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NOTE

One-Pot Stereoselective Synthesis of Dimethyl-(*Z*)-2-(ethanimidoylsulfanyl)-2-butenedioate from Dimethyl Acetylendicarboxylate and Thioacetamide in Presence of Zinc Oxide Powder

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Thioacetamide reacts with dimethyl acetylenedicarboxylate in presence of acetone to form dimethyl (*Z*)-2-(ethanimidoylsulfanyl)-2-butenedioate. Zinc oxide powder was found to catalyze the reaction in solvent-free conditions at 90ºC in 1 h.

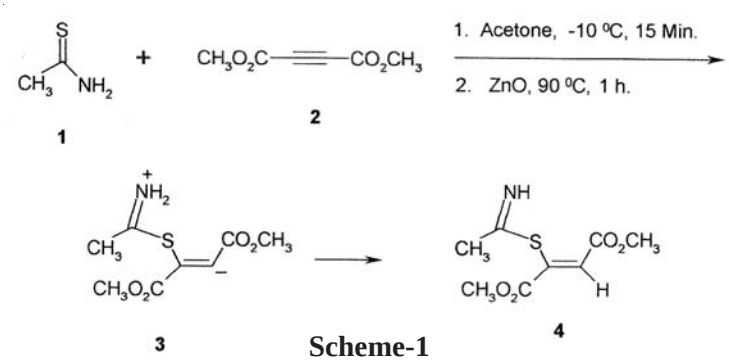
Key Words: Acetylenic ester, Michael addition, Zinc oxide, Catalyst, Solvent-free conditions.

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

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

Preparation of dimethyl-(*Z*)-2-(ethanimidoylsulfanyl)-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 10ºC over 15 min. The mixture was then stirred at 10ºC for 15 min. The mixture was allowed to warm up to room temperature. Thermally activated dry zinc oxide powder (2 g) was added and the solvent was evaporated. Zinc oxide powder and the residue were heated at 90ºC 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 proton transfer of the 1:1 adduct **3**. Zinc oxide powder was found to catalyze the reaction in solvent-free conditions at 90ºC in 1 h. (**Scheme-1**), in fairly high conversion. In the absence of zinc oxide powder, the reaction was completed in acetone in 12 h[10]. Zinc oxide powder may have efficient roll in the proton transfer step of the reaction (**Scheme-1**).



Scheme-1

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

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