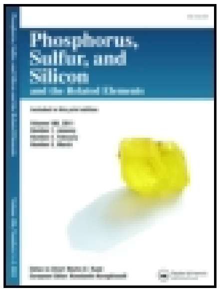

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POLY [N-(4-PYRIDINIUM DICHROMATE)-P-STYRENE SULPHONAMIDE] AS AN EFFICIENT REAGENT FOR OXIDATION OF ALCOHOLS

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POLY [*N*-(4-PYRIDINIUM DICHROMATE)-*P*-STYRENE SULPHONAMIDE] AS AN EFFICIENT REAGENT FOR OXIDATION OF ALCOHOLS

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Poly [N-*(4-pyridinium dichromate)-*p-*styrene sulphonamide] is readily prepared. It is a stable, mild, and efficient oxidizing reagent that can be used for oxidation of different alcohols to their corresponding carbonyl compounds in approtic solvents. This polymer can be synthesized from the reaction between poly [* N-*(4-pyridyl)-*p-*styrene sulphonamide] and* CrO_3 *in a minimum amount of water. The latter polymer was prepared by free radical polymerization of [* N-*(4-pyridyl)-*p-*styrene sulphonamide] by using azobis(isobutyronitrile) (AIBN) as an initiator.* N-*(4-pyridyl)-*p-*styrene sulphonamide was synthesized from commercial 4-vinyl benzene sulphonic acid sodium salt and 4-amino pyridine. Poly [* N-*(4-pyridinium dichromate)-*p-*styrene sulphonamide] can oxidize both aliphatic and aromatic alcohols in good yields at a temperature of 38°C and in* CH_2Cl_2 *as solvent. One advantage in using this reagent is the mild condition of the reaction system. The synthesized compounds including polymeric reagent and carbonyl compounds were identified by HNMR and IR spectroscopy.*

Keywords: Alcohols; oxidation; polymer support; reagent; synthesis

An increasing number of polymeric reagents have been developed for synthetic use. Polymeric reagents are greatly used in single step reactions. Their main advantages over monomeric reagents is their insolubility in the reaction medium and consequently the easier separation of products from the reaction mixtures, in most cases by simple filtration.

The reaction often can be driven to completion by using excess of these reagents without fear of separating the unspent reagents or the polymeric by-products from the desired reaction products. In addition,

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the spent polymeric reagents can usually be recovered quantitativilly at the end of the reactions and in ideal cases they can be regenerated to their initial activities.

A variety of polymer-supported oxidizing reagents with different functionalities have been reported in literature.[1–12]

Among these, polymer-bound metallic oxidants and specially polymer-supported chromium (VI) reagents have received considerable attention.

In connection with studies on the preparation and application of recyclable polymeric reagents for use in simple one-step processes, we have described the polymeric reagent poly [*N*-(4-pyridinium dichromate)-*p*-styrene sulphonamide] which is an efficient reagent in the oxidation of alcohols to the corresponding aldehydes and ketones.

RESULTS AND DISCUTION

This nonacidic polymeric reagent can be prepared easily by treatment of poly [*N*-(4-pyridyl)-*p*-styrene sulphonamide] with a slight excess of CrO_3 in water at room temperature (Scheme 1). After being washed with water to remove any unbound chromium (VI), the reagent can be used directly without drying in oxidation reaction or dried in vacuum to a yellow-brown powder, which is quite stable to prolonged storage. The IR spectrum of the polymer showed peaks at 765 and 930 cm^{-1}, which confirmed that it was a dichromate.[13]

SCHEME 1

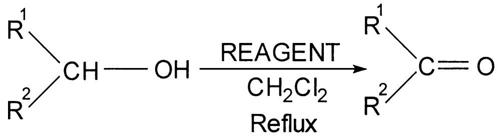
It should be noted that the reagent could be prepared and handled safely in molar amount, a definite advantage over more classical CrO_3 based reagents.

TABLE I Oxidation of Alcohols with Poly [*N*-(4-Pyridinium dichromate)-*p*-styrene Sulphonamide]

Alcohol	Product	Molar ratio	Reaction times (h)	Yield (%)
Benzyl alcohol	Benzaldehyde	1.1:1	2	95
1-Butanol	Butanal	1.1:1	6	80
2-Butanol	2-Butanone	1.1:1	10	80
1-Pentanol	Pentanal	1.1:1	9	90
1-Hexanol	Hexanal	1.1:1	10	90
1-Heptanol	Hepanal	1.1:1	10	85
1-Octanol	Octanal	1.1:1	10	85
Cyclopentanol	Cyclopentanone	1.1:1	8	90
Cyclohexanol	Cyclohexanone	1.1:1	8	90

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

The best results were obtained by using the wet reagent in the oxidation reaction (Table I). The reaction of alcohols with polymeric reagent afforded carbonyl compounds without the formation of side products (Scheme 2). As expected, in the absence of water the dry reagent is ineffective. Isolation of the aldehydes after reaction was greatly facilitated by the fact that no chromium ions were leached from the polymer. The results obtained in the oxidation of a number of different alcohols are reported in Table I. As expected the rate of reaction increased when the molar ratio of Cr(VI) to alcohol was increased, and very fast reactions could be obtained by using four-fold excess of reagent. However, the reagent was still quite effective in almost equimolar amount. As expected, the initial rate of the reaction with the polymer is usually quite high but the reaction slows down as the reactive sites are consumed. It should be noted that, although the reaction times are sometimes quite long, no products of overoxidation were detected with any of the alcohols tested.



SCHEME 2

Recycling of the reagent can be accomplished by using a simple washing-reactivation procedure in which the spent reagent is washed to remove the spent chromium salts. After regeneration of the polymer addition of CrO_3 and water reactivates the polymer.

EXPERIMENTAL

Apparatus

IR and H NMR spectra were recorded using a Shimadzu 435-U04 spectrophotometer, (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively.

General Reagents

Commercial 4-vinylbenzenesulphonic acid sodium salt was obtained from Fluka AG. All other chemicals were obtained from Merck.

*Procedure for the Preparation of Poly [*N*-(4-pyridyl)-*p*-styrene sulphonamide]*

To a solution of 0.02 mmol of [*N*- (4-pyridyl)-*p*-styrene sulphonamide] in 100 ml of DMSO was added 1.5 mmol of AIBN and then heated at 100°C for 27 h under a N_2 atmosphere. Then addition of water precipitated the polymer. The yield of product was 80%.

*Procedure for the Preparation of Poly [*N*-(4-pyridinium dichromate)-*p*-styrene sulphonamide]*

To a suspension of 0.05 mmol of poly [*N*-(4-pyridyl)-*p*-styrene sulphonamide] in 100 ml of water was added 0.06 mmol of CrO_3. Formation of the reagent occurred very smoothly and no heat was evolved when the mixture was stirred for several hours. After filtration, the reagent was washed repeatedly with water until the filtrate was colorless. In general the reagent was used without drying.

Procedure for the Oxidation of Alcohols

The standard procedure involved the reaction of 2.2 mmol of polymeric reagent with 2 mmol of alcohols in 10 ml of CH_2Cl_2 at 38°C.

The progress of some reactions was monitored by TLC. After completion of the reaction the products could be obtained after filtration of the polymer in the filtrate.

The main advantage associated with the use of a polymeric reagent is the ease of purification of the final product since both the initial polymer, which may be used in excess to help drive the reaction to completion and its by-product are insoluble and can be separated by simple filtration.

CONCLUSION

The procedure reported here is a convenient and high-yielding method for the oxidation of alcohols to their 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 reaction.

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