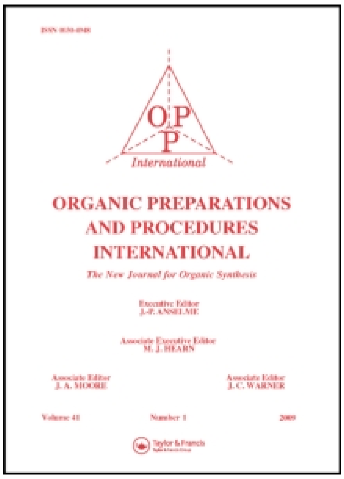

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FACILE OXIDATIVE DECARBOXYLATION OF AROMATIC α-HYDROXY ACIDS BY SODIUM METAPERIODATE IN THE PRESENCE OF DIBENZO-[18]-CROWN-6 AND PTC

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FACILE OXIDATIVE DECARBOXYLATION OF AROMATIC α-HYDROXY ACIDS BY SODIUM METAPERIODATE IN THE PRESENCE OF DIBENZO-[18]-CROWN-6 AND PTC

Submitted by
(03/29/94)

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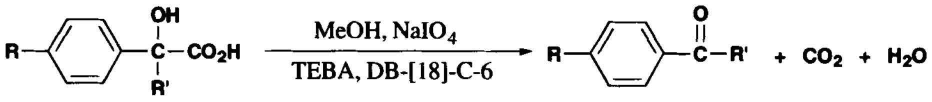
Alkaline sodium hypochlorite oxidizes α-hydroxy acids to the corresponding aldehydes and acids,[1] the ratio of products depending either on electronic factors or on the concentration of hypochlorite. Oxidation with tetrabutylammonium periodate (TBAP) in refluxing dioxane[2] and with polymer supported (Amberlyst A-26 or Amberlite IRA-400) periodate forms of some commercial anion exchange resins in refluxing ethanol,[3] give aldehydes as the only products in yields similar to or greater than those using hypochlorite.[1] The oxidation of arylacetic acids by tetrabutylammonium periodate has been rationalized by initial hydroxylation of the relatively activated methylenes followed by oxidative cleavage of the intermediate 2-hydroxy acids to the next lower carbonyl compounds.[2] However, these require reflux conditions and prolonged reaction times (8 to 48 hrs).[2,4] We now report a very effective and rapid method of oxidative decarboxylation of α-hydroxy acids including benzylic acids with sodium metaperiodate in the presence of benzyltriethylammonium chloride (TEBA) as a phase-transfer catalyst and a catalytic amount of dibenzo-(18)-crown-6 (DB-18-C-6) or 15-crown-5 under mild reaction conditions; 15-crown-5 was equally effective in catalyzing this reaction. The absence of either the phase-transfer reagent or dibenzo-(18)-crown-6 led to lower yields. Benzylic acids with electron-withdrawing substituents such as nitro group are readily decarboxylated whereas compounds containing electron-donating substituents such as methoxy group are decarboxylated more slowly at room temperature. No oxidation of the aliphatic α-hydroxy acid, lactic acid, was observed even after 3 hrs.



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EXPERIMENTAL SECTION

IR spectra were determined as KBr pellets on a Perkin-Elmer-783 model. ^{1}H NMR spectra were obtained in $CDCl_3$ on a Perkin-Elmer Spectrometer R-32 using TMS as an internal standard.

General Procedure for Oxidative Decarboxylation of α-Hydroxy Acids.- A mixture of the α-hydroxy acid (5 mmol) and sodium metaperiodate (5.5 mmol) with benzyltriethylammonium chloride (TEBA) (15 mg) and dibenzo-18-crown-6 (7 mg) was stirred in methanol (25 mL) for the time specified (See Table). The course of the reaction was monitored by TLC. The solvent was evaporated to afford a residue to which dichloromethane (15 mL) was added and the solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel elution with pet ether-ethyl acetate (1:1). The products obtained were characterised by ^1H NMR and comparison with authentic samples.

TABLE 1. Oxidative Decarboxylation of Aromatic α-Hydroxy Acids[a]

R	Substrate R'	Time (hrs)	Yield (%)	mp. (bp) (°C)	Lit.[b]
H	H	0.30	92	(176-177)	(177-179)
H	C_6H_5	0.35	83	47-48	47-49
NO_2	$4\text{-}NO_2C_6H_4$	0.35	93	188-189	189
Cl	$4\text{-}ClC_6H_4$	2.1	88	145-146	144-147
OMe	$4\text{-}MeOC_6H_4$	3.0	88	143-144	142-145

a) All reactions were carried out in methanol at room temperature. b) Handbook of Chemistry & Physics, 1985-1986, 66th Edition.

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