A New Procedure for the Preparation of Aldehydes and Ketones by the Oxidation of Primary and Secondary Alcohols with Potassium Dichromate in a Neutral Benzene–Water System†

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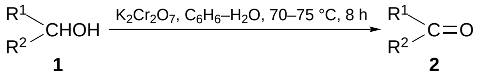
A new and convenient procedure for the preparation of aldehydes and ketones by the oxidation of the corresponding primary and secondary alcohols with potassium dichromate in a neutral benzene–water system is described.

The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is one of the most important reactions in organic chemistry. Potassium dichromate ($K_2Cr_2O_7$), a readily available and inexpensive reagent, has for some time been used as an oxidant in this reaction. Unfortunately, the traditional $K_2Cr_2O_7$ oxidation methods in this transformation are limited by the very low solubility of $K_2Cr_2O_7$ in most organic solvents and by the oxidation procedure occurring only under acidic conditions.[1–5] In order to overcome these limitations, milder $K_2Cr_2O_7$ oxidation methods, such as oxidation under phase-transfer catalysis,[6] oxidation with supported reagents[7–9] and oxidation in polar aprotic media,[10] have been developed that allow the reaction to be conducted in organic media and under neutral conditions. However, even these improved methods possess disadvantages, *e.g.*, the need to use phase-transfer catalysts, the difficulty of preparing the supported reagents, or the use of expensive polar aprotic solvents.

We report here a new and convenient procedure for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with $K_2Cr_2O_7$ in a benzene–water system under neutral conditions. The present method is simpler and more convenient than all the previously improved methods described above, and thus it offers special promise for the oxidation of alcohols with $K_2Cr_2O_7$ under more usual oxidation conditions.

The procedure involves addition of a solution of $K_2Cr_2O_7$ in water over 30 min to a stirred solution of the alcohol **1** in benzene‡ at about 70–75 °C. After 8 h the benzene layer is separated and the product **2** is isolated. The experimental results are summarized in Table 1.



1,**2**	R^1	R^2
a	$CH_3CCl{=}CH$	H
b	Ph	H
c	*p*-$MeOC_6H_4$	H
d	$PhCH{=}CH$	H
e	Et	Me
f	Ph	Ph

Table 1 Oxidation of alcohols **1**

Substrate	Product[a]	Yield (%)[b]
1a	**2a**	92
1b	**2b**	86
1c	**2c**	86
1d	**2d**	90[c]
1e	**2e**	68[c]
1f	**2f**	90[c]

[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. [b]Distilled product. [c]Isolated as the 2,4-dinitrophenylhydrazone.

Experimental

Typical Procedure: Oxidation of Benzyl Alcohol.—Benzene (100 ml), benzyl alcohol (**1b**) (10.8 g, 0.1 mol) and water (20 ml) were placed in a flask fitted with a condenser, the mixture was stirred with an electromagnetic stirrer and a solution of potassium dichromate ($K_2Cr_2O_7$) (29.4 g, 0.1 mol) in water (100 ml) was added over 30 min at 70–75 °C. After the reaction mixture had been maintained between 70 and 75 °C with stirring for a further 8 h, the organic phase was separated. The aqueous phase was extracted with benzene (3 × 20 ml) and the extracts were added to the organic phase. The combined organic extracts were washed sequentially with water, saturated sodium hydrogen carbonate solution and water, and dried with magnesium sulfate, and were then distilled through a short Vigreux column to give benzaldehyde (**2b**) (9.1 g, 86%).

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References

1 L. T. Sandborn, *Org. Synth.*, 1941, Coll. Vol. 1, 340.
2 L. F. Fieser, *Org. Synth.*, 1941, Coll. Vol. 1, 383.
3 C. D. Hurd and R. N. Meinert, *Org. Synth.*, 1943, Coll. Vol. 2, 541.
4 D. Pletcher and S. J. D. Taid, *Tetrahedron Lett.*, 1978, 1601.
5 L. Lombardo, *Org. Synth.*, 1987, **65**, 81.
6 R. O. Hutchins, N. R. Natale and W. J. Cook, *Tetrahedron Lett.*, 1977, 4167.
7 E. Santaniello and P. Ferraboschi, *Nouv. J. Chim.*, 1980, **4**, 279.
8 T. Tatsumi, H. Ohta and H. Tominaga, *Nippon Kagaku Kaishi*, 1988, 1759 (*Chem. Abstr.*, 1989, **110**, 191884p).
9 M. S. Climent, J. M. Marinas and J. V. Sinisterra, *React. Kinet. Catal. Lett.*, 1989, **38**, 13 (*Chem. Abstr.*, 1989, **111**, 56795r).
10 E. Santaniello, P. Ferraboschi and P. Sozzani, *Synthesis*, 1980, 646.
11 S. Budavari, *The Merck Index*, Merck & Co., Rahway, N.J., 11th edn., 1989, p. 166.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡**NB**. In view of the health and safety hazards of using benzene,[11] we have recently investigated, and now recommend, the use of toluene in place of benzene in this two-phase oxidation reaction.