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OXIDATION OF ALCOHOLS WITH POLYMERIC REAGENT OF POLY [VINYL (PYRIDINIUM FLUOROCHROMATE)]

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Abstract: Poly [Vinyl (Pyridinium Fluorochromate)] is a new reagent for the selective oxidation of primary and secondary alcohols under mild conditions. It also oxidises aromatic and α,ß - unsaturated alcohols to the corresponding aldehydes and ketones in good yield.

Primary and secondary alcohols have been oxidized by a number of Cr(VI) reagents [1,2]. Corey introduced pyridinuium chlorochromate (PCC) and pyridinium dichromate for the selective oxidation of alcohols to aldehydes [3,4]

We were primarily interested in the selective oxidation of the hydroxyamino acid residues present in the protein collagen to the corresponding aldehydes or ketones. Due to poor solubility of Cr(VI)

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reagents reported prior to pyridinium chlorochromate in water, these reagents were not useful for the oxidation of collagen. We have successfully used pyridinium chlorochromate for the selective oxidation of collagen[5,6]. We have also synthesised a number of new oxidizing agents based on Cr(VI) like Quinolinium chlorochromate (QCC) [7] Quinolinium dichromate QDC [8], Isoquinolinium Dichromate (IQDC)[9], Isoquinolinium fluorochromate IQFC[10], etc. These reagents have been very useful for the oxidation of alcohols.

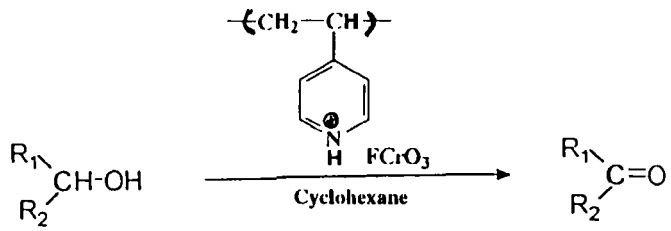
This note describes the synthesis and oxidation studies of Poly [vinyl (pyridinium fluorochromate)]. We have found that this reagent has certain advantages over similar oxidizing agents in terms of amount of oxidant and solvent required, selectivity in oxidation etc.

Polymeric reagents [11] have been used in simple processes such as epoxidation [12], Oxidation [13], halogenation [14] reactions. In all these applications, advantage is taken of the insolubility of the polymeric reagent and its by product which allows for the easy removal of the excess reagent or spent material from the desired product. In addition to being insoluble, polymeric reagents should be easy to prepare and have a capacity sufficient for use on a practical scale.

The results obtained with poly [vinyl (pyridinium Flurochormate)] are very satisfactory and shows the new reagent as a valuable addition to the existing oxidizing agents. Poly [vinyl (pyridinium fluorochromate)] oxidizes primary and secondary alcohols to the corresponding aldehydes or ketones in high yields (as shown in Table 1).

TABLE I: OXIDATION OF ALCOHOLS WITH PVPFC IN CYCLOHEXANE AT 80°C

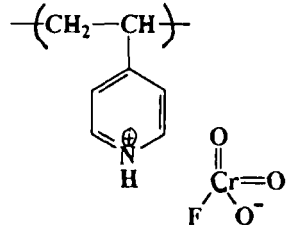
Sl. No.	Substrate	Reaction Time	Product	Yield (%)	M.P (°C)	B.P. (°C)
1.	Benzylalcohol	15 min	Benzaldehyde	95		179
2.	3,4,5-Trimethoxy benzylalcohol	5 h	3,4,5-Trimethoxy benzaldehyde	96	74	
3.	Cyclohexanol	5 h	cyclohexanone	95		155
4.	Cinnamylalcohol	30 min	Cinnamaldehyde	98		248
5.	1-Octanol	5 h	1-Octanal	85		171
6.	Benzoin	5 h	Benzil	97	95	
7.	1-Phenylethanol	3.5 h	Acetophenone	97		202



Poly [vinyl (Pyridinium Flurochromate)] is a bright orange stable solid. This is prepared by adding CrO_3 and HF to PVP resin suspended in water. After filtration and washing with water, the reagent was dried in vacuum. The capacity of the reagent was measured easily by titration with an appropriate reducing agent, and was usually found to be in the range of 3.9 4.2 mmol of oxidizing agent (expressed as fluorochromate) per gram of dry polymer.

The titration of the fluorochromate resin was done directly by titration of the chromate displaced from the resin by reaction with aqueous 2N potassium hydroxide overnight. A freshly prepared solution of ferrous ammonium sulphate was used to reduce the chromate after acidification with phosphoric acid and using diphenylamine sulfonate as indicator. Thus, the PVPFC resin obtained in similar preparation contained upto 4.25 mmol of chlorochromate per gram. In most cases for the reaction the PVPFC resins need not dried thoroughly before use, but simply air dried after washing with water.

The structure of PVPFC is confirmed by the infrared spectrum. The absorption bands were obtained at ν = 750 cm^{-1} and 960 cm^{-1}. The structure is thus confirmed and depicted as :



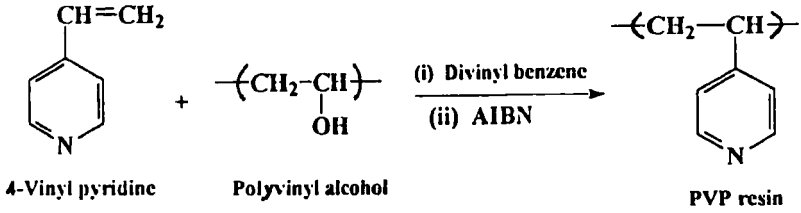
The spent polymeric reagent, after the first oxidation could be regenerated easily to poly (vinyl pyridine) by complete removal of the chromium salts using consecutive washings with HCl and sodium hydroxide. The recycled poly (vinylpyridine) which is slightly darker than the starting PVP resin could then be treated with CrO_3 and HF to produce PVPFC with an activity comparable to that of the original material.

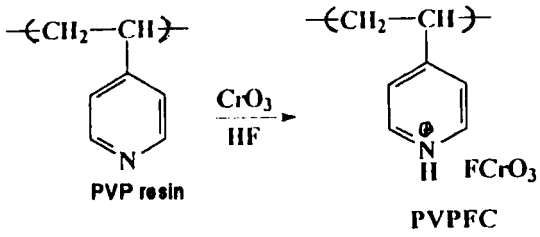
The cross - linked Poly (Vinyl Pyridine) resin

About 2.4 g of polyvinyl alcohol is dissolved in 550ml of hot distilled water and the solution is kept in a 2 litres resin kettle, equipped with a reflux condenser, a nitrogen inlet and a mechanical stirrer. The contents were kept stirred at 80°C and a solution of 25.6ml of 4-vinylpyridine and 1.5g of divinylbenzene in 50ml toluene was added rapidly. After the addition of 1g of azobisisobutyronitrile the polymerisation was allowed to proceed. Polymer beads started to appear rapidly. The mixture was left overnight. The beads were collected by filtration, washed extensively with water, acetone, dichloromethane and methanol. After drying in vacuum, 25g of almost pure PVP resin beads was obtained.

Poly [Vinyl (Pyridinium Fluorochromate)] (PVPFC)

10 g of PVP resin above suspended in 20 ml water was taken in a polythene beaker. 9 g of CrO_3 and 4.8 ml of concentrated HF were added to the resin. The mixture was stirred at room temperature for 1 hr and filtered and the resin was washed with distilled water until the filtrate was clear. The bright orange PVPFC was dried in vacuum and stored in a polythene bottle.





General Procedure for the oxidation of alcohols with Poly (Vinyl (pyridinium Fluorochromate)]

PVPFC (1.9g) was suspended in cyclohexane (5 ml) and the alcohol (1.7 m mol) was added at room temperature. The mixture was heated to 80°C and kept stirred at this temperature. Small aliquots were withdrawn at regular time intervals for tlc determination. After

completion, the reaction mixture was filtered and the resin was washed with ether and dichloromethane to extract the aldehyde or ketone. The solvent was evaporated and the product was charactertised by m.p. or b.p and gas chromatography.

The PVP resin was easily regenerated by washing with 2N HCl and 2N HNO_3 followed by 2N NaOH and rinsing with water. This treatment effectively removed the chromium salts from the polymer and regenerated the PVP resin.

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