Chemistry of Heterocyclic Compounds, Vol. 45, No. 4, 2009

LETTERS TO THE EDITOR

SYNTHESIS OF 3-BENZYL-5-(4-NITROPHENYL)-THIAZOLE-2(3H)-THIONE FROM 4-NITROPHENYL-OXIRANE, BENZYLAMINE, AND CARBON DISULFIDE

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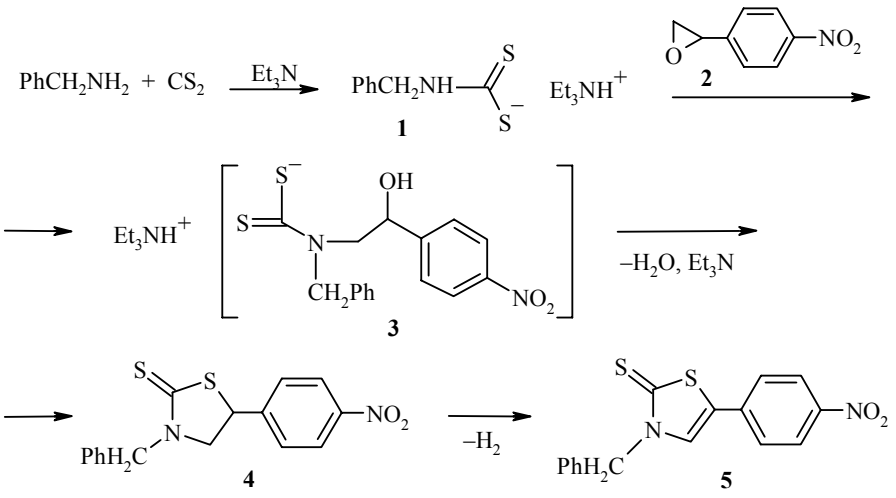
Keywords: benzylamine, 3-benzyl-5-(4-nitrophenyl)thiazole-2(3H)-thione, 4-nitrophenyloxirane, carbon disulfide.

Dithiocarbamates obtained by the reaction of carbon disulfide with amines are commonly used for the synthesis of sulfur heterocycles, in particular, thiazolidines [1, 2]. Accordingly, we have synthesized triethylammonium benzyldithiocarbamate (**1**), which was used without isolation for opening of the oxirane ring in 4-nitrophenyloxirane (**2**). This reaction was carried out in ethanol with equimolar amounts of the reagents.



We unexpectedly found that the reaction of the product, triethylammonium benzyldithiocarbamate **1** with *p*-nitrophenyloxirane **2** at about 45°C in ethanol is accompanied not only by cyclization to give thiazolidinethione **4**, by its subsequent aromatization to give thiazolinethione **5**.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 631-632, April, 2009. Original article submitted November 5, 2008.

This reaction probably proceeds through the intermediate formation of dithiocarbamate **1**, the nucleophilic opening of oxirane by **2** to give an intermediate dithiocarbamate derivative, namely, aminoethanol **3**, the spontaneous cyclization of **3** to give thiazolidine **4**, and, finally, oxidative aromatization to give 3-benzyl-5-(4-nitrophenyl)thiazole-2(3H)-thione (**5**), which is a bright-yellow crystalline compound.

Elderfield [1] has described the formation of thiazolidinethiones from monoethanolamine derivatives and carbon disulfide. However, oxiranes have not been used for the synthesis of thiazolidinethiones. An interesting finding is the oxidative aromatization of intermediate thiazolidinethione **4** to give thiazolinethione **5**. This latter process can probably be attributed to the nitro group in the starting compound. The Skraup quinoline synthesis is an analogous process, in which nitrobenzene is the oxidizing agent of the dihydro derivative formed [3, 4].

In order to confirm the participation of the nitro group in the dehydrogenation of thiazolidinethione **4** to give thiazolinethione **5**, we carried out the analogous reaction, in which a twofold excess of nitrobenzene was added in the final step. The product of the reduction of nitrobenzene, namely, aniline, was detected in the reaction mixture by gas-liquid chromatography. The yield of thiazolinethione **5** in this case was increased almost to 50%.

The IR spectrum was taken on an Avatar-320 spectrometer. The ^{1}H NMR spectrum was taken on a Bruker DRX500 spectrometer at 500 MHz in DMSO-d_6 with TMS as the internal standard, while the ^{13}C NMR spectrum was taken on a Bruker AM300 spectrometer at 75 MHz in DMSO-d_6. The electron impact mass spectrum was taken on a Finnigan MAT Incos 50 mass spectrometer with direct inlet of the sample into the ion source at 70 eV. The gas-liquid chromatography was carried out on a Kristall 5000.1 chromatograph with a flame ionization detector at 200-250°C using a 30 m×0.25 mm Zebron-50 column with 50% phenyl polysiloxane, 50% dimethyl polysiloxane as the stationary phase, and helium as the gas carrier.

3-Benzyl-5-(4-nitrophenyl)thiazole-2(3H)-thione (5). A solution of carbon disulfide (0.76 g, 0.01 mol) in ethanol (10 ml) was added with stirring to a solution of benzylamine (1.07 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in ethanol (15 ml) cooled to 0-5°C and stirred for about 2 h. Then, *p*-nitrophenyloxirane (1.65 g, 0.01 mol) was added, starting at room temperature and gradually warming to 45°C. The solvent was distilled off after 5 h and the oily, dark-yellow residue was crystallized by adding hexane. Two recrystallizations gave 0.95 g (29%) thione **5** as bright-yellow needles, mp 211-212°C (ethanol). IR spectrum (KBr), ν, cm^{-1}: 1530 (–C=S), 1515, 1345 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.42 (2H, s, CH_2); 7.38 (5H, m, Ar–H); 7.76 (2H, d, *J* = 8.9, 2CH–Ar); 8.27 (2H, d, *J* = 8.9, 2CH–ArNO_2); 8.55 (1H, s, N–CH). ^{13}C NMR spectrum, δ, ppm: 52.05 (CH_2); 123.71 (1C, N–CH); 124.46 (2C-3, Ar–NO_2); 125.86 (2C-2, 1C-4 Ar); 127.91, 128.00 (2C-2 Ar–NO_2); 128.68 (2C-3 Ar); 132.09 (S–C); 135.31 (1C-1 Ar); 135.65 (1C-1 Ar–NO_2); 146.42 (1C-4 Ar–NO_2); 186.11 (N–C=S). Mass spectrum, *m/z* (I_{rel}, %): 328 $[M]^+$ (45), 295 (28), 91 (100), 65 (37). Found, %: C 58.91; H 4.07; N 8.24. $C_{16}H_{12}N_2O_2S_2$. Calculated, %: C 58.52; H 3.68; N 8.53.

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