Tungsten Hexachloride (WCl_6) in the Presence of Dimethylsulfoxide Promoted Facile and Efficient One-Pot Ring Expansion-Chlorination Reactions of 1,3-Dithiolanes and 1,3-Dithianes

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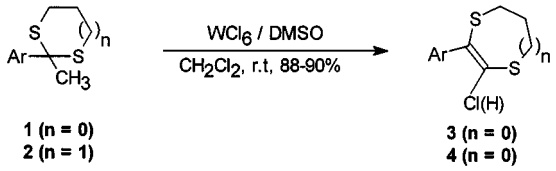
Abstract: Tungsten hexachloride (WCl_6) in the presence of DMSO could be efficiently used for the conversion of 1,3-dithiolanes and 1,3-dithianes to their corresponding chlorinated derivatives of dihydro-1,4-dithiin and dihydro-1,4-dithiepine in high yield, respectively.

Key words: 1,3-dithiolanes, tungsten hexachloride, 1,3-dithianes, ring-enlargement, dimethylsulfoxide

The annelation reactions of 1,3-dithiolane and 1,3-dithianes for the construction of larger rings containing hetero-sulfur atoms have been of interest from different point of views.[1-7] Nevertheless, less attention has been paid to the development of new improved methodologies based on rearrangement reactions. In recent years we have been exploring new applications for tungsten hexachloride (WCl_6). In this regard halode-hydroxylation and dihalo-oxo-bissubstitution reactions,[8] thioacetalization of carbonyl compounds, transthioacetalization and deprotection of acetals[9, 10] have been reported. In continuation of these studies we now report an efficient and highly regioselective ring expansion-chlorination reaction of 2-aryl-2-methyl-1,3-dithiolanes **1a,b** and 1,3-dithianes **2a,b** with electron-donating substituent on aromatic rings to produce the corresponding chlorinated dihydro-1,4-dithiin **3a,b** and 1,4-dithiepines **4a,b** by using WCl_6/DMSO in CH_2Cl_2 (Scheme1, Table).

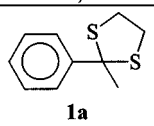
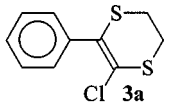
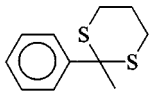
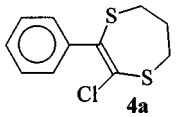
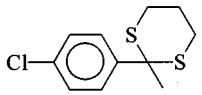
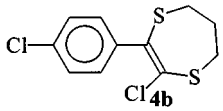
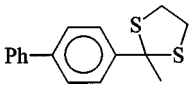
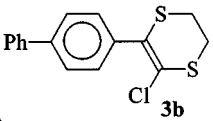
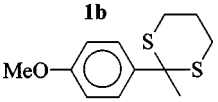
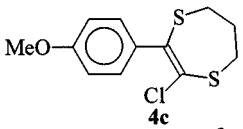
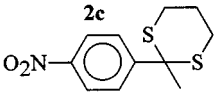
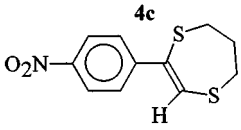
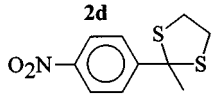
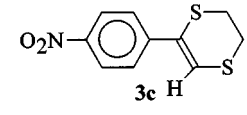


1 (n = 0)
2 (n = 1)

3 (n = 0)
4 (n = 0)

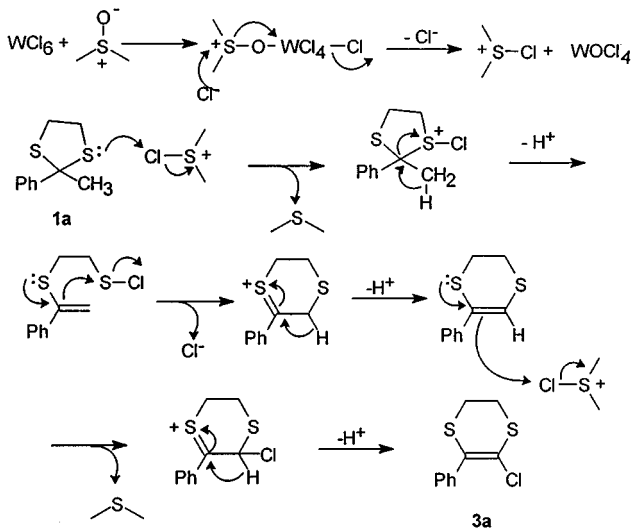
Scheme 1

Table. Ring Expansion-Chlorination of 1,3-Dithiolanes and 1,3-Dithianes by WCl_6 /DMSO in CH_2Cl_2

Substrate 1, 2	Product 3, 4	Time (min)	Yield [a, b] (%)
 1a	 3a	30	90
 2a	 4a	30	91
 2b	 4b	20	88
 1b	 3b	12	89
 2c	 4c	30	30[c,d]
 2d	 4d	15	95
 1c	 3c	15	90

a) Yields refer to isolated products. b) The molar ratio of substrates/ WCl_6 / DMSO were 1 / 0.8 / 3. c) 4-methoxy acetophnone was formed in 60% yield. d) NMR yield.

^{1}H-NMR, ^{13}C-NMR, and mass spectra of the isolated products clearly showed the formation of the chlorinated products.[11] However, the presence of a nitro group as an electron withdrawing group on aromatic ring (**1c, 2c**) strongly retards the chlorination reaction, and only the rearrangement product **3c, 4c** were formed in excellent yields (Table).[11] This observation indicates that the formation of the chlorinated products probably goes through cationic intermediates. In all reactions fast liberation of dimethyl sulfide was also detected, therefore, we propose here a potential mechanism, which indicates the role of DMSO, cationic character of reaction intermediates, and the formation of the chlorinated products (Scheme 2). The reactions proceeded cleanly without formation of polymeric material and the analytical data were also in accord with the proposed structures. This method is not suitable for aliphatic substrates that produce a mixture of unidentified products.



Scheme 2

To the best of our knowledge this method is the first example of one-pot ring expansion-chlorination of 1,3-dithianes and 1,3-dithiolanes derived from the corresponding substituted acetophenones.

Further investigations about the new synthetic applications of WCl_6 and its related compounds are under study in our laboratories.

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(11) *A typical experimental procedure is as follows:* To a solution of 2-phenyl-2-methyl-1,3-dithiolane **1a** (393 mg, 2mmol), and dry DMSO (469 mg, 6 mmol), in dry CH_2Cl_2 (20 mL) was added WCl_6 (634 mg, 1.6 mmol) and the resulting solution was stirred at room temperature. The progress of the reaction was monitored by TLC (CCl_4 as eluent). After completion (30 min), the reaction was quenched with an aqueous solution of NaOH (10%, 25 mL), and extracted with CH_2Cl_2 (3 × 25 mL). The organic extracts were washed successively brine (15 mL), and water (2 × 10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the crude product. Further purification was performed using chromatography over a short column of silica gel (CCl_4 as eluent) which after evaporation of the solvent afforded the desired oily pure product **3a** (412 mg, 90% yield).
3a: ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.10 (m, 4H), 7.18 (m, 5H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 30.21, 32.20, 113.14, 126.28, 128.36, 128.46, 129.67, 145.75; MS (20 eV) m/z (relative intensity) 228 (M^+, 74.0), 200 (M^+ - CH_2=CH_2, 26.3), 165 (36.3), 121 (100), 77 (15.9).
4a : ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 2.18 (m, 2H), 3.50-3.75 (m, 4H), 7.24-7.48 (m, 5H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 30.38, 31.97, 33.40, 120.58, 128.42, 129.67, 134.56, 140.01; MS (20 eV) m/z (relative intensity) 242 (55.1), 168 (16.7), 136 (9.4), 121 (M/2, 12.0), 89 (25.7), 73 (100).
4b: ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 2.10-2.20 (m, 2H), 3.45-3.50 (m, 4H), 7.24-7.36 (m, 4H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 29.47, 33.12, 33.55, 121.29, 128.84, 131.44, 133.17, 134.54, 138.59; MS (20 eV) m/z (relative intensity) 276 (M^+, 30.2), 202 (10.7), 170 (8.4), 138 (M/2, 12.2), 123 (20.2), 73 (100).
3b: ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.15 (m, 4H), 7.35-7.50 (m, 9H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 29.72, 31.83, 112.95, 125.40-129.70 (8 carbon atoms), 138,93; MS (20 eV) m/z (relative intensity) 304 (M^+, 65.7), 276 (M^+ - CH_2=CH_2, 29.3), 241 (18.0), 197 (100.0), 153 (12.0).
3c: ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 3.27-3.33 (m, 4H), 6.64 (s, 1H), 7.82-8.30 (dd, 4H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 27.11, 27.17, 117.52, 123.85, 123.86, 125.67, 126.12, 146.15; MS (20 eV) m/z (relative intensity) 240 (M^+, 100), 211 (M^+ - CH_2=CH_2, 4.0), 166 (26.1), 121 (26.2), 89 (11.5).
4d: ^{1}H-NMR ($CDCl_3$, 250 MHz) δ = 2.20-2.29 (m, 2H), 3.30-3.70 (m, 4H), 6.28 (s, 1H), 7.61-8.15 (dd, 4H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ = 29.9, 30.74, 32.95, 121.28, 122.87, 123.57, 127.72, 127.75, 146.67; MS (20 eV) m/z (relative intensity) 254(M^+, 88.6), 166 (12.4), 150 (11.9), 106 (39.5), 89 (37.3).