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Silica Gel Supported γ-Picolinium Chlorochromate; A New and Efficient Reagent for Selective Conversion of Alcohols and Oximes into Carbonyl Compounds under Mild and Non-Aqueous Conditions

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The preparation of silica gel supported γ-picolinium chlorochromate and its application as an efficient reagent for selective oxidation of oximes and alcohols into carbonyl compounds is reported. The trimethylsilyloxy and ester groups survived under the reaction conditions.

Key words: γ-picolinium chlorochromate, oximes, alcohols, oxidation

Chlorochromate derivatives of basic organic compounds are among the most valuable class of Cr(VI) based oxidants [1]. Since the introduction of pyridinium chlorochromate as a stable and selective reagent for the oxidation of alcohols [2], many other chlorochromate salts of organic bases have been prepared and applied for the oxidation of organic functional groups [3–9]. Stabilization and/or enhancement of selectivity of the chlorochromate reagents can be attained by supporting them on solid surfaces [6,7,9,10].

We have recently applied γ-picolinium chlorochromate (γ-PCC) as an efficient reagent for the oxidative transformation of organic functional groups [8,11,12]. During its preparation, we had to remove the solvent under reduced pressure and it changed the color of the oxidant from orange to dark brown [8]. In this paper we wish to report the preparation of silica gel supported γ-picolinium chlorochromate as a stable and efficient reagent for the conversion of oximes and alcohols into carbonyl compounds. Supporting γ-PCC on silica gel enabled to improve its selectivity in the competitive reactions with acid sensitive groups.

Synthesis of oximes starting from non-carbonyl substrates followed by a deoximation step is an important pathway to prepare carbonyl compounds [14–16]. Pyridinium chlorochromate (PCC) is not an efficient reagent for regeneration of aldehydes and ketones from oximes [17]. PCC coupled with hydrogen peroxide seem to improve the yield of deoximation [18]. However, further oxidation of the produced aldehydes

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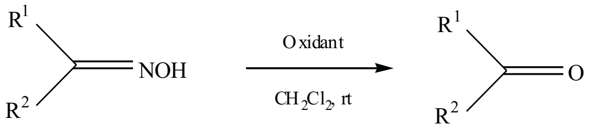
was observed. Recently efficient oxidation of oximes to carbonyl compounds by PCC has been reported in the absence of solvent [19]. Several efficient chlorochromate derivatives have also been used for this purpose [5,9,10,20].

RESULTS AND DISCUSSION

Different kinds of oximes were converted to the corresponding carbonyl compounds by 1.5 molar equivalents of silica gel supported γ-PCC in good to excellent yields (Scheme 1, Table 1). In all of the reactions a mixture of oxime and the oxidant was stirred in dichloromethane at room temperature, followed by a simple work-up procedure. Benzylic, allylic and linear aliphatic aldehydes were regenerated from aldoximes without any overoxidation of the products (Table 1, entries 1–11). The acid sensitive methoxy and benzyloxy groups remained intact during the reactions (Table 1, entries 1, 5). Aromatic and saturated cyclic ketoximes were also deoximated satisfactorily (Table 1, entries 12–20). In the case of benzoin oxime, the oxime group was oxidized selectively in the presence of benzylic hydroxy group and benzoin was obtained in 75% yield (Table 1, entry 17).

Scheme 1



Oxidant: Silica gel supported γ-PCC

Table 1. Conversion of oximes into carbonyl compounds by silica gel supported γ-PCC in dichloromethane at room temperature.

Entry	R^1	R^2	Time (h)	Oxid./Sub. (Mole ratio)	Yield (%)	M.p. of 2,4-DNP[a] (°C)	
						Found	Reported
1	2-$MeOC_6H_4$	H	3	1.5	88	250–252	253[22]
2	2-$O_2NC_6H_4$	H	7.5	1.5	83	262–263	264[22]
3	2-HOC_6H_4	H	7	1.5	72	247–249	248–252[22]
4	3-$O_2NC_6H_4$	H	9	1.5	71	291–294	293[22]
5	4-$PhCH_2OC_6H_4$	H	5	1.5	91	226–229	231–232[23]
6	4-MeC_6H_4	H	7	1.5	95	231–232	232.5[22]
7	4-ClC_6H_4	H	8	1.5	88	251–253	254[22]
8	4-BrC_6H_4	H	9	1.5	81	256–258	257[22]
9	4-$O_2NC_6H_4$	H	9	1.5	91	317–319	320[22]
10	PhCH=CH	H	2	1.5	84	254–255	255[22]
11	n-C_9H_{19}	H	8	1.5	91	100–102	104[22]

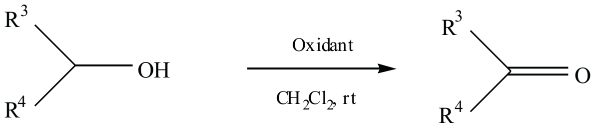
Table 1 (continuation)

12	C_6H_5	CH_3	8	1.5	82	246–248	248–249[22]
13	4-MeC_6H_4	CH_3	7	1.5	89	257–259	260[22]
14	4-BrC_6H_4	CH_3	5.5	1.5	93	255–257	257[22]
15	4-ClC_6H_4	CH_3	7	1.5	92	228–230	231[22]
16	Ph	Ph	4	1.5	95	237–238	238[22]
17	PhCHOH	Ph	8	1.5	75	131–133^b	134–136[24]
18	2-Naphthyl	CH_3	6	1.5	86	50–53^b	52–56[25]
19	$-CH_2(CH_2)_{10}CH_2-$		7	1.5	88	269–271	269–270[26]
20	$-CH_2(CH_2)_4CH_2-$		4	1.5	93	157–159	261[22]

^{a}Melting point of 2,4-dinitrophenylhydrazone derivative.
^{b}Melting point of carbonyl product.

Chlorochromates are among the most efficient and selective reagents for oxidation of alcohols to carbonyl compounds, especially for controlled oxidation of primary alcohols to aldehydes [1–4,8,19]. We investigated the reaction of various primary and secondary alcohols in the presence of silica gel supported γ-PCC in dichloromethane at room temperature (Scheme 2, Table 2). The reaction of primary benzylic alcohols with electron-donating and electron-withdrawing substituents produced the corresponding aldehydes in good to excellent yields (Table 2, entries 1–7). The acetal group in piperanyl alcohol survived in the reaction conditions (Table 2, entry 6). Cinnamyl alcohol and 1-octanol were also oxidized satisfactorily and cinnamaldehyde and octanal were isolated in 90% and 95% yields, respectively (Table 2, entries 8, 9). Silica gel supported γ-PCC was also the reagent of choice for the oxidation of aromatic as well as aliphatic and cyclic secondary alcohols (Table 2, entries 10–14). Most of the reactions were completed in the presence of 1.5 molar equivalents of the reagent that showed its efficiency in comparison with other chlorochromate salts.

Scheme 2



Oxidant: Silica gel supported γ-PCC

Many of hydroxy compounds can be protected by their conversion to trimethylsilyl ethers [21]. In Scheme 3 we showed the survive of aliphatic trimethylsilyloxy group in the oxidation of oximes and alcohols by silica gel supported γ-PCC at room temperature. Ester group also remained intact under similar conditions.

In conclusion silica gel supported γ-PCC is a very efficient and stable reagent for selective conversion of oximes and alcohols into carbonyl compounds. The reactions take place under mild conditions and the work-up procedure is very simple.

Scheme 3

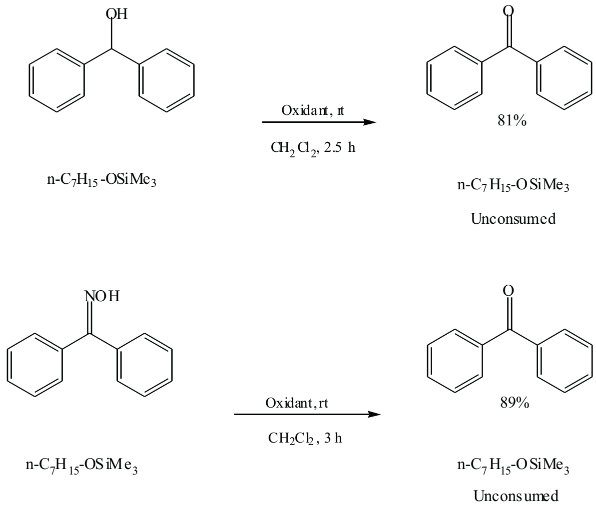
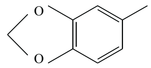
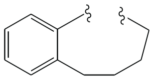
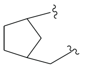


Table 2. Oxidation of primary and secondary alcohols by silica gel supported γ-PCC in dichloromethane at room temperature.

Entry	R^3	R^4	Time (h)	Oxid./Sub. (Mole ratio)	Yield (%)	M.p. of 2,4-DNP[a] (°C)	
						Found	Reported
1	Ph	H	1.5	1.5	84	235–236	237[22]
2	4-MeC_6H_4	H	1.5	1.5	90	231–232	232.5[22]
3	4-$MeOC_6H_4$	H	4	1.5	78	248–250	253[22]
4	4-$PhOC_6H_4$	H	11	1.5	94	212–215	214–216[26]
5	4-$PhCH_2OC_6H_4$	H	3	1.5	82	228–229	231–232[23]
6		H	4	1.5	83	262–264	264[22]
7	2-$O_2NC_6H_4$	H	12	1.5	62	262–264	264[22]
8	PhCH=CH	H	11	1.5	90	253–254	255[22]
9	n-C_7H_{15}	H	10	2	95	102–104	106[22]
10	Ph	Ph	2.5	1.5	86	238–239	238[22]
11			4	1.5	85	202–204[b]	203–205[26]
12	n-C_6H_{11}	CH_3	14	2	69	86–88	89[22]
13			13	2	97	91–93	93–96[25]
14	-$CH_2(CH_2)_4CH_2$-		6	2	95	144–146	148[22]

[a] Melting point of 2,4-dinitrophenylhydrazone derivative.
[b] Melting point of carbonyl product.

EXPERIMENTAL

Products were characterized by comparison of their spectral data (^{1}H NMR, IR) and melting point of their 2,4-dinitrophenylhydrazone derivatives with those reported in the literature [22–26]. Reaction monitoring was accomplished by TLC on SIL G/UV 254 sheets. All yields refer to isolated products.

Preparation of silica gel supported γ-picolinium chlorochromate. CrO_3 (3.0 g, 30 mmol) was added gradually to 6M HCl (5.6 ml, 33 mmol) with stirring at room temperature. After 5 min the homogeneous solution was cooled to 0℃ and γ-picoline (2.8 g, 30 mmol) was added slowly to the mixture over 15 min. The mixture was stirred for another 4 h at room temperature. Silica gel (15.7 g, Merck, Kiselgel 40, 70–230 mesh) was gradually added to the solution over 30 min and finally an orange solid material was obtained.

General procedure for conversion of oximes into carbonyl compounds by silica gel supported γ-PCC. Silica gel supported γ-PCC (containing 3 mmol of γ-PCC) was added to a solution of oxime (2 mmol) in dichloromethane (7 ml). The mixture was stirred magnetically at room temperature until the complete consumption of the oxime (Table 1). The mixture was filtered on a sintered glass funnel and the residue was washed with dichloromethane (15 ml). Evaporation of the solvent afforded the carbonyl compounds in 71–95% yields.

General procedure for the oxidation of alcohols by silica gel supported γ-PCC. In a round-bottomed flask a solution of alcohol (2 mmol) in dichloromethane (7 ml) was prepared. The oxidant (equal to 3–4 mmol of γ-PCC) was added and the mixture was stirred for the appropriate period (Table 2) at room temperature. Progress of the reaction was followed by TLC (eluent: n-hexane/ethyl acetate; 2/1). The mixture was filtered and the residue was washed with dichloromethane (15 ml). Evaporation of the solvent gave the carbonyl compounds in 62–97% yields.

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