Monatsh Chem (2009) 140:607–610
DOI 10.1007/s00706-008-0100-8

ORIGINAL PAPER

Catalytic oxidation of urazoles and bis-urazoles to their corresponding triazolinediones using aluminium nitrate and a catalytic amount of silica sulfuric acid

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Received: 31 July 2008 / Accepted: 29 October 2008 / Published online: 10 December 2008

Abstract A simple and efficient catalytic oxidation of urazoles and a bis-urazole to the corresponding triazolinediones by treatment with $Al(NO_3)_3.9H_2O$ in the presence of a catalytic amount of silica sulfuric acid is described. A good range of urazole derivatives was selectively oxidized in CH_2Cl_2 at room temperature in good to excellent yields.

Keywords Urazoles · Bis-urazole · Triazolinediones · Aluminium nitrate · Silica sulfuric acid · Oxidation

Introduction

In the last few years, heterogeneous reagents and catalysts have been used increasingly in organic synthesis [1–4]. The development of efficient and new catalytic systems for various organic transformations is an active research area with the aim of developing milder reaction conditions [5].

4-Substituted-1,2,4-triazole-3,5-diones (TADs) have been used both as substrates and reagents in various organic reactions such as electrocyclic and oxidation reactions [6–11]. However, the unusual reactivity which makes 1,2,4-triazoline-3,5-diones (**2**, **4**) of interest to organic chemists also makes them difficult to prepare and purify [12].

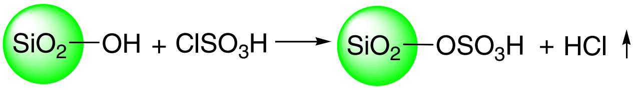
Even though urazole derivatives can be easily oxidized by a wide variety of oxidizing agents [13–23], this transformation is not easy because these compounds are very sensitive to the nature of the oxidizing agent and to the reaction conditions. In addition, most of the reported reagents produce by-products, which either destroy the product or which are difficult to remove. Many methods also suffer from other drawbacks, for example low yield, tedious work-up, toxicity, or expensive reagents.

Results and discussion

In order to overcome the above-mentioned limitations and in continuation of our ongoing program on the functionalization of organic compounds [24–29] we became interested in the use of new catalytic media, based on in-situ generation of nitric acid for selective oxidation of urazoles and bis-urazoles to triazolinediones.

Silica sulfuric acid is an efficient solid acidic source which has been used for different organic transformations [30]. It can be easily prepared by reaction of chlorosulfonic acid with silica gel (Scheme 1) [31]. Therefore, we decided to use silica sulfuric acid as an efficient acidic catalyst in the oxidation of urazoles and bis-urazoles with aluminium nitrate.

Consequently, we wish to report here selective oxidation of different types of urazole **1** or bis-urazole **3a** to the



Scheme 1

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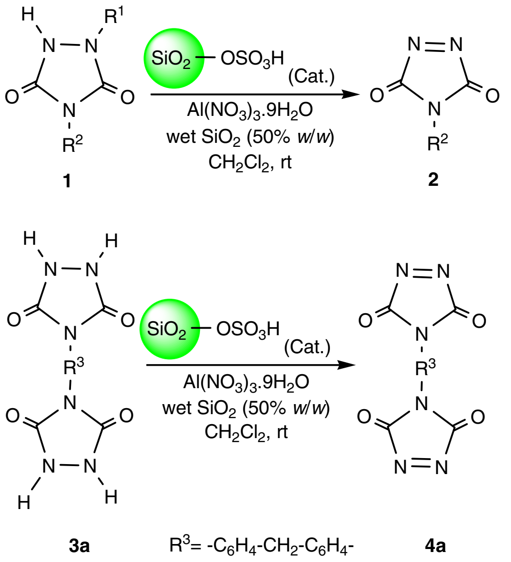


1	R^1	R^2
a	H	Et
b	Na	*n*-Pr
c	H	*n*-Bu
d	H	Cyclohexyl
e	H	Ph
f	H	3,4-Cl_2-Ph
g	H	4-NO_2-Ph
h	H	1-Naphtyl
i	H	4-MeO-Ph

Scheme 2

corresponding triazolinediones **2** or **4a** using $Al(NO_3)_3 \cdot 9H_2O$ (**I**) and a catalytic amount of SiO_2–OSO_3H (**II**) in the presence of wet SiO_2 (50% *w*/*w*) (Scheme 2).

The oxidation reactions were carried out under heterogeneous conditions in dichloromethane at room temperature giving excellent yields (Table 1).

The catalytic oxidation procedure is very simple. All reaction components except triazolinediones are insoluble in dichloromethane; therefore products can be easily obtained by simple filtration and evaporation of CH_2Cl_2.

To show the efficiency of the described system in comparison with previously reported procedures, we compared our results obtained for oxidation of 4-phenylurazole (as a typical example) with the best of the well-known data from the literature, as shown in Table 2.

A plausible mechanism of this oxidation is outlined in Scheme 3 which proposes that the oxidation reaction occurs at the surface of wet SiO_2 via in-situ generation of HNO_3.

In summary, herein we report an efficient catalytic method for selective oxidation of urazoles and one bis-urazole under mild heterogeneous conditions with good to high yields. This method offers the advantage of shorter reaction times, high selectivity, cost effective reagent or catalyst, and easy workup.

Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Silica sulfuric acid was prepared as described elsewhere [31]. The spectral data (IR, ^1H NMR, and ^{13}C NMR) and melting points of products **2a**–**2i** agreed well with literature data (**2a**–**2g** [13, 15], **2h**–**2i** [20]).

*Oxidation of 4-cyclohexylurazole (**1d**) to 4-cyclohexyl-1,2,4-triazoline-3,5-dione (**2d**) with $Al(NO_3)_3.9H_2O/SiO_2$–OSO_3H, a typical experiment*

A suspension of 0.183 g **1d** (1 mmol), 0.344 g $Al(NO_3)_3.9H_2O$ (1.2 mmol), 3.03 g SiO_2–OSO_3H, and 0.3 g wet SiO_2 (50% *w*/*w*) in 5 cm^3 dichloromethane was stirred at room temperature for 150 min and then filtered. The residue was washed with 20 cm^3 CH_2Cl_2. Anhydrous Na_2SO_4 (1.5 g) was added to the filtrate and then removed by

Table 1 Oxidation of urazoles and bis-urazole to their corresponding triazolinediones using $Al(NO_3)_3.9H_2O$ (**I**) and catalytic amounts of SiO_2–OSO_3H (**II**) in the presence of wet SiO_2 (50% *w*/*w*) in dichloromethane at room temperature

Entry	Substrate[a]	Product	**I** (substrate/mmol $mmol^{-1}$)	**II** (substrate/g $mmol^{-1}$)	Time (min)	Yield (%)[b]
1	**1a**	**2a**	1.2	0.03	150	100[c]
2	**1b**	**2b**	1.2	0.18	160	98
3	**1c**	**2c**	1.2	0.03	145	95
4	**1d**	**2d**	1.2	0.03	150	99
5	**1e**	**2e**	1.2	0.03	120	98
6	**1e**	**2e**	1.2	–	5 h	–[d,e]
7	**1f**	**2f**	1.2	0.03	185	97
8	**1 g**	**2 g**	1.2	0.03	185	90
9	**1 h**	**2 h**	1.2	0.03	145	96
10	**1i**	**2i**	1.2	0.03	160	99
11	**3a**	**4a**	2.4	0.06	210	97

[a] Wet SiO_2 (50% *w*/*w*)/substrate = 0.3 g/mmol

[b] Isolated yields

[c] Conversion

[d] Without silica sulfuric acid

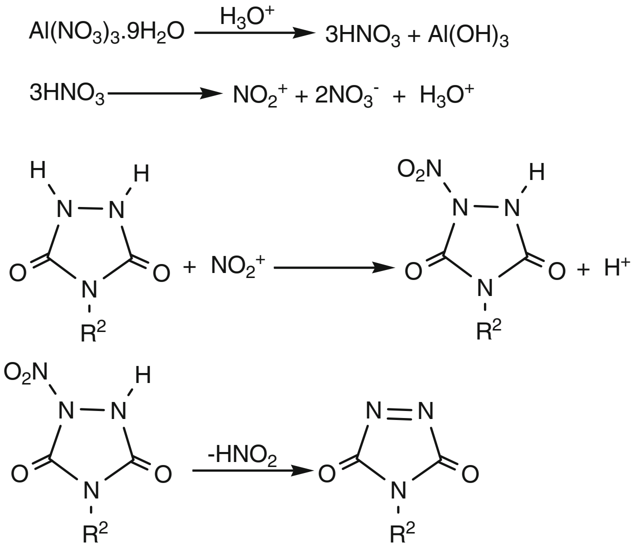
[e] Reaction not complete

Table 2 Comparison of the different methods used for the oxidation of 4-phenylurazole

Entry	Reagent	Reagent (substrate/mmol mmol^{-1})	Time (min)	Yield (%)[a]	Ref.
1	$Al(NO_3)_3.9H_2O$:SiO_2–OSO_3H	1.2:0.03[b]	120	98	This work
2	*N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonylamide	0.5	120	83	[15]
3	Trichloromelamine	3	180	87	[15]
4	HIO_3:$NaNO_2$	3:3.5	90	86	[16]
5	1.3-Dichloro-5,5-dimethylhydantoin	1	120	80	[18]
6	1,4-Diazabicyclo[2.2.2]octane-bromine	0.2	120	80	[20]
7	$NaNO_2$:oxalic acid	2:2	60	80	[32]
8	Silica chloride:$NaNO_2$	10:7	180	98	[33]
9	($KHSO_4.2KHSO_5.K_2SO_4$):$NaNO_2$	1.5:4.5	90	94	[34]

[a] Isolated yield

[b] The amount of SiO_2–OSO_3H is given in g/mmol



Scheme 3

filtration after 20 min. Finally, CH_2Cl_2 was removed by evaporation and 0.179 g **2d** (99%) was obtained. The product was identical with that described elsewhere [13, 15].

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

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