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Facile regeneration of carbonyl compounds from oximes using poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide]

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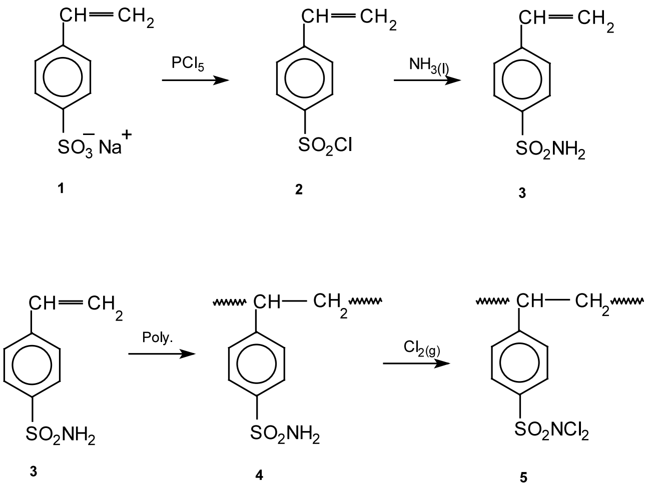
Abstract—Oximes of aldehydes and ketones are oxidized to the corresponding carbonyl compounds in good yields under mild conditions by poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide]. © 2002 Elsevier Science Ltd. All rights reserved.

Regeneration of carbonyl compounds from oximes is an important reaction and has assumed added importance not least because such derivatives of carbonyl compounds can serve as protecting groups for aldehydes and ketones in organic synthesis.[1–7] There has therefore been considerable interest in the development of novel techniques for the conversion of oximes back into carbonyl compounds, which work under mild conditions.

We have previously reported a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds[8] with *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis(*p*-toluenesulfonamide).[9]

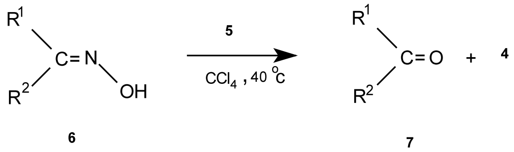


Scheme 1.

Herein, we now report a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds using a new reagent **5** that was prepared from sodium *p*-styrenesulfonate **1** (Scheme 1). The recovery of sulfonamide **4** in comparison to that previously reported by us is easier and we also synthesized some other aliphatic compounds with this polymeric reagent in high yields.

The first step of this work involved the preparation of the polymeric reagent. Poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] **5** was prepared by the reaction of **1** with PCl_5 and ammonia, polymerization with AIBN, and then chlorination with $Cl_{2(g)}$ to yield the corresponding chlorinated poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] in excellent yield as a semi-solid, which was identified by ^{1}H NMR and IR spectroscopy. Iodometric titration was used to determine the amount of chlorine. This new material proved to be a very powerful chlorinating agent, and was found to be easily recovered, regenerated and reused (Scheme 1). The second step is the reaction between the polymeric reagent and oximes in CCl_4.

The reaction of oximes **6** with reagent **5** in CCl_4 afforded carbonyl compounds **7** without the formation of side products (Scheme 2).



Scheme 2.

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Table 1. Deoximation with poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide]

Entry	R^1	R^2	Product[a]	Reaction times (h)	Yield (%)
1	CH_3	C_6H_5	Acetophenone	3	92
2	CH_3	p-ClC_6H_5	*p*-Chloroacetophenone	5	91
3	CH_3	p-$MeOC_6H_5$	*p*-Methoxyacetophenone	3	95
4	CH_3	p-BrC_6H_5	*p*-Bromoacetophenone	3	94
5	C_6H_5	C_6H_5	Benzophenone	5	92
6	C_6H_5	p-ClC_6H_5	*p*-Chlorobenzophenone	1	91
7	H	C_6H_5	Benzaldehyde	3	84
8	H	p-ClC_6H_5	*p*-Chlorobenzaldehyde	2	90
9	H	p-MeC_6H_5	*p*-Methylbenzaldehyde	3	90
10	H	o-$MeOC_6H_5$	*o*-Methoxybenzaldehyde	2	96
11	C_6H_5	$C_6H_5CH(OH)$	Benzoin	3	92
12	H	C_3H_7	Butyraldehyde	5	91
13	H	C_6H_{13}	Heptaldehyde	5	90
14	CH_3	C_4H_9	Isobutyl methyl ketone	5	92
15	H	$C_6C_2H_2$	Cinnamaldehyde	3	93
16	CH_3	CH_3CO	2,3-Butanedione	4	92

[a] Products were characterized by their physical properties, comparison with authentic samples and IR spectra.

The results of the conversion of various ketoximes and aldoximes to ketones and aldehydes are presented in Table 1.

The products of the reaction with **5** were isolated simply by filtering off **4** and evaporating the solvent from the filtrate. The method has advantage in terms of yields, simplicity of reaction conditions, short reaction times and no side products. The recovered starting polymer **4** was chlorinated and used many times without any reduction in its efficiency.

Commercial sodium *p*-styrenesulfonate (Fluka, A.G., Switzerland) was used as received. *p*-Styrene sulfonamide and poly(*p*-styrene sulfonamide) were prepared on 30 g scale from *p*-sodiumstyrene sulfonate, PCl_5, ammonia and AIBN according to the published procedure.[10]

Procedure for the preparation of poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide]. A sample of white finely divided powdered poly[4-vinylbenzenesulfonamide] (8.0 g) was dissolved in dry THF (50 ml). $Cl_{2(g)}$ was bubbled through the system for 30 min under ice-cooling to chlorinate the polymeric reagent. The color of the solution did not change. The mixture was refluxed for 2 h, until a dark brown color was produced. The solvent was evaporated, and the residue freed from the last traces of solvent in vacuum, to give the product (18.5 g). The compound was identified by NMR, IR, and molecular weight determination (functional groups titration). The mole number of N-bound chlorine was determined by iodometric titration.[11]

General procedure for deoximation with poly[4-vinyl-*N*,*N*-dichloro benzenesulfonamide]. A mixture of oxime (5 mmol), carbon tetrachloride (15 ml) and poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] **5** was refluxed at 40°C for the specific time (Table 1). After completion of the reaction, water (5 ml) was added to hydrolyze the intermediate, and the insoluble polymer **4** was removed by filtration and washed with carbon tetrachloride (10 ml). Removal of the solvent under reduced pressure gave the crude product. Solid products were recrystallized from diethyl ether, oily products being dissolved in ether and the ether solution washed, dried and concentrated.

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