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Microwave-assisted solvent-free synthesis of Thiocarbamic acid [(thiophene-2-yl) ethylidene]hydrazide

Azadeh Tadjarodi [1,*], Saeedeh Eslami Nezhad[1]

1 Chemistry Faculty, Iran University of Science and Technology, Narmak, Tehran, Iran
E-mail: tajarodi@iust.ac.ir

Abstract: A fast and efficient method has been developed for the synthesis of Thiocarbamic acid [(thiophene-2-yl) ethylidene]hydrazide, [TTEH], under microwave irradiation.
This compound has been characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR.

Keywords: thiosemicarbazide; microwave; 2-acetylthiophene; solvent free.

Introduction

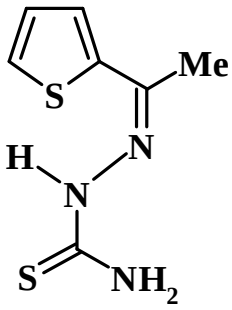
Thiosemicarbanzones have received considerable attention because of their pharmacological activities. They have numerous biological activities, e.g. anticarcinogenic, antibacterial, anti-HIV, anticancer, fungicides, antiviral, antifungal, antitumour, etc[1]. Lima and co-workers have been reported the synthesis of title compound by the direct reaction 2-acetylthiophene and thiosemicarbazide in boiling ethanol for 24 h[2]. We now to report the synthesis of Thiocarbamic acid [(thiophene-2-yl) ethylidene]hydrazide, [TTEH], through the reaction of 2-acetylthiophene and thiosemicarbazide in the presence of silica gel under solvent-free conditions using microwave irradiation. Solvent-free microwave irradiation is well known as environmentally benign method, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures[3,4]. Microwave irradiation presents a powerful tool toward organic reactions. This investigation showed that the used method and the results when compared with conventional processes were found to be inexpensive, more friendly and high yielding.

Results and Discussion

The structure of title compound has been assigned by spectroscopic data. In the IR spectrum, the absorption bands at 3236 and 3145 cm^{-1}, which may be assigned to $-NH_2$ and –NH group, respectively. The band ν(C=N) appeared at 1587 cm^{-1}. The stretching vibration at

1371 cm^{-1} are attributed to ν(CH) vibrations of CH_3 group. Also, ν(C=S) stretching frequency is observed in 1101 cm^{-1}.

The ^{1}H NMR spectrum displayed two signals at δ 6.94 and 7.01 *ppm* for the NH_2 group. The observed singlet peaks at δ = 2.3 and 9.04 *ppm* are assigned to methyl and hydrazide NH groups, respectively. There are seven signals in ^{13}CNMR spectrum. The peak at δ = 14.09 *ppm* could be assigned to the methyl group. The resonance at 178.61 *ppm* is related to C=S. Based on the presented ^{1}HNMR**,** ^{13}CNMR and FT-IR spectroscopy for this compound, structure can be proposed as shown in scheme 1.



Scheme 1. The structure of *[TTEH]*

Experimental Section

A mixture of 2-acetylthiophene (0.017 mol, 1.9 ml) and thiosemicarbazide (0.017 mol, 1.5 g) and 3g silica gel was mixed in mortar to provided a dark yellow soft powder, and then irradiated at 100W for 2 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, a solid product was washed with acetone and after the concentration of the solution, the yellow precipitate was obtained and washed with cold EtOH dried and purified by recrystallizaton from acetone. mp. 150-152 °C.

IR (KBr, *cm*$^{-1}$): 3236(m), 3145(m), 1587(s), 1502(s), 1371(m), 1294(m), 1101(m), 835(m).

^{1}HNMR (CD_3OD, *ppm*) δH: 2.3 (s, 3H, CH_3), 6.94 -7.01 (t, 2H, NH_2), 7.28-7.32 (m, 3H, C_4H_3 ring), 9.04 (s, 1H, NH).

^{13}CNMR (CD_3OD, *ppm*) δC: 14.09 (CH_3), 127.47, 127.68, 128.43, 142.26 (C_4H_3 ring), 144.18 (C=N), 178.61 (C=S).

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References

1. Sulekh Chandra; Anil Kumar. *Spectrochimica Aceta Part A*, **2007**, 68, 1410.
2. Lima de, G.M; Neto, J.L; Beraldo, H; Siebald, H. G. L; Duncalf, D.J. *Journal of Molecular Structure*, **2002**, 604, 287.
3. Zhang, X-H,; Wang, L-Y,; Zh-X,; Tan, Sh-H,; Zhang, Z-X. *dyes and pigments* , **2008**, 79, 205.
4. Loupy A. Microwaves in organic synthesis. Weinheim: *Wiley-VCH*; **2002**.