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[(4-Sulfanylidene-4*H*-1λ^4,3,2-dithiazol-5-yl)sulfanyl]formic acid derivatives: synthesis from 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride and structural characterization

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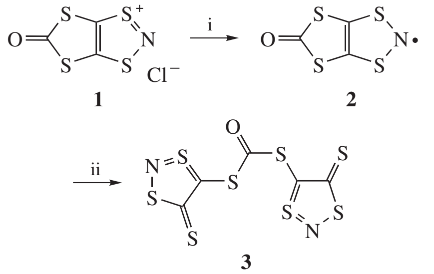
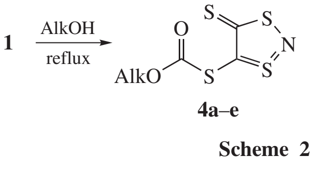
5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride was converted into [(4-sulfanylidene-4*H*-1λ^4,3,2-dithiazol-5-yl)sulfanyl]formic acid esters and amides upon treatment with alcohols and amines, respectively; the structure of propyl [(4-sulfanylidene-4*H*-1λ^4,3,2-dithiazol-5-yl)sulfanyl]formate was confirmed by X-ray diffraction.

Fused 1,2,3-dithiazolium salts are important precursors of stable dithiazolyl radicals.[1] Monocyclic derivatives react with ammonia, primary and tertiary amines[2,3] or reducing agents[4] to give rare 4*H*-1λ^{4}δ^2,3,2-dithiazoles with tetravalent sulfur atoms. Recently, we found that 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride **1** reacted with triphenylantimony in acetonitrile to afford [1,3]dithiolo[4,5-*d*]dithiazolyl radical **2**, which was identified by EPR and CV data.[5] Upon standing at room temperature, it decomposed with extrusion of carbon monoxide and dimerization to give compound **3** (Scheme 1), whose structure was confirmed by elemental analysis and spectral data. To characterize the chemical properties of salt **1** and reasons for the instability of radical **2**, we studied the reactions of salt **1** with alcohols and amines.



Scheme 1 *Reagents and conditions*: i, Ph_3Sb, 1 h, room temperature; ii, 5 h, room temperature.

5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride **1** was found inert towards phenol and benzyl alcohol. Treatment of salt **1** with methanol at reflux for 3 h afforded new product **4a**. Compound **4a** (29% yield), a deep violet solid, $C_4H_3NO_2S_4$, according to its mass spectra, elemental analysis and ^{1}H and ^{13}C NMR spectra, is a product of addition of methoxide group with extrusion of HCl. The structure of **4a** was finally proved by X-ray analysis of closely related propyl analogue **4c** (see below). We extended the reaction to other alcohols. 1,2,3-Dithiazoles **4** were obtained in moderate to low yields by refluxing salt **1** in corresponding alcohols (Scheme 2).†



a Alk = Me, 3 h, 29%
b Alk = Et, 3 h, 49%
c Alk = Pr, 2 h, 53%
d Alk = Pr^i, 8 h, 8%
e Alk = Bu, 3 h, 39%

Scheme 2

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† *General procedure for the preparation of (4*H*-1λ^4,3,2-dithiazol-5-yl)-sulfanylformic acid esters* **4** *and amides* **8**. A mixture of salt **1** (5 mmol) with alcohol (10 mmol) or amine (10 mmol) in THF (10 ml) was stirred under reflux or at room temperature up to disappearance of **1**. Solvents were evaporated, and the residue was separated by column chromatography (Silica gel Merck 60, light petroleum–CH_2Cl_2 mixtures).

New compounds were characterised by elemental analysis, ^{1}H and ^{13}C NMR (300 MHz for ^{1}H and 75.5 MHz for ^{13}C, $CDCl_3$ solutions), mass and IR (in KBr pellets) spectra.

4a: yield 29%, deep-violet crystals, mp 90–92 °C. ^{1}H NMR, δ: 3.99 (s, 3H, Me). ^{13}C NMR, δ: 56.6 (MeO), 167.9 (C=O), 171.4 (*sp*^{2} tertiary C), 203.3 (C=S). MS (EI, 70 eV), *m*/*z* (%): 225 (M$^+$, 40), 166 (20), 135 (30), 91 (100). IR (ν/cm^{-1}): 2948 (CH), 1696 (C=O). Found (%): C, 21.45; H, 1.29; N, 6.35. Calc. for $C_4H_3NO_2S_4$ (%): C, 21.32; H, 1.34; N, 6.22.

4b: yield 49%, deep-violet crystals, mp 88–90 °C. ^{1}H NMR, δ: 1.45 (t, 3H, Me, *J* 7.3 Hz), 4.53 (q, 2H, CH_2, *J* 7.3 Hz). ^{13}C NMR, δ: 14.3 (Me), 67.0 (CH_2), 167.2 (C=O), 171.7 (*sp*^{2} tertiary C), 203.2 (C=S). MS (EI, 70 eV), *m*/*z* (%): 239 (M$^+$, 20), 166 (30), 135 (10), 105 (35), 88 (100). IR (ν/cm^{-1}): 2924 (CH), 1684 (C=O). Found (%): C, 25.23; H, 2.02; N, 5.98. Calc. for $C_5H_5NO_2S_4$ (%): C, 25.09; H, 2.11; N, 5.85.

4c: yield 53%, deep-violet crystals, mp 59–61 °C. ^{1}H NMR, δ: 1.02 (t, 3H, Me, *J* 7.3 Hz), 1.81 (m, 2H, CH_2), 4.42 (t, 2H, CH_2, *J* 6.6 Hz). ^{13}C NMR, δ: 10.1 (Me), 22.0 and 72.3 (2CH_2), 167.2 (C=O), 171.6 (*sp*^{2} tertiary C), 203.0 (C=S). MS (EI, 70 eV), *m*/*z* (%): 253 (M$^+$, 30), 166 (50), 135 (10), 120 (20), 105 (35). IR (ν/cm^{-1}): 2928 (CH), 1692 (C=O). Found (%): C, 28.65; H, 2.62; N, 5.74. Calc. for $C_6H_7NO_2S_4$ (%): C, 28.44; H, 2.78; N, 5.53.

4d: yield 8%, deep-violet crystals, mp 129–131 °C. ^{1}H NMR, δ: 1.42 (d, 6H, Me, *J* 6.6 Hz), 5.30 (sept., 1H, CH, *J* 6.6 Hz). ^{13}C NMR, δ: 21.9 (2Me), 76.3 (CH), 166.6 (C=O), 171.9 (*sp*^{2} tertiary C), 203.1 (C=S). MS (EI, 70 eV), *m*/*z* (%): 253 (M$^+$, 230), 194 (5), 167 (30), 121 (10). IR (ν/cm^{-1}): 2928 (CH), 1684 (C=O). Found (%): C, 28.52; H, 2.68; N, 5.67. Calc. for $C_6H_7NO_2S_4$ (%): C, 28.44; H, 2.78; N, 5.53.

4e: yield 39%, deep-violet crystals, mp 56–58 °C. ^{1}H NMR, δ: 0.98 (t, 3H, Me, *J* 7.3 Hz), 1.45 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 4.46 (t, 2H, CH_2, *J* 6.6 Hz). ^{13}C NMR, δ: 13.6 (Me), 18.9, 30.5 and 70.7 (3CH_2), 167.2 (C=O), 171.7 (*sp*^{2} tertiary C), 203.1 (C=S). MS (EI, 70 eV), *m*/*z* (%): 267 (M$^+$, 10), 167 (50), 135 (10), 121 (10). IR (ν/cm^{-1}): 2956 (CH), 1696 (C=O). Found (%): C, 31.62; H, 3.14; N, 5.38. Calc. for $C_7H_9NO_2S_4$ (%): C, 31.44; H, 3.39; N, 5.24.

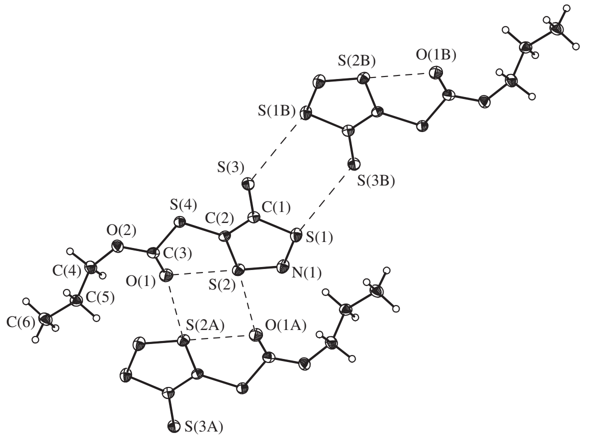
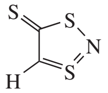


Figure 1 View of a part of the infinite chain formed by the molecules of **4c** in a crystal (thermal ellipsoids are shown for the 50% probability level).

Primary alcohols gave moderate yields of dithiazoles **4**, but reaction with isopropanol requires a longer period to be completed and the yield of **4d** is very low. Treatment of salt **1** with *tert*-butanol led to full decomposition, and no individual products were isolated.

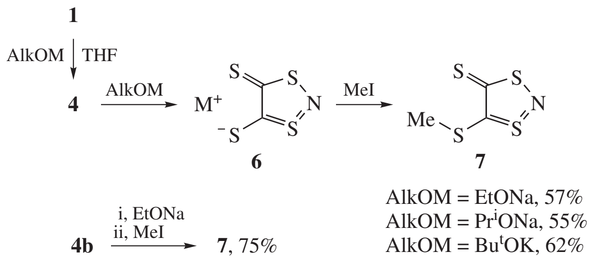
The molecular structure of dithiazole derivative **4c** is shown in Figure 1.[‡] The entire molecule except for the propyl group is close to planarity, the mean deviation from the plane is 0.016 Å. The structure of the dithiazole ring is close to that found in $4H$-1λ^4,3,2-dithiazole-4-thione **5**.[6]



5

The N(1)–S(1), N(1)–S(2), S(2)–C(2), C(1)–C(2), and S(1)–C(1) bond lengths are 1.6279(13), 1.6058(13), 1.7286(15), 1.417(2) and 1.6886(14), in **4c** and 1.621, 1.588, 1.648, 1.420, and 1.717 Å in **5**, respectively. The short intramolecular contact O(1)···S(2) 2.618(2) Å leads to the formation of the five-membered ring S(2)–C(2)–S(4)–C(3)–C(1) and additionally favors the planarity of the molecule. In a crystal, **4c** forms a network of intermolecular S···O and S···S interactions (see Figure 1, atoms A and B were obtained with the $-x-3$, $-y-1$, $-z$ and $-x-1$, $-y-1$, $-z+1$ symmetry transformations, respectively). The S(3)···S(1B) and O(1)···S(2A) distances are 3.530(1) and 2.969(1) Å, respectively. These contacts lead to the formation of infinite chains in the crystal, which are held together by π···π interactions between the carbonyl group and the S(2) atom of the dithiazole ring. The shortest distance S(2)···C(3C) ($-x-2$, $-y-1$, $-z+1$, not shown in Figure 1) between a pair of atoms for this interaction is 3.474(1) Å.

Taking into consideration that alkoxide anions could participate in the formation of esters **4**, we treated salt **1** with sodium ethoxide in THF for 2 h at room temperature, but dithiazole **4b** was not detected (TLC data). We proposed that the reaction proceeded further and salt **6** was formed; therefore, we added methyl iodide to the reaction mixture. Derivative **7**[2] was isolated in 57% yield. We then extended these conditions to other alkoxides, sodium isopropoxide and potassium *tert*-butoxide, and obtained S-methyl derivative **7** in 55 and 62% yields, respectively (Scheme 3).



Scheme 3

The difference in the reactivity of alcohols and alkoxides can be explained by the reaction of dithiazoles **4**, initially formed from salt **1**, with an alkoxide anion to give salt **6**. It was strictly confirmed by the reaction of dithiazole **4b** with sodium ethoxide followed by addition of methyl iodide: S-methyl derivative **7** was isolated in 75% yield.

The reactivity of salt **1** towards other nucleophiles (aliphatic amines) was investigated. Treatment of salt **1** with a primary aliphatic amine (isopropylamine) afforded dimer **3** in 48% yield. Results that are more interesting were obtained in the reactions of salt **1** with 2 equiv. of secondary amines – diethylamine, *N*-methylbutylamine, pyrrolidine, morpholine and piperidine. In all cases, [(4-sulfanylidene-$4H$-1λ^4,3,2-dithiazol-5-yl)sulfanyl]formic acid amides **8** were obtained in high to moderate yields (Scheme 4).[§]

[‡] *Crystallographic data*. Crystals of **4c** ($C_6H_7NO_2S_4$, $M = 253.37$) are triclinic, space group $P\bar{1}$, at 100 K: $a = 5.1394(5)$ Å, $b = 9.6019(9)$ and $c = 10.1765(10)$ Å, $\alpha = 94.8226(16)°$, $\beta = 96.5457(17)°$, $\gamma = 94.3943(17)°$, $V = 495.26(8)$ Å^3, $Z = 2$ ($Z' = 1$), $d_{calc} = 1.699$ g cm^{-3}, μ(MoKα) = 9.23 cm^{-1}, $F(000) = 260$. Intensities of 5875 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta < 56°$] and 2614 independent reflections [$R_{int} = 0.0193$] were used in a further refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H(C) atom positions were calculated and refined in an isotropic approximation in riding model with U_{iso}(H) parameters equal to $1.2U_{eq}(C_i)$ for CH_2 groups and $1.5U_{eq}(C_{ii})$ for Me ones, where $U(C_i)$ and $U(C_{ii})$ are the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. The refinement converged to $wR_2 = 0.0645$ and GOF = 1.019 for all independent reflections [$R_1 = 0.0253$ was calculated against F for 2264 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.[7]

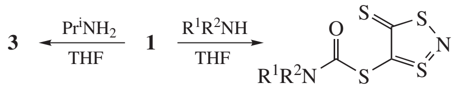
CCDC 779418 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

[§] **8a**: yield 69%, deep-violet oil. ^{1}H NMR, δ: 1.26 (t, 3H, Me, J 7.3 Hz), 1.35 (t, 3H, Me, J 7.3 Hz), 3.56 (m, 4H, 2CH$_2$). ^{13}C NMR, δ: 13.0 (Me), 13.8 (Me), 43.2 (CH$_2$), 44.2 (CH$_2$), 162.5 (C=O), 172.8 (sp^2 tertiary C), 201.8 (C=S). MS (EI, 70 eV), m/z (%): 266 (M$^+$, 10), 194 (5), 166 (5), 100 (50). IR (ν/cm^{-1}): 2928 (CH), 1640 (C=O). Found (%): C, 31.73; H, 3.52; N, 10.88. Calc. for $C_7H_{10}N_2OS_4$ (%): C, 31.56; H, 3.78; N, 10.51.

8b: yield 86%, deep-violet oil. ^{1}H NMR, δ: 0.96 (t, 3H, Me, J 7.3 Hz), 1.38 (m, 2H, 2CH$_2$), 1.65 (m, 2H, 2CH$_2$), 3.13 (s, 3H, Me), 3.51 (m, 2H, 2CH$_2$). ^{13}C NMR, δ: 13.8 (Me), 19.9 (Me), 29.3, 35.5 and 50.4 (3CH$_2$), 163.1 (C=O), 172.6 (sp^2 tertiary C), 201.7 (C=S). MS (EI, 70 eV), m/z (%): 280 (M$^+$, 10), 194 (5), 166 (5), 114 (35). IR (ν/cm^{-1}): 2928 (CH), 1644 (C=O). Found (%): C, 34.51; H, 4.12; N, 10.07. Calc. for $C_8H_{12}N_2OS_4$ (%): C, 34.26; H, 4.31; N, 9.99.

8c: yield 87%, deep-violet crystals, mp 138–140 °C. ^{1}H NMR, δ: 2.04 (m, 4H, 2CH$_2$), 3.59 (m, 4H, 2CH$_2$). ^{13}C NMR, δ: 24.7 and 25.8 (2CH$_2$), 47.3 and 48.7 (2CH$_2$), 160.7 (C=O), 172.5 (sp^2 tertiary C), 201.6 (C=S). MS (EI, 70 eV), m/z (%): 264 (M$^+$, 10), 166 (5), 98 (65). IR (ν/cm^{-1}): 2920 (CH), 1644 (C=O). Found (%): C, 31.95; H, 3.02; N, 10.77. Calc. for $C_7H_8N_2OS_4$ (%): C, 31.80; H, 3.05; N, 10.59.

8d: yield 82%, deep-violet crystals, mp 166–168 °C. ^{1}H NMR, δ: 3.69 (s, 4H, 2CH$_2$), 3.78 (s, 4H, 2CH$_2$). ^{13}C NMR, δ: 44.9 and 47.4 (2CH$_2$), 66.3 (2CH$_2$), 162.7 (C=O), 171.8 (sp^2 tertiary C), 202.2 (C=S). MS (EI, 70 eV), m/z (%): 280 (M$^+$, 15), 194 (5), 166 (5), 114 (50). IR (ν/cm^{-1}): 2916 (CH), 1644 (C=O). Found (%): C, 30.05; H, 2.64; N, 10.06. Calc. for $C_7H_8N_2O_2S_4$ (%): C, 29.98; H, 2.88; N, 9.99.



8a R^1 = R^2 = Et, 69%
8b R^1 = Me, R^2 = Bu, 86%
8c R^1 + R^2 = (CH$_2$)$_4$, 87%
8d R^1 + R^2 = (CH$_2$)$_2$O(CH$_2$)$_2$, 82%

Scheme 4

In summary, fused 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride **1** was found to react with strong (aliphatic amines) and weak (alcohols) nucleophilic reagents to afford [(4-sulfanylidene-4*H*-1λ^4,3,2-dithiazol-5-yl)sulfanyl]formic acid derivatives **8** and **4**, whereas treatment with alkoxides led to 5-(methylsulfanyl)-4*H*-1λ^4,3,2-dithiazole-4-thione **7**.

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