Fast selective oxidation of alcohols under solvent-free conditions

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Abstract A combination of acetic anhydride, H_2SO_4 -nano silica, wet-SiO₂ (60 %), and $K_2Cr_2O_7$ as a new oxidizing system for the selective oxidation of different types of alcohols to the corresponding aldehydes and ketones at room temperature under solvent-free conditions is introduced. Mild reaction conditions, high yields of the products, short reaction time, no further oxidation to the corresponding carboxylic acid, and easy work-up make this new system a useful method for oxidizing alcohols.

Keywords Selective oxidation · Alcohols · Acetic anhydride · Solvent-free

Introduction

The oxidation of the hydroxyl group to the corresponding carbonyl compounds is one of the most important reactions in synthetic organic chemistry, which have long been the objective of many research papers [1–6]. Chromium(VI) reagents such as Collins reagent [7], Jones reagent [8], chromic anhydride chlorotrimethylsilane [9], caffeinilium chlorochromate [10], guanidinium chlorochromate [11], cetyltrimethylammonium dichromate [12], *N*-methyl morpholine chlorochromate [13], benzyldimethyltelluronium dichromate [14], isoquinolinium bromochromate [15], pyridinium dichromate [16], pyridinium chlorochromate [17], Collins reagentacetic anhydride [18], chromium(VI) oxide-pyridine-acetic anhydride [19], and pyridinium dichromate-acetic anhydride [20] are widely used for this transformation. Unfortunately, most of these methods suffer from one or more disadvantages, such as a long reaction time, formation of a hemiacetal, overoxidation, use of toxic

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solvent, strongly acidic conditions, high temperatures, stoichiometric amounts of oxidant, tedious work-up, detrimental side reactions, and unsatisfactory yields.

In spite of a large number of methods reported for the oxidation reaction, there is still a need to develop a more efficient, simple, milder, and high-yielding product using laboratorial and industrial oxidants. Herein, we wish to report, for the first time, a combination of potassium dichromate ($K_2Cr_2O_7$), sulfuric acid immobilized on nano silica, and acetic anhydride as an affective oxidizing system for the oxidation of alcohols to their corresponding aldehydes or ketones in solvent-free conditions at room temperature (Scheme 1).

Experimental

Commercial reagents from Fluka, Merck, and Aldrich chemical companies were used without further purification. The composition of the synthesized powder was obtained by Fourier transform infrared (FT-IR) spectroscopy (IR Prestige-21, Shimadzu) in the wavelength range of 400–4,000 cm⁻¹. Information about the phase was obtained by an X-ray powder diffractometer (Philips, CuK_{α}, $\lambda = 1.54178$ Å) in the Bragg angle ranging between 10° and 60°.

Preparation of H₂SO₄-nano silica

 H_2SO_4 -nano silica was synthesized according to the previously reported procedure [21]. To a slurry of silica gel (10 g) in CCl₄ (50 ml) was added commercially available concentrated H_2SO_4 (3 ml) with shaking for 5 min. The solvent was evaporated and the produced H_2SO_4 -nano silica was then dried at 110 °C for 3 h. The amount of H^+ in the H_2SO_4 -nano silica was determined by acid–base titration (by standard NaOH) and it was 0.11 mmol (0.1 g H_2SO_4 -nano silica, equal to 0.11 mmol of H^+) [22].

The prepared catalyst was characterized with FT-IR and X-ray diffraction (XRD). The XRD spectrum of H₂SO₄-nano silica is shown in Fig. 1. This pattern exhibits a broad peak ($2\theta = 15-30^{\circ}$), attributed to amorphous nano silica.

In the FT-IR spectrum, the band at about 800 cm⁻¹ belongs to the Si–OH bond stretching vibration (Fig. 2). The band in the region 1,040–1,230 cm⁻¹ is attributed to the stretching vibrations of the Si–O–Si and S=O bonds. A peak appeared at about 3,400 cm⁻¹, due to the stretching of OH groups in the SO₃H.



Scheme 1 Selective oxidation of alcohols



Fig. 1 X-ray diffraction (XRD) pattern of H₂SO₄-nano silica



Fig. 2 Fourier transform infrared (FT-IR) spectrum of H₂SO₄-nano silica

General procedure for the selective oxidation of alcohols

A typical reaction was carried out as follows: 1 mmol of alcohol was added to a suspension of 1.5 mmol of acetic anhydride, 0.2 mmol of $K_2Cr_2O_7$, 0.3 g of H_2SO_4 -nano silica, and an appropriate amount of wet-SiO₂ (60 %). The mixture was stirred under solvent-free conditions at room temperature for various lengths of time (Table 1). The progress of the reaction was monitored by thin layer chromatography (TLC) (eluent; diethyl ether: CCl₄, various ratios). After the completion of the reaction, 20 ml CH₂Cl₂ was added to the heterogeneous mixture, and it was then filtered. The organic layer was washed with water, dried over MgSO₄, and the solvent was removed. The residue was chromatographed on a silica gel column. All of the products are known compounds and were identified by comparison of their physical data with those of authentic samples.

Results and discussion

The oxidation of 3-nitrobenzyl alcohol (m-NO₂–C₆H₄–CH₂OH) was first investigated as a model reaction. The oxidation provided 3-nitrobenzaldehyde in excellent

Entry	Substrate	Product ^a	Time (min)	Yield (%) ^b
1	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	m-NO ₂ -C ₆ H ₄ -CHO	3	96
2	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	<i>m</i> -NO ₂ -C ₆ H ₄ -CH ₂ OCOCH ₃	120	88
3	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	No detection of aldehyde	3	-
4	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	<i>m</i> -NO ₂ -C ₆ H ₄ -CHO	60	92
5	m-NO2-C6H4-CH2OH	<i>m</i> -NO ₂ –C ₆ H ₄ –CHO	30	91
6	m-NO ₂ -C ₆ H ₄ -CH ₂ OH	<i>m</i> -NO ₂ -C ₆ H ₄ -CHO	30	90
7	<i>m</i> -NO ₂ -C ₆ H ₄ -CH ₂ OH	Mixture of <i>m</i> -NO ₂ –C ₆ H ₄ –CHO and <i>m</i> -NO ₂ –C ₆ H ₄ –CH ₂ OCOCH ₃	30	50>
8	o-NO2-C6H4-CH2OH	o-NO2-C6H4-CHO	3	91
9	o-Br-C ₆ H ₄ -CH ₂ OH	o-Br-C ₆ H ₄ -CHO	2.5	95
10	p-Br-C ₆ H ₄ -CH ₂ OH	p-Br-C ₆ H ₄ -CHO	3	94
11	o-H ₃ CO-C ₆ H ₄ -CH ₂ OH	o-H ₃ CO–C ₆ H ₄ –CHO	5	89
12	p,o-Cl2C6H3CH2OH	<i>p</i> , <i>o</i> -Cl ₂ –C ₆ H ₃ –CHO	2	96
13	o-F-C ₆ H ₄ -CH ₂ OH	o-F-C ₆ H ₄ -CHO	2	95
14	p-H ₃ C-C ₆ H ₄ -CH ₂ OH	<i>p</i> -H ₃ C–C ₆ H ₄ –CHO	5	88
15	PhCH ₂ CH ₂ OH	PhCH ₂ CHO	2.5	94
16	PhCH(OH)CH ₂ CH ₃	PhCOCH ₂ CH ₃	2	95
17	PhCH ₂ CH ₂ CH ₂ OH	PhCH ₂ CH ₂ CHO	3	93
18	n-CH ₃ (CH ₂) ₆ CH ₂ OH	n-CH ₃ (CH ₂) ₆ CHO	5	91
19	CH ₃ (CH ₂) ₅ CH(OH)CH ₃	CH ₃ (CH ₂) ₅ COCH ₃	3	93
20	CH ₃ CH ₂ CH ₂ CH ₂ OH	CH ₃ CH ₂ CH ₂ CHO	4	92
21	CH ₃ CH ₂ CH(OH)CH ₃	CH ₃ CH ₂ COCH ₃	3	94

Table 1 Selective oxidation of different types of alcohols in the presence of acetic anhydride/ $K_2Cr_2O_7/H_2SO_4$ -nano silica/wet-SiO₂ (60 %) under solvent-free conditions at room temperature

 a Reaction carried out in a molar ratio of substrate:acetic anhydride: $K_2 Cr_2 O_7$ of 1:1.5:0.2 under solvent-free conditions at room temperature

^b All of the products are known compounds and were identified by comparison of their physical data with those of authentic samples

yield when the reaction was allowed to stir in the presence of acetic anhydride, $K_2Cr_2O_7$, H_2SO_4 -nano silica, and wet-SiO₂ (60 %) under solvent-free conditions at room temperature. No overoxidation to 3-nitrobenzoic acid was observed.

In order to improve the yields, we performed reactions using different quantities of reagents. The best result was obtained using a 1:1.5:0.2 mol ratio of alcohol, acetic anhydride, and $K_2Cr_2O_7$ at 3 min (Table 1).

To illustrate the need for a catalyst, oxidant, and acetic anhydride for this reaction, a series of experiments was carried out. As the first try, in the absence of $K_2Cr_2O_7$, the treatment of 3-nitrobenzyl alcohol with acetic anhydride and H_2SO_4 -nano silica yielded the corresponding 3-nitrobenzyl acetate, which the obtained product did not produce in the main oxidation reaction (Table 1, entry 2). Next, 3-nitrobenzyl acetate was reacted with $K_2Cr_2O_7$ to give the expected product, 3-nitrobenzaldehyde, but the reaction did not occur. This result showed that $K_2Cr_2O_7$ as an oxidant is necessary for the oxidation of alcohols and, in this process,

an ester as an intermediate was not formed. Furthermore, it is noted that, when the reaction of 3-nitrobenzyl alcohol with $K_2Cr_2O_7$ and H_2SO_4 -nano silica in the absence of acetic anhydride was conducted under the same conditions and at 3 min, the expected product was not detected. With continuing the reaction for 60 min, 3-nitrobenzaldehyde was produced in excellent yield (Table 1, entries 3 and 4). It is interesting that, with adding wet-SiO₂ (60 %) to the above reaction mixture, the reaction time decreased to 30 min (Table 1, entry 5). Finally, we examined the effect of different solvents in this reaction. When the reaction was carried out in CH₂Cl₂, good yield was observed at 30 min (Table 1, entry 6). The reaction in acetic acid gave different products, such as 3-nitrobenzyl acetate and 3-nitrobenzyl aldehyde in moderate yields at 30 min (Table 1, entry 7). However, the reaction under solvent-free conditions gave excellent yields at 3 min.

Due to the excellent results obtained, we applied the optimal protocol to various aromatic benzyl alcohols carrying either electron-donating or electron-withdrawing substituents in different positions (*ortho*, *meta*, and *para*). It was observed that the presence of $-OCH_3$ and $-CH_3$ on the phenyl ring increase the time of oxidation (Table 1, entries 11 and 14), whereas $-NO_2$, -Cl, -Br, and -F groups decrease the time of oxidation under the same conditions (Table 1, entries 1, 8–10, 12, and 13). The lower times of electron-withdrawing groups substituted benzyl alcohols in comparison to electron-donating derivatives in this study can be related to the electronic effects of substituents. Another advantage of this procedure is its efficiency for the high yield synthesis of aliphatic aldehydes and ketones from aliphatic alcohols at short times, which normally show very poor yields in traditional oxidation (Table 1, entries 18–21).

Based on previous works [14–16] and our experimental results, a plausible mechanism for the selective oxidation of alcohols is proposed in Scheme 2.



Scheme 2 A plausible mechanism for the selective oxidation of alcohols

Entry	Oxidant	Substrate to oxidant (molar ratio)	Time	Yield (%)	Reference
1	Quinaldinium fluorochromate	1:1.5	2–4 h	74–94	[11]
2	Quinaldinium dichromate	1:1.5	3–4 h	62–77	[11]
3	SSA/sodium dichromate	1:0.35	30 min	70–95	[22]
4	Na ₂ Cr ₂ O ₇	1:3	20-30 min	83–97	[24]
5	N-methyl morpholine chlorochromate	1:1.5	45–55 min	90–96	[13]
6	Cetyltrimethylammonium dichromate	1:17	0.5–6 h	80–100	[12]
7	Quinoxalinium dichromate	1:1.5	2 h	71–92	[23]
9	K ₂ Cr ₂ O ₇ /acetic anhydride	1:0.2	2-5 min	88–96	This work

Table 2 Comparison of the results obtained in this work with other groups

In the presence of H_2SO_4 -nano silica as a catalyst, first, the acetic anhydride (2) is activated to form a protonated intermediate (3). Then, the *O*-nucleophilic dichromate (4) attacks the carbonyl of an intermediate (3) to produce acetic acid and an intermediate (5), which, in turn, affords an intermediate (7) through protonation by H_2SO_4 -nano silica and then Cr–O bond cleavage with the nucleophilic attack of H_2O , respectively. Subsequently, *O*-nucleophilic attack of alcohol on the Cr–OCOCH₃ bond of an intermediate (7) produces an intermediate (8), which follows by proton transfer and Cr–O bond cleavage to yield the corresponding aldehyde and HCrO₃.

In order to show the excellent activity of the introduced oxidizing system, we compared our results (time, yield, and molar ratio of substrate to oxidant) with the results obtained by other reagents [11-13, 23-25] (Table 2). The comparison of results indicated that our oxidizing system oxidized the alcohols in a lower molar ratio of substrate to oxidant, shorter reaction time, and solvent-free conditions than the other reagents, especially in the case of aliphatic alcohols and benzyl alcohols with the electron-withdrawing substituents.

Conclusion

In this study, we have demonstrated, for the first time, the efficiency of the combination of acetic anhydride, H_2SO_4 -nano silica, wet-SiO₂ (60 %), and $K_2Cr_2O_7$ as an oxidizing system for the selective oxidation of different types of alcohols to the corresponding aldehydes and ketones. Mild reaction conditions, high yields of the products, short reaction time, no further oxidation to the corresponding carboxylic acid, and easy work-up make this new system a useful method for oxidizing alcohols.

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References

- 1. H.O. House, Modern Synthetic Reactions, 2nd edn. (W.A. Benjamin, New York, 1972)
- 2. M. Hudlicky, Oxidations in Organic Chemistry (American Chemical Society, Washington DC, 1990)
- 3. J. Luo, F. Peng, H. Yu, H. Wang, Chem. Eng. J. 204, 98 (2012)
- 4. B. Gao, M. Wan, J. Men, Y. Zhang, Appl. Catal. A Gen. 439, 156 (2012)
- 5. X. Wang, G. Wu, N. Guan, L. Li, Appl. Catal. B 115, 41 (2012)
- 6. Y. Leng, J. Wang, P. Jiang, Catal. Commun. 27, 101 (2012)
- 7. J.C. Collins, W.W. Hess, F.J. Frank, Tetrahedron Lett. 9, 3363 (1968)
- 8. K. Bowden, I.M. Heilbron, E.R.H. Jones, B.C.L. Weedon, J. Chem. Soc. 148, 39 (1946)
- 9. S. Goswami, A. Kar, Synth. Commun. 41, 2500 (2011)
- 10. F. Shirini, I. Mohammadpoor-Baltork, Z. Hejazi, P. Heravi, Bull. Korean Chem. Soc. 24, 517 (2003)
- 11. N. Degirmenbasi, B. Ozgun, Monatsh. Chem. 135, 407 (2004)
- 12. S. Patel, M. Kuanar, B.B. Nayak, H. Banichul, B.K. Mishra, Synth. Commun. 35, 1033 (2005)
- 13. S. Chandrappa, M.P. Sadashiva, K.S. Rangappa, Synth. Commun. 38, 2638 (2008)
- 14. Y.H. Song, Synth. Commun. 36, 631 (2006)
- 15. S.V. Khansole, S.B. Patwari, A.Y. Vibhute, Y.B. Vibhute, Chin. Chem. Lett. 20, 256 (2009)
- 16. E.J. Corey, G. Schmidt, Tetrahedron Lett. 20, 399 (1979)
- 17. E.J. Corey, J.W. Suggs, Tetrahedron Lett. 16, 2647 (1975)
- 18. J.C. Collins, W.W. Hess, F.J. Frank, Tetrahedron Lett. 30, 3363 (1968)
- 19. P.J. Gareg, B. Samuelsson, Cabohydr. Res. 67, 267 (1978)
- 20. F. Andersson, B. Samuelsson, Cabohydr. Res. 129, C1 (1984)
- 21. V.K. Rajput, B. Roy, B. Mukhopadhyay, Tetrahedron Lett. 47, 6987 (2006)
- 22. K. Shimizu, E. Hayashi, T. Hatamachi, T. Kodama, Y. Kitayama, Tetrahedron Lett. 45, 5135 (2004)
- 23. B.B. Fatemeh Mirjalili, M.A. Zolfigolb, A. Bamoniric, A. Zareia, J. Chin. Chem. Soc. 51, 509 (2004)
- 24. N. Degirmenbasi, B. Ozgun, Monatsh. Chem. 133, 1417 (2002)
- 25. J.D. Lou, C.L. Gao, Y.C. Ma, L.H. Huang, L. Li, Tetrahedron Lett. 47, 311 (2006)