

## Oxidation of urazoles via *in situ* generation of Cl<sup>+</sup> by using N,N,2,3,4,5,6-heptachloroaniline or a UHP/MCl<sub>n</sub> system under mild conditions<sup>†</sup>

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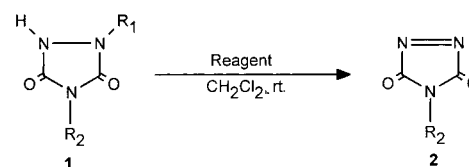
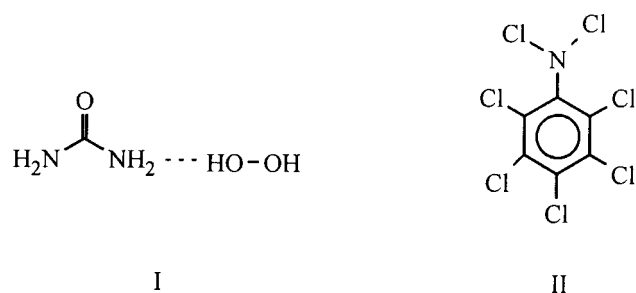
A combination of inorganic hydrolysable chloride salts and UHP (hydrogen peroxide–urea complex) in the presence of wet SiO<sub>2</sub> was used as an effective oxidising agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones under mild and heterogeneous conditions in good to excellent yields. Oxidation of urazoles and bis-urazoles also occurred with N,N,2,3,4,5,6-heptachloroaniline. The *in situ* generation of Cl<sup>+</sup> appears to be required for the oxidation of urazoles using these reagents.

**Keywords:** urazoles, N,N,2,3,4,5,6-heptachloroaniline

4-Substituted-1,2,4-triazole-3,5-diones (TADs) are notable for their ability to participate in a wide range of reactions, *e.g.* [4 + 2]<sup>1, 2</sup> and [2 + 2]<sup>3</sup> cycloadditions, ene reactions,<sup>4</sup> electrophilic aromatic substitution,<sup>5</sup> dehydrogenating properties<sup>6</sup> and oxidation of alcohols to aldehydes and ketones.<sup>7</sup> However, the unusual reactivity which makes 1,2,4-triazoline-3,5-diones (**2**, **4**) of interest to organic chemists, makes them difficult to prepare and purify. For example: 4-phenyl-1,2,3-triazoline-3,5-dione (**2e**) is an extremely reactive dienophile and enophile which is at least 1000 times more reactive than tetracyanoethylene (TCNE) in the Diels–Alder reaction with 2-chlorobutadiene and 2000 times more reactive than maleic anhydride.<sup>1</sup> All known methods of synthesis of these compounds require oxidation of the corresponding 1,2,4-triazolidine-3,5-diones (**1**, **3**), more commonly known as urazoles.

Although a wide variety of reagents are capable of effecting the oxidations of urazoles,<sup>8–11</sup> this transformation remains capricious because these compounds are very sensitive to the oxidising agents and reaction conditions. Moreover most of the reported reagents produce some by-products which are difficult to remove from the sensitive triazolinediones. Another major drawback to the older procedures is their use of reagents which are either highly toxic or produce serious disposal problems (or both).<sup>8</sup> Recently, we have demonstrated the remarkably practical use of N<sub>2</sub>O<sub>4</sub> gas *in situ* generated as a clean and efficient oxidant for this purpose.<sup>1,10,11</sup> It is known that gaseous N<sub>2</sub>O<sub>4</sub> is corrosive and highly toxic and must be generated under an

effective hood with caution. Therefore, we decided to develop a new reagent or reagent system in order to overcome the above limitations and provide a clean and easy work-up. Heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimisation of chemical wastes as compared to the solution phase counterparts.<sup>12</sup> Therefore, we attempted to find a heterogeneous system for urazole oxidation and we have investigated a number of different reaction conditions based upon the *in situ* generation of H<sub>2</sub>O<sub>2</sub>. In continuing our studies on the application of H<sub>2</sub>O<sub>2</sub> we found that UHP [(**I**) an addition compound of hydrogen peroxide and urea] is the best candidate for this purpose. A survey of the literature revealed that UHP (**I**) is an inexpensive, stable, and easy to handle source of pure H<sub>2</sub>O<sub>2</sub>.<sup>13</sup> In the last few years, there have been several reports on the use of UHP in the oxidations, namely for the conversion of amines to nitroalkane,<sup>14</sup> Baeyer–Villiger oxidations of ketones to lactones,<sup>15</sup> oxidations of sulfides to sulfones,<sup>16</sup> and more recently the conversion of pyridines to pyridine N-oxides under different conditions.<sup>17,18</sup> We wish to report a simple, cheap and convenient method for the effective conversion of urazoles and as well as bis-urazoles to their corresponding triazolinediones (**2**, **4**) under mild and heterogeneous conditions (Schemes 1 and 2).



Reagent: UHP(**I**)/MCl<sub>n</sub>/Wet SiO<sub>2</sub> or N,N,2,3,4,5,6-heptachloroaniline (**II**)

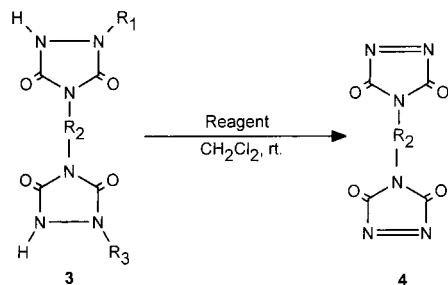
	R <sub>1</sub>	R <sub>2</sub>
<b>1</b>		
<b>a</b>	H	Me
<b>b</b>	H	Et
<b>c</b>	Na	<i>n</i> -Pr
<b>d</b>	H	<i>n</i> -Bu
<b>e</b>	H	Cyclohexyl
<b>f</b>	H	Ph
<b>g</b>	H	4-Cl-C <sub>6</sub> H <sub>4</sub>
<b>h</b>	H	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>

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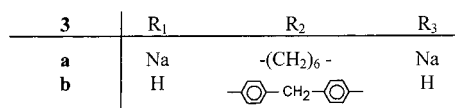
<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

**Scheme 1**

Although hydrogen peroxide or its derivatives (UHP, TetralinOOH<sup>9</sup>, etc.) does not affect urazoles even in the presence of strong inorganic acids such as H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, we observed that urazole oxidation occurred by UHP in the presence of concentrated hydrochloric acid. As might be expected, commercial hydrochloric acid contains a considerable amount of water and this destroyed triazolinediones (**2** and **4**). As a solution to this problem, hydrogen chloride (HCl gas) instead



Reagent: UHP(I)/MCl<sub>n</sub>/Wet SiO<sub>2</sub> or N,N,2,3,4,5,6-heptachloroaniline (II)



Scheme 2

**Table 1** Oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) with a combination of UHP (I) or N,N,2,3,4,5,6-heptachloroaniline (II), chloride salt [AlCl<sub>3</sub> (III), ZrCl<sub>4</sub> (IV), WCl<sub>6</sub> (V)] and wet SiO<sub>2</sub> (50% w/w) in dichloromethane at room temperature

Entry	Urazole or (bis)	Product <sup>a</sup>	(Reagent/Substrate) <sup>b</sup>					Time /h	Yield <sup>c</sup> /%	m.p./°C	
			I	II	III	IV	V			Found	Reported
1	<b>1a</b>	<b>2a</b> <sup>8</sup>	3	—	1	—	—	3.5	100 <sup>d</sup>	97-99	98-98.5 <sup>8</sup>
2	<b>1a</b>	<b>2a</b> <sup>8</sup>	3	—	—	0.75	—	3.5	100 <sup>d</sup>	97-99	98-98.5 <sup>8</sup>
3	<b>1a</b>	<b>2a</b> <sup>8</sup>	3	—	—	—	0.5	3.5	100 <sup>d</sup>	97-99	98-98.5 <sup>8</sup>
4	<b>1b</b>	<b>2b</b> <sup>19</sup>	3	—	—	—	0.5	3.5	100 <sup>d</sup>	54-56	53 <sup>9b</sup>
5	<b>1b</b>	<b>2b</b> <sup>19</sup>	3	—	—	0.75	—	3.5	100 <sup>d</sup>	54-56	53 <sup>9b</sup>
6	<b>1b</b>	<b>2b</b> <sup>19</sup>	3	—	—	—	0.5	3.5	100 <sup>d</sup>	54-56	53 <sup>9b</sup>
7	<b>1c</b>	<b>2c</b> <sup>11</sup>	4	—	3	—	—	2.5	80	43-44	44 <sup>11</sup>
8	<b>1c</b>	<b>2c</b> <sup>11</sup>	4	—	—	2.2	—	2.5	80	43-44	44 <sup>11</sup>
9	<b>1c</b>	<b>2c</b> <sup>11</sup>	2.5	—	—	—	0.66	3.5	83	43-44	44 <sup>11</sup>
10	<b>1d</b>	<b>2d</b> <sup>8</sup>	1.5	—	2	—	—	2.5	90	44-45	44-44.5 <sup>8</sup>
11	<b>1d</b>	<b>2d</b> <sup>8</sup>	3	—	—	0.75	—	2.5	80	44-45	44-44.5 <sup>8</sup>
12	<b>1d</b>	<b>2d</b> <sup>8</sup>	3	—	—	—	0.5	3.5	96	44-45	44-44.5 <sup>8</sup>
13	<b>1e</b>	<b>2e</b> <sup>8</sup>	3	—	1	—	—	3.5	97	97-98	95-96 <sup>8</sup>
14	<b>1e</b>	<b>2e</b> <sup>8</sup>	3	—	—	0.75	—	2.15	98	97-98	95-96 <sup>8</sup>
15	<b>1e</b>	<b>2e</b> <sup>8</sup>	3	—	—	—	0.5	3.5	98	97-98	95-96 <sup>8</sup>
16	<b>1e</b>	<b>2e</b> <sup>8</sup>	—	1	—	—	—	2	75	97-98	95-96 <sup>8</sup>
17	<b>1f</b>	— <sup>e</sup>	3	—	1	—	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
18	<b>1f</b>	— <sup>e</sup>	3	—	—	0.75	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
19	<b>1f</b>	— <sup>e</sup>	3	—	—	—	0.5	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
20	<b>1f</b>	<b>2f</b> <sup>8,10</sup>	—	1	—	—	—	1	100 <sup>d</sup>	169-175	170-178 <sup>10</sup>
21	<b>1g</b>	— <sup>e</sup>	3	—	1	—	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
22	<b>1g</b>	— <sup>e</sup>	3	—	—	0.75	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
23	<b>1g</b>	— <sup>e</sup>	3	—	—	—	0.5	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
24	<b>1g</b>	<b>2g</b> <sup>20</sup>	—	1	—	—	—	1	100 <sup>d</sup>	134-135	130-132 <sup>20</sup>
25	<b>1h</b>	— <sup>e</sup>	3	—	1	—	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
26	<b>1h</b>	— <sup>e</sup>	3	—	—	0.75	—	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
27	<b>1h</b>	— <sup>e</sup>	3	—	—	—	0.5	3.5	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
28	<b>1h</b>	<b>2h</b> <sup>8</sup>	—	1	—	—	—	1	100 <sup>d</sup>	125-126	128-129 <sup>8</sup>
29	<b>3a</b>	<b>4a</b> <sup>5,21</sup>	6	—	8	—	—	6.5	82	145-150	146-149 <sup>21</sup>
30	<b>3a</b>	<b>4a</b> <sup>5,21</sup>	6	—	—	6	—	5.5	81	145-150	146-149 <sup>21</sup>
31	<b>3a</b>	<b>4a</b> <sup>5,21</sup>	7.5	—	—	—	2	10	78	145-150	146-149 <sup>21</sup>
32	<b>3a</b>	<b>4a</b> <sup>5,21</sup>	—	2	—	—	—	2	100 <sup>d</sup>	145-150	146-149 <sup>21</sup>
33	<b>3b</b>	— <sup>e</sup>	6	—	—	6	—	6	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
34	<b>3b</b>	<b>4b</b> <sup>5,21</sup>	—	2	—	—	—	2	100 <sup>d</sup>	180	f 185 <sup>21</sup>

<sup>a</sup>All of the isolated products are known and their spectra and physical data have been reported in the literature.

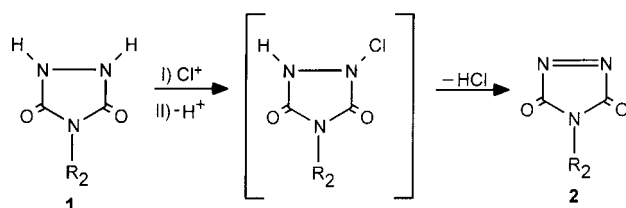
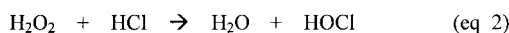
<sup>b</sup>Wet SiO<sub>2</sub>: substrate (mono) (0.4 g: 1 mmol) and wet SiO<sub>2</sub>: substrate (bis) (1.6 g: 1 mmol).

<sup>c</sup>Isolated yields. <sup>d</sup>Conversion. <sup>e</sup>Complexation occurred and no product was obtained. <sup>f</sup>Decomposition point.

of hydrochloric acid was used and the same result was obtained *i.e.* oxidation of urazoles and destruction of triazolinediones occurred simultaneously. The inorganic hydrolysable chloride salts [*e.g.* AlCl<sub>3</sub> (**III**), ZrCl<sub>4</sub> (**IV**) and WCl<sub>6</sub> (**V**)] and wet SiO<sub>2</sub> were used for the *in situ* generation of HCl in the reaction vessel. Promising results were obtained by using UHP/MCl<sub>n</sub>/wet SiO<sub>2</sub> system and oxidation of urazoles occurred without any destruction of 4-alkyl substituted triazolinediones (Table 1, entries 1–16 and 29–32). However, we found that the 4-aryl substituted triazolinediones (**1f–h** and **3b**) gave interesting stable complexes with this salt but we could not identify the real role of aryl moiety of urazoles. Hence, this method (UHP/MCl<sub>n</sub>/wet SiO<sub>2</sub>) was not suitable for the production of 4-aryl substituted triazolinediones.

Different kinds of urazoles and bis-urazoles were subjected to oxidation reaction in the presence of **I**, a chloride salt (*e.g.* **III–V**), and wet SiO<sub>2</sub> (50% w/w) in dichloromethane (Schemes 1 and 2). The oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature to give moderate to excellent yields (Table 1).

This oxidation reaction can be readily carried out only by placing **I**, chloride salt (one of *e.g.* **III–V**), **1** or **3**, wet SiO<sub>2</sub> (50% w/w) and CH<sub>2</sub>Cl<sub>2</sub> as the best solvent in a reaction vessel and efficiently stirring the resulting heterogeneous mixture at room temperature for 1–10 hours. The triazolinedione (**2**) or bis-triazolinedione (**4**) can be obtained by simple filtration and evaporation of the solvent. The results and reaction conditions are given in the Table 1.



Scheme 3

This new system *e.g.* a combination of inorganic chloride salts and UHP (**I**) is an effective source for the *in situ* generation of HOCl (eqn 2) and  $\text{Cl}^+$  (eqn 3) which behaves like  $\text{N}_2\text{O}_4$  ( $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+\text{NO}_3^-$ ).<sup>1a</sup> Since, in previous work it has been shown that *N,N,2,3,4,5,6*-heptachloroaniline (**II**) can generate  $\text{Cl}^+$ ,<sup>22</sup> thus we applied it alone as the oxidant for the oxidation of urazoles. The oxidation reaction was performed for 10 minutes without any destruction of triazolinediones (**2**, **4**). Oxidation of urazoles by *N,N,2,3,4,5,6*-heptachloroaniline (**II**) further supports the above idea (*e.g.* *in situ* generation of  $\text{Cl}^+$ ). Moreover this reagent was suitable for the oxidation of both alkyl and aryl substituted urazoles. Oxidation of urazoles (**1**, **3**) was also carried out by using HOCl or  $\text{H}_2\text{SO}_4/\text{SiO}_2/\text{Ca}(\text{OCl})_2$  but the purity and yield of the reaction products was rather low. Therefore, on the basis of our results and, previously reported results concerning the applications of *N,N,2,3,4,5,6*-heptachloroaniline (**II**),<sup>22</sup> the following mechanism may be proposed (Scheme 3).

In conclusion, practical and efficient oxidations of urazoles and bis-urazoles have been achieved by the new methodology described. The heterogeneous nature, cheapness and availability of the reagents, easy procedure and work-up make this method attractive for large-scale operations.

## Experimental

**General:** Chemicals were purchased from Fluka, Merck, Riedel-dehaen AG and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterised by comparison of their spectral (IR, UV,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ ) and physical data with the authentic samples. *N,N,2,3,4,5,6*-heptachloroaniline (**II**), was synthesised according to the literature.<sup>23</sup> All urazoles and bis-urazoles were synthesised according to our previously reported procedures.<sup>1, 4, 5, 10, 11, 21</sup>

**Oxidation of 4-cyclohexyl urazole (1e) to 4-cyclohexyl-1,2,4-triazoline-3,5-dione (2e) with UHP/ $\text{MCl}_n$  system, a typical procedure:** A suspension of compound **1e** (0.366 g, 2 mmol), **I** (0.564 g, 6 mmol), wet  $\text{SiO}_2$  (50% w/w) (0.4 g) and  $\text{WCl}_6$  (0.396 g, 1 mmol) in dichloromethane (20 ml) was stirred at room temperature for 3.5 hours and then filtered. Anhydrous  $\text{Na}_2\text{SO}_4$  (5 g) and  $\text{H}_2\text{SO}_4/\text{SiO}_2$  [(30% w/w) 1 g] were added to the filtrate and then stirred. After 15 minutes, the resulting mixture was filtered. Dichloromethane was removed by water bath (40–50 °C)<sup>24</sup> under simple distillation. The yield was 0.354 g (98%) of crystalline red solid (**2e**), m.p. 97–98 °C [lit.<sup>8</sup> m.p. 95–96 °C].  $^1\text{H-NMR}$  (FT-90 MHz,  $\text{CDCl}_3$  / TMS):  $\delta$  3.90 (quintet, 1H), 1.82–1.26 (m, 10H).  $^{13}\text{C-NMR}$  (FT-90 MHz,  $\text{CDCl}_3$  / TMS):  $\delta$  158.77, 53.93, 28.72, 24.96, 24.28.

**Oxidation of hexamethylenebis-urazole disodium salt (3a) to 1,6-bis(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (4a) with UHP/ $\text{MCl}_n$  system. A typical procedure:** A mixture of **3a** (0.366 g, 1 mmol), **I** (0.564 g, 6 mmol), wet  $\text{SiO}_2$  (50% w/w) (0.4 g) was crushed to a fine powder with a mortar and pestle. The resulting mixture was added to the dichloromethane (60 ml).  $\text{ZrCl}_4$  (1.4 g, 6 mmol) was also added to the reaction mixture and vigorously stirred. Anhydrous  $\text{Na}_2\text{SO}_4$

(10 g) and  $\text{H}_2\text{SO}_4/\text{SiO}_2$  [(30% w/w) 2 g] were added to the filtrate and then stirred. After 20 minutes, the resulting mixture was filtered. Dichloromethane was removed by simple distillation. The yield was 0.227 g (81%) of crystalline pink solid (**4a**) m.p. 145–150 °C [lit.<sup>21</sup> m.p. 146–149 °C].  $^1\text{H-NMR}$  (FT-90 MHz,  $\text{CDCl}_3$  / TMS):  $\delta$  3.65 (t, 4H), 1.62–1.33 (m, 8H).

**Oxidation of 4-cyclohexyl urazole (1e) to 4-cyclohexyltriazolinedione (2e) with *N,N,2,3,4,5,6*-heptachloroaniline.** A typical procedure: A suspension of compound **1e** (0.366 g, 2 mmol) and **II** (0.668 g, 2 mmol) in dichloromethane (20 ml) was stirred at room temperature for 2 hours. Dichloromethane was removed by water bath (40–50 °C)<sup>24</sup> and simple distillation. The residue was sublimed at 50 °C. The yield was 0.325 g, (90%) of crystalline pale red solid (**2e**).

**Preparation of *N,N,2,3,4,5,6*-heptachloroaniline<sup>23</sup>:** Pentachloroaniline (2.0 g, 7.5 mmol) was added gradually to a freshly prepared ethereal solution of hypochlorous acid (1.22 g, 22.8 mmol, in 40 ml ether) at –16 °C. The solution was stirred for 0.5 hour, during which time a yellow solid precipitated. The mixture was cooled to –68 °C in Cardice (to remove the water) and filtered very quickly. The filtrate was evaporated *in vacuo* and the yellow solid residue were washed with cold (*ca* –60 °C) pentane. It was then dried under vacuum to produce *N,N,2,3,4,5,6*-heptachloroaniline (2.1 g, 6.2 mmol) in 84% yield, m.p. 108 °C [lit.<sup>23</sup> m.p. 111 °C],  $^{13}\text{C-NMR}$ ( $\text{CDCl}_3$ /TMS):  $\delta$  147.6, 135.6, 132.9, 131.9 ppm., IR(Nujol), 1470, 1380, 780, 740, 610  $\text{cm}^{-1}$ .

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