

# Mild and heterogeneous oxidation of urazoles to their corresponding triazolinediones via in situ generation $\text{Cl}^+$ using silica sulfuric acid/ $\text{KClO}_3$ or silica chloride/oxone system

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Received 6 January 2006; received in revised form 17 March 2006; accepted 14 April 2006

Available online 21 April 2006

## Abstract

A combination of silica sulfuric acid and potassium chlorate or oxone<sup>®</sup> and silica chloride in the presence of wet  $\text{SiO}_2$  was used as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones under mild and heterogeneous conditions with moderate to excellent yields.

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**Keywords:** Urazoles; Bis-urazoles; Triazolinediones; Oxone<sup>®</sup>; Silica sulfuric acid; Silica chloride

## 1. Introduction

4-Substituted-1,2,4-triazole-3,5-diones (**TADs**) are notable for their ability to participate in a wide range of concerted and stepwise reactions [1–7]. Considerable attention has been paid to their additions to activated alkenes [1–4], electrophilic aromatic substitution [5], dehydrogenating properties [6], and oxidation of alcohols to aldehydes and ketones [7]. Very recently 4-substituted-1,2,4-triazole-3,5-diones were used for the aromatization of 1,4-dihydropyridines and pyrazolines [8]. The unusual reactivity which makes **TADs** (**2**, **4**) of interest also makes them hard to prepare and purify.

Although a variety of reagents are capable of effecting oxidations of urazoles (**1**, **3**) to **TADs**, this transformation is not easy because these compounds are very sensitive to

the oxidizing agents and reaction conditions. However, most of the reported reagents produce by-products, which either destroy, or are difficult to remove from, the sensitive triazolinediones. Another major drawback to the older procedures is their use of reagents which are either highly toxic or impart serious disposal problems (or both) [9–14]. Recently we, among many others, have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions, and the minimization of chemical wastes as compared to their liquid phase counterparts [15].

Also acids are widely used as catalysts in industry for producing more than  $1 \times 10^8$  mt/year of products. The most commonly used are HF,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ , and  $\text{H}_3\text{PO}_4$  (in liquid form or supported on Keiselguhr). Since solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal. Also, wastes and by-products can be minimized or avoided by

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developing cleaner synthesis routes. On the other hand, any reduction in the amount of liquid acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage, and environment protection. Among of solid acids, oxone<sup>®</sup> which contains potassium peroxymonosulfate,  $\text{KHSO}_5$  as the oxidizing species is commercially available as the triple salt  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ . There are more than one hundred reports in literature where oxone<sup>®</sup> is used as an oxidizing source for organic substrates [16]. Also it has been used as a solid acid and proceeded acid catalyzed reaction such as the other solid acid i.e., heteropoly acids [17], silica sulfuric acid [18], silica chloride [19], and nafion-H [20].

## 2. Results and discussion

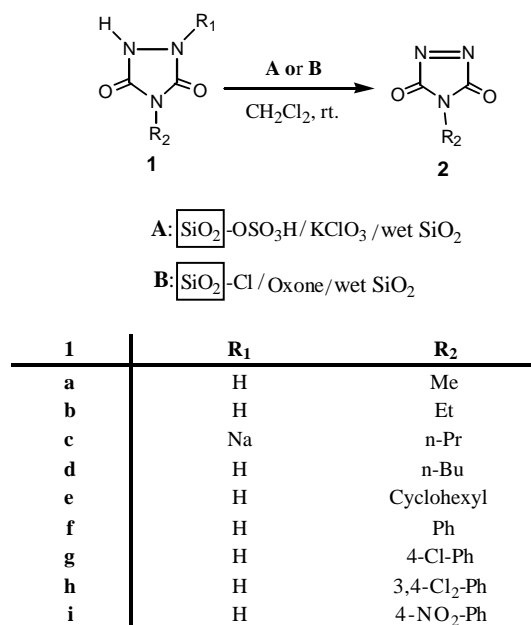
In continuation of our studies on using of oxone<sup>®</sup> in organic transformation [21], we have found that this reagent has been used by others as excellent system for different purposes when it combined with sodium or potassium halide [16].

Therefore, we were interested in finding a new form of heterogeneous system for the urazoles oxidation and thus, we have found that a combination of silica sulfuric acid and potassium chlorate or silica chloride and oxone<sup>®</sup> in the presence of wet  $\text{SiO}_2$  act as oxone-halide system [16], and generate  $\text{Cl}^+$  as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones. Thus, in this article we wish to report a simple, cheap, and convenient method for the effective oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) under mild and heterogeneous conditions (Schemes 1 and 2).

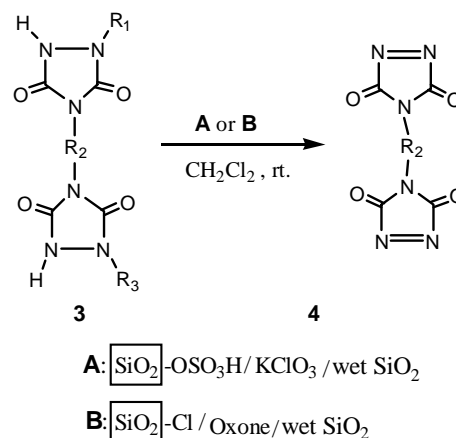
Different types of urazoles (**1**) and bis-urazoles (**3**) were subjected to the oxidation reaction with a combination of silica sulfuric acid (**I**) and  $\text{KClO}_3$  (**III**) (method A) or silica chloride (**II**) and oxone<sup>®</sup> [ $\text{KHSO}_4 \cdot 2\text{KHSO}_5 \cdot \text{K}_2\text{SO}_4$ ] (**IV**) namely oxone<sup>®</sup> ( $\text{p}K_a \approx 1$ ) [21] (method B) in the presence wet  $\text{SiO}_2$  (50% w/w) in dichloromethane (Schemes 1 and 2).

The oxidation reactions were performed under mild and completely heterogeneous conditions, at room temperature with moderate to excellent yields (Table 1).

The present oxidation reaction can be readily carried out only by placing, silica sulfuric acid (**I**), and  $\text{KClO}_3$  (**III**) or silica chloride (**II**) and oxone<sup>®</sup> (**IV**), with urazoles (**1**) or bis-urazoles (**3**), wet  $\text{SiO}_2$  (50% w/w), and  $\text{CH}_2\text{Cl}_2$  as the best solvent in a reaction vessel and efficiently stirring the resulting heterogeneous mixture at room temperature. The triazolinediones (**2**) and bis-triazolinediones (**4**) are obtained by simple filtration and evaporation of the solvent. The results and reaction conditions are tabulated in Table 1. As mentioned above the oxidation reactions are heterogeneous because urazoles and bis-urazoles [(**1**, **3**) white solids] are insoluble in dichloromethane whereas



Scheme 1.



Scheme 2.

all of the triazolinediones and bis-triazolinediones [(**2**, **4**), red and pink, respectively] are very soluble in dichloromethane. Therefore, the oxidation reaction has been performed at the surface of wet  $\text{SiO}_2$  via in situ generation of  $\text{Cl}^+$  (Scheme 3). The described methods are not suitable for 4-substituted aryl moieties which has electron donating groups (Scheme 4).

Oxidation of 4-phenyl urazole (**1f**) to 4-phenyl-1,2,4-triazole-3,5-dione (**2f**) with various solid acids and  $\text{KClO}_3$  in

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