Benzaldehydes from Propenylbenzenes and Cinnamic Acids

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Introduction

The preparation of aldehydes by the oxidative cleaveage of carbon-carbon double bonds is a useful reaction, but often one that is difficult to acheive. Among the methods currently available, ozonolysis gives the most reliable results [...].

The experimental procedure, which involves mixing premanganate with a solid support, is very simple. The oxidant and support are placed in a flask containing the reductant dissolved in dichloromethane and stirred either at room temperature or under reflux. When the reaction is complete, as indicated from TLC analysis, the spent oxidant and solid support are separated by filtration and a nearly pure product obtained by evaporation of the solvent.

In this paper we wish to describe a method for the preparation of benzaldehydes in good yields from the oxidative cleavage of styrene and cinnamic acid derivatives by permanganate under hetrogeneous conditions, to note some limitations to the reaction and to compare results obtained by the use of alumina and a cation exchange resin as solid supports.

The results from oxidation of a number of styrene and cinnamic acid derivatives having various structural features are summerized in Table 1. From these data it is possible to conclude the following:

- I. Substituents on the side chain (entries 1-7) have little to no impact on the reaction
- II. Carboxylic acid groups on the side chain are also tolerated (entries 5 and 8-18)
- III. A carboxylic acid group on the aromatic ring results in an intractable product mixture (entry 19)
- IV. A vareity of other ring substitutants, including hydroxyls (entry 10) do not affect the reaction
- V. Heteroatoms as part of the aromatic ring have little of no impact on the reaction (entries 23 and 24)

Table 1

Products obtained from the oxidation of styrene and cinnamic acid derivatives by KMnO4 under hetrogeneous conditions and room temperature

Entry	Reductant	Conditions	Product	Yield %
1	Styrene	а	Benzaldehyde	90
2	beta-Methylstyrene	а	Benzaldehyde	83
3	beta-Methoxystyrene	а	Benzaldehyde	50
5	Cinnamic Acid	b	Benzaldehyde	90
7	Anethole	С	p-Anisaldehyde	94
8	4-Methylcinnamic acid	d	4-Methyl-benzaldehyde	96
13	4-Methoxycinnamic acid	d	p-Anisaldehyde	90
15	3-Bromocinnamic acid	d	3-Bromo-benzaldehyde	99
16	4-Chlorocinnamic acid	d	4-Chloro-benzaldehyde	85

Conditions

- a. Reductant (1 mmol) and KMnO4/alumina reagent (4.65 gr) were stirred in DCM overnight.
- b. Reductant (1 mmol), Amberlite IR-120/H2) (1.17 g) and KMnO4 (0.49 g) were stirred in DCM 10-40 min.
- c. Reductant (1 mmol) and KMnO4/alumina (4.65 g) were stirred in DCM for 4 hours.
- d. Reductant (1 mmol) and KMnO4/alumina reagent (4.65 g) were stirred in DCM for 10-40 min.

Preparation of the KMnO4/Alumina Reagent

The KMnO4/Alumina reagent was made by combining KMnO4 (0.78 g), Al2O3 (acidic, Brockmann 1, 3.12 g) and H2O (0.78 g) in a mortar and grinding until homogeneous (about 3 min). The solid support prepared from cation exchange resin was made by grinding Amberlite IR-120 (0.80 g) and H2O (0.4 g) in a mortar for about 3 min.

Oxidation of Styrene and Cinnamic acid derivatives by KMnO4 under hetrogeneous Conditions

Conditions b: 4-Methylbenzaldehyde: Amberlite IR-120 (Mallinickrodt, 0.8 g) and H2) (0.4 mL) were ground in a mortar for 3 min to give a wet powder and added to 4-methylcinnamic acid (162 mg, 1.0 mmol) dissolved in CH2Cl2 (5 mL)

followed by finely ground KMnO4 (490 mg, 3.00 mmol). This mixture was stirred at r.t. for 20 min and then filtered through Celite. The residue was washed with CH2Cl2 (3 x 10 mL). The filtrate and washings were combined, dried (MgSO4) and concentrated to give 4-methyl- benzaldehyde (117 mg, 97%) as a colorless oil.

Conditions c: p-Anisaldehyde: To a solution of anethole (0.148 g, 1.0 mmol) in CH2Cl2 (35 mL) was added KMnO4/alumina reagent (4.65 g). The heterogeneous mixture was stirred at r.t until TLC analysis indicated that the reaction was complete (4 h). The contents of the flask were filtered through Celite and washed with CH2Cl2 (3 x 15 mL). The product was separated by evaporation of the solvent to give p-anisaldehyde (0.128 g, 94%).

Reference: Sheng Lai, and Donald G. Lee, Synthesis 1645 (2001)