Tetrahedron Letters, Vol.30, No.7, pp 819-822, 1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

# REACTIONS OF 2-LITHIO-1,3-BENZODITHIOLE WITH CARBON DISULFIDE : FORTH AND BACK PROCESSES

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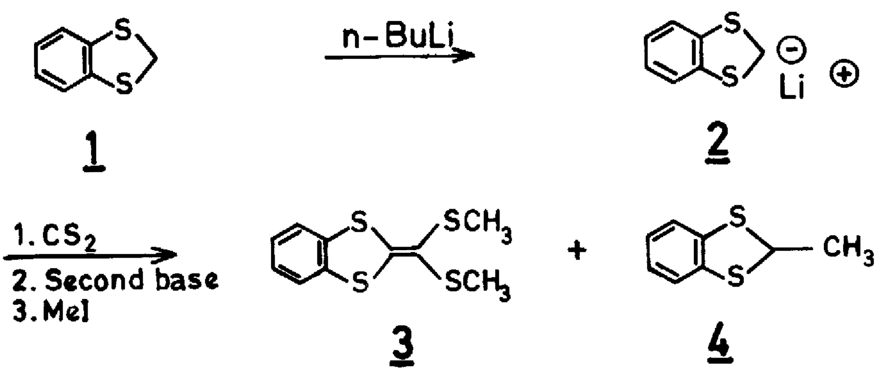
Abstract : Carbophilic reaction of 2-lithio-1,3-benzodithiole with $CS_2$, followed by the addition of a second base equivalent and quenching with MeI, yields 2-[bis(methylthio)methylene]-1,3-benzodithiole. An unexpected pathway mediated by $MeS^-$ and leading to the reformation of the 1,3-benzodithiole anion is described.

Many syntheses of dithioacids and keten dithioacetals are based on the reactions of carbanions, derived from active methylene compounds, with carbon disulfide[1,2]. An analogous approach has been used for the preparations of a variety of unsymmetrically substituted tetrathioethylenes[3], and 2-[bis(alkylthio)methylene]-1,3-dithioles[4].

We have recently extended this methodology and synthesized 2-[bis(methylthio)methylene] 1,3-benzodithiole 3, starting with the carbonion 2 derived from 1,3-benzodithiole 1 [5] (scheme 1). We wish to report here the unexpected results obtained during this study and to describe an intringuing ancillary pathway involved in these reactions.

Scheme 1



We first reacted one equivalent of 1,3-benzodithiole 1, successively with n-BuLi, $CS_2$, MeLi [6] and excess of MeI. 2-[Bis(alkylthio)methylene]-1,3-benzodithiole 3, was obtained together with a small but significant amount of the monomethylated 1,3-benzodithiole 4. The ratio of the two products (GLC) was 9:1 (Table, entry 2). Thus it was logical to assume that the formation of 4 in the first experiment stems from an uncomplete reaction of the carbanion 2 with $CS_2$, which in turn, was alkylated in the subsequent stage by methyl iodide. Indeed, alkylation of 2-lithio-1,3-benzodithiole 2 [7] with MeI gave high yield of product 4 (Table, entry 1).

In order to suppress completely the formation of 4, we decided to increase the amounts of the added $CS_2$. Then, an unexpected effect emerged. The ratio of 4/3 (Table, entry 3) was significantly modified; however, the modification took place in the wrong way : the relative amount of 4 was now much larger than in entry 2. Excess of $CS_2$ caused enhancement of the formation of 4, contradictory to our expectation. It seems that carbanion 2 formed in the first stage is not the exclusive precursor of 4 and experiments 2 and 3 point to a possible formation of that carbanion at a later ($CS_2$-dependent) stage of the process. A careful examination of the behaviour of the reagents used in excess (MeLi + $CS_2$) was needed.

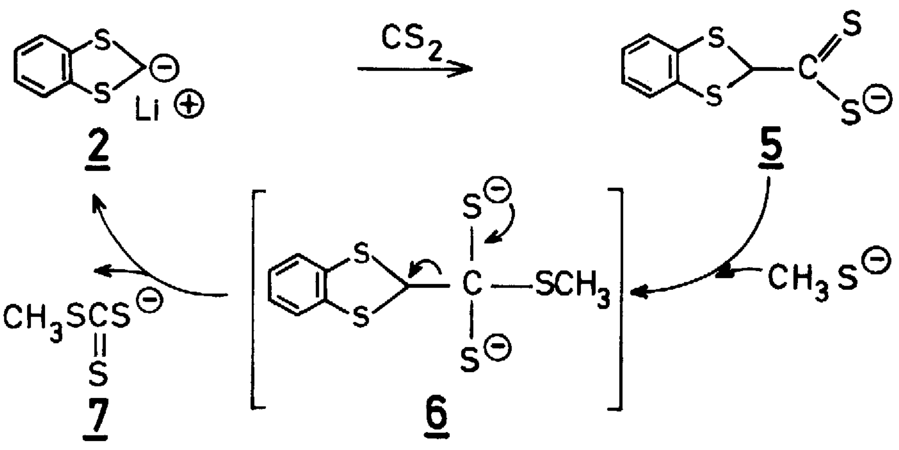
While the thiophilic addition of organo-lithium reagents to thiocarbonyl compounds is well documented [4], the possibility of thiophilic addition to $CS_2$, has attracted attention, only recently [8,9]. Thus, it was shown that aryl and heteroaryl reagents can react with $CS_2$ forming RSLi :

$$R\,Li + CS_2 \xrightarrow[\text{attack}]{\text{thiophilic}} RS - \underset{Li^+}{\overset{-}{C}} = S$$

$$\xrightarrow{\qquad\qquad} RS^-Li^+ + [(C{=}S)]$$

Assuming a similar mechanism in our system, $CH_3SLi$ might be formed from $CH_3Li$ reacting with the excess of $CS_2$. Formation of $CH_3S\,Li$ opens a second pathway which leads to reformation of carbanion 2 (scheme 2) : the dithioacid 5 initially formed can add now $CH_3S^-$ yielding the intermediate 6 which splits to the trithiocarbonate anion 7 and the anion 2.[10]

Scheme 2



TABLE

Ratio of compounds 3 and 4 obtained from Carbanion 2[a]

| Entry | $CS_2$ (equivs) | second base (equivs) | ratio of products[b] | |
|---|---|---|---|---|
| | | | 3 | 4 |
| 1 | 0 | 0 | 0 | 100 [c] |
| 2 | 1 | MeLi [d](1) | 90 | 10 |
| 3 | 2.5 | MeLi (2.5) | 60 | 40 |
| 4 | 2.5 | Li TMP[e](2.5) | 100[f] | 0 |
| 5 | 2.5 | MeSLi[g] (excess)<br>LiTMP[e] | 65 | 35 |

(a) *Carbanion 2 was generated by n-BuLi; after completion all reactions were* quenched with exces MeI. (b) Ratios of 3/4 were estimated by GC/MS (CP-sil 25 m capillary column and Nermog R10-10 mass spectrometer) from crude reaction mixtures. (c) The yield of isolated and purified 4 was 82%, $^1$H-NMR :($\delta$ in ppm relative to TMS)1.6 (d,3H, J= 7Hz), 4.9(q, 1H, J= 7 Hz), 6.9-7.2 (m,4H). (d) see ref.6. (e) TMP = 2,2',6,6'-tetramethyl piperidine. (f) The yield of isolated and purified 3 was 60%, m.p = 58°C (pentane) $^1$H-NMR : $\delta$: 2.3(s, 6H); 7.05-7.15 (m,4H). (g) Prepared according to ref.11, see ref.12.

The validity of this $CH_3S^-$ - mediated process was substantiated by the following experiments. First, the formation of $CH_3S^-$ can be totally excluded if a lithium amide is used in place of the alkyl lithium as second base; thus, using Li TMP (Table, entry 4), the formation of 4 is completely suppressed and reasonable yields of compoud 3 are obtained, from much cleaner mixtures. Second, if in an analogous Li TMP - catalyzed run, an excess of externally generated $CH_3S$ Li [11] was added [12], before the second base, then the formation of 4 is restored back (Table, entry 5). The following experiment provides details of a typical procedure needed to *synthesize 3. Addition of 1.82 ml of 1.6 M n-BuLi in hexane to 0.45 g(2.6 mmole) of 1,3-ben*zodithiole 1 in 8 ml of dry THF, under Argon, at - 30°C, produced a solution of 2.
To this carbanion 0.5 g (6.6 mmole) of $CS_2$ were added and the mixture stirred at the same temperature for 30 min. A solution of LiTMP (6.6 mmole), prepared by the addition of 4.35 ml (6.6 mmole) n-BuLi to 0.5 g (6.6 mmole) of 2,2', 6,6'-tetramethylpiperidine in 10 ml of dry THF, was added *via* a syringe, followed, after continued stirring for 1 h, by an excess of MeI (0.8 ml, 12.6 mmole). After the solvents were evaporated water was added to the mixture, and extracted with ether; ethereal extracts were dried on $MgSO_4$. The compound 3 was isolated by flash chromatography on silica gel with cyclohexane/toluene (80/20) as the eluant.

In summary, beside the synthesis of molecule 3 we discovered an unprecedented pathway mediated by $MeS^-$ and leading to the reformation of the 1,3-benzodithiole anion. While $MeS^-$ is known to cleave carbon-oxygen bonds in hindered esters or in methyl aryl ethers,[11] we demonstrate here the first example of a carbon-carbon $\sigma$ bond cleavage by this reagent . The scope of this reaction is now under further investigation.

## Acknowledgements

The C.N.E.T. is gratefully acknowledged for generous financial support.

## References and notes

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6. MeLi was used instead of n-BuLi, as the second base equivalent, in order to avoid any possible thiophilic addition reaction with the intermediate dithiocarboxylate 5; see ref.4.
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10. In fact, reacting $CH_3Li$ with $CS_2$, in our reaction conditions (see Table) and quenching by an excess n-butylbromide, did not yield detectable amounts of the compound (butyl ester of the dithioacetic acid) from the carbophilic attack. The main compound formed was n-butyl, methyl trithiocarbonate. The formation of the latter involves the intermediate production of $CH_3SLi$ (from the thiophilic addition of $CH_3Li$ on $CS_2$ (see the text)) and subsequent reaction with the excess $CS_2$, before alkylation by n-butylbromide.
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12. Solid $CH_3SLi$ is barely soluble in THF at -30°C, and the process reported in the table (entry 5) is a heterogeneous,probably slow reaction; this might account for the surprisingly high amount of 3, still present in the mixture.

(Received in France 14 December 1988)