

SYNLETT Spotlight 169

Triazolinediones (TADs)

Compiled by Gholamabbas Chehardoli



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

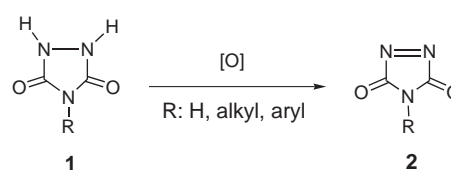
Gholamabbas Chehardoli was born in Malayer/Jokar, Iran, in 1973. He received his B.Sc. in chemistry from Bu-Ali Sina University, Hamadan, Iran in 1999, and his M.Sc. in organic chemistry from the same university. He is currently in the final stage of his PhD studies under the supervision of Professor Mohammad Ali Zolfigol. His research interests focus on the synthesis of new hydrogen peroxide adducts and their application in organic reactions. The purpose of this research is according to green chemistry.

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Introduction

4-Substituted-1,2,4-triazoline-3,5-diones (TADs, **2**) were first synthesized by Thiele in 1894.¹ These compounds were prepared via oxidation of urazoles (**1**, Scheme 1).² Urazoles and their oxidation products (TADs) are commercially available.³ Recently, several heterogeneous systems have been reported for the oxidation of urazoles to their corresponding triazolinediones.⁴ Triazolinediones are red or pink crystalline solids which are very reactive

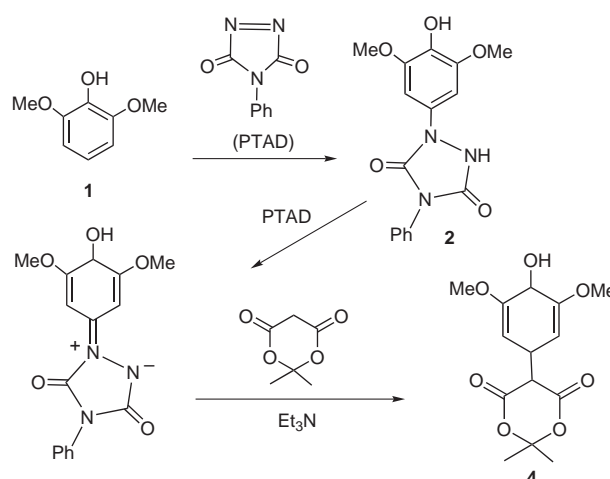
and able to participate in a wide range of reactions such as [2+2] and [4+2] cycloadditions, ene reactions, and electrophilic aromatic substitutions, etc.⁵⁻⁷



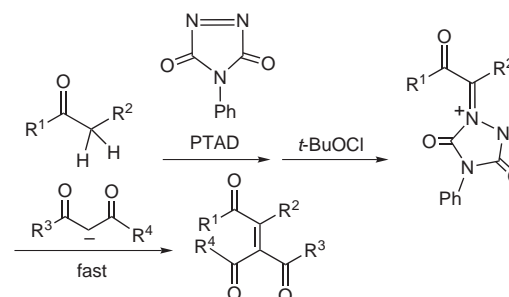
Scheme 1

Abstracts

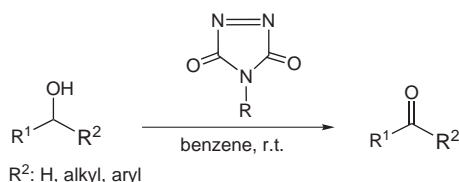
(A) Reaction of 2,6-dimethoxyphenol (**1**) with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) produces the arylated urazole **2** which can be oxidized to the stable dienone ylide **3** upon treatment with either *tert*-butyl hypochlorite or excess PTAD. When ylide **3** is formed in situ and treated with Meldrum's acid and triethylamine, the orange *p*-quinone methide **4** is obtained.⁸



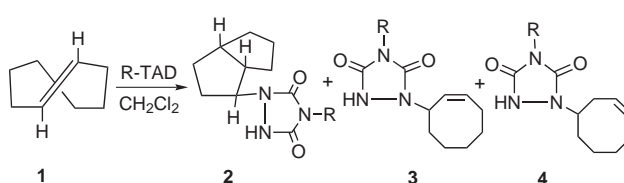
(B) Triazolinediones react with ketones and after oxidation give triazolinedione ylides. The resulting ylides, usually generated in situ, undergo condensations with enolate species to form acylated olefins in synthetically useful yields. The tri- and tetraacylolefins produced by this method are susceptible to subsequent Michael addition of enolates.⁹



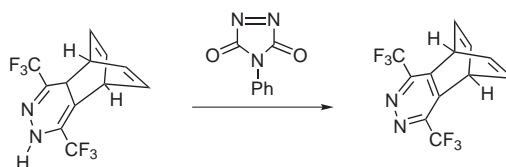
(C) PTAD oxidizes alcohols to aldehydes or ketones at room temperature in a few hours with high yields. Dry benzene is a convenient solvent, from which the phenylurazole separates during the reaction.¹⁰



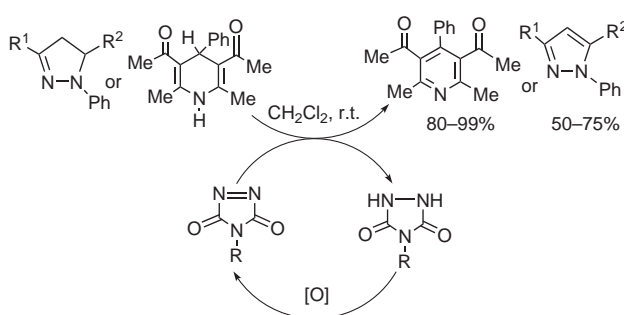
(D) 4-Substituted-1,2,4-triazoline-3,5-diones ($R = \text{Me}$ or Ph) react stereospecifically with *trans*-cyclooctene **1** to give addition products **2**, **3**, and **4**.¹¹



(E) Dehydrogenation of various annulated dihydropyridazines occurred with 4-phenyl-1,2,4-triazoline-3,5-dione as dehydrogenating agent.¹²



(F) 4-Substituted-1,2,4-triazoline-3,5-diones were used as effective and recyclable oxidizing agents for the oxidation of both 1,4-dihydropyridines¹³ and 1,3,5-trisubstituted-pyrazolines¹⁴ to their corresponding pyridines and pyrazoles, respectively under mild conditions with moderate to excellent yields. Simple oxidation procedures of urazoles regenerate TADs.^{13,14}



References

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