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SYNTHESIS OF 6,7-DIHYDRO-5H-[1,3,4]THIADIAZOLO-[2,3-*b*][1,3]THIAZINIUM SYSTEM DERIVATIVES

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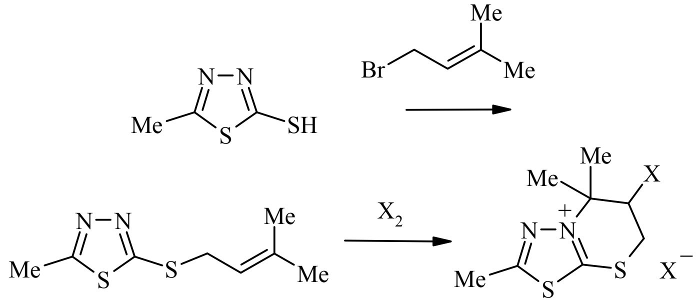
Keywords: 6-halo-2,5,5-trimethyl-6,7-dihydro-5H-[1,3,4]thiadiazolo[2,3-*b*][1,3]thiazinium halide, 2-methyl-5-[(3-methylbut-2-en-1-yl)sulfanyl]-1,3,4-thiadiazole, X-ray structural analysis.

It has been shown that the reaction of 5-methyl-2-prenylsulfanyl-1,3,4-thiadiazole (**1**) with bromine and iodine gives halocyclization products involving the nitrogen atom of the thiadiazole ring, i.e. the 6-halo-2,5,5-tri-methyl-6,7-dihydro-5H-[1,3,4]thiadiazolo[2,3-*b*][1,3]thiazinium halides **2a,b**. Formation of significant amounts of reaction products at the sulfur atom was not noted. The 6,7-dihydro-5H-[1,3,4]thiadiazolo[2,3-*b*]-[1,3]thiazinium system has previously been synthesized by reaction of 2,5-disulfanyl-1,3,5-thiadiazole with 1,3-dibromopropane [1].



1

2a,b

2 a X = I, **b** X = Br

Compound **1** was prepared by the reaction of 5-methyl-2-sulfanyl-1,3,4-thiadiazole with 1-bromo-3-methylbut-2-ene. The structures of the products were proved by ^{1}H NMR spectroscopic data and that of the iodide **2a** additionally by X-ray analysis.

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^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) in DMSO-d$_6$ with TMS as internal standard. The X-ray structural analysis was carried out on an automatic four circle Xcalibur 3 X-ray diffractometer using a standard procedure (MoKα radiation, graphite monochromator, 295(2) K, ω/2θ scanning). A fragment of the light-yellow prismatic crystal of size 0.226×0.095×0.034 mm was used for the analysis. The crystal is monoclinic with space group $P2_1/n$ and unit cell parameters a = 6.7607(2), b = 18.4770(6), c = 10.6587(3) Å, β = 100.836(2)°, V = 1307.72(7) Å^3, for the empirical formula $C_8H_{12}I_2N_2S_2$: Z = 4, d_{calc} = 2.307 g/cm^3, μ = 5.097 mm^{-1}. 9153 Reflection were collected in the range 2.94 < θ < 30.50° of which 3914 were independent (R_{int} = 0.0185) including 2821 with $I > 2\sigma(I)$, for θ = 30.50 the completeness was 98.0%. Corrections for absorption were made analytically [2] using the polyhedral crystal model. The structure was solved and refined using the *SHELX* [3] program package. All of the non-hydrogen atoms were refined in the anisotropic approximation, hydrogen atoms were included in the geometrically calculated positions and included in the refinement using the "riding" model with related isotropic thermal parameters. The final refinement structural parameters were: R_1 = 0.0314, wR_2 = 0.0781 (for reflections with $I > 2\sigma(I)$), R_1 = 0.0449, wR_2 = 0.0802 (for all reflections with a quality S factor of 1.029). Peak maxima and minima for the residual electron density were Δρ = 2.099 and -1.637 e/Å^3. The crystallographic information has been placed in the Cambridge Structural Database, deponent CCDC 793711. This data can be freely accessed at the address www.ccdc.cam.ac.uk/data_request/cif.

2-Methyl-5-[(3-methylbut-2-en-1-yl)sulfanyl]-1,3,4-thiadiazole (1). 5-Methyl-1,3,4-thiadiazole-2-thiol (0.53 g, 4 mmol) and prenyl bromide (0.47 ml, 4 mmol) were added to a solution of metallic sodium (0.1 g, 4 mmol) in ethanol (10 ml) and refluxed for 2 h. After cooling, ethanol was evaporated from the filtrate and the residue was treated with ether. Evaporation of the ether gave compound **1** as a yellow oil. Yield 0.5 g (63%). Found, %: C 47.65; H 6.01; N 32.04; S 13.86. $C_8H_{12}N_2S_2$. Calculated, %: C 47.97; H 6.04; N 32.01; S 13.98.

6-Iodo-2,5,5-trimethyl-6,7-dihydro-5H-[1,3,4]thiadiazolo[2,3-*b*][1,3]thiazinium Iodide (2a). A solution of iodine (0.51 g, 2 mmol) in ethanol (4 ml) was added to a solution of compound **1** (0.2 g, 1 mmol) in ethanol (2 ml). After 24 h the solution was decanted, the residue was dissolved in acetone (3 ml), and a solution of $NaI \cdot 2H_2O$ (0.37 g, 2 mmol) in acetone (3 ml) was added to it. The light-yellow precipitate formed was filtered off. Yield 0.32 g (97%); mp 116ºC (ethanol, decomp.). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.79 (3H, s, CH_3); 1.83 (3H, s, CH_3) 2.77 (3H, s, CH_3 arom.); 3.91 (1H, dd, J = 14.1, J = 7.1, SCH_2); 4.17 (1H, dd, J = 14.1, J = 3.1, SCH_2); 5.29 (1H, m, CHI). Found, %: C 21.02; H 2.54; I 55.96; N 6.28; S 14.03. $C_8H_{12}I_2N_2S_2$. Calculated, %: C 21.16; H 2.66; I 55.89; N 6.17; S 14.12.

6-Bromo-2,5,5-trimethyl-6,7-dihydro-5H-[1,3,4]thiadiazolo[2,3-*b*][1,3]thiazinium Bromide (2b). A solution of Br_2 (0.028 ml, 0.5 mmol) in chloroform (3 ml) was added dropwise with cooling in ice to a solution of compound **1** (0.11 g, 0.5 mmol) in chloroform (3 ml). After 24 h the chloroform was evaporated and the residue was treated with acetone and filtered. Yield 0.19 g (67%); mp 196-200ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.74 (3H, s, CH_3); 1.85 (3H, s, CH_3); 2.78 (3H, s, CH_3 arom.); 3.89 (1H, dd, J = 14.4, 5.5, SCH_2); 4.22 (1H, dd, J = 14.4, J = 2.8, SCH_2); 5.44 (1H, m, CHBr). Found, %: C 26.53; H 3.18; Br 44.59; N 7.87; S 17.64. $C_8H_{12}Br_2N_2S_2$. Calculated, %: C 26.68; H 3.36; Br 44.37; N 7.78; S 17.81.

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