

## Metal-Free Catalytic Oxidation of Urazoles under Mild and Heterogeneous Conditions via Combination of Ammonium Nitrate and Catalytic Amounts of Silica Sulfuric Acid

A. Ghorbani-Choghamarani<sup>a,\*</sup>, M.A. Zolfigol<sup>b,\*</sup>, M. Hajjami<sup>b</sup> and S. Mallakpour<sup>c</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Ilam University, P.O. Box 69315516, Ilam, Iran

<sup>b</sup>Faculty of Chemistry, Bu-Ali Sina University, P.O. Box 6517838683, Hamadan, Iran

<sup>c</sup>Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

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Highly efficient production of 4-substituted-1,2,4-triazole-3,5-diones from urazole derivatives using ammonium nitrate and silica sulfuric acid ( $\text{SiO}_2\text{-OSO}_3\text{H}$ ), as a cheap and nontoxic catalyst, in the presence of wet  $\text{SiO}_2$  (50% w/w) under mild and heterogeneous conditions is reported. The process presented here is operationally simple, environmentally benign and produces high yield.

**Keywords:** Urazole, Bis-urazole, Triazolinedione, Ammonium nitrate, Silica sulfuric acid

### INTRODUCTION

In recent years, there has been rapid growth in the development of new supported reagents on solid bases [1,2]. In view of the environmental and economical reasons, there is a constant effort to substitute the conventional catalysts with newer solid acids [3]. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research [4]. Moreover, an important aspect of clean technology is the use of environmentally friendly catalysts [5].

1,2,4-Triazole-3,5-diones belong to an important class of five-member heterocyclic compounds, which can be prepared from the oxidation of urazoles and bis-urazoles. They have been used both as substrates and reagents in various organic transformations such as reaction of allylsilanes with triazolinedione [6], triazolinedione-alkene reaction [7], reaction of a triazolinedione with alkenes [8], reaction of

triazolinedione with carbon nanotubes [9], oxidation of 1,4-dihydropyridines [10], oxidation of alcohols to aldehydes and ketones [11], and oxidative coupling of thioles [12]. High sensitivity and unusual reactivity of 1,2,4-triazole-3,5-diones make them of interest to organic chemists, though difficult to prepare and purify. Therefore, developing oxidizing systems, which would safely and mildly convert urazoles to their corresponding triazolinediones is of great importance.

### EXPERIMENTAL

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterized by the comparison of their spectral (IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) and physical data with those of authentic samples.

#### General Procedures

**Synthesis of silica sulfuric acid.** A 500 ml suction flask containing silica gel (60 g) was equipped with a constant-

\*Corresponding authors. E-mail: arashghch58@yahoo.com; Zolfi@basu.ac.ir

pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and gas inlet tube to conduct HCl gas into water. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately (Scheme 1). Then the mixture was shaken for 30 min. A white solid (silica sulfuric acid) of 76.0 g was obtained [2].

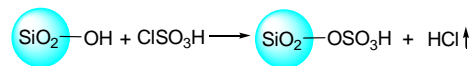
**Oxidation of 4-tert-butylurazole to 4-tert-butyl-1,2,4-triazole-3,5-dione with ammonium nitrate, silica sulfuric acid and wet SiO<sub>2</sub>.** To a mixture of 4-tert-butylurazole (0.157 g, 1 mmol), wet SiO<sub>2</sub> (0.2 g) and ammonium nitrate (0.16 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml), 0.05 g of silica sulfuric acid was added. The mixture was stirred at room temperature for 85 min, and then filtered. The residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (20 ml). Anhydrous Na<sub>2</sub>SO<sub>4</sub> (1.5 g) was added to the filtrate and filtered off after 20 min. Finally, CH<sub>2</sub>Cl<sub>2</sub> was removed and 4-tert-butyl-1,2,4-triazole-3,5-dione was obtained in 99% yield (0.153 g) as crystalline pink solid, m.p.: 120-124 °C.

## RESULTS AND DISCUSSION

Following our newly published works [13-20] on the application of mild and heterogeneous conditions in organic transformations, we thought of developing a new and efficient catalytic medium for the oxidative preparation of 4-substituted-1,2,4-triazole-3,5-diones from urazole derivatives. Consequently, we designed a heterogeneous medium *via* combining ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), catalytic amounts of silica sulfuric acid (SiO<sub>2</sub>-OSO<sub>3</sub>H) and wet SiO<sub>2</sub> (50% w/w) for a mild oxidation of urazoles and bis-urazoles.

Initially, to investigate the catalytic ability of silica sulfuric acid (SiO<sub>2</sub>-OSO<sub>3</sub>H) and to determine an appropriate amount of the catalyst, 4-phenylurazole was subjected to the oxidation reaction. The oxidation of 4-phenylurazole was performed using mixtures containing 1 mmol of 4-phenylurazole, ammonium nitrate (2 mmol), wet SiO<sub>2</sub> (0.2 g) and different amounts of the catalyst (silica sulfuric acid) in dichloromethane (5 ml) at room temperature (Table 1).

The results of the preparation of 4-phenyl-1,2,4-triazole-3,5-dione as a function of the amounts of silica sulfuric acid are shown in Fig. 1. The optimal amount of silica sulfuric acid to convert 4-phenylurazole to 4-phenyl-1,2,4-triazole-3,5-dione is 0.05 grams, which was used in all oxidation reactions

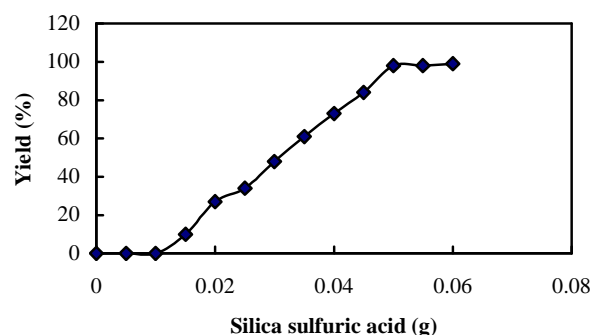


Scheme 1

**Table 1.** Conversion of 4-Phenylurazole to the Corresponding Triazolinedione with Ammonium Nitrate Different Amounts of Silica Sulfuric Acid in the Presence of wet SiO<sub>2</sub> (50% w/w) in Dichloromethane at Room Temperature<sup>a</sup>

Entry	Silica sulfuric acid (g)	Yield (%) <sup>b</sup>
1	0.000	0
2	0.005	0
3	0.010	0
4	0.015	10
5	0.020	27
6	0.025	34
7	0.030	48
8	0.035	61
9	0.040	73
10	0.045	84
11	0.050	98
12	0.055	98
13	0.06	99

<sup>a</sup>Reaction time: 40 min. <sup>b</sup>Isolated yield.



**Fig. 1.** Oxidation of 4-phenylurazole by ammonium nitrate and catalytic amounts of silica sulfuric acid in the presence of wet SiO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Reaction time = 40 min.

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(except entries 10 and 14 in Tabel 2).

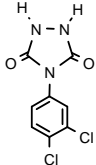
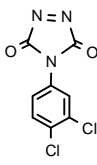
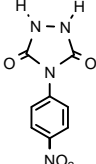
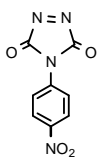
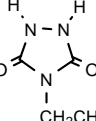
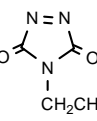
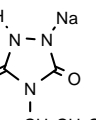
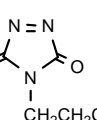
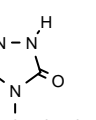
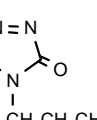
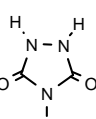
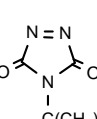
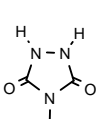
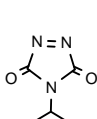
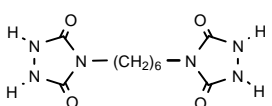
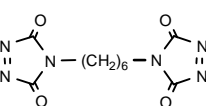
Herein, we would like to report a new heterogeneous catalytic method for the effective oxidation of a wide range of urazoles to the corresponding triazolinediones using ammonium nitrate and catalytic amounts of silica sulfuric acid ( $\text{SiO}_2\text{-OSO}_3\text{H}$ ) in the presence of wet  $\text{SiO}_2$  (50% w/w) in dichloromethane at room temperature in good to excellent yields (Scheme 2 and Table 2).

Oxidation reaction took place heterogeneously under mild conditions. All reaction components except pink-to-red color triazolinedione were insoluble in the reaction solvent. Consequently, 4-substituted-1,2,4-triazole-3,5-diones were obtained easily by mixing urazole, ammonium nitrate, wet  $\text{SiO}_2$  and a catalytic amount of silica sulfuric acid; then, the mixture was stirred at room temperature. Pure products were easily isolated from the reaction medium by washing the

**Table 2.** Oxidation of Urazole Derivatives to the Corresponding Triazolinediones Using  $\text{NH}_4\text{NO}_3$  and Catalytic Amounts of Silica Sulfuric Acid in the Presence of Wet  $\text{SiO}_2$  (50% w/w) in Dichloromethane at Room Temperature<sup>a</sup>

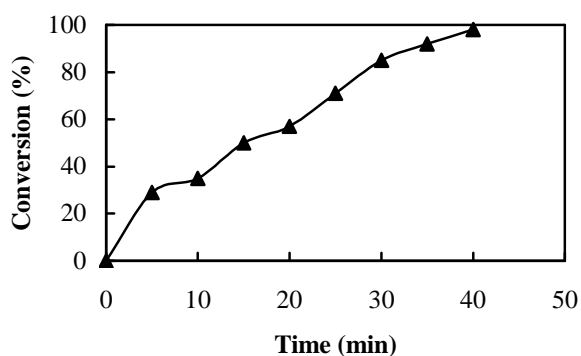
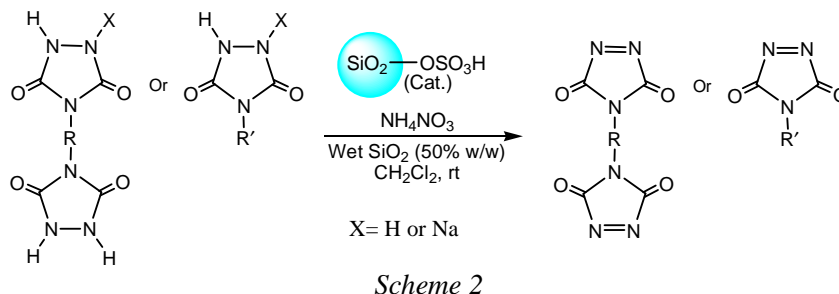
Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>	TON <sup>c</sup>	TOF ( $\text{min}^{-1}$ ) <sup>d</sup>
1			40	98	7.42	0.185
2			6.5 h	94 <sup>e</sup>	7.12	0.018
3			4.5 h	85 <sup>f</sup>	6.43	0.024
4			5.5 h	93 <sup>g</sup>	7.04	0.021
5			105	94	7.12	0.068
6			90	93	7.04	0.078

Table 2. Continued

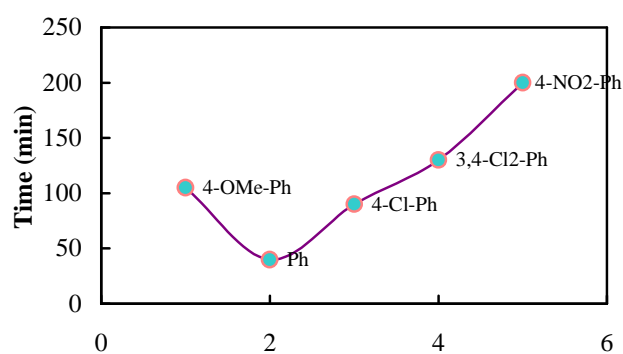
7			130	98	7.42	0.057
8			200	94	7.12	0.036
9			70	94	7.12	0.102
10			210	91	1.38	0.0065
11			120	99	7.50	0.063
12			85	99	7.50	0.088
13			85	99	7.50	0.088
14			80	97	1.05	0.013

<sup>a</sup>Molar ratio of reagents: urazole/ammonium nitrate/silica sulfuric acid/wet SiO<sub>2</sub> for entries 1-9 and 11-12: (1 mmol/2 mmol/0.05 g/0.2 g); for entry 10: (1 mmol/2 mmol/0.25 g/0.2 g); for entry 14: (1 mmol/2 mmol/0.35 g/0.2 g). <sup>b</sup>Isolated yields. <sup>c</sup>TON = turn over number. <sup>d</sup>TOF = turn over frequency. <sup>e</sup>Reaction performed in the absence of wet SiO<sub>2</sub>. <sup>f</sup>Reaction performed in the absence of wet SiO<sub>2</sub> but one drop of water added. <sup>g</sup>Reaction performed in the presence of dry SiO<sub>2</sub>.

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**Fig. 2.** The kinetic progress of the oxidation of 4-phenylurazole.



**Fig. 3.** Effect of functional groups on the oxidation of 4-aromatic substituted groups.

reaction mixture with dichloromethane, simple filtration and evaporation of the solvent.

To investigate the kinetic progress of the described system, oxidation of 4-phenylurazole was carried out in different periods of time. The results are outlined in Fig. 2. As the results show, the triazolinedione yield rises gradually and steadily with increasing reaction time.

As Table 2 shows, the reaction rate slightly rises with increasing the electron donation of the functional groups on aromatic rings which is clearly visible in Fig. 3.

In summary, in this paper we presented a mild, catalytic and efficient methodology for the oxidation of 4-substituted urazoles using ammonium nitrate and catalytic amounts of silica sulfuric acid. This new heterogeneous method exhibits the following features: (a) the mild reaction condition was found convenient to oxidize urazole derivatives, (b) cost effective, commercially available, highly stable and environment friendly reagents were used, (c) reasonable turn

over number (TON) and turn over frequency (TOF) of the catalyst were observed, (d) reagents and the catalyst were easily separated, and (e) waste was minimization.

## ACKNOWLEDGMENTS

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