Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Supported Nitric Acid on Silica Gel and Polyvinyl Pyrrolidone (PVP) as an Efficient Oxidizing Agent for the Oxidation of Urazoles and Bis-urazoles

Arash Ghorbani-Choghamarani [a], Zahra Chenani [a] & Shadpour Mallakpour [b]

[a] Department of Chemistry, Faculty of Science, Ilam University, Ilam, Iran

[b] Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

Published online: 29 Oct 2009.

Synthetic Communications®, 39: 4264–4270, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902898619

Taylor & Francis
Taylor & Francis Group

Supported Nitric Acid on Silica Gel and Polyvinyl Pyrrolidone (PVP) as an Efficient Oxidizing Agent for the Oxidation of Urazoles and Bis-urazoles

Arash Ghorbani-Choghamarani,[1] Zahra Chenani,[1] and Shadpour Mallakpour[2]
[1]Department of Chemistry, Faculty of Science, Ilam University, Ilam, Iran
[2]Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

Abstract: A method for the oxidation of a good range of urazoles and bis-urazoles to the corresponding triazolinediones by supported nitric acid on silica gel (SiO_2-HNO_3) and/or polyvinyl pyrrolidone (PVP-HNO_3) is described. Reactions have been carried out heterogeneously at room temperature in dichloromethane with good to excellent yields.

Keywords: Bis-urazoles, oxidation, polyvinyl pyrrolidone, triazolinediones, urazoles

INTRODUCTION

In the past few years, supported reagents[1–4] have become increasingly used in organic synthesis, mainly because the reactions are carried out under mild conditions and the organic products are easily isolated. In addition, the stability, low cost, heterogeneous nature of the reactions, good yields of the products, short reaction times, and reusability are other important advantages of these reagents.[5]

Received January 12, 2009.
Address correspondence to Arash Ghorbani-Choghamarani, Department of Chemistry, Faculty of Science, Ilam University, P. O. Box 69315516, Ilam, Iran. E-mail: arashghch58@yahoo.com

4-Substituted-1,2,4-triazole-3,5-diones constitute an important class of heterocyclic compounds, which can be prepared from the oxidation of urazoles and bis-urazoles. They have been used both as substrate and reagent in various organic transformations such as the reaction of allylsilanes with triazolinedione,[6] oxidation of 1,4-dihydropyridines,[7] oxidation of alcohols to aldehydes and ketones,[8] oxidative coupling of thioles,[9] and [6 + 2] cycloadditions.[10] High sensitivity and unusual reactivity of 1,2,4-triazoline-3,5-diones make them of interest to organic chemists but also make them difficult to prepare and purify.

There are several reports on the oxidation of urazoles and bis-urazoles in the literature.[11–19] Despite these intensive efforts, this transformation is not easy because these compounds are very sensitive to the oxidizing agents and reaction conditions, and most of the oxidants produce by-products, which either destroy the product or are difficult to remove from the sensitive triazolinedione. In addition, most of oxidizing systems require use of strong and toxic oxidants,[20] harsh conditions,[17,18] long reaction times,[13–15] excess reagent,[13,19] or tedious workup[15] or generate poor yields of products.[17]

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, ^{1}H NMR, and ^{13}C NMR) and physical data with authentic samples.

Preparation of SiO_2-HNO_3

In a 50-mL, round-bottomed flask, 2.82 g of HNO_3 (65%, 3.2 mL) and 2.0 g of silica gel were stirred for 10 min, and a white solid (SiO_2-HNO_3) was obtained.

Preparation of PVP-HNO_3

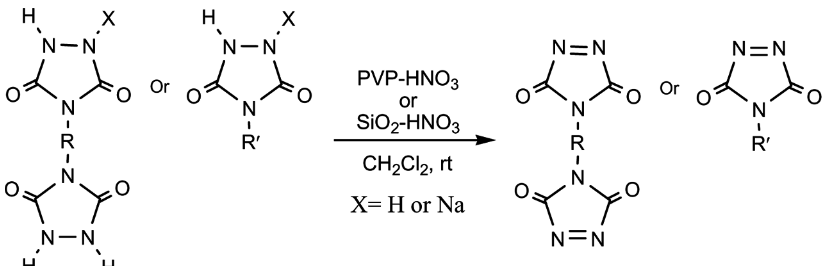
In a 50-mL, round-bottomed flask, 2.82 g of HNO_3 (65%, 3.2 mL) and 4.8 g of polyvinyl pyrrolidone (PVP) (4 g, 3.24 mmol) were stirred for 10 min, and a white solid (PVP-HNO_3) was obtained.

Oxidation of 4-Naphthylurazole 1b to 4-Naphthyl-1,2,4-triazoline-3,5-dione 2b by PVP-HNO_3

A suspension of 4-naphthylurazole **1b** (0.227 g, 1 mmol) and PVP-HNO_3 (0.25 g) in dichloromethane (DCM, 5 mL) was stirred at room temperature for 110 min and then filtered. The residue was washed with CH_2Cl_2 (20 mL). Anhydrous Na_2SO_4 (1.5 g) was added to the filtrate and filtered off after 20 min. Finally, CH_2Cl_2 was removed, and 4-naphthyl-1,2,4-triazoline-3,5-dione **2b** was obtained in 99% yield (0.222 g).

RESULTS AND DISCUSSION

In continuation of our recent investigations on the application of new reagents on the functionalization of organic compounds,[21,22] we became interested in introducing an efficient supported reagent for the selective oxidation of urazoles and bis-urazoles to the corresponding triazolinediones. Therefore, we used SiO_2-HNO_3 and PVP-HNO_3 to prepare a mild oxidizing reagent.



1	X	R	R′
a	H	---	Ph
b	H	---	1-Naphtyl
c	H	---	4-OMe-Ph
d	H	---	4-Cl-Ph
e	H	---	3,4-Cl_2-Ph
f	H	---	4-NO_2-Ph
g	H	---	Et
h	Na	---	n-Pr
i	H	---	n-Bu
j	H	---	tert-Bu
k	H	---	Cyclohexyl
l	H	-C_6H_4-CH_2-C_6H_4-	---
m	Na	-$(CH_2)_6$-	---

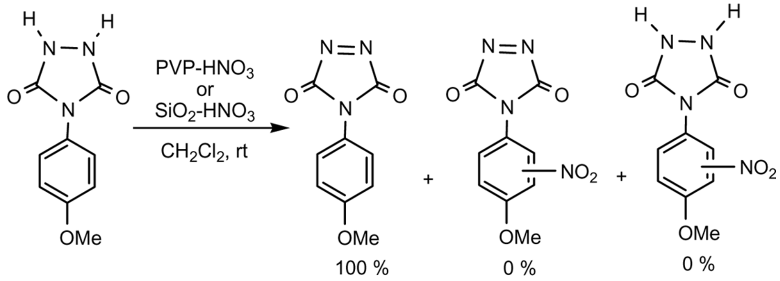
Scheme 1. Efficient oxidation of urazoles and bis-urazoles.

Recently, we have used PVP-HNO_3 and SiO_2-HNO_3 for the oxidation of sulfides to sulfoxides.[21] To investigate the scope and limitation of these supported reagents, we decided to apply them in diffrent oxidation reaction. Herein, we disclose a new heterogeneous protocol for the oxidation of a wide variety of urazoles and bis-urazoles **1** to the corresponding triazolidione **2** using SiO_2-HNO_3 and/or PVP-HNO_3 in DCM with good to excellent yields (see Scheme 1 and Table 1).

Table 1. Oxidation of urazole derivatives to the corresponding triazolinediones using PVP-HNO_3 **I** and/or SiO_2-HNO_3 **II** in dichloromethane at room temperature

			Substrate/Reagents[a]			
Entry	Substrate	Product	I	II	Time (min)	Yield (%)[b]
1	**1a**	**2a**	0.25	—	60	75
2	**1a**	**2a**	—	0.2	35	99
3	**1b**	**2b**	0.25	—	110	99
4	**1b**	**2b**	—	0.2	10	99
5	**1c**	**2c**	0.25	—	55	99
6	**1c**	**2c**	—	0.2	5	99
7	**1d**	**2d**	0.25	—	65	98
8	**1d**	**2d**	—	0.2	10	95
9	**1e**	**2e**	0.25	—	70	97
10	**1e**	**2e**	—	0.2	50	98
11	**1f**	**2f**	0.4	—	150	99
12	**1f**	**2f**	—	0.32	35	91
13	**1g**	**2g**	0.25	—	100	100[c]
14	**1g**	**2g**	—	0.2	15	100[c]
15	**1h**	**2h**	0.4	—	90	90
16	**1h**	**2h**	—	0.32	35	85
17	**1i**	**2i**	0.25	—	120	96
18	**1i**	**2i**	—	0.2	15	94
19	**1j**	**2j**	0.25	—	35	99
20	**1j**	**2j**	—	0.2	10	99
21	**1k**	**2k**	0.25	—	120	99
22	**1k**	**2k**	—	0.2	5	99
23	**1l**	**2l**	0.5	—	55	98
24	**1l**	**2l**	—	0.4	15	99
25	**1m**	**2m**	0.5	—	65	81
26	**1m**	**2m**	—	0.4	75	84

[a]**I** and **II** refer to grams of PVP-HNO_3 and SiO_2-HNO_3.
[b]Isolated yields.
[c]Conversion.



Scheme 2. Chemoselective oxidation of 4-methoxyphenyl urazole to 4-methoxyphenyl-1,2,4-triazoline-3,5-dione.

As is evident from Table 1, the reaction proceeds more efficiently and rapidly with SiO_2-HNO_3 than with PVP-HNO_3.

The oxidation reactions were carried out under completely heterogeneous conditions by mixing urazole or bis-urazole **1** with supported nitric acid on silica or PVP in DCM. Reactants and reagents are insoluble in DCM but red or pink product **2** is soluble in the reaction solvent; therefore, triazolinediones can be readily obtained by simple filtration and evaporation of CH_2Cl_2.

To investigate chemoselectivity and mildness of this procedure, a urazole containing an activated aromatic moiety (4-methoxyphenyl urazole) was subjected to oxidation reaction with supported nitric acid on silica gel and PVP, and surprisingly, no nitrated product was obsereved (Table 1, entries 5 and 6; Scheme 2).

The mechanism of this transformation initiates with auto-ionization of nitric acid, which generates in situ nitronium ion (NO_2^+). Then nucleophilic attack of nitrogen of urazole on the NO_2^+ followed by elimination of HNO_2 gives the corresponding triazolinedione. In the next step, HNO_2 might generate NO^+, which oxidize another molecule of urazole.

In summary, herein we report an efficient and heterogenous method for the selective oxidation of urazoles and bis-urazoles under mild conditions. This method offers the advantage of shorter reaction times, high selectivity, nontoxicity, cost-effective reagent or catalyst, and easy workup.

ACKNOWLEDGMENT

We are grateful to Ilam University, Ilam, Iran, for research facilities and financial support of this research project.

REFERENCES

1. Tapia, R.; Torres, G.; Valderrama, J. A. Nitric acid on silica gel: A useful nitrating reagent for activated aromatic compounds. *Synth. Commun.* **1986**, *16*, 681.
2. Gao, Y.; Lam, Y. Polymer-supported *N*-phenylsulfonyloxaziridine (Davis reagent): A versatile oxidant. *Adv. Synth. Catal.* **2008**, *350*, 2937.
3. Abraham, S.; Rajan, P. K.; Sreekumar, K. Poly(methyl methacrylate) supported pyrazolinium permanganate: A new oxidizing reagent. *Polym. J.* **1997**, *29*, 12.
4. Goudarzian, N.; Ghahramani, P.; Hossini, S. Polymeric reagent (I): Polyethyleneimine-supported silver dichromate as a new oxidizing agent. *Polym. Int.* **1996**, *39*, 61.
5. Shirini, F.; Zolfigol, M. A.; Salehi, P.; Abedini, M. Applications of some metal hydrogen sulfates in organic transformations. *Curr. Org. Chem.* **2008**, *12*, 183.
6. Dey, R. T.; Haque, S. A.; Hazra, A.; Basak, S.; Sarkar, T. K. A reinvestigation of the reaction of allylsilanes with *N*-phenyltriazolinedione: Stereoselective synthesis of substituted urazoles by [3 + 2] cycloaddition. *Tetrahedron Lett.* **2007**, *48*, 6671.
7. Zolfigol, M. A.; Ghorbani-Choghamarani, A.; Shahamirian, M.; Safaiee, M.; Mohammadpoor-Baltork, I.; Mallakpour, S. E.; Abdollahi-Alibeik, M. 4-Phenyl-1,2,4-triazole-3,5-dione as reusable reagent for the aromatization of 1,4-dihydropyridines under mild conditions. *Tetrahedron Lett.* **2005**, *46*, 5581.
8. Cookson, R. C.; Stevens, I. D. R.; Watts, C. T. A new reagent for oxidation of alcohols to ketones in neutral solution at room temperature. *Chem. Commun.* **1966**, 744.
9. Christoforou, A.; Nicolaou, G.; Elemes, Y. *N*-Phenyltriazolinedione as an efficient, selective, and reusable reagent for the oxidation of thiols to disulfides. *Tetrahedron Lett.* **2006**, *47*, 9211.
10. Sugimura, T.; Im, C. Y.; Okuyama, T. [6 + 2]-Cycloaddition of N-phenyltriazolinedione with cycloheptatriene derivatives mediated and stereodirected by a chiral 3-oxy substituent. *Tetrahedron Lett.* **2004**, *45*, 1519.
11. Zolfigol, M. A.; Bagherzadeh, M.; Mallakpour, S.; Chehardoli, G.; Kolvari, E.; Ghorbani-Choghamarani, A.; Koukabi, N. Mild and heterogeneous oxidation of urazoles to their corresponding triazolinediones via in situ generation Cl^+ using silica sulfuric acid/$KClO_3$ or silica chloride/oxone system. *Catal. Commun.* **2007**, *8*, 256.
12. Zolfigol, M. A.; Bagherzadeh, M.; Mallakpour, S.; Chehardoli, G.; Ghorbani-Choghamarani, A.; Koukabi, N.; Dehghanian, M.; Doroudgar, M. The first report on the catalytic oxidation of urazoles to their corresponding triazolinediones via in situ catalytic generation of Br^+ using periodic acid or oxone/KBr system. *J. Mol. Catal. A Chem.* **2007**, *270*, 219.
13. Zolfigol, M. A.; Ghorbani-Vaghei, R.; Mallakpour, S.; Chehardoli, G.; Ghorbani-Choghamarani, A.; Hosain-Yazdi, A. Simple, convenient, and heterogeneous method for conversion of urazoles to triazolinediones using

N,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonylamide or trichloromelamine under mild and heterogeneous conditions. *Synthesis* **2006**, 1631.
14. Zolfigol, M. A.; Chehardoli, G.; Shirini, F.; Mallakpour, S. E.; Nasr-Isfahani, H. Oxidation of urazoles to their corresponding triazolinediones under mild and heterogeneous conditions via in situ generation of $NO^+IO_x^-$. *Synth. Commun.* **2001**, *31*, 1965.
15. Zolfigol, M. A.; Nasr-Isfahani, H.; Mallakpour, S.; Safaiee, M. Oxidation of urazoles with 1,3-dihalo-5,5-dimethylhydantoin, both in solution and under solvent-free conditions. *Synlett*. **2005**, 761.
16. Zolfigol, M. A.; Chehardoli, G.; Ghaemi, E.; Madrakian, E.; Zare, R.; Azadbakht, T.; Niknam, K.; Mallakpour, S. *N*-Bromo-reagent-mediated oxidation of urazoles to their corresponding triazolinediones under mild and heterogeneous conditions. *Monatsh. Chem.* **2008**, *139*, 261.
17. Karami, B.; Mallakpour, S.; Farahi, M. Silica-supported ICl as a novel heterogeneous system for the rapid oxidation of urazoles to triazolinediones. *Heteroatom. Chem.* **2008**, *19*, 389.
18. Menard, C.; Doris, E.; Mioskowski, C. Ph_3BiCO_3: A mild reagent for in situ oxidation of urazoles to triazolinediones. *Tetrahedron Lett.* **2003**, *44*, 6591.
19. Zolfigol, M. A.; Salehi, P.; Mallakpour, S. E.; Torabi, M. 1,4-Diazabicyclo[2.2.2]octane 1,4-bis(oxide)-bis(hydrogen peroxide)/MCl_x as a novel heterogeneous system for the oxidation of urazoles under mild conditions. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1673.
20. Mohammadpoor-Baltork, I.; Sadeghi, M. M.; Mallakpour, S. E.; Hajipour, A. R.; Adibi, A.-H. Efficient and convenient oxidation of urazoles to their corresponding triazolinediones under solvent-free conditions. *Synth. Commun.* **2002**, *32*, 3445.
21. Zolfigol, M. A.; Amani, K.; Hajjami, M.; Ghorbani-Choghamarani, A.; Ayazi-Nasrabadi, R.; Jafari, S. Chemo- and homoselective catalytic oxidation of sulfides to sulfoxides with supported nitric acid on silica gel and polyvinyl pyrrolidone (PVP) catalyzed by KBr and/or NaBr. *Catal. Commun.* **2008**, *9*, 1739.
22. Zolfigol, M. A.; Bagherzadeh, M.; Niknam, K.; Shirini, F.; Mohammadpoor-Baltork, I.; Ghorbani-Choghamarani, A.; Baghbanzadeh, M. Oxidation of 1,4-dihydropyridines under mild and heterogeneous conditions using solid acids. *J. Iran. Chem. Soc.* **2006**, *3*, 73.