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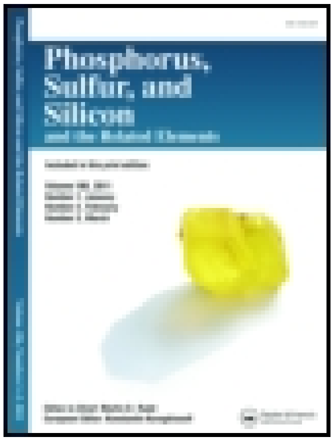

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Chromium Trioxide Supported onto Wet Silica Gel: Rapid Oxidation of Alcohols to Carbonyl Compounds Under Microwave Irradiation in Solventless System

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Published online: 27 Oct 2010.

To cite this article: Majid M. Heravi , Nasrin Farhangi , Yahya Sh. Beheshtiha , Karim Assadolah , Mitra Ghassemzadeh & Koroush Tabar-Hydar (2002) Chromium Trioxide Supported onto Wet Silica Gel: Rapid Oxidation of Alcohols to Carbonyl Compounds Under Microwave Irradiation in Solventless System, Phosphorus, Sulfur, and Silicon and the Related Elements, 177:12, 2883-2885, DOI: 10.1080/10426500214883

To link to this article: http://dx.doi.org/10.1080/10426500214883

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Phosphorus, Sulfur and Silicon, 2002, Vol. 177:2883–2885
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1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290146929

CHROMIUM TRIOXIDE SUPPORTED ONTO WET SILICA GEL: RAPID OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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(Received April 4, 2002)

In an environmentally benign system, alcohols are rapidly oxidized to carbonyl compounds using CrO_3 supported onto wet silica gel as an oxidant under microwave irradiation.

Keywords: Carbonyl compounds; chromium trioxide; oxidation of alcohols; silica gel

The oxidation of alcohols to carbonyl compounds is an important transformation in organic chemistry attracting much interest.[1–3] Although a large number of methods are known in the literature for such a transformation, there still appears a need either to improve the existing oxidation methods[4] or to introduce newer reagents to permit better selectivity under milder conditions and with easy work-up procedures.[5]

Chromium based reagents have been used extensively in organic synthesis.[6] A drawback against such oxidants and their use in multistage organic synthesis in spite of their power is their lake of selectivity, for example, overoxidation of aldehydes to carboxylic acids and the degradation of unsaturated substrates are often unavoidable side reactions. Moreover oxidants based on chromium are corrosive and they are irritants for the skin and for sensitive parts of the body such as eyes.[7] Introduction of reagents on solid supports have shown some of

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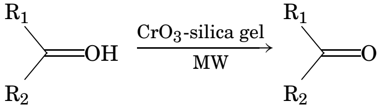
TABLE I Oxidation of Alcohols Using CrO_3/Wet Silica Gel under Microwave Irradiation in Solvent-Free Conditions



Entry	Substrate	Time (sec)	Product	Yield[a] (%)
1	Benzylalcohol	60	Benzaldehyde	96
2	2-Nitrobenzylalcohol	60	2-Nitrobenzaldehyde	98
3	2-Methylbenzylalcohol	120	2-Methylbenzaldehyde	98
4	Benzohydrol	60	Benzophenone	98
5	Cinnamylalcohol	180	Cinnamaldehyde	70
6	Cyclohexanol	120	Cyclohexanone	98
7	n-Amylalcohol	180	n-Amylaldehyde	96
8	Iso-Amylalcohol	180	Iso-Amylaldehyde	96

[a] Unoptimized yields of isolated products that exhibited physical and spectral properties in accur with the assigned structure.

these problems, but still affords an attractive route in organic synthesis in view of the selectivity and associated ease of manipulation.[8] In continuation of our investigations on organic reactions in solventless systems under microwave irradiation, we report an efficient and rapid oxidation of alcohols to the corresponding carbonyl compounds using CrO_3-wet silica gel under microwave irradiation in a solventless system.

The reaction is conducted by mixing finely ground wet silica gel-chromium (VI) oxide with neat alcohols and exposed the mixture on microwave irradiation for a very short time (Table I). We discovered that in the absence of wet silica gel the reactions do not proceed and in the presence of dry silica gel the reactions are sluggish and considerable amounts of alcohols are recovered unchanged even after reaction for extended periods of time. The reactions are relatively clean with no tar formation which is typical for many chromium trioxide oxidations. Interestingly, no overoxidation to carboxylic acids was observed.

The oxidation of cinnamyl alcohol with this method gave a moderate yield of cinnamaldehyde (70%) and benzaldehyde (30%) showing the carbon-carbon bonds are prone to cleavage by this procedure.

In conclusion, this communication affords a valuable extension of the use of chromium trioxide as oxidant. High yields, very short reaction time, easy work-up procedure, and solventless conditions are advantages of this methodology.

EXPERIMENTAL SECTION

All oxidation products are known compounds. They were identified by their physical and spectroscopic data.

Wet Silica Gel Supported Chromium (VI) Oxide

Silica gel (10 g, Aldrich Brockmann 60) was shaken with distilled water (2 mL). This mixture (2.4 g) was mixed with chromium trioxide (0.8 g, 8 mmol) using a pistle and mortar.

Oxidation of Alcohols to Carbonyl Compounds

General Procedure

In a beaker, neat alcohol (1 mmol) was mixed with the above catalyst (1 mmol). An exothermic reaction started with darkening of the orange color of the reagents. The completion of the reaction was confirmed by TLC (hexane: EtOAc; 8:2). The product was extracted with CH_2Cl_2 and was passed through a small bed of alumina (1 cm) to afford the corresponding carbonyl compound (Table I). (*Caution*: Although this reaction worked safely in our hand, using an efficient hood is strongly recommended.)

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