

# Lead Tetraacetate/Chromic Anhydride Combination as a Novel Reagent for the Selective Oxidation of Methylene Dioxide Function

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## Abstract

$\text{Pb}(\text{OAc})_4/\text{CrO}_3$  combination was found to be able to oxidize methylene dioxide function in the presence of diphenylmethane moiety.

Among the variety of agents available for the oxidation of organic compounds<sup>1-2</sup>, the most commonly used are derivatives of hexavalent chromium or heptavalent manganese. Chromium anhydride and sodium dichromate are converted to the chromium (III) ion in the course of such oxidations, for a net transfer of three electrons to each chromium atom. Studies of the mechanisms of oxidations with chromium compounds<sup>3,4</sup> have been complicated by the fact that each stage in the oxidation of organic molecules is accompanied by the net transfer of two electrons although the oxidizing agents normally accept a total of three or five electrons. It is therefore evident that intermediate valence states of chromium are important to the overall process.

Lead tetraacetate<sup>5</sup>, is commonly used as a solution in acetic acid or benzene for the oxidation of organic compounds<sup>6</sup>. Neither chromic anhydride, nor lead tetraacetate can easily oxidize methylene dioxide function. From another point of view chromic anhydride can easily oxidize the methylene function in molecules such as diphenylmethane<sup>7</sup>.

In this report, we wish to show that a combination of  $\text{Pb}(\text{OAc})_4/\text{CrO}_3$  is able to oxidize selectively methylene dioxide function in the presence of diphenylmethane moiety. Thus compounds **1a-b** were transformed to **2a-b** by means of  $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$  in methanol (90%). Oxidation of **2a-b** with  $\text{Pb}(\text{OAc})_4/\text{CrO}_3$  (1:1) in acetic acid gave compounds **3a-b** (50%).

It should be noted that compound **2b** was converted to **2c** by the aid of  $\text{Zn}/\text{KOH}$  in ethanol<sup>7</sup>. However, the similar oxidation reaction in the case of **2c** failed and resulted in the cleavage of the acetal linkage.

## Experimental Section

General Remarks: see Ref. 8.

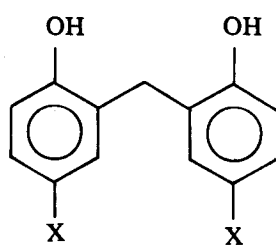
Preparation of Compounds **3a-b**. Both compounds were characterized by IR., MS., and elemental analysis. The following is a representative procedure.

Conc.  $\text{H}_2\text{SO}_4$  (d. 1.84, 40 ml) was added to a solution of 2,2'-dihydroxy-5, 5'-dichlorodiphenyl methane (**1a**, 1.5 g,  $5.6 \times 10^{-3}$  mol) in methanol (40 ml). Formalin (20 ml) was added dropwise for 1 h while stirring. After 3 h, the mixture was allowed to stand for 24 h at 25°C. The mixture was poured onto ice (200 g) and stirred. The precipitate was filtered, washed with 2N NaOH, water and dried to afford **2a** (1.9 g, 90%), m.p. 160 - 170°. recrystallization from ethanol gave **2a** (1g, 60%), m.p. 182 - 185°. IR. (KBr): 2980, 1500 - 1590, 1085  $\text{cm}^{-1}$ . MS. : 352.0 M<sup>+</sup> (Cl-cluster).

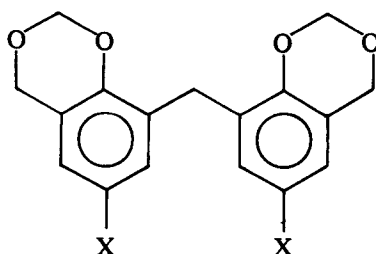
Anal. Calc. for  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Cl}_2$  (352.36): C 57.95, H 3.97, Cl 19.88;

Found: C 57.95, H 3.94, Cl 19.36.

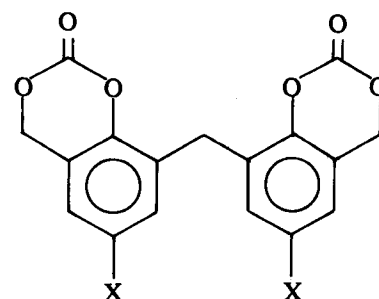
Compound **2a** (1g,  $2.8 \times 10^{-3}$  mol) and  $\text{Pb}(\text{OAc})_4$  (1.25 g) in acetic acid (20 ml) was refluxed for 2 h. The solution was cooled for 1 h, and  $\text{CrO}_3$  (3g) in water (1 ml) was



1a X = Cl 1b X = Br



2a X = Cl 2b X = Br 2c X = H



3a X = Cl 3b X = Br

added to the stirred solution. The mixture was refluxed for 4 h and then poured into cold water. After 12 h the precipitate was filtered, washed with water and dried to give **3a** (50%). Sublimation at 0.01 mm Hg, and 200 – 210° gave crystalline prisms of compound **3a**, m.p. 248 – 250°. IR. 1760, 2980, 1500, 1095  $\text{cm}^{-1}$ . MS.: 380  $\text{M}^+$  (Cl-cluster).

Anal. Calc. for  $\text{C}_{17}\text{H}_{10}\text{O}_6\text{Cl}_2$  (380.23): C 53.54, H 2.63, Cl 18.63;

Found: C 54.00, H 2.66, Cl 18.46.

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