis will go through a series of chemical transformations and finally will give corresponding carbonyl compounds in high yield.

CONCLUSION

From this work it is clear that the poly[4-vinyl-*N,N'*-dichlorobenzene-sulphonamide] reagent is an important and valuable reagent for the conversion of oximes to their corresponding carbonyl compounds. The reactions are simple, fast and the resulting polymeric reagent can be recovered, activated and reused. It is interesting to mention that deoxygenation reaction with polymer reagent **I** under solution conditions will take 360-1800 min while this reaction under microwave conditions will take 0.67-1.0 min, which indicates an increase in the rate of reaction between 537-1800 times. Therefore, deoxygenation reaction under microwave irradiation will save plenty of energy and time which makes this method industrially useful and economical.

ACKNOWLEDGEMENTS

We are grateful to the Research Council of Isfahan University of Technology and the Research Council of Bu-Ali Sina University for the financial supports.



Scheme II

REFERENCES

- Bandgar B.P., Lalita B.K. and Thote J.L., Deoximation with *N*-haloamides, *Synth. Commun.* **27**, 1149-1152 (1997).
- Goswami P. and Chowdhury P.K., Deoximation of oximes to carbonyl compounds through in situ generation of nitrosyl chloride, *Ind. J. Chem.* **40(B)**, 156-158 (2001).
- Edmont D. and Williams D.M., A new and versatile synthesis of 5-substituted pyrrolo[2,3-d] pyrimidines, *Tetrahedron Lett.* **41**, 8581-8586 (2000).
- Mikshiev Y.M., Kornilov V.I., Paidak B.B. and Zhdanov, Y.A., Synthesis of higher 3-deoxy-2-ketoaldonic acids by construction and deoximation of their hydroxyiminoesters, *Russ. J. Gen. Chem.*, **69**, 476-482 (1999).
- Tamami B. and Kiasat A.R., Microwave promoted rapid oxidative deoximation of oximes under solvent-free conditions, *Synth. Commun.*, **30**, 4129-4156 (2000).
- Ponnusamy S. and Pitchumani K., Facile PTSH-catalyzed Beckmann rearrangement of ketoximes in solid state, *Ind. J. Chem.* **38(B)**, 861-864 (1999).
- Shim S.B., Kim K., and Kim Y.H., Direct conversion of oximes and hydrazones into their ketones with dinitrogen tetroxide, *Tetrahedron Lett.* **28**, 645-648 (1987).
- Maloney J.R., Lyle R.E., Scavedra J.E., and Lyle G.G., Oxidative deoximation with pyridinium chlorochromate, *Synthesis*, 212 -213(1987).
- Aizpurua J.M., Juaristi M., Lecea B., Palomo C., Reagents and synthetic methods. Halosilanes/chromium trioxide as efficient oxidizing reagents, *Tetrahedron*, **41**, 2903-2911 (1987).
- Laszlo P. and Polla E., Carbonyl regeneration from semicarbazones, tosylhydrazones, and phenylhydrazones by clay-supported ferric nitrate, *Synthesis*, 439-440 (1985).
- Bandgar B.P., Kale R.R., and Kunde L.B., Selective regeneration of carbonyl compounds from oximes with *N*-Bromosuccinimide under neutral and mild conditions, *Monatsh. Chem.* **129**, 1057-1060 (1998).
- Varma R. and Meshram H.M., Solid state deoximation with ammonium persulphate-silica gel: Regeneration of carbonyl compounds using microwaves, *Tetrahedron Lett.* **38**, 5427-5428 (1997).
- Mikshiev Y.M., Levitan G.E., Kornilov V.I., and Zhdanov Y.A., Transformations of oximes derived from 3-deoxyaldulose into higher saccharides of new types, *Russ. J. Gen. Chem.* **66**, 1857-1861 (1996).
- Mahto S.K., Hamal S., and Gajurel C.L., Oxidative cleavage of ketoximes, *Ind. J. Chem.* **35(B)**, 998-1000 (1996).
- Edmont D. and Williams D.M., A new and versatile synthesis of 5-substituted pyrrolo[2,3-d]pyrimidines, *Tetrahedron Lett.* **41**, 8581-8586 (2000).
- Hajipour A.R., Mallakpour S.E., and Baltork I.M., Oxidative deprotection of trimethylsilyl ethers, tetrahydropyranyl ethers, and ethylene acetals with benzyltriphenylphosphonium peroxy monosulfate under microwave irradiation, *Synth. Commun.* **31**, 1625-1631 (2001).
- Hajipour A.R., Mallakpour S.E., Baltork I.M., and Abibi H., Conversion of oximes, phenylhydrazones, and semicarbazones to corresponding carbonyl compounds with benzyltriphenylphosphonium peroxy monosulfate ($\text{BzPh}_3\text{P}^+\text{HSO}_5^-$) in the presence of bis-muth chloride under non-aqueous conditions, *Synth. Commun.* **31**, 3401-3409 (2001).
- Ghiaci M. and Asghari J., Copper (II) nitrate-silica gel mediated regeneration of carbonyl compounds from oximes under microwave irradiation, *Synth. Commun.* **30**, 3865-3872 (2000).
- Khazaei A., Mehdipour E., and Roodpeyma B., Poly(*p*-*N*-chlorostyrenesulphonamide): A new and efficient chlorinating agent for aromatic rings, *Iran. J. Chem. Chem. Eng.* **14**, 77-80 (1995).
- Khazaei A., Ghorbani Vaghei R., and Tajbakhsh M., The application of *N,N'*-dibromo-*N,N'*-1,2-ethanediyldis(*p*-toluenesulphonamide) as a powerful reagent for deoximation of various oximes, *Tetrahedron Lett.*, **42**, 5099-5100 (2001).
- Khazaei A. and Ghorbani Vaghei R., Facile regeneration of carbonyl compounds from oximes using poly[4-vinyl-*N,N'*-dichlorobenzenesulphonamide], *Tetrahedron Lett.* **43**, 3073-3074 (2002).
- Zolfigol M.A., Bagherzadeh M., Chehardoli G., Mallakpour S.E., and Mamaghani M., Oxidation of urazoles via in situ generation of Cl^+ by using *N,N'*-2,3,4,5,6-heptachloroaniline or a UHP/ MCl_n system under mild conditions, *J. Chem. Research (S)*, 390-393 (2001).