SYNLETT
Spotlight 61

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

PCC: Novel Oxidation Reactions

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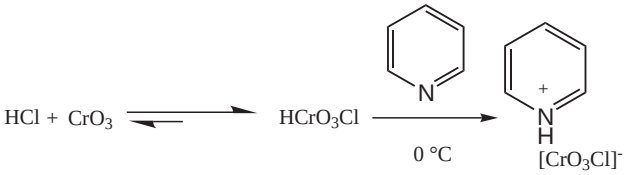
Introduction

Until the studies of Corey and co-workers (1975),[1] the reactivity of pyridinium chlorochromate (PCC) had been investigated little. The first report on the chlorochromate anion dates back to 1833.[2] In 1899, the first synthesis of PCC was achieved.[3] PCC is prepared easily and safely.[1] It shows a high capability to convert primary alcohols exclusively to aldehydes. Mere filtration, washing of the residue with diethyl ether, and concentration of the filtrate furnish virtually pure product. PCC shows a slightly acidic character and for acid-labile groups the reaction could be buffered with NaOAc. The applications of PCC are not limited to oxidation reactions, but several rearrangements and useful conversions are mediated by PCC, which makes it a versatile reagent in organic synthesis.

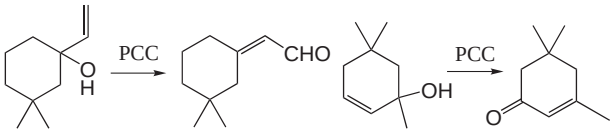


Preparation

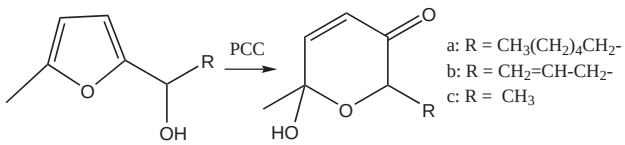
The addition of CrO_3 to 6 N HCl furnishes the unstable chlorochromic acid and subsequent addition of pyridine at 0 °C immediately gives a yellow-orange solid of PCC which is not appreciably hygroscopic.[1]

Abstracts

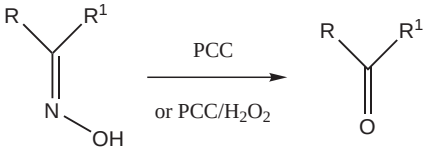
(A) The oxidant and slightly acidic character of PCC is able to convert allylic tertiary alcohols or tertiary vinyl alcohols into α,β-unsaturated carbonyl compounds.[4]



(B) PCC shows an unusual behavior as dienophile and oxidant in the ring enlargement of 2-furyl carbinols to pyran derivatives.[5]



(C) The deoxamination of oximes to regenerate the carbonyl compound is also mediated using PCC.[6a] However, PCC/H_2O_2 system is more effective as a deblocking agent.[6b]



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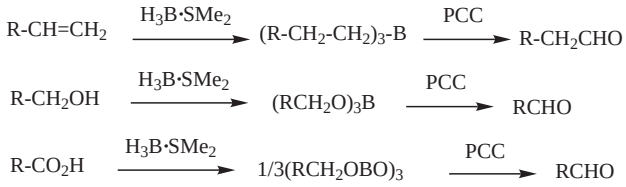
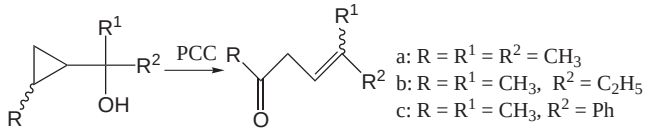
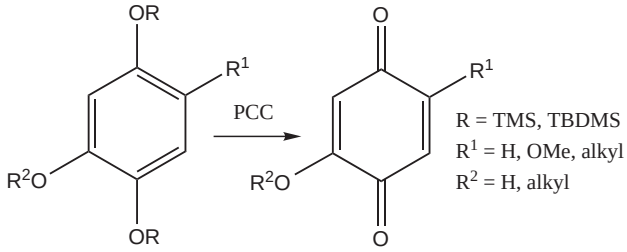
(D) Hydroboration of 1-alkenes give trialkyl boranes which on subsequent oxidation with PCC furnish aldehydes.[7a] PCC oxidation of borate esters or boroxines also give aldehydes.[7b,c]



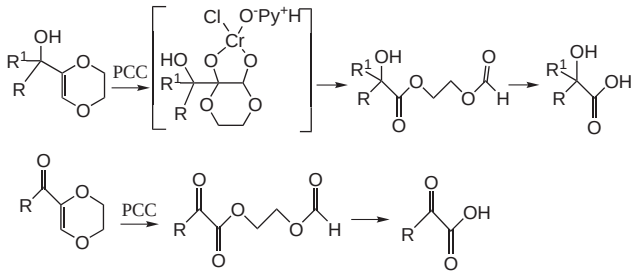
(E) PCC oxidation of tertiary 2-alkyl cyclopropyl carbinols furnished transposed β,γ-enones, making the overall process a synthetically useful method for 1,4-carbonyl transposition.[8]



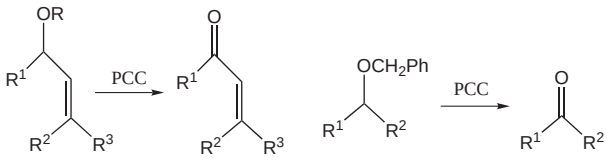
(F) PCC can release quinone from hydroquinone silyl ethers.[9]



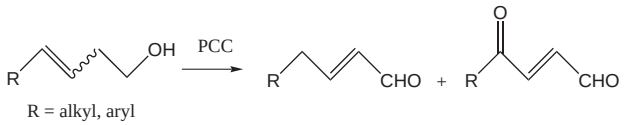
(G) The allylic alcohols obtained from lithiated 1,4-dioxene and ketones or aldehydes undergo regiospecific oxidative cleavage with PCC at the dioxene double bond to furnish, after saponification, α-hydroxy acids. Extension of this reaction to α,β-unsaturated ketones affords α-keto acids.[10]



(H) Specific oxidative cleavage of allylic and benzylic ethers is known with PCC.[11]



(I) Oxidation of homoallylic alcohol with excess of PCC gave products arising from alcohol oxidation, double bond migration with isomerization from the *cis*- to the *trans*-olefin and subsequent allylic oxidation. Thus, this constitutes a synthetically useful conversion of homoallylic alcohols to 1,4-dicarbonyl-2-ene compounds. [12]



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