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PYRIDINIUM CHLOROCHROMATE: AN IMPROVED METHOD FOR ITS SYNTHESIS AND USE OF ANHYDROUS ACETIC ACID AS CATALYST FOR OXIDATION REACTIONS

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Abstract : An improved procedure for the preparation of Corey's reagent--Pyridinium chlorochromate has been described. The method is less hazardous and gives better yield. Synthetic utility of the reagent has been shown to increase in the presence of anhydrous acetic acid, used for the first time as catalyst, for the oxidation of alcohols.

INTRODUCTION

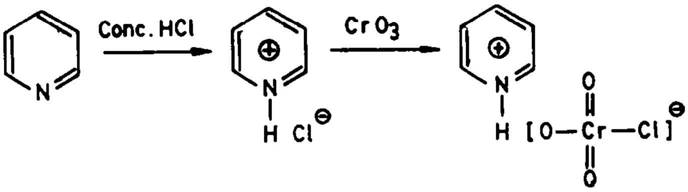
Pyridinium chlorochromate (PCC) is a mild, selective and stable reagent for the oxidation of a wide variety of alcohols to the corresponding carbonyl compounds with high efficiency[1]. Synthetic application of PCC, especially its use for industrial scale preparations, are well known[2,3,4]. The reagent is prepared by Corey's method in 75-80% yield[5]. However, the main disadvantage of this method is the formation of chromyl chloride, a very toxic and hazardous compound, during the first step of the PCC synthesis.

Literature review revealed that the oxidation of alcohols by PCC has been catalyzed by using acidic compounds. A number of acid catalysts, eg. p-toluene sulphonic acid (TsOH)[6], trichloro acetic acid (TCA)[7] and dichloro acetic acid (DCA)[8] have been used to study the mechanism of PCC oxidations. Molecular sieves[9] have also been used as catalyst for the synthetic applications of PCC.

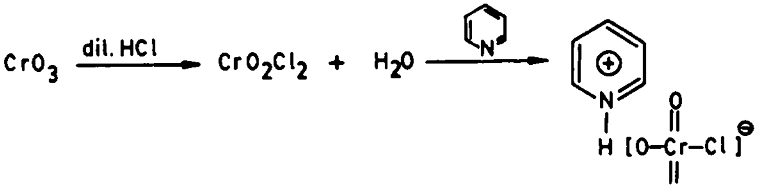
The present work deals with the development of a new method for the synthesis of PCC in improved yield via a less hazardous procedure. Use of anhydrous acetic acid as catalyst for the oxidation of alcohols is also being described for the first time. Six alcohols of varying structural features have been oxidized by PCC and catalyzed and uncatalyzed oxidation reactions have been performed.

RESULTS AND DISCUSSION

An alternative method for the synthesis of PCC by doing away with the formation of chromyl chloride has successfully been developed. The first step of the present scheme involves the formation of pyridinium chloride, which is much less toxic than chromyl chloride formed in Corey's method. Pyridinium chloride is then added dropwise to dry CrO_3 to give an yellow-orange solid of PCC in 90-97% yield (Scheme I). Another advantage of the present method is that concentrated hydrochloric acid (12 N) instead of 6 N hydrochloric acid can easily be used without any danger of toxicity. In Corey's method (Scheme II) more the concentration of hydrochloric acid used, more is the possibility of chromyl chloride vapours escaping out, making the procedure more and more hazardous with decreasing yield of PCC. As a compromise, 6 N hydrochloric acid has been used in Corey's method. But the amount of water present in dilute acid (6 N) lowers the yield of PCC as it is soluble in water. In our method, since chromyl chloride is not formed, concentrated hydrochloric acid (12 N) can easily and safely be used with enhancing the yield of PCC.



Scheme -I



Scheme -II

Both catalyzed and uncatalyzed oxidation reactions for six alcohols have been performed in dry chloroform and the results are presented in Table I. The results clearly demonstrate the catalytic effect of anhydrous acetic acid on the reactions. The reaction in all the cases, except in the case of borneol, is markedly accelerated and the reaction time is reduced to half. In most cases there is some improvement in the overall yield of the product as well. The apparent inactivity of the catalyst in the case of borneol may be due to the hindered nature of the hydroxyl group present in borneol.

TABLE I

Oxidation of alcohols with PCC in chloroform

ALCOHOL	PRODUCT	% YIELD		TIME (hr)	
		UNCATALYZED	CATALYZED	UNCATALYZED	CATALYZED
1-OCTANOL	OCTANAL[a]	94	94	1.2	0.6
1-HEXANOL	HEXANAL[a]	86	89	2.0	1.0
CYCLOHEXANOL	CYCLOHEXANONE[a]	87	90	2.5	1.0
BORNEOL	CAMPHOR[a]	70	72	2.6	2.5
CITRONELLOL	CITRONELLAL[b]	90	92	2.0	0.8
GERANIOL	CITRAL[b]	90	92	2.0	1.0

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

The chief advantage of the catalyzed reaction over the others reported so far is that the reaction proceeds smoothly with no side reactions. Also, the removal of the catalyst from the reaction mixture is very easy, which can be achieved by evaporating the column fractions under reduced pressure in rotary evaporator without causing any decomposition to the product.

EXPERIMENTAL

Improved and modified procedure for the synthesis of Corey's reagent-PCC :

Concentrated hydrochloric acid (12 N, 1.84 ml, 0.022 mole) was added dropwise to cold dry pyridine (1.61 ml,0.02 mole) with constant stirring. The solution was cooled to 0°C and was then added dropwise to dry chromium trioxide (2 g, 0.02 mole) with vigrous stirring. Recooling to 0°C gave a yellow-orange solid of PCC which was isolated by filtration. The filtered mass was pressed between the folds of filter-papers and dried in vacuum. If necessary 2-3 drops of water were added to the reaction mixture to dissolve the traces of CrO_3 left unreacted in pyridinium chloride. Yield: 4.18 g (97%), mp 204°C (lit 205°C).

Anal. ($C_5H_6NO_3CrCl$) : N; calcd, 6.48; found, 6.31%.

Typical procedure for the oxidation of alcohols :

Substrate (alcohol, 0.001 mole) was added neat to the well stirred solution of PCC (0.001 mole) in purified dry chloroform (10 ml) with constant stirring at room temperature. The progress of the reaction was followed by TLC (solvent, 9:1, Benzene:Ethylacetate, 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 (2x15 cm) of silica gel. The elution of the carbonyl compound was performed by using solvent ether. The etherial eluent was concentrated and 2,4-dinitro phenyl hydrazone derivative prepared. However, in those cases where it was desirable to prepare 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 the same with the melting points listed in literature.

In the case of catalyzed oxidation reactions, 100 μl of anhydrous acetic acid were added to the well stirred solution of PCC in chloroform. After stirring for atleast 5 minutes, alcohol was added neat to the oxidant-catalyst solution. Rest of the procedure is same as with the uncatalyzed oxidation reaction.

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