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Electrophilic halogenation of thioethers: 5-chloro- and 5,6-dichloro-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-one and an efficient synthesis of vinylenedithiotetrathiafulvalene (VDT-TTF)

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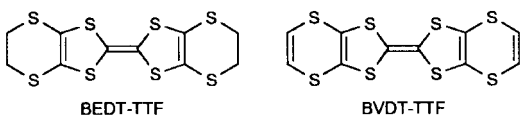
The SO_2Cl_2 chlorination of 5,6-dihydro-1,3-dithiolo[4,5-*b*]-[1,4]dithiine-2-one affords the corresponding mono- and *trans*-di-chloro derivatives which eliminate HCl upon treatment with KF/18-crown-6 or LiBr/HMPA, offering an easy route to the unsaturated vinylenedithiotetrathiafulvalene (VDT-TTF).

Halogen···halogen intermolecular interactions[1] have been recently used for the resolution of racemic bromoalkanes[2] and for the elaboration of novel organic conductors based on bromo- or iodo-tetrathiafulvalenes.[3,4] The strongly decreased donor ability of the analogous chlorinated TTFs prompted us to look for novel derivatives where the halogen atoms are not conjugated with the π-redox TTF core. Since the direct halogenation of the ethylenedithio moieties of the oxidation-sensitive bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is not possible, we investigated the electrophilic halogenation of its precursor, *i.e.* 5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-one[5] **1** and report here on the synthesis and reactivity of the mono- and dichloro derivatives of **1**.



The chlorination of **1** was efficiently performed with 1 equiv. of SO_2Cl_2 in refluxing CCl_4 to afford racemic (*R*,*S*)-**2** in 91% yield (Scheme 1).† With two equiv. of sulfuryl chloride, *trans*-5,6-dihydro-5,6-dichloro-1,3-dithiolo[4,5-*b*][1,4]dithiine-2-one **3** was obtained in 60% yield as a racemic mixture of (*R*,*R*) and (*S*,*S*) enantiomers without any (*R*,*S*) isomer, as confirmed by the presence of a single ^{1}H NMR signal and the X-ray crystal structure resolution of **3** (Fig. 1).‡ The molecule is located on an *mm*2 site in which the two chlorine atoms adopt axial positions while the carbon atoms are disordered, a consequence of the (*R*,*R*) and (*S*,*S*) racemic mixture. This *trans* addition, also observed in the dichlorination of 1,4-dithiane,[6] derives from the lowered nucleophilicity of the sulfur atom of **2**, α to the CHCl group (Scheme 2). The electrophilic reagent thus reacts on the second sulfur atom and the migration of the Cl^+ moiety occurs on the less hindered side, followed by HCl elimination to afford **3**. Note also that only traces of the trichloro derivative were obtained with an excess of chlorinating agent, while prolonged refluxing only led to product degradation.

In an attempt to obtain the corresponding mono- and difluoro derivatives of **1** by substitution of the chlorine atoms, **2** and **3** were reacted with KF/18-crown-6 as described, for example, in the reaction of $PhSCH_2Cl$ to give $PhSCH_2F$.[7] Under those conditions however, we observed that HCl elimination took place instead, affording in both cases the corresponding vinylic derivatives **4** and **5** in 50 and 60% yield, respectively (Scheme 1). This reaction thus provides easy access to the vinylic dithiolone **4**, otherwise prepared in low yield from the $dmit^{2-}$ dianion.[8,9] This is all the more appealing since **4** can be used as a starting material for a number of attractive target molecules, such as bisvinylenedithiotetrathiafulvalene (BVDT-TTF),[10] the unsymmetrically substituted vinylenedithiotetrathiafulvalene (VDT-TTF) as well as metal dithiolene complexes which can now be prepared from **4**.

A first illustration of this potential is given here by the chloro diester derivative **7**, obtained by $P(OMe)_3$ cross-coupling of **2** with **6**,[11] which directly affords VDT-TTF in 60% yield upon treatment with LiBr/HMPA in a one-pot reaction (Scheme 3) in which the two ester groups are hydrolysed and decarboxylated

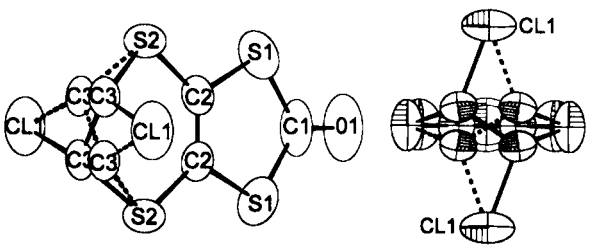
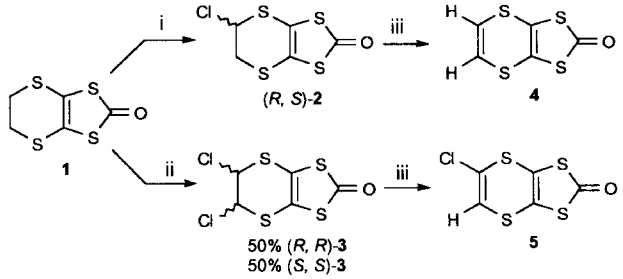
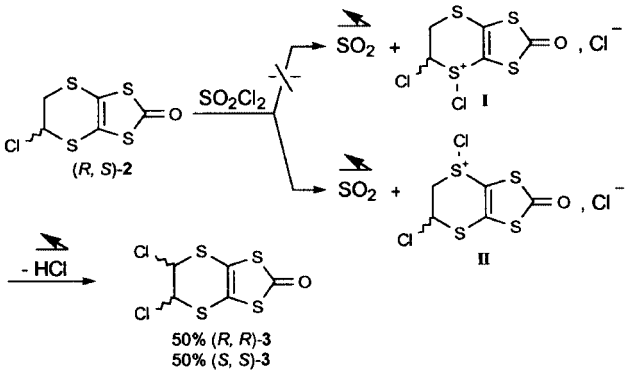


Fig. 1 Two views of the dichloro derivative **3**, showing the statistical distribution of the (*R*,*R*) (unbroken line bonds) and (*S*,*S*) (dashed line bonds) enantiomers in the crystalline form.



Scheme 1 *Reagents and conditions:* i, 1 equiv. SO_2Cl_2, CCl_4, reflux, 24 h; ii, 2 equiv. SO_2Cl_2, CCl_4, reflux, 24 h; iii, 4 equiv. KF, 0.2 equiv. 18-crown-6, MeCN, reflux, 18 h.



Scheme 2 Postulated mechanism for the chlorination of **2**.

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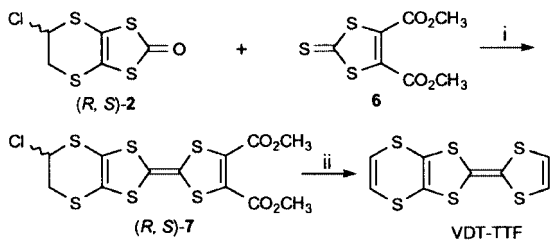

Scheme 3 *Reagents and conditions:* i, $P(OMe)_3$, reflux, 3 h; ii, 11 equiv. LiBr, HMPA, 80 °C, 30 min, 150 °C, 60 min.

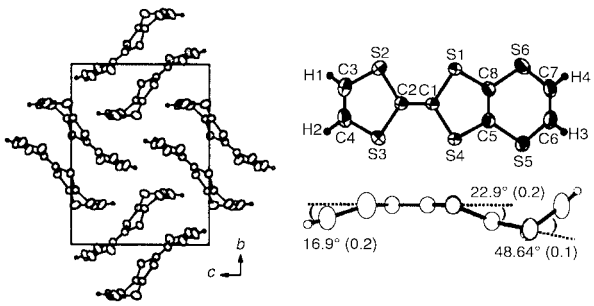

Fig. 2 The X-ray crystal structure of VDT-TTF. Left: projection view of the unit cell along *a*. Right: ORTEP view and numbering scheme of the VDT-TTF molecule (with 50% probability displacement ellipsoids) and folding angles of the dithiole and dithiine rings.

while HCl is simultaneously eliminated under these basic conditions. Note that the reported synthesis of VDT-TTF involved the coupling of **4** with **6** in 8% yield and further decarboxylation in 18% yield.[12] Recrystallization from toluene afforded red crystals the X-ray crystal structure of which prove them to be isostructural with the saturated EDT-TTF analogue (Fig. 2).‡ Of particular note are the folding angles of the five- and six-membered rings along the S···S axes, 16.9(2) and 22.9(2)° in the dithiole rings along S2···S3 and S1···S4, respectively and 48.6(1)° along S5···S6 in the dithiine ring.[13] The availability of VDT-TTF will allow thorough investigations of its radical cation salts with various counter anions as well as reactivity studies, particularly in lithiation experiments where both types of vinylic hydrogen atoms of VDT-TTF might compete for metallation.

The efficient halogenation reactions described here, and the reactivity of the chlorinated species will prompt us to investigate the preparation of the corresponding halogenated tetrathiafulvalenes and their radical cation salts. Furthermore, other chlorinating agents are also being investigated with **1** for the synthesis of the tetrachloro derivative, while preliminary results on its direct fluorination showed the Selectfluor® reagent to be effective.

Notes and references

† *Selected data* for **2**: white crystals; mp 84 °C (CCl_4), δ_H(200 MHz, $CDCl_3$): 3.39 (dd, ^3J 13.5, 6.9 Hz, 1H), 3.66 (dd, ^3J 13.5, 3.3 Hz, 1H), 5.79 (dd, ^3J 6.9; 3.3 Hz, 1H). δ_C(50 MHz, $CDCl_3$): 188.7, 114.4, 114.1, 59.2, 39.7. ν_{max}(KBr)/cm^{-1}: 1675 (C=O). MS (70 eV, EI): *m/z* (%) 244 (6), 243 (52), 242 (13, $M^{\bullet+}$), 241 (91), 213 (57), 88 (63), 76 (100) (Anal. Calc for $C_5H_3ClOS_4$ (242.795): C, 24.73; H, 1.25; Cl, 14.60. Found: C, 24.80; H, 1.11; Cl, 14.88%). For **3**: light yellow platelets; mp 157 °C (CCl_4), δ_H(200 MHz, $CDCl_3$): 5.52 (s, 2H). δ_C(50 MHz, $CDCl_3$): 187.1 (1C), 110.5 (2C), 62.1 (2C). ν_{max}(KBr)/cm^{-1}: 1670 (C=O). MS (70 eV, EI): *m/z* (%) 278 (17), 276 (54, $M^{\bullet+}$), 247 (45), 151 (49), 88 (90), 76 (100). (Anal. Calc. for $C_5H_2Cl_2OS_4$ (277.240): C, 21.66; H, 0.73; Cl, 25.58; S, 46,26. Found: C, 21.68; H, 0.76; Cl, 25.36; S, 45.64%). For **4**: light yellow needles; mp 99 °C (MeCN), δ_H(200 MHz, $CDCl_3$): 6.61 (s, 2H). δ_C(50 MHz, $CDCl_3$): 192.3 (1C), 123.9 (2C), 117.2 (2C). ν_{max}(KBr)/cm^{-1}: 1665 (C=O). MS (70 eV, EI): *m/z* (%) 206 (84, $M^{\bullet+}$), 178 (100), 88 (78), 76 (78) (Anal. calc. for $C_5H_2OS_4$ (206.334): C, 29.11; H, 0.98; S, 62.16. Found: C, 29.07; H, 0.92; S, 60.30%). For **5**: white crystals; mp 160 °C (CCl_4), δ_H(200 MHz, $CDCl_3$): (s, 1H). δ_C(50 MHz, $CDCl_3$): 191.2, 127.7, 120.1, 119.0, 118.4. ν_{max}(KBr)/cm^{-1}: 1663 (C=O). MS (70 eV, EI): *m/z* (%) 239 (96, $M^{\bullet+}$), 211 (88), 136 (100), 76 (57) (Anal. Calc for C_5HClOS_4 (239.860): C, 24.94; H, 0.42; Cl, 14.72; S, 53.27. Found: C, 25.07; H, 0.52; Cl, 14.84; S, 51.77%). For **7**: black needles; mp 128 °C (toluene–cyclohexane, 3:7), δ_H(200 MHz, $CDCl_3$): 3.30 (dd, ^3J 13.4, 7.0 Hz, 1H), 3.50 (dd, ^3J 13.4, 3.6 Hz, 1H), 3.83 (s, 6H), 5.72 (dd, ^3J 3.6, 7.0 Hz, 1H). δ_C(50 MHz, $CDCl_3$): 159.8 (2C), 131.9, 129.0, 116.0 (2C), 115.4 (2C), 59.1, 53.5 (2C), 39.5. ν_{max}(KBr)/cm^{-1}: 1720 (C=O). MS (70 eV, EI): *m/z* (%) 444 (28, $M^{\bullet+}$), 381 (63), 261 (100), 218 (38), 76 (29) (Anal. Calc. for $C_{12}H_9ClO_4S_6$ (445.046): C, 32.39; H, 2.04; Cl, 7.97; O, 14.38; S, 43.23. Found: C, 32.88; H, 1.99; Cl, 8.00; O, 14.23; S, 42.04%). For VDT-TTF: red platelets; mp 185 °C (toluene), δ_H(200 MHz, $CDCl_3$): 6.34 (s, 2H), 6.54 (s, 2H). δ_C(50 MHz, $CDCl_3$): 129.0, 128.3, 125.3, 124.7 (2C), 118.9 (2C). MS (70 eV, EI): *m/z* (%) 291 (59, $M^{\bullet+}$), 146 (100), 88 (38) (Anal. Calc. for $C_8H_4S_6$ (291.864): C, 32.85; H, 1.38; S, 65.77. Found: C, 33.05; H, 1.32; S, 65.73%).

‡ X-Ray data for **3** and VDT-TTF were collected on a Stoe Imaging Plate Diffractometer (IPDS) with Mo-Kα radiation, λ = 0.71073 Å at T = 293(2) K. The structures were solved by direct methods and refined against F^2 using the SHELXTL5.04 set of programs. Hydrogen atoms in VDT-TTF were found in the Fourier difference map and refined isotropically.

Crystal data for **3**: $C_5H_2Cl_2OS_4$, M = 277.240, orthorhombic, space group *Pmmn*, a = 7.0595(21), b = 7.4252(20), c = 9.3827(22) Å, V = 491.8(4) Å^3, Z = 2, D_c = 1.875 g cm^{-3}, μ = 1.456 mm^{-1}, data collected = 2833, unique data = 2091 (R_{int} = 0.0337) of which 323 with $I > 2\sigma(I)$, $R(F)$ = 0.0357, $R_w(F^2)$ = 0.0871.

For VDT-TTF: $C_8H_4S_6$, M = 292.47, monoclinic, space group $P2_1/n$, a = 6.4203(13), b = 14.905(3), c = 11.648(2) Å, V = 1112.4(4) Å^3, Z = 4, D_c = 1.746 g cm^{-3}, μ = 1.182 mm^{-1}, data collected = 8649, unique data = 2142 (R_{int} = 0.0515) of which 5988 with $I > 2\sigma(I)$, $R(F)$ = 0.0268, $R_w(F^2)$ = 0.0565.

CCDC 182/1640. See http://www.rsc.org/suppdata/cc/b0/b001996h/ for crystallographic data in .cif format.

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13 Similar folding angles are observed in the structure of the neutral BVDT-TTF. See ref. 8.