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Wet Alumina Supported Chromium(VI) oxide: Selective Oxidation of Alcohols in Solventless System

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Abstract: A simple and selective method for the oxidation of alcohols to carbonyl compounds is described that occurs on wet alumina supported chromium(VI) oxide under solvent-free conditions and is expedited by microwave irradiation. Aliphatic primary alcohols provide the corresponding esters in moderate yield.

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Chromium based reagents have been extensively used in organic synthesis.[1] 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 of product isolation and waste disposal. Introduction of reagents[2] on solid supports has circumvented some of these problems and provided an attractive alternative in organic synthesis in view of the selectivity and associated ease of manipulation. Therefore, it is not surprising that a large number of chromium(VI)-based oxidants impregnated on solid support have been explored.[3a-i] Chromium trioxide (CrO_3) in the presence of wet aluminum oxide and in an aprotic solvent oxidizes secondary and aromatic alcohols.[4a-b] However, these reactions, under inert atmosphere, require 15-24 h for completion. In a heterogeneous environment, CrO_3-silica selectively oxidizes alcohols,[4c] but the prior drying of the reagent for 4 h is required and the yields are low. Consequently, there is scope for the development of rapid and solventless methods that have manipulative advantages over heterogeneous reactions.

In continuation of our investigations on organic reactions in solventless systems,[5] we now report a facile and selective oxidation of alcohols to carbonyl compounds using CrO_3-wet alumina under solvent-free conditions that is accelerated, in some cases, by exposure to microwaves (MW). The reaction is conducted by mixing finely-ground wet alumina chromium(VI) trioxide with neat alcohols. We discovered that in the absence of wet alumina the reactions are slow and considerable amount of alcohols are recovered unchanged in reactions at room temperature or even upon irradiation to microwaves for an extended period of time. As an example, the reaction of 4-methylbenzyl alcohol with dry alumina-CrO_3 results in the formation of only 30% 4-methylbenzaldehyde whereas the yield increases to 83% in the case of premoistened reagent.

In most cases, the reactions are completed upon simple mixing; gentle warming by microwaves accelerates[5] some others (Table). The reactions are relatively clean with no tar formation, typical of many CrO_3 oxidations. Interestingly, no overoxidation to carboxylic acids is observed (entries 1-4). The oxidation of primary aliphatic alcohols, however, does not proceed to desired aldehydes; esters are readily obtained in moderate yields e.g. hexyl alcohol affords only hexyl hexanoate in 52% yield. The stabilization of the inorganic anhydride species[3j] on alumina surface and their thermal activation may be responsible for this facile oxidation.

The oxidation of benzyl alcohol is representative of general procedure employed. Wet-alumina is prepared by shaking neutral aluminum oxide (10 g, Aldrich, Brockmann I, ~150 mesh) with distilled water (2 mL). The reagent is prepared by mixing CrO_3 (0.8 g, 8 mmol) with wet-alumina (2.4 g) using a pastle and mortar. This reagent is gradually added to the benzyl alcohol (0.432 g, 4 mmol) and mixed with a spatula. An exothermic reaction ensues with darkening of the orange color of the reagent and is completed almost immediately as confirmed by TLC (hexane:AcOEt, 8:2). The product is extracted into methylene chloride (2x25 mL) and is passed through a small bed of alumina (1 cm) to afford pure benzaldehyde. In some cases, brief microwave irradiation (inside an alumina bath in an unmodified household microwave oven) completes the reaction.[5n,o]

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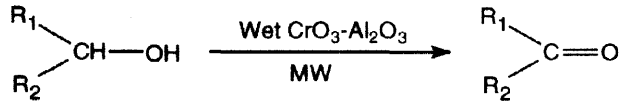

Table: Oxidation of alcohols with wet alumina supported chromium(VI) oxide

Entry	R_1	R_2	Mole ratio CrO_3/alcohol	Time (sec)	Yield (%)[a]
1.	C_6H_5	H	2.0	-	76
2.	4-Me-C_6H_4	H	2.0	-	83
3.	4-MeO-C_6H_4	H	2.0	-	80
4.	4-NO_2-C_6H_4	H	2.0	40	76
5.	C_6H_5	C_6H_5	2.0	35	87
6.	C_6H_5	CH_3	2.0	-	84
7.	C_6H_5CO	C_6H_5	3.0	30	72
8.			2.0	40	90
9.			2.0	-	87

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

In conclusion, oxidation with CrO_3-wet alumina under solvent-free conditions is a rapid, manipulatively simple and selective protocol when compared to the conventional solution phase or heterogeneous reactions.

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