

[a003]

## Quantitative Regeneration of Carbonyl Compounds from Oximes and hydrazones by Gaseous Nitrogen Dioxide

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### Abstract

Treatment of various oximes and phenylhydrazones with gaseous nitrogen dioxide at room temperature afforded the corresponding carbonyl compounds in high to quantitative yields and a simple and solventless method.

### Introduction

Nitrogen derivatives of aldehydes and ketones such as oximes are highly crystalline compounds. They constitute a very efficient method for the isolation, purification, and characterization of carbonyl compounds.<sup>1</sup> Oximes not only serve as protecting groups for carbonyl compounds<sup>2</sup> but also can be transformed to nitriles<sup>3</sup> and amides via Beckmann rearrangement<sup>4a</sup>, or can serve for activating the carbonyl group<sup>5</sup>. In addition, oximes can be prepared from non-carbonyl compounds<sup>6</sup> and therefore, regeneration of carbonyl compounds from oximes is an important synthetic route. Some of the methods reported earlier for deoxygenation of carbonyl compounds consist of oxidative<sup>7a</sup> or reductive methods<sup>7c</sup>, using for example trimethylsilyl chlorochromate<sup>8</sup>, titanium silicalite-1<sup>9</sup>, dimethyl dioxirane, *t*-butylhydroperoxide<sup>10</sup>, *o*-iodoxybenzoic acid (IBX)<sup>11</sup>, manganese triacetate<sup>12</sup>, ammonium persulphate-silica<sup>13</sup>, Dess–Martin periodinane<sup>14</sup>, quinolinium fluorochromate<sup>15</sup>, peroxymonosulfate on silica gel<sup>16</sup>, 3- carboxypyridinium chlorochromate<sup>17</sup>, etc. Some of these reagents suffer from one or other disadvantages such as long reaction times, difficulties in isolation of products, expense and also the potential to cause explosions by excessive heating during preparation. Moreover, many of the methods cited in the literature describe the deoxygenation of aldoximes, which afford low yields of aldehydes as the liberated aldehydes are overoxidized.

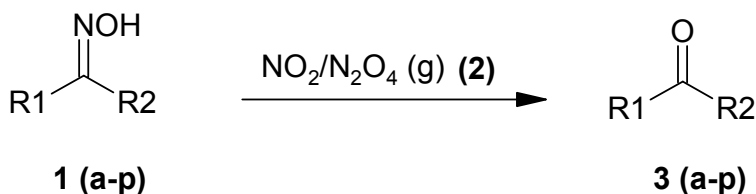
In this paper, we wish to report gaseous nitrogen dioxide as an efficient reagent for the oxidative deprotection of oximes and phenylhydrazone to their carbonyl compounds in high to quantitative yield in a simple and solventless method.

### Results and Discussions

The absolutely solvent-free reaction of 50 mg *p*-chlorobenzaldehyde oxime with 0.6 bar gaseous nitrogen dioxide affords the corresponding aldehyde with 100% yield in less than 5 minutes. The method is superior as it regenerates the corresponding aldehyde quantitatively, whereas some known methods yields much less, e.g. 78% yield on oxidative deprotection by metalloporphyrin and heteropoly acid<sup>18</sup>, 89 % yield on oxidative deprotection of reactants by 2, 6-dicarboxypyridinium chlorochromate<sup>19</sup>, 90%

yield on oxidative deprotection by poly [4-vinyl-*N,N*-dichlorobenzenesulfonamide]<sup>19</sup> and 80% yield on cleavage of C=N bond by Zr(HSO<sub>4</sub>)<sub>4</sub><sup>20</sup>.

Adopting the above method, various aldehydes and ketones have been regenerated from the corresponding oximes (Scheme 1, Table 1).



Scheme 1. Quantitative regeneration of carbonyl compounds from oximes

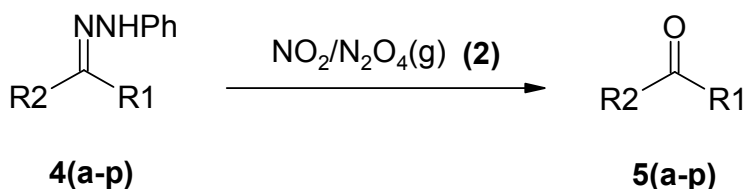
The method did not produce any waste or over-oxidized product (acid) and is suitable for aliphatic aldoximes (**1i**, **1n**), as well as aromatic ones. Ketoximes such as acetophenone oxime (**1p**) and *p*-nitroacetophenone oxime (**1o**) react also quantitatively to the corresponding ketones. In most cases no further purification is needed. MPs and IRs of the crude reaction products correlate well with the literature values.

Table 1. Conversion of oximes to carbonyl compounds

entry	R1	R2	Temp.(°C)	Time.(min)	Conversion (%)
<b>1a</b>	H	<i>p</i> -ClPh	-4	3	100 <sup>a</sup>
<b>1b</b>	H	<i>m</i> -NO <sub>2</sub> Ph	-5	1.5	100
<b>1c</b>	H	<i>o</i> -NO <sub>2</sub> Ph	-8	3	100
<b>1d</b>	H	<i>p</i> -NO <sub>2</sub> Ph	-5	2	100 <sup>b</sup>
<b>1e</b>	H	<i>p</i> -CNPh	0	6	100
<b>1f</b>	H	<i>p</i> -N(Me) <sub>2</sub> Ph	0	3	100
<b>1g</b>	H	<i>p</i> -MePh	r.t	2	100 <sup>c</sup>
<b>1h</b>	H	<i>p</i> -OMePh	r.t	3	100
<b>1i</b>	H	CH(Me) <sub>2</sub>	r.t	2	100
<b>1j</b>	H	<i>p</i> -BrPh	r.t	5	100
<b>1k</b>	H	<i>p</i> -OHPh	r.t	2	100 <sup>d</sup>
<b>1l</b>	H	<i>o</i> -OMe-Ph	r.t	3	100
<b>1m</b>	H	PhCH=CH <sub>2</sub>	r.t	1	100
<b>1n</b>	H	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub>	r.t	1.5	100
<b>1o</b>	Me	<i>p</i> -NO <sub>2</sub> Ph	r.t	5	100
<b>1p</b>	Me	Ph	r.t	3	100 <sup>e</sup>

<sup>a,b,c,d,e</sup> Typical isolated yields are 99, 97.6, 98.3, 98, 99 % respectively.

Not only oximes but also phenylhydrazones (**4**) can be transformed to corresponding aldehydes and ketones in a similar manner (Scheme 2).



Scheme 2. Quantitative regeneration of carbonyl compounds from phenylhydrazones

Again, the reaction is very simple, clean and produces no waste. Various carbonyls were regenerated from corresponding phenylhydrazones (Table 2).

Table 2. Conversion of phenylhydrazones to carbonyl compounds

Entry	R1	R2	Temp.(°C)	Time.(min)	Conversion (%)
<b>4a</b>	H	<i>p</i> -ClPh	r.t	2	100 <sup>a</sup>
<b>4b</b>	H	<i>m</i> -NO <sub>2</sub> Ph	-5	5	100
<b>4c</b>	H	<i>o</i> -NO <sub>2</sub> Ph	-5	5	100
<b>4d</b>	H	<i>p</i> -NO <sub>2</sub> Ph	-4	6	100 <sup>b</sup>
<b>4e</b>	H	<i>p</i> -CNPh	r.t	3	100
<b>4f</b>	H	<i>p</i> -N(Me) <sub>2</sub> Ph	r.t	1	100
<b>4g</b>	H	<i>p</i> -MePh	r.t	1.5	100 <sup>c</sup>
<b>4h</b>	H	<i>p</i> -OMePh	r.t	4	100
<b>4i</b>	H	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub>	r.t	2	100
<b>4j</b>	H	<i>p</i> -BrPh	r.t	3	100
<b>4k</b>	H	<i>p</i> -OHPh	r.t	1	100 <sup>d</sup>
<b>4l</b>	H	<i>o</i> -OMePh	r.t	5	100
<b>4m</b>	H	PhCH=CH <sub>2</sub>	r.t	4	100
<b>4n</b>	vaniline		r.t	2	100
<b>4o</b>	Me	<i>p</i> -NO <sub>2</sub> Ph	r.t	5	100
<b>4p</b>	Me	Ph	r.t	4	100 <sup>e</sup>

<sup>a,b,c,d,e</sup> Typical isolated yields are 98.5, 99, 98.6, 97.8, 98.5% respectively.

## Experimental Section

All the products were identified by comparison of their spectral data and/or melting point with those reported in literatures.<sup>21, 22</sup>

### **General procedure for the regeneration of carbonyl compounds from oximes.**

In a typical experiment, a 100 mL round-bottom flask was charged with oxime (1 mmol) and then evacuated. The flask was filled with NO<sub>2</sub> at a pressure of 0.6 bar. The progress of the reaction was monitored by TLC. After the required time, dichloromethane (3-10 mL) and water (3 -10 mL) was added. The organic layer was washed with water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave the carbonyl compound which was crystallized from 96% ethanol, if necessary. The product obtained was identified by comparing of its spectral data and m.p. with those of authentic samples and literature references. The results are summarized in Table 1.

### **General procedure for the regeneration of carbonyl compounds from phenylhydrazones**

Principally the similar protocol as for oximes was followed for the regeneration of carbonyls from their phenylhydrazones.

### **Conclusion**

Gaseous NO<sub>2</sub> is a very efficient reagent for oxidative regeneration of carbonyls from oximes and phenylhydrazones in a solvent-free procedure. The method is very simple, produces no waste and needs generally short reaction times.

### **Acknowledgment**

We acknowledge Iran University of Science and Technology (IUST) for partial financial support of this work.

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