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PYRIDINIUM CHLOROCHROMATE IN THE ORGANIC SYNTHESIS: A CONVENIENT OXIDATION OF ENOL-ETHERS TO ESTERS AND LACTONES

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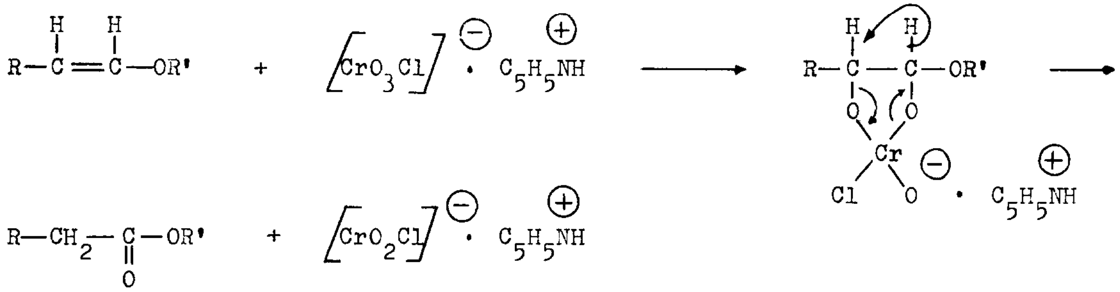
Pyridinium chlorochromate (PCC) is a stable reagent introduced by Corey and at present is used for the oxidation of primary and secondary alcohols to carbonyl compounds[1]. Recently we have described an unusual synthetic application of PCC in the oxidative enlargement of 2-furylcarbinols to pyran derivatives which show antimicrobial and anticoccidial properties[2].

In this paper we wish to report a novel and convenient synthetic use of PCC, in oxidizing linear and cyclic enol-ethers to esters and lactones with high efficiency; the reagent behaves as an oxidizing, weakly electrophilic species, capable of attacking particularly nucleophilic olefins, such as enol-ethers (generally PCC does not react with simple double bonds[1]).

In a typical experiment, the enol-ether (5 mmol in 10 ml of CH_2Cl_2) was rapidly added at room temperature to a suspension of PCC (10 mmol) in CH_2Cl_2 (10 ml). After 1 hour the reaction, which was followed by TLC, was complete and the crude product was isolated as described by Corey[1] and purified by column chromatography on SiO_2. Elution with benzene or benzene-diethyl ether afforded the pure esters and lactones in excellent yields (Table 1).

A possible reaction mechanism could involve initial electrophilic attack upon the olefin by the PCC to afford an unstable intermediate[3]. Heterolytic cleavage of the Cr-O bond, accompanied by a 1,2 hydride shift, can give then the carbonyl compound.



This reaction is the first example of the direct conversion of enol-ethers to esters or lactones and the simplicity of the procedure and the high yields obtained make it useful for preparative purposes.

Table 1

Enol-ether	Product [a]	C=O (I.R.)	b.p.	m.p.	Yield [b]
5-cholesten-3β-vinyl-ether	cholesteryl 3β-acetate	1723 cm^{-1}	-	113-15°C	95%
5α-pregnan-3β-acetate-20-vinyl-ether [c]	5α-pregnan-3β, 20-diacetate [c]	1720 cm^{-1}	-	120-26°C	90%
ethyl-vinyl-ether	ethyl acetate	1735 cm^{-1}	77-78°C/ 760 mm Hg	-	75%
2,3-dihydro-4H-pyran	δ-valerolactone	1728 cm^{-1}	112-14°C/ 14 mm Hg	-	90%
2,3-dihydro-furan	γ-butyrolactone	1770 cm^{-1}	88-90°C/ 13 mm Hg	-	85%

a) All the products were characterized by comparison with authentic materials (P.M.R., I.R., and the physical constants b.p. or m.p.)
b) All the yields refer to isolated products
c) Both the starting material and the final product were a mixture of C_{20} epimers

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References

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