



Trade Science Inc.

# Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 3(3), 2007 [118-121]

## Synthesis of 2-Methyl Terephthalic Acid By Selective Oxidation Of 2,4-Dimethyl Benzoic Acid Using $\text{KMnO}_4$

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Received: 9<sup>th</sup> May, 2007 ; Accepted: 14<sup>th</sup> May, 2007

### ABSTRACT

A simple and environmental-friendly procedure to synthesize 2-methyl terephthalic acid by selectively oxidizing 2,4-dimethylbenzoic acid was reported. 2,4-Dimethylbenzoic acid reacts in alkalic solution with potassium permanganate ( $\text{KMnO}_4$ ) to afford 2-methyl terephthalic acid. The reaction is highly selective and takes only 5 hours. The chemical structure of the product was confirmed by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy. The pathways of the procedure and the mechanism of the selective oxidation reactions were discussed.

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### KEYWORDS

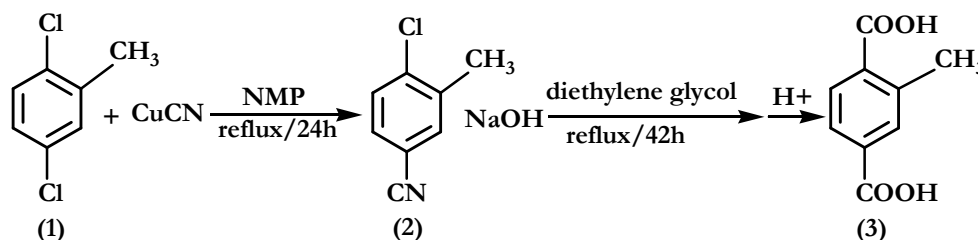
2-Methyl terephthalic acid;  
Synthesis;  
 $\text{KMnO}_4$ ;  
Oxidation;  
2,4-dimethyl benzoic acid.

### INTRODUCTION

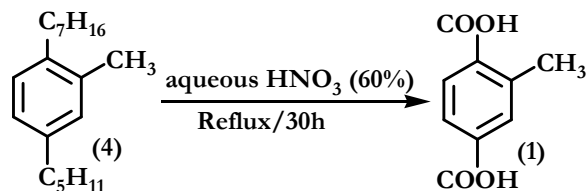
2-Methyl terephthalic acid (**1**) is one of the substituted terephthalic acids. As terephthalic acid and other substituted terephthalic acids, (**1**) was used in preparing polymers. For instance, Hotta<sup>[1]</sup> used 2-methyl terephthalic acid to prepare poly(2-methyl paraphenylenebenzobisthiazole), which was

used as reinforcing materials. Different from terephthalic acid, (**1**) has a methyl group of 2-position in its phenyl bone, so that (**1**) can be used to synthesize some new chiral polymers and special liquid crystalline materials<sup>[2,3]</sup>.

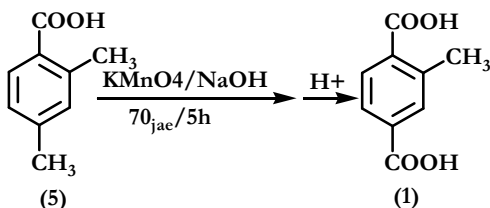
Based on references<sup>[4,5]</sup>, (**1**) can be synthesized through the following two routes: (**1**) 2,5-dichlorotoluene (**2**) reacts with cuprous cyanide to give 2-



SCHEME 1 : Synthesis of 2-methyl terephthalic acid using 2,5-dichlorotoluene



**SCHEME 2 :** Synthesis of 2-methyl terephthalic acid using 2-methyl-4-amyl-phenyl heptane



**SCHEME 3 :** Synthesis of 2-methyl terephthalic acid using 2, 4-dimethyl benzoic acid

methyl terephthalic acid (3), then (1) is obtained by alkaline hydrolysis of (3) (SCHEME 1) (1) can also be prepared by oxidation of 2-methyl-4-amyl-phenyl heptane (4) using 60% (W/W) aqueous  $\text{HNO}_3$  (SCHEME 2). It is known that SCHEME 1 is feasible, pure product can be obtained, but there is inevitably a little halogen ion residue, which has adverse effect on the quality of the product. Moreover, cyanide ion is virulent and very harmful. Meanwhile, this procedure is very complicated and need a long reaction time. SCHEME 2 is easy to operate. However, it also needs a long reaction time owing to its two-phase reaction system. Besides, NO as the gas waste of the reaction will inevitably cause atmosphere pollution.

Potassium permanganate ( $\text{KMnO}_4$ ) has long been used as an oxidant for a variety of organic functional groups<sup>[6]</sup>. It is known that  $\text{KMnO}_4$  can oxidize alkyl group of aromatic hydrocarbon to afford carboxyl group, if there is  $\alpha\text{-H}$ <sup>[7]</sup> in the alkyl group. In this paper, a simple procedure for synthesizing 2-methyl terephthalic acid by selectively oxidizing 2, 4-dimethylbenzoic acid using  $\text{KMnO}_4$  as oxidant is put forward (SCHEME 3).

## EXPERIMENTAL

### Apparatuses assay

2,4-Dimethyl benzoic acid was technical grade. Other chemicals used were of analytical reagent

grade. All the chemicals were used directly without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a BRUKER AV300 with TMS as the internal standard,  $\text{DMSO-}d_6$  as solvent and chemical shifts were given on the scale. IR Spectra were measured on a Nicolet 5700 FT-IR spectrometer by the incorporation of the samples in KBr disks. HPLC analysis was carried out on an Waters 1515 HPLC with a Waters C-18 column (4.6×150mm) and a UV detector (Waters Inc., USA). The wavelength of detection was 287nm and the flow rate was  $1.0\text{ml min}^{-1}$ . Elution solvent was a mixture of  $0.2\text{mol L}^{-1}$  aqueous  $\text{NaH}_2\text{PO}_4$  and methanol (57: 43, v/v). The injection volume was  $10\mu\text{l}$ . Before injection, the sample was filtered through a  $0.22\text{-}\mu\text{m}$  organic filtration membrane.

### General procedure

$\text{NaOH}$  (0.8g, 0.02mol) was dissolved in water (300ml). The solution was poured into the flask with stirring apparatus. A sample of (4) (3.0g, 0.02mol) and  $\text{KMnO}_4$  (6.64g, 0.042mol) were added overall. The mixture was heated to  $70^\circ\text{C}$ , stirred at  $70^\circ\text{C}$  for 5 hours, and then filtrated, washed with considerable water. Brown mud-like filter residue and light yellow transparent filtrate were obtained. The filtrate was acidified to pH 1-2 with 2mol/L aqueous hydrochloric acid and white precipitate appeared. Filtration, washing the filter residue with water ( $3\times 100\text{ml}$ ) and cold 95% ethanol ( $3\times 30\text{ml}$ ), drying the precipitate under vacuum at  $60^\circ\text{C}$  for more than 5 hours afforded white powders (called raw product). Then sublimating the white powders with oil bath under vacuum afforded pure white crystal (called refined product, 1.95g, yield 54.2%).

IR(KBr)  $\text{vcm}^{-1}$ : 2980(O-H), 1700(C=O), 1570, 1500 (phenyl), 1420(C-H methyl), 1270 (C-O).  $^1\text{H}$ -NMR (TMS),  $\delta\text{ppm}$ : 13.17(s, 2H, COOH), 7.90-7.81 (m, 3H, phenyl), 2.56, 2.51, 2.51(t,  $J=8\text{Hz}$ , 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR(TMS),  $\delta\text{ppm}$ : 168.2(COOH), 166.7 (COOH), 138.9(phenyl), 134.5(phenyl), 133.1(phenyl), 132.1 (phenyl), 130.2(phenyl), 126.6(phenyl), 20.9( $\text{CH}_3$ ).

## RESULTS AND DISCUSSION

The selectivity of reaction is very important in

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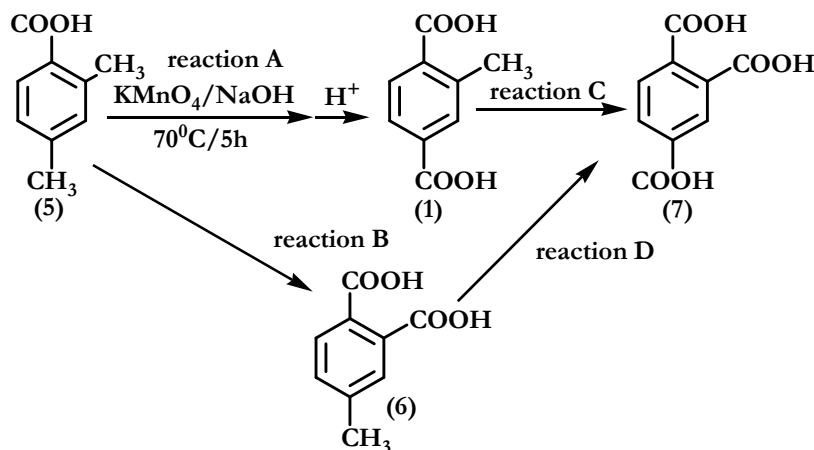


Figure 1 : Pathways of the procedure

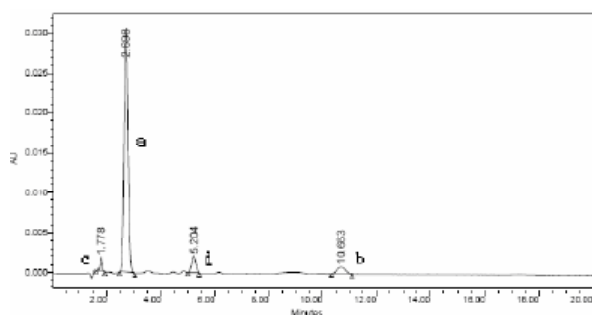


Figure 2 : HPLC analysis of the raw product

organic synthesis. In this procedure, the reactant, 2, 4-dimethyl benzoic acid has two methyl groups, both of which have the possibility to be oxidized by  $\text{KMnO}_4$  to form carboxyl group. Therefore the oxidation product of 2, 4-dimethyl benzoic acid may be 2-methyl terephthalic acid and 4-methyl phthalic acid. Meanwhile the two dicarboxylic acids can be further oxidized to trimellitic acid. That's to say, there are probably four reactions (see figure 1), labeled as A, B, C and D. However, it was found that 2-methyl terephthalic acid was the predominant product under this reaction conditions. This means that the oxidation reaction has high selectivity and reaction A is the main reaction. To study the pathways and the mechanism of the reaction, HPLC analysis was carried out.

HPLC analytical result of the raw product using the method described earlier was shown in figure 2. As can be seen, a satisfactory separation with reasonable retention times was obtained. There are four sharp peaks (i.e. four compounds in the raw prod-

uct) in the chromatogram. The retention times are 2.70min (a), 10.66min (b), 1.78min (c), 5.20min (d), respectively. Through application of sample test and comparison between the HPLC chromatogram of authentic standards, the peaks a, b and d in figure 2 were identified as 2-methyl terephthalic acid, 2,4-dimethylbenzoic acid and 4-methyl phthalic acid respectively. 2,4-Dimethylbenzoic acid used here is technical grade. Compound c may come from the raw material, which is confirmed by HPLC analysis. Besides trimellitic acid was found in the acidic filtrate, which was observed by HPLC. Thus, the three products (2-methyl terephthalic acid, 4-methyl phthalic acid and trimellitic acid) were all found. The results mean that the four reactions shown in figure 1 all took place in the process. Moreover, the average yield of 2-methyl terephthalic acid under our reaction conditions is ~55%, which shows that in the competition among reaction A, B, C, and D, reaction A is predominant.

The high selectivity may be attributed to steric hindrance and inductive effect. On the one hand, in the structure of (5), methyl group of 2-position has greater steric hindrance than that of 4-position. Furthermore, permanganate ion ( $\text{MnO}_4^-$ ) has considerable ionic size, so it is impacted by steric hindrance to some extent. Therefore 4-methyl group may be more easily to be oxidized by  $\text{KMnO}_4$  than 2-methyl group. On the other hand, the two carboxyl groups of (6) occupy ortho-position, while those of (1) locate in para-position. Such symmetric structure of (1) make it stabler than (6). Owing to the two fac-

tors described above (1) is more likely to be obtained than (6). It is well known that 4-carboxyl group of (1) is an electron drawing group, while 4-methyl group of 5 is an electron donating groups. Thus comparing with 1, 2-methyl group of (5) has more electron cloud, so it is easily to be oxidized. That is to say, under some conditions  $\text{KMnO}_4$  would oxidize (1) to form (7) rather than oxidize (5) to form (7). But when  $\text{KMnO}_4$  is excessive, both the methyl groups of (1) will be oxidized and the oxidation product will be completely (7). Therefore the reaction conditions especially the dosage of  $\text{KMnO}_4$  are very important.

The oxidizing ability of  $\text{KMnO}_4$  varies with pH value. In the procedure reported here,  $\text{KMnO}_4$  is deoxidized to  $\text{MnO}_2$  owing to the weak alkaline system. Oxidizing one mole (5) to (1) or (6) also consumes approximate two mole  $\text{KMnO}_4$ . At the same time, (1) and (6) simultaneously consumes a little  $\text{KMnO}_4$  to give trimellitic acid. The result of experiments showed that when the mole ratio of  $\text{KMnO}_4$  and (5) was about 2.2, the highest yield of (1) was obtained. When the ratio was more than 4.0, no 1 was gotten. Reaction B, C and D is side reactions for (1) production; the quantities of the by-products (6,7) change under different reaction conditions. By choosing suitable reaction conditions, good results can be obtained for (1).

## CONCLUSION

A simple procedure to synthesize 2-methyl terephthalic acid by selectively oxidizing 2, 4-dimethylbenzoic acid was reported. The average yield of 2-methyl terephthalic acid is ~55%. By choosing suitable reaction conditions, better results can be obtained for (1). The pathways and mechanism of the selective oxidation reactions was discussed. The high selectivity may be attributed to steric hindrance and inductive effect. It has to be noticed that the explanation is still dubious and further studies are needed.

Compared with the other two methods (SCHEME 1 and SCHEME 2) of synthesizing 2-methyl terephthalic acid, the procedure reported here (SCHEME 3) has more advantages. The deoxidizing product of

$\text{KMnO}_4$ ,  $\text{MnO}_2$  can be recycled. The reaction condition is very mild and the device is simple. In addition, the reaction time is very short. Therefore the route of synthesizing 2-methyl terephthalic acid by selectively oxidizing 2,4-dimethylbenzoic acid will have broad application foreground.

## Supplementary information available statement

FT-IR spectra, UV-spectra,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analysis of the product are provided as supplementary information. According to the results of the analysis, the product was identified to be 2-methyl terephthalic acid.

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