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SOLVENT-FREE, MICROWAVE ASSISTED OXIDATION OF ALCOHOLS WITH 4-HYDROXYPYRIDINIUM CHLOROCHROMATE FUNCTIONALIZED SILICA GEL

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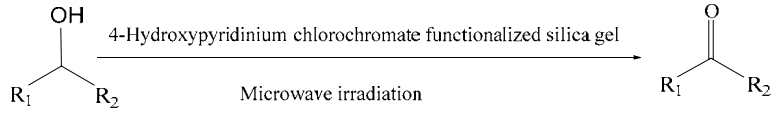
4-Hydroxypyridinium chlorochromate functionalized silica gel was found to be an efficient and reusable oxidant for the very fast oxidation of primary and secondary alcohols to the corresponding carbonyl compounds under solvent-free conditions and microwave irradiation in excellent yields.



R_1, R_2= H, alkyl, allyl, aryl

INTRODUCTION

Oxidation of alcohols to the carbonyl compounds is an important transformation in organic synthesis[1]. Solid supports such as silica gel have found wide application in organic reactions.[2–8] There are a few example using supported organic molecules on silica gel as oxidizing agents.[9–13] Since 1986 microwave irradiation has become an increasingly popular method for accelerating synthetic reactions. This technology offers a clean, effective and convenient method of heating, which often results in higher yields, shorter reactions times and easier workup procedure. Organic reactions such as oxidation of alcohols that are assisted by microwave irradiation have attracted considerable attention.[14–19] Chromium oxidants were used for oxidation of organic compounds consistently.[20] Pyridinium chlorochromate adsorbed on alumina,[21–22] on silica,[23] chromic acid activated carbon,[24] ammonium chlorochromate on silica,[25] and chromyl chloride on silica-alumina[26] have been reported to give better yields under milder conditions as compared to the unsupported oxidants. However, most of these methods have some disadvantages including vigorous reaction conditions and tedious workup, use of solvents and long time of reactions. Thus, there is still a scope for further development of mild, simple and environment-friendly method for oxidation of alcohols to their corresponding carbonyl compounds. During the course of our systematic study on the development of supported reagents and catalysts for the oxidation of organic compounds,[27–32] we have previously presented a convenient method for oxidation of alcohols to corresponding carbonyl compounds with 4-aminopyrinium chlorochromate supported on silica gel.[32] In this paper we wish to report use of eco-friendly heterogeneous oxidant based on 4-hydroxypyridinium chlorochromate functionalized silica gel as an eco-friendly heterogeneous oxidant for the oxidation of alcohols to the corresponding carbonyl compounds.

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RESULTS AND DISSCUSION

Our approach to a fast and efficient method for the oxidation of alcohols to the corresponding carbonyl compounds is to make use of 4-hydroxypyridinium chlorochromate supported on silica gel (Figure 1). It is a stable solid and can be prepared from the reaction of 4-aminopyridine with activated silica gel, which is then reacted with a solution of chromium trioxide in water.

Initially, the control experiments focused on limiting the quantity of reagent in the mixture, and control of the reaction time. The results are summarized in the Table 1.

As can be seen from Table 1, the best results were obtained with use of Substrate: oxidant ratio (1:1) under 3 min microwave irradiation (entry 10) and additions the irradiation time and the amount of oxidant were unprofitable (entries 2–8, 13). Forde more the reaction was not completed by use of 4-hydroxypyridinium chlorochromate in the absence of silica gel (entry 12). For subsequent experiments on other alkyl, aryl and allyl alcohols, we found that a 1:1 mixture 4-hydroxypyridinium chlorochromate functionalized silica gel and alcohols, was produced the corresponding carbonyl compounds under solvent- free conditions and microwave irradiation (Scheme 1, Table 2). Interestingly, in the oxidation of primary alcohols further oxidation of the liberated aldehydes to the corresponding carboxylic acids didn't occur even with higher mole ratio of 4-hydroxypyridinium chlorochromate functionalized silica gel further oxidation didn't perform by reaction time elongation (Table 2 entries 1–24). The chemoselectivity of method also have been investigated using cinnamyl alcohol, in this case the C=C stayed intact during the reaction time (Table 2, entries 17–19, 35).

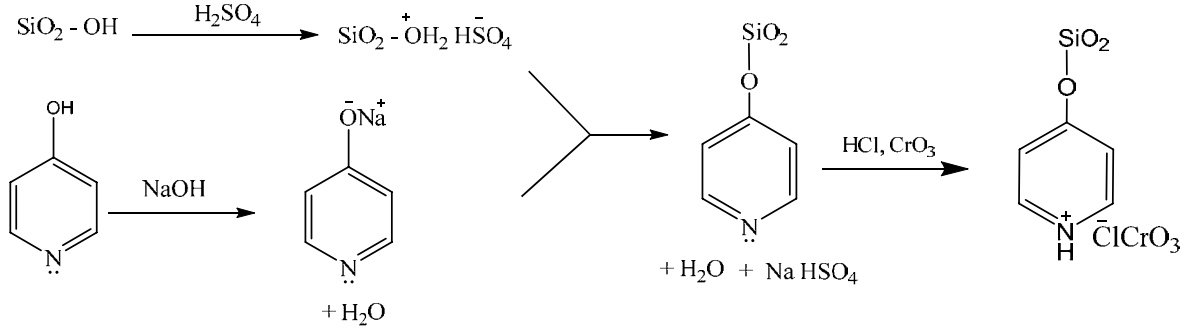


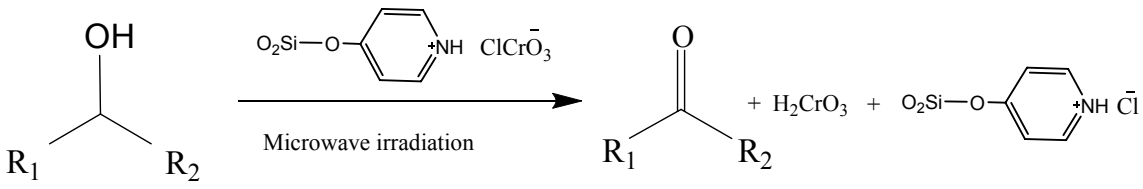
Fig. 1.

Table 1

Optimization of conditions in the reaction of benzyl alcohol with 4-hydroxypyridinium chlorochromate functionalized silica gel

Entry[a]	**Substrate: oxidant**[b]	**Irradiation time(min)**	**Conversion**[c]	**MW Power (W)**	**Yield (%)**[d]
1	1:3	(stirred at reflux conditions for 2 h)	50	-	45
2	1:3	6	90	300	85
3	1:3	7	93	300	85
4	1:3	5	100	400	92
5	1:3	4	100	400	92
6	1:3	2	100	400	94
7	1:2	5	100	400	98
8	1:2	4	100	400	98
9	1:1	4	100	400	100
10	1:1	3	100	400	100
11	1:1	2	>97	400	>94
12e	1:2	8	>28	900	>20
13	1:1	3	100	500	75

[a] Reaction conditions: solvent- free conditions under microwave irradiation.
[b] Molar ratio.
[c] Determinated by GC.
[d] Isolated product.
[e] In the absence of silica gel.



R_1, R_2= H, alkyl, allyl, aryl

Scheme 1 – Oxidation of alcohols with 4-hydroxypyridinium chlorochromate functionalized silica gel.

Table 2

Oxidation of alcohols with 4-hydroxypyridinium chlorochromate functionalized silica gel

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M. p. (°C)	
					Found	Reported
1	Benzyl alcohol	Benzaldehyde	2	98	Liq.	
2	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	2	100	Liq.	
3	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	2	98	104-105	103-106
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	2	100	Liq.	
5	2,4-Dimethoxybenzyl alcohol	2,4- Dimethoxybenzaldehyde	2	100	70	67-69
6	3-Chlorobenzyl alcohol	3-Chlorobenzaldehyde	3	98	Liq.	
7	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	3	99	56	57-58
8	2-Hydroxybenzyl alcohol	2-Hydroxybenzaldehyde	2	100	Liq.	
9	3-Hydroxybenzyl alcohol	3-Hydroxybenzaldehyde	2	99	104	100-102
10	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	3	97	63-64	64-69
11	5-Bromo-2-hydroxybenzyl alcohol	5-Bromo-2-hydroxybenzaldehyde	3	99	102	100-102
12	2-Hydroxy-3-methoxybenzyl alcohol	2-Hydroxy-3-methoxybenzaldehyde	2	98	41-43	40-42
13	4-(Dimethylamino)benzyl alcohol	4-(Dimethylamino)benzaldehyde	2	94	77	72-75
14	3,4,5-Trimethoxybenzyl alcohol	3,4,5-Trimethoxybenzaldehyde	2	97	71.5	72-74
15	2-Fluorobenzyl alcohol	2-Fluorobenzaldehyde	4	96	Liq.	
16	2-Phenylethyl alcohol	Phenylacetaldehyde	2	98	Liq.	
17	Cinnamyi alcohol	Cinnamaldehyde	2	91	Liq.	
18	3-Buten-1-ol	Methylviny ketone	3	90	Liq.	
19	1-Pentenol	Pentenal	4	93	Liq.	
20	3-Methyl-1 butanol	3-Methybutanal	4	94	Liq.	
21	Butanol	Butanal	4	87	Liq.	
22	2.2-Dimethyl-1-propanol	2.2-Dimethylpropanal	4	90	Liq.	
23	1-Hexanol	Hexanal	4	94	Liq.	
24	1-Octanol	Octanal	4	92	Liq.	
25	1-Phenylethyl alcohol	Acetophenone	2	100	Liq.	
26	Benzhydrol	Benzophenone	2	100	45	47-51
27	9,10-Dihydroxy-9,10-dihydroanthracene	Anthraquinone	2	100	280	282-285
28	2,4- Dihydroxypentane	Acetylacetone	3	87	Liq.	
29	4-Chlorobenzhydrol	4-Chlorobenzophenone	4	91	76.5	74-76
30	4-Nitrobenzhydrol	4-Nitrobenzophenone	4	93	133-135	136-138
31	2-Amino-9,10-dihydroxy-9,10-dihydroanthracene	2-Aminoanthraquinone	4	92	290	291-294
32	1-Amino-9,10-dihydroxy-9,10-dihydroanthracene	1-Aminoanthraquinone	4	92	250-252	251-254
33	3-Nitrobenzhydrol	3-Nitrobenzophenone	4	92	81	75-78
34	3-Phenyl-1-propanol	3-Phenyl-1-propanal	4	88	Liq.	
35	1-Octene-3-ol	1-Octene-3-one	4	90	Liq.	
36	3-Methyl-2-butanol	3-Methyl butanone	4	89	Liq.	
37	2-Methyl-1-propanol	2- Methylpropanal	4	88	Liq.	
38	Cyclohexanol	Cyclohexanone	4	91	Liq.	
39	2-Methylcyclopentanol	2-Methylcyclopentaone	4	91	Liq.	

[a] Isolated product.

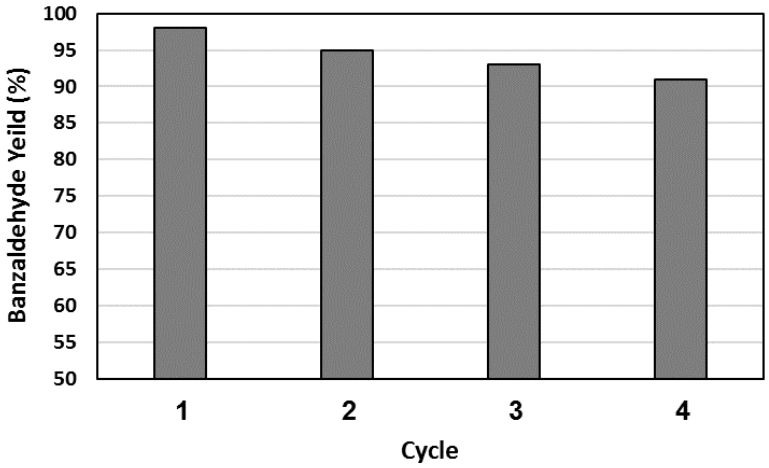


Fig. 2 – Effect of the catalyst recycling on the yield of benzaldehyde for the MW-assisted oxidation of benzyl alcohol with 4-hydroxypyridinium chlorochromate functionalized silica gel.

The reusability of the oxidant has also been investigated. One of the most important features of this heterogeneous can be recycled. 4-Hydroxypyridine functionalized silica gel after reusing for more than four times was recovered quantitatively after each experiment and was activated with a fresh solution of chromium trioxide hydrochloric acid. The activity of the functionalized oxidant was also examined. It was found that the activity decreased gradually, and the obtained benzaldehyde reduced from 100% to 91% after four runs (Figure 1). A 1:1 mixture of alcohol /oxidant in a 2 min period was used. The IR spectrum of the recovered reagent exhibited signals at v= 887 and 1069 cm^{-1} corresponding to Si-O-C stretching.

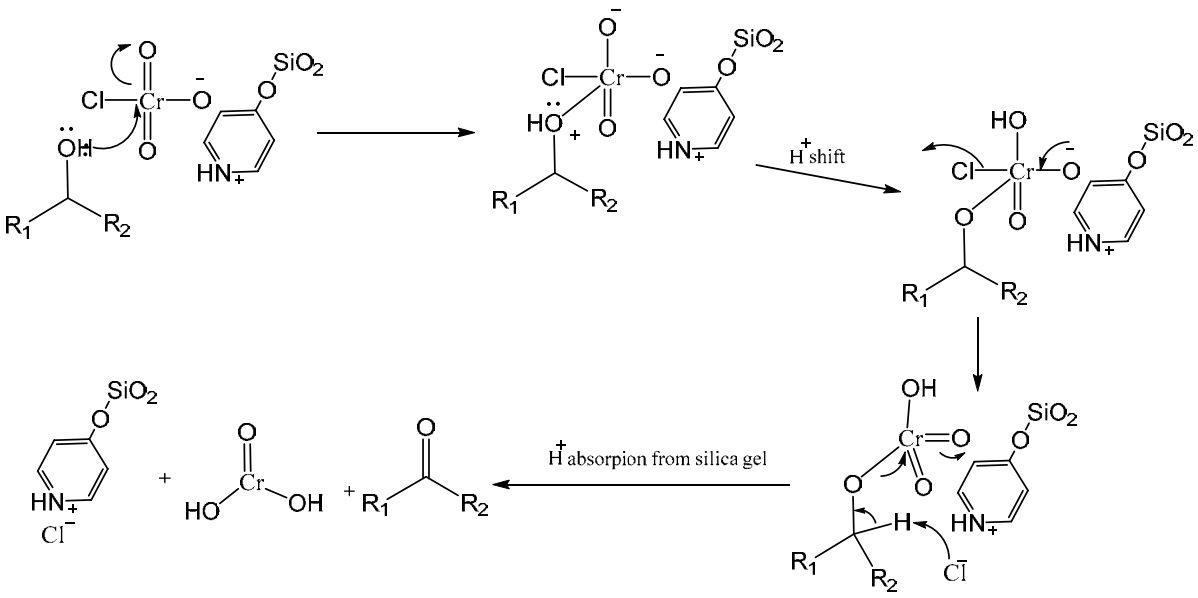
Efficiency and applicability of 4-hydroxypyridinium chlorochromate functionalized silica for the oxidation of alcohols were compared with some of those reported methods.[13, 16, 32–35] As shown in Table 3, 4-hydroxypyridinium chlorochromate functionalized silica functions better than previously reported reagents in yields and reaction times for oxidation of primary and secondary alcohols to the corresponding carbonyl compounds under solvent-free conditions and microwave irradiation.

Table 3

Comparison the results of present method with some of those reported in the literature

Entry	Substrate	Product	Reaction Conditions	Yield (%)	Time	Ref.
1	Benzyl alcohol	Benzaldehyde	Ratio of 1:1.5 alcohol: 4- aminopyridinium chlorochromate	97	2 (h)	32
2	Benzyl alcohol	Benzaldehyde	Ratio of 1:1 alcohol: SSDT reagent at the reflux conditions	95	1 (h)	13
3	Benzyl alcohol	Benzaldehyde	Rh /NACcatalysts, T= 100 °C	50	24 (h)	33
4	Benzyl alcohol	Benzaldehyde	benzyl alcohol (1 mmol), Pd@TiC (25 mg), CH_3CN (2 mL), 20 W domestic bulbs, Air.	97	8 (h)	35
5	Benzyl alcohol	Benzaldehyde	--	100	2 (min)	-[a]
6	Benzhydrol	Benzophenone	Ratio of 1:1 alcohol: SSDT reagent at the reflux conditions	83	1.5 (h)	13
7	Diphenylcarbinol	Benzophenone	--	98	2 (min)	-[a]
8	1-Hexanol	Hexanal	Ratio of 1:1 alcohol: Cetyltrimethylammonium Chlorochromate under microwave irradiation	92	8 (min)	16
9	1-Hexanol	Hexanal	--	94	4 (min)	-[a]
10	1-Phenylethyl alcohol	Acetophenone	Ratio of 1:1: 2 alcohol: MnO_2 :TBHP, RT	84	7 (h)	34
11	1-Phenylethyl alcohol	Acetophenone	--	100	2 (min)	-[a] 34

[a] Present work



Scheme 2. Suggested mechanism for oxidation of alcohols with 4-hydroxypyridinium chlorochromate functionalized silica gel.

The reaction mechanism depicted in Scheme 2. The first step is attack of oxygen on the chromium to form the Cr-O bond. Then, a proton on the (now positive) OH is transferred to one of the oxygens of the chromium, and a chloride ion is then displaced. The C-O double bond is formed when a base (Cl^-) removes the proton on the carbon adjacent to the oxygen.

EXPERIMENTAL

Materials and Instruments

Chemicals were purchased from Merck, Aldrich, Fluka and used without further Purification. Experiments were carried out in closed vessel multi-mode Microsynth Milstone laboratory microwave oven. All experiments had good reproducibility by repeat the experiments in same conditions. The melting points were determined on Electrothermal 9100 apparatus. IR spectra were recorded on a Bruker Tensor 27 spectrometer. ^{1}H NMR and ^{13}C NMR spectra of selected products were recorded on a Bruker 250 MHz spectrometer. To determine substrate conversion, An Agilent 7890A GC was used. All products are known compounds and they were identified by comparison of their physical and spectral data with those of authentic samples. All yields refer to pure isolated products.

Preparation of 4-hydroxypyridine functionalized silica gel

A fresh solution of 1.9 g of 4-hydroxypyridine (20 mmol) in 20 cm^3 of NaOH added to 6 g silica gel (nano powder, 99%, 600 m^2/g) that was activated by 12.8 cm^3 of 4.75 M sulfuric acid and the mixture was stirred at 40 °C for 10 min until a milky solid was formed.

Preparation of 4-hydroxypyridinium chlorochromate functionalized silica gel

To a fresh solution of 2 g of chromium trioxide (20 mmol) in 25 mL of 6 N hydrochloric acid, 4-hydroxypyridine functionalized silica gel (7.9 g, contain 1.9 g, 20 mmol 4-hydroxypyridine) was added within 5 min below 7-12 °C, and the mixture was stirred at ambient temperature for 30 min until a lemon solid was formed. After the evaporation of the solvent, the solid was dried at 50 °C for 2h. The supported reagent can be kept for weeks in dark without losing its activity. This synthesized reagent (0.1 g) was titrated by a standard solution of NaOH (0.1 N) to obtain its [H^+] concentration which was 3.6 meq per gram of the powder.

General procedure

In a small-scale experiment 4-hydroxypyridinium chlorochromate functionalized silica gel (3.95 g, contain 10 mmol of 4-hydroxypyridinium chlorochromate) an alcohol (10 mmol) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time. The mixture was irradiated for the time indicated in the table by microwave radiation (Table 2). The progresses of the reactions were monitored by TLC. After cooling to room temperature the product was extracted with diethyl ether (2 × 10 mL) and filtered. Evaporation of solvent gave a crude product which was passed through a short silica gel column by ethylacetate: pet. ether (1:7) as eluent to afford the pure product. The structures of the products were confirmed by their melting point, IR and /or NMR spectral data and comparison with commercially available authentic samples.[36–38]

Spectra data

Benzaldehyde Yield: 100%.; IR (neat) 3064, 3030, 2850, 2821, 2733, 1704, 1655, 1600, 1584, 1456, 1392, 1167, 829 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.81-7.89 (m, 2H), 7.42- 7.63 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 190.91, 136.22, 134.34, 130.12, 129.87.

4-Methoxybenzaldehyde Yield: 98%. M.p.: 104-105 °C.; IR (neat) 2994, 2960, 2852, 1701, 1606, 1538, 1345, 1195, 855 cm^{-1}. ^{1}H NMR (250 MHz, DMSO) δ 9.83 (s, 1H), 7.82 (d, 2H), 7.05(d, 2H), 3.80 (s, 3H). ^{13}C NMR (63 MHz, DMSO) δ 191.36, 132.09, 130.08, 114.75, 55.87.

3-Chlorobenzaldehyde Yield: 98%.; IR (KBr) 3383, 3064, 2938, 2833, 2699, 1696, 1474, 1388, 1195, 790 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.43-7.78 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 191.3, 138.22, 136.17, 134.09, 131.23, 130.02, 126.74.

2-Hydroxybenzaldehyde Yield: 100 %.; IR (neat) 2994, 2960, 2852, 1701, 1606, 1538, 1345, 1195, 855 cm.$^{-1}$ 13C NMR (63 MHz, DMSO) δ 197.03, 162.53, 136.29, 132.86, 121.45, 120.37, 116.71.

2-Hydroxy-3-methoxybenzaldehyd: Yield: 98 %. M.p.: 41-43 °C.; IR (KBr) 3448, 1640, 1587, 1454, 1255 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) 10.913 (s, 1H), 9.72 (s, 1H), 6.76 - 6.99 (m, 4H), 3.67(s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 196.54, 151.33, 148.02, 124.32, 120.63, 119.46, 117.82, 56.02.

4-(Dimethylamino)benzaldehyde Yield: 94 %. M.p.: 77 °C.; IR (KBr) 3447, 2923, 2714, 1661, 1596, 1547, 1359, 1162, 812 cm.$^{-1}$ ^{1}H NMR (250 MHz, DMSO) δ 9.81 (s, 1H), 7.84 (d, 2H), 6.73 (d, 2H), 2.98 (s, 6H). ^{13}C NMR (63 MHz, DMSO) δ 191.13, 155.43, 132.67, 126.20. 111.36, 40.17.

2-Fluorobenzaldehyd Yield: 96 %.; IR (neat) 3448, 2827, 2738, 1699, 1598, 1296, 833 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 10.16 (d, 1H), 7.56 (d, 1H), 7.33 (dd, 1H), 7.15 (dd, 1H), 7.46.984 (d, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 185.93, 158.19, 135.57, 129.19, 123.77, 122.92, 115.83.

Cinnamaldehyde Yield: 91 %.; IR (neat) 3063, 2993, 2816, 1678, 1123, 975, 748 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.58 (d, 1H), 7.41-7.57 (5H), 7.51 (d, 1H), 6.72 (d, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 192.61, 151.95, 133.88, 130.84, 128.21, 127.76, 127.19.

Octanal: Yield: 92 %.; IR (neat) 2960, 2874, 1730, 1411 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.68 (t, 1H), 2.33 (m, 2H), 1.60 (m, 2H), 1.25-1.29 (m, 8H), 0.82 (t, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 192.47, 43.13, 31.05, 30.10, 29.24, 23.37.

Acetophenone Yield: 100 %.; IR (neat) 3080, 3025, 1696, 1605, 1365, 1268, 762 cm.$^{-1}$, ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.57-7.83 (m, 5H), 2.47(s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 190.78, 135.94, 129.92, 129.14, 128.96, 25.88.

Acetylacetone Yield: 87 %.; IR (neat) 3443, 2360, 1716, 1623 cm.$^{-1}$ ^{1}H NMR (250 MHz, DMSO) δ 3.59 (s, 2H), 1.989 (s, 6H), [15.4(O-H), 5.6 (vinyl H in enol form)]. ^{13}C NMR (63 MHz, DMSO) δ 203.13, 57.98, 30.55, [191.46, 100.51, 29.50, 24.43, in enol form].

4-Chlorobenzophenone Yield: 91 %. M.p.: 76.5 °C.; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.82 (d, 2H), 7.63 (d, 2H), 7.53 (dd, 1H), 7.42 (dd, 2H), 7.39 (d, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 194.86, 137.82, 136.64, 136.02, 131.91, 130.63, 128.85, 128.12, 127.50.

4-Nitrobenzophenone Yield: 93 %. M.p.: 133-135 °C; IR (KBr) 3382, 2751, 1666, 1278, 763 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.17 (d, 2H), 7.86 (d, 2H), 7.75 (d, 2H), 7.53 (m, 1H), 7.44 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 194.15, 149.91. 142.86, 137.25, 130.41, 128.87, 127.53, 126.27, 123.46,

2-Aminoanthraquinone Yield: 92 %. M.p.: 290 °C.; IR (KBr) 3447, 1587, 1454, 1256,1215, 1161, 1058, 946,761 cm^{-1}. ^{1}H NMR (250 MHz, DMSO) δ 6.62 – 8.04 (8H), 2.46 (2H). ^{13}C NMR (63 MHz, DMSO) δ 183.72, 180.49, 155.09, 135.27, 134.62, 134.05, 129.95, 126.73, 121.58, 118.49, 110.10.

1-Aminoanthraquinone Yield: 92 %. M.p.: 250-252 °C.; IR (KBr) 3419, 2359, 1637, 1607, 1283, 1013, 801 cm.$^{-1}$ ^{1}H NMR (250 MHz, DMSO) δ 8.12(m, 1H), 8.03 (d, 1H), 7.66(m, 1H), 7.41(m, 1H), 7.38(d, 1H), 7.22 (m, 1H), 7.06 (d, 1H), 2.78 (s, 2H). ^{13}C NMR (63 MHz, DMSO) δ 183.30, 182.91, 153.11, 135.51, 134.70, 133.28, 132.09, 131.81, 131.03, 127.41, 124.68, 122.27, 116.37, 110.89.

2- Methylpropanal Yield: 88 %.; IR (neat) 2742, 1727, 1120, 933 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.74 (d, 1H), 2.77 (m, 1H), 1.15 (d, 6H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 203.87, 42.01, 16.76.

2-Methylcyclopentaone Yield: 91 %.; IR (neat) 3473, 2971, 2927, 1745, 1453, 1228, 1156, 898 cm.$^{-1}$ ^{1}H NMR (250 MHz, $CDCl_3$) 2.40 (m, 1H), 2.28 (m, 1H),.2.17 (m, 1H), 1.96 (m, 1H), 1.75 (m, 1H), 1.51 (m, 1H), 1.13 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 222.35, 44.28, 38.16, 32.84, 21.07, 15.26.

CONCLUSION

In conclusion, we have designed to synthesize 4-hydroxypyridinium chlorochromate functionalized silica as an efficient and recoverable oxidant for controlled oxidation of alcohols to their corresponding carbonyl compounds. Efficiency, high yields, short reaction times, clean reaction profile, solvent-free condition, simplicity of preparation and recyclability of oxidant are some advantages of the described protocol.

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