

A Convenient Method for One Step Oxidative Decarboxylation by KMnO_4 in Non Aqueous Media[†]

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A simple and efficient method for one step oxidative decarboxylation of some aromatic carboxylic acids, using potassium permanganate in non-aqueous media is described.

The conversion of a carboxylic acid (or derivative) to an aldehyde or ketone with loss of one carbon atom plays an important role in organic chemistry.^{1,2} This degradation is an important tool in the structural elucidation and characterization of natural products.³ It also allows carboxylic acid derivatives to serve as synthetic equivalents of other structural fragments. The oxidative decarboxylation of carboxylic acids has been studied extensively. Many of the oxidants used for this reaction are metallic ones such as sodium perborate⁴, copper (II) bromide-lithium *tert*-butoxide⁵, lead (IV)⁶, cobalt (III)⁷, silver (II)⁸, thallium (III)⁹, and cerium (IV)¹⁰, but non-metallic oxidants^{11,12} have also been used. In addition, oxidative decarboxylations have been affected photochemically.^{13,14}

In this report a novel application of potassium permanganate, a stable, non-toxic, widely available and inexpensive chemical, as an oxidant in organic chemistry is described.

Potassium permanganate is normally employed as a neutral or alkaline aqueous solution. If an organic compound is not soluble in water, it may be investigated as a suspension in the aqueous permanganate solution, or a co-solvent such as *t*-butyl alcohol or acetic acid may be employed.¹⁵

According to this research, the reaction of potassium permanganate with phenylacetic acid, (4-methoxyphenyl) acetic acid, (4-hydroxyphenyl) acetic acid, and benzilic acid in an organic solvent (CH_2Cl_2 or CHCl_3) resulted in preparation of benzaldehyde, (4-methoxy) benzaldehyde, (4-hydroxy) benzaldehyde, and benzophenone, respectively. Surprisingly, benzylmalonic acid reacted with potassium permanganate under the same conditions and benzaldehyde formed.

It is noteworthy that, in all of the mentioned reactions no vigorous conditions (heat or reflux) and no catalyst (acid or alkali media) were used. The reactions were simply performed in high yields only with stirring at room temperature. The MnO_2 and CO_2 that were obtained as side-products in the reactions were tested by conventional methods. The optimized conditions for oxidative decarboxylation reactions were listed in Table 1.

Under the reaction conditions no further oxidation of the obtained product (aldehyde or ketone) to corresponding acids was observed. Presence of the activated benzylic hydrogen seems to be an important factor in oxidative decarboxylation reaction.

Although different methods and reagents have been reported for oxidative decarboxylation of arylacetic acids, the

Table 1 Oxidative decarboxylation of aromatic carboxylic acids by KMnO_4

Substrate	Product	Yield	Solvent	Stirring time (h)	Substrate/ KMnO_4 molar ratio
		75%	CH_2Cl_2	20	2/3
		80%	CH_2Cl_2	30	1/2
		80%	CH_2Cl_2	30	1/2
		90%	CHCl_3	20	2/3
		75%	CH_2Cl_2	20	1/2

Yields refer to isolated compounds, characterized by comparison with authentic samples, (IR, H-NMR, TLC, and HPLC)

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main advantages of this method are: high-yielding, performance of the reactions at room temperature, direct use of potassium permanganate in non aqueous solvents, no requirement to acid or alkali media, and negligible side reactions (no further oxidation of products).

Experimental

The typical procedure for the oxidative decarboxylation reaction is as follows.

Into a 250-mL, round-bottomed flask was placed 0.03 mol of phenylacetic acid, 0.045 mol of KMnO₄, and about 170 mL of CH₂Cl₂. The suspension was stirred at room temperature for 20 h. During this time, progress of the reaction was monitored by thin-layer chromatography. Then the reaction mixture was filtered and the product was recovered by evaporation of the solvent. Evaporation of the solvent afforded nearly pure product but, further purification can be accomplished by thick-layer chromatography. The proposed structure of the product was confirmed by spectroscopic (IR, H-NMR) and chromatographic (TLC, HPLC) methods.

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