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Fast Synthesis of Aromatic Aldehydes from Benzylic Bromides without Solvent under Microwave Irradiation

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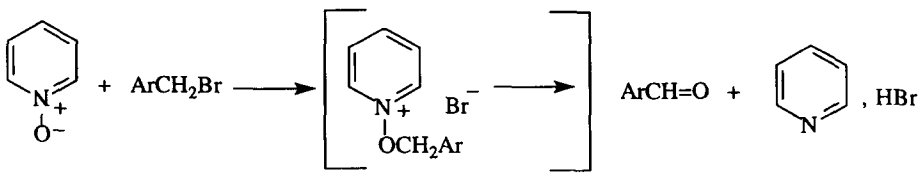
Abstract : Pyridine N-oxide reacts in a single step with benzylic bromides under microwave irradiation to afford high yields of aromatic aldehydes. Copyright © 1996 Published by Elsevier Science Ltd

Very few oxidations have been conducted under microwave irradiation : Gedye et al[1] have reported the rapid transformation of toluene with permanganate to benzoic acid but attempts to optimize the process led to an explosion ; Avarez et al[2] have aromatised dihydropyridines to pyridines with nitric acid and bentonite.

Formation of the N-alkoxy salts from heterocyclic N-oxides and alkyl halides is a well-known reaction[3] ; evolution of these salts with bases may lead to (i) regeneration of the heterocyclic N-oxide, (ii) formation of an alkene by proton abstraction from the carbon β to the oxygen and (iii) formation of a carbonyl derivative by proton abstraction from the carbon α to the oxygen, which corresponds to a mild oxidation of the alkyl halide to a carbonyl . Use of weak nucleophilic bases as 1,8-diazabicyclo(5,4,0)undecene (DBU) favors the elimination pathways.



The similarity of this reaction to the Kornblum reaction with alkoxysulfonium salts[4] is noteworthy.

We report the fast one-step preparation of aromatic aldehydes from pyridine N-oxide and benzylic halides under microwave irradiation and without solvent and base. The reaction affords high yields of aldehydes with aromatic bromides substituted by electrowithdrawing groups or poor electrodonating groups ; when the benzenic ring is substituted by highly electrodonating groups, the reaction requires an excess of pyridine N-oxide during a shorter time to give good yields of aldehyde (Table 1).

Table 1 - Reaction of benzylic bromides with pyridine N-oxides under microwave irradiation.

Benzylic bromides	Pyridine N-oxide %*	Power (W)	Time (s)	Yields %
p-nitrobenzyl bromide	120	160	120	90
benzyl bromide	120	160	120	90
p-methylbenzyl bromide	120	160	120	80
p-acetoxybenzyl bromide	120	350	40	40 **
p-methoxybenzyl bromide	120	160	120	3
p-methoxybenzyl bromide	200	350	40	92
2-(bromomethyl)naphtalene	120	160	120	30***
cinnamyl bromide	100	160	120	15

* with regard to the bromide ** with 60% unreacted bromide; longer times or larger amounts of N-Oxide lead to degradation products. *** with 10% unreacted bromide

In a typical procedure, benzyl bromide (0.85g, 5mmol) and pyridine N-oxide (0.57g, 6mmol) are placed in a microwave oven and irradiated for 2 mn (160 W). After cooling, diluted HCl is added and the aldehyde is extracted with ether. The organic layer is washed with diluted NaOH and dried over $MgSO_4$. Evaporation of the solvent gives the crude product of high chemical purity. Similar results are obtained with double or triple the amount and adjusting the irradiation power.

Studies of this reaction with aliphatic halides and deuterated halides are in progress.

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