

## Oxidation of $\alpha$ -Hydroxy Carboxylic Acids with Sodium Hypochlorite

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The oxidative decarboxylation of  $\alpha$ -hydroxy carboxylic acids can be carried out with a variety of reagents, e.g. periodate,<sup>1</sup> permanganate,<sup>2</sup> chromic acid<sup>3</sup> and lead tetraacetate.<sup>4</sup> We were interested in developing methods for the transformation of  $\alpha$ -hydroxy carboxylic acids directly into aldehydes having one carbon atom less. A few examples of this type of reactivity have appeared in the literature. Thus *N*-iodosuccinimide,<sup>5</sup> bromine in water<sup>6</sup> and sodium bismuthate in acid medium<sup>7</sup> effect this transformation well, but are expensive or inconvenient for large scale preparations, and often undesirable by-products are formed. Sodium (or calcium) hypochlorite, on the other hand, is an attractive reagent because of its availability and low cost.

Recently Keehn<sup>8</sup> and co-workers reported that this reagent, under slightly acidic conditions (acetic acid), converts  $\alpha$ -hydroxy carboxylic acids into the lower carboxylic acid homolog.

In this paper we report that if acetic acid is omitted in the Keehn procedure, aldehydes or ketones are formed as the exclusive products:



A series of  $\alpha$ -hydroxy acids (Table 1) were oxidized with sodium hypochlorite in a two-phase ether-water solvent system. Aldehydes or ketones were formed in essentially quantitative yields.

The fact that aldehydes rather than carboxylic acids are obtained as the major products, can be ascribed to the alkaline reaction conditions which ensure that hypochlorite is the principal oxidation agent present in the reaction mixture, and that the concentrations of hypochlorous acid and its decomposition products are kept low. HClO is a weak acid ( $\text{p}K_{\text{A}} 7.53$ ), and is easily formed from the sodium salt in e.g. acetic acid solution. The difference in reactivity of hypochlorite in acetic acid solution may possibly be related to the difference in oxidation potential between hypochlorous acid (1.49 V) and sodium hypochlorite (0.90 V).

Further work dealing with the mechanistic details of the described reaction, and the synthetic application is in progress.

**General Procedure.** A solution containing 10 mmol of the  $\alpha$ -hydroxy carboxylic acid in 25 ml of diethyl ether was cooled in an ice-bath. Then 40 ml of a commercial bleach solution (containing 4.2 % sodium hypochlorite and 0.5 % sodium hydroxide), 22 mmol, was added over a 3 min period. The reaction mixture was then allowed to warm up to room temperature and stirred at this temperature for 2–3 h. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate and the solvent evaporated. The crude product was purified by molecular distillation or recrystallization.

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Table 1. Oxidation of  $\alpha$ -Hydroxy Carboxylic Acids.

Entry	Substrate	Reaction time, h	Product	Yield, %
1	PhCHOHCOOH	2	PhCHO	95
2	Ph <sub>2</sub> COHCOOH	1	Ph <sub>2</sub> CO	91
3	PhC(CH <sub>3</sub> )OHCOOH	1	PhCOCH <sub>3</sub>	93
4	C <sub>6</sub> H <sub>11</sub> CHOHCOOH	2	C <sub>6</sub> H <sub>11</sub> CHO	85
5	(CH <sub>3</sub> ) <sub>2</sub> CHCHOHCOOH	2	(CH <sub>3</sub> ) <sub>2</sub> CHCHO	47
6	PhCHOHCOONa	2	PhCHO	93
7	5-androsten-3 $\beta$ ,17 $\alpha$ -diol-17-carboxylic acid	3	5-androsten-3 $\beta$ -ol-17-one	85

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