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The Oxidation of Methoxy Aromatic Aldehydes With the system O_2 / iPrCHO / Metal Catalyst

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Abstract: The oxidation of methoxy aromatic aldehydes by the system O_2 / iPrCHO / metal catalyst proceeds in high yields of formates, almost without the formation of important quantities of carboxylic acids.

Various oxidations using molecular oxygen (1 atm) in the presence of metal catalysts and co-reactant aldehydes have been reported since the first oxidation of olefins to epoxides by Mukaiyama[1]. They include oxygenation of cyclic or acyclic ketones into the corresponding lactones or esters[2,3], aldehydes into carboxylic acids[4], enolates into the corresponding α-hydroxy carbonyl compounds[5]. We expected that oxidation of methoxy aromatic aldehydes, never reported to our knowledge, could be achieved, constituting an efficient alternative to the use of peracids. As modifications of the method frequently occur in the literature[6,7] involving the oxidation of the other functional groups cited above, we would like to report, in this Letter, our more significant results (Table).

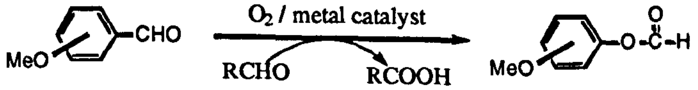

Table- Oxidation of methoxy aromatic aldehydes [a)]

Entry	Aromatic aldehyde	Metal catalyst (1 mole %)	Formate(%)	Remaining aldehyde(%)	Other products (%)
1[b)]	4-methoxy-	$Cu(OAc)_2.4\ H_2O$	87	8	4 (acid)
2	-	$Cu(acac)_2$	83	0	5 (acid); 3 (phenol)
3	-	$Ni(acac)_2$	67	0	26(acid); 5 (phenol)
4	2,4-dimethoxy-	$Ni(acac)_2$	94	2	
5	-	$Ni(dmp)_2$[1]	100	0	
6[c)d)]	-	K10-montmorillonite/$Ni(acac)_2$	100	0	
7	3,4-dimethoxy-	$Ni(acac)_2$	94	6	
8[d)]	-	$Ni(OAc)_2.4\ H_2O$	88	4	
9[e)]	2,5-dimethoxy-	$Cu(acac)_2$	75	17	7 (phenol)
10[f)]	-	$Cu(acac)_2$+$Ni(acac)_2$	87	8	
11[e)]	2,4,6-trimethoxy-	$Cu(acac)_2$	86	6	
12[f)]	3,4,5-trimethoxy-	$Cu(acac)_2$+$Ni(acac)_2$	25	75	

a) Reaction conditions:aromatic aldehyde 1.0 mmol., metal catalyst (1 mole%), isobutyraldehyde 3.0 mmol. in 1,2-dichloroethane (6.0 ml), 1atm. O_2, r.t., 21 h in dark. The percentages of products are determined by capillary chromatography. Identification by comparison of their retention times with those of authentic samples (also by 1H NMR for the formates). b) without co-reactant aldehyde. c) K 10-montmorillonite (50 mg) impregnated with $Ni(acac)_2$ according to ref 8. d) in ordinary light. e) 2 mole % of catalyst and 6.0 mmol of iPrCHO. f) 6.0 mmol.iPrCHO and 1mole% of each catalyst.

These oxidations are easily performed and very selective: oxidations of aldehydes into carboxylic acids are almost never observed, only formates being obtained in high yields. The only limitation lies in the differences of reactivity of aromatic aldehydes. The order of reactivities is as follows: 2,4-dimethoxy > 3,4-dimethoxy # 4-methoxy > 2,5-dimethoxy > 2,4,6-trimethoxy > 3,4,5-trimethoxy. Dimethoxy aryl groups are more reactive than trimethoxy and for both a methoxy substituent in para is important. But as the whole sequence cannot be easily interpreted, we intend to use theoretical methods of calculations to verify if a correlation exists between the number and the position of methoxy substituents and the HOMO coefficients of the carbons of the aryl groups participating in the transposition of Baeyer-Villiger (The peroxy group O-O of the intermediate reacts through its LUMO). Entry 1 apart (table 1), the recourse to an aldehyde co-reactant, serving as a sacrificial auxiliary, is mandatory, as is the use of a metal catalyst. Tetraphenylcyclopentadienone (TCPN), known as a quencher of singlet oxygen[9] ($^1O_2$) completely inhibits the reaction. Benzoquinone (BQ), a quencher of radicals, seems a little less efficient. These results agree with the supposed attachment of molecular oxygen to the metallic center, a situation favoring its transformation into a singlet oxygen active species able to react with methoxy aromatic aldehydes[9]. The Baeyer-Villiger transposition may then take place, probably through a radical clivage of the peroxy group O-O of the intermediate: one of the oxygen atoms is found in the formate, the other one is quenched by iPrCHO, an effective co-reactant for this purpose. Baeyer-Villiger oxidation of aromatic aldehydes bearing electron-donating substituents has been performed by using peracids[10], such as mCPBA ou MPSA (monopersuccinic acid, an easy to use and efficient compound we are experimenting in our laboratory). As formates are easily hydrolysable in basic media, the method may be considered as an interesting potential transformation of aromatic aldehydes into the corresponding phenols, some of them being difficult to obtain by standard methods.

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