SYNLETT
Spotlight 179

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

Pyridinium Dichromate – A Mild Oxidizing Reagent in Synthetic Organic Chemistry

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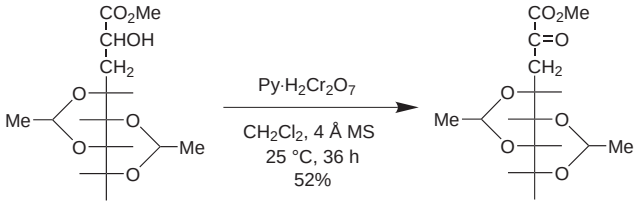
Introduction

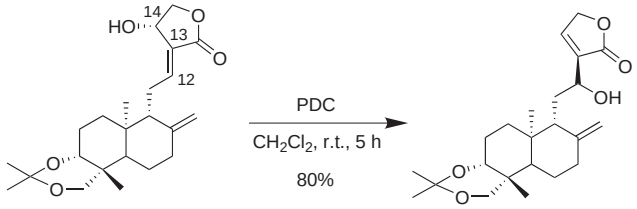
Pyridinium dichromate (PDC) is a mild and selective oxidizing agent mainly used to oxidize primary[1] and secondary alcohols.[2] It has several other applications such as in the rearrangement of allylic hydroxyl groups,[3] in the preparation of heterocycles,[4] the production of metal-free dienones,[5,6] the oxidation of carbon–boron bonds[7] as well as in the preparation of enones[8] and in multicomponent reactions.[9] This reagent was discovered by E. J. Corey and G. Schmidt in 1979.[10] It is stable in solvents like DMF, DMSO, acetonitrile; it is sparingly soluble in dichloromethane, chloroform and acetone. PDC is commercially available and easily prepared by addition of pyridine to a cooled solution of CrO_3 in water at –30 °C. The resulting solution is diluted with acetone at –20 °C forming orange crystals that are collected by filtration.

Abstracts

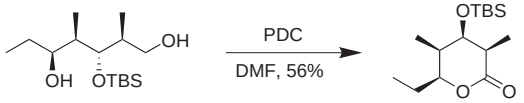
(A) Kornilov et al. reported that methyl heptonate was oxidized to the desired pyruvate ester with PDC in dichloromethane in the presence of 4 Å molecular sieves (25 °C, 36 h) in 52% yield.[2]



(B) Shrinivas and workgroup showed that the treatment of the substrate with a catalytic amount of PDC (0.05 equiv) led to rearrangement of the allylic hydroxyl group at C-14 to give 3-[1-hydroxy-2-(3,3,6a,10b-tetramethyl-8-methylene-decahydronaphtho[2,1-*d*][1,3]dioxin-7-yl)-ethyl]-5*H*-furan-2-one.[3]



(C) Chênevert et al. reported that PDC oxidizes selectively primary alcohols to acids, followed by lactonization. To a solution of alcohol in anhydrous DMF was added PDC. After stirring for 24 h at room temperature the product was isolated and purified to give lactone in 56% yield.[4]



TBS = *tert*-butyldimethylsiloxy

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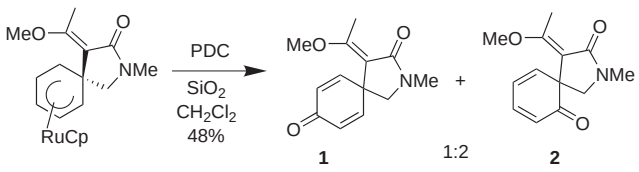
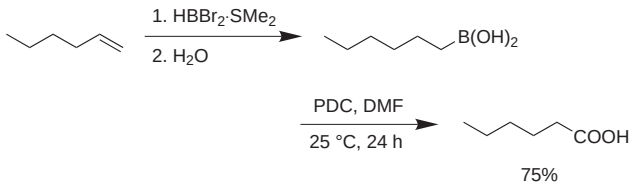
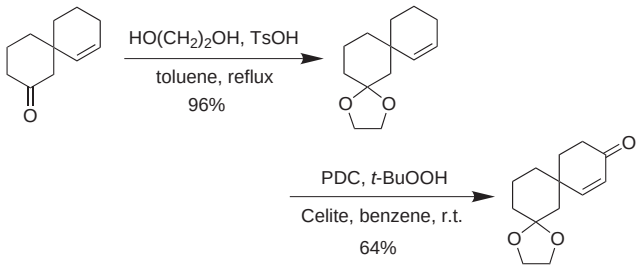
(D) Pigge and coworkers reported that the ruthenium complex when exposed to 3 equiv of PDC, SiO_2, CH_2Cl_2, r.t.,[5] gives metal-free dienones **1** and **2** (1:2 ratio, respectively), albeit in somewhat modest 48% overall yield.[6]



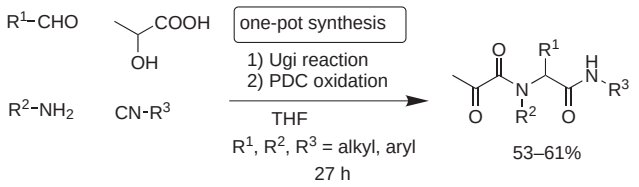
(E) Brown et al. showed that a primary-carbon–boron bond can be cleaved and oxidized to carboxylic acid by using PDC in DMF.[7]



(F) Schepens et al. described that after protection of the carbonyl group as ethylene ketal (96% yield) the allylic position can be oxidized to an enone with PDC and *tert*-butylhydroperoxide in 64% yield.[8]



(G) Nakamura et al. reported a two-step one-pot synthesis Ugi reaction by PDC that easily affords the α-keto amides in short reaction times.[9]



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