1-Methylimidazolium Chlorochromate: A New Cr(VI) Oxidant and Use of Anhydrous Acetic Acid as the Catalyst for the Oxidation of Primary and Secondary Alcohols

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The synthetic potential of a new Cr(VI) reagent, *viz.*, 1-methylimidazolium chlorochromate, analogous to Corey's reagent-PCC, has been examined. Anhydrous acetic acid has been found to catalyze the oxidation reaction.

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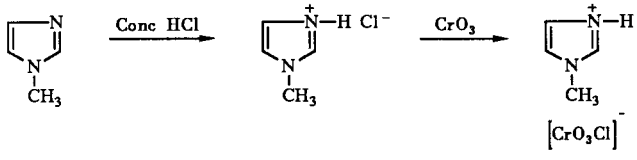
Heterocyclic complexation agents have been frequently employed with reactive transition metals to provide selectivity, stability, and solubility in organic solvents. For example, Vanadium(II) as a pyridine complex provides a highly selective bis-aryl coupling agent [2]; pyridine-borane complex has been used to reduce aldehydes and ketones in organic solvents [3]. Similarly, Chromium(VI) has been made more selective as an oxidant by its co-ordination to such heterocycles as pyridine [4-7], 2,2′-bipyridine [8], the complex of pyridinium chlorochromate with pyrazole and 3,5-dimethylpyrazole have also been used for selective oxidation of allylic alcohols [9,10]. The use of heterocyclic compounds made Cr(VI) not only a mild oxidant, less hygroscopic and less hazardous than chromium trioxide but also as a most useful oxidant for industrial purposes.

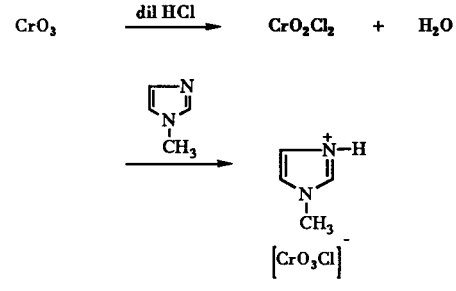
We have synthesized 1-methylimidazolium chlorochromate (MCC) [11] and studied the mechanism for the oxidation of primary and secondary alcohols. The present communication deals with the synthetic potential of this reagent. During the study, it has been found that MCC has certain advantages over the other similar oxidants in terms of amounts of solvent and oxidant used, easy removal conditions and smooth running of the reaction. Thus, the results obtained by oxidizing six alcohols of varying structural features with MCC show that it is a valuable addition to the existing oxidizing agents.

Scheme I



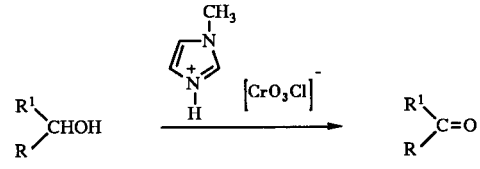
We have prepared MCC in two ways-1) by using Corey's method of PCC (Scheme I) [5] and 2) by using our improved method for preparing PCC in a less hazardous way and with increased yield [11,12] (Scheme II). It has been found that when MCC was synthesized by Corey's method, the yield was only 70-75% against the 91% yield obtained by our method [11]. One more advantage is that it is very

Scheme II



much less hygroscopic and can be used after one year of its preparation without any decomposition, which is not the case with PCC and other similar Cr(VI) reagents.

MCC in dry chloroform oxidizes primary and secondary alcohols to the corresponding aldehydes or ketones in high yield.



In the course of our investigation, we have found that anhydrous acetic acid catalyzes the reaction by efficiently reducing the reaction-time almost to half and in some cases even the product yield was also increased. All the results, catalyzed and uncatalyzed, are presented in Table I.

Table I

Alcohol	Uncatalyzed Time, hours	Uncatalyzed Yield %	Catalyzed Time, hours	Catalyzed Yield %	Product
1-Octanol	1.5	66	0.75	73	Octanal [a]
Hexanol	3.0	78	2.0	80	Hexanal [a]
Cyclo-hexanol	3.4	82	2.5	85	Cyclohexanone [a]
Borneol	2.5	60	2.3	60	Camphor [a]
Citronellol	3.5	85	1.0	85	Citronellal [b]
Geraniol	3.7	86	1.5	80	Citral [b]

[a] The % yield was determined on the basis of the 2,4-DNP derivative. [b] The % yield was determined on the basis of the semicarbazone derivative.

It is evident from the Table I that the reaction in all cases, except in the case of borneol, is markedly accelerated and the reaction-time is reduced to almost half. The apparent inactivity of the catalyst in the case of borneol may be due to the hindered alcoholic function present in borneol. The chief advantage of anhydrous acetic acid is that the reaction is smooth without any side reactions and acetic acid can easily be removed from the column fractions by evaporating it under reduced pressure without causing any decomposition to the product.

EXPERIMENTAL

Typical Procedure for the Oxidation of Alcohols.

At room temperature the substrate (alcohol, 0.001 mole) was added neat to the well-stirred solution of the oxidant (MCC, 0.001 mole) in dry purified chloroform (10 ml) with constant stirring. The progress of the reaction has been followed by tlc (solvent, 9:1, benzene:ethyl-acetate, v/v). After the completion of the reaction, solvent ether was added to the reaction mixture which was then passed through a previously prepared short column of silica gel (2 x 15 cm). The elution of the carbonyl compound was performed by using solvent ether as the eluent. The etherial eluent was then concentrated and the 2,4-dinitrophenylhydrazone derivative was prepared. However, in some cases where it was desirable to prepare the semicarbazone derivative of the carbonyl compound, the etherial eluent was evaporated to dryness under reduced pressure in a rotary evaporator. Both the 2,4-DNP and semicarbazone derivatives were characterized by their melting points and comparing them with the melting points of those listed in the literature.

In the case of catalyzed oxidation reactions, 100 $\mu\ell$ of anhydrous acetic acid were added to the well-stirred solution of MCC in chloroform. After stirring for at least 5 minutes, alcohol was added to the oxidant-catalyst solution. The rest of the procedure is the same as with the uncatalyzed oxidation reaction.

Further work on the industrial applications of MCC are in progress and will be reported in due course of time.

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