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Oxidation of Secondary Alcohols Using Molecular Oxygen and Benzaldehyde in the Absence of Metal Catalysts

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OXIDATION OF SECONDARY ALCOHOLS USING MOLECULAR OXYGEN AND BENZALDEHYDE IN THE ABSENCE OF METAL CATALYSTS[+]

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ABSTRACT: A simple and convenient method for the oxidation of secondary alcohols using molecular oxygen, benzaldehyde in 1,2dichloroethane in the absence of metal catalysts is described for the first time.

The search for new and improved methods to oxidise alcohols to corresponding carbonyl compounds endures as a major pursuit in chemical synthesis[1]. From an economical and environmental point of view, molecular oxygen is an attractive oxidant and in recent past there was a great interest in the development of mild metal catalyzed aerobic process with the aid of sacrificial reagent, aldehyde[2,3] However, *Kaneda et .al.* reported that a peracid generated *in situ* from the system of a molecular oxygen and an aldehyde alone, devoid of

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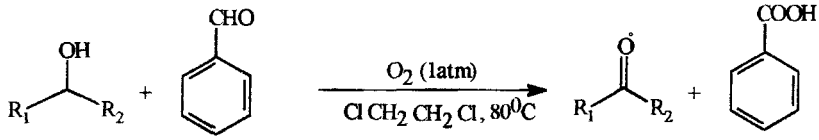
any metal catalyst was found to be an efficient oxidant for epoxidation of olefins[4] and Baeyer-Villiger oxidation of ketones[5]. Herein, we report a simple and convenient method for oxidation of secondary alcohols using molecular oxygen and benzaldehyde in dichloroethane in the absence metal catalysts for the first time.



Secondary alcohols are selectively oxidised to ketones in good yields(Table-1). However, both cyclohexanone and caprolactone, the Baeyer-Villiger product[6] (entry 3) are obtained in the oxidation of cyclohexanol. It was found that benzaldehyde is the best reagent for the oxidation of alcohols. Yields are low with isobutyraldehyde (entry 4). In a plausible mechanism, the oxidation of secondary alcohol is initiated by HCl catalyzed[7,8] addition of alcohol to the perbenzoic acid which is generated *in situ* from molecular oxygen and benzaldehyde to give an intermediate(I), which decomposes with loss of a proton to yield ketone and benzoic acid.

Thus, the present methodology provides a convenient and simple route for the synthesis of ketones by *in situ* generated perbenzoic acid and hydrochloric acid. Dispensing the direct use of peracid, a hazardous material difficult in handling and transportation is the practical advantage envisaged in this process.

EXPERIMENTAL

A typical procedure for the oxidation of alcohol to ketone is as follows.

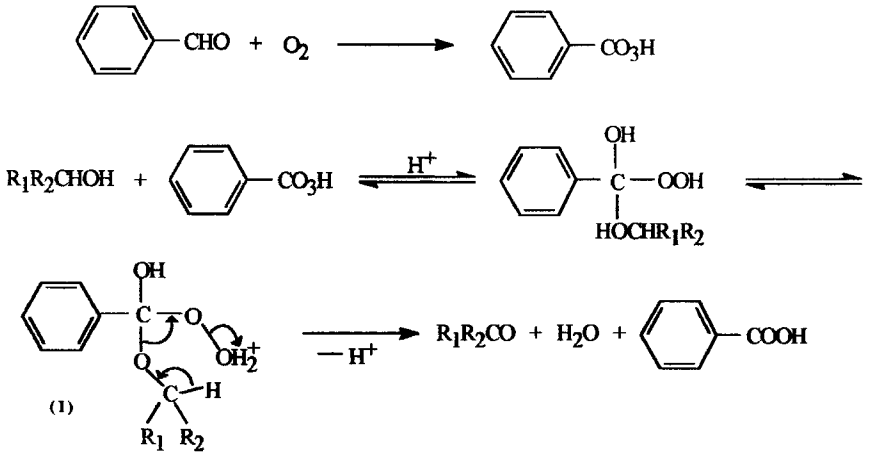


Table-1: Oxidation of secondary alcohols to ketones.

Entry	Compound	Product	Time(h)	Yield(%)[a]
1	2-octanol	2-octanone	26	80
2	cyclododecanol	cyclododecanone	26	85
3	cyclohexanol	cyclohexanone + caprolactone	36	50 + 20
4	cyclohexanol	cyclohexanone	36	30[b]
5	cyclopentanol	cyclopentanone	36	45
6	menthol	menthone	36	60
7	1-phenyl ethanol	acetophenone	26	60
8	norborneol	norcamphor	36	40
9	2-methyl cyclohexanol	2-methyl cyclohexanone	28	62

a) isolated yield b) isobutyraldehyde used in place of benzaldehyde

Benzaldehyde(5mmol-freshlydistilled),cyclododecanol(2mmol), 1,2 dichloroethane (10 ml) were refluxed under oxygen (balloon) atmosphere in a 100 ml two necked round bottomed flask for 26 hrs. The reaction mixture was cooled and benzoic acid was removed by successive treatments with saturated aqueous sodium bicarbonate solution. The oxygenated product in 1,2 dichloroethane was concentrated and cyclododecanone was isolated (85%) by column chromatography on silicagel.

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7. There is a report that the aging process of perbenzoic acid on chlorinated solvent generates catalytic amounts of HCl from the decomposition of solvent

by oxygen and peracid (see ref.8). While using toluene as solvent in place of 1,2 dichloroethane the yields are very poor (< 20%).

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