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Sodium Percarbonate: A Convenient Reagent for the Dakin Reaction

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Abstract: Sodium percarbonate, a readily available, inexpensive and easy to handle reagent efficiently oxidizes hydroxylated benzaldehydes and hydroxylated acetophenones to hydroxyphenols.

Phenols and their derivatives are fundamentally important substrates used extensively in organic synthesis. In the Dakin reaction, hydroxylated benzaldehydes are converted to hydroxy-phenols through the replacement of formyl groups by a hydroxyl moiety using alkaline hydrogen peroxide.[1] Other reagents have been employed to oxidize aromatic aldehydes to arylformates; these include peroxyacetic acid,[2] peroxybenzoic acid,[3] *m*-chloroperoxybenzoic acid[4] and organoperoxyselenic acid.[5]

Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) is a very inexpensive large scale industrial chemical which is extensively used in the detergent industry as a bleaching agent.[6] It has been used for the oxidation of sulfides,[7] amines,[7,8] organoboranes[9] as well as for the epoxidation of olefins[7] and hydrolysis of nitriles to amides.[10] We now wish to report that sodium percarbonate oxidizes hydroxylated benzaldehydes and acetophenones to hydroxy phenols in good yields (Table.)

In a typical procedure, a mixture of aromatic aldehyde (3.0 mmol) and sodium percarbonate (3.0 mmol) is dissolved in tetrahydrofuran (10.0 ml) and water (4.0 ml) and sonicated in an ultrasound bath under an argon atmosphere. The reaction is quenched with acetic acid (1.0 ml) and the solvent removed under vacuum. Methanol is added to the residue and the mixture filtered. The filtrate is concentrated under reduced pressure and chromatographed (silica gel; 30% ethyl acetate in hexanes).

para-Hydroxybenzaldehydes react more slowly than the corresponding *ortho*-hydroybenzaldehydes. *meta*-Hydroxybenzaldehyde fails to undergo oxidation. 4-Hydroxy-3-nitrobenzaldehyde also failed to react with $Na_2CO_3 \cdot 1.5H_2O_2$ which may be due to intramolecular hydrogen bonding. In addition to aromatic aldehydes, we examined the conversion of hydroxylated acetophenones to hydroxyphenols. 2-Hydroxyacetophenones (entries 11 and 13) were oxidized to catechols while 4-hydroxyacetophenones (entries 12 and 14) failed to undergo oxidation.

Dedication: Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

Table. Oxidation of Hydroxylated Benzaldehydes and Acetophenones to Hydroxyphenols

Entry	Substrate	Time (h)	Product	Yield (%)
1	Salicyladehyde	5	Catechol	91
2	4-Hydroxybenzaldehyde	8	Hydroquinone	86
3	3-Hydroxybenzaldehyde	20	-----------------------------	----
4	*o*-Vanillin	1	3-Methoxycatechol	95
5	2-Hydroxy-4-methoxybenzaldehyde	2	4-Methoxycatechol	83
6	Vanillin	4	2-Methoxyhydroquinone	93
7	5-Chloro-2-hydroxybenzaldehyde	5	4-Chlorocatechol	92
8	2-Chloro-4-hydroxybenzaldehyde	7	2-Chlorohydroquinone	62
9	2-Hydroxy-5-nitrobenzaldehyde	7	4-Nitrocatechol	60
10	4-Hydroxy-3-nitrobenzaldehyde	20	------------------------------	----
11	2-Hydroxyacetophenone[a]	8	Catechol	90
12	4-Hydroxyacetophenone	20	------------------------------	----
13	2-Hydroxy-4-methoxyacetophenone	7	4-Methoxycatechol	78[b]
14	3,5-Dimethoxy-4-hydroxyacetophenone	20	------------------------------	----

[a] A mixture of THF-DMF-H_2O (3:1:l) was used as a solvent for acetophenone reactions.
[b] Based on 80% conversion of the starting material.

In conclusion, we describe a safe and mild method for oxidizing hydroxylated benzaldehyde and hydroxylated acetophenones to hydroxyphenols.

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References:

1. Hassall, C.H. "Org. Reactions"; Wiley, New York, **1957**, vol. 9, pp. 73-106.
2. Boeseken, J.; Cohen, W. D.; Kip, C. J. *Rec. Trav. Chim. Pays-Bas.* **1936**, *55*, 815.
3. Ogata, Y.; Sawaki, Y. *J. Org. Chem.* **1969**, *34*, 3985.
4. Camps, F.; Coll, J.; Messeguer, A.; Pericas, M.A. *Tetrahedron Lett.* **1981**, *22*, 3895.
5. Syper, L. *Synthesis*, **1989**, 167.
6. Das, T. K.; Mandavawalla, A. K.; Dalta, S. K. *Colourage* **1983**, *301*, 25.
7. Ando, T.; Conk, D. G.; Kimura, T. *Chem. Lett.* **1986**, 665.
8. Zajac, W. W.; Walters, T.R.; Woods, J. M. *Synthesis*, **1988**, 808.
9. Kabalka, G. W.; Wadgaonkar, P. P.; Shoup, T.M. *Organometallics*, **1990**, *9*, 1316.
10. Kabalka, G. W.; Deshpande, S. M.; Wadgaonkar, P. P.; Chatla, N. *Syn. Commun.* **1990**, *20*, 1445.

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