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SODIUM PERBORATE: A CONVENIENT REAGENT FOR BENZYLIC HYDROPEROXIDE REARRANGEMENT

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Abstract: Sodium perborate in boron trifluoride etherate has been found to be an effective reagent for the hydroperoxide rearrangement of electron rich and highly substituted benzylic tertiary alcohols to phenols in good yields.

Hydroperoxide rearrangement of benzylic alcohols is an excellent alternative to the Baeyer-Villiger oxidation for preparing phenols from acyl aromatics.[1] Benzylic secondary and tertiary alcohols, which are derived from hindered and electron-rich acetophenones, are ideal substrates for hydroperoxide formation and subsequent rearrangement to provide phenolic derivatives.[2] Generally, the conversion of benzylic secondary and tertiary alcohols to the corresponding phenols involves the use of 30–90% hydrogen peroxide in the presence of various acids such as *p*-toluene sulfonic acid,[2] boron trifluoride etherate,[3] and mixtures of acetic acid and perchloric acid.[4] We have discovered that sodium perborate will convert these benzylic alcohols to phenols under relatively mild conditions.

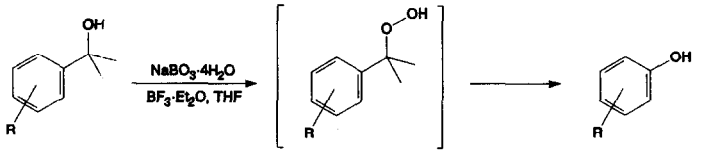
Sodium perborate ($NaBO_3 \cdot 4H_2O$) is an inexpensive, stable and easily handled oxidant which has an excellent shelf life.[5] It is commonly used as a bleaching agent in detergents. Sodium perborate-boron trifluoride etherate (1:5 mol ratio) was found to be a suitable reagent for the oxidation of 1-(4-methoxyphenyl)ethanol to 4-methoxyphenol in 84% yield.

The reaction is incomplete when the ratio of sodium perborate to boron trifluoride etherate was either 1:4 or 1:3 even after 24 h. Although both secondary and tertiary alcohols undergo benzylic hydroperoxide rearrangement, tertiary alcohols provide higher yields of product. Benzylic hydroperoxide rearrangement of tertiary alcohols (obtained from either acetophenones or benzoate esters) to the corresponding phenols are detailed in Table.

In a typical procedure, boron trifluoride etherate (20 mmol, 2.46 ml) is added to a suspension of sodium perborate (4 mmol, 616 mg) in dry tetrahydrofuran (20 ml) contained in an argon flushed flask cooled to 0 °C. The mixture is stirred for 30 min and then the alcohol (2.0 mmol in 5.0 ml of dry THF) is added. The reaction is allowed to proceed until the alcohol is completly reacted (TLC). The reaction is then quenched with sodium

sulfite, the product extracted into ether and dried over $MgSO_4$. Removal of solvent followed by column chromatography yields the hydroxylated compound.

Benzylic Hydroperoxide Rearrangements



Entry	Substrate	Temp. (°C)/Time (h)	Yield (%)[a]
a	R = 4-Methoxy	0/1.0	93
b	R = 3,4-Dimethoxy	0/1.0	87
c	R = 2,4-Dimethoxy	0/1.0	90
d	R = 2,6-Dimethoxy	0/1.0	93
e	R = 3,4,5-Trimethoxy	0/1.0	87
f	R = 4-Methyl	50/1.0	73
g	R = 2,4-Dimethyl	50/1.0	73
h	R = 4-Bromo	50/36	23

[a] All yields refer to isolated analytically pure compounds characterized by ^1H and ^{13}C NMR and IR.

In conclusion sodium perborate provides a safe, relatively mild method for benzylic hydroperoxide rearrangement of benzylic tertiary alcohols to produce phenols.

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