

## MICROWAVE-EXPEDITED SYNTHESIS OF AROMATIC ALDEHYDES AND KETONES FROM ALKYL HALIDES WITHOUT SOLVENT USING WET MONTMORILLONITE K 10 SUPPORTED IODIC ACID AS OXIDANT

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### Abstract

The efficient microwave-assisted synthesis of aldehydes and ketones over wet montmorillonite K 10 using HIO<sub>3</sub> as oxidizing agent is described. This fast oxidation protocol is applicable to variety of alkyl halides.

**Key words:** alkyl halides, iodic acid, Montmorillonite K10

### Introduction

Recently microwave-assisted solvent-free synthesis in organic reactions has been of growing interest as an efficient, economic and clean procedure ('green chemistry').<sup>1-9</sup> Over the past few years, a considerable number of reactions have been developed in which inorganic solid supports such as alumina, silica gel and montmorillonite appeared to be useful in terms of mildness of conditions, yield and convenience.<sup>10-12</sup>

Synthesis of aldehydes and ketones from alkyl halides is an important method for the preparation of aldehydes and ketones. In this regard various reagents have been developed: dimethyl sulfoxide,<sup>13-14</sup> *N,N*-dimethyl-4-nitrosoaniline,<sup>15</sup> nitronate anion and Pd(PPh<sub>3</sub>),<sup>16</sup> pyridine *N*-oxides,<sup>17</sup> and other amine oxides,<sup>18</sup> chromate and dichromate systems,<sup>19</sup> silver nitrate,<sup>20</sup> hexamethylene tetraamine,<sup>21</sup> pyrazinyl sulfoxides.<sup>22</sup>

Some of these reagents or catalysts give low yields,<sup>13,14,17,18,21</sup> others require the use of high temperature,<sup>13,14,21</sup> long reaction time,<sup>15,16,22</sup> bulk requirement of the solid bed.<sup>12</sup>

Barbry and Champagne have reported a solvent free procedure under microwave irradiation for the oxidation of benzylic bromides to aromatic aldehydes using pyridine

*N*-oxide as oxidant.<sup>23</sup> By this method only benzylic bromides can be oxidized to their corresponding aromatic aldehydes.

Recently NaIO<sub>4</sub>-DMF,<sup>24</sup> bromate exchange resin,<sup>25</sup> 2-dimethylamino-*N,N*-dimethylaniline *N*-oxide<sup>26</sup> and photooxidation of alkyl bromides with mesoporous silica FSM-16<sup>27</sup> have been reported for the conversion of alkyl halides to the aldehydes and ketones. However these procedures have some limitations such as long reaction time.

Oxidation of alkyl halides and alkyl tosylates to their corresponding aldehydes and ketones by molecular oxygen catalyzed by Kieselghur supported CuCl is another method, which was developed by our group.<sup>28</sup>

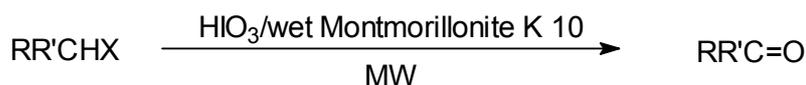
### Results and discussion

Herein we wish to report a fast and convenient procedure for the one step oxidation of alkyl halides to the aldehydes and ketones using HIO<sub>3</sub>/wet montmorillonite K 10 under microwave irradiation and without solvent (Table 1). This method offers some advantages in terms of simplicity of performance, solvent-free conditions, no side product formation, very low reaction time and also a wide range of alkyl halides can be converted to their corresponding aromatic aldehydes and ketones. In addition the montmorillonite K 10 clay can be recycled after activation (yields remained 86% after 3 re-uses for the oxidation of benzyl chloride to benzaldehyde).

Some experiments have been performed to check the efficiency of microwave irradiation in our synthesis. When this reaction was done in methanol, or benzene under reflux condition, after 12 hours only starting materials were observed on the TLC plate. In the absence of the montmorillonite K 10 yields are much lower in longer time.

### Conclusions

In summary we have extended successfully the application of montmorillonite K 10 supported iodic acid under microwave irradiation and without solvent. This method offers some advantages in terms of simplicity of performance, solvent free condition, no side product formation and very low reaction time. In addition, the montmorillonite K 10 clay can be recycled after activation.



Scheme 1

**Table 1.** Microwave-assisted oxidation of alkyl halides to the corresponding aldehydes and ketones over wet montmorillonite K 10 using HIO<sub>3</sub> as oxidant.

Entry	Substrate <sup>a</sup>	Reaction time (sec.)	Product	Yield <sup>b</sup> %
1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	60.0	C <sub>6</sub> H <sub>5</sub> CHO	91
2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	50.0	C <sub>6</sub> H <sub>5</sub> CHO	97
3	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	60.0	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub> CHO	90
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	120.0	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	87
5	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	90.0	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	89
6	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	90.0	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	85
7	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	90.0	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	93
8	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	90.0	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> CHO	86
9	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> I	40.0	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	90
10	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHBr	90.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	94
11	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCl	120.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	88
12	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHCl	120.0	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CO	93
13	α-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> Br	100.0	α-C <sub>10</sub> H <sub>7</sub> CHO	87
14	α-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> Cl	90.0	α-C <sub>10</sub> H <sub>7</sub> CHO	92

<sup>a</sup>α-C<sub>10</sub>H<sub>7</sub> is 1-naphthyl, <sup>b</sup>the yields of isolated products.

## Experimental

**Typical procedure for the oxidation of benzyl chloride to benzaldehyde:** Wet montmorillonite K 10 was prepared by the addition of 50 mL of distilled water into 450 g of dry montmorillonite K 10 (surface 200 m<sup>2</sup>/g, Fluka) followed by mixing for 30 minutes; it must be stored in a well closed container.

Benzyl chloride (0.56 g, 5 mmol), iodic acid (1.76 g, 10 mmol) and wet montmorillonite K 10 (5 g) were taken in a microwave oven (Butane household apparatus) and irradiated (1000 W) for 1 min. The progress of the reaction was monitored by thin layer chromatography (10% ethyl acetate in petroleum ether). After completion of the reaction, the product was extracted into dichloromethane (3×15 mL) followed by decolorisation with activated charcoal, then it was filtered after 5 minutes and dried over sodium sulfate. Evaporation of the solvent followed by distillation of the residue gave 0.48 g (91% yield) of benzaldehyde, which was identified by its boiling point, IR and <sup>1</sup>H-NMR spectroscopic properties.

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### Povzetek

Opisana je sinteza aldehydov in ketonov z oksidantom HIO<sub>3</sub> na vlažnem montmorilonitu K 10 s pomočjo mikrovalov. Metoda je uporabna na različnih alkil halidih.