

# SYNLETT Spotlight 179

## Pyridinium Dichromate – A Mild Oxidizing Reagent in Synthetic Organic Chemistry



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

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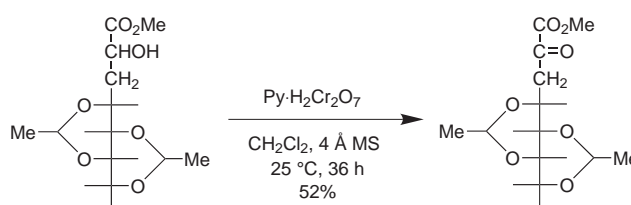
### Introduction

Pyridinium dichromate (PDC) is a mild and selective oxidizing agent mainly used to oxidize primary<sup>1</sup> and secondary alcohols.<sup>2</sup> It has several other applications such as in the rearrangement of allylic hydroxyl groups,<sup>3</sup> in the preparation of heterocycles,<sup>4</sup> the production of metal-free dienones,<sup>5,6</sup> the oxidation of carbon–boron bonds<sup>7</sup> as well as in the preparation of enones<sup>8</sup> and in multicomponent reactions.<sup>9</sup> This reagent was discovered by E. J. Corey and

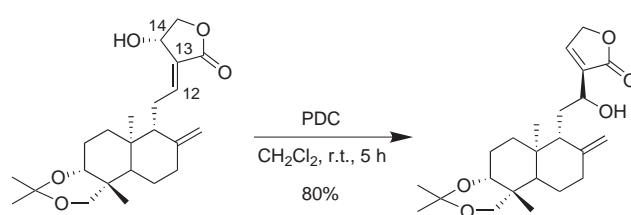
G. Schmidt in 1979.<sup>10</sup> It is stable in solvents like DMF, DMSO, acetonitrile; it is sparingly soluble in dichloromethane, chloroform and acetone. PDC is commercially available and easily prepared by addition of pyridine to a cooled solution of CrO<sub>3</sub> in water at –30 °C. The resulting solution is diluted with acetone at –20 °C forming orange crystals that are collected by filtration.

### Abstracts

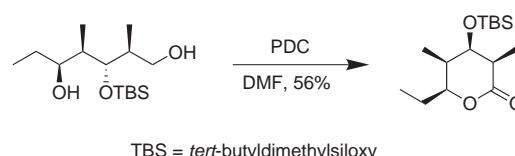
(A) Kornilov et al. reported that methyl heptonate was oxidized to the desired pyruvate ester with PDC in dichloromethane in the presence of 4 Å molecular sieves (25 °C, 36 h) in 52% yield.<sup>2</sup>



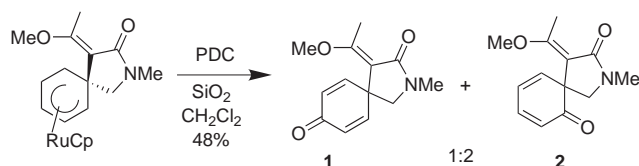
(B) Shrinivas and workgroup showed that the treatment of the substrate with a catalytic amount of PDC (0.05 equiv) led to rearrangement of the allylic hydroxyl group at C-14 to give 3-[1-hydroxy-2-(3,3,6a,10b-tetramethyl-8-methylene-decahydronaphtho[2,1-d][1,3]dioxin-7-yl)-ethyl]-5H-furan-2-one.<sup>3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



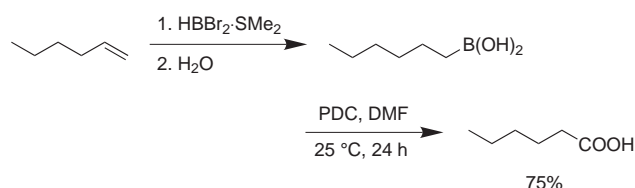
(C) Chênevert et al. reported that PDC oxidizes selectively primary alcohols to acids, followed by lactonization. To a solution of alcohol in anhydrous DMF was added PDC. After stirring for 24 h at room temperature the product was isolated and purified to give lactone in 56% yield.<sup>4</sup>



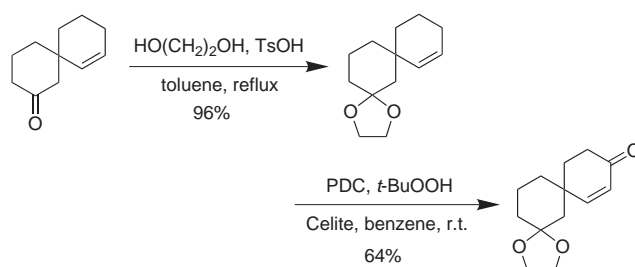
(D) Pigge and coworkers reported that the ruthenium complex when exposed to 3 equiv of PDC, SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, r.t.,<sup>5</sup> gives metal-free dienones **1** and **2** (1:2 ratio, respectively), albeit in somewhat modest 48% overall yield.<sup>6</sup>



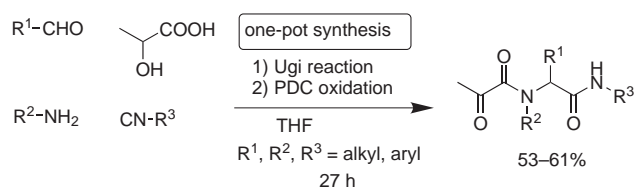
(E) Brown et al. showed that a primary-carbon-boron bond can be cleaved and oxidized to carboxylic acid by using PDC in DMF.<sup>7</sup>



(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.<sup>8</sup>



(G) Nakamura et al. reported a two-step one-pot synthesis Ugi reaction by PDC that easily affords the  $\alpha$ -keto amides in short reaction times.<sup>9</sup>



## References

- (1) Piancatelli, G. *Handbook of Reagents for Organic Synthesis – Oxidizing and Reducing Agents*; Paquette, L. A., Ed.; Wiley & Sons: Chichester, **1999**, 330.
- (2) Kornilov, V. I.; Glebova, Z. I.; Sudareva, T. P. *Russ. J. Gen. Chem.* **2005**, *75*, 811.
- (3) Siva, S. R. T.; Vijay, K. N.; Shrinivas, N. *Tetrahedron Lett.* **2004**, *45*, 9357.
- (4) Chênevert, R.; Courchene, G.; Caron, D. *Tetrahedron: Asymmetry* **2003**, *14*, 2567.
- (5) Alcudia, A.; Arrayás, R. G.; Liebeskind, L. S. *J. Org. Chem.* **2002**, *67*, 5773.
- (6) Pigge, F. C.; Coniglio, J. J.; Rath, N. P. *J. Org. Chem.* **2004**, *69*, 1161.
- (7) Brown, H. C.; Kulkarni, S. V.; Khanna, V. V.; Patil, V. D.; Racherla, U. S. *J. Org. Chem.* **1992**, *57*, 6173.
- (8) Schepens, W.; Haver, D. V.; Vandewalle, M.; De Clercq, P. J.; Bouillon, R.; Verstuyf, A. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3889.
- (9) Nakamura, M.; Inoue, J.; Yamada, T. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2807.
- (10) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *5*, 399.