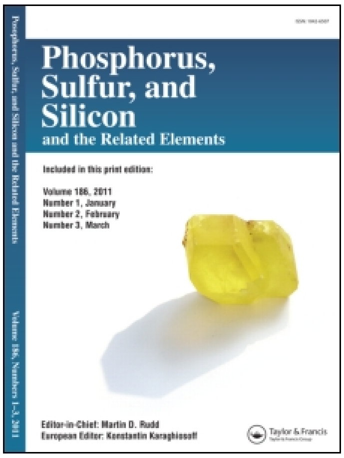

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MOLYBDENUM PENTACHLORIDE (MOCL$_5$) PROMOTES EFFICIENT RING-EXPANSION AND RING-EXPANSION-CHLORINATION OF 1,3-DITHIOLANES AND 1,3-DITHIANES IN THE PRESENCE OF DMSO. PART 3[1]

Habib Firouzabadi[a]; Babak Karimi[a]
[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran

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MOLYBDENUM PENTACHLORIDE ($MOCL_5$) PROMOTES EFFICIENT RING-EXPANSION AND RING-EXPANSION-CHLORINATION OF 1,3-DITHIOLANES AND 1,3-DITHIANES IN THE PRESENCE OF DMSO. PART 3[1]

HABIB FIROUZABADI* and BABAK KARIMI

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

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Ring-expansion and ring-expansion-chlorination of 1,3-dithiolanes and dithianes conducted in the presence of $MoCl_5$ and DMSO are described.

Keywords: Molybdenum pentachloride; thioacetals; ring-expansion; ring- expansion-chlorination; dithiolanes; dithianes; dimethylsulfoxide

INTRODUCTION

The annelation reactions of 1,3-dithiolanes and 1,3-dithianes generally have been employed for the construction of rings fused to heterocyclic molecules (Scheme 1).

Surveying the literature reveals that very few examples of ring enlargement of 1,3-dithiolanes and 1,3-dithianes are known and their chemistry is little explored. Wilson in 1965 showed that treatment of 2,2-dimethyl-1,3-oxathiolane with chlorine in a refluxing mixed solvent CH_2Cl_2 / CCl_4 afforded 2-methyl-1,4-oxathiene in 54% isolated yield (Scheme 2). This method has been also applied successfully to other compounds.[2]

Phenyl selenyl chloride [PhSeCl] has been also used for mild ring enlargement of 1,3-dithiolanes and 1,3-dithianes (Scheme 3).[3]

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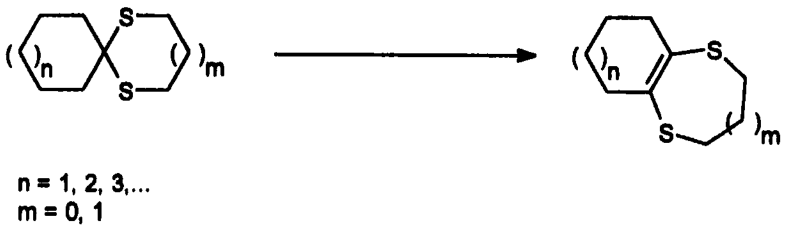
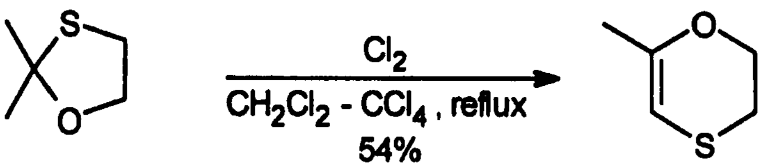
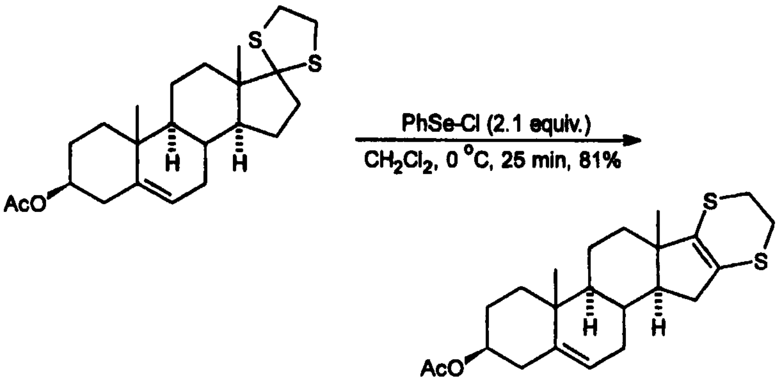
* Corresponding Author: E mail: firouzabadi@chem.susc.ir, Fax: Int. (0711) 2220027,



SCHEME 1

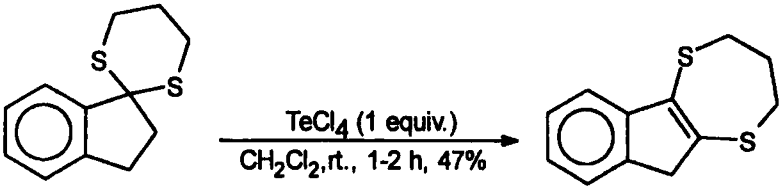


SCHEME 2



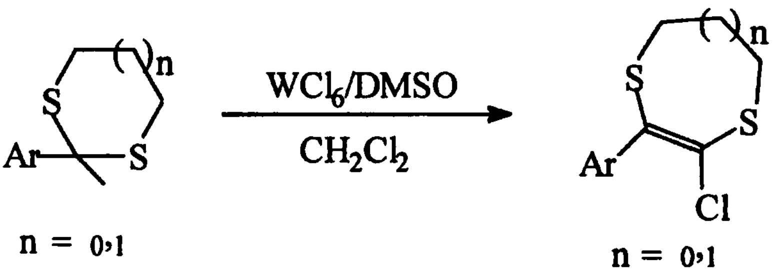
SCHEME 3

Ring expansion of 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes in the presence of $TeCl_4$ has been recently reported (Scheme 4).[4,5]



SCHEME 4

We have reported that WCl_6 was able to promote this type of transformation efficiently under mild reaction conditions. In addition, for the first time,[6] we explored and reported that WCl_6 in CH_2Cl_2 was able to conduct a useful one-pot ring-enlargement-chlorination of some 1,3-dithianes and 1,3-dithiolanes (Scheme 5). This reaction was quite solvent dependent and e.g. in CH_3CN only ring-expansion had occurred.



SCHEME 5

Now, in this article, we report the reactions of dithioacetals, 1,3-dithiolanes and 1,3-dithianes in the presence of molybdenum pentachloride ($MoCl_5$) and DMSO in CH_2Cl_2.

RESULTS AND DISCUSSION

In this study first 2-phenyl-2-methyl-1, 3-dithiolane was subjected to react in the presence of $MoCl_5$ as a catalyst in dry DMSO. TLC monitoring of the reaction mixture showed that a single product was formed. Surprisingly, this product was neither a ketone nor the starting *S,S*-acetal. ^{1}H-NMR spectrum of the product showed two single multiplet one at 6 = 7.18 (m, 5H) and the other at δ= 3.10 (m, 4H). The appearance of a single multiplet around δ3.10 ppm and the absence of absorption for a methyl group in the ^{1}H-NMR spectrum of this product strongly suggested the existence of the dihydro-1, 4-dithiin moiety (Fig. 1) in the skeletal structure of the product in this investigation.

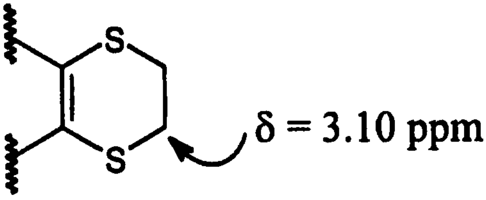
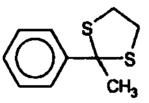
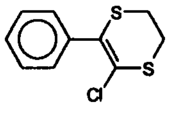
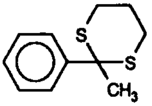
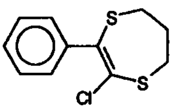
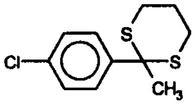
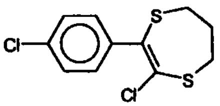
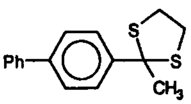
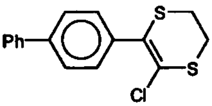
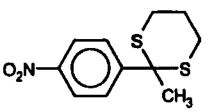
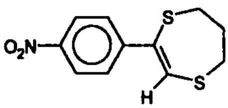
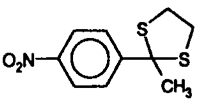
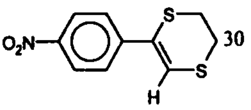


FIGURE 1 Skeletal structure of the dihydro-1, 4-dithiin moiety

^{13}C-NMR spectrum of the product at 63 MHz showed the following bands: δ = 30.21, 32.20, 113.14, 126.28–126.67 (4 peaks, aromatic region), 145.75. The peaks around δ 30–32 ppm belong to the saturated ring carbons, which are bonded to sulfur atoms. The absorption bands between 126–127 are clearly due to the presence of a phenyl group and the peaks at 113.14 and 145.75 are related to a sp^2 olefinic carbon-carbon double bond. However, the absorption bands around 145.75 are deshielded, presumably due to the bonding of an electronegative group (perhaps a chlorine atom) to the olefinic carbons. Interestingly, the mass spectral fragmentation pattern for this compound was in quiet agreement with 2-chloro-3-phenyl-5, 6-dihydro-1, 4-dithiin **1** and (Scheme 6).

The novelty of the reaction prompted us to apply this method for the one-pot ring expansion-chlorination of 1,3-dithiolanes and 1,3-dithianes in the presence of $MoCl_5$ as a catalyst and dry DMSO in CH_2Cl_2. Various types of 2-aryl-2-methyl-1,3-dithiolanes and 2-aryl-2-methyl-1,3-dithianes with electron-donating and electron-withdrawing substituents were examined. Treatment of 1,3-dithiolanes and 1,3-dithianes of arylalkyl ketones with $MoCl_5$ (0.9 equiv.) and dry DMSO (3 equiv.) in CH_2Cl_2 resulted in the corresponding chlorinated dihydro-1, 4-dithiins and dihydro-1, 4-dithiepines in good yields (Table I, entriesl-4).

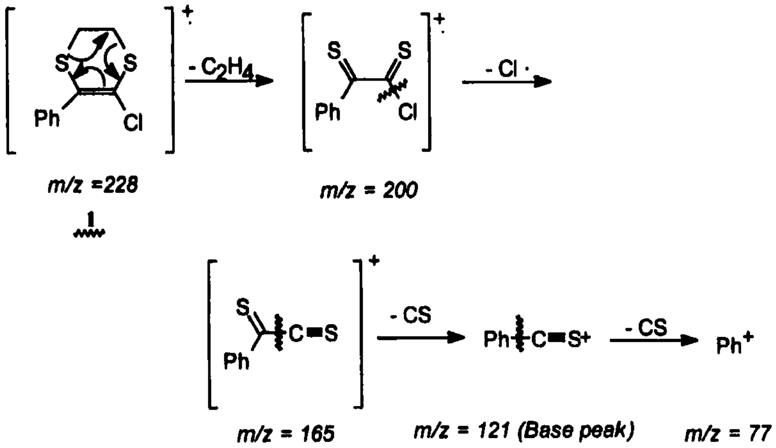
TABLE I Ring Expansion and Ring-Expansion-Chlorination of 1,3-Dithiolanes and 1,3-Dithianes by $MoCl_5$/DMSO in CH_2Cl_2

entry	*substrate*	*product*	*time* *(min)*	*yield*^{a,b} *(%)*
1			40	85
2			60	75
3			70	80
4			40	79
5			30	89
6			30	82

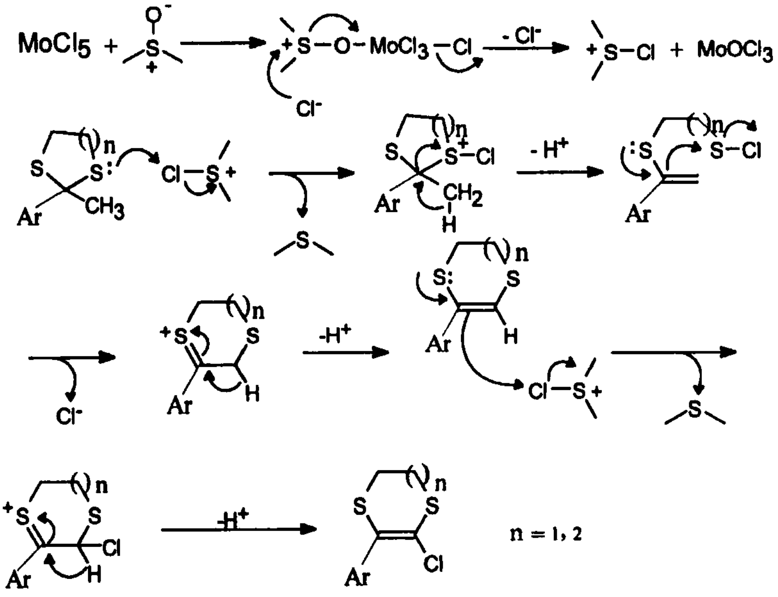
a. Yields refer to isolated products.

b. The molar ratio of the substrates/ $MoCl_5$ / DMSO were 1 / 0.9 / 3.

A chlorination reaction was not observed for the substrates in which the aromatic ring carries a strong electron-withdrawing group such as $-NO_2$ (Table I, entries 5,6). This observation suggests that the formation of a carbonium ion intermediate in the reaction pathway is probable. Therefore, by considering this proposal, we have suggested the following reaction pathway (Scheme 7).



SCHEME 6



SCHEME 7

EXPERIMENTAL

General

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Companies. Most of the products were purified by column chromatography or recrystallization from appropriate solvents and were identified by comparison of their mp, bp, IR, MS, NMR with those reported for the authentic samples. Progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates or by GC using a Shimadzu gas chromatograph GC-14A, equipped with a flame ionization detector and a 3 meters length glass column packed with DC-200 stationary phase and nitrogen as the carrier gas. IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. NMR spectra were recorded using a Bruker Avance DPX 250 MHz instrument. Mass spectra were run on a Shimadzu GC MS-QP 1000 EX.

Ring-expansion-chlorination of 2-phenyl-2-methyl-1, 3-dithiolane with $MoCl_5$ in the presence of dry DMSO in dry CH_2Cl_2: a typical procedure

To a solution of 2- phenyl-2-methyl-1, 3-dithiolane (392 mg, 2 mmol), and dry DMSO (468 mg, 6 mmol), in dry CH_2Cl_2 (20 ml) was added $MoCl_5$ (492 mg, 1.8 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 (40 min), the reaction was quenched with an aqueous solution of NaOH (10%, 30 ml), and extracted with CH_2Cl_2 (3 × 25 ml). The organic extracts were combined and were washed successively with brine (15 ml), and water (2 × 15 ml). The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the oily pure product in 85% yield (TableI, entry 1). ^{1}H-NMR ($CDCl_3$, 250 MHz) $\delta = 3.10$ (m, 4H), 7.18 (m, 5H); ^{13}C-NMR ($CDCl_3$, 63 MHz) $\delta = 30.21$, 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).

Elemental analysis calculated for $C_{10}H_9S_2Cl$; C: 52.5%, H: 3.9%, Cl: 15.53%, S: 28%; found; C: 52.65 %, H: 4%, Cl: 15.22%, S: 27.9%.

Acknowledgements

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