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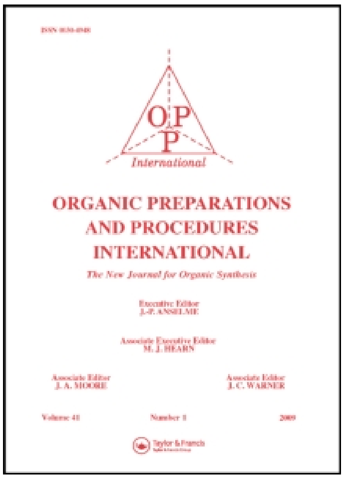

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o-HYDROXYMETHYLBENZHYDROL

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o-HYDROXYMETHYLBENZHYDROL[1]

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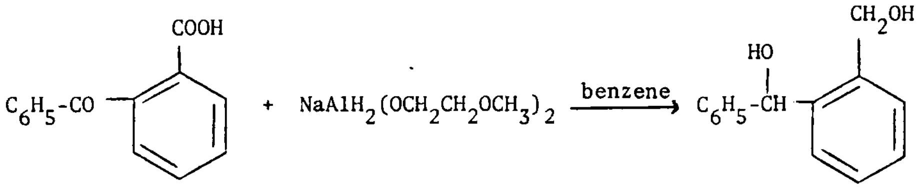

The reduction of carboxylic acids by $LiAlH_4$ has always represented a synthetic problem fraught with experimental difficulties. In most cases, the initially generated carboxylate salt precipitates from the ethereal medium, and subsequent reduction is slow and/or incomplete. Several reviewers have commented on this difficulty and have recommended reduction of the carboxylate ester.[2,3] The reduction of o-aroylbenzoic acids is particularly bothersome in that a highly insoluble, slowly reducible salt precipitates in either THF or ether upon treatment with $LiAlH_4$.

A smooth reduction to the diol, o-hydroxymethylbenzhydrol, can be achieved from the benzoyl pseudo esters, 3-alkoxy-3-phenylphthalides[4] or from the normal esters, alkyl o-benzoylbenzoates[4,5]. The preparation of such esters naturally requires additional synthetic steps. "Aged" $LiAlH_4$-pyridine solutions presumably containing lithium tetrakis(N-dihydropyridyl)aluminate will reduce the aroylbenzoic acids to 3-arylphthalides.[5] The claim has been made that freshly prepared solutions of $LiAlH_4$ in pyridine do give reasonable yields of the fully reduced diol (conversions are unspecified) from the parent aroylbenzoic acids.[6]

We wish to report the utilization of a commercially available metal hydride, sodium dihydro-bis(2-methoxyethoxy)aluminate which rapidly and quantitatively reduces o-benzoylbenzoic acid to its diol without complicating salt formation. This hydride is supplied as a 70% by weight solution in benzene[7] and can be conveniently handled in air without danger of fire or significant hydrolysis.

EXPERIMENTAL

2-Benzoylbenzoic acid (0.10 mole, 22.6 g) was dissolved in 400 ml of benzene and charged to a three-necked, one liter, round bottom flask. The solution was stirred mechanically, and 84 ml (0.60 hydride equivalents) of the sodium dihydro-bis(2-methoxyethoxy)aluminate were added dropwise. Although there was an initial vigorous reaction, gas evolution and formation of a white precipitate, the reflux was easily controlled by a West condensor. As more reagent was added, the precipitate redissolved and gas evolution diminished, but the reaction continued to be exothermic. The solution darkened in color and by the termination of the addition (1 hr) it was deep red. The mixture was stirred overnight at room temperature and hydrolyzed by the dropwise addition of 60 ml of water. The white solids which precipitated were filtered off, washed well with benzene, and the combined benzene phases dried over $MgSO_4$ and concentrated *in vacuo*. A pale yellow glass resulted which crystallized upon treatment with 1:1 hexane:ether. A total of 18.7 g (87%) of 2-hydroxymethylbenzhydrol, mp 65-67^o, was obtained. An analytical sample was prepared by recrystallization from hexane: ether, mp 72-72.5^o. The material was spectrally identical with a sample prepared by the published ester-reduction method.[4]

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