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Pyridinium Chlorochromate in Organic Synthesis. A Facile and Selective Oxidative Cleavage of Enol Ethers

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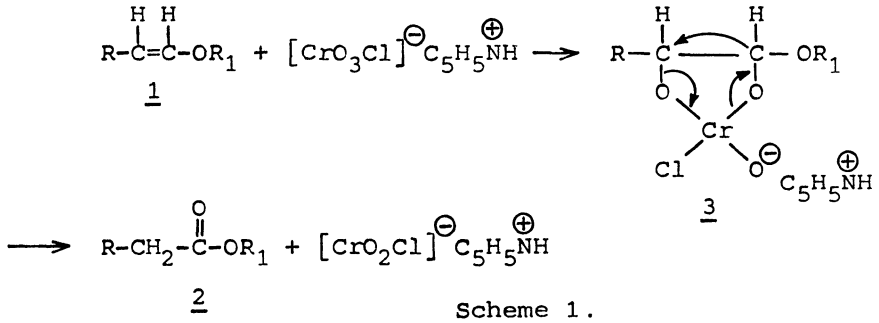
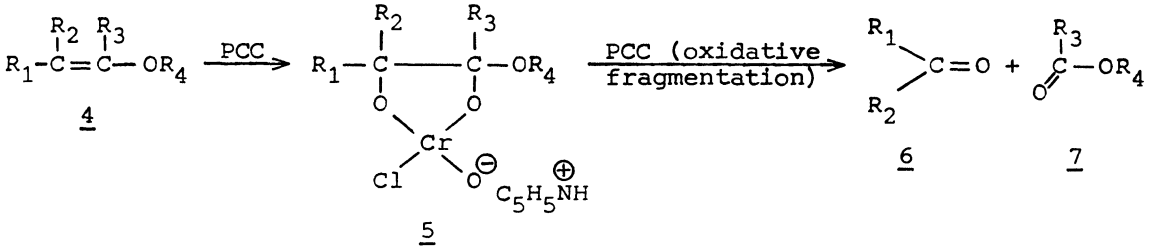
Pyridinium chlorochromate (PCC) has been found to be selective reagent for the oxidative cleavage of enol ethers to esters or keto lactones in high yields.

Pyridinium chlorochromate introduced by Corey[1] has found extensive use in organic synthesis for carrying out a wide variety of oxidative transformations.[2] One of the unusual reactions of pyridinium chlorochromate (PCC) reported by Piancatelli[3] was the oxidation of enol ethers 1 to esters 2. The mechanism that was proposed involved the initial electrophilic attack upon the olefin by the PCC to afford an unstable intermediate 3 which then by heterolytic cleavage of the Cr-O bond, accompanied by a 1,2-hydride shift gave the ester (Scheme 1).



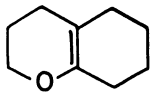
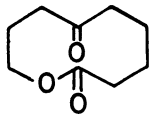
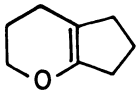
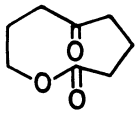
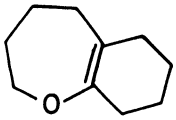
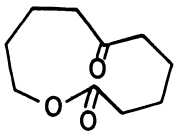
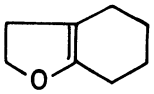
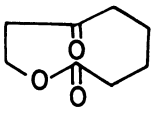
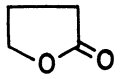
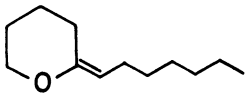
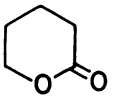
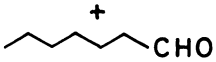
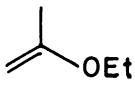
Scheme 1.

In the course of our studies on oxidative cyclization of ω-hydroxyl olefins to γ- and δ-lactones with oxotransition metal species,[4,5] we anticipated that enol ethers of the type 4 would behave differently with pyridinium chlorochromate. 4 would be expected to form the cyclic chromate ester 5 with PCC and since there is no possibility for a 1,2-hydride shift as in 3, this would undergo an oxidative fragmentation to yield carbonyl compounds 6 and 7 (Scheme 2).



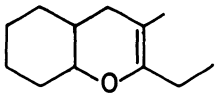
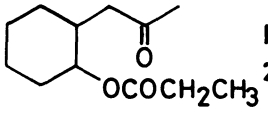
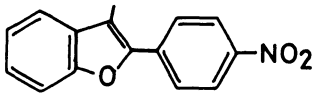
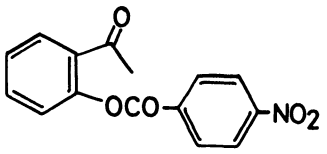
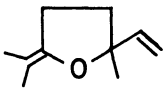
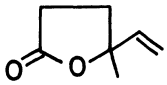
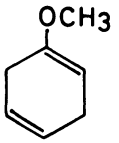
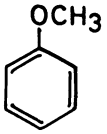
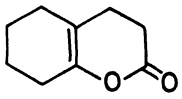
Scheme 2.

Table 1.

Entry	Substrate[a]	Product[b]	Reaction condition	% Yield[c]
1			PCC, CH_2Cl_2 25 °C, 1 h	85
2			PCC, CH_2Cl_2 25 °C, 1 h	75
3			PDC, ØH 80 °C, 4 h	64
4			PCC, CH_2Cl_2 25 °C, 1 h	63
5			PCC, ØH 80 °C, 4 h	45
	"	"	PDC, ØH 80 °C, 4 h	57
6		 + 	PCC, CH_2Cl_2 25 °C, 2 h	62 45
7		CH_3COOEt	"	65

[a] [b] [c]

Table 1. (continued)

Entry	Substrate[a]	Product[b]	Reaction condition	% Yield[c]
8			PCC, CH_2Cl_2 25 °C, 2 h	78
9			PCC, ØH 80 °C, 4 h	70
10			PCC, CH_2Cl_2 25 °C, 2 h	90
11			PCC, CH_2Cl_2 25 °C, 1 h	100
12		—	PCC, CH_2Cl_2 40 °C, 48 h	No reaction
	"	—	PCC, ØH 80 °C, 48 h	No reaction

a) Substrates in entries 1-4 and 8 were prepared according to the procedure in the Ref. 7; entry 5, Ref. 10; entry 6, Ref. 11; entry 9, Ref. 12; entry 10, Ref. 13.

b) Satisfactory spectral data were obtained for the purified, chromatographically homogeneous material.

c) Yield refers to pure, isolated products.

In this paper we wish to report the realization of such a strategy for effecting a smooth oxidative cleavage of nucleophilic olefins such as cyclic enol ethers to keto lactones with pyridinium chlorochromate. In a typical experiment the enol ether (2 mmol in 5 ml of CH_2Cl_2 or benzene) was rapidly added to a suspension of PCC (8 mmol) and Celite (1.5 g) in CH_2Cl_2 or benzene (15 ml). After stirring for 1-48 h (25 °C-80 °C), ether (50 ml) was added, filtered through a pad of Celite and silica gel and evaporation of solvent and chromatographic purification yielded the product. Either dichloromethane or benzene can be used as a solvent for these reactions and pyridinium dichromate[6] was also found to be effective. A number of examples of facile oxidation of enol ethers to esters or keto lactones are given in Table 1. Entry 10 in Table 1 is a typical example of a substrate where a highly selective oxidative cleavage of enol ether double bond is effected while the other carbon-carbon double bond remains unaffected. Entry 9 illustrates the oxidation of benzofuran ring systems, albeit slowly. Enol lactones (entry 12) are inert to the reaction conditions while the dihydroaromatic systems (entry 11) undergo a ready aromatization.

It is pertinent to point out that similar oxidative cleavage of cyclic enol ethers to keto lactones have been achieved by reaction with m-chloroperbenzoic acid,[7] ozone[8] and ruthenium tetroxide.[9] However, all these reagents do not offer selectivity in the presence of other double bonds in the substrate. The present methodology uses readily accessible, inexpensive reagents for effecting a useful transformation. Reaction condition is generally mild and the yield of the products are good. Application of this methodology to the synthesis of natural products is in progress.

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