Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2010, **20**, 282–284

Mendeleev Communications

Synthesis of 2-iminothiophen-3(2*H*)-ones from 3*H*-1,2-dithiol-3-ones

Vladimir A. Ogurtsov,[a] Yurii V. Karpychev,[a] Dar'ya A. Pestravkina,[a] Pavel A. Belyakov,[a] Yulia V. Nelyubina[b] and Oleg A. Rakitin*[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: orakitin@ioc.ac.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085*

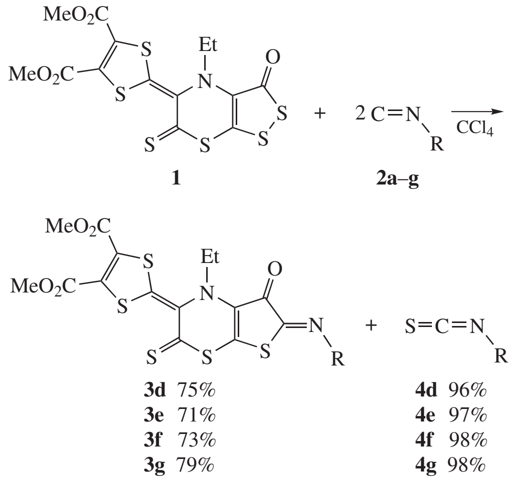
DOI: 10.1016/j.mencom.2010.09.015

3*H*-1,2-Dithiol-3-ones undergo a new transformation into 2-iminothiophen-3(2*H*)-ones upon treatment with isonitriles; the structure of iminothiophenone 10 was confirmed by X-ray diffraction analysis.

In recent years, 1,2-dithioles have attracted much attention due to their anticancer activity and versatile chemical reactivity.[1] It is known that 1,2-dithiole-3-thiones can be easily involved in various chemical transformations, especially, in 1,3-dipolar cycloaddition reactions. There are substantially less examples of such reactions for 1,2-dithiol-3-ones. They undergo insertion reactions of nucleophilic nitrogen functions (hydrazines,[2] amines[3] or azides[4]) with the formation of nitrogen heterocycles (pyrazoles or isothiazoles) and elimination of sulfur atoms.

Recently, we have reported that the reaction of 1,2-dithiole-3-thiones with isonitriles at room temperature afforded imino-1,3-dithietanes.[5] The reaction was found reversible and the rise of the temperature shifted the equilibrium to the starting compounds. To continue our investigation into the synthetic utility of 1,2-dithioles, we studied the reaction of 1,2-dithiol-3-ones with isonitriles.

Aliphatic isonitriles **2a**–**c** were found inert towards dithiolone **1** at room temperature in CCl_4. Heating under reflux for a few hours led to the decomposition of starting materials; no isolable products were detected (TLC data). Aromatic isonitriles **2d**–**f** were more reactive towards **1**. The reaction between **1** and **2d** was investigated in detail. If the process was carried out in a protic solvent, such as ethanol, or in strong aprotic dipolar solvents, such as DMSO, isonitrile **2d** was decomposed and starting dithiolone **1** was isolated in practically quantitative yield. The reaction between **1** and **2d** did not proceed in acetonitrile at room temperature, and heat under reflux resulted in the decomposition of starting materials. The reaction in an inert solvent (carbon tetrachloride) at room temperature occurred slowly; after heating the reaction mixture under reflux for 1 h, new product **3d** was formed. Compound **3d** (75% yield), a black solid with $C_{22}H_{18}N_2O_6S_5$ according to mass spectra, elemental analysis, and ^1H and ^{13}C NMR spectra is formally the product of addition of isonitrile **2d** to compound **1** and elimination of sulfur from the latter with another molecule of isonitrile. Isothiocyanate **4d** was isolated from the reaction mixture in practically quantitative yield (Scheme 1).† Treatment of dithiolone **1** with 2 equiv. of arylisonitriles **2e**,**f** in CCl_4 under reflux for



a R = CH_2Ts
b R = CH_2Ph
c R = CH_2CO_2Et
d R = 4-$MeOC_6H_4$
e R = Ph
f R = 4-$NO_2C_6H_4$
g R = $C(CO_2Et)CHNMe_2$

Scheme 1

---

† *General procedure for the preparation of 2-iminothiophen-3(2*H*)-ones* **3d**–**g**, **7**, **8**, **10**–**13**. A mixture of 1,2-dithiol-3-one **1**, **5**, **6** or **9** (0.05 mmol) and isonitrile **2** (0.1 mmol) in CCl_4 (10 ml) was stirred at room temperature or under reflux up to the disappearance of 1,2-dithiol-3-one or isonitrile (TLC data). The reaction mixture was separated by column chromatography (Silica gel Merck 60; light petroleum, light petroleum–CH_2Cl_2 and CH_2Cl_2–acetone mixtures).

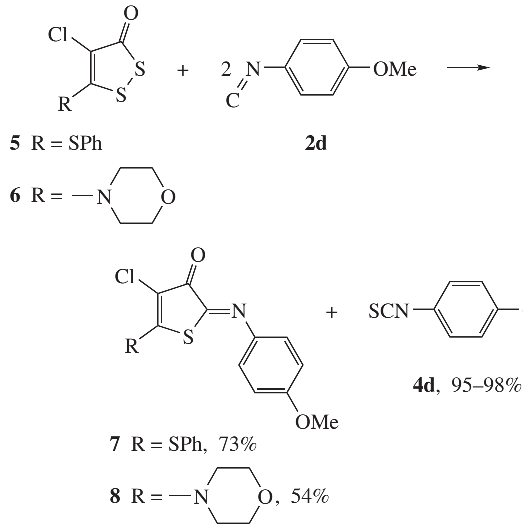
New compounds were characterised by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy ($CDCl_3$ solutions, 300 and 75.5 MHz for ^1H and ^{13}C, respectively) and mass spectrometry (EI, 70 eV).

3d: reflux for 1 h, yield 75%, black powder, mp 106–108 °C. ^1H NMR, δ: 1.21 (t, 3H, $MeCH_2$, *J* 7.1 Hz), 3.26 (dq, 1H, CH_2Me, *J* 14.3 Hz, *J* 7.1 Hz), 3.61 (dq, 1H, CH_2Me, *J* 14.3 Hz, *J* 7.1 Hz), 3.85 (s, 3H, OMe), 3.93 (s, 3H, CO_2Me), 3.95 (s, 3H, CO_2Me), 6.97 (d, 2H, H_{Ar}, *J* 8.8 Hz), 7.31 (d, 2H, H_{Ar}, *J* 8.8 Hz). ^{13}C NMR, δ: 13.4 ($MeCH_2$), 48.1 ($MeCH_2$), 53.9 (CO_2Me), 54.1 (CO_2Me), 55.7 (OMe), 114.9 (2CH), 124.5 (2CH), 124.6, 131.1, 132.0, 133.1, 134.6, 140.5, 148.0, 153.8, 159.6, 160.1 and 160.3 (11*sp*^{2} tertiary C), 177.1 (C=O), 191.4 (C=S). IR (KBr, ν/cm^{-1}): 2952 (CH), 1732 and 1684 (C=O). MS, *m*/*z* (%): 566 (M$^+$, 3), 404 (100), 376 (65), 274 (68), 165 ($SCNC_6H_4OMe$, 38), 150 (42), 133 (36). Found (%): C, 46.71; H, 3.23; N, 4.87. Calc. for $C_{22}H_{18}N_2O_6S_5$ (%): C, 46.63; H, 3.20; N, 4.94.

3e: reflux for 6 h, yield 71%, black powder, mp 191–192 °C. ^1H NMR, δ: 1.24 (t, 3H, $MeCH_2$, *J* 7.1 Hz), 3.29 (dq, 1H, CH_2Me, *J* 14.2 Hz, *J* 7.1 Hz), 3.63 (dq, 1H, CH_2Me, *J* 14.2 Hz, *J* 7.1 Hz), 3.95 (s, 3H, OMe), 3.97 (s, 3H, OMe), 7.20 (d, 2H, H_{Ar}, *J* 7.7 Hz), 7.28–7.35 (m, 1H, H_{Ar}), 7.43–7.49 (m, 2H, H_{Ar}). ^{13}C NMR, δ: 13.3 ($MeCH_2$), 48.1 ($MeCH_2$), 53.9 (CO_2Me), 54.0 (CO_2Me), 120.9, 128.0 and 129.6 (5CH), 131.1, 131.8, 133.1, 134.5, 148.4, 151.7, 154.7, 159.6 and 160.4 (10*sp*^{2} tertiary C), 176.7 (C=O), 191.0 (C=S). IR (KBr, ν/cm^{-1}): 2952 (CH), 1744, 1720 and 1676 (C=O). MS, *m*/*z* (%): 536 (M$^+$, 9), 404 (33), 376 (26), 274 (33), 135 (SCNPh, 13). Found (%): C, 47.08; H, 2.69; N, 5.09. Calc. for $C_{21}H_{16}N_2O_5S_5$ (%): C, 47.00; H, 3.00; N, 5.22.

6 and 30 h, respectively, afforded new products **3e**,**f** in high yields. The reaction of dithiolone **1** with isonitrile **2g** proceeded at room temperature in CCl_4, and product **3g** was formed after 1 h in high yield (79%). The structure of iminothiophenones **3** was finally proved by X-ray analysis of closely related analogue **10** (see below).

1,2-Dithiol-3-ones fused with aromatic (benzene and pyridine) rings – 3*H*-1,2-benzodithiol-3-one and 3*H*-[1,2]dithiolo[3,4-*b*]pyridin-3-one – were found inert towards isonitriles **2**, and they were recovered in practically quantitative yields from the reaction mixtures after heating under reflux for 20 h. On the other hand, monocyclic 1,2-dithiol-3-ones **5**, **6** reacted with 2 equiv. of isonitrile **2d** in CCl_4 to afford thiophenones **7**, **8** in high to moderate yields (Scheme 2).



Scheme 2

Interesting results were obtained for bis[1,2]dithiolo[1,4]thiazine dione **9**, in which two 1,2-dithiol-3-one rings can be involved in the reaction with isonitriles **2**. Treatment of dione **9** with 2 equiv. of isonitrile **2d** or **2g** at room temperature in CCl_4 led to a mixture of monothiophenones **10** or **11**, bis(thiophenones) **12** or **13** together with starting bis(1,2-dithiole) **9**. Further reaction of monothiophenones **10** or **11** with another 2 equiv. of **2d** or **2g** at room temperature for 20 h gave **12** or **13** in moderate yields (45 and 57%, respectively) (Scheme 3). It means that the reactivity of 1,2-dithiole rings in **9** and in monothiophenones is comparable.

The structure of imine **10** was confirmed by X-ray analysis[‡] (Figure 1). According to its results, this monothiophenone crystallizes with four independent molecules in a unit cell, which are related by pseudo-symmetry elements – inversion centre and translation. The latter manifests itself in the similarity of the geometrical parameters for the independent species; all of them fall in the ranges typical of this type of heterocyclic compounds. As thiophenone **10** lacks any convenient proton donor, the strongest intermolecular interactions are C=O···S ones [O···S

3f: reflux for 30 h, yield 73%, black powder, mp 208–210 °C. ^{1}H NMR, δ: 1.24 (t, 3H, *Me*CH$_2$, *J* 6.8 Hz), 3.22–3.39 (m, 1H, C*H*$_2$Me), 3.52–3.70 (m, 1H, C*H*$_2$Me), 3.94 (s, 3H, OMe), 3.97 (s, 3H, OMe), 7.24 (d, 2H, H$_{\rm Ar}$, *J* 8.3 Hz), 8.31 (d, 2H, H$_{\rm Ar}$, *J* 8.3 Hz). ^{13}C NMR, δ: 13.3 (*Me*CH$_2$), 48.5 (Me*C*H$_2$), 53.9 (CO$_2$*Me*), 54.0 (CO$_2$*Me*), 120.5 (2CH), 125.4 (2CH), 131.2, 131.5, 133.2, 134.5, 146.3, 154.1, 154.2, 154.8, 159.4 and 160.8 (11*sp*^{2} tertiary C), 176.0 (C=O), 190.0 (C=S). IR (KBr, ν/cm^{-1}): 2960 (CH), 1740 and 1688 (C=O), 1344 (NO$_2$). MS, *m*/*z* (%): 582 (M$^+$ + 1, 1), 274 (9), 238 (11), 219 (18), 206 (40), 192 (18), 180 (SCNC$_6$H$_4$NO$_2$, 11). Found (%): C, 43.21; H, 2.47; N, 7.00. Calc. for $C_{21}H_{15}N_3O_7S_5$ (%): C, 43.36; H, 2.60; N, 7.22.

3g: room temperature, 1 h, yield 79%, brown powder, mp 148–150 °C. ^{1}H NMR, δ: 1.16 (t, 3H, *Me*CH$_2$N, *J* 7.0 Hz), 1.31 (t, 3H, *Me*CH$_2$O, *J* 7.1 Hz), 3.19 (dq, 1H, MeC*H*$_2$N, *J* 14.1 Hz, *J* 7.0 Hz), 3.30 (br. s, 3H, MeN), 3.56 (dq, 1H, MeC*H*$_2$N, *J* 14.1 Hz, *J* 7.0 Hz), 3.73 (br. s, 3H, MeN), 3.90 (s, 3H, CO$_2$Me), 3.91 (s, 3H, CO$_2$Me), 4.23 (q, 2H, MeC*H*$_2$O, *J* 7.1 Hz), 7.65 (s, 1H, CH). ^{13}C NMR, δ: 13.3 (*Me*CH$_2$N), 14.7 (*Me*CH$_2$O), 41.2 (MeN), 48.0 (Me*C*H$_2$N), 49.2 (MeN), 53.8 (Me), 53.8 (CO$_2$*Me*), 60.5 (Me*C*H$_2$O), 105.9, 130.4, 131.3, 132.9, 132.9, 134.5, 152.5, 159.0, 159.8, 159.9 and 163.9 (11*sp*^{2} tertiary C), 151.5 (CH), 178.2 (C=O), 194.6 (C=S). IR (KBr, ν/cm^{-1}): 2952 and 2920 (CH), 1716, 1652 and 1620 (C=O). MS, *m*/*z* (%): 599 (M$^+$ – 2, 1), 404 (1), 376 (2), 274 (6), 200 [SCNC(CO$_2$Et)=CH(NMe$_2$), 5]. Found (%): C, 44.01; H, 3.97; N, 6.83. Calc. for $C_{22}H_{23}N_3O_7S_5$ (%): C, 43.91; H, 3.85; N, 6.98.

7: reflux for 12 h, yellow powder, mp 153–154 °C. ^{1}H NMR, δ: 3.79 (s, 3H, Me), 6.88 (d, 2H, H$_{\rm Ar}$, *J* 8.8 Hz), 7.15 (d, 2H, H$_{\rm Ar}$, *J* 8.8 Hz), 7.45–7.50 (m, 2H, Ph), 7.54–7.63 (m, 3H, Ph). ^{13}C NMR, δ: 55.6 (Me), 114.8 (2CH, Ar), 124.4 (2CH, Ar), 130.0, 131.8 and 136.1 (5CH, Ph), 117.2, 125.4, 140.4, 147.9, 160.0 and 167.3 (6*sp*^{2} tertiary C), 177.4 (C=O). IR (KBr, ν/cm^{-1}): 2992 and 2836 (CH), 1688 (C=O). MS, *m*/*z* (%): 363 (M$^+$ + 2, 25), 361 (M$^+$, 60), 230 (12), 228 (30), 202 (5), 200 (15). Found (%): C, 56.26; H, 3.17; N, 4.04. Calc. for $C_{17}H_{12}ClNO_2S_2$ (%): C, 56.42; H, 3.34; N, 3.87.

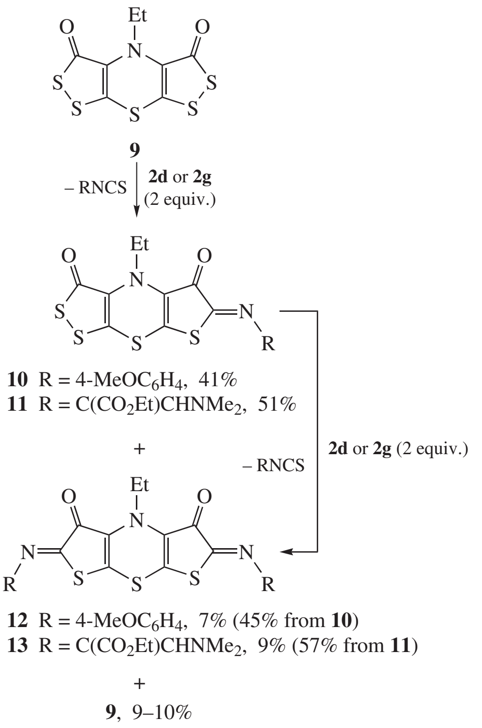
8: room temperature, 30 h, yield 54%, yellow powder, mp 185–187 °C. ^{1}H NMR, δ: 3.82–3.84 (m, 7H, 2CH$_2$ + MeO), 3.97–4.00 (m, 4H, 2CH$_2$), 6.95 (d, 2H, H$_{\rm Ar}$, *J* 8.8 Hz), 7.19 (d, 2H, H$_{\rm Ar}$, *J* 8.8 Hz). ^{13}C NMR, δ: 51.4 (2CH$_2$), 55.6 (Me), 66.7 (2CH$_2$), 98.6, 141.7, 148.7, 159.2 and 163.1 (5*sp*^{2} tertiary C), 114.7 (2CH), 123.1 (2CH), 178.9 (C=O). IR (KBr, ν/cm^{-1}): 2924 and 2852 (CH), 1652 (C=O). MS, *m*/*z* (%): 340 (M$^+$ + 2, 8), 338 (M$^+$, 24), 210 (36), 208 (100), 179 (6), 177 (24), 165 (17). Found (%): C, 53.24; H, 4.57; N, 8.23. Calc. for $C_{15}H_{15}ClN_2O_3S$ (%): C, 53.17; H, 4.46; N, 8.27.

10: room temperature, 20 h, yield 41%, black crystals, mp 149–150 °C. ^{1}H NMR, δ: 1.26 (t, 3H, *Me*CH$_2$N, *J* 7.1 Hz), 3.84 (s, 3H, MeO), 3.87 (q, 2H, MeC*H*$_2$N, *J* 7.1 Hz), 6.97 (d, 2H, H$_{\rm Ar}$, *J* 9.0 Hz), 7.31 (d, 2H, H$_{\rm Ar}$, *J* 9.0 Hz). ^{13}C NMR, δ: 14.1 (*Me*CH$_2$N), 42.6 (Me*C*H$_2$N), 55.7 (MeO), 114.9 (2CH), 124.6 (2CH), 133.8, 133.9, 140.0, 142.8, 147.1, 147.7 and 160.4 (7*sp*^{2} tertiary C), 175.67 (C=O), 182.97 (C=O). IR (CDCl$_3$, ν/cm^{-1}): 2936 (C-H), 1684 and 1656 (C=O). MS, *m*/*z* (%): 408 (M$^+$, 19), 376 (24), 348 (5), 275 (87), 247 (45), 243 (100), 232 (37), 219 (78). Found (%): C, 47.05; H, 2.79; N, 6.82. Calc. for $C_{16}H_{12}N_2O_3S_4$ (%): C, 47.04; H, 2.96; N, 6.86.

11: room temperature, 1.5 h, yield 51%, dark brown powder, mp 155–156 °C. ^{1}H NMR, δ: 1.17 (t, 3H, *Me*CH$_2$N, *J* 7.3 Hz), 1.26 (t, 3H, *Me*CH$_2$O, *J* 6.9 Hz), 3.27 (s, 3H, MeN), 3.63 (s, 3H, MeN), 3.78 (q, 2H, MeC*H*$_2$N, *J* 7.3 Hz), 4.18 (q, 2H, MeC*H*$_2$O, *J* 6.9 Hz), 7.61 (s, 1H, CH). ^{13}C NMR, δ: 13.7 (*Me*CH$_2$N), 14.6 (*Me*CH$_2$O), 41.1 (MeN), 42.4 (Me*C*H$_2$N), 49.2 (MeN), 60.3 (Me*C*H$_2$O), 104.9, 130.8, 132.4, 133.8, 144.0, 145.8 and 163.7 (7*sp*^{2} tertiary C), 151.5 (CH), 176.3 (C=O), 183.4 (C=O). IR (KBr, ν/cm^{-1}): 2920 (CH), 1660 and 1620 (C=O). MS, *m*/*z* (%): 443 (M$^+$, 26), 411 (17), 300 (17), 275 (36), 228 (26), 219 (58). Found (%): C, 43.22; H, 3.94; N, 9.53. Calc. for $C_{16}H_{17}N_3O_4S_4$ (%): C, 43.32; H, 3.86; N, 9.47.

12: room temperature, 20 h, yield 11%, dark brown powder, mp 177–178 °C. ^{1}H NMR, δ: 1.24 (t, 3H, Me, *J* 7.1 Hz), 3.85 (s, 6H, 2OMe), 4.03 (q, 2H, CH$_2$, *J* 7.1 Hz), 6.97 (d, 4H, H$_{\rm Ar}$, *J* 8.9 Hz), 7.31 (d, 4H, H$_{\rm Ar}$, *J* 8.9 Hz). ^{13}C NMR, δ: 14.1 (Me), 42.3 (CH$_2$), 55.7 (2MeO), 115.0 (4CH), 124.7 (4CH), 132.1, 140.3, 143.0, 146.1 and 160.5 (10*sp*^{2} tertiary C), 175.8 (2C=O). IR (KBr, ν/cm^{-1}): 2928 (CH), 1676 and 1664 (C=O). MS, *m*/*z* (%): 509 (M$^+$, 1), 199 (12), 165 (100). Found (%): C, 47.05; H, 2.79; N, 6.82. Calc. for $C_{16}H_{12}N_2O_3S_4$ (%): C, 47.04; H, 2.96; N, 6.86.

13: room temperature, 1.5 h, yield 9%, dark brown powder, mp 185–186 °C. ^{1}H NMR, δ: 1.12 (t, 3H, *Me*CH$_2$N, *J* 7.0 Hz), 1.29 (t, 6H, 2*Me*CH$_2$O, *J* 7.1 Hz), 3.28 (br. s, 6H, 2MeN), 3.67 (br. s, 6H, 2MeN), 3.93 (q, 2H, MeC*H*$_2$N, *J* 7.0 Hz), 4.21 (q, 4H, 2MeC*H*$_2$O, *J* 7.1 Hz), 7.61 (s, 1H, CH). ^{13}C NMR, δ: 13.4 (*Me*CH$_2$N), 14.7 (2*Me*CH$_2$O), 41.1 and 49.0 (2br. s, 4Me), 42.1 (Me*C*H$_2$N), 60.4 (2Me*C*H$_2$O), 105.4, 125.0, 131.2, 143.3 and 163.9 (10*sp*^{2} tertiary C), 151.1 (2CH), 176.9 (2C=O). IR (KBr, ν/cm^{-1}): 2980 and 2896 (CH), 1640 and 1624 (C=O). MS, *m*/*z* (%): 579 (M$^+$, 1), 453 (1), 240 (8), 228 (20), 211 (12), 200 (SCNR, 16), 171 (16), 154 (30), 139 (13), 126 (10), 109 (21), 89 (49), 83 (100). Found (%): C, 49.85; H, 5.14; N, 11.99. Calc. for $C_{24}H_{29}N_5O_6S_3$ (%): C, 49.72; H, 5.04; N, 12.08.



Scheme 3

3.296(2)–3.309(2) Å] assembling three of the independent molecules into trimers. A slightly weaker C=O···S contact [O···S 3.410(3) Å] links these associates with the fourth monothiophenone molecule to give corrugated tapes along the crystallographic plane *ac*. A number of weaker interactions, such as C–H···S, C–H···O, H···H, complete the formation of a 3D framework.

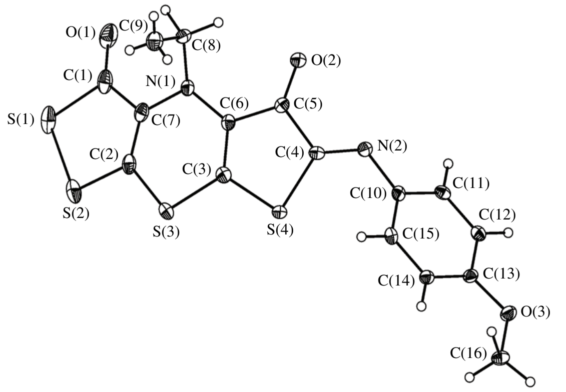
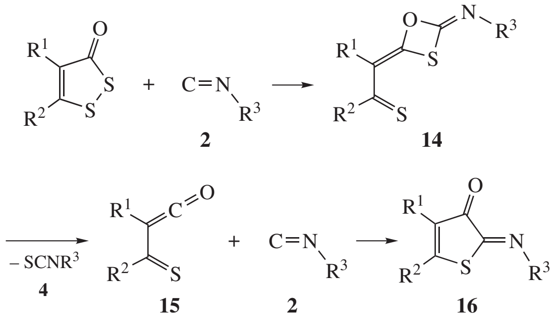


Figure 1 General view of an independent molecule in the crystal of **10** in representation of atoms *via* thermal ellipsoids at a 50% probability level.



Scheme 4

The above reactions are the novel conversions of 1,2-dithiol-3-one into thiophenone ring through the insertion of isonitrile and the elimination of sulfur with another molecule of isonitrile (isothiocyanate formation). The most plausible pathway (Scheme 4) includes the cycloaddition of dithiolone and isonitrile **2** to give 1,3-oxathietane **14**, which can release the molecule of isothiocyanate **4** and form the key intermediate – ketene **15**. Isonitrile **2** is likely to react with ketene **15** to produce thiophenone **16**.

References

1 (*a*) C. Th. Pedersen, *Adv. Heterocycl. Chem.*, 1982, **31**, 63; (*b*) C. Th. Pedersen, *Sulfur Rep.*, 1995, **16**, 173; (*c*) D. M. McKinnon, in *Comprehensive Heterocyclic Chemistry II*, ed. I. Shinkai, Pergamon, Oxford, 1996, vol. 3, chapter 3.11, p. 593; (*d*) R. Marković and A. Rašović, in *Comprehensive Heterocyclic Chemistry III*, ed. J. A. Joule, Elsevier, Oxford, 2008, vol. 4, chapter 4.11, p. 893.
2 B. Böttcher and F. Bauer, *Liebigs Ann. Chem.*, 1950, **568**, 227.
3 K. H. Baggaley, L. J. A. Jennings and A. W. R. Tyrrell, *J. Heterocycl. Chem.*, 1982, **19**, 1393.
4 M. S. Chauhan and D. M. McKinnon, *Can. J. Chem.*, 1976, **54**, 3879.
5 V. A. Ogurtsov, Yu. V. Karpychev, P. A. Belyakov, Yu. V. Nelyubina, K. A. Lyssenko and O. A. Rakitin, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 422 (*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 430).
6 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

Received: 31st March 2010; Com. 10/3499

---

‡ *Crystallographic data.* Crystals of **10** ($C_{16}H_{12}N_2O_3S_4$, $M = 408.52$) are monoclinic, space group $P2_1/n$, at 100 K: $a = 28.9379(13)$, $b = 7.4455(3)$ and $c = 31.7694(14)$ Å, $\beta = 102.5740(10)°$, $V = 6680.8(5)$ Å^3, $Z = 16$ ($Z' = 4$), $d_{\text{calc}} = 1.625$ g cm^{-3}, μ(MoKα) = 5.88 cm^{-1}, $F(000) = 3360$. Intensities of 72870 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 56°$] and 16112 independent reflections ($R_{\text{int}} = 0.0677$) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation in riding model. For **10**, the refinement converged to $wR_2 = 0.1006$ and GOF = 1.003 for all independent reflections [$R_1 = 0.0430$ was calculated against F for 10900 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.[6]

CCDC 786198 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.