Tetrahedron Letters No. 18, pp 1601 - 1602, 1978. 0040-4039/78/0429-1601. $02.00/0.

A PROCEDURE FOR THE OXIDATION OF ALCOHOLS TO ALDEHYDES BASED ON PHASE TRANSFER CATALYSIS

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(Received in UK 10 March 1978; accepted for publication 17 March 1978)

A recurring problem in synthesis has been the low selectivity of the methods available for the oxidation of alcohols to aldehydes. As a result a number of sophisticated procedures have been developed (for example those based on dimethylsulphoxide[1,2], chromium trioxide[3,4,5] or ruthenium tetroxide[6]) but none are totally satisfactory. This paper describes a method using potassium dichromate and a phase transfer catalyst which is generally applicable to acid stable alcohols and which is both simple and rapid. Indeed the oxidation can be carried out in a few seconds in a separating funnel and the work up is straightforward.

The alcohol (10 mmol) in 25 cm^3 of methylene chloride was shaken briefly with the stoichiometric amount of potassium dichromate (3.3 mmol) in 25 cm^3 of 9M sulphuric acid after the addition of tetrabutylammonium bisulphate (0.9 mmol). The methylene chloride phase was allowed to separate from the aqueous chromic sulphate solution and the aldehyde content determined by g.l.c. and n.m.r..

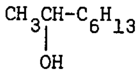
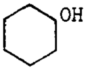
The yields of aldehyde from twelve primary alcohols and of ketones from two secondary alcohols are reported in the table. The yields are sensitive to the amount of dichromate used; while a large excess could never be tolerated, the stoichiometric quantity is not necessarily the optimum and it was sometimes advantageous to have a slight excess present (see the table).

With many alcohols the yield of aldehyde or ketone compares favourably with other procedures. The exceptions were (a) the water soluble smaller aliphatic alcohols (b) p-methoxybenzyl alcohol which was not stable to the acid under the reaction conditions (c) cinnamyl alcohol where the double bond appeared to be oxidised. In contrast, the alcohol with the isolated double bond, ω-undecylenyl alcohol, gave a good yield of the expected aldehyde and no attack on the double bond was apparent.

It should be noted that each mol of dichromate oxidises three mols of alcohol and thus the mechanism probably involves disproportionation of Cr^V or Cr^{IV} species. Indeed in the absence of concentrated acid the chromium percipitates as a mixed valence oxyspecies and one advantage of the conditions described is that the reaction is clean and easily worked up since the chromium ends up as chromic sulphate in solution in the aqueous acid. The second advantage of using highly acidic aqueous phase is the rate of the reaction. With 9M sulphuric acid the reactions are over in a few seconds at room temperature and it is possible to oxidise totally unactivated alcohols but with neutral dichromate the oxidation of benzyl alcohol takes 15 hours at 55°C and aliphatic alcohols give only low conversions to aldehydes[7]. Intermediate acidity conditions may allow the conversion to aldehydes of alcohols which were sensitive to the conditions employed here.

In the absence of an alcohol, the methylene chloride phase becomes strongly orange-yellow when shaken with acid dichromate but only after addition of the tetrabutylammonium ion. Certainly the alcohols are only oxidised in the presence of tetrabutylammonium ion and this confirms that the reaction between the alcohol and dichromate occurs in the organic phase; thus this is a further example of an oxidation reaction occurring by phase transfer catalysis[7,8,9].

TABLE

Alcohol	Yield[a] Aldehyde	Alcohol	Yield[a] Aldehyde/ Ketone
$C_6H_5CH_2OH$	92	C_2H_5OH	5
$p\text{-}CH_3\text{-}C_6H_4CH_2OH$	95	$1\text{-}C_4H_9OH$	34
$p\text{-}NO_2C_6H_4CH_2OH$	55	$1\text{-}C_8H_{17}OH$	82
$p\text{-}CH_3O\text{-}C_6H_4CH_2OH$	1	$1\text{-}C_{16}H_{33}OH$	90
$C_6H_5CH_2CH_2OH$	62	$CH_2{=}CH\text{-}(CH_2)_9$	95
	91*		
$C_6H_5CH_2CH_2CH_2OH$	80	 $CH_3CH(OH)\text{-}C_6H_{13}$	95
	90*		
$C_6H_5CH{=}CHCH_2OH$	0		65

a. determined by g.l.c. and checked by n.m.r. using the aldehyde absorption.

* reaction carried out with 4.1 mmol $K_2Cr_2O_7$

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