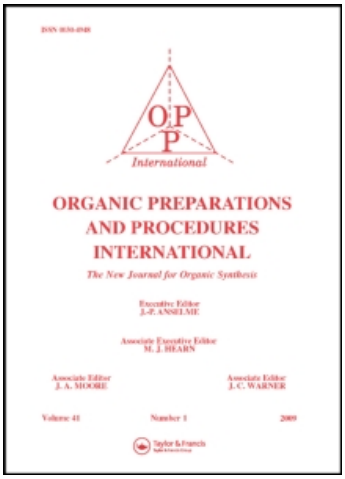

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A CONVENIENT SYNTHESIS OF p-HYDROXYBENZAL DEHYDES

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A CONVENIENT SYNTHESIS OF p-HYDROXYBENZALDEHYDES

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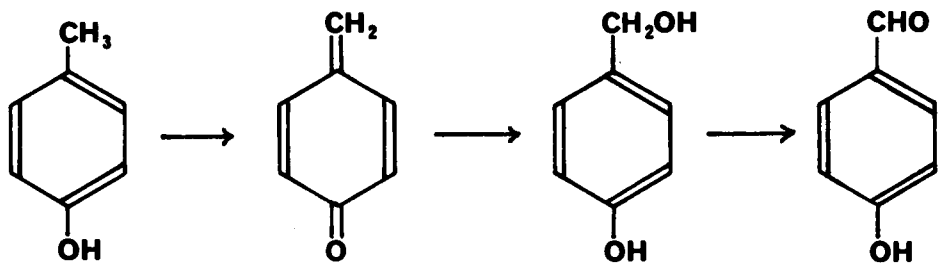
p-Hydroxybenzaldehydes are prepared conventionally by the formylation of an appropriate phenolic precursor through application of the Gatterman or Villsmeier reaction. Disadvantages of this approach include lack of selectivity of the substitution reaction, instability of other substituents to the reaction conditions, and the necessity of protecting the formyl group if it is incompatible with any subsequent reactions. Although the oxidation of p-alkylphenols to p-acylphenols by 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) is well established[1], there appear to be only two recorded examples of the oxidation of p-methylphenols to p-hydroxybenzaldehydes[2,3]. Further, there is little information on which to judge the compatibility of DDQ with other functional groups under the conditions appropriate for these oxidations.



TABLE

4-Hydroxybenzaldehyde	mp(°C)	Yield (%)
Unsubstituted	115-6°	84
2-Methyl	109-110°	78
3,5-Dimethyl[a]	-	83
3,5-Dibromo	179-80°	81
3-Methoxy	82-3°	71
3-Nitro	140-2°	47
3-(3-Methylbutanoyl)[b]	-	74

a) From Ref. 2, yield based on amount of DDQ used. b) From Ref. 3.

As the oxidation of p-methylphenols with DDQ appeared to offer an attractive alternate route to p-hydroxybenzaldehydes, we have surveyed its applicability to a range of substrates. The results summarised in the Table show that a variety of substituents are tolerated including acyl, bromo, methoxyl and nitro. However, oxidation of 3,4,5-trimethylphenol proceeded only as far as 4-hydroxy-2,6-dimethyl-benzyl alcohol (63%). This indicates that steric encumbrance of the methyl group undergoing oxidation could be a limiting factor in the application of this method. Additionally, this observation provides compelling evidence for the oxidation pathway formulated above.

EXPERIMENTAL

General Procedure.- DDQ (4.5g., 0.02 mol) in methanol (30 ml.) was added to a stirred solution of the phenol (0.01 mol) in methanol (10 ml) at room temperature. A deep blue colour developed instantaneously and eventually turned to yellow-brown. Stirring was continued for a further 1.5-2 hrs, when the pale yellow solution was evaporated to dryness in vacuo. The residue was extracted with chloroform and the insoluble hydroquinone recovered by filtration. The filtrate was evaporated and the residue eluted through a short column of silica gel with ethyl acetate. The eluate was evaporated and the residue recrystallised. All products had mps in close agreement with literature values[4], as well as consistent IR and NMR spectra

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