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Shaken not stirred; oxidation of alcohols with sodium dichromate

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Abstract—Efficient and selective oxidation of primary alcohols to the corresponding aldehydes with sodium dichromate at room temperature under solvent-free conditions by shaking is described. This new procedure can also successfully oxidise secondary alcohols.

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1. Introduction

The oxidation of alcohols to the carbonyl compounds is an important reaction in synthetic organic chemistry. Sodium dichromate dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$), an oxidising agent used in organic chemistry for over a century, is one of the most versatile and vigorous of the commonly used oxidants for the above transformation.[1–4]

Over the years, sodium dichromate dihydrate has been continually developed and modified to overcome the typical problems that occur for the reactions, for example, especially to overoxidation that exist during the selective preparation of aldehydes from the corresponding alcohols.

2. Results and discussion

Sodium dichromate in aqueous sulfuric acid under rather vigorous conditions (high temperature and/or an aqueous strongly acidic environment) is used for a variety of oxidations including some primary alcohols to aldehydes[5] and secondary alcohols to ketones. Acidic dichromate is not a generally useful reagent for the oxidation of primary alcohols. 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. To avoid further oxidation to the corresponding acid, the aldehyde has to be removed as rapidly as possible, for example, by distillation through a fractionating column. In addition, under acidic medium, the aldehyde product and unreacted alcohol react to give a hemiacetal that is rapidly oxidised to an ester. The most important problem in sodium dichromate dihydrate oxidations is that overoxidation can occur during the reaction process. In an attempt to circumvent this problem the main trend has been to develop the use of non-aqueous complexes, for instance, the Collins reagent[6] [$(C_5H_5N)_2CrO_3$], pyridinium chlorochromate[7] [PCC, $(C_5H_5NH)ClCrO_3$] and pyridinium dichromate[8] [PDC, $(C_5H_5NH)_2{}^+Cr_2O_7{}^{2-}$]. The latter two are currently the reagents of choice, particularly for the oxidation of α,β-unsaturated primary and secondary alcohols to the corresponding unsaturated aldehydes and ketones. Furthermore, most of improved $Na_2Cr_2O_7$-based oxidants previously reported are performed at vigorous conditions.[9,10]

We now report here that the oxidation of primary alcohols with $Na_2Cr_2O_7$ at room temperature under solvent-free conditions[11] by shaking, is a new system that offers a very simple, efficient, and 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

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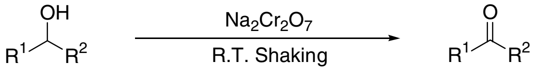
comparison with the complexes described above, the main advantage of the present method is that no preparation of the complexes is needed. Convenient operation, high yield, and simple work-up are additional benefits of the present method. In addition, the shaking machine is first employed for this reaction, which is very easy for performance. We find that shaking is much more effective than using a stirrer for this kind of reactions. For example, some other previously reported chromium(VI) oxidation methods, sometimes, are needed to be heated and/or with a long reaction time.[1] In the present work, heating is unnecessary and the reaction time is quite short. The present method is the first letter to report using shaking in oxidations of alcohols under solvent-free conditions. It offers special promise for the preparation of aldehydes by the oxidation of alcohols, but can be also successfully employed in the oxidation of secondary alcohols to the corresponding ketones.



In the present procedure, commercial $Na_2Cr_2O_7$ by grinding to a fine power and a 1:1 molar ratio of $Na_2Cr_2O_7$ to substrate are employed with shaking machine at room temperature for the oxidation. The reaction progress is monitored by TLC. In general, the oxidations are complete within 30 min. The product is of acceptable purity for most purposes. 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 high yield.

In conclusion, this solvent-free oxidation of alcohols using $Na_2Cr_2O_7$ as an oxidant at room temperature by shaking is a new and efficient method for the preparation of the corresponding aldehydes and ketones.

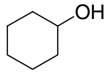
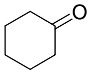
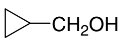
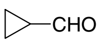
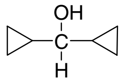
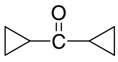
3. Experimental

Oxidation of benzyl alcohol to benzaldehyde. Typical procedure: a mixture of benzyl alcohol (108 mg, 1 mmol) and $Na_2Cr_2O_7{\cdot}2H_2O$ (298 mg, 1 mmol; finely and carefully to grind into around 200–300 mesh in advance) in a normal test tube is shaken mechanically (Oscillation frequency: 220 times per minute; Horizontal oscillator, Model: HY-2, Zhengji Instrument Co. Ltd) at room temperature for 20 min. The progress of the reaction is monitored by TLC (plates: aluminium-backed silica gel Merck 60 GF_{254}) using hexane–ethyl acetate (8:2) as eluent. The reaction mixture is then washed with dichloromethane (3 × 5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane–ethyl acetate (8:2) to afford 103 mg (97%) benzaldehyde.

4. Note

This oxidation is exothermic, and precautions should be taken to avoid it running amuck. Even though we have

Table 1. Solvent-free sodium dichromate oxidations by shaking

Substrate[a]	Scale (mg/mmol)	Reaction time (min)	Product[b]	Yield[c] (%)	Bp (°C/mm)		Mp (°C) of 2,4-DNP	
					Found	Reported[13]	Found	Reported[13]
n-$CH_3(CH_2)_4CH_2OH$	306/3	30	n-$CH_3(CH_2)_4CHO$	83	130–131/760	131	104–105	104
$CH_3CCl{=}CHCH_2OH$	320/3	20	$CH_3CCl{=}CHCHO$	91	34–35/10	145[14]	130	129–130[14]
$PhCH_2OH$	108/1	20	PhCHO	97	57–58/10	178–179	238–239	237
$PhCH{=}CHCH_2OH$	134/1	20	$PhCH{=}CHCHO$	95	121–122/10	248	255–257	255
p-H_3CO–C_6H_4–CH_2OH	138/1	20	p-H_3CO–C_6H_4–CHO	95	122–123/10	248	252–254	254
$CH_2{=}CHCH(OH)CH_3$	144/2	20	$CH_2{=}CHC(O)CH_3$	87[d]			140–141	139.5–140.5
$CH_3CH_2CH(OH)CH_3$	222/3	30	$CH_3CH_2C(O)CH_3$	90	79–80/760	80	113–115	115
	501/5	30		95	153–155/760	155	161–162	161–162
PhCH(OH)Ph	184/1	20	PhC(O)Ph	97	117–118/0.9	305	48–49.5[e]	48–49[e]
$PhCH(OH)COOC_2H_5$	180/1	20	$PhCOCOOC_2H_5$	95	127–129/10	130/10		
$C_{15}H_{31}CH(OH)CH_2COOC_2H_5$	329/1	30	$C_{15}H_{31}COCH_2COOC_2H_5$	90			36–38[f]	37–38[f]
$PhCH(OH)CH_2OH$	138/1	20	$PhCOCH_2OH$	93	110–113/10	118–120/11	233–234	233–236
	216/3	30		89	106–109/760	97–100/740	185–186	182–185
	336/3	30		96	60–63/10	162.5–163	192–194	193–194

[a] All the substrates are commercially available.

[b] 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.

[c] Yield of isolated product.

[d] Isolated as the 2,4-dinitrophenylhydrazone.

[e] Mp of benzophenone.

[f] Mp of ethyl 3-oxooctadecylate.

run each reaction at least three times on the amounts ranging from 100 to 1000 mg in high yields without encountering any problem, we nevertheless advise that any user should certainly never run on a large scale. Sodium dichromate dihydrate is a highly toxic agent. All chromium(VI) reagents must be handled with care. The mutagenicity of chromium(VI) compounds is well documented.[12] Special care must always be exercised in adding sodium dichromate dihydrate to organic media.

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