Oxidation of urazoles to triazolinediones under solvent-free conditions using peroxymonosulfate and alumina-supported permanganate

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Received 13 June 2001; accepted (revised) 10 December 2001

Treatment of urazoles with potassium permanganate leads to a simple and mild oxidation reaction, which produces triazolinediones. The reaction is conducted under solvent-free conditions and triazolinediones can be isolated in good to high yields by a simple work-up procedure. The reaction with alumina-supported permanganate enhances the rate and yield.

Triazolinedione exhibit a wide range of reactivity and reaction types, e.g. [4+2] and [2+2] cycloadditions, diene reactions, electrophilic aromatic substitution, dehydrogenating properties and oxidation of alcohols to aldehydes and ketones. The unusual reactivity that makes 1,2,4-triazoline-3,5-diones of interest also makes them hard to prepare and purify. For example, 4-phenyl-1,2,4-triazoline-3,5-dione 2a-f is an extremely reactive dienophile and enophile which is at least 1000 times more reactive than tetraacyanoethylene in the Diels-Alder reaction with 2-chlorobutadiene and 2000 times more reactive than maleic anhydride. All known methods of synthesis of these compounds require oxidation of the corresponding 1,2,4-triazolidine-3,5-diones 1a-f, more commonly known as urazoles.

In recent years, a wide variety of reagents have been reported for this transformation, but this transformation is a difficult step because these compounds are sensitive to the oxidizing agents and reaction conditions. The use of the reported reagents results in several by-products, which either destroy, or are difficult to separate from the sensitive triazolinediones. Another major drawback to the older procedures is using of reagents, which are either highly toxic or present serious disposal problems. Recently we have introduced a new methodology for the oxidation of different types of urazoles under solvent-free conditions with benzyltriphenylphosphonium peroxymonosulfate.

Adsorption on the surface of solid supports is known to cause a change in the chemical properties of many reagents. One of the most striking examples is with the well-known oxidant, potassium permanganate. Oxidation of organic compounds by permanganate adsorbed on a solid support has two major advantages over that take place in homogeneous conditions: (a) the products can be easily isolated by filtration, followed by evaporation of the solvent; and (b) heterogeneous permanganate oxidation often exhibit greater reactivity and selectivity. Recently, for conversion of oximes to carbonyl compounds and also for oxidation of alcohols to aldehydes and ketones under solvent-free conditions potassium permanganate supported on alumina is reported.

In continuation of our ongoing program to develop environmentally benign methods using solid supports, we wish to report the oxidation of urazoles 1a-f to their corresponding triazolinediones 2a-f using potassium permanganate and alumina-supported potassium permanganate under solvent-free conditions. Initially the oxidation of 4-phenylurazole 1a with potassium permanganate (1 mmole) under solvent-free conditions without alumina was carried out. It was found that the duration of the oxidation is more and resulted in less yield (Table 1). Then, the reaction was carried out in the presence of alumina as a supporting agent. It resulted in the reaction to proceed in a shorter time with better yield. The process involves a simple mixing of potassium permanganate and potassium permanganate supported on alumina and urazoles 1a-f in a mortar and grinding the mixture for the time specified in Table 1 at room temperature. The yields of triazolinediones 2a-f are good to high and the reaction periods are exceedingly short (Scheme I and Table 1).

In conclusion, it is important to note that this simple and easy method under solid-state conditions, affords triazolinediones from urazoles in a shorter reaction period with potassium permanganate and alumina-supported potassium permanganate. Moreover,
the oxidation of urazoles takes place at room temperature and in the absence of solvent.

**Experimental Section**

Urazoles 1 were synthesized according to reported procedures. Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR, UV, 1H NMR) and physical data with the authentic samples. All 1H NMR spectra were recorded at 90 MHz in CDCl₃. All IR spectra were recorded on a Shimadzu 435 IR spectrometer. All reactions were carried out under solvent-free conditions.

**Typical procedure for the oxidation of urazoles 1 to triazolinediones 2 using potassium permanganate under solvent-free condition:** A mixture of 4-phenylurazole (1a 1 mmole, 0.177 g) and KMnO₄ (1 mmole, 0.16 g) in a mortar was ground with a pestle for the time specified in Table 1 until a deep-red colour appeared. When TLC showed complete disappearance of starting material, which required 8 min (Table 1). Dichloromethane (10 mL) was added to the reaction mixture and after vigorous stirring the mixture was filtered and the solvent evaporated. 4-Phenyltriazolinedione 2a was obtained in 90% yield (0.16 g). m.p. 170-75°C (dec.) [Lit. m.p. 170-78°C].

**Acknowledgement**

We are thankful to the Isfahan University of Technology Research Council for the partial support of this work.

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