

Simple and efficient heterogeneous media for the oxidation of urazole derivatives to their corresponding triazolinediones *via in situ* generation of Cl⁺

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A new procedure for the oxidation of urazole derivatives to their corresponding triazolinediones was developed using ZrCl₄ and polyvinylpyrrolidone-supported hydrogen peroxide (PVP-H₂O₂) in dichloromethane under very mild reaction conditions. This procedure is very simple and works efficiently at room temperature with excellent yields of products.

Keywords: Polyvinylpyrrolidone; PVP-H₂O₂; Urazole; Triazolinedione; Oxidation.

INTRODUCTION

4-Substituted-1,2,4-triazoline-3,5-diones are notable for their ability to participate in a wide range of reaction types such as [4+2] [1-2] and [2+2] [3] cycloadditions, ene reactions [4], electrophilic aromatic substitution [5], dehydrogenation [6] and oxidation of alcohols to aldehydes and ketones [7]. Oxidation of urazoles is a common way for the preparation of triazolinediones and a wide variety of methods and reagents have been reported in the literature for this purpose, such as *N,N,N,N*-tetrabromobenzene-1,3-disulfonylamide (TBBDA) or trichloromelamine (TCM) [8], Ph₃BiCO₃ [9], ICl-SiO₂ [10], periodic acid or oxone/KBr system [11], 1,4-diazabicyclo[2.2.2]octane 1,4-bis(oxide)-bis (hydrogen peroxide)/MCl_x [12], 4-(*p*-chloro) phenyl-1,2,4-triazole-3,5-dione [13] and *N*-bromo reagent [14]. However, most of the reported reagents produce byproducts, which either destroy, or are difficult to remove from the sensitive triazolinediones. Another major drawback of the older procedures is the use of reagents which are either highly toxic or impart serious disposal problems (or both) [15-18]. Therefore, the preparation of these compounds under mild conditions is of practical importance for synthetic organic chemists and is still in demand. Heterogeneous reactions facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years. The advantages of these methods over conventional homogeneous

reactions are: higher selectivity, enhanced reaction rates, cleaner products, and simplicity of manipulation [19].

EXPERIMENTAL

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

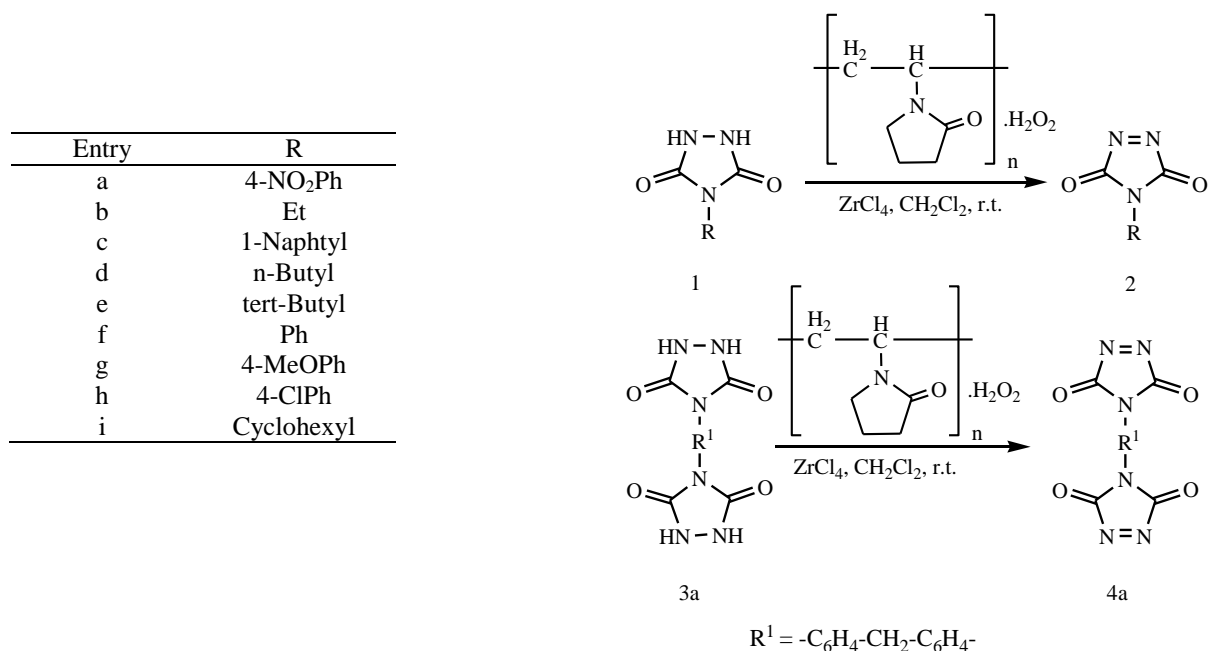
Oxidation of 4-cyclohexylurazole (1i) to 4-cyclohexyl-1,2,4-triazoline-3,5-dione (2i), as a typical experiment:

A mixture of 4-cyclohexylurazole (**1i**, 0.183 g, 1 mmol), polyvinylpyrrolidone-supported hydrogen peroxide (PVP-H₂O₂, 0.29 g), and ZrCl₄ (0.097 g, 0.417 mmol) in 5 mL dichloromethane was stirred at room temperature for 105 min and then filtered. The residue was washed with CH₂Cl₂ (20 mL). Anhydrous Na₂SO₄ (1.5 g) was added to the filtrate and then removed by filtration. Finally, evaporation of the solvent gave 4-cyclohexyl-1,2,4-triazoline-3,5-dione (**2i**). The yield of the crystalline red solid was 97%.

RESULTS AND DISCUSSION

In continuation of our ongoing work on development of environmentally benign methods using solid supported reagents [20-24], and in order to complete our studies on the functionalization of organic compounds [25-30] we investigated the

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Scheme 1. Oxidation of different types of urazoles **1** or bis-urazole **3a** to their corresponding triazolinediones **2** or **4a**

oxidation of urazole derivatives by polyvinylpyrrolidone-supported hydrogen peroxide (PVP-H₂O₂) and ZrCl₄. PVP-H₂O₂ was prepared *via* the reported procedure by Pourali and Ghanei [31]. The oxidation of different types of urazoles **1** or bis-urazole **3a** to their corresponding triazolinediones **2** or **4a** using a combination of polyvinylpyrrolidone-supported hydrogen peroxide (PVP-H₂O₂) and ZrCl₄, which *in situ* generate Cl⁺, is delineated in Scheme 1.

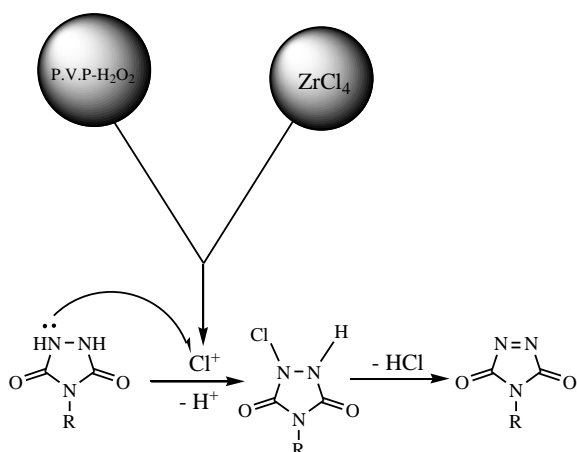
As shown in Table 1, different kinds of urazoles (**1**) and bis-urazole (**3a**) are oxidized to their corresponding triazolinediones by PVP-H₂O₂ in the

presence of ZrCl₄ and dichloromethane as a solvent under stirring the resulting heterogeneous mixture at room temperature. The triazolinediones **2** and bis(triazolinedione) **4a** are obtained by simple filtration and evaporation of the solvent. The oxidation reactions of urazoles are heterogeneous because urazoles and bis-urazole [(**1**, **3a**) white solids] are insoluble in dichloromethane whereas all triazolinediones and bis(triazolinedione) [(**2**, **4a**), red and pink, respectively] are extremely soluble in dichloromethane. A plausible mechanism of this oxidation is outlined in Scheme 2.

Table 1. Oxidation of urazole derivatives to their corresponding triazolinediones with PVP-H₂O₂ (**I**) and ZrCl₄ (**II**) in CH₂Cl₂ at room temperature

Entry	Substrate	Product	I (g)	II (mmol)	Time (min)	Yield ^a (%)
1	1a	2a	0.29	0.417	120	96
2	1b	2b	0.29	0.417	90	96
3	1c	2c	0.29	0.417	120	98
4	1d	2d	0.29	0.417	90	95
5	1e	2e	0.29	0.417	75	98
6	1f	2f	0.29	0.417	90	98
7	1g	2g	0.29	0.417	120	98
8	1h	2h	0.29	0.417	90	99
9	1i	2i	0.29	0.417	105	97
10	3a	4a	0.58	0.834	210	98

^a Isolated yield.



Scheme 2. Plausible mechanism

In conclusion, we report an efficient and versatile procedure for the oxidation of urazoles and bis-urazole with the following advantages: (a) the reagent used is inexpensive and easily handled; (b) the procedure is very simple and works efficiently without any additives at room temperature; (c) the isolation of the product is straightforward and this system could be used for the oxidation of a wide variety of urazole derivatives under mild and safe conditions.

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REFERENCES

1. S.E. Mallakpour, M.A. Zolfigol, *Indian J. Chem.* 34, 183 (1995).
2. G. Desimoni, G. Faita, P.P. Righetti, A. Sulcini, D. Tsyganov, *Tetrahedron* 50, 1821 (1994).
3. J.H. Hall, G. Krishnan, *J. Org. Chem.* 49, 2498 (1984).
4. S.E. Mallakpour, G.B. Butler, H. Aghabozorg, G. Palanik, *J. Macromolecules* 18, 342 (1985).
5. S.E. Mallakpour, G.B. Butler, *J. Polym. Sci., Polym. Chem Ed*, 27, 217 (1989).
6. T. Klindert, G. Seitz, *Synth. Commun.* 26, 2587 (1996).
7. R.C. Cookson, I.D.R. Stevens, C.T. Watts, *Chem. Commun.*, 744 (1966).
8. M.A. Zolfigol, R. Ghorbani-Vaghei, S. Mallakpour, G. Chehardoli, A. Ghorbani Choghamarani, A. Hosain Yazdi, *Synthesis*, 10, 1631 (2006).
9. C. Me'nard, E. Doris and C. Mioskowski, *Tetrahedron Letters*, 44, 6591 (2003).
10. B. Karami, S. Mallakpour, and M. Farahi, *Heteroatom Chemistry*, 19, 389 (2008).
11. M. A. Zolfigol, M. Bagherzadeh, S. Mallakpour, G. Chehardoli, A. Ghorbani-Choghamarani, N. Koukabi, M. Dehghanian, M. Doroudgar, *Journal of Molecular Catalysis A: Chemical*, 270, 219 (2007).
12. M. A. Zolfigol, Peyman Salehi, S. E. Mallakpour and M. Torabi, *Bull. Chem. Soc. Jpn.*, 76, 1673 (2003).
13. M. A. Zolfigol, D. Azarifar, S. Mallakpour, I. Mohammadpour-Baltork, A. Forghaniha, B. Maleki and M. Abdollahi-Alibeik, *Tetrahedron Letters*, 47 833 (2006).
14. M. A. Zolfigol, G. Chehardoli, E. Ghaemi, E. Madrakian, R. Zare, T. Azadbakht, K. Niknam, and S. Mallakpour, *Monatsh. Chem.* 139, 261 (2008).
15. V.P. Arya, S. Shenoy, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* 14, 883 (1976).
16. H. Warnho, K. Wald, *Org. Prep. Proced. Int.*, 7, 251 (1975).
17. S.E. Mallakpour, *J. Chem. Educ.*, 69, 238 (1992).
18. S.E. Mallakpour, M.A. Zolfigol, *J. Sci. Islamic Republic Iran*, 4, 199 (1993).
19. I. Mohammadpour-Baltork, M.M. Sadeghi, S.E. Mallakpour, A.R. Hajipour, A.H. Adibi, *Synthetic Commun.*, 32, 3445 (2002).
20. A. Ghorbani-Choghamarani, M. Nikoorazm, H. Goudarziafshar, L. Shiri, Z. Chenani, *Bull. Korean Chem. Soc.* 30, 972 (2009).
21. M.A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi, S. Jafari, *Catal Commun.*, 9, 1739 (2008).
22. A. Ghorbani-Choghamarani, Z. Chenani, S. Mallakpour, *Synthetic Commun.*, 39, 4264 (2009).
23. A. Ghorbani-Choghamarani, M.A. Zolfigol, M. Hajjami, K. Darvishi, L. Gholamnia, *Collect. Czech. Chem. Commun.*, 75, 607 (2010).
24. A. Ghorbani-Choghamarani, G. Azadi, *J. Iran. Chem. Soc.*, 8, 1082 (2011).
25. M.A. Zolfigol, F. Shirini, A. Ghorbani-Choghamarani, I. Mohammadpour-Baltork, *Green Chem.*, 4, 562 (2002).
26. M.A. Zolfigol, F. Shirini, A. Ghorbani-Choghamarani, M. Hajjami, M. Sedaghat, *Mendeleev Commun.*, 15, 113 (2005).
27. M.A. Zolfigol, F. Shirini, A. Ghorbani-Choghamarani, *Synthesis*, 2043 (2006).
28. M.A. Zolfigol, M. Bagherzadeh, K. Niknam, F. Shirini, I. Mohammadpour-Baltork, A. Ghorbani-Choghamarani, M. Baghbanzadeh, *J. Iran. Chem. Soc.*, 3, 73 (2006).
29. M.A. Zolfigol, K. Amani, M. Hajjami, A. Ghorbani-Choghamarani, *Monatsh. Chem.* 139, 895 (2008).
30. A. Ghorbani-Choghamarani, M. Hajjami, H. Goudarziafshar, M. Nikoorazm, S. Mallakpour, F. Sadeghizadeh, G. Azadi, *Monatsh. Chem.*, 140, 607 (2009).
31. A.R. Pourali, M. Ghanei, *Bull. Korean Chem. Soc.*, 27, 1674 (2006).

ПРОСТИ И ЕФЕКТИВНИ ХЕТЕРОГЕННИ СРЕДИ ЗА ОКИСЛЕНИЕТО НА УРАЗОЛОВИ
ПРОИЗВОДНИ ДО СЪОТВЕТНИТЕ ТРИАЗОЛИНДИОНИ ЧРЕЗ *IN SITU* ГЕНЕРИРАНЕ
НА Cl^+

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(Резюме)

Разработена е нова процедура за окисление на уразолови производни до съответните им триазолиндиони. Използвани са $ZrCl_4$ и водороден пероксид в поливинил-полипиролон ($PVP-H_2O_2$) в среда от дихлорметан при меки реакционни условия. Методът е много прост и работи ефективно при стайни температури с отличен добив на продуктите.