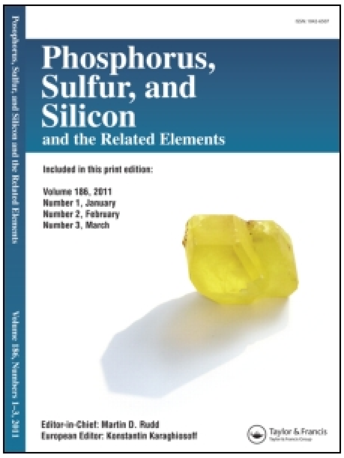



**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# CHROMIUM TRIOXIDE SUPPORTED ONTO COPPER SULFATE AS AN EFFICIENT OXIDIZING AGENT FOR OXIDATION OF ALCOHOLS UNDER SOLVENT FREE CONDITIONS

Ali Reza Kiasat[a]; Foad Kazemi[a]; Kazem Nourbakhsh[a]
[a] Shahid Chamran University, Ahvaz, Iran

Online publication date: 12 August 2010

**To cite this Article** Kiasat, Ali Reza , Kazemi, Foad and Nourbakhsh, Kazem(2004) 'CHROMIUM TRIOXIDE SUPPORTED ONTO COPPER SULFATE AS AN EFFICIENT OXIDIZING AGENT FOR OXIDATION OF ALCOHOLS UNDER SOLVENT FREE CONDITIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 457 — 461

**To link to this Article: DOI:** 10.1080/10426500490262630

**URL:** http://dx.doi.org/10.1080/10426500490262630

*Phosphorus, Sulfur, and Silicon*, 179:457–461, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490262630

# CHROMIUM TRIOXIDE SUPPORTED ONTO COPPER SULFATE AS AN EFFICIENT OXIDIZING AGENT FOR OXIDATION OF ALCOHOLS UNDER SOLVENT FREE CONDITIONS

*Ali Reza Kiasat, Foad Kazemi, and Kazem Nourbakhsh*
*Shahid Chamran University, Ahvaz, Iran*

(Received August 26, 2003)

*Alcohols are rapidly oxidized to carbonyl compounds using $CrO_3$ supported onto $CuSO_4$ under solvent free conditions. Over-oxidation of aldehydes to carboxylic acids and damage to carbon-carbon double bond is not observed by this method.*

*Keywords:* Chromium trioxide; copper sulfate; oxidation; solvent free



The oxidation of alcoholic groups to carbonyl compounds is a fundamental transformation that is encountered at all levels of organic synthesis[1] and, because of its significant role, the development of newer methods is attracting much current interest in spite of the availability of numerous methods reported in the literature.[2,3]

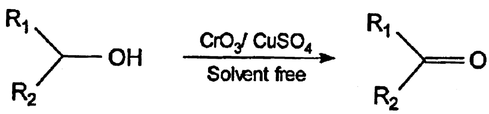
Chromium trioxide, $CrO_3$, based oxidants are one of the most widely used of all oxidizing reagents for this transformation.[4,5] Over the years they have been continually developed and modified to overcome the typical problems that occur during the oxidation and to accept wider ranges of substrates with improved selectivity.[5] A drawback against such oxidants and their use in multistage organic synthesis in spite of their power is their lack of selectivity, for example, overoxidation of aldehydes to carboxylic acids and the degradation of unsaturated substrates are often unavoidable side reactions.[3] Moreover the utility of chromium (VI) reagents in the oxidative transformation is compromised due to their inherent toxicity, cumbersome preparation and potential danger (ignition or explosion) in handling of its complexes, difficulties in terms

Authors acknowledge the partial support of this work by Shahid Chamran Ahvaz University Research Council.

Address correspondence to Ali Reza Kiasat, Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, Iran.

of product isolation and waste disposal.[6] Application of heterogeneous systems especially by introduction of reagents on solid supports and under solvent-free conditions has circumvented some of these problems and provided an attractive alternative in organic synthesis.[7] The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products, and manipulative simplicity.[8,9] Moreover the absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel.

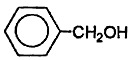
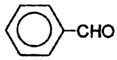
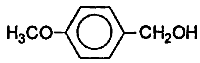
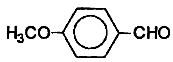
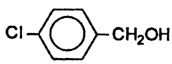
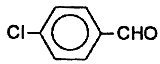
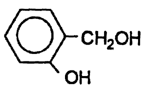
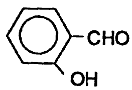
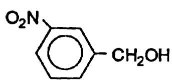
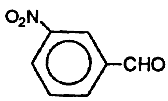
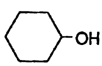
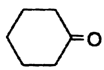
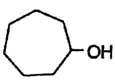
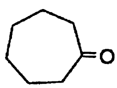
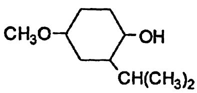
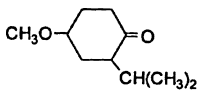
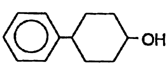
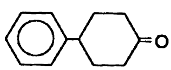
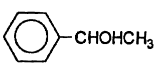
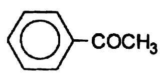
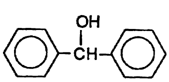
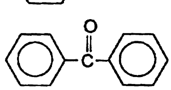
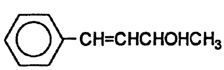
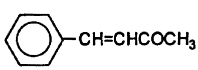
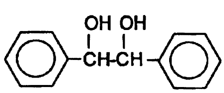
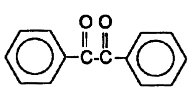
Very recently Heravi et al. have reported that $CrO_3$ supported onto both wet silica gel[3] and Zeolite HZSM-5[10] can be used as oxidizing agents for the oxidation of alcohols to carbonyl compounds under microwave irradiation in solvent less system. They discovered that in the absence of inorganic supports the oxidation reactions under microwave irradiation are sluggish and considerable amounts of starting materials were recovered unchanged. In 2002, a report by Ji-Dong Lou et al.[5] outlined that $CrO_3$ can slowly oxidize primary alcohols to the corresponding aldehydes in solvent free conditions at room temperature. Having the above facts in mind, now we wish to report an extremely convenient method for oxidation of alcoholic groups into their corresponding carbonyl compounds with $CrO_3$ supported onto $CuSO_4$ under solvent free conditions.




Chromium trioxide supported on copper sulfate was prepared by simply cogrinding $CuSO_4$ with $CrO_3$ in the ratio 10:1 (w/w) in an agate mortar. In this simple and efficient method the starting alcohols were converted to the corresponding carbonyl compounds in a mortar with grinding by a pestle in the presence of supported $CrO_3$ on $CuSO_4$. The feasibility of the present oxidation of alcohol was first examined using benzyl alcohol as a model substrate. Thus, benzyl alcohol was thoroughly mixed with 2 equivalent of $CrO_3/CuSO_4$ in a mortar with a pestle and in an ambient air environment at room temperature and benzaldehyde was obtained in 75% yield within 7 min. It is noteworthy that the oxidation did not proceed to completion even after prolonged hours of reaction when less than 2 equivalents of the oxidant were used.

With the first successful result in hand, oxidation of other alcohols with $CrO_3/CuSO_4$ were carried out under similar reaction conditions. The results obtained are presented in Table I. As shown in Table I,

**TABLE I** Conversion of Alcohols to Carbonyl Compounds Using $CrO_3$ Supported onto $CuSO_4$[a]

| Entry | Substrate | Product | Time (min) | Yield[b,c] (%) |
|---|---|---|---|---|
| 1 | $CH_3(CH_2)_5CH_2OH$ | $CH_3(CH_2)_5CHO$ | 7 | 59 |
| 2 | $CH_3(CH_2)_6CH_2OH$ | $CH_3(CH_2)_6CHO$ | 7 | 70 |
| 3 |  |  | 7 | 75 |
| 4 |  |  | 6 | 80 |
| 5 |  |  | 6 | 87 |
| 6 |  |  | 7 | 68 |
| 7 |  |  | 10 | 93 |
| 8 |  |  | 8 | 53 |
| 9 |  |  | 8 | 88 |
| 10 |  |  | 8 | 90 |
| 11 |  |  | 9 | 81 |
| 12 |  |  | 6 | 74 |
| 13 |  |  | 8 | 80 |
| 14 |  |  | 7 | 85 |
| 15 |  |  | 9 | 80 |

[a]Molar ratio of reagent to substrate was 2:1.
[b]Yields refer to pure isolated products.
[c]Products were characterized by comparsion of their physical data, IR, NMR spectra with known samples.

primary and secondary saturated aliphatic, benzylic, and the heterocyclic alcohols were oxidized to the corresponding carbonyl compounds in good to excellent isolated yields with very short times (5–10 min). Overoxidation of primary benzylic alcohols to carboxylic acids, which is common for some other reagents was not observed. One of the interesting properties of this reagent was its ability to convert hydrobenzoin to benzoin contrasting to the results obtained by many other reagents, which cleave the carbon-carbon bond to give the corresponding aldehyde or acid. 4-Phenyl-but-3-en-2-ol as a $\alpha,\beta$-unsaturated alcohol was easily converted to 4-phenyl-but-3-en-2-one in 85% yield showing that carbon-carbon double bonds are not prone to cleavage using this method and no isomerization of double bonds is observed.

The promoting effect of $CuSO_4$ was definitely confirmed by comparing our results with those previously reported by Ji-Dong Lou et al.[5] that applied $CrO_3$ in the absence of inorganic support for the oxidation of primary alcohols to the corresponding aldehydes in solvent free conditions at room temperature. For example, the oxidation of benzyl alcohol with $CrO_3$ was completed under solvent free condition after 3 h, while with $CrO_3/CuSO_4$, the required time for completion of oxidation reaction is 7 min.

The rapid and selective formation of oxidation products demonstrates the efficiency of this new method. The structure of all the products were established from their analytical and spectral (IR, $^1H$ NMR) data and by direct comparison with authentic samples.

In conclusion, oxidation of primary and secondary alcohols with $CrO_3/CuSO_4$ in solvent-free conditions is a rapid, manipulatively simple, selective, and environmentally friendly protocol when compared to the conventional solution phase or heterogeneous condition, and should have utility in contemporary organic synthesis.



## EXPERIMENTAL

### General

Alcohols, $CrO_3$, and $CuSO_4$ were purchased from Fluka and Merck. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates.

### General Procedure for the Oxidation of Alcohols Using $CuSO_4/CrO_3$

$CuSO_4$ (2 g) and $CrO_3$ (0.2 g, 2 mmol) were crushed together in a mortar so as to form an intimate mixture. A neat alcohol (1 mmol) and two drops of t-BuOH were added to this mixture. The reaction mixture was ground for the time specified in the Table I. The progress of reaction was monitored by TLC using ether-$CCl_4$. Then the reaction mixture was poured into a mixture of ether (20 ml) and water (10 ml). The organic layer was passed through a small bed of alumina and evaporated to dryness using a rotary evaporator to give the pure corresponding carbonyl compound (Table I). (Caution: Chromium is listed by the Environmental Protection Agency as one of 129 priority pollutants. $CrO_3$ is a highly toxic agent. All chromium (VI) reagents must be handled with care. The mutagenicity of chromium (VI) compounds is well documented.[11]

## REFERENCES


[1] a) R. C. Larock, *Comprehensive Organic Transformations* (VCH, Weinheim, 1989); b) M. Hudlicky, *Oxidation in Organic Chemistry* (ACS Manograph 86, American Chemical Society, Washington DC, 1990).

[2] R. S. Varma and R. K. Saini, *Tetrahedron Lett.*, **39,** 1481 (1988).

[3] M. M. Heravi, N. Farhangi, Y. S. Beheshtiha, K. Assadolah, M. Ghassemzadeh, and K. Tabar-hydar, *Phosphorus, Sulfur and Silicon*, **177,** 2883 (2002).

[4] S. V. Ley, A. Madin, *In Comperehensive Organic Stnthesis*, edited by B. M. Trost and I. Fleming. (Pergamon Press, London, 1991), Vol. 7, p. 251.

[5] J. D. Lou and Z. N. Xu, *Tetrahedron Lett.*, **43,** 6095 (2002).

[6] M. M. Heravi, R. Kiakojoori, and K. Tabar-Hydar, *J. Chem. Research*, 658 (1998).

[7] D. Laszlo, ed., *Preparative Chemistry Using Supported Reagents*, (Academic Press, San Diego, 1987).

[8] M. Balogh and P. Laszlo, *Organic Chemistry Using Clays* (Springer Verlag, Berlin, 1993).

[9] M. M. Heravi, N. Farhangi, Y. S. Beheshtiha, K. Assadolah, M. Ghassemzadeh, and K. Tabar-hydar, *Phosphorus, Sulfur and Silicon*, **177,** 2843 (2002).

[10] M. M. Heravi, D. Ajami, K. Tabar-Hydar, and M. Ghassemzadeh, *J. Chem. Research*, 334 (1999).

[11] D. Y. Cupo and K. E. Wetterhahn, *Cancer Res.*, **45,** 1146 (1985).