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Solvent Free Oxidations of Epoxides and Polycyclic Aromatic Hydrocarbons with Chromium(VI)-Based Oxidants. Zinc Chlorochromate Nonahydrate [Zn $(ClCrO_3)_2$. $9H_2O$] vs Pyridinium Chlorochromate [PyCl CrO_3H].

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Abstract : Zinc chlorochromate nonahydrate (ZCCNH) and pyridinium chlorochromate (PCC) are used for the oxidation of epoxides under neat conditions at room temperature. Oxidation of naphthalene and anthracene produce their quinones with ZCCNH. PCC is not an effective oxidant for this purpose and the hydrocarbons are isolated intact.

Key words: Oxidation of epoxides, Hydrocarbons, Neat condition, Benzoquinone, Aldehyde, Ketone.

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Oxidations with chromium trioxide, sodium or potassium dichromate as the source of chromium (VI) are usually performed under aqueous acidic conditions. Sometimes co-solvents like acetone, benzene, methylene chloride, or ether are used in order to solubilize water insoluble organic compounds. Under the conditions mentioned, the reagents oxidize almost every oxidizable functional groups ranging from carbon-hydrogen bonds to aromatic nuclei. However, the low pH of the reaction medium in the presence of water enhances hydrolytic reactions which restricts the use of this class of reagents for acid sensitive molecules.[1]

In order to improve on the selectivity of oxidation and also the mildness of the reaction conditions, a number of oxochromium amine complexes have been developed in the last two decades.[2-12] Zirconium hydroxide chromate[6-8] and also organosilicon derivatives of chlorochromate are of interest and trimethylsilyl chlorochromate was prepared and reported as an efficient oxidant[13]. Investigation of the oxidation ability of the metal analogues of pyridinium chlorochromate[14] is also of interest and recently potassium and magnesium chlorochromates[15] are reported for the oxidations of different types of organic compounds. We have found that zinc cation activates oxoanions and make them useful for the oxidation of organic substrates in aprotic organic solvents.

Recently, we have introduced zinc dichromate trihydrate[16] and zinc chlorochromate nonahydrate[17] as useful and versatile reagents.

In recent years, attention has been paid to reactions which are performed under neat conditions.[18,19]. Therefore, the idea and the reports prompted us to investigate the oxidation abilities of pyridinium chlorochromate (PCC) and zinc chlorochromate nonahydrate (ZCCNH) for the oxidation of varieties of organic substrates under solvent free conditions at room temperature.

Both reagents are suitable for the oxidation of hydroquinone to benzoquinone with high rates and yields under solvent free conditions. Overoxidation of the aldehydes to carboxylic acids has not been observed in the reactions. The rates of the reactions are usually faster with ZCCNH than with PCC for this type of oxidations.

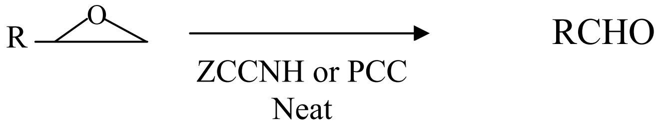
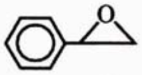
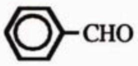
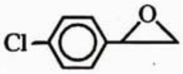
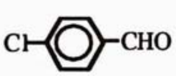
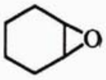
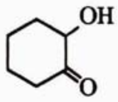
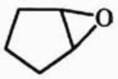
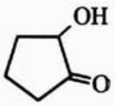


Table 1. Oxidation of Epoxides with (I) ZCCNH and (II) PCC.

Entry	Substrate	Product	Solvent Free Oxid./Subst.(h) Yield%^{a} I	 II	In Solution Oxid./Subst.(h) Yield%^{a} I[17]	 II[19]
1			1(b)80	2(b)81	1.5(2)80	2(0.3)76
2			1.2(b)91	2(b)83	2(3)85	2(0.5)78
3			0.9(b)88	3(b)87	2(2)75-80	3(0.5)70
4			0.9(b)89	3(b)85		3(0.5)68

a) Isolated yield after column chromatography

b) Reaction was completed immediately.

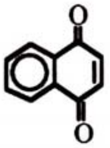
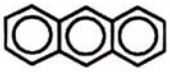
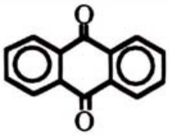
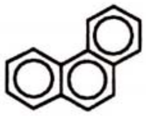
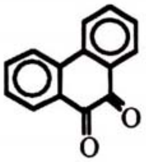
Epoxides, under neat conditions, are converted either to their corresponding hydroxyl carbonyl compounds or via the cleavage of carbon-carbon bonds to produce the respective carbonyl compounds with high yields. In comparison with those reported in the solution[17], the reactions proceeded immediately with lower molar ratios of the oxidants (Table 1).

Oxidation of aromatic hydrocarbons to their corresponding quinones, under mild conditions, is important, Surprisingly, we have found that naphthalene needs harsh reaction conditions to oxidize to 1,4–naphthoquinone with ZCCNH, i.e. 1h in 80% yield at room temperature under neat condition. Phenanthrene and anthracene are also converted to 9,10-anthraquinone and 9,10-phenanthroquinone in 2 h with 60% and 30% yields respectively. PCC is not an effective oxidant for these transformations, and the hydrocarbons are isolated from the reaction mixture intact. Comparisons of the results under neat condition with the reactions performed in solutions are tabulated in (Table 2).

In conclusion, under solvent free conditions zinc chlorochromate nonahydrate (ZCCNH) is a more efficient oxidant than pyridinium chlorochromate (PCC) for the oxidation of a variety of functional groups. Less molar ratios of the oxidations are used under neat conditions in comparison with the corresponding reactions in solution which makes this method more attracting for medium to large-scale operation.

The rate and yields are usually higher under solvent free conditions than those reported for the reaction in solution.

Table 2. Oxidation of Aromatic Hydrocarbons with (I) Zinc chlorochromate Nonahydrate (ZCCNH) and (II) Pyridinium Chlorochromate (PCC).

Entry	Substrate	Product	Solvent Free		In Solution	
			Oxid./Subst.(h) Yield%^{a}		Oxid./Subst.(h) Yield%^{a}	
			I	II	I^{17}	II
1			10(1)80	10(5) -^{b}	-^{b}	-^{b}
2			10(2)60	10(5) -^{b}	8(3)83	-^{b}
3			10(2)30	10(5) -^{b}	-^{b}	-^{b}

a) Isolated yield after column chromatography
b) Reaction does not procced.

Experimental

General: Chemicals were either prepared in our laboratories or were purchased from Fluka, Merck, B.D.H., Aldrich and Riedel Dehaen AG Chemical Companies. Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to the isolated product. IR Spectra were recorded on a Perkin Elmer 781 Spectrophotometers. NMR Spectra were recorded on a Bruker DPX250 NMR spectrometer. Mass Spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity determinations of the products were accomplished by TLC on silica gel polygram SILG/UV 254 Plates or GLC on a Shimadzu GC-14A instrument. All the solvents were completely dried and predistilled.

Oxidation of Styrene Oxide with Zinc Chlorochromate Nonahydrate (ZCCNH)[17] under solvent free conditions, a typical procedure:

A mixture of styrene oxide (0.12 g, 1 mmo1) and ZCCNH (0.498 g, 1 mmo1) was prepared. The reaction was completed immediately. To the resulting mixture, silica gel (4 g) was added and mixed throughly. The resulting solid was applied on a silica gel column and eluted with petroleum ether/acetone (8/1, 50 ml).

The mixture was concentrated and the desired aldehyde was precipitated as its 2,5–dinitrophenylhydrazone derivative 0.085 g, 80% yield. (Table 1)

Oxidation of Naphthalene with Zinc Chlorochromate Nonahydrate (ZCCNH) under solvent-free conditions, a typical procedure:

A mixture of naphthalene (0.128 g, 1mmol) and ZCCNH (4.98 g, 10 mmo1) was prepared. The reaction mixture was magnetically agitated at room temperature. The progress of the reaction was monitored by TLC and was completed after 1 h. To the resulting mixture silica gel (4 g) was added and mixed throughly. The resulting solid was applied on a silica gel column and eluted with petroleum ether/acetone (8/1, 50 ml) to afford 1,4–

naphthoquinone 0.126 g, 80% yield, mp 123 °C, [lit.[18, 20] mp 123–125 °C] (Table 2).

Acknowledgments

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