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Polymeric reagent

I. Polymer supported silver dichromate complex as an oxidizing agent

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Summary

Poly(4-vinylpyridine)(I) and poly(2-vinylpyridine)(II) supported silver dichromates are readily prepared and used as mild, efficient and easy to handle oxidizing agents for hydroxy compounds. Polymeric reagent (II) is more reactive than (I).

Introduction

Polymer-supported chromium (VI) oxidizing reagents such as polymer-bound chromate based on commercial Amberlyst A-26 resin (1), polyvinylpyridinium chlorochromate (2), and polyvinylpyridinium dichromate (3) have been developed and reported in the literature. The main advantages of these polymeric agents over their monomeric forms (4,5) are the ease of purification of the final oxidized products and the regenerability of the reagents.

Recently monomeric reagent tetrakis(pyridine) silver dichromate was reported (6), and later commercialized (7), for oxidation of benzylic and allylic alcohols in high yields. Among the advantages of this reagent over the already reported chromium (VI) reagents were its stability at room temperature, neutrality and not being photosensitive and hygroscopic. However, while the work up of the reaction mixture is clean and easy, purification of the final oxidized product necessitates column chromatography due to some soluble chromium complex compounds.

To add to already a few polymeric oxidizing compounds based on chromium (VI), we now wish to report the preparation and uses of the polymeric analogues of pyridine silver dichromate complex as efficient oxidizing agents.

Results and Discussion

Pyridine silver dichromate was fixed onto poly(4-vinylpyridine)(I) and poly(2-vinylpyridine)(II)(8) to give stable dark brown color fine powders. These insoluble reagents are non acidic and can be effective in acetone, dichloromethane, benzene and toluene. They can be used in equimolar amounts with respect to the substrates. Polymeric reagent (II) proved to be considerably more reactive than (I). The infrared spectrum of the polymers showed the presence of the dichromate anions. The capacity of the polymers were determined to be about 1.4 mmol $Cr_2O_7^{=}$ per gram of the reagent (9). No products of over oxidation were detected with any of the alcohols tested. Our preliminary abservation showed that addition of catalytic amount of glacial acetic acid enhanced the rate of oxidation

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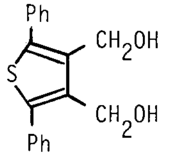
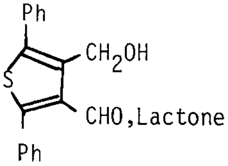
Table (I). Oxidation of Hydroxy Compounds to their Corresponding Carbonyl Compounds with Polyvinylpyridine Silver Dichromate Complex.

No.	$-CH_2OH$	$-CHO$	Time(min)	Yield%
1	Benzyl Alcohol	Benzaldehyde	20 10	100^a 100^b
2	Cinnamyl Alcohol	Cinnamaldehyde	120 40	100^a 100^b
3	Hydroquinone	Quinone	45 10	100^a 100^b
4	Furoin	Furil	150 60	95-100^a 95-100^b
5	Piperonol	Piperonal	150 50	95-100^a 95-100^b
6	Methylphenyl-carbinol	Acetophenone	120 40	100^a 100^b
7	Benzoin	Benzil	150 45	80^a 95-100^b
8			90 240	80-85^b Trace of lactone 90-95^b lactone
9	4,4'-Dibromo benzoin	4,4'-Dibromo-benzil	150 150	90^a 100^b

a. Oxidized with poly(4-vinylpyridine) Supported Reagent
b. Oxidized with poly(2-vinylpyridine) Supported Reagent

reaction (10). And finaly the chromium ions remain firmly bound to the insoluble polymer after the oxidation reactions, a fact which makes this reagent advantageous over its monomeric form.

In comparison to the already reported chromium (VI) based polymeric oxidants (1,2,3) our reagents can be used in equimolar amounts with respect to the substrates. They are non acidic and useful for oxidation of acid sensetive compounds. No wetting of the dry reagents in needed prior to oxidation reactions, a fact which was reported essential in the use of polyvinylpyridinium dichromate (3). This makes them suitable for oxidation of water sensetive compounds. In addition the work-up of the reaction mixture is as easy as of those reported for the other polymeric oxidizing agents.

Investigation about the preparation and uses of metal dichromate complexes of polyvinylpyridines and polyvinylpyridine-oxides as oxidizing reagents are underway.

Experimental Part

Preparation of Polyvinylpyridine Supported Silver Dichromate: A solution of poly(4-vinylpyridine)(I) or poly(2-vinylpyridine)(II),(1.5g) is methanol (60 ml) was added dropwise to a stirred methanolic solution of silver nitrate (4.7 g). A white precipitate formed which was filtered and washed several times with methanol. It was then added slowly to an excess saturated solution of potassium dichromate in water and the suspension stirred for 1hr. The brown precipitate was filtered and washed with water until the filtrate was colorless. The dried resins weighed 3.9 grams.

General Procedure for the Oxidation of Hydroxy Compounds: Polymeric reagent (2.4 g) was added to a stirred solution of the alcohol (6 mmole) in dry toluene. The reaction started under reflux condition and was monitored by TLC. On completion of the reaction the product was obtained in the soluble phase by simple decantation and washing of the resin. The solvent was evaporated and the desired carbonyl compound was obtained and in some cases purified by column chromatography. The results are shown in table (I).

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