

Oxidative Deprotection of Cyclic Acetals and Trimethylsilyl Ethers by γ -Picolinium Chlorochromate Under Nonaqueous Conditions*

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Abstract—Deprotection of cyclic acetals and oxidative desilylation of trimethylsilyl ethers into the corresponding carbonyl compounds with γ -picolinium chlorochromate (γ -PCC) under nonaqueous conditions at room temperature is described. Oxidation of aldehydes to carboxylic acids was not observed in any case.

The protection of certain functional groups and their deprotection constitute important processes in synthetic reactions [1]. Although there are several methods for deprotection of acetals [2–18] and silyl ethers [19–27], many of them suffer from low yields, unavailability and instability of the reagent, severe reaction conditions, and oxidation of recovered aldehydes. Therefore new mild and convenient methods are still in demand.

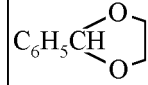
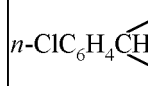
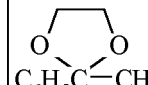
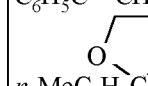
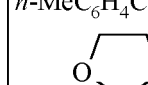
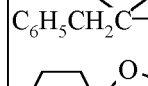
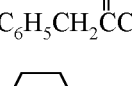
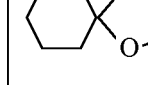
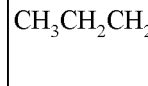
Recently we introduced γ -picolinium chlorochromate (γ -PCC) as a new and efficient reagent for oxidation of alcohols and oximes into carbonyl compounds under nonaqueous conditions [28, 29]. We now report on a mild and convenient method for deprotection of cyclic acetals and oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds in good yields with the use of γ -PCC.

Different types of cyclic ketals and acetals were subjected to deprotection by γ -PCC in dichloromethane at room temperature (Scheme 1, Table 1).

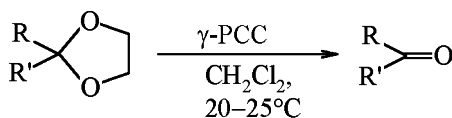
Benzaldehyde and *p*-chlorobenzaldehyde were recovered from the corresponding 1,3-dioxolanes in good yields (Table 1, runs nos. 1, 2). Different methyl-

ketones such as acetophenone, *p*-methylacetophenone, and benzyl methyl ketone were also deprotected in 79–89% yield (Table 1, runs nos.3–5). Cyclohexanone as a saturated cyclic ketone as well as

Table 1. Deprotection of acetals to carbonyl compounds with γ -picolinium chlorochromate at room temperature

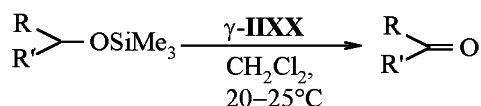
Run no.	Substrate	Time, h	Reaction product	Yield, %
1		15	C_6H_5CHO	75
2		13	<i>n</i> -ClC ₆ H ₄ CHO	80
3		8	$C_6H_5C(=O)CH_3$	79
4		6	<i>n</i> -MeC ₆ H ₄ C(=O)CH ₃	85
5		11	$C_6H_5CH_2C(=O)CH_3$	89
6		15		77
7		17	$CH_3CH_2CH_2CHO$	71
8		12	$CH_3(CH_2)_4C(=O)CH_3$	75

Scheme 1.



* The article was submitted in English.

Scheme 2.



butyraldehyde and 2-heptanone as saturated linear aldehydes and ketones were obtained by deacetalization of the corresponding acetals in satisfactory amounts (Table 1, runs nos. 6–8). No excessive oxidation of aldehydes was observed in any case.

We have also studied the application of γ -PCC to oxidative deprotection of trimethylsilyl ethers providing aldehydes and ketones (Scheme 2, Table 2).

Benzylic silyl ethers with different substituents were reacted with γ -PCC at room temperature to afford the corresponding carbonyl compounds with no excessive oxidation of the aromatic aldehydes (Table 2, runs nos. 1–7). Cinnamaldehyde as an allyl model compound formed safely under the reaction conditions in 76% yield (Table 2, run no. 8). The other saturated trimethylsilyl ethers were subjected

Table 2. Oxidative deprotection of trimethylsilyl ethers with γ -picolinium chlorochromate at room temperature providing carbonyl compounds

Run no.	Substrate	Time, h	Reaction product	Yield, %
1	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	5	$p\text{-ClC}_6\text{H}_4\text{CHO}$	88
2	$p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	5	$p\text{-MeOC}_6\text{H}_4\text{CHO}$	78
3	$p\text{-BrC}_6\text{H}_4\text{CHOSiMe}_3$	5	$p\text{-BrC}_6\text{H}_4\text{CHO}$	85
4	$m\text{-PhOC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	4	$m\text{-PhOC}_6\text{H}_4\text{CHO}$	82
5	$\text{C}_6\text{H}_5\text{CH}(\text{OSiMe}_3)\text{C}_6\text{H}_5$	3	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	90
6	$\alpha\text{-C}_{10}\text{H}_7\text{CH}(\text{OSiMe}_3)\text{Me}$	6	$\alpha\text{-C}_{10}\text{H}_7\text{COCH}_3$	85
7	$\text{C}_6\text{H}_5\text{-C}(\text{OSiMe}_3)(\text{H})\text{-C}(\text{OSiMe}_3)\text{-C}_6\text{H}_5$	4	$\text{C}_6\text{H}_5\text{-C}(\text{O})\text{-C}(\text{O})\text{-C}_6\text{H}_5$	95
8	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OSiMe}_3$	5	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	76
9	$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OSiMe}_3$	10	$\text{CH}_3(\text{CH}_2)_5\text{CHO}$	65
10	$\text{CH}_3(\text{CH}_2)_4\text{CHOSiMe}_3$	12	$\text{CH}_3(\text{CH}_2)_4\text{C=O}$	65
11	$\text{cyclo-C}_6\text{H}_{11}\text{OSiMe}_3$	15	$\text{cyclo-C}_6\text{H}_{10}=\text{O}$	60

to oxidative deprotection and the corresponding carbonyl compounds were isolated in good yields (Table 2, runs nos. 9–11).

Mild reaction conditions, good yields of products, simple work-up procedure, and stability and ease of the reagent preparation are among the advantages of this procedure which make it an attractive supplement to the previously reported methods.

EXPERIMENTAL

All the products are known compounds and were identified by comparison of their spectral data (IR, ^1H NMR) and by melting points of their 2,4-dinitrophenylhydrazones, in particular mixed with authentic samples. The reaction progress was monitored by thin layer chromatography on silica gel Polygram SIL G/UV 254 plates. The yields are derived from the weight of the corresponding 2,4-dinitrophenylhydrazones.

General procedure for deprotection of acetals to carbonyl compounds with γ -PCC. γ -Picolinium chlorochromate (25 mmol) was added to acetal (5 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature until acetal was no longer detectable. The progress of reaction was monitored by TLC (eluent toluene–ethyl acetate, 2:1). Hydrochloric acid (20%, 25 ml) was added to the resulting mixture. The product was extracted into ethyl ether (3 \times 30 ml). On evaporation of the solvent the corresponding carbonyl compound was obtained in 71–89% yield and was characterized as 2,4-dinitrophenylhydrazone derivative.

General procedure for oxidative deprotection of trimethylsilyl ethers with γ -PCC. A mixture of trimethylsilyl ether (5 mmol) and γ -PCC (25 mmol) was prepared in dichloromethane. The solution was stirred at room temperature for an appropriate time (see Table 2). The completion of reaction was confirmed by TLC (eluent *n*-hexane–ethyl ether, 5:1). The reaction mixture was treated with HCl (20%, 25 ml) followed by extraction with diethyl ether (3 \times 30 ml). The organic layer was separated and dried with Na_2SO_4 and then concentrated to obtain the carbonyl compounds in 60–90% yield. The latter were isolated as the corresponding 2,4-dinitrophenylhydrazones.

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