



Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 4(2), 2008 [125-127]

A convenient method for the rapid oxidation of alcohols to carbonyl compounds by using $\text{CrO}_3/\text{Na}_2\text{CO}_3$ under solvent free conditions

Digambar D.Gaikwad^{1*}, Sayed Abed¹, Babasaheb V.Kendre², Anil W.Vadal²,
Rajendra P.Pawar³, Dipak T.Tayade⁴

¹Dept. of Chemistry, Govt College of Arts And Science, Aurangabad, (INDIA)

²Dept. of Chemistry, Vaidyanath College, Parli Vajinath, (INDIA)

³Dept. of Chemistry, Dnyanopasak College, Parbhani, (INDIA)

⁴Dept. of Chemistry, Mahatma Fule College, Warud Amravati, (INDIA)

E-mail: gaikwad_dd@yahoo.com

Received: 28th December, 2007 ; Accepted: 2nd January, 2008

ABSTRACT

Using CrO_3 supported on anhydrous sodium carbonate the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds are efficiently carried out under solvent free conditions without over oxidation. © 2008 Trade Science Inc. -INDIA

KEYWORDS

Alcohol;
Chromium trioxide;
Sodium carbonate;
Aldehyde;
Ketone etc.

INTRODUCTION

Aldehydes and ketones are very important reactive intermediates and their synthesis by the oxidation of alcohols has gained much importance in recent years [1-3]. Among the transition metal oxidants [4-5], Cr(VI) oxidants are very versatile and efficient. Their use for the conversion of alcohols to carbonyl compounds is well known. Cr(VI) oxidants are highly economical, water soluble, stable and commercially available. Cr(VI) oxidants can act as powerful oxidizing agents in the presence of solvents and in absence of inorganic support, but these oxidants suffer from serious drawbacks during commercial isolation such as toxicity and environmental hazardness [6-7]. In order to overcome these difficulties there is a definite need to develop convenient methods, in which chromium trioxide is used along with some solid support.

Recently, oxidation of alcohols using CrO_3 supported on inorganic solids under solvent free conditions has gained much attention because of the mild reaction conditions, short reaction time, giving high yields of pure products and ecofriendly nature. Oxidizing agents prepared by using CrO_3 supported on Graphite [8], Halosilane [9], Silica gel [10], Aluminum Silicate [11], Kieselguhr [12], Zirconium (IV) Oxide [13] in the presence of solvents have been reported earlier. Microwave assisted oxidation of alcohols to Carbonyl compounds using CrO_3 supported on Wet alumina [14], Wet Silica gel & Zeolite HZSM-5 [15] in solvent less system have been previously reported methods. In super critical Carbon Dioxide [16] reaction medium, the application of CrO_3 supported on SiO_2 has been recently reported. It is observed that in the absence of inorganic support the oxidation reactions under microwave irradiation are sluggish and large amount of starting material remains

Full Paper

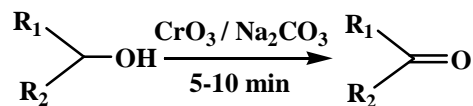
as it is. It is recently reported that the oxidation of alcohols using CrO_3 supported on Copper Sulphate^[17], Sodium Bisulphate^[18] and alumina^[19] under solvent free conditions are quite useful methods for getting pure products.

RESULTS AND DISCUSSION

The above reported methods promote us to synthesize carbonyl compounds using CrO_3 supported on anhydrous Na_2CO_3 under mild reaction conditions. In a mortar with a pestle chromium trioxide supported on sodium carbonate was prepared by simply co-grinding powdered sodium carbonate with CrO_3 for 1 min. in the ratio of 5:1. To the above-prepared reagent an alcohol was added. The mixture was ground with a pestle for 5-minutes at room temperature. The TLC examination of mixture taken after 5-minutes showed the disappearance of the starting material. We tried first the oxidation of benzylalcohol and cyclohexanol to see the feasibility of oxidation by mixing 1 equivalent of alcohols with 2 equivalents of reagent at room temperature. This proportion of alcohol and reagent is necessary for effective oxidation process.

Interesting feature of this reagent was the conversion of benzylalcohol to benzaldehyde without over oxidation to benzoic acid. The oxidation reactions of other alcohols were also carried out and it was found that all the reactions proceeded to completion within 5-10 minutes giving high purity products in good yields. The results obtained are given in TABLE 1. This reported method is rapid, cost effective, highly efficient, facile, mild, completely free from any by products and is environmentally benign. Using this method aliphatic, benzylic and heterocyclic alcohols are converted into corresponding carbonyl compounds in excellent yields under solvent free conditions.

G.Cainelli^[20], reported the oxidation of cyclohexanol and benzylalcohol using CrO_3 supported on anion exchange resin in the presence of solvent. The time required for the completion of reaction was about 2-3 hours when refluxed. In Ji-Dong Lou et al.^[21] method, benzyl alcohol oxidation was carried out in the absence of inorganic support under solvent less conditions at room temperature. The time required was more than 3 hours, while in present method reactions proceed to



Where, R_1 and $\text{R}_2 = \text{H}, \text{Alkyl}$ or Aryl

SCHEME

TABLE 1 : Oxidation of primary and secondary alcohols to carbonyl compounds using CrO_3 supported on Na_2CO_3

Entry	Substrate	Product	M.P. Time Yield		
			/B.P.	$^{\circ}\text{C}$ (Min)	%
1.	1-Butanol	Butanal	76	5	71
2.	1-Heptanol	Heptanal	155	7	72
3.	1-Octanol	Octanal	171	6	72
4.	Benzylalcohol	Benzaldehyde	180	5	85
5.	4-Nitrobenzylalcohol	4-Nitrobenzaldehyde	109	10	92
6.	Cycloheptanol	Cycloheptanone	131	7	75
7.	Cyclobutanol	Cyclobutanone	101	6	80
8.	Cyclohexanol	Cyclohexanone	153	7	90
9.	Benzhydrol	Benzophenone	50	8	90
10.	Hydrobenzoin	Benzoin	136	6	83
11.	Benzoin	Benzil	97	5	80
12.	Menthol	Menthone	208	8	89
13.	4-Methyl Cyclohexanol	4-Methyl Cyclohexanone	172	5	91

completion within 5-10 minutes. This demonstrates the efficiency of this newly prepared reagent.

The work reported here thus provides a rapid, facile, and direct method for the conversion of primary and secondary alcohols to the corresponding carbonyl compounds under solvent free conditions at room temperature.

In conclusion, we have developed a simple environmental conscious method for the synthesis of carbonyl compounds in excellent yields by grinding solid-solid or solid-liquid reactants at solvent free conditions. The short reaction time, mild reaction condition, cheapness and commercial availability of the reagent, cleaner product, easy workup and ecofriendly nature are advantages of this method.

EXPERIMENTAL

Physical constants were determined in open capillaries in paraffin oil bath and are uncorrected. TLC analyses were done using glass plates coated with silica gel-G. ^1H NMR spectra were recorded on Avance 300MHz spectrometer using TMS as internal standard in CDCl_3 solvent. IR spectra were recorded in KBr on a JASCO-FTIR 5300 spectrometer. All the yields re-

fer to isolated products. The products were identified in comparison with the physical constants of authentic samples and ¹HNMR, IR spectral values. Chromium trioxide, sodium carbonate and alcohols were purchased from s. d. Fine chem. Ltd.

Procedure

In a mortar the mixture of Na₂CO₃ (1g) and CrO₃ (0.2g) was taken and ground with a pestle for 1 min. Then Benzylalcohol (1mmol) was added to the above mixture. The reaction mixture was ground for 5 mins. The progress of the reaction was followed by TLC using hexane-ethyl acetate (8:2). The reaction mixture extracted with ether and dried with sodium sulphate. The obtained product was purified by column chromatography.

Yield = 85 %; B.P. =180°C

ACKNOWLEDGMENT

Authors are thankful to the Head, Department of Chemistry & Principal, Vaidyanath College Parli-Vajnath, for providing Laboratory Facilities.

REFERENCES

- [1] H.C.Brown, C.P.Garg, K.T.Liu; J.Org.Chem., **36**, 971, 387 (1971).
- [2] R.C.Larok; Comprehensive Organic Transformations, (1989).
- [3] M.M.Heravi, N.Farhangi, Y.S.Beheshtiha, K. Assadolah, M.Ghassemzadeh, K.Tabar Hydar; Phosphorus, Sulfur and Silicon, **177**, 2883 (2002).
- [4] E.J.Eisenbraun; Org. Synth, **4**, 310 (1973).
- [5] J.Meinwald, J.Crandall, W.E.Hymans; Org.Synth., **45**, 77 (1965).
- [6] M.M.Heravi, R.Kiakojoori, K.Tabar Hydar; J. Chem.Res., 658 (1998).
- [7] D.Y.Cupo, K.E.Wetterhahn; Cancer.Res., **45**, 1146 (1985).
- [8] J.M.Lalancette, G.Rollin, P.Dumas; Can.J.Chem., **50**, 3058 (1972).
- [9] J.M.Aizpuruan, C.Palomo; Tetrahedron Lett, **24**, 4367 (1983).
- [10] E.Santaniello, F.Ponti, A.Manzocchi; Synthesis, 534 (1978).
- [11] J.D.Lou, Y.Wu; Synth Commun, **17**, 1717 (1987).
- [12] J.D.Lou; Synth Commun, **19**, 1841 (1989).
- [13] H.Nakamura, H.Matsushashi; Bull.Chem.Soc.Jpn, **68**, 997 (1995).
- [14] R.S.Varmar, R.K.Saini; Tetrahedron Lett, **39**, 1481 (1998).
- [15] M.M.Heravi, D.Ajami, K.Tabar Hydar, M. Ghassemzadeh; J.Chem.Res., 334 (1999).
- [16] Maria Elena Conzaler Nunez, Rossella Mello, Andrea Olmos, Rafael Acerete, Gregoria Asensia; J. Org.Chem., **71**, 1039 (2006).
- [17] A.R.Kiasat, F.Kazemi, K.Nourbakhsh; Phosphorus, Sulfur and Silicon related, 457 (2004).
- [18] F.Shirini, M.A.Zolfigol, S.Torabi; Letters in Organic Chemistry, **2**, 544 (2005).
- [19] A.R.Kiasat, F.Kazemi, K.Nourbakhsh; Indian J. Chem., **44**, 1524 (2005).
- [20] G.Cainelli, G.Cardillo, M.Orena, S.Sandri; J.Am. Chem.Soc., **98**, 6737 (1976).
- [21] J.D.Lou, Z.N.Xu; Tetrahedron Lett, **43**, 6095 (2002).