SHORT COMMUNICATIONS

One-Pot Synthesis of 2-Ylidene-1,3-dithiolanes

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Abstract—A one-pot synthesis of 2-ylidene-1,3-dithiolanes, involving the reaction of carbon disulfide with methylene-active compounds in the presence of sodium ethylate followed by adding 1,2-dichloralkanes to the reaction mixture, is developed.

Keywords: sulfur-containing heterocycles, dithiolanes, one-pot synthesis, methylene-active compound, multicomponent synthesis

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1.3-Dithiolanes bearing electron-acceptor substituents are applied in the synthesis of compounds with valuable optical and electronic properties [1-7]. For this reason, searching for rational synthetic approaches to such 1,3-dithiolanes is an urgent problem. We previously reported a method of synthesis of 2-ylidene-1,3-dithiolanes, which involves the of sodium 2,2-disubstituted reaction 1.1ethenebisthiolates with 1,2-dichloroalkanes [8] and described a one-pot synthesis of dithiolanes from malononitrile and cyanoacetamide. Proceeding with this research, we found that other methylene-active compounds, too, can be involved in the threecomponent reaction. As a result, a one-pot synthesis of 2-ylidene-1,3-dithiolanes 1a, 1b and 2a, 2b, which includes the reaction of carbon disulfide with a methylene-active compounds in the presence of ethylate followed by adding 1,2sodium dichloroalkanes to the reaction mixture (Schemes 1 and 2). The yields of the reaction products were 85-96%. As methylene-active compounds we used

dimedone (5,5-dimethylcyclohexane-1,3-dione) (Scheme 1) and ethyl cyanoacetate (Scheme 2).

The reaction with ethyl cyanoacetate gives, according to the NMR data, a 1 : 1 mixture of the E and Z isomers of ethyl 2-cyano-2-(4-methyl-1,3-dithiolan-2-ylidene)acetate **2b**.

The structure of the synthesized compounds was confirmed by IR and ¹H NMR spectroscopy and mass spectrometry.

The IR spectra of dithiolanes 1 and 2 display strong stretching absorption bands of the C=O and C=C bonds at 1706–1715 and 1458–1468 cm⁻¹, respectively. The IR spectra of compounds 2 also contain characteristic signals of the conjugated cyano group. The ¹H NMR spectra of compounds 1a and 1b show alkyl proton signals at 0.95–4.04 ppm. The ¹H NMR spectra of compounds 2a and 2b also contain signals of the ester alkyl groups. The mass spectra display molecular ion peaks (20–100%).





 $R = H(a); CH_3(b).$

Dithiolanes **1b** and **2b** were synthesized for the first time, and the method of synthesis of compounds **1a** and **2a** is much more facile that those reported in [9–11].

Thus, we developed an original one-pot synthesis of 2-ylidene-1,3-dithiolanes, which allows heterocycles of complex structures to be prepared in one stage. The developed method contains less stages and takes less time.

5,5-Dimethyl-2-(1,3-dithiolan-2-ylidene)cyclohexan-1,3-dione (1a). A solution of 0.28 g (0.002 mol) of dimedone in 1 mL of ethanol was added to sodium ethylate obtained from 0.05 g (0.002 mol) of sodium and 1 mL of ethanol. Carbon disulfide, 0.15 mL (0.002 mol), and a new portion of sodium ethylate from 0.05 g (0.002 mol) of sodium and 1 mL of ethanol were then successively added to the mixture. The precipitate that formed was dissolved in 4 mL of DMF, and 1 g (0.01 mol) of dichloroethane was added to the solution. The reaction mixture was stirred until reaction completion (1 h by TLC) and diluted with 4–5 volumes of water. The precipitate that formed was filtered off, washed with water, and recrystallized from propan-2-ol.

Yield 0.41 g (85%), mp 202°C (201–202°C [9], 200°C [10]). IR spectrum, v, cm⁻¹: 1710 (C=O), 1458 (C=C). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 0.96 s (6H, 2CH₃), 2.47 s (4H, 2COCH₂), 3.39 s (4H, 2SCH₂). Mass spectrum, *m/z* (*I*_{rel}, %): 242 (30) [*M*]⁺. Found, %: C 54.75; H 5.99. C₁₁H₁₄O₂S₂. Calculated, %: C 54.52; H 5.82. *M* 242.35.

Compounds 1b, 2a, and 2b were prepared in a similar way.

5,5-Dimethyl-2-(4-methyl-1,3-dithiolan-2-ylidene)cyclohehane-1,3-dione (1b). Yield 0.46 g (90%), mp 175–176°C. IR spectrum, v, cm⁻¹: 1715 (C=O), 1460 (C=C). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 0.95 s (3H, CCH₃), 0.97 s (3H, CCH₃), 1.35 d (3H, J 6.7 Hz, CHC<u>H₃</u>), 2.46 m (4H, 2COCH₂), 3.19–3.23 d.d (1H, J 12.1, 6.8 Hz, SCH₂), 3.46–3.50 d.d (1H, J 12.1, 5.8 Hz, SCH₂), 3.97–4.04 m (1H, C<u>H</u>CH₃). Mass spectrum, *m/z* (I_{rel} , %): 256 (50) [*M*]⁺. Found, %: C 56.38; H 6.45. C₁₂H₁₆O₂S₂. Calculated, %: C 56.22; H 6.29. *M* 256.38.

Ethyl 2-cyano-2-(1,3-dithiolan-2-ylidene)acetate (2a). Yield 0.4 g (92%), mp 104–105°C (104°C [10], 105–106°C [11]). IR spectrum, v, cm⁻¹: 2200 (C=N), 1706 (C=O), 1461 (C=C). ¹H NMR spectrum (DMSO d_6), δ, ppm: 1.22–1.25 t (3H, J 7.1 Hz, CH₃), 3.68– 3.75 m (4H, 2SCH₂), 4.18–4.23 q (2H, J 7.1 Hz, CH₂). Mass spectrum, *m/z* (*I*_{rel}, %): 215 (20) [*M*]⁺. Found, %: C 44.85; H 4.40. C₈H₉NO₂S₂. Calculated, %: C 44.63; H 4.21. *M* 215.29.

Ethyl 2-cyano-2-(4-methyl-1,3-dithiolan-2ylidene)acetate (2b). Yield 0.44 g (96%), mp 169– 170°C. IR spectrum, v, cm⁻¹: 2207 (C=N), 1711 (C=O), 1468 (C=C). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.22–1.25 m (3H, CH₂CH₃), 1.22–1.25 m (3H, CH₂CH₃)*, 1.44 m (3H, CHCH₃), 1.44 m (3H, CHCH₃)*, 3.49–3.58 m (1H, SCH₂), 3.49–3.58 m (1H, SCH₂)*, 3.79–3.84 m (1H, SCH₂), 3.79–3.84 m (1H, SCH₂)*, 4.17–4.23 m (2H, CH₂CH₃), 4.17–4.23 m (2H, CH₂CH₃)*, 4.33–4.41 m (1H, CHCH₃), 4.33–4.41 m (1H, CHCH₃)*. Mass spectrum, m/z (I_{rel} , %): 229 (100) [M]⁺. Found, %: C 47.35; H 5.03. C₉H₁₁NO₂S₂. Calculated, %: C 47.14; H 4.84. M 229.31.

The purity of the synthesized compounds was controlled by TLC (eluent – ethyl acetate) of Sorbfil PTSKh-AF-A-UF plates in with development in UV light or iodine vapor, or by heating. The melting points were measured on an OptiMelt MPA100 instrument. The IR spectra were obtained on a FSM-1202 FTIR spectrometer in mineral oil. The NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500 (¹H) MHz in DMSO- d_6 , internal reference TMC. The mass spectra were measured on a Shimadzu GCMS-QP 2010 SE system (electron ionization, 70 eV). Elemental analysis was performed on a Perkin Elmer-2400 CHN analyzer.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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