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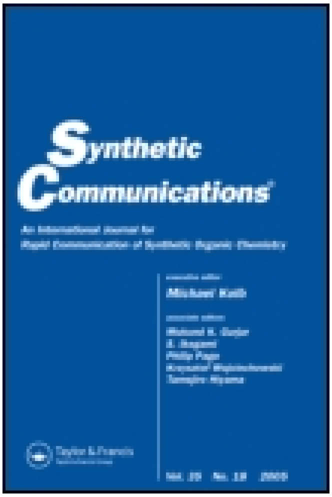

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Chromium(VI) Based Oxidants III.[1,2] Ferric Dichromate, Polyvinylpyridine Supported Zinc, and Ferric Dichromates as New Oxidizing Agents

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SYNTHETIC COMMUNICATIONS, 21(20), 2077-2088 (1991)

CHROMIUM(VI) BASED OXIDANTS III.[1,2]

FERRIC DICHROMATE, POLYVINYLPYRIDINE SUPPORTED ZINC, AND FERRIC DICHROMATES AS NEW OXIDIZING AGENTS

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Summary: *Ferric dichromate, polyvinylpyridine supported zinc and ferric dichromates complexes are prepared and used as stable, mild, and efficient oxidizing reagents for the oxidation of different organic compounds. Ferric dichromate complex is more efficient.*

Oxidations with potassium dichromate in aqueous media are pH dependent and encounter problems in organic synthesis.[3,4] Oxidation of organic compounds in organic solvents under aprotic condition is of importance for the pH sensitive compounds. For this purpose different chromium(VI) based oxidants are reported.[5,6]

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The reported reagents suffer from at least one of the following drawbacks; 1)powerful oxidant without selectivity, 2)high acidity of the reaction media, 3)photosensitivity of the reagent, 4)unstability, 5)hygroscopicity, 6)dangerous procedure for their preparation, 7)long reaction time,and 8)tedious work-up of the reaction mixture. Therefore, search for the new methodology is always a demand few synthetic purposes. In this line of research, we have introduced for chromium(VI) based oxidants. These reagents also suffer from disadvantages which are described.[1,2,7]

Supported agents,[8-10] specially the polymeric ones, have found wide applications in organic synthesis. Several polymer supported chromium(VI) oxidizing agents have been reported in the literature.[9] Recently polyvinylpyridine supported silver dichromate has been introduced for the oxidation of hydroxy compounds.[11] This reagent is expensive, hence not suitable for large-scale oxidations. Therefore, preparation of dichromates with inexpensive cations would be of interest and their polymer supported reagents might be of practical importance. Along this line, copper dichromate was prepared and identified as a weak oxidizing agent under aprotic condition. Ferric dichromate was also prepared and exhibited high reactivity as an oxidant in organic solvents. The acidity of ferric dichromate (pH of a 0.01 molar solution: 2.19) is less pronounced than that reported for pyridinium chlorochromate (pH of a 0.01 molar solution:1.75) and is higher than that reported for zinc dichromate trihydrate (pH of a 0.01 molar solution 2.85).[2]

With the above reagent, benzylic alcohols are converted to their corresponding carbonyl compound, in high yields. Naphthalene and anthracene are converted to 1,4 and 9,10 quinones respectively. sec-Saturated alcohols are converted to their ketones. Styrene is converted to benzaldehyde and trans-stilbene to benzil and benzaldehyde. Acyloins are transformed to their diketones and p-hydroquinones to their corresponding quinones. Saturated primary alcohols produced their carboxylic acids (Table 1).

Zinc dichromate trihydrate which is much cheaper than its silver analogue is reported to be an effective oxidant for the conversion of different functional groups.[2]

Here we also report the preparation and uses of poly 2- and 4-vinylpyridine supported zinc and ferric dichromates as new members of the polymer supported metal dichromate oxidizing agents. The presence of the dichromate anion in these polymeric reagents is confirmed by their IR spectra. They all show bands at 930 cm^{-1} and 765 cm^{-1} characteristic peaks for the dichromates.[12]

The capacities of these reagents were determined by atomic absorption technique and iodometric titration method.[13,14] The values obtained were 1.6, 1.9 and 2.4 for poly(2-vinylpyridine) supported zinc dichromate, poly 4-zinc dichromate and poly 2-or 4-ferric dichromates respectively as mmoles of $Cr_2O_7^=$ per gram of the reagents. The difference in capacity between poly 2-and poly 4-zinc dichromate complexes is probably due to the structural difference between the two supports and consequently different

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Table I. Oxidation of Organic Compounds with $Fe_2(Cr_2O_7)_3$ in CH_3CN.

No.	Substrate	Product	Isolated Yield %	Oxid./Subst.	RXn Time (hr)
1	Benzyl Alcohol	Benzaldehyde	75	2	1.5
2	p-Methoxybenzyl Alcohol	p-Methoxybenzaldehyde	85	2	1.4
3	p-Nitrobenzyl Alcohol	p-Nitrobenzaldehyde	98.8	4	7
4	p-Chlorobenzyl Alcohol	p-Chlorobenzaldehyde	78	1.5	1.5
5	9-Methylhydroxy Anthracene	9-Anthracene Carboxaldehyde	70	2	2.5
6	Phenylmethyl carbinol	Acetophenone	90	2.5	2.7
7	Benzhydrol	Benzophenone	95	2.8	2.7
8	Piperonol	Piperonal	98	2	0.3
9	2-Octanol	2-Octanone	84.7	2	1.5
10	Menthol	Menthone	94	3	3
11	Cinnamyl Alcohol	Benzaldehyde + Cinnamaldehyde	60 30	0.6	2.5
12	Naphthalene	1,4-Naphthoquinone	60	3	4.5
13	Anthracene	9,10-Anthraquinone	98.5	4	3
14	trans-Stilbene	Benzil + Benzaldehyde	86 14	4	0.3
15	Styrene	Benzaldehyde	60	3	4

(continued)

Table I. Continued.

16	Benzoin	Benzil	89	1.5	1
17	Furoin	Furil	93.5	2.8	1.5
18	p-Hydroquinone	p-Benzoquinone	86	0.5	0.75
19	1,4-Dihydroxy Naphthalene	1,4-Naphthoquinone	86	2	3
20	1-Octanol	1-Octanoic Acid	94	3	3
21	1-Heptanol	1-Heptonoic Acid	88	3.5	3

complexation with the zinc cation. As seen, the ferric dichromate complex has the highest capacity and this is an advantage of this reagent over the zinc dichromate complex or the already reported silver dichromate complex.[11]

These polymeric oxidizing reagents are stable, insoluble in water and most organic solvents. They can be effective in dichloromethane, benzene, and toluene. They can be used in equimolar amounts with respect to the substrates. The chromium ions remain firmely bound to the insoluble polymer support during the reactions. The work-up of the reaction mixture is easy and comparable to other reported polymeric oxidizing reagents.[11,15]

As shown in Table II, primary benzylic and secondary benzylic alcohols, acyloins and hydroquinone were oxidized to their corresponding carbonyl compounds in high yields. As for selectivity and reactivity of these reagents in the oxidation of different hydroxy compounds, a few points worth mentioning.

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Table II. Oxidation of Hydroxy Compounds to their Carbonyl Compounds with Polyvinylpyridine Supported Zinc and Ferric Dichromates.

No.	Substrate	Product	Rxn Time (hr)				Yield %			
			(P_2Zn)	(P_4Zn)	(P_2Fe)	(P_4Fe)	(P_2Zn)	(P_4Zn)	(P_2Fe)	(P_4Fe)
1	Benzyl Alcohol	Benzaldehyde	0.5	1	0.15	0.25	95	95	97	98
2	p-Nitrobenzyl Alcohol	p-Nitrobenzaldehyde	0.5	1	0.3	0.5	95	90	95	95
3	p-Chlorobenzyl Alcohol	p-Chlorobenzaldehyde	0.5	1	0.3	0.5	90	90	95	90
4	p-Methoxybenzyl Alcohol	p-Methoxybenzaldehyde	1.5	3.5	1.6	3	70	65	93	90
5	Piperonol	Piperonal	1.5	3.2	1	2.5	80	75	95	90
6	Furfuryl Alcohol	Furfural	0.5	1	0.2	0.4	85	80	98	98
7	Methylbenzyl Carbinol	Acetophenone	1	0.3	1.7	1.6	85	70	100	100
8	Benzhydrol	Benzophenone	0.5	2	0.3	1.5	85	80	100	90

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Table II. Continued.

9	Benzoin	Benzil	0.7	2	0.3	0.8	80	80	100	95
10	Furoin	Furil	2	4	1	3.2	80	55	95	90
11	p-Hydroquinone	p-Benzoquinone	0.25	0.6	0.15	0.5	100	100	100	95
12	Cinnamyl Alcohol	Cinnamaldehyde	2	3	1	1.4	70	65	70	95

P_2Zn: Poly(2-vinylpyridine) supported zinc dichromate.

P_2Fe: Poly(2-vinylpyridine) supported ferric dichromate.

P_4Zn: Poly(4-vinylpyridine) supported zinc dichromate.

P_4Fe: Poly(4-vinylpyridine) supported ferric dichromate.

Firstly, it is seen that as in the case of the reported polyvinylpyridine supported silver dichromate[12] and polyvinylpyridinium dichromate,[15] poly 2-isomers are more efficient than poly 4-isomers. Secondly, polymer supported ferric dichromates are considerably more reactive than polymer supported zinc dichromates, with poly 2-isomer being the most reactive one.

In Table III we have compared the results of our experiments with some of those previously reported in the literature.[2,11]

Investigation about the preparation and uses of crosslinked polyvinylpyridine supported metal dichromate reagents and their regenerations are underway.

EXPERIMENTAL

Poly 2- and poly 4-vinylpyridines were prepared by suspension polymerization of the corresponding monomers. Polymer samples of close molecular weights were used as supports[9]. Capacities were determined by titration and atomic absorption technique. Oxidized products were identified by comparison of their spectra and physical data with those of the authentic samples.

Preparation of Polyvinylpyridine Supported Zinc and Ferric Dichromate.

Polyvinylpyridine supported zinc chloride and ferric nitrate were prepared by dropwise addition of the methanolic

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Table III. Several Comparisons of Ferric Dichromate, (FeD), and poly(4-vinylpyridine) supported Ferric Dichromate (P_4Fe), with zinc Dichromate trihydrate (ZnDT) for the Oxidation of Organic Compounds.

No.	Reactant	Product	Yields % (FeD)	(P_4Fe)	(ZnDT)
1	Benzyl Alcohol	Benzaldehyde	75	98	95
2	p-Nitrobenzyl Alcohol	p-Nitrobenzaldehyde	98.8	95	50
3	Benzhydrol	Benzophenone	95	90	95
4	Cinnamyl Alcohol	Cinnamaldehyde	30	95	5
5	Benzoin	Benzil	89	95	90
6	Naphthalene	1,4-Naphthoquinone	60	--	10
7	Anthracene	9,10-Anthraquinone	98.5	--	80
8	trans-Stilbene	Benzil	86	--	50

solution of the polymer to solutions of excess anhydrous zinc chloride and ferric nitrate nonahydrate in methanol respectively. The precipitates were washed first with methanol and then with dichloroethane and dried. They were both hygroscopic and were used immediately for the preparation of the reagents.

A suspension of polyvinylpyridine supported zinc chloride or ferric nitrate (4 g.) in acetone (20 ml) was added to

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a stirred solution of the excess chromium trioxide (15 g., 0.15 mol) in a minimum amount of water, which was diluted by the slow addition of acetone (150 ml) with stirring. Stirring was continued for 1 hr. and then the resulting mixture was refrigerated overnight. The light brown precipitates were isolated by simple filteration and washed with methanol-acetone mixture (1/1) and dried in vacuum at 50°C to produce the stable and non-hygroscopic oxidants in a >90% yield.

General Procedure for Oxidation of Hydroxy Compounds with the Polymeric Agents.

To a solution of the hydroxy compounds (5 mmol) in toluene, polymeric reagent (2.6 mmol based on the capacity) was added and refluxed for 0.15-4 hrs. The progress of the reaction was monitored by TLC (eluent: hexane-ether). On completion of the reaction the product was obtained by simple filtration and washing of the resin. The combined filtrates were evaporated and the desired carbonyl compound was obtained and if necessary purified by column chromatography. The results are shown in Table II.

Preparation of Ferric Dichromate[16].

To a solution of CrO_3(3.36 g, 0.022 mol) in water (50 ml) freshly prepared ferric hydroxide (2.5 g, 0.24 mol) was added and the resulting mixture was refluxed for 4 hrs. The reaction mixture was filtered and the filtrate was evaporated on a rotatory evaporater. The resulting viscous material was

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dried in a vacuum desicator in the presence of P_2O_5 at 40°C overnight to yield ferric dichromate (~ 90%). The purity of the obtained dichromate was determined to be ~ 92%.

Oxidation of Organic Substrates with Ferric Dichromate.

To a solution of substrate (1 mmol) in acetonitrile (10 ml) the oxidant (0.5-4 mmol) was added to the reaction mixture while magnetically being stirred and refluxed for 0.3-7 hrs. The reaction mixture was filtered and the filtrate was evaporated. The resulting material was purified by either column or preparative layer chromatography to give the desired products in 30-98.8% yields.

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References:

1. Firouzabadi, H., Iranpoor, N., Kiaeezadeh, F., Toofan, J., Tetrahedron, 1986, 42, 719.
2. Firouzabadi, H., Sardarian, A.R., Moosavipour, H., Afshari, G.M., Synthesis, 1986, 285.
3. Fieser, L.F., Fieser, M., "Reagents for Organic Synthesis", Vol. 1, New York, 1967, p. 941-952.
4. Augustine, R.L., "Oxidation", Vol. 1, Marcel Dekker, Inc., New York, 1969, P. 28, 30-38.

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5. Cainelli, G., Cardillo, G., "Chromium Oxidations in Organic Chemistry, Reactivity and Structure Concepts in Organic Chemistry", vol. 19, Springer-Verlag, Berlin, 1984.

6. Luzzio, F.A., Guziec, F.S., Org. Prep. and Procedure _Int._, 1988, _20_, 533.

7. Firouzabadi, H., Sardarian, A.R., Gharibi, H., _Synthetic Commun._, 1984, _14_, 84.

8. a. McKillop, A., Young, D.W., _Synthesis_, 1979, 401.
   b. Akelah, A., _Synthesis_, 1981, 413.

9. Akelah, A., Sherrington, D.C., _Chem. Rev._, 1981, _81_, 557.

10. Sherrington, D.C., Hodge, P., "Synthesis and Separation Using Functional Polymers", John-Wily and Sons, England, 1988.

11. Tamami, B., Hatam, M., Mohadjer, D., _Polymer Bull._, 1989, _21_, 531.

12. Acharya, S.P., Cited by Rav, G.G., Radhakrishna, A.S., Singh, B.B., Bhatnagar, S.P., _Synthesis_, 1983, 808.

13. Skoog, D.A., West, D.M., "Fundamental of Analytical Chemistry" 4th ed., Holt-Saunders Int. Ed., 1982, P. 582.

14. Fritz, J.S., Schenk, G.H., "Quantitative Analytical Chemistry", 4th ed, Allyn and Bacon Ed., 1979, P. 276.

15. Tamami, B., Goudarzian, N., _Polymer Bull._, 1990, _23_, 295.

16. Husain, S., Partington, J.R., _Chem. N._ 1926, 133, 386.

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