

Oxidation of Benzaldehydes Catalyzed by Methyltrioxorhenium with Hydrogen Peroxide

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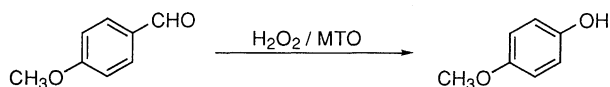
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Methyltrioxorhenium-catalyzed oxidation of benzaldehydes with hydrogen peroxide gives corresponding phenols in good yield. Benzaldehydes substituted with methoxy or hydroxyl groups at 2- and/or 4-position are good substrates for this reaction.

Oxidative synthesis of phenols from benzaldehydes by Baeyer-Villiger oxidation or Dakin reaction using percarboxylic acid or hydrogen peroxide is one of the important organic synthetic procedures.¹

Recently methyltrioxorhenium (MTO) was reported as an effective oxygenation catalyst with H_2O_2 for the epoxidation of olefins,² oxidation of (thiolato)cobalt complex,³ and oxygen transfer to bromide ion.⁴ The organorhenium compound forms peroxo complexes in the presence of H_2O_2 , and the peroxo species catalyze the oxygenations.^{5,6}

Here I wish to report the results of MTO-catalyzed H_2O_2 oxidation of benzaldehydes. For example, the oxidation of 4-methoxybenzaldehyde with H_2O_2 proceeds smoothly to form 4-methoxyphenol in 74% yield in the presence of 2 mol% catalyst.



A typical reaction procedure is as follows; 4-methoxybenzaldehyde (0.40 g, 2.9 mmol) was dissolved in oxidation

solution^{2,7} (H_2O_2 /EtOH, 1.0 M, 11 mL, 12 mmol) which was dried over anhydrous $MgSO_4$, and MTO (0.015 g, 0.059 mmol) was added to the mixture. MTO dissolved immediately with the change of the color of the solution to yellow which indicated the formation of peroxo complex.^{5,6} The mixture was stirred at 50°C for 24 hours. After the complete consumption of the aldehyde, the excess H_2O_2 was decomposed by pouring the mixture into aqueous sodium thiosulfite, and then the aqueous solution was acidified with conc. HCl. The products were extracted with diethyl ether, and were separated by silica gel column chromatography (dichloromethane as the eluent). 4-Methoxyphenol (0.27 g, 74%) was obtained as the main product with 4-methoxybenzoic acid (0.05 g, 11%) and ethyl 4-methoxybenzoate (0.03 g, 6%) as byproducts.

Several reaction conditions were examined using 4-methoxybenzaldehyde as the substrate. The results were summarized in Table 1. 4-Methoxyphenol was obtained as the main product with 4-methoxybenzoic acid and its ester in the cases of alcoholic solvents. The solvent affected the reactivity and the yield of phenol. Alcohols and tetrahydrofuran (THF) were found to be effective as the solvent. Ethanol was most effective among them for the synthesis of phenols, and *tert*-butyl alcohol, the most effective solvent for MTO-catalyzed epoxidation, was an inferior solvent to ethanol in this oxidation (entry 11). The non-alcoholic solvent like THF gave comparable yield with ethanol (entry 12). The oxidations of 4-methoxybenzaldehyde at 50°C and at 70°C gave the phenol in good yields. However the oxidations of 4-methoxybenzaldehyde at 30°C was slow and the yield of the phenol was very low (entry 3, 4, 5). Higher H_2O_2 concentration increased the yield of the benzoic acid, and lower

Table 1. Oxidation of 4-methoxybenzaldehyde with H_2O_2 / MTO in various conditions ^a

entry	oxidation solution		MTO mol%	temp., °C	conv. %	yield / % ^b		
	solvent	(H_2O_2 conc./M)				phenol ^c	benzoic acid ^d	ester
1	EtOH	1	1	50	97	46	14	12 ^e
2		0.5	2	50	90	41	9	7 ^e
3		1	2	30	54	8	12	18 ^e
4		1	2	50	100	74	11	6 ^e
5		1	2	70	100	75	11	8 ^e
6		3	2	50	100	61	17	5 ^e
7		1	5	50	88	51	15	7 ^e
8		1	10	50	68	24	18	6 ^e
9	MeOH	1	2	50	100	49	15	22 ^f
10	<i>iso</i> -PrOH	1	2	50	97	51	13	3 ^g
11	<i>tert</i> -BuOH	1	2	50	87	44	21	3 ^h
12	THF	1	2	50	100	67	11	-

^a Reaction conditions: 4-methoxybenzaldehyde (2.9 mmol), 50°C, 24h, 4 equivalent of H_2O_2 . ^b Isolated yield. ^c 4-Methoxyphenol.

^d 4-Methoxybenzoic acid. ^e Ethyl 4-methoxybenzoate. ^f Methyl 4-methoxybenzoate. ^g Isopropyl 4-methoxybenzoate.

^h *tert*-Butyl 4-methoxybenzoate.

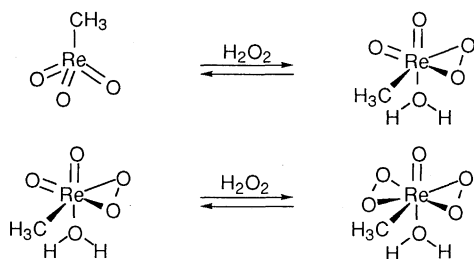
Table 2. Oxidation of benzaldehydes with H₂O₂ / MTO^a

entry	benzaldehyde	OS ^b	temp	time	conv.	yield / % ^c		
		equiv.	°C	h	%	phenol	benzoic acid	ester ^d
1	4-methoxy	4	50	24	100	74	11	6
2	2,4-dimethoxy	3	rt ^e	6	100	86	nd ^f	nd
3	3,4-dimethoxy	3	50	24	100	57	13	8
4	2,3,4-trimethoxy	4	rt	16	100	76	nd	nd
5	2,4,6-trimethoxy	4	rt	16	100	66	nd	nd
6	2-hydroxy	4	rt	24	>90	71	nd	nd
7	4-hydroxy	4	rt	17	100	72	11	3

^a 2 mol% MTO (entry 5, 6 mol%). ^b Oxidation solution, 1.0 M H₂O₂ / EtOH. ^c Isolated yield. ^d Ethyl ester of corresponding benzoic acid. ^e Room temperature. ^f Not determined.

H₂O₂ concentration decreased the rate of the reaction and the yield of phenol (entry 6, 4, 2). Though the oxidation of 4-methoxybenzaldehyde in ethanolic oxidation solution without MTO gave a small amount of the phenol very slowly, MTO was essential for the formation of phenol in THF. Interestingly, use of large amount of catalyst (~10 mol%) decreased the conversion and the yield of phenol (entry 7, 8).

As shown previously in the literature, MTO react with H₂O₂ to form monoperoxo and diperoxo complexes.³⁻⁶ These η²-peroxo complexes were suggested as the catalytically active species respectively for the epoxidation, oxidation of (thiolate)cobalt complex and bromide ion. In these cases, the reactions proceed via nucleophilic attack of the substrates to the peroxo oxygen of the complexes.³⁻⁵



The first step of the oxidation of benzaldehyde described here must involve the reaction of electrophilic carbonyl carbon of the aldehyde and the rhenium peroxo complex, and form peroxo intermediate (the true structure is unknown so far) which decompose with aryl migration like Baeyer-Villiger oxidation. This indicates that the peroxo-rhenium adduct plays an opposite role as nucleophile to the reported oxidations.³⁻⁵

Application of this catalytic Baeyer-Villiger type oxidation to other benzaldehyde substrates was performed using ethanolic oxidation solution. The results were summarized in Table 2.

Benzaldehydes substituted with methoxy group(s) at 2- and/or 4-position could be converted to the corresponding phenols in good yields. Hydroxylated benzaldehydes such as salicylaldehyde and 4-hydroxy-benzaldehyde were also oxidized to catechol and hydroquinone respectively in over 70% yield. The oxidation of 4-methyl- and 4-chlorobenzaldehyde gave corresponding benzoic acids and their ethyl esters as the major products with a small amount of corresponding phenols as byproducts. The oxidation of 1-phenylpropionaldehyde gave 1-phenylpropionic acid and its ethyl ester under the same conditions.

In summary, a variety of phenols have been effectively prepared from benzaldehydes by MTO-catalyzed hydrogen peroxide oxidation in good yield. The application of this catalytic system to other organic synthetic procedures is now in progress.

References and Notes

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- Preparation of oxidation solution: EtOH (290 mL) was mixed with 30% H₂O₂ (30 mL). The solution was stirred with anhydrous MgSO₄ (25 g) for 3h and then filtered. The oxidation solution was titrated and stored in a refrigerator.