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

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Received: 27th December, 2011; Accepted: 17th January, 2012

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.

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-Alder¹⁻¹⁰, ENE¹¹⁻²², and [2+2] cycloaddition reactions²³⁻²⁴, as well as unconcerted reactions, for example neucleophilic and addition reactions²⁵⁻²⁸, can be pointed out. Modification of polydienes via ENE reactions is an example of application of triazolinediones in polymer area²⁹.

Triazolinediones are also used as oxidating agents, for example, in conversion of ketones to 1,2-diketones³⁰, as well as oxidation of 1,3,5-trisubstituted pyrazolines under mild conditions³¹ and aromatization of 1,4-dihydropyridines³².

In addition to the nitrogen dioxide manner³³, 4-sustituted triazolinediones are prepared using different common methods of oxidation for urazoles such as silica chloride/NaNO₂³⁴, silica sulfuric acid/NaNO₂³⁵, Ph_BiCO³⁶, KMnO₄/Al₂O₃³⁷, 1,4-diazabicyclo[2.2.2]octane, 1,4-bis(oxide)-bis(hydrogen peroxide)/MCl³⁸, NO⁺crown H(NO₃)₂⁻³⁹, Ca(OCl)₂⁴⁰, K₂Cr₂O₇/AlCl₃⁴¹, silica sulfuric acid/KClO₃⁴², silica chloride/oxone⁴², 1,3-Dihalo-5,5-dimethylhydantoin⁴³, periodic acid, and oxone®/KBr⁴⁴.

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
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), NaNO\(_2\) (0.035 g, 0.5 mmol), and wet SiO\(_2\) (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 CH\(_2\)Cl\(_2\) (2×10 ml). The filtrate was dried over anhydrous Na\(_2\)SO\(_4\) (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 NaNO\(_2\) in the presence of wet SiO\(_2\) generate NO\(^+\) as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinodiones. 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-line-diones under mild and heterogeneous conditions. Different types of urazoles (1) and bis-urazoles (3) were subjected to the oxidation reaction with a combination of molybdatophosphoric acid and NaNO\(_2\) in the presence of wet SiO\(_2\) (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 NaNO\(_2\) with urazoles (1) or bis-urazoles (3), wet SiO\(_2\) (50% w/w), and CH\(_2\)Cl\(_2\) as the best solvent in a reaction vessel, and efficiently stirring the resulting heterogeneous mixture at room temperature. The

<table>
<thead>
<tr>
<th>Urazole Code</th>
<th>Urazole Code (mg)</th>
<th>H(<em>3)[P(MoO(</em>{10}))] mg (mmol)</th>
<th>NaNO(_2) mg (mmol)</th>
<th>Wet SiO(_2) mg (mmol)</th>
<th>CH(_2)Cl(_2) mL</th>
<th>Time (min)</th>
<th>Triazolinodione code</th>
<th>Triazolinodione mg</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>92 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2a</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>1b</td>
<td>106 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2b</td>
<td>88</td>
<td>83</td>
</tr>
<tr>
<td>1c</td>
<td>123 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2c</td>
<td>82</td>
<td>67</td>
</tr>
<tr>
<td>1d</td>
<td>111 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2d</td>
<td>85</td>
<td>77</td>
</tr>
<tr>
<td>1e</td>
<td>83 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2e</td>
<td>61</td>
<td>86</td>
</tr>
<tr>
<td>1f</td>
<td>79 (0.5)</td>
<td>0.913 (0.5)</td>
<td>67 (1.0)</td>
<td>200</td>
<td>10</td>
<td>90</td>
<td>2f</td>
<td>67</td>
<td>87</td>
</tr>
<tr>
<td>3a</td>
<td>164(0.5)</td>
<td>1.825 (1.0)</td>
<td>135 (2.0)</td>
<td>200</td>
<td>15</td>
<td>90</td>
<td>4a</td>
<td>98</td>
<td>70</td>
</tr>
<tr>
<td>3b</td>
<td>183 (0.5)</td>
<td>1.825 (1.0)</td>
<td>135(2.0)</td>
<td>200</td>
<td>15</td>
<td>90</td>
<td>4b</td>
<td>113</td>
<td>63</td>
</tr>
</tbody>
</table>
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.

ACKNOWLEDGMENT

The authors are grateful to the Research Council of Shahrood University of Technology for the financial support of this work.

REFERENCES

[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 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-ethyl)-methane: pink crystal, mp 190–185 °C (dec), Lit. [43] 185 °C (dec).