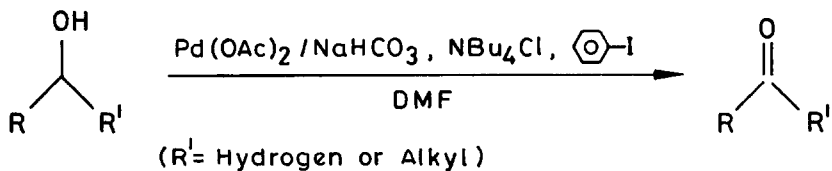


PALLADIUM CATALYSED OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS UNDER
SOLID-LIQUID PHASE TRANSFER CONDITIONS

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Summary: Palladium acetate catalysed the oxidation of primary and secondary alcohols to aldehydes and ketones respectively at room temperature and atmospheric pressure under solid-liquid phase transfer conditions.

Heck-type reaction is reported for vinylation of organic halides¹ and vinylic halides² under solid-liquid phase transfer conditions at room temperature. Yoshida³ reported the oxidation of secondary alcohols to ketones with Pd(PPh₃)₄ in presence of bromobenzene at 100°C. We now report the first instance of a solid-liquid phase transfer catalytic system that oxidises both primary and secondary alcohols in good yields at room temperature and atmospheric pressure using palladium acetate as catalyst, tetrabutylammonium chloride as phase transfer agent and sodium hydrogen carbonate as base.



A representative experiment is as follows: A flask was charged with 10 mg (0.045 mmol) of palladium acetate, 467 mg (1.68 mmol) of tetrabutylammonium chloride, 590 mg (7.0 mmol) of sodium hydrogen carbonate, 571 mg (2.8 mmol) of iodobenzene and 300 mg (2.8 mmol) of benzyl alcohol in 10 ml of DMF. The entire reaction mixture was stirred vigorously under inert atmosphere at room temperature for 48 h. Conversion of benzyl alcohol in the reaction was monitored by means of gas chromatography. The reaction mixture was diluted with water and extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate, followed by filtration and removal of solvent under reduced pressure. The residual oil is purified by column chromatography on silica gel to afford benzaldehyde, 279.5 mg (95%).

This versatility of the catalytic system is demonstrated in oxidation of primary and secondary alcohols in reasonable yields as exemplified in Table 1. The yields depend upon the nature and concentration of the phase transfer reagent. Tetrabutylammonium chloride is much more efficient than

tetrabutylammonium bromide, tetrabutylammonium iodide, tetraethylammonium chloride and tetramethylammonium chloride, and the rate of reaction increases with increasing concentration of phase transfer reagent. The optimum concentration of tetrabutylammonium chloride is 0.6 equiv. to 1 equiv. of the substrate. No significant reaction is observed in the absence of phase transfer agent.

The best yields are obtained using palladium acetate that is closely followed by palladium chloride, while $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ affords very sluggish reaction. No palladium metal deposition is observed.

Thus the scope of the application of phase transfer reagents in organometallic chemistry is further widened with these results

Table 1: Palladium catalysed oxidation of primary and secondary alcohols^a.

Entry	Alcohol	Product	Yield (%)
1	1-propanol	1-propanal	97 ^b
2	1-butanol	1-butanal	80 ^b
3	2-methylpropanol	2-methylpropanal	50 ^b
4	1-heptanol	1-heptanal	75 ^c
5	3-methyl-1-butanol	3-methyl-1-butanal	55 ^b
6	benzyl alcohol	benzaldehyde	95 ^c
7	2-propanol	acetone	100 ^b
8	cyclohexanol	cyclohexanone	95 ^c
9	2-octanol	2-octanone	90 ^b

a) Reaction time 48 h

b) GLC yields

c) Isolated yields

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