

## Simple, Efficient and Solvent-Free Method for Quantitative Regeneration of Carbonyl Compounds from Oximes by Gaseous Bromine

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Ketoximes and aldoximes are efficiently deprotected to their corresponding carbonyl compounds using bromine in the gas form under solvent-free conditions. This method is high yielding, fast, clean and more suitable for practical organic synthesis.

**Key Words:** Oximes, Gaseous bromine, Solvent-free conditions.

### INTRODUCTION

Oximes of aldehydes and ketones are generally solid and crystalline compounds. They constitute an efficient method for the isolation, purification and characterization of carbonyl compounds<sup>1</sup>. In addition they can be prepared from non-carbonyls<sup>2a-c</sup> and therefore, their transformation to the corresponding carbonyl compounds is an important reaction to prepare aldehydes and ketones. So far, a good number of methods based on hydrolytic<sup>3</sup>, reductive<sup>4</sup> and oxidative<sup>5</sup> reactions have been developed for deoxygenation. The oxidative reactions methods make use of different kinds of oxidizing agents. These include pyridinium chlorochromate<sup>5</sup>, methyl triphenylphosphonium peroxydisulfate<sup>6</sup>, aqueous hydrogen peroxide activated by ammonium heptamolybdate catalyst<sup>7</sup>, chromic anhydride, chlorotrimethylsilane<sup>8</sup>, ionene supported peroxydisulfates<sup>9</sup>, ammonium persulfate-silica gel<sup>10</sup> and others such as mixed-addenda vanadomolybdophosphate,  $H_6PMo_9V_3O_{40}$ <sup>11</sup>, dinitrogen tetroxide<sup>12</sup>, silphos[ $PCl_3-n(SiO_2)_n$ ]<sup>13</sup>,  $MoO_2(acac)_2$ <sup>14</sup>, periodic acid<sup>15</sup> and photosensitized oxidative by platinum(II) terpyridyl acetylidate complex<sup>16</sup>.

Herein, the authors reported gaseous bromine, as a fast, efficient and clean reagent for the deprotection of oximes under solvent-free conditions. The method is superior as the reactions occur at room temperature with rapid rate, with no formation of over oxidation products, with high yields and is easy work up.

### EXPERIMENTAL

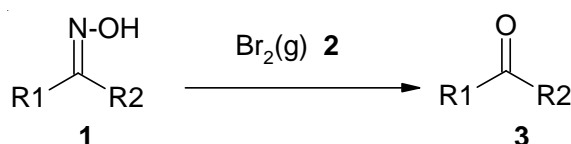
All chemicals were purchased from Merck, Aldrich or Fluka and used as received. Melting points were measured by using the capillary tube method with an electrothermal 9200 apparatus and are uncorrected. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. Infrared (IR) spectra were recorded on a Perkin-Elmer 1720-X FT-IR spectrometer using KBr pellets.

**General procedure for the regeneration of carbonyl compounds from oximes:** To obtain gaseous bromine, a 100 mL flask is filled with 100 mg of liquid bromine, cool it in an ice-water bath and connect it to a vacuum pump. After evacuation, the flask was warmed up to room temperature affording the required gaseous bromine. In a typical experiment, another 100 mL round-bottom flask was charged with oxime (1.0 mmol) and then evacuated. The flask was filled with gaseous bromine (1.3-1.5 mmol) at a pressure of 0.25 bars. After required time, the flask was evacuated. The progress of the reaction was monitored by TLC. To the reaction mixture hexane (5 mL) was added and the organic layer was washed with H<sub>2</sub>O (3-5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave the corresponding carbonyl compound.

**Detection method:** The products obtained were identified by comparing of their spectral data and m.p. with those of authentic samples and literature references.

## RESULTS AND DISCUSSION

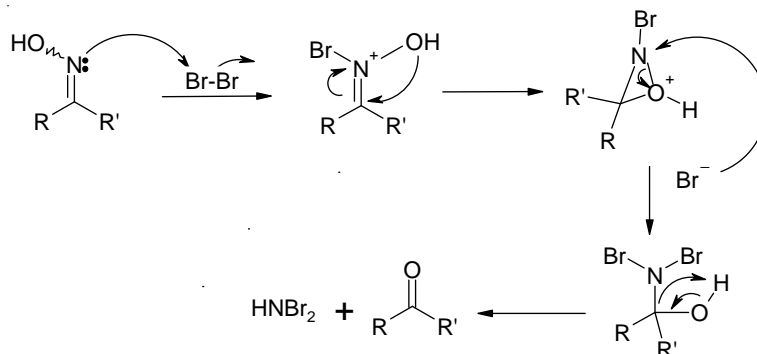
In continuation of our previous studies on the selective oxidative deprotection of carbonyl derivatives to the corresponding aldehydes or ketones by gaseous NO<sub>2</sub><sup>17</sup>, it is observed that by exposing the oximes products (**1**) with excess bromine gas (**2**) at room temperature, a rapid exothermic reaction takes place. Subsequent workup afforded the desired carbonyl compounds (**3**) in almost high yields (**Scheme-I**). To optimize the reaction conditions, 4-chlorobenzaldehyde oxime was used as a model compound and effect of different amounts of Br<sub>2</sub> gas on its oxidative cleavage to 4-chloro benzaldehyde was studied.



**Scheme-I:** Regeneration of carbonyls from oximes by bromine gas

The complete conversion of the model compound was observed, when at least 1.0 equivalent of bromine gas was used. Direct TLC of the crude reaction product after evacuation (without addition of water) has proved that the producing of the carbonyl functional group does not require any external oxygen donor. It means that the oxygen atom of the oxime appears in the final aldehyde. The odour of the crude product was significantly from 4-chlorobenzaldehyde. The detailed mechanism of the reaction is not clear at this stage and is under further investigations, but a plausible mechanism is suggested in **Scheme-II**.

Having the optimal reaction conditions in hand, the reactivity of various aldehyde and ketone oximes were investigated in the next step. The results have been summarized in Table-1.



**Scheme-II:** Suggested mechanism of regeneration of carbonyls from oximes by Br<sub>2</sub>

TABLE-1  
DEPROTECTION OF OXIMES UNDER SOLVENT-FREE CONDITIONS

Entry	R	R'	Temp. (°C)	Time (min)	Yield (%)
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	25	5	100
2	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	25	5	94
3	<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	25	5	91
4	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	25	5	76
5	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	H	25	5	67
6	<i>p</i> -NMe <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	H	25	5	78
7	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	H	25	5	95
8	<i>p</i> -OMeC <sub>6</sub> H <sub>4</sub>	H	25	5	84
9	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	H	25	5	74
10	<i>o</i> -OMeC <sub>6</sub> H <sub>4</sub>	H	25	5	88
11	Furyl	H	25	5	70
12	Thiophenyl	H	25	5	72
13	CH(Me) <sub>2</sub>	H	25	5	62
14	PhCH=CH <sub>2</sub>	H	25	5	84
15	CH <sub>3</sub> CH=CH	H	25	5	75
16	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Me	25	5	62
17	C <sub>6</sub> H <sub>5</sub>	Me	25	5	75

As evident from Table-1, the reaction is rather general; oximes of aromatic aldehydes and ketones as well as aliphatic and  $\alpha,\beta$ -unsaturated aldehydes reacted smoothly to regenerate the desired carbonyl compounds in high yields within very short reaction times. The  $\alpha,\beta$ -unsaturated compounds such as cinnamaldehyde oxime (**14**) and crotonaldehyde oxime (**15**) underwent chemoselective regeneration in high yields without affecting the C=C bond.

### Conclusion

Gaseous bromine is a very efficient reagent for oxidative regeneration of carbonyls from oximes and in a solvent-free procedure. The method is very simple, produces no waste and needs generally short reaction times.

### ACKNOWLEDGEMENT

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