

# The reaction of (*N*-isocyanimino)triphenylphosphorane with dialkyl acetylenedicarboxylates in the presence of 1,3-diphenyl-1,3-propanedione: a novel three-component reaction for the stereoselective synthesis of dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates

Ali Souldozi,<sup>a</sup> Ali Ramazani,<sup>a,\*</sup> Nouri Bouslimani<sup>b</sup> and Richard Welter<sup>b</sup>

<sup>a</sup>Department of Chemistry, The University of Zanjan, PO Box 45195-313, Zanjan, Iran

<sup>b</sup>Laboratoire DECOMET, ILB, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France

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**Abstract**—Reactions of dialkyl acetylenedicarboxylates with (*N*-isocyanimino)triphenylphosphorane in the presence of 1,3-diphenyl-1,3-propanedione proceed smoothly at room temperature to afford dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates in high yields. The stereochemistry of the final products were confirmed by single crystal X-ray structure determination. The reaction is completely stereoselective.

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## 1. Introduction

Compounds containing the oxadiazepine skeleton<sup>1–5</sup> have attracted interest in bio-organic, natural products and medicinal chemistry. They are an important class of heterocyclic compounds that have pharmaceutical and biological activities including antimicrobial, anti-fungal, and anticancer.<sup>1–4</sup>

For several years acetylenic esters have attracted the attention of organic chemists and are reactive systems that can take part in many chemical syntheses,<sup>6</sup> for example, as Michael acceptors.<sup>7</sup> In recent years, there has been increasing interest on the applications of acetylenic esters in the multi-component<sup>8–11</sup> synthesis. Due to the atom economy, convergent character and simplicity of one-pot procedures, multi-component condensation reactions (MCRs) have an advantageous position among other reactions. The development of novel

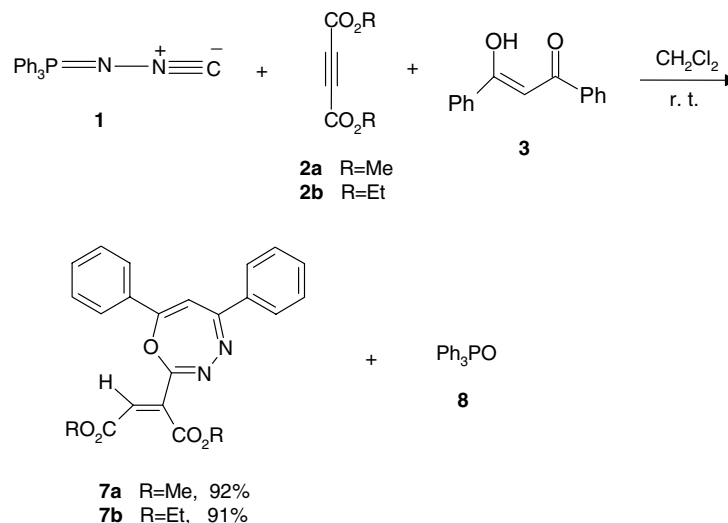
MCRs is receiving growing interest from industrial chemistry research groups and represents a challenge for organic chemists.<sup>12,13</sup>

A few methods have been reported in the literature for the synthesis of oxadiazepine heterocycles which are multi-step in nature.<sup>14,15</sup> Based on our literature survey, reports on the synthesis of 1,3,4-oxadiazepine heterocycles are rare.<sup>14,15</sup>

In recent years, several synthetic methods have been reported for the preparation of (*N*-isocyanimino)triphenylphosphorane (CNNPPh<sub>3</sub>) **1** (Scheme 1), there are several reports on the use of **1** in the synthesis of metal complexes.<sup>16,17</sup> However, application of **1** in the synthesis of organic compounds is rare.<sup>18,19</sup> As part of our ongoing program to develop efficient and robust methods for the preparation of heterocyclic compounds,<sup>20–22</sup> we sought to develop a convenient preparation of dialkyl 2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates **7**. Herein we report a hitherto unknown, one-pot three-component reaction, which, starting from readily available dialkyl acetylenedicarboxylates **2** affords dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates **7**.

**Keywords:** Acetylenic ester; (*N*-Isocyanimino)triphenylphosphorane; 1,3-Diphenyl-1,3-propanedione; 1,3,4-Oxadiazepine; Aza-Wittig reaction.

\* Corresponding author. Tel.: +98 241 5152572; fax: +98 241 5283100; e-mail: [aliramazani@yahoo.com](mailto:aliramazani@yahoo.com)



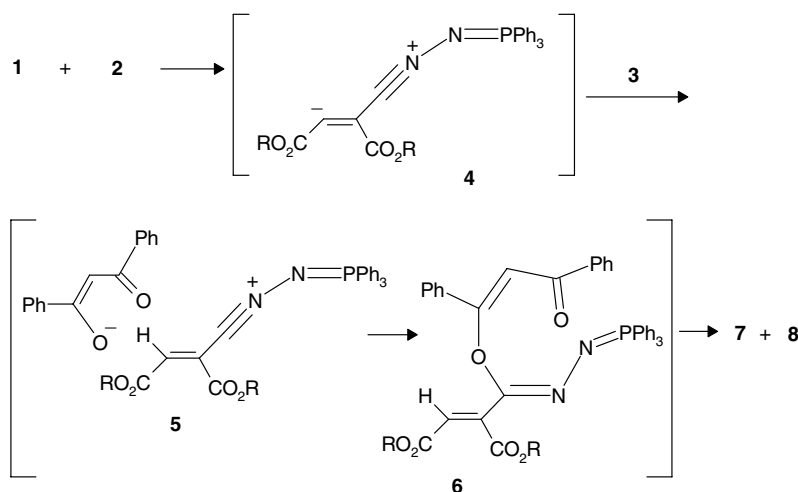
Scheme 1.

(*N*-Isocyanimino)triphenylphosphorane **1**, dialkyl acetylenedicarboxylates **2**, and 1,3-diphenyl-1,3-propanedione **3** were reacted in a 1:1:1 ratio in dichloromethane at room temperature to give dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates **7** and triphenylphosphine oxide **8** (Scheme 1). The reaction proceeded smoothly and cleanly under mild conditions and no side reactions were observed. The mechanism of the three-component reaction between **1**, **2**, and **3** has not been established experimentally, however, a possible explanation is proposed in Scheme 2. On the basis of the well established chemistry of isocyanides,<sup>6,23</sup> it is reasonable to assume that compound **7** could result from the initial addition of **1** to acetylenic ester **2** followed by protonation of 1:1 adduct **4** by 1,3-diphenyl-1,3-propanedione **3**. Subsequent attack of the enolate anion on the positively charged ion **5** forms iminophosphorane **6**, which undergoes an intramolecular aza-Wittig<sup>24</sup> reaction under the conditions employed, to produce dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates **7** and triphenylphosphine oxide **8** (Scheme 2). Based on TLC monitoring of the reaction

and NMR analyses of the products, only *Z* stereoisomers (**7a** and **7b**) were observed.

The structures of products **7a–b** were deduced from their IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* values. The <sup>1</sup>H NMR spectrum of **7b** consisted of two triplets for the methyl groups (OCH<sub>2</sub>CH<sub>3</sub>, δ = 1.25 and 1.36 ppm), two quartets for the methylene groups (OCH<sub>2</sub>CH<sub>3</sub>, δ = 4.17 and 4.37 ppm), two singlets for the oxadiazepine ring and vinylic protons, δ = 6.56 and 6.58 ppm and a multiplet for the aromatic ring (δ = 7.44–7.80 ppm). The <sup>1</sup>H decoupled <sup>13</sup>C NMR spectrum of **7b** showed 20 distinct resonances, partial assignment of these resonances is given in Section 2. Finally, the structure of **7b** was confirmed unambiguously by single crystal X-ray analysis (Fig. 1).

We believe that the reported method offers a mild, simple and efficient route for the preparation of dialkyl (*Z*)-2-(5,7-diphenyl-1,3,4-oxadiazepin-2-yl)-2-butenedioates



Scheme 2.

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