Poly(vinyl pyridine) supported silver dichromates as versatile, mild and efficient oxidants for different organic compounds

B. Tamami*, M. Hatam and D. Mohadjer
Department of Chemistry, Shiraz University, Shiraz, Iran
(Received 22 May 1990; revised 31 August 1990; accepted 31 August 1990)

Poly(4-vinyl pyridine) (I) and poly(2-vinyl pyridine) (II) supported silver dichromates are readily prepared. They are stable, mild and efficient polymeric oxidizing reagents which can be used in equimolar amounts for oxidation of different hydroxy compounds to their corresponding carbonyl compounds in aprotic solvents. Oximes, amines, thiols and aromatic hydrocarbons can also be oxidized by these reagents. Polymeric reagent II is more efficient in oxidation reactions than (I).

(Keywords: polymeric oxidizing reagent; poly(vinyl pyridine); silver dichromate)

INTRODUCTION

An increasing number of polymeric reagents have been developed for use in organic synthesis[1-3]. Polymeric reagents are generally used in single-step reactions. Their main advantage 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 reactions can often be driven to completion by using excess of these reagents without the fear of separating the unspent reagents or the polymeric by-products from the desired reaction products. In addition, the spent polymeric reagents can usually be recovered quantitatively at the end of the reactions and, in ideal cases, they can be regenerated to their initial activities.

As methods for the functionalization of polymers have improved, parallel to the development of different types of polymeric reagents, synthesis and uses of polymeric oxidizing reagents have become the natural goals. A variety of polymer-supported oxidizing reagents with different functionalities have been reported in the literature[4]. Among these, polymer-bound metallic oxidants and especially polymer-supported chromium (VI) reagents have received considerable attention.

Polymer-supported chromium (VI) oxidizing reagents, such as polymer-bound chromate based on commercial Amberlyst A-26 resin[5], poly(vinyl pyridinium chlorochromate)[6], poly(vinyl pyridinium dichromate)[7] and polymer-supported quaternary ammonium complex chromates[8], have been developed and reported in the literature for oxidation of different types of alcohols.

Monomeric metal dichromates, such as tetrakis (pyridine)-silver dichromate[9] and zinc dichromate trihydrate[10], have recently been made and reported as mild and efficient reagents for oxidation of a few types of organic substrates, especially different hydroxy compounds. The former reagent has been commercialized (Aldrich, catalogue no. 31788-8). As far as we know, no polymer-supported metal dichromates have been reported in the literature. Recently we described the polymeric analogues of tetrakis (pyridine)-silver dichromate as mild and efficient reagents for oxidation of alcohols[11]. It was shown that linear poly(2-vinyl pyridine) and poly(4-vinyl pyridine) supported silver dichromates could oxidize different hydroxy compounds to their corresponding carbonyl compounds. In this paper we describe fully the preparation and application of these linear, as well as crosslinked, polymeric reagents in the oxidation of a variety of organic compounds, such as hydroxy compounds, oximes, thiols and aromatic hydrocarbons.

EXPERIMENTAL

2- and 4-vinyl pyridines were commercial products obtained from Fluka. These monomers were purified by distillation under reduced pressure immediately before use. Linear poly(vinyl pyridine)s were prepared by suspension polymerization of the corresponding monomers[12]. The polymer samples used had similar molecular weights in the range $7.2-8.8 \times 10^4$, as determined by their intrinsic viscosities[13]. Crosslinked porous poly(vinyl pyridine)s (2% divinyl benzene), were purchased from Fluka. Solvents were dried prior to use. All oxidation products were known compounds and were identified by comparison of their spectra and physical data with those of the authentic samples. Melting points were determined in open capillaries on a Buchi 510 apparatus. The progress of reactions was followed by thin layer chromatography (t.l.c.) on silica gel Polygram SIL G/ $u.v._{254}$ plates and separation of the products was conducted on silica gel columns.

Infra-red and nuclear magnetic resonance spectra were run on a Perkin-Elmer i.r. 157G and Pye Unicam SP9 n.m.r. spectrometer respectively.

Functionalization of poly(vinyl pyridine)s

A solution of poly(4-vinyl pyridine) or poly(2-vinyl pyridine) (1.5 g) in methanol (60 ml) was added dropwise

* To whom correspondence should be addressed

0032-3861/91/142666-05

to a stirred methanolic solution of silver nitrate (4.7 g). A white precipitate formed which was filtered and washed several times with methanol. For crosslinked polymers a suspension of the resin (1.2 g) in aqueous solution of silver nitrate (3.7 g) was stirred for 10 h, and the white precipitate was filtered and washed with water and then methanol. In each case the white precipitate was added to an excess saturated solution of potassium dichromate in water and the suspension was stirred for 1 h. The brown precipitate was filtered and washed with water until the filtrate was colourless. The reagents were dried in vacuum at 40°C.

The infra-red spectrum of the reagents showed bands at 930 and 765 cm^{-1}, characteristic of the dichromate anions[14]. The capacities of these reagents were determined by atomic absorption. The values were 1.4 and 1.2 mmol $Cr_2O_7^{2-}$/g reagent for linear and crosslinked reagents respectively.

General procedure for oxidation of hydroxy compounds

Linear or crosslinked reagent (5.5 mmol, based on the capacities) was added to a solution of the hydroxy compound (10 mmol) in dry toluene in a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer, and was refluxed for 10 min to 6 h. Both types of reagent were completely insoluble in the reaction medium. Progress of the reaction was followed by t.l.c. (with n-hexane ether as eluent). The mixture was cooled to room temperature and filtered. The solid material was washed several times with suitable solvents such as acetone, chloroform or carbon tetrachloride. The combined filtrates were evaporated and the desired carbonyl compound was obtained and in some cases purified on a silica gel column with appropriate eluent. Evaporation of the solvent afforded pure oxidized compounds (10–100% yield) (see *Table 1*).

General procedure for oxidation of oximes, amines, thiols and hydrocarbons

A solution of the substrate (1 mmol) in toluene (15 ml) was prepared in a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer. Poly(2-vinyl pyridine) supported silver dichromate (1–8 mmol, based on the capacity) was added to this solution and refluxed for 10 min to 10 h. The progress of the reaction was monitored by t.l.c. The reaction mixture was cooled to room temperature and filtered. The solid material was washed with chloroform several times and the combined filtrates were evaporated on a rotary evaporator. The resulting crude material was purified on a silica gel column and the desired component was separated (0–100% yield) (see *Table 2*).

RESULTS AND DISCUSSION

Linear and crosslinked poly(4-vinyl pyridine) (I) and poly(2-vinyl pyridine) (II) supported silver dichromate were prepared by complexation of the corresponding polymers with silver nitrate and then exchanging the nitrate anions with the dichromates. The infra-red spectra of the polymers showed the presence of the dichromate anions[14]. These dark brown fine powder reagents were stable for months and were insoluble in solvents such as acetone, dichloromethane, benzene and toluene. The capacities of these oxidizing reagents were determined by atomic absorption, and were found to be about 1.2–1.4 mmol $Cr_2O_7^{2-}$/g reagents. Toluene was the solvent of choice and all oxidation reactions were carried out in this solvent. The chromium ions remained firmly bound to the insoluble polymer supports after the oxidation reactions, a fact which makes these reagents advantageous over their monomeric form. The product isolation and purification were performed simply by filtration of the reaction mixture, evaporation of the solvent, and if necessary further separation of the unreacted starting material or by-products by column chromatography.

In comparison to the previously reported chromium (VI) based polymeric oxidants[5–8] used for oxidation of alcohols, these reagents can be used in equimolar amounts with respect to the substrates. They are non-acidic and useful for oxidation of acid-sensitive compounds. No wetting of the dry reagents is needed prior to the oxidation reactions, a fact which was reported as essential in the use of poly(vinyl pyridinium dichromate)[7]. This makes them suitable for oxidation of water-sensitive compounds.

Linear and crosslinked polymeric reagents I and II were effective in the oxidation of various types of hydroxy compounds such as primary and secondary benzylic and allylic alcohols and acyloins to their corresponding carbonyl compounds in good yields (*Table 1*). The reagents selectively oxidized the benzylic hydroxy group. They could change a few hydroquinones to their corresponding quinones. No product of over-oxidation was detected in the reaction mixtures at the end of oxidation reactions.

An interesting result obtained from these studies was that in all oxidation reactions on different hydroxy compounds, both linear and crosslinked polymeric reagent II supported silver dichromates were more reactive than polymeric reagent I. Considering that the capacities of these polymeric reagents were almost identical, the molecular weights of the linear polymer supports (as determined by their intrinsic viscosities) were close and the same sort of behaviour was observed in different solvents (such as acetone, methylene chloride, benzene and toluene), we have come to the conclusion that such differences are mainly due to the structural difference between the two isomeric polymers. Fixation of $Ag_2Cr_2O_7$ onto poly(2-vinyl pyridine) is probably by a different process than with poly(4-vinyl pyridine). In the former the nitrogen atoms of the rings are close to the main chain compared to the latter polymer in which they are exposed and far away from the chain. In addition polymeric reagent II probably has a more compact structure due to slight interactions between the hydrogens of the chain and the nitrogens of the rings[15,16]. No such interactions are possible for the polymeric reagent I. Considering these assumptions one can suggest that the higher efficiencies of polymeric reagent II compared to I are probably due to the higher local concentration and/or better availability of $Cr_2O_7^{2-}$ groups on these polymer supports for reaction with the interacting substrates. We have noticed this sort of difference in efficiencies between 2- and 4-isomers for poly(vinyl pyridinium dichromate), a well known commercialized polymeric analogue of pyridinium dichromate, in a study on the effect of the polymer structure and tacticity on the oxidizing ability of this polymeric reagent[13]. Even more enhanced

Table 1 Oxidation of hydroxy compounds to their corresponding carbonyl compounds with poly(vinyl pyridine) supported silver dichromates (reactions proceeded under reflux condition in toluene, with substrate:oxidant molar ratio of 1:1.1)

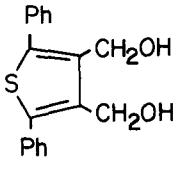
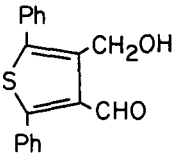
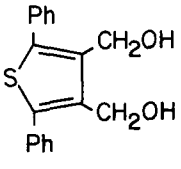
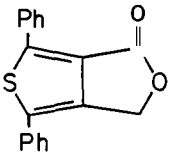
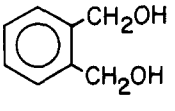
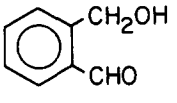
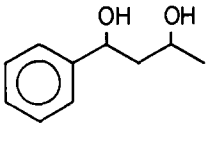
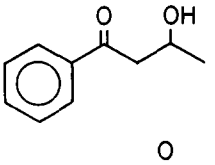
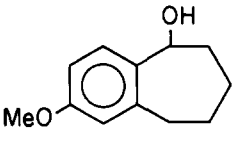
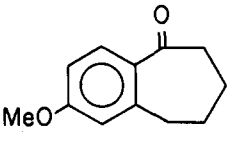
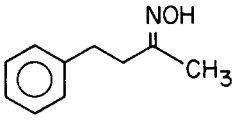
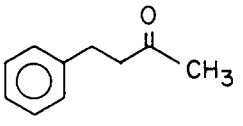
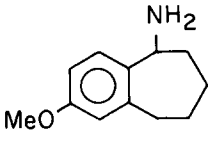
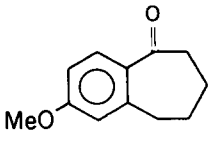
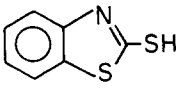
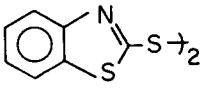
No.	Substrate	Product[a]	Time (min)	Yield (%)
1	Benzyl alcohol	Benzaldehyde	20[b], 100[d]	
			10[c], 40[e]	100[b–e]
2	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	40[b]	100[b,c]
			20[c]	
3	*p*-Chlorobenzyl alcohol	*p*-Chlorobenzaldehyde	40[b]	
			20[c]	95[b,c]
4	Anisyl alcohol	Anisaldehyde	180[b]	95[b]
			100[c]	80[c]
5	Cinnamyl alcohol	Cinnamaldehyde	120[b], 90[d]	95–100[b], 30[d]
			40[c], 90[e]	95–100[c], 55[e]
6	Furforyl alcohol	Forfural	25[b]	100[b,c]
			15[c]	
7	Piperonol	Piperonal	150[a], 230[d]	95–100[b], 60[d]
			60[c], 110[e]	95–100[c], 80[e]
8			130[b]	80[b,c]
			90[c]	Trace of lactone
9			180[b]	90–95[b,c]
			130[c]	
10			150[b]	85–90[b,c]
			90[c]	
11	Methylphenyl carbinol	Acetophenone	120[b], 160[d]	100[b], 60[d]
			40[c], 120[e]	100[c], 75[e]
12	Benzylphenylcarbinol	Benzylphenyl ketone	360[b]	80[b]
			120[c]	90[c]
13	1,2-Diphenylglycol	Benzil	150[b]	80[b]
			45[c]	95–100[c]
14	α-Tetralol	α-Tetralone	250[b]	80[c]
			100[c]	90[c]
15			120[b]	80[b]
			60[c]	90[c]
16			360[b]	85[b]
			120[c]	95[c]
17	Diphenyl carbinol	Benzophenone	100[b]	95–100[b]
			30[c]	100[c]
18	Benzoin	Benzil	40[b], 230[d]	100[b], 60[d]
			20[c], 160[e]	100[c], 80[e]
19	Furoin	Furil	150[b], 150[d]	95–100[b], 30[d]
			60[c], 150[e]	95–100[c], 50[e]
20	Hydroquinone	Benzoquinone	45[b]	100[b]
			10[c]	100[c]
21	Dihydroxy anthracene	Anthraquinone	95[b]	95[b,c]
			45[c]	

Table 2 Oxidation of oximes, amines, thiols and aromatic hydrocarbons with poly(2-vinyl pyridine) supported silver dichromate (reactions proceeded under reflux condition in toluene)

No.	Substrate	Product[a]	Ratio of oxidant/ substrate	Time (h)	Yield (%)
1	Acetophenone oxime	Acetophenone	3	5	85
2	Benzophenone oxime	Benzophenone	3	5	90
3	Benzaldoxime	Benzoldehyde	1	3	80
4	*p*-Chlorobenzaldoxime	*p*-Chlorobenzaldehyde	1	3.5	80
5	*p*-Methoxybenzaldoxime	*p*-Methoxybenzaldehyde	3	5	65
6	Salicylaldoxime	Salicylaldehyde	3	5	60
7	α-Benzoin oxime	Benzoin and benzil	2	4	65 30
8			3	5	0
9	*p*-Toluidine	4,4′-Dimethylazobenzene	3	3	30
10	*p*-Chloroanilin	4,4′-Dichloroazobenzene	3	3	20
11	Benzylamine	Benzaldehyde	3	3	60
12	α-Naphthylamine	1,1-Azonaphthalene	4	3	0
13	*p*-Hydroxyaniline	4,4′-Dihydroxy azobenzene	3	3	30
14			4	4	65
15	Thiophenol	Phenyldisulphide	1	0.25	100
16	Benzylthiol	Benzyldisulphide	1	0.167	100
17	Cyclohexyl thiol	Cyclohexyldisulphide	1	2.5	80
18			1	1.5	80
19	Anthracene	9,10-Anthraquinone	8	8	60
20	Phenanthrene	9,10-Phenanthroquinone	8	10	30
21	Diphenylmethane	Benzophenone	8	10	50
22	Diphenylacetylene	Benzil	6	8	75

[a]All oxidation products were identified by comparison of their spectra and physical data with those of authentic samples

differences have been noticed in the case of poly(vinyl pyridine *N*-oxide) supported chromium (VI) reagents[17].

Oximes, amines, thiols and aromatic hydrocarbons were oxidized by the more efficient polymeric reagent (II) (*Table 2*).

Aldoximes and ketoximes were successfully converted to their corresponding aldehydes and ketones in good yields, using up to three-fold excess of the oxidant. Oxidation of aromatic amines was accompanied by long reaction time and poor yields of the corresponding azo-compounds. In the case of benzylic amines the corresponding carbonyl compounds were obtained in moderate yields. The polymeric reagent oxidized thiols to their corresponding disulphides in almost quantitative yields in short time. Finally, aromatic hydrocarbons could be oxidized with excess of polymeric reagent in considerable yields.

ACKNOWLEDGEMENT

We are grateful to Shiraz University Research Council for partial support of this work, and to Professor H. Firouzabadi for helpful discussions.

Table 1 — *footnotes*
[a]All oxidation products were identified by comparison of their spectra and physical data with those of authentic samples
[b]Oxidation with poly(4-vinyl pyridine) supported silver dichromate (I)
[c]Oxidation with poly(2-vinyl pyridine) supported silver dichromate (II)
[d]Oxidation with crosslinked I
[e]Oxidation with crosslinked II

REFERENCES

1 Akelah, A. and Sherrington, D. C. *Chem. Rev.* 1981, **81**, 557
2 Sherrington, D. C. and Hodge, P. 'Synthesis and Separation Using Functional Polymers', J. Wiley, Chichester, 1988
3 Soutif, J. C. and Brosse, J. C. *React. Polym.* 1990, **12**, 3
4 Taylor, R. T. *Am. Chem. Soc. Symp. Ser.* 1986, **308**, 132
5 Cainelli, G., Cardillo, G., Osena, G. and Sandri, S. *J. Am. Chem. Soc.* 1976, **98**, 6737
6 Frechet, J. M. J., Warmack, J. and Farral, M. J. *J. Org. Chem.* 1978, **43**, 2618
7 Frechet, J. M. J., Darling, P. and Farral, M. J. *J. Org. Chem.* 1981, **46**, 1728
8 Brunelet, T., Jauitteau, C. and Gelbard, G. *J. Org. Chem.* 1986, **51**, 4016
9 Firouzabadi, H., Sardarian, A. and Gharibi, H. *Synth. Commun.* 1984, **14**, 89
10 Firouzabadi, H., Sardarian, A., Moosavipour, H. and Afshari, G. M. *Synthesis* 1986, **4**, 285
11 Tamami, B., Hatam, M. and Mohadjer, D. *Polym. Bull.* 1989, **21**, 531
12 Holt, P. F. and Tamami, B. *Polymer* 1973, **14**, 645
13 Tamami, B. and Goudarzian, N. *Polym. Bull.* 1990, **23**, 295
14 Miller, F. A. and Wilkins, C. H. *Anal. Chem.* 1952, **24**, 1253
15 Holt, P. F. and Lindsay, H. *J. Chem. Soc. B* 1969, 54
16 Geusken, G., Lubikulu, J. C. and David, C. *Polymer* 1966, **7**, 63
17 Tamami, B. and Hatam, M. unpublished results