Russian Journal of Organic Chemistry, Vol. 38, No. 4, 2002, pp. 591–592. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 4, 2002, pp. 617–619.

Reactions of Tri(1-propenyl)amine with Elemental Sulfur

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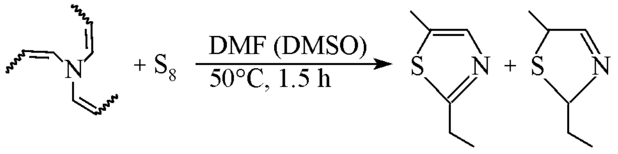
Received May 11, 2001

Abstract—The reaction of tri(1-propenyl)amine with elemental sulfur in bipolar aprotic solvent (DMF, DMSO) at 50°C within 1.5 h furnished 5-methyl-2-ethylthiazole in 62% yield. 2*H*,5*H*-5-methyl-2-ethylthiazole, 2-hydroxy-5-methylbenzaldehyde were found among the side products. The formation paths of the compounds obtained are suggested.

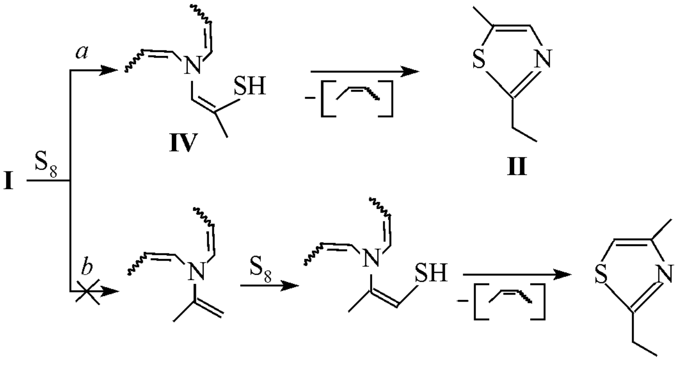
Reactions of aliphatic enamines with sulfur in DMF at room temperature result in thioamides [1–3], and substituted thiophenes arise at heating [4].

It was found that a reaction of tri(1-propenyl)amine (**I**) with elemental sulfur in DMF at 50°C within 1.5 h afforded 5-methyl-2-ethylthiazole (**II**) 2*H*,5*H*-5-methyl-2-ethylthiazole (**III**) in an overall yield of 65%.



I **II** **III**

The reaction at room temperature takes the same direction, but is considerably decelerated: complete conversion of compound I is attained in 10 h. Similar results were obtained at replacing DMF by DMSO. Triallylamine did not react with elemental sulfur under the above conditions. Also, the elemental selenium was not involved in the reaction with compound **I** in DMF. Taking into account that reaction of sulfur with enamines occurs when a hydrogen atom is present in β-position of the latter and that thioenols arise at the initial stage [4], it is reasonable to assume that *N*-2-mercapto-1-propenyl-di(propenyl)amine (*IV*) forms in the reaction in question that compound **II** (path *a*) furnishes through cyclization-elimination. According to published data [2, 4] the reaction of elemental sulfur with enamines in DMF occurs with isomerization of the initial enamine. Compound **I** in reaction with sulfur in DMF does not undergo isomerization: this process should inevitably result in formation of 4-methyl-2-ethyl-1,3-thiazole (**V**) (path *b*).



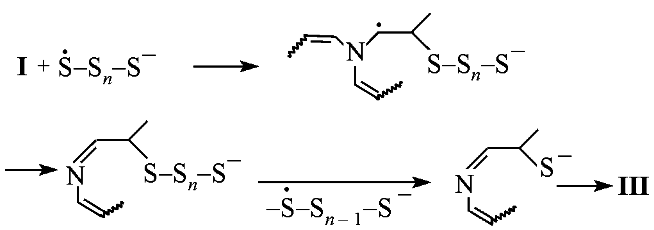
In the ^{1}H NMR spectrum of the synthesized substituted thiazole appears a signal from fragment =CHN (7.26 ppm, q) corresponding to compound **II** and is not observed a signal from group =CH–S of compound **V** that should be present at ~6.69 ppm.

Since in the absence of a solvent the reaction between compound **I** and elemental sulfur does not occur it should be assumed that sulfur is activated by bipolar aprotic solvent to form zwitter-ions **VI** and ion-radicals **VII**. Just these species take part in the observed chemical processes.

$$\begin{array}{ll} S_8 + \bar{S}\text{–}S_n\text{–}S\text{–}\overset{+}{X} + [S\text{–}\bar{S}_{n-1}\text{–}\dot{S} + \dot{S}\text{–}\overset{+}{X}] & \\ \quad\;\; \rightleftharpoons & \qquad\qquad\quad \mathbf{VII} \\ {}^{-}S\text{–}S_n\text{–}\overset{+}{S} + X & \\ \quad\; \mathbf{VI} & \end{array}$$

X = DMSO, DMF.

In reaction of compound **I** with elemental sulfur carried out in the presence of hydroquinone the content of compound **II** in the reaction mixture decreased by 22%, and compound **III** was not detected by GC-MS method. In keeping with this fact the formation of compound **III** may be presented as follows.



According to ^{1}H NMR data compound **III** is an equilibrium mixture of *erythro*- and *threo*-isomers.

The GLC and GC-MS analysis of the reaction mixture revealed the presence of compound **VIII** with *m/z* 136 in 11–13% content. From ^{1}H NMR spectrum [5] the structure of compound **VIII** was deduced as 2-hydroxy-5-methylbenzaldehyde. It was shown experimentally that the yield of this compound is not affected by carrying out the reaction in the presence of hydroquinone.

EXPERIMENTAL

GLC analysis of reaction mixtures was performed on Chrom-5 instrument, column 1000 × 4 mm, stationary phase 10% SE-30 on Chromaton N-AW-DMCS. Compounds obtained were isolated for identification by preparative chromatography on device PAKhV-0.7, column 1000 × 6 mm, stationary phase the same as for analysis. Mass spectra were measured on GC-MS instrument LKB-2091. ^{1}H and ^{13}C NMR spectra were recorded on spectrometer Bruker DPX-400 at 400.13 and 100.62 MHz respectively. As solvent was used $CDCl_3$, as internal reference HMDS.

Reaction of tri(1-propenyl)amine with sulfur. (a) A mixture of 1.6 g (0.01 mol) of compound **I**, 0.6 g (0.02 mol) of sulfur, and 25 ml of DMF was heated to 50°C for 1.5 h. Then the reaction mixture was diluted with water, the reaction products were extracted into ether, the extracts were washed with water, dried on $CaCl_2$, and subjected to fractional distillation. We obtained 1.1 g of a mixture containing according to GLC data 82% of compound **II** and 12% of compound **VIII**. GC-MS analysis demonstrated that the peak corresponding to compound **II** included also ~8% of compound **III**. The yields of compounds obtained are as follows: **II**, 56%; **III**, 5%; **VIII**, 8%; unidentified compounds, 6.4%.

^{1}H NMR spectrum of compound **II**, δ, ppm: 1.34 t (3H, CH_3CH_2), 2.40 d (3H, CH_3CS), 2.94 q (2H, CH_2CS), 7.26 q (1H, HC=). ^{13} NMR spectrum of compound **II**, δ, ppm: 11.98 ($CH_3C=$), 14.18 (CH_3CH_2), 26.95 (CH_3CH_2), 132.55 ($CH_3C=$), 139.70 (HC=C), 171.34 (C=N). Mass spectrum of compound **II**, *m/z*: 127.

^{1}H NMR spectrum of compound **III**, δ, ppm, *J* Hz: 0.99, 1.05 t (3H, CH_3CH_2, ^3J 7.4), 1.44, 1.46 d.d (3H, CH_3CH, ^3J 7.29), 1.75, 1.99 d.q (2H, CH_3CH_2, ^3J 7.4), 4.36 q.t (1H, $CHCH_3$, ^3J 7.3, $^4J_{HCSCH}$ 1.5); 4.35 q.d.d (1H, $CHCH_3$, ^3J 7.3, $^4J_{HCSCH}$ 0.9), 5.64 m (1H, CHC_2H_5), 7.23, 7.20 d.d. (1H, CH=N, $^4J_{CH=NCH}$ 2.5). ^{13} NMR spectrum of compound **III**, δ, ppm: 10.68, 10.54 (CH_3CH_2), 21.42, 20.82 (CH_3CH), 32.28, 31.56 (CH_2), 54.45, 54.14 ($CHCH_3$), 86.16, 85.46 ($CHCH_2CH_3$), 164.45, 164.37 (CH=N). Mass spectrum of compound **III**, *m/z*: 129.

(b) A reaction of a mixture of 1.6 g (0.01 mol) of compound **I**, 0.8 g (0.02 mol) of sulfur, and 25 ml of DMF was carried out for 10 h at room temperature. After standard workup we obtained 1 g of mixture containing according to GLC data 79% of compound **II** and 13% of compound **VIII**. GC-MS analysis demonstrated that the peak corresponding to compound **II** included also ~5% of compound **III**. The yields of compounds obtained are as follows: **II**, 63%; **III**, 3%; **VIII**, 8%; unidentified compounds, 8%.

(c) To a mixture of 0.7 g (0.005 mol) of compound **I**, 0.2 g (0.006 mol) of sulfur, and 25 ml of DMF was 10 wt% of hydroquinone (calculated on the weight of the reaction mixture). The reaction mixture was heated to 50°C for 1.5 h and subjected to usual workup. We isolated 0.49 g of mixture containing according to GLC data 13% of compound **I**, 60% of compound **II**, and 11% of compound **VIII**. GC-MS analysis demonstrated the absence of compound **III**. The yields of compounds obtained are as follows: **II**, 49%; **VIII**, 9%; unidentified compounds, 16%.

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