

## An efficient and selective method for conversion of oximes, semicarbazones and phenylhydrazones to the corresponding carbonyl compounds under solvent-free conditions

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### ABSTRACT

*o*-Xylylenebis (triphenylphosphonium peroxymonosulfate) (1) was easily prepared from an aqueous solution of oxone and *o*-xylylenebis(triphenylphosphonium bromide). This Compound (1) is a useful and selective reagent for conversion of oximes, semicarbazones and phenylhydrazones to the corresponding carbonyl compounds. The reaction was carried out under solvent-free conditions and in the presence of catalytic amount of aluminium chloride. This method shows a good selectivity in oxidation of oximes, semicarbazones and phenylhydrazones in the presence of aliphatic and aromatic alcohols. The advantages of the present method include good functional group tolerance, high yields of products, simple experimental procedure and purification, no solvent and short reaction times.

**Keywords:** Oxidation; Oxime; Semicarbazone; Phenylhydrazone; Solvent-free.

### 1. Introduction

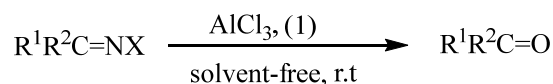
Oximes, semicarbazones and phenylhydrazones are highly crystalline compounds, which are very useful for the purification and characterization of carbonyl compounds. These derivatives are also used as efficient protecting groups for aldehydes and ketones [1]. Since, the regeneration of carbonyl compounds under mild conditions is important, extensive studies on the cleavage of these derivatives to the parent carbonyl compounds have been carried out. Several deprotection procedures have been developed [2] that have some advantages over the classical hydrolysis method [3], but some of the published methods require strongly oxidative or reducing conditions, basic or acidic media, tedious procedures or expensive reagents [4]. Therefore, there is still demand to investigate a mild, selective, non-hazardous and inexpensive reagent for this transformation. On the other hand, heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years [5].

The advantage of these methods over conventional homogenous reaction is that they provide greater selectivity, enhanced reaction rates, cleaner products, and manipulative simplicity. In continuation of our ongoing program to develop environmentally benign methods using solid supports [6], here we report the conversion of C=N derivative using *o*-xylylenebis (triphenylphosphonium peroxy-monosulfate) (1) under very mild conditions.

*o*-Xylylenebis (triphenylphosphonium peroxymonosulfate) was easily prepared from an aqueous solution of oxone and *o*-xylylenebis-(triphenylphosphonium bromide) [7] in a quantitative yield at room temperature which was used for the selective oxidation of benzylic alcohols and hydroquinones [8].

Using compound (1) in the presence of 0.1 molar ratio of aluminium chloride, various oximes, semicarbazones and phenylhydrazones have been successfully deprotected to their corresponding aldehydes and ketones in good to excellent yields. The process involves simply mixing reagent (1), aluminium chloride, and oximes, semicarbazones or phenylhydrazones in a mortar and grinding the mixture at ambient temperature (Scheme 1).

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$\text{R}^1, \text{R}^2 =$  alkyl, aryl

$\text{X} = \text{OH}, \text{NHPH}, \text{NHCONH}_2$

**Scheme 1.** Deprotection of oximes, semicarbazones and phenylhydrazones to their corresponding aldehydes and ketones.

## 2. Experimental

### 2.1. General procedure

A mixture of substrate (1 mmol), reagent (1) (1 mmol) and aluminum chloride (0.1 mmol) was ground in a mortar and pestle until TLC showed complete disappearance of starting substrate. Diethyl ether (10 mL) was added to the reaction mixture and, after vigorous stirring, the mixture was washed with water and filtered. The filtrate was dried and evaporated to give almost pure products. If necessary, the product was purified by column chromatography.

## 3. Results and Discussion

All the products are known compounds and were characterized by  $^1\text{H}$ NMR, IR analysis and physical characteristics. To find the optimum conditions, acetophenone oxime as a model substrate was treated with different molar ratio of oxidant and different Lewis acids such as  $\text{AlCl}_3$ ,  $\text{BiCl}_3$  and  $\text{FeCl}_3$ . The best result obtained using molar ratio of oxime to oxidant (1:1) with 0.1 molar ratio of aluminum chloride (Table 1).

We have also examined the reaction of acetophenone oxime under optimum conditions with oxone and observed that even at higher temperature and longer reaction time, no product was formed. This indicates that *o*-xylylenebis(triphenylphosphonium) cation as a counterion for  $\text{HSO}_5^-$  has an extensive effect in this transformation. However using our method, a wide variety of alkyl, aryl oximes, semicarbazones and phenylhydrazones were converted to their corresponding carbonyl compounds, in high yields within short reaction times (Table 2).

As shown in Table 2, a variety of oximes (aliphatic and aromatic), semicarbazones and phenylhydrazones were transformed to their corresponding carbonyl compounds under optimum reaction conditions. These results indicate the generality of this method. The procedure is effective for the cleavage of sterically hindered oxime (Table 2, entry 13). It is interesting to mention that many functional groups such as halogens, methyl, methoxy, hydroxyl and nitro, remained intact under this reaction conditions. Another advantage of this method is that the unsaturated derivatives of cinnamaldehyde converted very efficiently to the

corresponding carbonyl compounds without affecting C=C bond (Table 2, entries 14 and 21).

A plausible mechanism for reaction is shown in Scheme 2. Reagent (1) being an electrophilic oxygen donor oxidized oxime I to intermediates II which can exist in equilibrium with unstable intermediates III leads to parent carbonyl compounds [9].

We have further studied the selectivity of this method in oxidation of oximes, semicarbazones and phenylhydrazones in the presence of aliphatic and aromatic alcohols. As an example, when a mixture of an equimolar amount of cyclohexanone oxime and 2-phenylethylalcohol was treated with reagent (1), only the oxime was selectively converted to cyclohexanone and 2-phenylethylalcohol recovered quantitatively from reaction mixture.

However, treatment of cyclohexanone oxime in the presence of benzyl alcohol, led to exclusive formation of benzaldehyde in 96% yield and the oxime remained intact. This selectivity was not observed with other similar reagents.

In order to investigate see the drawbacks and advantages of this method, we have compared some of our results with those reported in the literature (Table 3). As it can be seen in Table 3, that *o*-xylylenebis(triphenylphosphonium peroxymonosulfate) can transform C=N derivatives to their corresponding carbonyl compounds, under solid phase conditions at room temperature with higher yield and shorter reaction time.

## 4. Conclusions

In conclusion, we have introduced an easy method under solid-state conditions which offers carbonyl compounds from their C=N derivatives in a short reaction time and excellent yield. This oxidation system is able not only to convert complicated oximes to their parent carbonyl but also shows a good selectivity in oxidation of oximes in the presence of aliphatic alcohols and in the oxidation of aromatic alcohols in the presence of oximes.

## Acknowledgment

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**Table 1.** Catalyst effect on the reaction.

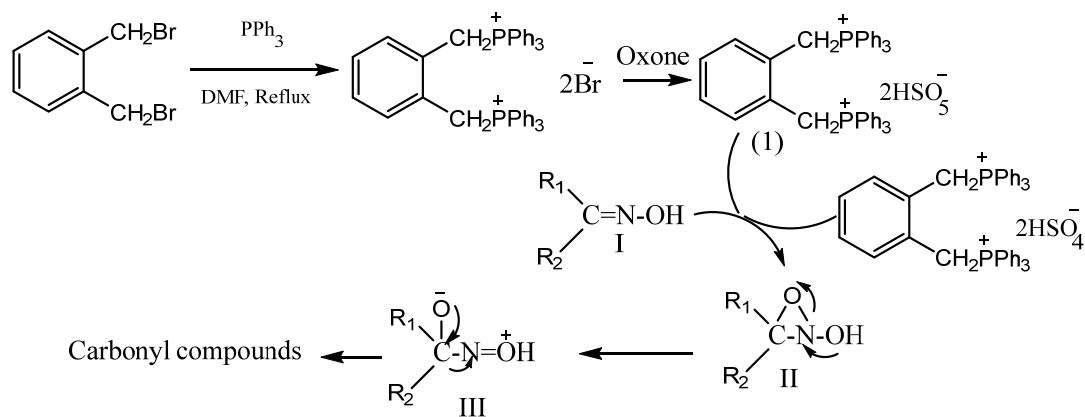
Entry	Catalyst	Yield (%) <sup>a</sup>
1	$\text{AlCl}_3$	96
2	$\text{FeCl}_3$	38
3	$\text{BiCl}_3$	35

<sup>a</sup>Acetophenone oxime (1mmol), reagent (1) (1mmol), 0.1 molar ratio of catalyst.

**Table 2.** Conversion of oximes, semicarbazones and phenylhydrazones to carbonyl compounds with reagent (1).<sup>a</sup>

Entry	Substrate	Time (min)	Yield (%) <sup>b</sup>	m.p.(°C) or b.p.(°C)	
				Found	Reported <sup>d</sup>
1	(Ph) <sub>2</sub> CNOH	25	90	47-49	48.5-49
2	(Ph)(Me)CNOH	15	96	201-203	202
3	(Ph)(C <sub>2</sub> H <sub>5</sub> )CNOH	10	98	216-220	218
4	3-Pyridine carboxaldehyde oxime	25	80	78-81	78-81
5	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CHNOH	10	90	212-214	213-214
6	2,6-Dichlorobenzaldehydeoxime	15	88	70-73	71
7	2-Tetralone oxime	10	96	119-121	131-133
8	Cyclohexanone oxime	5	95	154-157	154-156
9	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CHNOH	15	88	57-60	59-60
10	(PhCO)(Me)CNOH	20	96	221-224	222
11	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )(Me)CNOH	25	85 <sup>c</sup>	234	232
12	( <i>p</i> -PhC <sub>6</sub> H <sub>4</sub> )(Me)CNOH	25	90 <sup>c</sup>	116-118	117-119
13	Camphor oxime	25	89 <sup>c</sup>	117-179	179
14	Cinnamaldehyde oxime	18	91	252-254	252
15	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHNNHPh	15	96	44-47	47
16	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CHNNHPh	15	94	57-59	57
17	( <i>P</i> -PhC <sub>6</sub> H <sub>4</sub> )(CH <sub>3</sub> )CNNHPh	18	89	118-120	120-121
18	<i>o</i> -OHC <sub>6</sub> H <sub>4</sub> CHNNHPh	15	90	195-198	197
19	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CHNNHPh	10	92	203-205	204-205
20	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CHNNHPh	16	95	246-247	248
21	Cinnamaldehyde phenylhydrazone	15	91	252-254	252
22	(Ph) <sub>2</sub> CNNHPh	20	90	48-50	48.5-49
23	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CHNNHCONH <sub>2</sub>	10	95	56-58	57
24	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHNNHCONH <sub>2</sub>	20	96	46-47	47
25	<i>p</i> -OHC <sub>6</sub> H <sub>4</sub> CHNNHCONH <sub>2</sub>	25	78	114-116	115-116
26	PhCHNNHCONH <sub>2</sub>	20	79	178-180	179
27	<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHNNHCONH <sub>2</sub>	30	70	41-43	179
28	(Ph)(Me)CHCHNNHCONH <sub>2</sub>	25	85	81-83	104-105

<sup>a</sup>All the products were identified by comparing IR, NMR and m.p with those of authentic samples.<sup>b</sup>Yields refer to isolated products.<sup>c</sup>This reaction was carried out with oxidant(1)/substrate: (2/1) molar ratio.<sup>d</sup>All reported data was from Ref. [10].



Scheme 2. A plausible mechanism for conversion of oximes.

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Table 3. Deprotection of acetophenone oxime using (1) in comparison with other reagents.

Entry	Reagent	Time (h)	Temp. (°C)	Yield (%)	Ref.
1	(1)	0.1	r.t.	96	This work
2	3-CPCC	1	Reflux/CH <sub>2</sub> Cl <sub>2</sub>	90	[10a]
3	NCS	6	r.t.	85	[10b]
4	2,6-DCPFC	0.2	r.t.	90	[10c]
5	MCC/SiO <sub>2</sub>	4	38-40	81.9	[10d]
6	QFC	4-6	Reflux/CH <sub>3</sub> CN	87	[10e]
7	MCC/alumina	2	58-60	76	[10f]
8	PFC/H <sub>2</sub> O <sub>2</sub>	4	0-10	92	[10g]
9	CrO <sub>3</sub> /DMSO	0.6	r.t.	82	[10h]
10	Poly[4-vinyl- <i>N,N'</i> -dichlorobenzenesulphonamide]	0.012	microwave	90	[10i]
11	H <sub>2</sub> O <sub>2</sub> /PCWP	1.5	H <sub>2</sub> O/CHCl <sub>3</sub> , 30	95	[10j]

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