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NOTE

Synthesis of Dimethyl (*Z*)-2-(Ethanimidoylsulfanyl)-2-butenedioate from Dimethyl Acetylendicarboxylate and Thioacetamide

HAMID ARJMANDFAR, NAFISEH NAMJOU and ALI RAMAZANI*
Department of Chemistry, University of Zanjan, P.O.Box 45195-313, Zanjan, Iran
E-mail: aliramazani@gmail.com

Thioacetamide reacts with dimethyl acetylenedicarbo-xylate in acetone to form dimethyl (*Z*)-2-(ethanimidoyl-sulfanyl)-2-butenedioate. Sodium hydrogen carbonate powder was found to catalyze the reaction in solvent-free conditions at 90ºC in 1 h.

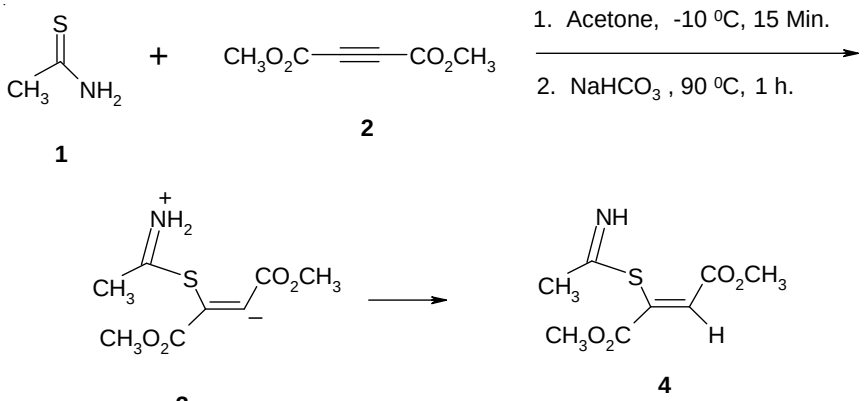
Key Words: Acetylenic ester, Michael addition, Thioacetamide, Sodium hydrogen carbonate, Solvent-free conditions.

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

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-rapid analyzer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively. Mass spectra were recorded on a Finnigan-matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

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 dropwise 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 and allowed to warm

up to room temperature. Thermally activated dry sodium hydrogen carbonate powder (2 g) was added and the solvent was evaporated. Dry sodium hydrogen carbonate powder and the residue were heated at 90ºC for 1 h and then placed over a column of silica gel (10 g) (**Scheme-1**). 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. m.p. 148-149ºC (dec.), IR (KBr (ν_{max}, cm^{-1}): 3173; 3065; 1703, 1611. ^1H NMR ($CDCl_3$) δ_H : 1.97 (3H, s, CH_3); 3.26 and 3.83 (6H, 2 s, 2 OCH_3); 6.79 (1H, s, =CH); 8.29 (1H, s, =NH). ^{13}C NMR ($CDCl_3$) δ_C : 30.66 (CH_3), 51.10 and 52.61 (2 OCH_3), 97.46 (=CH), 113.72 (C=NH), 147.58 (=CS), 166.59 and 167.63 (2 C=O). MS (m/z, %): 218 (MH^+,7); 217 (M^+, 42); 186 (47); 144 (49); 116 (86); 85 (90); 74 (100), 42 (100). Analysis: Calc. for $C_8H_{11}NO_4S$ (217.25): C, 44.23; H, 5.10; N, 6.45%. Found: C, 44.20; H, 5.10; N, 6.50%.



Scheme-1

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**). Sodium hydrogen carbonate 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 sodium hydrogen carbonate powder, the reaction was completed in acetone[10] in 12 h. Sodium hydrogen carbonate powder may be to have efficient roll in the protontransfer step of the reaction (**Scheme-1**).

Conclusion

A new and high efficient, one-pot stereoselective method for preparing of compound **4** in the presence of sodium hydrogen carbonate powder in solvent-free conditions has been developed. Other aspects of this process are under investigation.

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