Reactions of Silica Chloride (SiO_2Cl)/DMSO, a Heterogeneous System for the Facile Regeneration of Carbonyl Compounds from Thioacetals and Ring-Expansion Annelation of Cyclic Thioacetals

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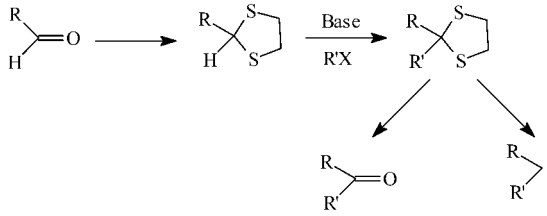
Silica chloride (SiO_2Cl)/DMSO, as a heterogeneous system, has been efficiently used for deprotection of thioacetals into aldehydes in dry CH_2Cl_2 at room temperature. Thioketals without enolizable hydrogens adjacent to a sulfur atom are converted easily to the corresponding ketones in high yields under similar reaction conditions. However, thioketals with enolizable methyl and methylene groups undergo ring-expansion reactions to afford 1,4-dithiepins and 1,4-dithiins in dry CH_2Cl_2 at room temperature in good yields.

Introduction

Protection of carbonyl groups, as their cyclic thioacetals, is an important functional group transformation. Thioacetals often serve as precursors of acyl anion equivalents and masked methylene functions (Scheme 1).[1] High stability of *S*,*S*−acetals in comparison with *O*,*O*-acetals toward different reaction conditions reveals the significance of thioacetals as protecting groups in organic synthesis. Conversion of thioacetals at mild reaction conditions into carbonyl compounds is an important transformation but is not a straightforward process. Therefore, a plethora of methods using heavy metal salts,[1] such as $HgCl_2$, $HgO/BF_3{\cdot}Et_2O$, CAN, SeO_2,[2] which are very toxic, nonmetallic reagents such as the oxide of nitrogen,[3a] trisethyloxonium tetrafluoroborate,[3b] and methyl fluorosulfonate,[3c] are used for this purpose. The preparation of these reagents and also their handlings are not so easy, especially for the large-scale operations.

Photolytic methods and electrochemical techniques have also been used,[4] but they require expensive equipment even though they are safe to the environment. Bi$(NO_3)_3$[5a] and clay-supported Fe$(NO_3)_3$[5b] have been successfully used in solution and also under solvent-free conditions for this aim. Some other reported methods included the use of clay-supported ammonium nitrate (clayan),[6a] bis(trifluoroacetoxy)iodobenzene,[6b] DDQ,[6c] gallium chloride/H_2O or MeOH/O_2,[6d] zirconium sulfenyl phosphonate $\{Zr(O_3Pme)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}\}$,[6e] a mixture of DMSO with I_2,[6f] HCl/H_2O/dioxane,[6g] trimethylsilyl chloride (TMSCl),[6h] and *tert*-butyl bromide.[6i] Natural kaolinitic clay has also been used as a reusable solid catalyst for the selective dethioacetalization.[7] Very recently, reagents for the preparation and cleavage of 1,3-dithiolanes have been reviewed.[8]

Scheme 1



Scheme 2

The ring-expansion annelation reactions of cyclic thioacetals as 1,3-dithiolanes and 1,3-dithianes can be primarily used for the construction of larger rings containing sulfur atoms (Scheme 2).

A literature review shows that very few examples of ring enlargement reactions of 1,3-dithiolanes and 1,3-

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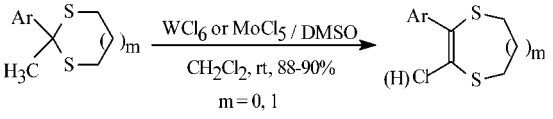
Scheme 3



dithianes are reported. Treatment of 1,3-dithiolanes and 1,3-dithianes with phenyl selenyl chloride (PhSeCl) resulted in ring-expansion reactions in some steroidal compounds.[9] 2,2-Dimethyl-1,3-oxathiolane with chlorine in a refluxing mixed solvent, CH_2Cl_2/CCl_4, produced 2-methyl-1,4-oxathiene in only 54% isolated yield. This method has also been used successfully for other compounds.[10] $TeCl_4$ has also mediated the ring-expansion reactions of 1,3-dithiolanes, 1,3-dithianes, and 1,3-oxathiolanes.[11]

In recent years, we have been involved in exploring some new applications of tungsten hexachloride (WCl_6), molybdenum pentachloride ($MoCl_5$), and zirconium tetrachloride ($ZrCl_4$) in organic synthesis.[12] Along this line, we have found that WCl_6 and $MoCl_5$ in the presence of DMSO are efficient reagents for the facile deprotection of thioacetals and one-pot ring-expansion and ring-expansion chlorination of cyclic thioacetals. Ring-expansion chlorination reaction is the first reported in the literature (Scheme 3).

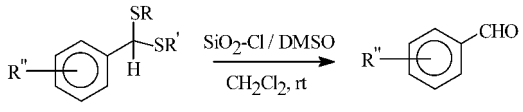
Silica gel treated with thionyl chloride has been used as a catalyst for the selective thioacetalization of carbonyl compounds.[13] We have recently reported a modified procedure for the production of a highly efficient silica chloride that has been used for the transthioacetalization of acetals, transformation of acylals into thioacetals, and dehydration of tertiary benzylic alcohols to olefins.[14] Now we report dethioacetalization of thioacetals into carbonyl compounds, ring-expansion annelation, and one-pot ring-expansion chlorination of cyclic thioacetals using solid silica chloride (SiO_2Cl) in the presence of DMSO.

Results and Discussion

Silica chloride can be prepared very easily from cheap starting materials with high yields. This solid polymeric compound is a mild oxophilic reagent, and its handling is much easier than those of $SOCl_2$ and TMSCl, which have toxic and corrosive vapors. In this study we have applied SiO_2Cl/DMSO as a new heterogeneous system for deprotection of thioacetals into aldehydes in dry CH_2Cl_2 at room temperature (Scheme 4, Table 1). The reactions were easy and clean and proceeded under mild reaction conditions in high yields.

As shown in Table 1, open-chain and cyclic thioacetals (1,3-dithiolanes or 1,3-dithianes) of aromatic aldehydes were cleanly converted into their corresponding aldehydes in excellent yields (Table 1, entries 1a−1k, 1q, and 1r). 2-Cinnamyl-1,3-dithiane and its 1,3- dithiolane derivative were successfully converted to cinnamaldehyde in high yields (Table 1, entries 1l and 1m). In these reactions silica chloride acts as an oxophilic and activating reagent for DMSO to generate dimethylsulfonium chloride. DMSO also acts as a source of oxygen in these reactions. We believe that dimethylsulfonium chloride is the responsible intermediate for these reactions to occur. Therefore, we have generated this active species by independent known methods[6h,15] and added it to the solution of 2-(4-toluyl)-1,3-dithiane to obtain toluyl aldehyde in a high yield. In all reactions, a sticky polymeric material plus fast liberation of dimethyl sulfide was also detected. Therefore, we have proposed a mechanism in which the role of DMSO, silica chloride, and dimethylsulfonium chloride in the dethioacetalization reactions is clarified (Scheme 5).

Scheme 4

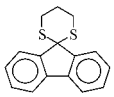


1 **2**

R, R' = -CH_2CH_2-, -$CH_2CH_2CH_2$-, R = R' = n-butyl

R" = H, 4-Me, 4-Cl, 3-MeO, 4-MeO

Table 1. Deprotection of Thioacetals with SiO_2Cl/DMSO in CH_2Cl_2

Entry	R"	R, R'	time (min.)	Yield[a,b,c,d] (%)[l]
1a	H	-CH_2CH_2-	40	94
1b	H	-$CH_2CH_2CH_2$-	35	92
1c	4-CH_3-	-CH_2CH_2-	35	96
1d	4-CH_3-	-$CH_2CH_2CH_2$-	30	94
1e	4-CH_3O-	-CH_2CH_2-	40	91
1f	3-CH_3O-	-$CH_2CH_2CH_2$-	45	90
1g	2-CH_3-	-$CH_2CH_2CH_2$-	40	91
1h	3-CH_3-	-$CH_2CH_2CH_2$-	35	93
1i	4-Br	-$CH_2CH_2CH_2$-	60	91
1j	4-NO_2	-$CH_2CH_2CH_2$-	90	89
1k	4-Cl	-$CH_2CH_2CH_2$-	75	90
1l		2-Cinnamyl-1,3-dithiolane	60	91
1m		2-Cinnamyl-1,3-dithiane	65	92
1n		2,2-diphenyl,1-3-dithiolane	60	95
1o		2,2-diphenyl,1-3-dithiane	65	96
1p			60	90
1q	H	n-Bu	70	88
1r	2-Cl	n-Bu	95	89

[a] Isolated yields. [b] Structures are confirmed by IR, ^1H NMR, ^{13}C NMR, and mp/bp. [c] GC purity >95%. [d] The ratio of the substrate/SiO_2Cl/DMSO was 1 mmol/1.4 g/6−8 mmol.

Thioacetals derived from ketones show quite a different behavior. In the case of thioacetals derived from ketones without enolizable hydrogen, deprotection proceeded very well to give the corresponding ketones in high yields (Table 1, entries 1n−1o) in CH_2Cl_2 at room temperature. It is important to note that cyclic thioacetals derived from ketones with enolizable hydrogen rearranged to the corresponding dihydro-1,4-dithiins or -1,4-dithiepins in good yields (Scheme 6, Table 2).

When silica chloride was added to the solution of 2-methyl-2-phenyl-1,3-dithiane and DMSO in dry CH_2-

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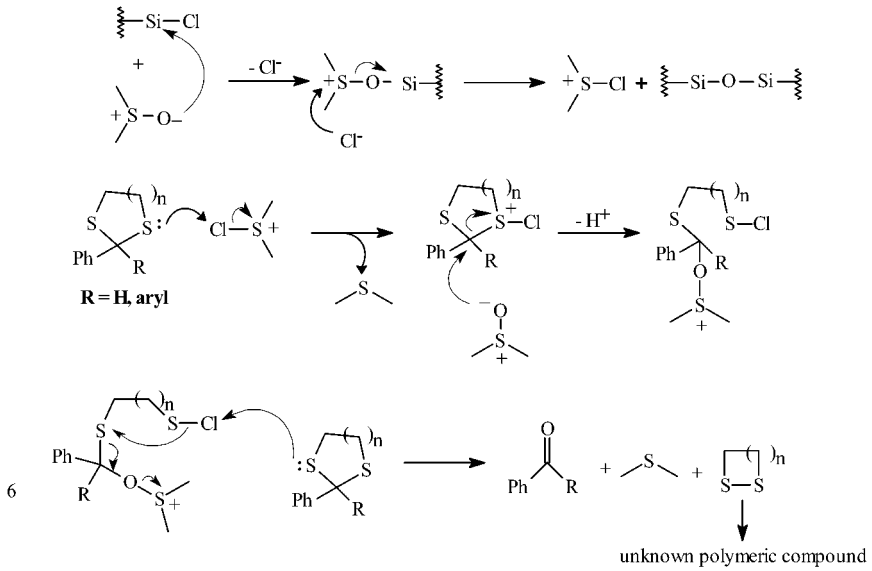
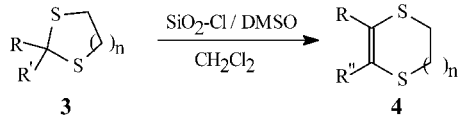
Scheme 5

Suggested mechanism 1



Scheme 6

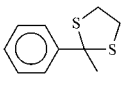
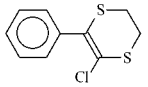
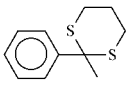
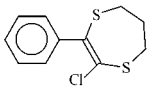
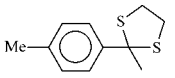
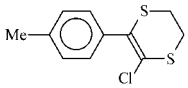
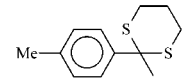
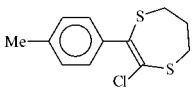
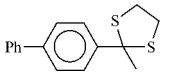
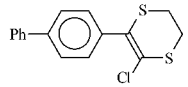
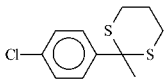
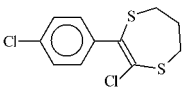
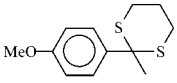
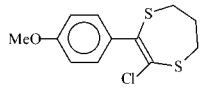
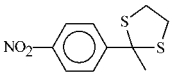
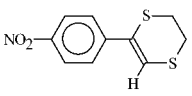
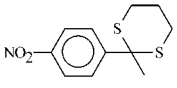
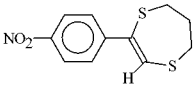


R = Ph, Benzyl, 4-Cl-C_6H_4, 4-NO_2-C_6H_4, 4-MeO-C_6H_4, $PhCOCH_2$,
R' = Me, Et, Benzyl, R" = Ph, Me, Cl, n = 1,2

Cl_2, 2-chloro-3-phenyl-5,6,7-trihydro-1,4-dithiepin was produced in a high yield (Table 2, entry 3a). When we applied a similar reaction to 1,3-dithianes and 1,3-dithiolanes derived from different acetophenones, ring-expansion chlorination reaction also proceeded very smoothly and the chlorinated products were obtained in good to high yields (Table 2, entries 3a−3f). 2-Methyl-2-(4-methoxyphenyl)-1,3-dithiolane undergoes ring-expansion chlorination and dethioacetalization reactions to produce the expected products in 27% and 65−70% yields, respectively (Table 2, entry 3g). However, the presence of a nitro group as a strong electron-withdrawing group on the aromatic ring (Table 2, entries 3h and 3i) effectively retards the chlorination reaction, and only the rearrangement products 4h and 4i were obtained in 89% and 87%, respectively. This observation indicates that cationic intermediates may be involved in the formation of the chlorinated products. In addition, in all reactions in this study, fast liberation of dimethyl sulfide was also detected. Therefore, we proposed a mechanism in which the role of DMSO, the cationic character of the reaction intermediates, and the formation of the chlorinated products are clarified (Scheme 7).

We have also extended the application of the method to thioacetals prepared from ketones with enolizable methylene groups to prepare different derivatives of 1,4-dithiepins and 1,4-dithiins. For this purpose several 1,3-dithiolanes and a 1,3-dithiane were synthesized and subjected to SiO_2Cl/DMSO in CH_2Cl_2 at room temperature.[14] We have found that 2,2-bisbenzyl-1,3-dithiolane was converted successfully to 2-phenyl-3-benzyldihydro-1,4-dithiin as a purple-red viscous liquid in 75% yield (Table 3, entry 3j). 2-Ethyl-2-phenyl-1,3-dithiolane under similar reaction conditions was converted to 2-methyl-3-phenyl-

Table 2. Ring-Expansion Chlorination of 1,3-Dithiolanes and 1,3-Dithianes by SiO_2Cl/DMSO in CH_2Cl_2

Entry	Substrate	Product	Time (h)	Yield [a, b)12] (%)
3a			1.5	80
3b			1.5	82
3c			2	65
3d			2.2	60
3e			2	85
3f			1.5	84
3g			0.8	27
3h			1	89
3i			1	87

[a] Yields refer to isolated product. [b] The molar ratio of substrates/SiO_2Cl/DMSO was 1 mmol/1.8 g/3−4 mmol.

dihydro-1,4-dithiin as an off white oil in 80% yield (Table 3, entry 3k). 1,3-Dithiolane derived from 4-phenylcyclohexanone was converted into its corresponding dithiin

Scheme 7

Suggested mechanism 2:

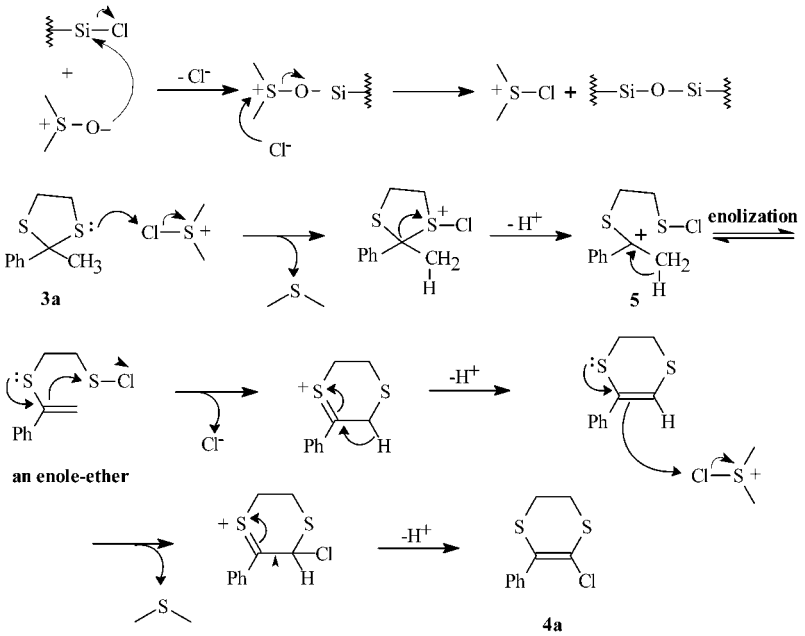
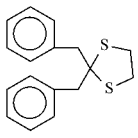
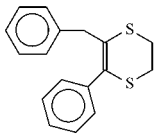
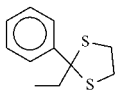
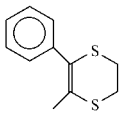
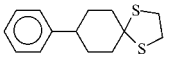
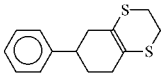
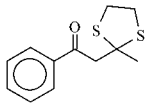
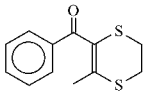
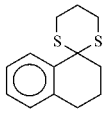
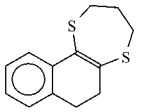


Table 3. Preparation of Substituted 1,4-Dithiins and Dithiepins by Ring-Expansion Reactions of 2,2-Substituted 1,3-Dithiolanes and 1,3-Dithianes in the Presence of SiO_2Cl/DMSO in CH_2Cl_2

Entry	Substrate	Product	Time (h)	Yield [a, b][11] (%)
3j			1.8	75
3k			1.5	80
3l			2	65
3m			1.5	87
3n			1.6	60

[a] Yields refer to isolated products. [b] The molar ratio of substrates/SiO_2Cl/DMSO was 1 mmol/1.2 g/3−4 mmol.

as an off white oily material in 65% yield (Table 3, entry 3l).

To show that the methylene groups with more enolizable hydrogen undergo rearrangement reactions, we have selectively prepared 2-methyl-2-(benzoylmethyl)-1,3-dithiolane.[16] Then, this compound was reacted with SiO_2-Cl/DMSO in CH_2Cl_2 at room temperature, and as was expected, 2-methyl-3-benzoyldihydro-1,4-dithiin was isolated as a light green oily compound in 87% yield (Table 3, entry 3m). 1,3-Dithane derived from α-tetralone was also rearranged into the corresponding dithiepin in 60% yield as a red oily compound (Table 3, entry 3n).

The reactions proceeded cleanly without the formation of polymeric materials at room temperature. However, the amounts of polymeric materials and carbonyl compounds increase at higher temperatures. This method does not work properly for aliphatic thioacetals and always gives a mixture of products that are not identified.

Conclusions

In conclusion, we have introduced a new method for the deprotection of thioacetals derived from aldehydes and ketones without enolizable hydrogens. We have also shown that, by this method, cyclic thioacetals with enolizable hydrogens undergo ring-expansion, one-pot ring-expansion chlorination, and ring-expansion annelation reactions with good yields. We believe that this method is general and could be employed for the synthesis of complex derivatives of dithiins and dithiepins.

Experimental Section

General Procedure for Dethioacetalization of Thioacetals and Thioketals with DMSO/SiO_2Cl in CH_2Cl_2. To a solution of 1,3-dithiolanes or 1,3-dithianes, substituted benzaldehyde (2 mmol), and dry DMSO (12−16 mmol) in dry CH_2Cl_2 (25 mL) was added silica chloride (2.8 g), and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After completion (30−95 min), the reaction was quenched with an aqueous solution of NaOH (10%, 25 mL) and extracted with CH_2Cl_2. The organic extracts were combined together, washed successively with brine and water, separated, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford the almost pure product(s). Further puri-

(16) Firouzabadi, H.; Iranpoor, N.; Amani, K. *Synthesis* **2002**, 59−62.

fication was achieved by column chromatography on silica gel (eluent, petroleum ether (60−80 °C)/EtOAc, 5/1) to give the desired product(s) in good to excellent yields (Table 1, entries 1a−1r; 88−96%).

Ring-Expansion Chlorination of 2-Phenyl-2-methyl-1,3-dithiolane to the Corresponding Chlorinated Dihydro-1,4-dithiin with SiO_2Cl/DMSO in Dry CH_2Cl_2 as a Typical Procedure. To a solution of 2-phenyl-2-methyl-1,3-dithiolane (0.40 g, 2 mmol) and dry DMSO (0.47 g, 8 mmol) in dry CH_2Cl_2 (25 mL) was added silica chloride (3.6 g), and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (CCl_4 as eluent). After completion (80 min), the reaction was quenched with an aqueous solution of NaOH (10%, 25 mL) and extracted with CH_2Cl_2. The organic extracts were washed successively with brine and water, separated, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product. Further purification was achieved by column chromatography using a short column of silica gel (CCl_4 as eluent) to afford the desired pure product as a light brown oily compound (Table 2, entry 3a; 0.34 g, 80% yield): ^{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 ppm; MS (20 eV) *m*/*z* (relative intensity) 230 ($M^+ + 2$, 25.2), 228 (M^+, 74.0), 200 ($M^+ - CH_2{=}CH_2$, 26.3), 165 (36.3), 121 (100), 77 (15.9).

General Procedure for the Ring Expansion of 2,2-Disubstituted Thioacetals to the Corresponding Dihydro-1,4-dithiin and Dithiepins with SiO_2Cl/DMSO in Dry CH_2Cl_2. To a solution of 2,2-disubstituted thioacetals (2 mmol) and dry DMSO (0.35 g, 6 mmol) in dry CH_2Cl_2 (25 mL) was added silica chloride (2.4 g), and the resulting mixture was stirred at room temperature. After completion (1.6−2 h, monitored by TLC, eluent CCl_4), the reaction was quenched with an aqueous solution of NaOH (10%, 25 mL), and extracted with CH_2Cl_2. The organic extracts were combined together, washed successively with brine and water, separated, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude products. Further purification was achieved by preparative thin-layer chromatography (CCl_4 as eluent) to afford pure products (Table 3, entries 4j−4n; 60−87%).

Data for 2-Phenyl-3-benzyldihydro-1,4-dithiin (4j): purple-red viscous liquid; 0.43 g, 75% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 3.18−3.26 (m, 4H), 3.49 (s, 2H), 7.18−7.48 (m, 10H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 29.25, 31.28, 41.55, 124.37, 127.18, 127.58, 128.29, 128.66, 129.77, 130.05, 139.65, 140.12, 145.75; MS (20 eV) *m*/*z* (relative intensity) 284 (M^+, 100), 223 ($M^+ - SC_2H_5$, 28.5), 191 (23.4), 121 (31.5), 91 (28.6). CHN Anal: C (calcd 71.78, found 71.45), H (calcd 5.67, found 5.64).

Data for 2-Methyl-3-phenyldihydro-1,4-dithiin (4k): off white oil; 0.33 g, 80% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.82 (s, 3H), 3.27 (m, 4H), 7.18−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 22.51, 29.73, 30.09, 121.12, 124.60, 127.92, 128.21, 129.99, 140.29; MS (20 eV) *m*/*z* (relative intensity) 208 (M^+, 100), 180 ($M^+ - C_2H_4$, 22.9), 147 ($M^+ - SC_2H_5$, 31.4), 121 (44.7). CHN Anal.: C (calcd 63.42, found 63.22), H (calcd 5.81, found 5.80).

Data for Dithiin (4l): off white oil; 0.37 g, 65% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.89−1.97 (m, 2H), 2.29−2.34 (m, 4H), 2.81−3.10 (m, 1H), 3.20−3.47 (m, 4H), 7.17−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 28.79, 30.54, 34.08, 40.13, 41.39, 43.27, 119.36, 119.69, 126.53, 126.74, 128.88, 145.93; MS (20 eV) *m*/*z* (relative intensity) 248 (M^+, 100), 189 (9.9), 149 (13.9), 144 (51.1), 131 (89.2), 105 (27.2), 91 (10.2). CHN Anal.: C (calcd 67.92, found 67.85), H (calcd 6.49, found 6.45).

Data for 2-Methyl-3-benzoyldihydro-1,4-dithiin (4m): light green oil; 0.41 g, 87% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.88 (s, 3H), 3.10−3.27 (m, 4H), 7.34−7.52 (m, 3H), 7.80−7.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 23.33, 27.35, 32.74, 121.85, 128.41, 129.00, 130.01, 133.75, 137.16, 193.70; MS (20 eV) *m*/*z* (relative intensity) 236 (M^+, 62.2), 176 ($M^+ - SC_2H_4$, 22.5), 147 (5.0), 119 (25.9), 105 (100), 77 (32.9). CHN Anal.: C (calcd 60.98, found 61.01), H (calcd 5.12, found 5.12).

Dithiepin (4n): break oily compound; 0.28 g, 60% yield; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.80−1.92 (m, 1H), 2.14−2.18 (m, 1H), 2.39−2.42 (m, 1H), 2.68−2.87 (m, 5H), 3.22−3.28 (m, 2H), 7.05−7.77 (m, 4H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 29.14, 30.91, 32.41, 34.20, 37.38, 124.41, 126.86, 128.66 133.73, 135.08, 136.04, 136.60, 140.94; MS (20 eV) *m*/*z* (relative intensity) 234 (M^+, 100), 205 (7.6), 160 (9.3), 129 (10.1), 115 (7.7), 73 (6.9). CHN Anal.: C (calcd 66.62, found 66.45), H (calcd 6.02, found 6.01).

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