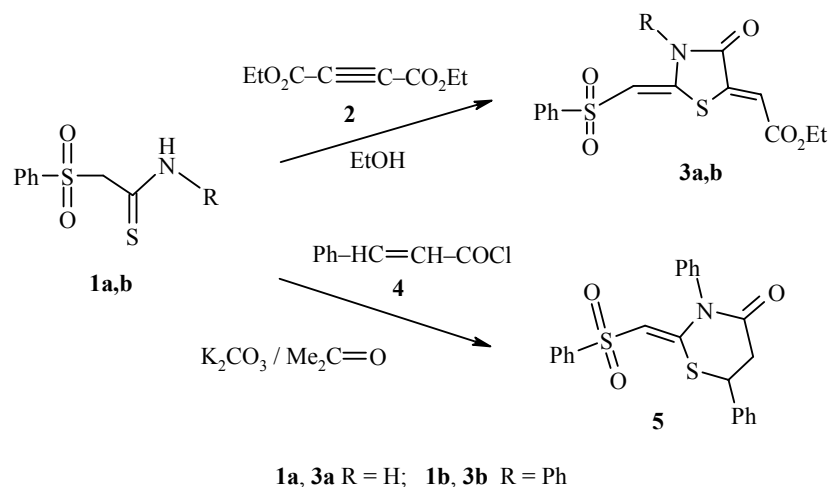


CYCLOACYLATION OF PHENYLSULFONYL-N-R-THIOACETAMIDES BY COMPOUNDS CONTAINING AN ACTIVATED MULTIPLE BOND

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In continuing studies of the reactions of thioamides with compounds containing an activated multiple bond [1], we have established that phenylsulfonyl-N-R-thioacetamides **1a,b** react with acetylenedicarboxylic ester, forming one of the two possible ([3+2] and [3+3]) cyclocondensation products [2]: ethyl 4-oxo-2-phenylsulfonylmethylidene-3-R-1,3-thiazolidine-5-methylidenecarboxylates **3a,b**. When thioacetamide **1b** reacts with 3-phenyl-2-propenoyl chloride (**4**), rather than three possible products (as in the case of cycloacylation of N-aryl-3-oxobutanethioamides [1]), only one product is formed: 3,6-diphenyl-2-phenylsulfonylmethylidene-5,6-dihydro-4H-1,3-thiazin-4-one (**5**).



These results are most likely explained by the low acidity of the methylene group and steric hindrances created by the sulfonyl group in phenylsulfonyl-N-R-thioacetamides [3], which makes it impossible (in contrast to N-aryl-3-oxobutanethioamides) to acylate them at the methylene group.

The structure of the synthesized compounds was proven using IR and ¹H NMR spectra, and the composition was proven using elemental analysis data. The ¹³C NMR spectrum of thiazolidine **3a** also is

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evidence for the formation of a thiazole ring, since the C=O carbon signal (164.7 ppm) in the ^{13}C NMR spectrum, recorded without spin–spin decoupling, appears as a doublet ($J = 5.4$ Hz) due to spin–spin coupling with the proton in the CH= moiety.

Ethyl 4-Oxo-2-phenylsulfonylmethylidene-1,3-thiazolidine-5-methylidenecarboxylate (3a). A solution of phenylsulfonylthioacetamide **1a** (2.15 g, 0.01 mol) and acetylenedicarboxylic ester **2** (1.87 g, 0.011 mol) in ethanol (15 ml) was boiled for 1 h and cooled down. The precipitate was filtered out. Yield 2.44 g (72%); mp 192–193°C (ethanol). IR spectrum (KBr), ν , cm^{-1} : 3250, 3100, 1730 (C=O), 1700 (C=O), 1610, 1460, 1380, 1320, 1280, 1150. ^1H NMR spectrum (DMSO- d_6 , 300 MHz, TMS), δ , ppm (J , Hz): 1.30 (3H, t, $J = 6.9$, $\text{CH}_3\text{CH}_2\text{O}$); 4.26 (2H, q, $J = 6.9$, $\text{CH}_3\text{CH}_2\text{O}$); 6.17 (1H, s, $\text{CH}=\text{C}_{(2)}$); 6.61 (1H, s, $\text{CH}=\text{C}_{(5)}$); 7.62 (3H, m, C_6H_5); 7.87 (2H, m, C_6H_5); 12.45 (1H, s, NH). ^{13}C NMR spectrum, (DMSO- d_6 , 75 MHz), δ , ppm: 14.0 ($\text{CH}_3\text{CH}_2\text{O}$); 61.5 ($\text{CH}_3\text{CH}_2\text{O}$); 102.2 ($\text{CH}=\text{C}_{(2)}$); 114.9 ($\text{CH}=\text{C}_{(5)}$); 126.3 (C_{Ar}); 129.6 (C_{Ar}); 133.5 (C_{Ar}); 142.1 (C_{Ar}); 147.1 (C-5); 150.5 (C-2); 164.7 ($\text{O}=\text{C}_{(4)}$); 165.5 ($\text{O}=\text{C}$). Found, %: C 49.79; H 4.10; N 3.93. $\text{C}_{14}\text{H}_{13}\text{NO}_5\text{S}_2$. Calculated, %: C 49.55; H 3.86; N 4.13.

Ethyl 4-Oxo-2-phenylsulfonylmethylidene-3-phenyl-1,3-thiazolidine-5-methylidenecarboxylate (3b) was obtained as for compound **3a**. Yield 68%; mp 183–185°C (ethanol). IR spectrum (KBr), ν , cm^{-1} : 3100, 1720 (C=O), 1700 (C=O), 1580, 1500, 1460, 1380, 1320, 1260, 1160. ^1H NMR spectrum (DMSO- d_6 , 300 MHz, TMS), δ , ppm (J , Hz): 1.32 (3H, t, $J = 6.8$, CH_3CH_2); 4.30 (2H, q, $J = 6.8$, $\text{CH}_3\text{CH}_2\text{O}$); 5.63 (1H, s, $\text{CH}=\text{C}_{(2)}$); 6.75 (1H, s, $\text{CH}=\text{C}_{(5)}$); 7.36 (2H, m, C_6H_5); 7.43–7.69 (6H, m, C_6H_5); 7.85 (2H, m, C_6H_5). Found, %: C 58.04; H 3.86; N 3.66. $\text{C}_{20}\text{H}_{17}\text{NO}_5\text{S}_2$. Calculated, %: C 57.82; H 4.12; N 3.37.

3,6-Diphenyl-2-phenylsulfonylmethylidene-5,6-dihydro-4H-1,3-thiazin-4-one (5). A solution of compound **4** (1.67 g, 0.01 mol) in acetone (5 ml) was added with stirring at 25°C to a solution of phenylsulfonyl-N-phenylthioacetamide **1b** (2.91 g, 0.01 mol) in anhydrous acetone (10 ml) containing K_2CO_3 (2.07 g, 0.015 mol). The mixture was stirred for 1 h at 40°C and then cooled. The precipitate was filtered out and washed with water (3×5 ml). Yield 2.02 g (48%); mp 272–273°C (AcOH). IR spectrum (KBr), ν , cm^{-1} : 3000, 1690 (C=O), 1520, 1490, 1450, 1340, 1300, 1250, 1130. ^1H NMR spectrum (DMSO- d_6 , 300 MHz, TMS), δ , ppm: 3.24 (1H, m, H-5); 3.59 (1H, m, H-5); 4.98 (1H, m, H-6); 5.04 (1H, s, CH=); 7.14 (2H, m, C_6H_5); 7.38 (5H, m, C_6H_5); 7.57 (6H, m, C_6H_5); 7.77 (2H, m, C_6H_5). Found, %: C 65.77; H 4.30; N 3.03. $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{S}_2$. Calculated, %: C 65.54; H 4.54; N 3.32.

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