

Hindawi Publishing Corporation  
Organic Chemistry International  
Volume 2011, Article ID 497852, 3 pages  
doi:10.1155/2011/497852

## Research Article

# Organic Solid Acid/ $\text{NaNO}_2$ : An Efficient System for the Oxidation of Urazoles and Bis-Urazoles under Mild and Heterogeneous Conditions

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Received 12 October 2011; Revised 25 November 2011; Accepted 26 November 2011

Academic Editor: Dipakranjan Mal

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Various organic solid acids/ $\text{NaNO}_2$  were used as effective oxidizing agents for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones under mild and heterogeneous conditions at room temperature with good-to-excellent yields.

## 1. Introduction

4-Substituted-1,2,4-triazole-3,5-diones (TADs) have been used both as substrates and reagents in various organic reactions, such as Diels-Alder-reaction, ene reactions, [2+2] cycloadditions, dehydrogenation reactions, electrophilic aromatic substitution, condensation of dicarbonyl compounds, and oxidation of alcohols to aldehydes and ketones [1–4]. Very recently aromatization of 1,4-dihydropyridines and pyrazolines and oxidation of thiols with TADs as well have been reported [5–7]. The unusual reactivity of TADs makes them interesting and also hard to prepare and purify [8]. It is interesting to note that, 4-phenyl-1,2,4-triazoline-3,5-dione is an extremely reactive dienophile and enophile which is at least 1000 times more reactive than tetracyanoethylene in the Diels-Alder reaction with 2-chlorobutadiene and 2000 times more reactive than maleic anhydride [1–4]. All known methods for the preparation of these compounds (1,2,4-triazolidine-3,5-diones) require oxidation of the corresponding urazoles.

Although a variety of reagents are capable of efficient oxidations of urazoles to TADs, this transformation is not easy because these compounds are very sensitive to the oxidizing

agents and reaction conditions. In addition, most of the reported reagents produce byproducts which either destroy the sensitive triazolinediones, or are difficult to remove from the reaction product. Another major drawback of the older procedures is their use of reagents which are either highly toxic or impose serious disposal problems (or both) [9–13].

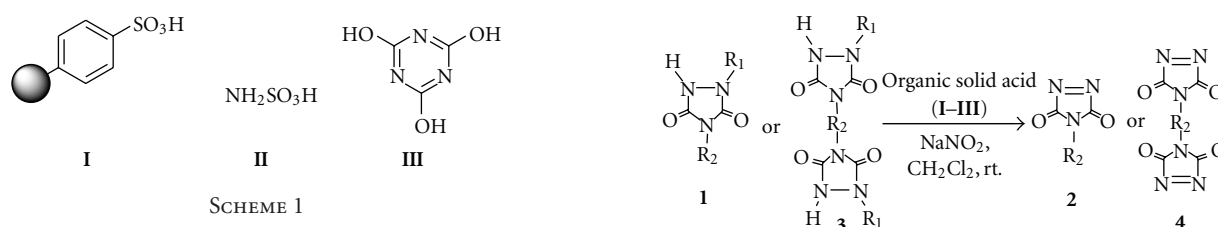
It has been demonstrated that application of heterogeneous systems, for the above reported oxidations, has many advantages over their liquid phase counterparts such as simple experimental procedures, mild reaction conditions and minimization of chemical waste materials [14, 18].

Polymer-supported sulfonic acid {(I) sulfonated polystyrenes (Dowex-50, Amberlite IR-112, Permutit-Q)} [10], sulfamic acid (II) [10], and isocyanuric acid (III) [10] are three stable and suitable organic solid acids that are commercially available. Easy workup and the stability of these reagents make them safe and convenient source of proton in comparison to liquid acids. These reagents are transformed during reaction into easily removable products. There are several reports that demonstrate the use of these reagents for various organic transformations under mild conditions (Scheme 1) [15].

TABLE 1: Oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) with either one of the Polymer-supported sulfonic acid (**I**), sulfamic acid (**II**) or isocyanuric acid (**III**) in the presence of NaNO<sub>2</sub> in dichloromethane at room temperature.

Entry	Urazole	Product	Reagent/substrate (mmol)			Time (h)			Yields <sup>a</sup> (%)		
			<b>I</b>	<b>II</b>	<b>III</b> <sup>b</sup>	<b>I</b>	<b>II</b>	<b>III</b>	<b>I</b>	<b>II</b>	<b>III</b>
1	<b>1a</b>	<b>2a</b>	2	0.2	0.75	1	2	0.0	100 <sup>c</sup>	100 <sup>c</sup>	100 <sup>c</sup>
2	<b>1b</b>	<b>2b</b>	2	0.2	0.75	1	2	0.0	100 <sup>c</sup>	100 <sup>c</sup>	100 <sup>c</sup>
3	<b>1c</b>	<b>2c</b>	2	0.2	0.75	1	2	0.0	90	72	91
4	<b>1d</b>	<b>2d</b>	2	0.2	0.75	1	2	0.0	99	99	90
5	<b>1e</b>	<b>2e</b>	2	0.2	0.75	1	2	0.5	90	85	90
6	<b>1f</b>	<b>2f</b>	2	0.2	1	1	2	0.5	91	80	95
7	<b>1g</b>	<b>2g</b>	2	0.2	1	1	2	0.5	94	83	89
8	<b>1h</b>	<b>2h</b>	2	0.2	1.25	1	2	0.5	90	92	80
9	<b>1i</b>	<b>2i</b>	2	0.2	1	1	2	0.5	89	81	100 <sup>c,d</sup>
10	<b>1j</b>	<b>2j</b>	2	0.2	1	1	2	0.5	93	75	70
11	<b>1k</b>	<b>2k</b>	2	0.2	1	1	2.5	0.5	98	94	96
12	<b>1l</b>	<b>2l</b>	2	0.2	1.25	1	2.5	0.5	87	80	84
13	<b>3a</b>	<b>4a</b>	4	0.4	2	2	4	0.5	85	82	94
14	<b>3b</b>	<b>4b</b>	4	0.4	2	2.5	5	0.5	90	99	93

<sup>a</sup> Isolated yields. <sup>b</sup> In the presence of a few drops of water. <sup>c</sup> Conversion. <sup>d</sup> 4-Nitrophenyl triazolinedione is very labile. Therefore, it was destructed in the course of passing through a pad of silica gel.



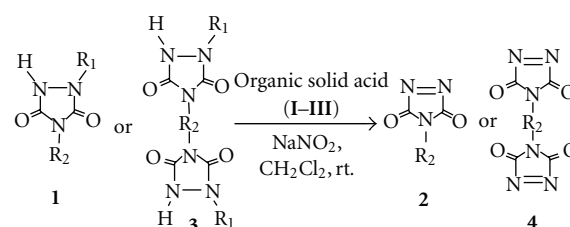
## 2. Results and Discussion

In continuation of our studies on the use of *solid acids* in organic transformations [16, 17], we found that polymer-supported sulfonic acid (**I**), sulfamic acid (**II**) and isocyanuric acid (**III**) in the presence of NaNO<sub>2</sub> could be used as oxidizing agents for the oxidation of urazoles and bis-urazoles under mild and heterogeneous conditions (Scheme 2).

Herein, we wish to report a simple, inexpensive, and convenient method for the effective oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) by using the described reagents **I–III**.

A good range of urazoles (**1**) and bis-urazoles **3** were subjected to the oxidation reaction in the presence of the solid acids (**I–III**)/NaNO<sub>2</sub> in dichloromethane. All oxidation reactions were performed under mild and completely heterogeneous conditions, at room temperature with good to excellent yields (Table 1).

As reported above the oxidation reactions are heterogeneous because urazoles and bis-urazoles ((**1**, **3**) as a white solids) are insoluble in dichloromethane whereas all of the triazolinediones and bis-triazolinediones ((**2**, **4**), red, pink or brown solids) are very well soluble in dichloromethane. According to our previously reported results with other



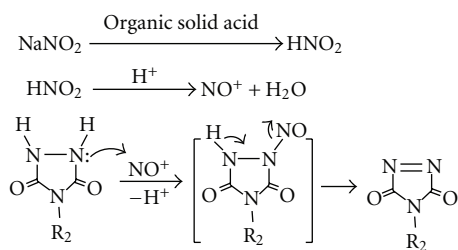
Urazole	R <sub>1</sub>	R <sub>2</sub>
<b>1a</b>	H	Me
<b>1b</b>	H	Et
<b>1c</b>	Na	n-Pr
<b>1d</b>	H	n-Bu
<b>1e</b>	H	Cyclohexyl
<b>1f</b>	H	Ph
<b>1g</b>	H	4-Cl-Ph
<b>1h</b>	H	3,4-Cl <sub>2</sub> -Ph
<b>1i</b>	H	4-NO <sub>2</sub> -Ph
<b>1j</b>	H	4-OMe-Ph
<b>1k</b>	H	4- <i>t</i> -Bu-Ph
<b>1l</b>	H	4-Naphtyl
<b>3a</b>	Na	-(CH <sub>2</sub> ) <sub>6</sub> -
<b>3b</b>	H	

SCHEME 2

reagents [14, 16–18], the following mechanism for the oxidation reaction via *in situ* generation of NO<sup>+</sup> may be suggested (Scheme 3).

Although Nafion-H is a very useful solid acid [10], unfortunately, several attempts for the oxidation of urazoles by Nafion-H have failed. Therefore, this reagent is not practical and suitable for this purpose.

In summary, we have described a practical, efficient, and convenient method for the oxidation of urazoles and bis-



SCHEME 3

urazoles. We suggest that these systems could be used for the oxidation of a wide variety of urazole derivatives under mild and safe conditions.

### 3. Experimental Section

**3.1. General.** Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR and  $^1\text{H-NMR}$ ) and physical data with authentic samples which were produced by other reported procedures.

**3.2. Oxidation of 4, 4'-(4, 4'-Diphenylmethylene)-bis-urazole (3b) to bis(p-3, 5-Dioxo-1, 2, 4-triazoline-4-ylphenyl) Methane (4b): A Typical Procedure.** A mixture of compound **3b** (0.366 g, 1 mmol), **I–III** (see Table 1), and  $\text{NaNO}_2$  (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred for the specified time in Table 1. Then the reaction mixture was filtered and washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). Dichloromethane was removed by water bath ( $40\text{--}50^\circ\text{C}$ ) and simple distillation. A crystalline pink solid (**4b**) is obtained in good-to-excellent yields. Mp =  $182\text{--}185^\circ\text{C}$ , and {lit. Mp =  $185^\circ\text{C}$  [14, 18]}.

### Acknowledgments

This paper is extracted from the M. S. thesis of Mr. M. Rasouli. The authors acknowledge financial support for this work from the research affairs of Hamedan University of Medical Sciences, Hamedan, Iran and partial support of this work by the Research Affairs Office of Bu-Ali Sina University (Grant no. 32-1716 entitled development of chemical methods, reagent and molecules.) and also Center of Excellence in Development of Chemical Method (CEDCM) Hamedan, Iran.

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