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Mild and heterogeneous oxidation of urazoles to their corresponding triazolinediones using molybdatophosphoric acid

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ABSTRACT

A combination of molybdatophosphoric acid and NaNO₂ in the presence of wet SiO₂ is used as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones under mild and heterogeneous conditions with moderate to excellent yields.

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KEYWORDS

Molybdatophosphoric acid;
Triazolinediones;
Urazole;
Oxidation;
Heterogeneous.

INTRODUCTION

4-Substituted 1,2,4-triazoline-3,5-diones (urazoles) are very important materials for their high reactivity in various kinds of chemical reactions. Among the different applications of this group of chemicals in research works, their use in the synthesis of new organic compounds as well as their use in the new and convenient methods for the preparation of organic compounds and the study of chemical reactions can be pointed out.

Among the wide range of applications of 4-Substituted 1,2,4-triazoline-3,5-diones, their applications as very reactive molecules in concerted reactions such as Diels-Alder^[1-10], ENE^[11-22], and [2+2] cycloaddition reactions^[23-24], as well as unconcerted reactions, for example nucleophilic and addition reactions²⁵⁻²⁸, can be pointed out. Modification of polydienes via ENE reactions is an example of application of triazolinediones in polymer area^[29].

Triazolinediones are also used as oxidizing agents, for example, in conversion of ketones to 1,2-diketones^[30], as well as oxidation of 1,3,5-trisubstituted pyrazolines under mild conditions^[31] and aromatization of 1,4-dihydropyridines^[32].

In addition to the nitrogen dioxide manner^[33], 4-substituted triazolinediones are prepared using different common methods of oxidation for urazoles such as silica chloride/NaNO₂^[34], silica sulfuric acid/NaNO₂^[35], Ph₃BiCO₃^[36], KMnO₄/Al₂O₃^[37], 1,4-diazabicyclo[2.2.2]octane, 1,4-bis(oxide)-bis(hydrogen peroxide)/MCl^[38], NO⁺ crown H(NO₃)₂^[39], Ca(OCl)₂^[40], K₂Cr₂O₇/AlCl₃^[41], silica sulfuric acid/KClO₃^[42], silica chloride/oxone^[42], 1,3-Dihalo-5,5-dimethylhydantoin^[43], periodic acid, and oxone®/KBr^[44].

In this article, we wish to report a new, simple, cheap, and convenient method for the effective oxidation of 4-substituted 1,2,4-triazolidine-3,5-diones to

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corresponding 1, 2, 4-triazoline-3, 5-diones.

EXPERIMENTAL

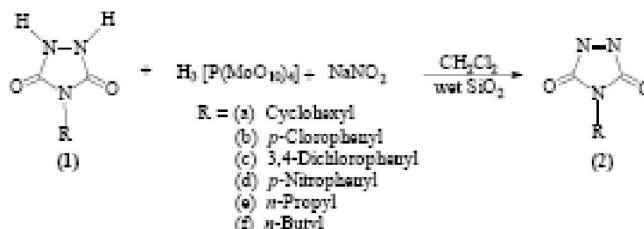
Oxidation of 4-cyclohexyl urazole (1a) to 4-cyclohexyl -1,2,4-triazoline-3,5-dione (2a): a typical procedure

Urazoles and bis-urazoles^[45-49] were synthesized according to previously reported procedures.

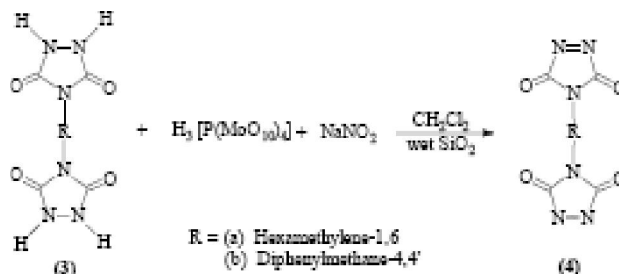
A suspension of compound 1a (0.092 g, 0.5 mmol), molybdatophosphoric acid (0.913 g, 0.5 mmol), NaNO₂ (0.035 g, 0.5 mmol), and wet SiO₂ (50% w/w) (0.1 g) was added to the dichloromethane (10 ml), and the suspension was vigorously stirred. The red suspension was allowed to stir for 90 min and was filtered. The residue was washed with CH₂Cl₂ (2×10 ml). The filtrate was dried over anhydrous Na₂SO₄ (5 g), and was filtered again. After 15 min, dichloromethane was removed by water-bath (40–50 °C)^[50] and simple distillation. The yield was 0.080 g (90%) of crystalline red solid (2a), m.p. 95-97 °C^[51], lit.^[43] 95-96 °C.

RESULTS AND DISCUSSION

In continuation of our studies on oxidation of urazoles, we have found that a combination of molybdatophosphoric acid and NaNO₂ in the presence of wet SiO₂ generate NO⁺ as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones. Thus in this article we wish to report a simple, cheap, and convenient method for the effective oxidation of urazoles and bis-urazoles to their corresponding triazo-linediones under mild and



Scheme 1 : Oxidation reaction of 4-substituted urazoles to their corresponding triazolinediones at room temperature



Scheme 2 : Oxidation reaction of bis-urazoles to their corresponding bis-triazolinediones at room temperature

heterogeneous conditions. Different types of urazoles (1) and bis-urazoles (3) were subjected to the oxidation reaction with a combination of molybdatophosphoric acid and NaNO₂ in the presence of wet SiO₂ (50% w/w) in dichloromethane (Schemes 1 and 2).

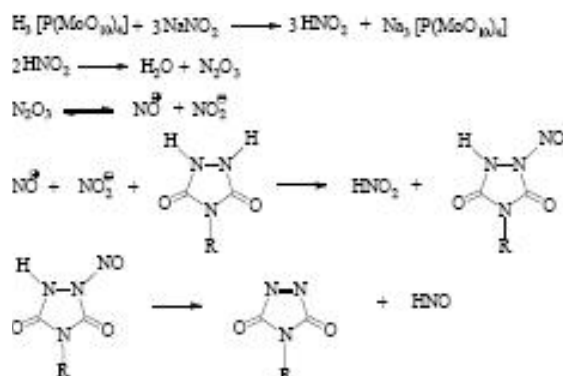
The oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature with moderate to excellent yields (TABLE 1). The present oxidation reaction can be readily carried out only by placing molybdatophosphoric acid and NaNO₂ with urazoles (1) or bis-urazoles (3), wet SiO₂ (50% w/w), and CH₂Cl₂ as the best solvent in a reaction vessel, and efficiently stirring the resulting heterogeneous mixture at room temperature. The

TABLE 1 : Oxidation of urazoles (1) and bis-urazoles (3) to their corresponding triazolinediones (2) and bis-triazolinediones (4) using molybdatophosphoric acid and NaNO₂ in the presence wet SiO₂ (50% w/w) in dichloromethane at room temperature

Urazole Code	Urazole mg (mmol)	H ₃ [P(MoO ₁₀) ₄] mg (mmol)	NaNO ₂ mg (mmol)	Wet SiO ₂ (mg)	CH ₂ Cl ₂ (mL)	Time (min)	Triazolinedione code	Triazolinedione mg	Yield (%)
1a	92 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2a	80	90
1b	106 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2b	88	83
1c	123 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2c	82	67
1d	111 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2d	85	77
1e	83 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2e	61	86
1f	79 (0.5)	0.913 (0.5)	67 (1.0)	200	10	90	2f	67	87
3a	164(0.5)	1.825 (1.0)	135 (2.0)	200	15	90	4a	98	70
3b	183 (0.5)	1.825 (1.0)	135(2.0)	200	15	90	4b	113	63

triazolinediones (2) and bis-triazolinediones (4) were obtained by simple filtration and evaporation of the solvent. The results and reaction conditions were tabulated in TABLE 1.

As mentioned above, the oxidation reactions are heterogeneous because urazoles and bis-urazoles [(1, 3) white solids] are insoluble in dichloromethane whereas, the triazolinediones and bis-triazolinediones [(2, 4), red and pink, respectively] are very soluble in dichloromethane. Therefore, the oxidation reaction was performed at the surface of wet SiO_2 via insitu generation of NO^+ (Scheme 3).



Scheme 3 : A proposed mechanism for insitu generation of NO^+ and its reaction with urazoles

In conclusion, a practical and efficient oxidation of urazoles and bis-urazoles was achieved. We suggest that these systems could be used for the oxidation of a wide variety of urazole derivatives under mild and safe conditions.

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- [50] These Compounds are Sensitive to Light, Heat, Alcohols, Ethers, Transition Metals, and Any Nucleophiles. Also, They are Very Volatile so That, If The Temperature Rises Over 50 °C In The Course of Removing of CH₂Cl₂, Some Tads are Removed With The Solvent Simultaneously. Therefore, The Temperature Must be Controlled and Dichloromethane is The Best Solvent For This Purpose.
- [51] Spectroscopic data: 2a: 4-Cyclohexyl-1,2,4-triazoline-3,5-dione: pink crystal, mp 95–97 °C, Lit. [43] 95–96 °C. ¹H NMR (CDCl₃): δ 1.26–1.8 (m, 10H), 3.90 (m, 1H). 2b: 4-(4-Chloro phenyl)-1,2,4-triazoline-3,5-dione: red crystal, mp 132–135 °C, Lit. [43] 130–132 °C. ¹H NMR (CDCl₃): δ 7.41 (s, 5H). 2c: 4-(3,4-Dichloro phenyl)-1,2,4-triazoline-3,5-dione: red crystal, mp 111–113 °C, Lit. [43] 113–115 °C. 2d: 4-(4-Nitro phenyl)-1,2,4-triazoline-3,5-dione: red crystal, mp 125–126 °C, Lit. [43] 128–129 °C. ¹H NMR CDCl₃): δ 7.89–8.40 (m, 5H). 2e: 4-n-Propyl-1,2,4-triazoline-3,5-dione: pink crystal, mp 40–42 °C, Lit. [43] 44 °C. ¹H NMR (CDCl₃): δ 0.94 (t, 3H), 1.68 (m, 2H), 3.63 (t, 2H). 2f: 4-n-Butyl-1,2,4-triazoline-3,5-dione: pink crystal, mp 42–43 °C, Lit. [43] 44–44.5 °C. ¹H NMR (CDCl₃): δ 0.86 (t, 3H), 1.21–1.53 (m, 4H), 3.5 (t, 2H). 4a: 1,6-Bis-(3,5-dioxo-1,2,4-triazoline-4-eyl)-hexane: pink crystal, mp 145–150 °C, Lit. [43] 146–149 °C. ¹H NMR (CDCl₃): δ 1.33–1.62 (m, 8H), 3.65 (t, 4H). 4b: Bis-(para-3,5-dioxo-1,2,4-triazoline-4-eyl-phenyl)-methane: pink crystal, mp 180–185 °C (dec), Lit. [43] 185 °C (dec).