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Silica chloride/$NaNO_2$ as a novel heterogeneous system for the oxidation of urazoles under mild conditions

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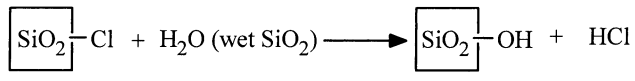
Abstract—Urazoles and bis-urazoles can be converted in excellent yields to their corresponding triazolinediones, with a combination of silica chloride (I), wet SiO_2 and sodium nitrite in dichloromethane at room temperature.

There is current general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.[1,2] In continuation of our studies on the application of heterogeneous systems we found that silica chloride[3,4] (I) is an excellent source for generation of HCl. It is interesting to note that the addition of wet SiO_2 to the reaction mixture containing silica chloride generates HCl in situ. Therefore, We used it for a different purpose. We were interested in using reagent (I) for the oxidation of urazoles and bis-urazoles via in situ generation of HNO_2 and NO^+, respectively when used in conjunction with $NaNO_2$, wet SiO_2 in an organic solvent (Scheme 1). We wish to report a simple method for the effective oxidation of urazoles and bis-urazoles under mild and heterogeneous conditions (Schemes 2 and 3).

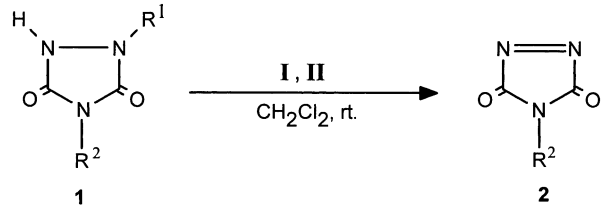
4-Substituted-1,2,4-triazole-3,5-diones are notable for their ability to participate in a wide range of concerted and stepwise conditions.[5–11] Considerable attention has been paid to their additions to activated alkenes,[5–8] electrophilic aromatic substitution,[9] dehydrogenating properties[10] and oxidation of alcohols to aldehyde and ketones.[11] The unusual reactivity which makes 1,2,4-triazoline-3,5-diones (**2**, **4**) of interest also makes them hard to prepare and purify.

Although a variety of reagents are capable of effecting these oxidations,[12–15] so far as we know 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 triazolinedione. Another major drawback to the older procedures is their use of reagents which are either highly toxic or present serious disposal problems (or both).[12] Very recently, we, among many others have demonstrated that the heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical waste as compared to the liquid phase counterparts.[16] In this article we wish to report a simple, cheap and convenient method for the effective conversion of urazoles and bis-urazoles to their



I

Scheme 1.



1 **2**

1	R^1	R^2
a	H	Me
b	H	Et
c	Na	*n*-Pr
d	H	*n*-Bu
e	H	Cyclohexyl
f	H	Ph
g	H	4-Cl-C_6H_4
h	H	4-NO_2-C_6H_4
i	H	3,4-Cl_2-C_6H_3

Scheme 2.

Keywords: oxidation; urazoles; bis-urazoles; triazolinediones; silica chloride.

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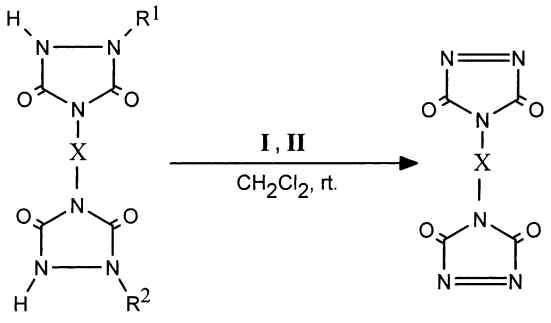
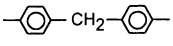


3	R^1	X	R^2
a	Na	-$(CH_2)_6$ -	Na
b	H		H

Scheme 3.

corresponding triazolinediones (**2**, **4**) under mild and heterogeneous conditions (Schemes 2 and 3).

Different types of urazoles (**1**) and bis-urazoles (**3**) were subjected to the oxidation reaction in the presence of silica chloride (I), $NaNO_2$ (II) and wet SiO_2 (50% w/w) in dichloromethane (Schemes 2 and 3). The oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature with good to excellent yields (Table 1). The triazolinediones (**2**) and bis-triazolinediones (**4**) were obtained by simple filtration and evaporation of the solvent. The oxidation reactions are heterogeneous because urazoles and bis-urazoles [(**1**, **3**) white solids] are insoluble in dichloromethane whereas all of the triazolinediones and bis-triazolinediones [(**2**, **4**), red and pink, respectively] are very soluble in dichloromethane. Therefore, the oxidation reaction presumably occurs at the surface of wet SiO_2 via in situ generation of HNO_2 in a small amount. Later on, the oxidation products (**2**, **4**) migrate to the liquid phase (CH_2Cl_2) immediately.

This new system effectively acts as N_2O_4 because a number of reactions are known in which nitrogen tetroxide ($N_2O_4 \Leftrightarrow NO^+NO_3^-$) acts as a nitrosating agent.[5,15,19] Therefore, we propose the following mechanism (i) on the basis of our observations, (ii) previously reported results about the applications of N_2O_4,[5,15,19] and (iii) products obtained (Scheme 4).

In conclusion, a cheap and easy procedure for the efficient oxidation of urazoles has been achieved.

1. Experimental

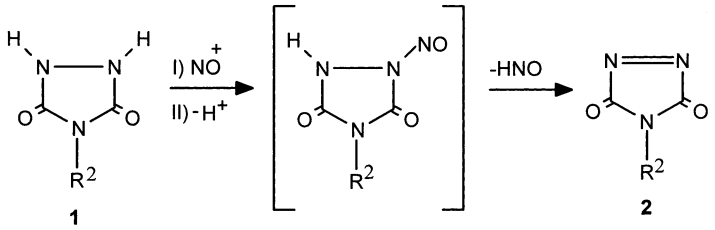
1.1. General

Chemicals were purchased from Fluka, Merck, Riedel-dehaen AG and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR, UV, ^1H

Table 1. Oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) with a combination of silica chloride (I), $NaNO_2$ (II) and wet SiO_2 (50% w/w) in dichloromethane at room temperature

Urazole or (bis)	Product	(Reagent/substrate)[a]		Time (h)	Yield[b] (%)	Mp °C	
		I	II			Found	Reported
1a	**2a**[12]	2	2	2	100[c]	97–99	98–98.5[12]
1b	**2b**[17]	2	2	2	100[c]	54–56	53[17a]
1c	**2c**[18]	5	2	3	80	42–54	44[15]
1d	**2d**[18]	4	2	2	80	43–45	44–45[18]
1e	**2e**[12]	4	2	3	84	97–98	95–96[12]
1f	**2f**[14]	10	7	3	98	168–175	170–178[14]
1g	**2g**[18]	10	7	3	98	134–135	130–132[12]
1h	**2h**[12]	10	7	3	95	125–126	128–129[18]
1i	**2i**[18]	12	7	3	82	110–113	113–115[18]
3a	**4a**[9]	16	7	3	90	145–150	146–149[9]
3b	**4b**[9]	10	7	3	81	182–185(dec.)[d]	185(dec.)[9]

[a] Wet SiO_2/substrate (mono) (0.4 g/1 mmol) and wet SiO_2/substrate (bis) (1 g/1 mmol).
[b] Isolated yields.
[c] Conversion.
[d] Decomposition point.



Scheme 4.

NMR, and ^{13}C NMR) and physical data with the authentic samples. Silica chloride was synthesized according to the reported procedure.[3,4] All urazoles and bis-urazoles were synthesized according to our previously reported procedures.[5,8,9,14,15]

1.1.1. Oxidation of 4-phenyl urazole (1f) to 4-phenyl-1,2,4-triazoline-3,5-dione (2f): a typical procedure. A suspension of compound **1f** (0.177 g, 1 mmol), I (0.955 g, 10 mmol)], wet SiO_2 (50% w/w) (0.4 g) and $NaNO_2$ (0.483 g, 7 mmol) in dichloromethane (10 mL) was stirred at room temperature for 3 h and then filtered. Residue was washed with CH_2Cl_2 (2×5 mL). Anhydrous Na_2SO_4 (3 g) was added to the filtrate. After 20 min, the resulting mixture was filtered. Dichloromethane was removed by water bath (40–50°C)[20] and simple distillation. The yield was 0.171 g (98%) of crystalline red solid (**2f**), mp 168–175°C, [lit.[14] mp 170–178°C].

1.1.2. 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 **3b** (0.366 g, 1 mmol), wet SiO_2 (50% w/w, 1 g) was crushed to a fine powder with a mortar and pestle. The resulting mixture was added to the dichloromethane (60 mL) and the suspension was vigorously stirred. Silica chloride [I (0955 g, 10 mmol)], and $NaNO_2$ (0.483 g, 7 mmol) were also added ($NaNO_2$ was added in four portions each addition after 30 min) to the reaction mixture. After the final addition the red suspension was allowed to stir for another 60 min and was filtered. Residue was washed with CH_2Cl_2 (2×10 mL). The filtrate was dried over anhydrous Na_2SO_4 (6 g) and was filtered again. Dichloromethane was removed by simple distillation. The yield was 0.292 g (81%) of crystalline pink solid (**4b**) mp 182–185°C (dec.) [lit.[9] mp 185>dec.°C].

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20. These compounds are sensitive to light, heat, alcohols, ethers, transition metals and any nucleophiles. Also they are very volatile so that, if temperature rises over than 50°C in the course of removing of CH_2Cl_2, some of TADs are removed with solvent simultaneously. Therefore, the temperature must be controlled and dichloromethane is the best solvent for this purpose.