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Novel reaction patterns of carbon disulfide with organolithium compounds via cleavage of C=S bonds or via cycloaddition reactions

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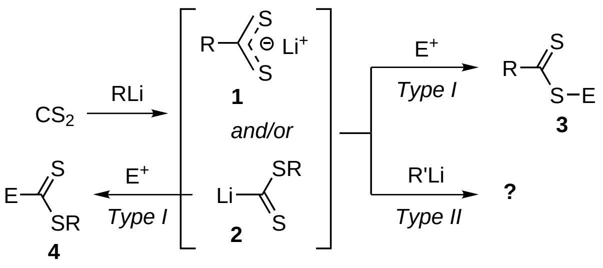
Abstract—Carbon disulfide reacted at room temperature with 1,4-dilithio-1,3-diene species via cleavage of the C=S double bonds affording multiply substituted thiophenes or via cycloaddition reactions affording thiopyran-2-thiones. © 2002 Elsevier Science Ltd. All rights reserved.

The dual nature of reactivities of thiocarbonyl groups including CS_2 has attracted much attention for the preparation of S-containing heterocycles as well as for investigations into reaction mechanisms.[1] Although addition reactions of thiocarbonyl compounds with organolithium regents have been known for decades, their reaction mechanisms are still in debate and synthetically useful methods based on these fundamental reactions are very rare.[1] The most promising synthetic application so far has been the preparation of dithiocarboxylates **1** (the carbophilic addition intermediates) and/or the thiophilic addition intermediates **2** and related compounds, by addition of organolithium reagents to CS_2 as shown in Scheme 1.[1,2] In principle, the in situ generated dithiocarboxylates **1** and/or the thiophilic addition intermediates **2** can undergo two types of further reactions (Scheme 1): Type I with electrophiles such as alkyl halides and Type II with nucleophiles such as RLi. There are several reports on Type I reactions, leading to the synthetically useful preparations of dithioesters **3** or **4**.[2–4] Although interesting selectivities and useful applications can be expected from Type II reactions, such types of reaction are surprisingly rare, probably due to poor chemo- and regioselectivities.[3,4]



Scheme 1.

We have recently demonstrated that 1,4-dilithio-1,3-dienes **5** have remarkably different reactivities from those of mono-lithium compounds.[5–8] The cooperation or chelation of the two alkenyl lithium moieties in **5** upon substrates and the highly electron-rich character of **5** are considered to be critical for the success of the novel reactions.[5–8] In order to investigate the Type II addition of lithium compounds to carbon disulfide, we applied 1,4-dilithio-1,3-dienes **5** as model compounds, since selectivities may be improved by the cooperation or chelation of the two alkenyl lithium moieties in **5**. In this communication, we would like to report a new type of reaction of organolithium compounds **5** with CS_2, forming thiophene derivatives **6** via cleavage of one of the C=S double bonds and/or thiopyran-2-thione derivatives **7** via a cycloaddition reaction (Scheme 2).

Reactions of 1,4-dilithio-1,3-dienes **5** with carbon dioxide afforded cyclopentadienones in excellent yields.[5] Therefore, cyclopentadienethiones were expected from the reaction of **5** with CS_2. However, very interestingly, as shown in Scheme 3, the reaction of **5** generated in situ from the corresponding diiodo compound **8** and 4

Keywords: carbon disulfide; lithium compounds; C=S cleavage; cycloaddition; sulfur heterocycles.

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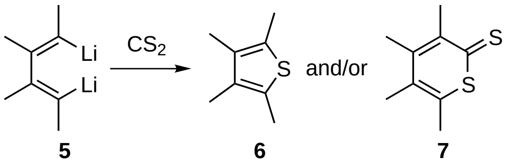
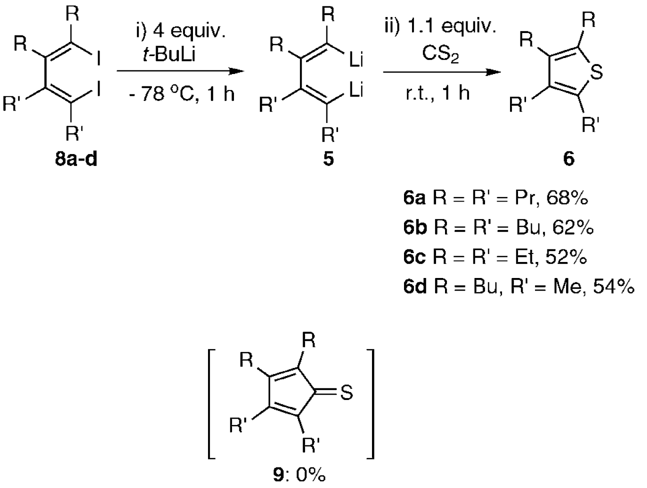


Scheme 2.



Scheme 3.

equivalents of *tert*-BuLi,[9,10] with carbon disulfide at room temperature afforded the thiophene derivatives **6** within 1 h in good isolated yields (**6a**: R = R′ = Pr, 68%; **6b**: R = R′ = Bu, 62%; **6c**: R = R′ = Et, 52%; **6d**: R = Bu, R′ = Me, 54%),[11] which are the same products as those obtained by using SCl_2. No formation of the expected cyclopentadienethiones **9** was detected. Although cleavage of the C=S bonds in CS_2 using transition metal complexes is known[12] and the use of organolithium compounds has been suggested by Seyferth,[2] this work represents an unprecedented reaction pattern for the RLi/CS_2 system.

When diiodo compounds **8e** and **8f** were used, the above reaction afforded a mixture of two S-containing products. In addition to the corresponding thiophene derivatives **6e** and **6f**, thiopyran-2-thione derivatives **10** and **11** were obtained (Fig. 1).[13] To the best of knowledge, substituted thiopyran-2-thiones such as **10** and **11** have not been reported in the literature. Although the yields could be improved, this reaction may provide a preparative method for the synthesis of such substituted thiopyran-2-thione derivatives.

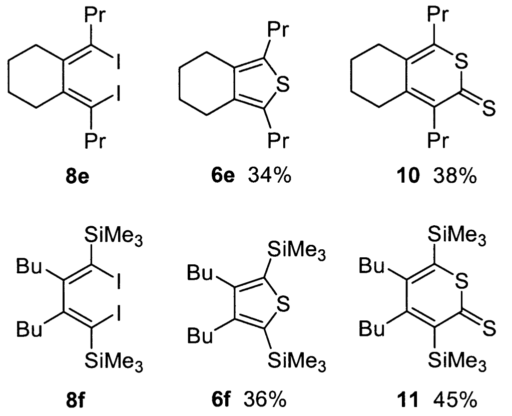
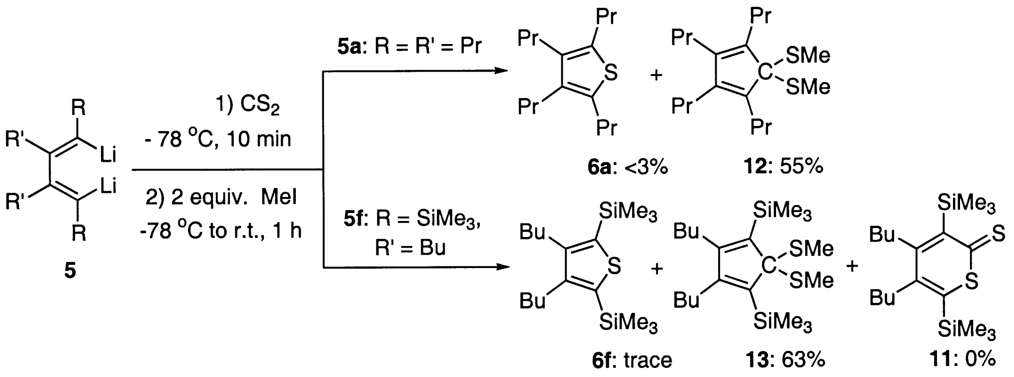


Figure 1.

The cooperation or chelation of the two alkenyl lithium moieties in **5** or the intramolecular reaction pattern of the second organolithium species is assumed to be critical for the success of these novel reactions. In the literature, at least three different reaction pathways have been proposed for the addition of organo-lithium and -magnesium reagents to thiocarbonyl groups.[1] In this reaction, although the mechanisms are not yet clear, the pathway for the formation of the thiophenes **6** is assumed to be different from that for the formation of the thiopyran-2-thiones **7**. Interestingly, when the reaction was carried out at a lower temperature and 2 equivalents of MeI were added as a trapping reagent, dimethylthiocyclopentadiene **12** was isolated in 55% yield along with <3% yield of **6a** after the reaction mixture had been stirred at room temperature for 1 h (Scheme 4). Similarly, when the dilithio compound **5f** was treated with CS_2, trapping with MeI afforded **13** in a 63% isolated yield, along with a trace amount of **6f** (Scheme 4).[14] No formation of **11** was detected. These results are in contrast to those obtained from the previous reactions when the temperature was immediately raised to room temperature without addition of trapping reagents. Based on these observations,

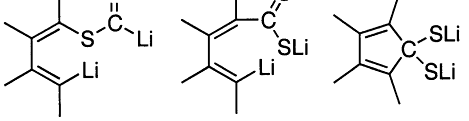


Scheme 4.

although further investigation is needed to understand the reaction mechanisms, the intermediacy of **14**, **15** and **16** might be proposed (Fig. 2). Thiophilic addition affords **14**, whilst carbophilic addition gives **15**. A second carbophilic addition of **15** may lead to the formation of **16**, which is trapped with MeI to afford **12** or **13**.

In conclusion, we have reported new reaction patterns for the RLi/CS_2 system. These findings are of significance for understanding the reaction mechanisms of such fundamental chemistry and for the development of preparative methods for S-containing heterocycles from RLi and CS_2.

Investigations into the reaction mechanisms and further applications for the synthesis of S-containing heterocycles are under progress.



14 **15** **16**

Figure 2.

Acknowledgements

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13. NMR data for **11**: ^1H NMR ($CDCl_3$, $SiMe_4$): δ 0.34 (s, 9H), 0.47 (s, 9H), 0.91–0.92 (m, 6H), 1.37–1.38 (m, 8H), 2.59 (t, $J=7.0$ Hz, 2H), 2.68 (t, $J=7.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, $SiMe_4$): δ 0.10, 4.00, 13.72, 13.84, 22.98 ($2CH_2$), 34.23, 34.25, 34.85, 35.18, 143.46, 149.77, 156.13, 157.64, 210.81. HRMS calcd for $C_{19}H_{36}S_2Si_2$: 384.1797, found: 384.1788.
14. NMR data for **13**: ^1H NMR ($CDCl_3$, $SiMe_4$): δ 0.26 (s, 18H), 0.93 (t, $J=6.9$ Hz, 6H), 1.35–1.43 (m, 8H), 1.60 (s, 6H), 2.28–2.36 (m, 4H); ^{13}C NMR ($CDCl_3$, $SiMe_4$): δ 12.08, 13.93, 23.45, 28.34, 34.41, 73.94, 146.84, 157.15. HRMS calcd for $C_{21}H_{42}S_2Si_2$: 414.2261, found: 414.2253.