

**NOTE****One-Pot Stereoselective Synthesis of Dimethyl-(Z)-2-(ethanimidoysulfanyl)-2-butenedioate from Dimethyl Acetylenedicarboxylate and Thioacetamide**

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Thioacetamide reacts with dimethyl acetylenedicarboxylate in acetone to form dimethyl-(Z)-2-(ethanimidoysulfanyl)-2-butenedioate. Dipotassium hydrogen phosphate powder was found to catalyze the reaction in solvent-free conditions at 90°C in 1 h.

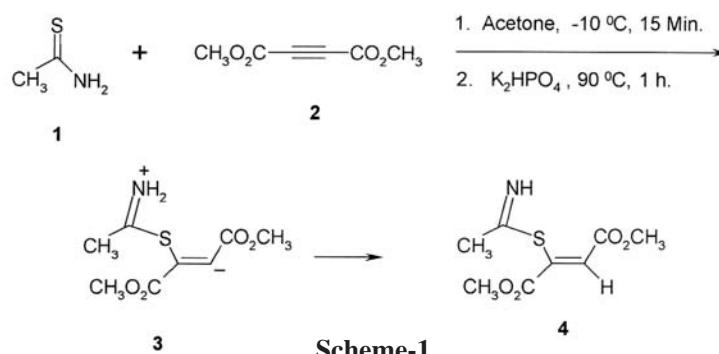
**Key Words:** Acetylenic ester, Michael addition, Dipotassium hydrogen phosphate, Solvent-free conditions, Catalyst.

Organosulfur chemistry has provided organic chemists with a wealth of reactions, many of which have found general application in organic synthesis<sup>1-3</sup>. Organosulfur compounds are important heterocycles in bio-organic chemistry and are present in many pharmaceuticals<sup>4-6</sup>. Many studies on the synthesis of the organosulfur compounds are available in literature<sup>1-10</sup>. Dimethyl acetylenedicarboxylate (**2**) is reactive system, which take part in many chemical reactions<sup>10-13</sup>. These results promoted us to examine the one-pot reaction of dimethyl acetylenedicarboxylate (**2**) with thioacetamide (**1**) (**Scheme-1**) in the presence of dipotassium hydrogen phosphate powder in solvent-free conditions.

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively.

**Preparation of dimethyl (Z)-2-(ethanimidoysulfanyl)-2-butenedioate (4):** To a magnetically stirred solution of thioacetamide (**1**) (0.075 g, 1 mmol) in acetone (3 mL) was added adropwise a mixture of dimethyl acetylenedicarboxylate (**2**) (1 mmol) in acetone (2 mL) at 10°C over 15 min. The mixture was then stirred at 10°C for 15 min. The mixture was allowed to warm up to room temperature. Thermally activated dry dipotassium hydrogen phosphate powder (2 g) was added and the solvent was evaporated. Dipotassium hydrogen phosphate powder and the residue were heated at 90°C for 1 h. (**Scheme-1**) and then placed over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether as eluent. The solvent was removed under reduced pressure and product **4** was obtained as light yellow crystals.

The compound **4** may result from initial addition of thioacetamide **1** to the acetylenic ester **2** and concomitant protontransfer of the 1:1 adduct **3**. Dipotassium hydrogen phosphate powder was found to catalyze the reaction in solvent-free conditions at 90°C in 1 h. (**Scheme-1**), in fairly high conversion. In the absence of dipotassium hydrogen phosphate powder, the reaction was completed in acetone in 12 h<sup>10</sup>. Dipotassium hydrogen phosphate powder may be to have efficient roll in the protontransfer step of the reaction (**Scheme-1**).



In summary, a new and high efficient, one-pot stereoselective method for preparing of compound **4** in the presence of dipotassium hydrogen phosphate powder in solvent-free conditions is developed (**Scheme-1**). Other aspects of this process are under investigation.

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