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Microwave Assisted Conversion of Oximes and Semicarbazones to Carbonyl Compounds Using Benzyltriphenylphosphonium Peroxymonosulfate

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Summary. Benzyltriphenylphosphonium peroxymonosulfate in the presence of catalytic amounts of bismuth chloride was found to be an efficient and mild reagent for the oxidative cleavage of oximes and semicarbazones to the corresponding carbonyl compounds under microwave irradiation.

Keywords. Benzyltryphenylphosphonium peroxymonosulfate; Carbonyl compounds; Microwave irradiation; Oxime; Semicarbazone.

Introduction

Oximes and semicarbazones are crystalline and stable compounds, which not only are used for the characterization and purification of carbonyl compounds but also play an important role in the protection of carbonyl compounds [1]. Thus, the regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. Recently, extensive studies on the oxidative cleavage of these derivatives have been carried out using various oxidants [2–15]. However, many of these methods use expensive, toxic or rare oxidizing reagents that are difficult to prepare, and they also use a higher molar ratio of reagent. Therefore, there is a need for a simple, less expensive and safer method for cleavage of oximes and semicarbazones.

Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is a strong, inexpensive, water-soluble and versatile oxidizing reagent that is commercially available, but this reagent is

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insoluble in organic solvents and buffering is needed due to its acidity [16]. Recently, we have reported the potency of benzyltriphenylphosphonium peroxymonosulfate (**1**) as a mild, inexpensive and efficient oxidizing reagent for oxidation of alcohols to the corresponding carbonyl compounds under solvent-free [17a] or non-aqueous conditions [17b], oxidation of urazoles to the corresponding triazolinediones under solid-state conditions [17c], oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and deprotection of ethylene acetals to the corresponding carbonyl compounds under aprotic conditions [17d], and solid state oxidation of sulfides and thiols to the corresponding sulfoxides and disulfides under solventless condition [17e]. In recent years, there has been a growing interest in the application of microwave irradiation in chemical reaction enhancement [18], because of its cleaner reactions, decreased reaction times and easier work-up. In continuation of our ongoing program to develop environmentally benign methods using solid-state conditions especially under microwave irradiation [19], we now report a facile oxidative cleavage of oximes and semicarbazones (**2**) using benzyltriphenylphosphonium peroxymonosulfate (**1**) in the presence of catalytic amounts of bismuth chloride and acceleration under microwave irradiation. The reaction proceeds efficiently in good to excellent yields at ambient pressure within a few minutes.

This reagent is a white powder, which is prepared by the dropwise addition of an aqueous solution of Oxone® to an aqueous solution of benzyltriphenylphosphonium chloride in quantitative yield at room temperature, and it can be stored for months without losing its potency [17]. The amounts of HSO_5^- in this reagent have been determined by an iodometric titration method [20] and the measurements are consistent with almost 99% ($24.24 \pm 0.6\%$ by weight) of active oxidizing agent. The reagent (**1**) is quite soluble in methylene chloride, chloroform, acetone, and acetonitrile and insoluble in non-polar solvents such as carbon tetrachloride, *n*-hexane, and diethyl ether.

Results and Discussion

Initially, the oxidative cleavage was carried out by mixing one equivalent of the reagent **1** and bismuth chloride with acetophenone oxime (**2c**) as a model compound in a mortar and ground the mixture with a pestle until the formation of a homogeneous mixture (1 min). Then, the reaction mixture was transferred to an *Erlenmeyer* flask and irradiated in a microwave oven (5 min). It was found that the starting material **2c** remained intact during solid-phase irradiation. So, we tested several solvents such as carbon tetrachloride, hexane, toluene, acetonitrile and dichloromethane. Finally, dichloromethane was found to be a microwave active solvent.

In order to evaluate the effect of bismuth chloride in this reaction, we carried out the oxidative deprotection of the model compound **2c** with the reagent **1** without using any catalyst. Since oxidative deprotection of **2c** under microwave irradiation with this reagent failed in the absence of catalyst, the catalytic effect of several *Lewis* acids such as $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, $AlCl_3$, and $BiCl_3$ was investigated. Surprisingly, only $BiCl_3$ was effective. The optimum molar ratio of bismuth chloride was 0.3 mol-equiv. Under these conditions, aldoximes and keto oximes **2**

Table 1. Conversion of oximes and semicarbazones **2** to carbonyl compounds **3** with reagent **1** under microwave irradiation[a,b]

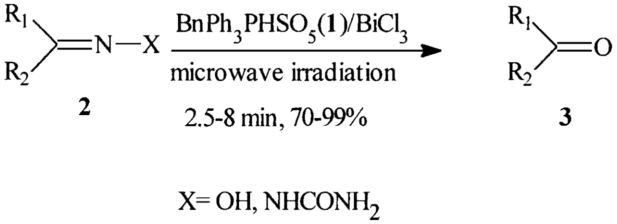
Entry	Substrates **2**	Products **3**	Time (min)	Yield (%)[c]
2a	Benzaldoxime	Benzaldehyde	2.5	99
2b	3-Nitrobenzaldoxime	3-Nitrobenzaldehyde	5	90
2c	Acetophenone oxime	Acetophenone	3	99
2d	Benzophenone oxime	Benzophenone	3	90
2e	4-Chloroacetophenone oxime	4-Chloroacetophenone	3	95
2f	4-Bromoacetophenone oxime	4-Bromoacetophenone	3	98
2g	4-Phenylacetophenone oxime	4-Phenylacetophenone	4	90
2h	3,4-Dimethoxyacetophenone oxime	3,4-Dimethoxyacetophenone	2.5	90
2i	5-Methylfurfuraldoxime	5-Methylfurfuraldehyde	3	80
2j	3-Methoxybenzaldoxime	3-Methoxybenzaldehyde	3	90
2k	Cyclohexanone oxime	Cyclohexanone	5	85
2l	9-Fluorenone oxime	9-Fluorenone	2.5	95
2m	α-Tetralone oxime	α-Tetralone	3	90
2n	Cinnamaldoxime	Cinnamaldehyde	3	93
2o	4-Phenylcyclohexanone oxime	4-Phenylcyclohexanone	4	80
2p	Acetophenone semicarbazone	Acetophenone	4	90
2q	4-Bromoacetophenone semicarbazone	4-Bromoacetophenone	5	85
2r	Benzophenone semicarbazone	Benzophenone	5	70
2s	3-Methoxybenzaldehyde semicarbazone	3-Methoxybenzaldehyde	4	80
2t	3-Chlorobenzaldehyde semicarbazone	3-Chlorobenzaldehyde	4	75
2u	4-Acetylpyridine semicarbazone	4-Acetylpyridine	5	75
2v	α-Tetralone semicarbazone	α-Tetralone	5	85
2w	5-Methylfurfural semicarbazone	5-Methylfurfuraldehyde	5	70
2x	3-Nitrobenzaldehyde semicarbazone	3-Nitrobenzaldehyde	8	70
2y	4-Phenylacetophenone semicarbazone	4-Phenylacetophenone	5	80
2z	Cinnamaldehyde semicarbazone	Cinnamaldehyde	5	70

[a] Oxidant/substrate/$BiCl_3$ (1:1:0.3); [b] confirmed by comparison with authentic samples (IR, ^1H NMR, TLC) [21]; [c] yield of isolated pure carbonyl compound

were converted to the corresponding carbonyl compounds **3** under microwave irradiation in high yields and short reaction times. The reagent **1** was also used to convert semicarbazones **2** to the corresponding carbonyl compounds **3** under microwave irradiation in the presence of bismuth chloride (0.3 mmol) in good to high yields (Table 1).

The mildness of the reagent **1** has been shown by the oxidative cleavage of α,β-unsaturated oximes and semicarbazones. When we treated α,β-unsaturated oxime or semicarbazone, only the C=N bond was selectively oxidized to the corresponding carbonyl compound and the reagent was ineffective in oxidizing the C=C double bond (Table 1). Notably, aldehydes did not undergo further oxidation to their carboxylic acids under the reaction conditions.

In conclusion, we have reported a new and efficient methodology for the regeneration of aldehydes and ketones from oximes and semicarbazones under microwave irradiation. The stability, the easy preparation of the reagent, and the easy



Scheme 1

work-up make this method a novel and useful one relative to the present methodologies for regeneration of carbonyl compounds from their derivatives under microwave irradiation.

Experimental

All of the yields refer to isolated products after purification. All of the products were characterized by comparison of their spectral (IR, ^{1}H NMR) and physical data (melting and boiling points) with those of authentic samples [21]. The reagent **1** was prepared according to our previous reported procedures [17]. All ^{1}H NMR spectra were recorded at 90 MHz in $CDCl_3$ relative to *TMS* as an internal standard and IR spectra were recorded on a Shimadzu 435 IR spectrometer. The apparatus used for the oxidative deprotection was a Samsung domestic microwave oven (2450 MHz, 900 W) without any modification, but all of the reactions were carried out in a hood with strong ventilation.

Typical procedure for the regeneration of carbonyl compounds **3** *from oximes and semicarbazones* **2** *using reagent* **1** *under microwave irradiation*

Benzophenone oxime **2d** (197 mg, 1 mmol), benzyltriphenylphosphonium peroxymonosulfate (**1**) (466 mg, 1 mmol) and bismuth chloride (95 mg, 0.3 mmol) were mixed together in a mortar and ground with a pestle to form a homogeneous mixture (1 min). After transferring the mixture to an *Erlenmeyer* flask and adding 3 ml of dichloromethane, it was irradiated in a microwave oven (2450 MHz, 900 W) for 3 min. After completion of the reaction (TLC examination), the reaction mixture was allowed to reach room temperature, washed with carbon tetrachloride (2 × 15 ml) and after vigorous stirring it was filtered through a sintered glass funnel. The solvent from the combined extracts was evaporated under vacuum and the crude product was passed through a bed of silica gel (1 cm) using carbon tetrachloride as an eluent to give benzophenone **3d** (163 mg, 90%), m.p. 50–51°C [Ref. [21] m.p. 49–51°C].

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