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Selective solvent-free oxidation of alcohols with potassium dichromate

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Abstract—Selective oxidation of primary alcohols to the corresponding aldehydes by potassium dichromate at room temperature under solvent-free conditions are described. This new procedure can also oxidise secondary alcohols. © 2002 Elsevier Science Ltd. All rights reserved.

The oxidation of primary alcohols to the corresponding aldehydes has been accomplished with large number of hexavalent chromium compounds.[1–4]

Potassium dichromate ($K_2Cr_2O_7$), a readily available and inexpensive reagent, has for some times been used as an oxidant in this reaction. Unfortunately, the traditional $K_2Cr_2O_7$ oxidation methods in this transformation are limited by performing in acidic aqueous solution. Under the reaction condition, the oxidising reagent can further oxidise the aldehyde to the acid, since in an aqueous medium, the aldehyde product can be hydrated to the geminal diol, which is further oxidised. Therefore, to isolate the aldehyde, it should be continuously removed as it is formed, usually by distillation. This technique can be used successfully only with relatively volatile aldehydes, and yields are moderate. In addition, under acidic medium, the aldehyde product and unreacted alcohol react to give a hemiacetal that is rapidly oxidised to an ester. Since oxidation with $K_2Cr_2O_7$ under anhydrous neutral media would appear to be a way to circumvent the overoxidation and the ester formation, in recent years the traditional $K_2Cr_2O_7$ oxidation has been modified. Improved $K_2Cr_2O_7$ oxidation methods, such as oxidation under phase-transfer catalysis,[5] oxidation with supported reagents,[6,7] and oxidation in polar aprotic media,[8,9] have been developed that allow the reaction to be conducted in organic media and under neutral conditions. Most of existing $K_2Cr_2O_7$ oxidations are performed at temperatures above ambient.

We now report here that the oxidation of primary alcohols with $K_2Cr_2O_7$ at room temperature under solvent-free conditions is a new system that offers a very simple and efficient selective oxidation method for the preparation of aldehydes. In the present method, overoxidation and formation of an ester can be prevented by the use of solvent-free conditions under which the aldehyde produced is stable. On the other hand, in comparison with the methods described above, the advantages of the present method are that it does not require the use of phase-transfer catalysis, the preparation of supported reagents, the usage of expensive polar aprotic solvents, and therefore it offers special promise for the preparation of aldehydes by the oxidation of alcohols into aldehydes. In addition, the present method can also successfully oxidise secondary alcohols to the corresponding ketones.

In the present experiments, commercial $K_2Cr_2O_7$ with grinding to a fine power and a 1:1 molar ratio of $K_2Cr_2O_7$:substrate is employed. First, the oxidant is carefully added to the substrate and the mixture is stirred magnetically at room temperature until TLC analysis indicates a completed reaction. In general, the oxidations are complete within 5 h. The reaction mixture is then worked up by dilution with dichloromethane or diethyl ether and filtration. Distillation of the solvent gives a product that is of acceptable purity for most purposes. For solid substrates, the best method for doing this oxidation is first to dissolve them with a minimum amount of dichloromethane or diethyl

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Keywords: selective oxidation; alcohols; aldehydes; ketones; potassium dichromate; solvent-free.

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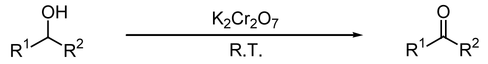
Table 1. Solvent-free potassium dichromate oxidations



Substrate	Reaction time (h)	Product[a]	Yield (%)
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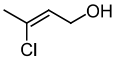
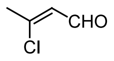
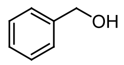
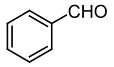
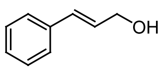
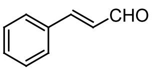
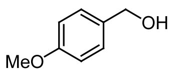
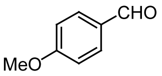
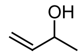
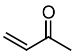
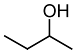
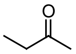
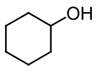
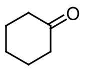
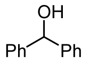
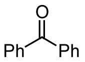
	3		85
	4		80
	3		92
	4		90
	3		82
	4		75
	4		80
	3		95

[a] All the aldehydes and ketones have been described previously in the literature and were identified by their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones.

ether at room temperature and then to perform the reaction. The results, which are shown in Table 1, show that the method is generally applicable to a wide range of alcohols, and gives the corresponding products in good yields.

In conclusion, this solvent-free oxidation of alcohols using $K_2Cr_2O_7$ as an oxidant at room temperature is a new and efficient method for the preparation of the corresponding aldehydes and ketones.

Caution: $K_2Cr_2O_7$ is a toxic agent. All chromium(VI) reagents must be handled with care. The mutagenicity of chromium(VI) compounds is well documented.[10] We have worked with quantities of 0.5–1 g of alcohols. Any mixture of potassium dichromate and an organic substance must be viewed as potentially unstable. Special care must always be exercised in adding $K_2Cr_2O_7$ to organic media.

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