Oxidation of 2,6-Bis(hydroxymethyl)phenols to 2-Hydroxyisophthalaldehydes by MnO_2

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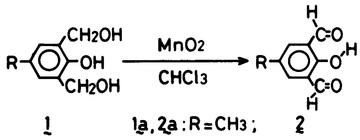
(Received January 20, 1984)

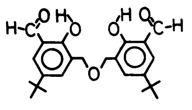
Synopsis. A facile and direct preparative method of 2-hydroxyisophthalaldehydes from 2,6-bis(hydroxymethyl) phenols using activated manganese(IV) oxide is described. The aldehydes are obtained in good yields.

2-Hydroxyisophthalaldehyde derivatives (**2**) are useful compounds for the investigation of binuclear metal complexes,[1–4)] and macrocyclic binuclear metal complexes.[5,6)] Since binuclear copper(II) complexes have been prepared from Schiff bases of **2a** by Robson[1a)] and Okawa[2a)], the investigatons have been directed toward the study of their molecular structures,[5,6b)] affinity[3b,6c)] for carbon monoxide and ethylene, intermolecular electron transfer process,[6a)] and redox behavior.[4,6)] All of these investigations adopted the Ullmann's method[7)] for the preparation of **2**, but the reaction is achieved through the following three-steps: conversion of 2,6-bis(hydroxymethyl)-4-methylphenol (**1a**) to the tosylated diol, its oxidation to the tosylated diformyl compound by sodium dichromate, and final formation of **2a** by treatment in sulfuric acid. This method is cumbersome and the yield of the compound is low. Once the aldehydes are synthesized, the route to the final ligand compounds is fairly straightfoward. Therefore, a facile and direct preparation of the aldehydes is an important factor for the synthesis of the binuclear metal complexes.

Recently, the reaction of **1b** with vanadyltriisopropylate was found to afford 3,3′-[oxybis(methylene)] bis[5-*t*-butyl-2-hydroxybenzaldehyde] (**3**) as the major product and **2b** as the by-product.[8)] Since manganese(IV) oxide prepared by heating a manganese(II) salt such as carbonate or oxalate at 220—280 °C, is known to oxidize salicyl alcohol to salicylaldehyde in good yield,[9)] the activated MnO_2 can be used for oxidation of **1** to **2**. In this paper, the author reports the results of the present procedure, and the desired products were obtained in 67—70% yields in a sufficiently pure state for most purposes.



1 1a, 2a: R=CH_3; 1b, 2b: R=t-Bu **2**



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Experimental

All melting points are uncorrected. The IR spectra were recorded on a Hitachi EPI-G3 spectrometer in KBr disks. The ^{1}H NMR spectra and mass spectra were recorded on a Hitachi R-24B spectrometer with TMS as the internal standard in $CDCl_3$ solution, and a Hitachi M-70 mass spectrometer, respectively.

Reagents. Compounds **1** were prepared by a modification of the literature method.[7)] Activated manganese(IV) oxide[10)] was prepared by heating manganese(II) carbonate at 250 °C for 5 h.

General Procedure. Compound **1** (10 g) was added to manganese(IV) oxide (80 g) suspended in 300 ml of $CHCl_3$ in a 500 ml Erlenmeyer flask, and the mixture was stirred by a magnetic stirrer at room temperature. The phenol which was slightly soluble in the solvent dissolved within about 3 h. After 2 d, the solution was filtered. The solid was washed twice thoroughly with 200 ml each of $CHCl_3$, and the washings were added to the original filtrate.[11)] The combined solution was evaporated to yield a pale yellow solid (6.5—6.9 g). The yields and analytical data of the products are described below.

2a: 67% yield, mp 130 °C (lit, mp 133.5 °C,[7)] mp 129—130 °C[4)]); IR (cm^{-1}) 2880 (formyl CH), 1682 (formyl C=O), 1668 (formyl C=O associated with OH), 1216 (phenolic C–O); ^{1}H NMR δ=2.83 (3H, s, methyl), 7.73 (2H, s, aromatic), 10.15 (2H, s, CHO), 11.35 (1H, s, OH); MS *m/z* 164 (M$^+$).

2b: 70% yield, mp 105 °C; IR (cm^{-1}) 2880 (formyl CH), 1692 (formyl C=O), 1662 (formyl C=O associated with OH), 1224 (phenolic C–O); ^{1}H NMR δ=1.24 (9H, s, methyl), 7.83 (2H, s, aromatic), 10.17 (2H, s, CHO), 11.28 (1H, s, OH); MS *m/z* 206 (M$^+$); Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.79; H, 6.84.

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10) Compounds **2** were obtained in low yields by heating with commercial manganese(IV) oxide at 250 °C for 5 h.

11) After filtration the remaining solid consisting mainly of manganese(IV) oxide was dried and treated in aq NaOH solution. The color of the solution changed to fluorescent greenish-yellow. By acidifying the solution, a small amount of compounds **2** was generally obtained.