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Pyrazine-Based Polymeric Complex of Oxodiperoxochromium (VI) Compound as a New Stable, Mild, Efficient and Versatile Oxidant in Organic Synthesis

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***Abstract*:** The title compound was prepared and characterized by conventional methods. Its uses as stoichiometric oxidizing agent for a variety of organic compounds are described. With this reagent alcohols are converted to the corresponding carbonyl compounds. With 1,2-dioles C-C bond cleavage occurs. Decarboxylation of α-hydroxy acids proceeds quantitatively. Also thiols are converted to disulfides, hydroxy phenols to quinones, benzylamines to carbonyl compounds, tertiaryamines to the N-oxides, phosphines to phosphine oxides, sulfides to sulfoxides, and anthracene and phenanthrene to quinones. Deprotection of oximes and oxidative deprotection of silyl ethers proceed easily.
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INTRODUCTION

There has been a continued interest in the development of new Cr (VI) based reagents for the effective oxidation of organic substrates, especially under mild aprotic conditions. For this purpose a number of monomeric Cr (VI) reagents have been reported in the literature[1]. Among these, several amine complexes such as Jones reagent[2] Scarett reagent[3], pyridinum dichromate[4], pyridinum chlorochromate[5], nicotinum dichromate[6], quinolium dichromate[7] and several metal dichromates such as zinc dichromate trihydrate[8], tetrakispyridine silver dichromate[9], and zinc chlorochromate[10] can be named. Also several regenerable polymer supported Cr (VI) reagents have been reported in the literature. These are polymer-bound chromates based on commercial Amberlyst A-26 resin[11], polyvinylpyrridinium chlorochromate[12] and dichromate[13], polyvinylpyridine N-oxide supported dichromates[14], polyvinylpyridine supported silver dichromate[15], and ferric dichromate and zinc dichromate.[16]

Peroxide forms of group VI transition metals, chromium, molybdenum, and tungsten, were reviewed recently.[17] Among these only oxodiperoxochromium (VI) compound CrO_5 , shows a general utility as an oxidizing reagent in organic synthesis. CrO_5 itself is an unstable compound and cannot be isolated in a solid form. When prepared, it is usually obtained as its blue etherial solution which is used directly in oxidation reactions and can be stored in a refrigerator for a few hours.[18] Several adducts of this compound with different bases have been studied and reported in the literature.[17] They are generally more stable than the parent compound. Among these, complexes of CrO_5 with pyridine[18,19], bipyridine[18], triphenylphosphine oxide[20,21] and hexamethylphosphortriamide[20,22] have particularly been used for oxidation of different organic compounds.

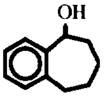
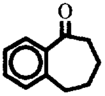
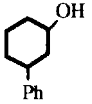
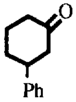
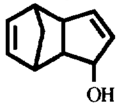
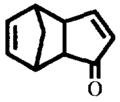
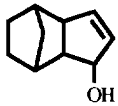
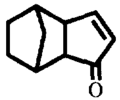
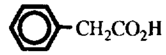
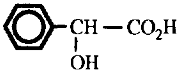
Coordination polymers exhibit novel optical, magnetic, electrical and catalytic properties.[23] However, there have been very few reports on the uses of such polymers as reagents in organic synthesis. We recently, reported the stabilization of the unstable zinc borohydride by forming its coordination polymer with pyrazine. The polymer was then utilized as an efficient and stable reducing agent.[24] Now in continuation of our interest along this line, we wish to introduce the coordination polymer of pyrazine and oxodiperoxochromium (VI) compound as a new stable form of CrO_5 for efficient oxidation of a wide variety of organic compounds.

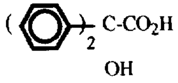
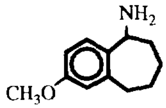
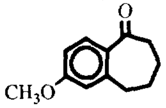
RESULTS AND DISCUSSION

The reagent was prepared by mixing the etherial solution of CrO_5 and pyrazine, which upon cooling gave the deep blue stable precipitate in good yield. It can be stored for months at room temperature and is quite stable towards hammer blows. According to the following evidences this complex of oxodiperoxochromium (VI) compound and pyrazine have a polymeric nature with bridge pyrazine molecules, $(Pyz\text{-}CrO_5)_n$, a) atomic absorption determination of the amount of chromium in a measured quantity of the complex showed a 1:1 molar ratio of chromium to pyrazine, b) the complex is sparingly soluble in common organic solvents such as dichloromethane, chloroform, benzene, toluene, n-hexane, cyclohexane, while pyridine complex of CrO_5, for example, is completely soluble in these solvents, c) absence of a peak at ca 1250 cm^{-1} due to terminal pyrazine and presence of a weak peak at ca 980 cm^{-1} due to bridging pyrazine in the IR spectra[25], d)the UV spectra of pyrazine shows two distinct absorptions at 260 nm and 316 nm which are related to $\pi - \pi^*$ and $n - \pi^*$ transitions[28] respectively, however in the UV spectra of the complex the $\pi - \pi^*$ transition is unaffected but the peak due to the $n - \pi^*$ transition is nearly diminished. This is good evidence for incorporation of both nitrogen of pyrazine molecule in the coordination sphere of chromium in a bridging manner.

Oxidation of different classes of organic compounds with $(Pyz\text{-}CrO_5)_n$ proceeded very well in CH_2Cl_2 at room temperature. As shown in Table 1, benzylic alcohols were converted to the corresponding carbonyl compounds in excellent yields. Oxidation of α-β-unsaturated alcohols and primary and secondary alcohols also proceeded well in high yields. α-Hydroxyketones were converted to the corresponding α-diketones, and 1,2-diphenylethylene glycol produced benzaldehyde as the major and benzil as the minor product. α-Hydroxyacids were decarboxylated to the corresponding carbonyl compounds quantitatively (Table 1). Hydroquinone, catechol, 1,4-dihydroxy naphthalene and 2-t-butylhydroquinone were oxidized very easily to their quinones in excellent yields. Phosphines were converted to phosphine oxides rapidly and almost quantitatively. Sulfides were converted to the sulfoxides as exclusive products without overoxidation to sulfones, and thiols were oxidized to their disulfides in high yields. Benzylic amines were converted to their corresponding carbonyl compounds, p-toluidine and α-naphthylamine produced the azo compound in poor yields, and triethylamine and N,N-dimethylaniline were changed to the N-oxides quantitatively (Table 1). Finally anthracene and phenanthrene were oxidized to the corresponding quinones in moderate yields.

Table 1: Oxidation of different organic compounds with $(Pyz\text{-}CrO_5)_n$

Substrate	Product	Time (h)	Yield(%)
Benzyl alcohol	Benzaldehyde	0.5	100
2-Naphthalenemethanol	2-Naphthalenecarboxaldehyde	0.6	99
9-Anthracenemethanol	9-Anthracenecarboxaldehyde	0.6	99
P-Anisylalcohol	P-Anisaldehyde	0.	100
Piperonol	Piperonal	0.3	95
P-Nitrobenzylalcohol	P-Nitrobenzaldehyde	0.4	98*
P-Chlorobenzylalcohol	P-Chlorobenzaldehyde	0.6	95
1-Phenylethanol	Acetophenone	0.4	96
Benzhydrol	Benzophenone	0.5	100
		0.6	95
2-Octanol	2-Octanone	1.5	97
1-Heptanol	1-Heptanone	1.5	99
Cyclohexanol	Cyclohexanone	1.5	93
		1.25	95
Borneol	Camphor	2	90
Cinamylalcohol	Cinamylaldehyde	1.5	90
		1.25	85
		1.25	90
Benzoin	Benzil	0.3	90*
Anisoin	Anisil	0.2	92*
Furoin	Furil	0.3	90*
1,2-Diphenylethrleneglycol	Benzaldehyde benzil	1.5	60 20
1-phenylethylene glycol	Benzaldehyde	1.5	75
	Benzaldehyde	0.3	100
	Benzaldehyde	0.3	100

	Benzophenone	0.3	100
P-Hydroquinone	P-Benzoquinone	0.2	96
O-Hydroquinone	O-Benzoquinone	0.6	80
2-t-Butyl-P-hydroquinone	2-t-Butyl-P-benzoquinone	0.4	90
1,4-dihydroxynaphthalene	1,4-Naphthoquinone	0.2	95
Triphenylphosphine	Triphenylphosphine oxide	0.1	100
Diphenylmethylphosphine	Diphenylmethylphosphine oxide	0.1	100
Tributyl phosphine	Triphenylphosphine oxide	0.15	99
Methylphenyl sulfide	Methylphenyl sulfoxide	1.5	90
Diphenyl sulfide	Diphenyl sulfoxide	1.5	90
Dibenzyl sulfide	Dibenzyl sulfoxide	1.1	90
Dibutyl sulfide	Dibutyl sulfoxide	1.5	90
α-Toluenethiol	Benzyl disulfide	0.1	95
Furfuryl mercaptan	Furyl disulfide	0.1	95
Thiophenol	Phenyl di sulfide	0.15	95
Cyclohexane thiol	Cyclohexyl disulfide	0.3	90
2-Mercaptobezothiazol	2-Mercaptobenzothiazoldisulfide	0.1	95
Benzylamine	Benzaldehyde	0.5	85
		0.5	80
1-Naphthylamine	1,1'-Azonaphthalene	1	20
P-Toluidine	4,4'-Dimethylazobenzene	1	20
Triethylamine	Triethylamine oxide	0.4	100**
N,N'-Dimethylaniline	N,N'-Dimethylaniline oxide	0.6	100**
Anthracene	Anthraquinone	4.5	50***
Phenanthrene	Phenanthroquinone	4.5	45***

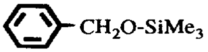
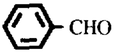
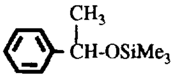
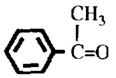
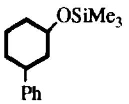
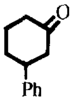
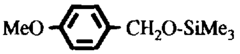
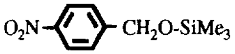
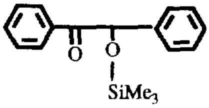
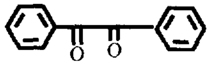
All reaction were performed in CH_2Cl_2 at room temp. with Oxid./Subst. = 2/1.

* Reactions were performed in benzene under reflux conditions.

** G.C. yield.

*** Reactions were performed with Oxid/Subst. = 5/1.

Table 2: Deoximation of oximes, and oxidative deprotection of silylethers with $(Pyz\text{-}CrO_5)_n$

Substrate	Product	Time(h)	Yield (%)
Benzaldehyde oxime	Benzaldehyde	0.8	85
9-Anthracenecarboxaldehyde oxime	9-Anthracecarboxaldehyde	0.9	90
P-Chlorobenzaldehyde oxime	P-Chlorobenzaldehyde	1	95
Camphor oxime	Camphor	1.5	90
Acethophenone oxime	Acetophenone	0.9	95
		0.6	99
		0.5	95
		1.5	95
		0.4	99
		0.4	95*
		0.4	95*

All reactions were performed in CH_2Cl_2 at room temp. with Oxid/Subst = 2/1

* Reactions were performed in benzene under reflux conditions.

Oximes and silylethers are important protecting groups for carbonyl compounds[29] and alcohols[30] respectively. Deoximation of different oximes and oxidative deprotection of sillyl ethers with $(\text{Pyz-CrO}_5)_n$afforded the corresponding carbonyl compounds in excellent yields (Table 2).

For comparison, some of the results obtained from the oxidation of organic compounds with this polymeric complex, $(\text{Pyz-CrO}_5)_n$, and some of those obtained from related monomeric analougues and two reported polymeric chromium (VI) based reagents are tabulated in Table 3.

Table 3: Comparison of oxidazing ability of $(\text{Pyz-CrO}_5)_n$ with some other oxidant

substrate	1	2	3	4	5	6
	Time(Yield%)	Time(Yield%)	Time(Yield%)	Time(Yield%)	Time(Yield%)	Time(Yield%)
Benzylalcohol	0.5(100)	0.5(100)	1(85)	1(95)	1(100)	1.7(100)
1-phenylethanol	0.5(96)	-	-	-	0.75(90)	2.7(60)
Cinamylalcohol	1.5(90)	2(90)	1.5(30)	1.25(100)	3(85)	1.5(30)
Benzoin	0.3(90)	0.1(100)	-	3(90)	2.5(80)	3(60)
Benzydrol	0.5(100)	0.5(65)	0.7(90)	1(95)	0.5(100)	-
Acetophenone oxime	0.9(95)	1.25(70)	1(20)	0.25(100)	3(25)	-
α-Toluenethiol	0.1(95)	0.02(100)	1(20)	0.25(100)	0.5(100)	-
Benzylamine	0.5(85)	2.5(30)	-	0.4(100)	4(70)	-

1 = $(\text{Pyz-CrO}_5)_n$, 2 = Pyridine -CrO_5 complex[18], 3 = CrO_5 etherate[18],4 = Bipyridine -CrO_5 complex[18],
5 = Polyvinylpyridine N-oxide supported dichromate[14],6 = Polyvinylpyridine supported silver dichromate[15]

In conclusion $(\text{Pyz-CrO}_5)_n$ is introduced as a new stable form of CrO_5 and can be used as a versatile and efficient oxidant in organic synthesis. Compared to many other Cr(VI) based oxidants reported in the literature, it offers at least one of the following advantages: preparation of the reagent is neither difficult nor dangerous, it is stable and nonhygroscopic, usually provides a high yield of product, no overoxidation of products occurs, reaction medium is neutral which is suitable for oxidation of acid labile compounds, molar ratio of oxidant to reactant is reasonable, and finally the work up of spent reagent because of its heterogeneous nature is easy.

EXPERIMENTAL

The chemicals were either prepared in our laboratories or purchased from Fluka,BDH, and Merck Chemical Companies.

All yields refer to isolated products, unless otherwise indicated. All oxidation products were known compounds, and are 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 apparatus. Reaction monitoring and purity determination of products were accomplished by GLC on a Shimadzu model GC-8A instrument with a flame-ionization detector using a cloumn of 15% carbowax 20m Chromosorb-W acid washed 60-80 mesh or by

TLC on silica-gel polygram Silg/uv 254 plate. IR-spectra were run on a Perkin-Elmer 781 Spectrophotometers. The NMR spectra were recorded on a Hitachi, R-2413, 60MHz spectrometer. The amount of chromium in the reagent was determined by atomic absorption technique.

Preparation of Polymeric Complex of Oxodiperoxochromium (VI) Compound and Pyrazine $(Pyz\text{-}CrO_5)_n$

Concentrated sulfuric acid (1.2 ml) and diethylether (150 ml) were added to a solution of potassium dichromate (5.88 gr) in distilled water (100 ml), at -5°C. To the resulting mixture hydrogen peroxide (40 ml, 30%) was added with vigorous stirring to produce a dark-blue solution of chromium peroxide, which was extracted into the etherial phase. The etherial phase was dried on Na_2SO_4 and filtered. Its CrO_5 content was about 45%, determined by quantitative precipitation with 2,2-bipyridine.[18] To this etherial solution of CrO_5 (18mmol), an equimolar amount of pyrazine (1.44 gr, 18 mmol) in diethyl ether (10 ml) was added. The mixture was cooled to 0°C and after 4h, a deep blue precipitate was filtered and washed with ether and dried at room temperature under vaccum (80% yield). mp 110° (dec.). capacity of the reagent was 4.7 mmol CrO_5 per gram of polymer.

General Procedure for Oxidation of Organic Substrates with $(Pyz\text{-}CrO_5)_n$

To a solution of a substrate (1 mmol) in dry CH_2Cl_2 (10 ml) the reagent (2 mmol) was added and the mixture was stirred for the appropriate time at room temperature. Progress of the reaction was monitored by TLC (eluent n-hexane; ether, 5:1) or by GLC. At the end of the reaction the solvent was evaporated and the resulting mixture was washed through a short pad of silica gel with benzene. The evaporation of solvent gave pure product in most cases but if necessary, the product was further purified by column chromatography on a silica gel column with non polar solvent as eluent.

General Procedure for Deoximation of Oximes and Oxidative Deprotection of Silylethers with $(Pyz\text{-}CrO_5)_n$

In a round-bottomed flask (25 ml) the substrate (1 mmol) was dissolved in dry CH_2Cl_2 (10 ml) and the reagent (2 mmol) was added while the mixture was being stirred for 0.4-1.5 h. At the end of reaction the solvent was evaporated and the resulting mixture was washed through a short silica pad, evaporation of solvent gave pure product. If necessary further purification was done by column chromatography on silica gel column with benzene as eluent.

ACKNOWLEDGEMENT

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