Imidazolium fluorochromate (IFC): A new, mild, stable and selective chromium(VI) oxidant

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The preparation of imidazolium fluorochromate (IFC), characterisation and its synthetic utility in the oxidation of primary and secondary alcohols, and in the oxidative deoxygenation of ketoximes to the corresponding carbonyl compounds at room temperature are reported.

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is most frequently accomplished by Cr(VI) reagents. Various Cr(VI) reagents have been developed with ligands such as pyridine, quinoline and 2,2'-bipyridine. Among these oxidants fluorochromates have been reported to be very stable and more reactive than other halochromates. Agarwal et al. have reported an improved and modified procedure for the synthesis of chlorochromates of pyridine, imidazole and 2-methylimidazole but the stability of imidazolium chlorochromate alone has not been reported. Obafemi has synthesised and characterised imidazolium and 2-methylimidazolium chlorochromates and reported that the former compound is hygroscopic and unstable in air in addition to low yield (19%).

In continuation of our studies on development of fluorochromates with heterocyclic bases we now report the preparation, characterisation and synthetic utility of imidazolium fluorochromate (IFC) with a view to minimising the existing difficulties encountered in the oxidation of organic compounds with Cr(VI) based oxidants. IFC has the following advantages over already reported Cr(VI) reagents: (i) quite stable at room temperature (ii) not photosensitive (iii) less hygroscopic and hence a suitable reagent for the oxidation of acid-sensitive and ring strained alcohols.

IFC is readily soluble in water, acetone, DMF, DMSO, acetic acid and acetonitrile but insoluble in dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, ethyl acetate, heptane and ether. The acidity of IFC (pH of a 0.01 M solution; 2.62) is less pronounced than those reported for the 0.01 M solutions of PCC (pH 1.75) and PFC (pH 2.45). IFC in acetonitrile oxidises primary and secondary alcohols to the corresponding carbonyl compounds and has been found to be an effective reagent in the mild oxidation of ketoximes to their corresponding ketones. The results of the oxidation reactions are summarised in Table 1.

**Experimental Section**

**General.** Alcohols used in this work were of extra pure quality (E. Merck, Fluka & Aldrich). The products of the oxidation reactions were identified by comparison with authentic samples (IR, GC analysis & melting point). Melting points were recorded using a Rangaswamy hot stage apparatus and are uncorrected. IR spectra were recorded in Hitachi IR spectrophotometer (model: 270-50) and GC analyses were carried out on a Hewlett Packard 5890A gas chromatograph.

**Preparation of imidazolium fluorochromate (IFC).** 40% Hydrofluoric acid (11.3 mL, 0.23 mole) was added dropwise to imidazole (13.62 g, 0.2 mole) cooled in ice in a polythene beaker with constant stirring. A clear solution was obtained within 5 min. Dry and well powdered chromium trioxide (20 g, 0.2 mole) was added to this solution slowly with stirring. The resulting mixture was then heated on a water-bath for 30 min and left overnight in a refrigerator. Bright red orange crystals of IFC formed were separated by filtration and dried *vacuum* for 2-3 hr. The reagent (IFC) can be stored in polythene containers without appreciable loss in its activity. Yield 29.34 g (78%); m.p: 126-28°C (Found: C, 19.02; H, 2.51; N, 14.48. Required: C, 19.6, H, 2.68; N, 14.89%). IR (KBr): 3150, 1590, 1425, 940, 760, 635 & 365 cm⁻¹ (similar to that of potassium chlorochromate).

**General procedure for oxidation.** The substrate (0.001 mole) in acetonitrile was added to a solution of IFC (0.001-0.002 mole) in acetonitrile with stirring. The reaction mixture was stirred at room temperature for the period indicated in Table 1. After completion of the reaction (found by GC analysis) the reaction...
mixture was diluted with dry diethyl ether (30 mL) and filtered through a short column of silica gel. The column was washed with dry diethyl ether (4×10 mL) and the combined filtrate was evaporated to isolate the crude product which upon distillation afforded the respective product.

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References