Oxidative Deoximation with Pyridinium Chlorochromate

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The recovery of the parent ketone or aldehyde from an oxime derivative has classically involved acid hydrolysis under suitable conditions which removes the hydroxylamine from the equilibrium[1]. This limits the scope of the reaction to eliminate acid sensitive ketones or aldehydes. The recent application of oxidative or reductive removal of the oximino function, therefore, led us to consider other reagents[2]. Because of the availability, convenience, and selectivity in oxidation by pyridinium chlorochromate[3], it was investigated as a deoximative reagent with the results shown in the Table.

A summary of the results showed that use of two molar equivalents of pyridinium chlorochromate gave better yields. The reaction required greater than 12 h at room temperature for maximum yields. Ketoximes were converted to the corresponding ketones in yields of 50–85%, benzaldoxime was converted to benzaldehyde with further oxidation, and oxime ethers were resistent to the reagent providing a degree of selectivity in the use of substituted imines as protecting groups for carbonyl compounds.

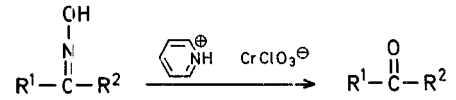

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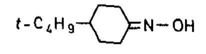
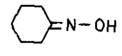
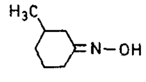
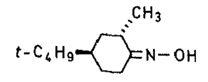
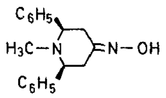
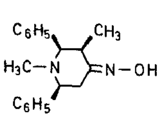
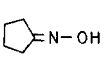
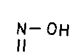
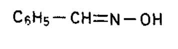
Table. Deoximations with Pyridinium Chlorochromate[a]

Oxime	Reaction time	Sodium acetate added (mol-equiv)[b]	Yield [%][c] of carbonyl	b.p./torr or m.p.	Lit. b.p./torr or m.p.
	24 h	2	76	116°/20 46–48°	112–116°/20[4] 43–48°
	18 h	—	47	155°/760	155°/760[5]
	15 h	—	53	73–74°/20	65°/15[5]
	18 h 94 h	— 2	46[d] 46[d]	120°/20	77°/3.5[6]
	12 h	2	85	150–152°	151–153°[7]
	15 h 20 h	— 2	56[e] 48[e]	—[f]	—
	18 h	2	28	128–129°/760	130°/760[5]
 $C_6H_5-\overset{\overset{\displaystyle N-OH}{\|\|}}{C}-CH_3$	15 h	—	61	60°/0.5	79°/10[5]
$C_6H_5-CH=N-OH$	15 h	—	56	70–71°/20	62°/10[5]
	24 h	—	0[g]		

[a] The reaction of a carbonyl derivative with a 2-molar amount of pyridinium chlorochromate in dichloromethane. The yields were based on distilled ketone or aldehyde, which were identified by boiling point and spectral data.

[b] Sodium acetate was added to retard epimerization of the α-methylketones and to avoid interference from the basic nitrogen of the piperidones.

[c] The purity of the products was determined by observing the N.M.R. spectra at high amplitude and by G.L.P.C. on 10% SE 30 on 80–100 mesh Chromosorb W and the purity of each product was 95% or greater. Cyclohexanone showed an impurity of approximately 5%, while the other compounds contained less than 2% impurity.

[d] The 18 h reaction gave 6.7 *trans*/1 *cis* while the 94 h reaction gave 2.3 *cis*/1 *trans*.

[e] The reaction without sodium acetate gave a 1:1 mixture of epimer while sodium acetate allowed only 10% epimerization.

[f] Identified as the picrate, m.p. 180–182°.

[g] The oxime ether was recovered in 91% yield after distillation (b.p. 52°/0.05 torr) in greater than 98% purity as shown by G.L.P.C.[c]

Deoximation with Pyridinium Chlorochromate; General Procedure:

To a rapidly stirred suspension of pyridinium chlorochromate[3] (6.37 g, 30 mmol) in dichloromethane (40 ml) is added the carbonyl derivative (15 mmol) in dichloromethane (30 ml). The mixture is stirred at room temperature for 15 h or longer and poured into ether (200 ml). The resultant mixture is filtered through a pad of Florisil and the solvent is removed by evaporation under reduced pressure. The resultant oil is distilled under reduced pressure and the product is identified by spectral and chromatographic studies. The results are given in the Table.

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