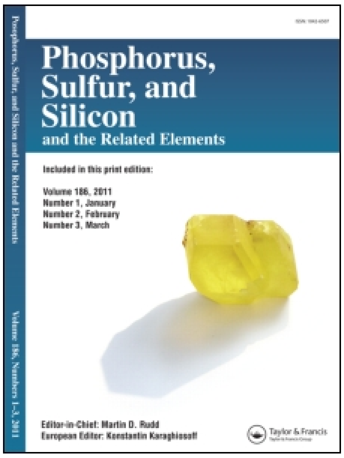

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POLY[*N*-(4-PYRIDINUMDICHROMATE)-*P*-STYRENESULPHONAMIDE] AS AN EFFICIENT REAGENT FOR THE CLEAVAGE OF C=N BONDS OF OXIMES

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Poly[N-(4-pyridinumdichromate)-p-styrenesulphonamide] (PPDSS) was found to be an efficient oxidant for the conversion of C=N of oximes to their corresponding carbonyl compounds in excellent yields.

Keywords: Carbonyl compounds; deoximation; deprotection; PPDSS

Protection of carbonyl compounds as C=N derivatives is of great interest to organic chemists, as they are highly stable and readily prepared compounds.[1] Oximes are extensively used to not only isolate and purify of carbonyl compounds but also to activate the carbonyl group.[2] Oximes also serve as the intermediates for many reactions such as the preparation of nitriles[3] or amides via Beckmann rearrangement.[4] Their synthesis from noncarbonyl compounds[5] provides an alternative pathway to aldehydes and ketones. Although a number of methods for the conversion of C=N derivatives to carbonyl compounds are available, the discovery of a milder, selective, nonhazardous reagent is still in demand. Some of the methods reported earlier for deoximation of carbonyl compounds consist of oxidative[6] or reductive,[7] clay-supported ammonium chlorochromate,[8] bis-(trimethylsilyl) chromate,[9] silica gel supported chromium trioxide,[10] N-methoxyimidoxyl bromides,[11] copper (II) chloride dihydrate,[12] 2-iodoxybenzoic acid (IBX) and Dess-Martin periodinane (DMP),[13] quinolinium fluorochromate,[14] and ammonium persulphate-silica.[15] Some of these reagents suffer from disadvantages

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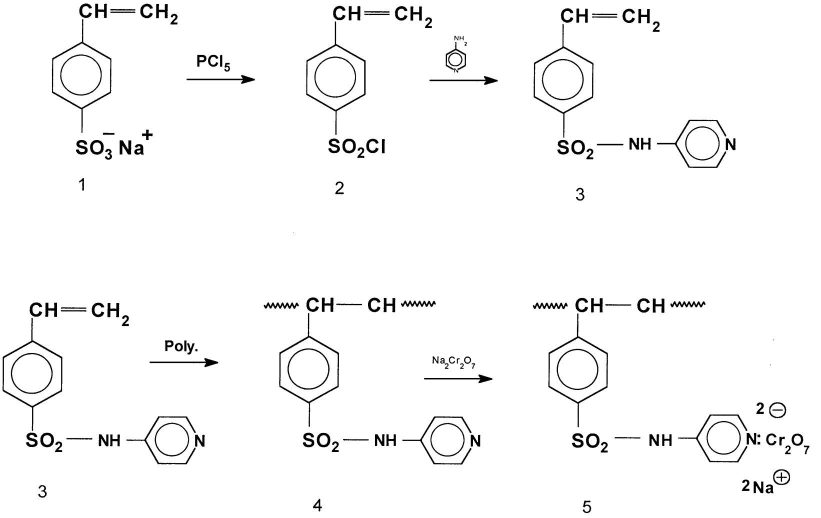
like long reaction time, difficulties in isolation of products; also some may be expensive and cause explosion under excessive heating during preparation. Moreover, many of the methods cited in the literature do not describe the deoximation of aldoximes, give low yields of aldehydes, or the liberated aldehydes are overoxidized. Benzaldoxime, for example, was deoximated in poor yield by pyridinium chlorochromate (PCC),[16] in 35% yield by PCC-H_2O_2,[7] in 56% yield by trimethylammonium chromate,[17] and in 72% yield by chromium trioxide-chlorotrimethylsilane.[18]

RESULTS AND DISCUSSION

We previously reported a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds with *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis (*p*-toluenesulfonamide)[19] and poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide].[20]

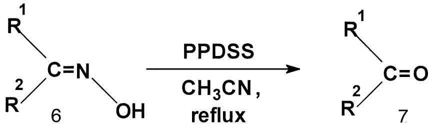
Herein, we report a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds using a new reagent PPDSS[21] that was prepared from sodium *p*-styrenesulfonate **1** (Scheme 1).



SCHEME 1

Poly[*N*-(4-pyridinumdichromate)-*p*-styrenesulphonamide] (PPDSS) was prepared by the reaction of **1** with PCl_5 and 4-aminopyridine, polymerization with AIBN, and then addition of a suspension of poly[*N*-(4-pyridine)-*p*-styrenesulphonamide] in water to a cold solution of $Na_2Cr_2O_7$ in a minimum amount of water. This orange-colored oxidizing agent is a stable compound and can be stored for months without losing its activity. It is not hygroscopic or light sensitive. The presence of the dichromate anion in the reagent was confirmed by the IR spectrum having bands at 930 and 765 cm^{-1}, and is characteristic for the dichromate anion.[22]

The reaction of oximes **6** with PPDSS in CH_3CN afforded carbonyl compounds **7** without the formation of side products (Scheme 2).



SCHEME 2

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

The products of the reaction with **5** (PPDSS) were isolated simply by filtering off PPDSS 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.

TABLE I Oxidative Cleavage of Oximes with PPDSS

Entry	R^1	R^2	Product[a]	Reaction times (h)	Yield (%)
1	CH_3	C_6H_5	Acetophenone	2.5	93
2	CH_3	*p*-$MeOC_6H_5$	*p*-Methoxyacetophenone	2.0	91
3	C_6H_5	C_6H_5	Benzophenone	2.0	95
4	C_6H_5	*p*-ClC_6H_5	*p*-Chlorobenzophenone	2.0	90
5	H	C_6H_5	Benzaldehyde	2.5	92
6	H	*o*-ClC_6H_5	*o*-Chlorobenzaldehyde	2.0	90
7	H	*o*-OHC_6H_5	*o*-Hydroxybenzaldehyde	2.5	91
8	H	*p*-ClC_6H_5	*p*-Chlorobenzaldehyde	2.0	90
9	C_6H_5	$C_6H_5CH(OH)$	Benzoin	3.0	91
10	C_6H_5	C_2H_5	Propiophenone	3.5	89
11	CH_3	C_6H_{13}	2-Octanone	4.0	91

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

CONCLUSION

The procedure reported here is a convenient and high-yielding method for the oxidation of oximes to the corresponding carbonyl compounds. Furthermore, another important advantage of this work is that the polymeric reagent can be stored for months without losing its activity. It is not hygroscopic or light sensitive. The insoluble polymer was removed by filtration after the reaction.

EXPERIMENTAL

General

Commercial sodium *p*-styrenesulfonate and 4-aminopyridine (Fluka, A.G., Switzerland) were used as received.

Procedure for the Preparation of Poly[N-(4-pyridinumdichromate)-p-styrenesulphonamide]

To a suspension of 0.05 mmol of poly[*N*-(4-pyridine)-*p*-styrenesulphonamide] in 100 ml of water was added a cold solution of 0.06 mmol of $Na_2Cr_2O_7$ in a minimum amount of water. Formation of the reagent occurred very smoothly. After filteration, the reagent was washed repeatedly with water until the filtrate was colorless.

General Procedure for Deoximation with Poly[N-(4-pyridinumdichromate)-p-styrenesulphonamide]

A mixture of oxime (5 mmol), acetonitrile (15 ml) and poly[*N*-(4-pyridinumdichromate)-*p*-styrenesulphonamide] was refluxed for 2–4 h (Table I). The reaction was monitored by TLC. After completion, it was diluted with ether (15 ml) and the insoluble polymeric reagent 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 recrystalized from diethyl ether; oily products were dissolved in ether and the ether solution washed, dried, and concentrated.

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