SHORT PAPER

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Tert-BuOK/BuLi-Induced facile cyclodehydrogenation of diphenyl sulfide to dibenzothiophene†

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Attempted double *ortho*-lithiation of diphenyl sulfide using two equivalents of butyllithium in the presence of potassium *tert*-butoxide in diethyl ether-THF at room temperature under argon resulted in facile cyclodehydrogenation to afford dibenzothiophene in moderate yield.

Keywords: dibenzothiophene, aromatic sulfides, butyllithium, cyclodehydrogenation

Aromatic *ortho*-lithiation mediated by heteroatom substituents has been an important tool for the functionalization of aromatic nucleus and a great number of polysubstituted aromatics and heterocycles have been synthesised using this methodology.[1] The major heteroatom elements involved therein are oxygen, nitrogen and sulfur. Among the sulfur-based functionalities, the sulfonyl (RSO_2-) and sulfinyl (RSO) groups are often employed for this purpose. In contrast to the oxygen counterparts, however, the sulfanyl function (RS-) is of limited use for directed lithiation of arenes. This is mainly due to the ease with which the thioether function is cleaved or metallated α to the sulfur in preference to the aromatic ring.[2] The hierarchy of heteroatom substituents in aromatic lithiation follows the order RO->R_2N->RS-.[3]

In connection with our program focused on the synthesis of bismuth-containing heterocycles, we were interested in double *ortho*-lithiation of diphenyl sulfide (**1**) with butyllithium. In previous papers,[4] successful double *ortho*-lithiation of diphenyl ether has been reported using butyllithium as reagent and diethyl ether or THF-diethyl ether as the solvent. In our attempted double lithiation under similar conditions, however, compound **1** underwent extensive decomposition to give a complex mixture of products, amongst which butylbenzene, biphenyl, thiophenol, butyl phenyl sulfide and diphenyl disulfide were identified as volatile components. Changing the solvent, substrate/reagent ratio or temperature, addition of TMEDA as a complexing agent, and use of different atmospheres all provided no promising results as to the desired double *ortho*-lithiation.

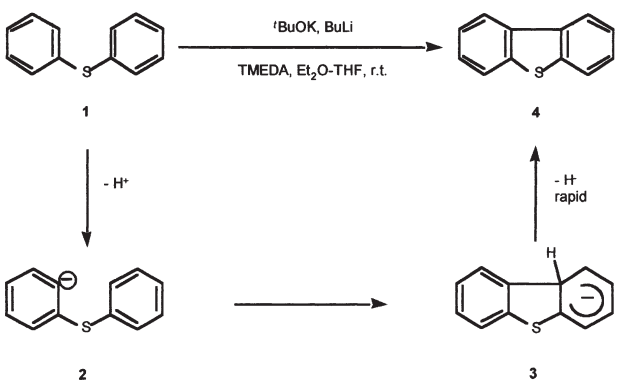
A combination of potassium *tert*-butoxide and butyllithium has been called a superbasic mixture.[5] When **1** was treated with two equivalents of butyllithium in the presence of potassium *tert*-butoxide and TMEDA in diethyl ether/THF at room temperature, rather surprisingly, dibenzothiophene (**4**) was obtained in yields as high as 65%. Other alkaline bases such as sodium ethoxide and sodium hydride failed to produce any cyclization product. Representative results are summarized in Table 1.

Treatment of the reaction mixture with a simple electrophile such as methyl iodide produced no substituted dibenzothiophene. Quenching of the reaction mixture with deuterium oxide provided no isotope labelling of **4**. Therefore, compound **4** is most likely to be formed via the intramolecular nucleophilic aromatic substitution involving rapid displacement of a ring hydrogen, as depicted in Scheme 1. The action of butyllithium on 1,4-dihydrodibenzothiophene has long been known to induce aromatisation to **4** via loss of two hydrogen atoms.[6] Such butyllithium-assisted hydride elimination of the initial monolithiated intermediate is supposedly a common occurrence with these polycondensed aromatic systems.[7] Since the amount of **4** formed was practically independent of the reaction time, the reaction of **1** with potassium *tert*-butoxide/butyllithium should proceed rapidly, via the competition between intramolecular cyclodehydrogenation leading to **4** and carbon–sulfur bond cleavage leading to various decomposition products. Recently, several papers have been published from our laboratory on nucleophilic aromatic substitutions under strongly alkaline conditions, in which the ring hydrogen atom is replaced by nucleophiles in preference to a nucleofugal substituent present.[8]

Table 1 *t*-BuOK/BuLi-induced cyclodehydrogenation of diphenyl sulfide to dibenzothiophene

Entry	Reagent[a]	Conditions	Conversion/%	Yield/%[b]
1	*t*-BuOK, BuLi	Et_2O, TMEDA, r.t.	96	54
2	*t*-BuOK, BuLi	THF, TMEDA, r.t.	100	52
3	*t*-BuOK, BuLi	Et_2O/THF, TMEDA, r.t.	100	65
4	*t*-BuOK, BuLi	Et_2O/THF, TMEDA, r.t.	100	53
5	*t*-BuOK, BuLi	Et_2O/THF, DME, r.t.	91	64
6	*t*-BuOK, BuLi	Et_2O/THF, r.t.	100	56
7	*t*-BuOK, BuLi	hexane, r.t.	29	4
8	EtONa, BuLi	Et_2O/THF, r.t.	20	0
9	NaH, BuLi	Et_2O/THF, r.t.	23	0
10	*t*-BuOK, BuLi	Et_2O/THF, 0 °C	100	53
11	*t*-BuOK, BuLi	Et_2O/THF, reflux	100	55
12[c]	*t*-BuOK, BuLi	Et_2O/THF, r.t.	100	56
13[d]	*t*-BuOK, BuLi	Et_2O/THF, r.t.	56	25
14[e]	*t*-BuOK, BuLi	Et_2O/THF, r.t.	45	21
15[f]	t-BuOK, BuLi	Et_2O/THF, LiCl, r.t.	97	48

[a]Except for entries 12–15, two equivalents of bases were employed. [b]Determined by GC using cyclododecane as internal standard. [c]*t*-BuOK: BuLi = 1 : 2. [d]*t*-BuOK: BuLi = 1 : 1. [e]*t*-BuOK : BuLi = 20 : 1. [f]*t*-BuOK : BuLi: LiCl = 1 : 2 : 1.



Scheme 1

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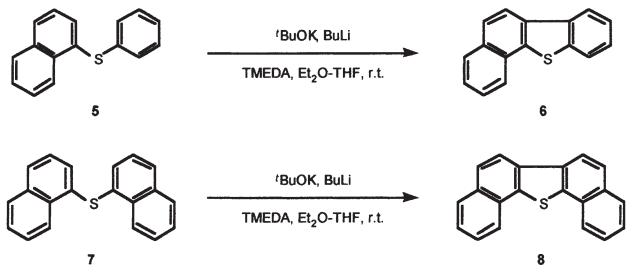
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 2

In an early paper,[9] diphenyl sulfide **1** was reported to cyclise on prolonged treatment with phenyllithium or phenylsodium, producing **4** in 10–34% yields along with other products. We confirm this, but in our case much better results were obtained within a short time. Known preparative routes[8] to **4** include the high temperature reaction of biphenyl with sulfur in the presence of aluminum chloride,[6] fusion of 2,2′-dihydroxybiphenyl with diphosphorus pentasulfide,[10] tetrazotisation of 2,2′-diaminobiphenyl followed by treatment with $K_3Cr(SCN)_6$,[11] partial desulfurisation of thianthrene with copper bronze,[12] and reductive cyclisation of diphenyl sulfoxide with sodium amide.[13]

On similar treatment, 1-naphthyl phenyl sulfide (**5**) and bis(1-naphthyl) sulfide (**7**) produced benzo[*b*]naphtho[2,1-*d*]thiophene (**6**) and dinaphtho[1,2-*b*; 2′,1′-*d*]thiophene (**8**) in 36 and 18% yields, respectively. Though the yields were moderate to low, this is compensated for by the single-step, one-pot and time-saving nature of the present procedure, since compounds **6** and **8** have previously been synthesised only through lengthy or tedious routes.[15,16]

Unfortunately, the present methodology has proved to be valid only for the construction of unsubstituted polycyclic thiophenes such as **4**, **6** and **8**. When cyclisation of substituted diphenyl sulfides such as bis(3- or 4-methoxyphenyl) sulfide or bis(4-methylphenyl) sulfide was attempted using potassium t-butoxide/butyllithium under similar conditions, there always resulted a complex mixture of decomposition products.

Experimental

Melting points were determined on a Yanaco MP S3 apparatus. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-A400 NMR spectrometer using tetramethylsilane as an internal reference. All reagents were reagent grade commercial products and used as received, with the exception of 1-naphthyl phenyl sulfide **5** and bis(1-naphthyl) sulfide **7**, which were prepared according to the literature.[17,18] All products are known and were characterised by m.p., ^{1}H and ^{13}C NMR or by comparison with authentic specimens.

1-Naphthyl phenyl sulfide (**5**): white prisms (1:1-ethanol/water): m.p. 39–40 °C (lit[17] 39.0–40.5 °C); ^{13}C NMR: δ 136.9, 134.2, 133.6, 132.5, 131.2, 129.2, 129.05, 129.0, 128.5, 126.9, 126.4, 126.1, 125.8, 125.6.

Bis(1-naphthyl) sulfide (**7**): pale yellow needles (ethanol): m.p. 102–104 °C (lit[18] 104–106 °C); ^{1}H NMR δ 8.42 (m, 1H), 7.90–7.31 (m, 6H); ^{13}C NMR: δ 134.1, 132.6, 132.4, 129.9, 128.6, 128.0, 126.7, 126.4, 125.85, 125.1.

Cyclisation of diphenyl sulfide (**1**) *to dibenzothiophene* (**4**). *Typical procedure*: To a stirred solution of diphenyl sulfide (**1**; 0.186g, 1 mmol) and potassium *tert*-butoxide (0.112g, 1 mmol) in diethyl ether-THF (1:2) was added dropwise butyllithium in hexane (1.3 mL, 2 mmol) at room temperature. The resulting dark red mixture was kept at the same temperature with stirring for 30 min, and then diluted with water. The organic phase was extracted with diethyl ether, the combined extracts were dried over $MgSO_4$ and evaporated to leave a solid residue, which was recrystallised from ethanol to give **4** as a white solid (0.101 g, 55%): m.p. 99–100 °C (lit[19] 99.5–100 °C); ^{1}H NMR: δ 8.18–8.16 (m, 1H), 7.87–7.85 (m, 1H), 7.47–7.45 (m, 2H); ^{13}C NMR: δ 139.4, 135.5, 126.7, 124.3, 122.8, 121.5.

Compounds **6** and **8** were prepared from sulfides **5** and **7**, respectively, in a manner similar to the preparation of compound **4**. Chromatographic purification of products was performed on a column packed with Merck silica gel (230–400 mesh), using a mixture of EtOAc and hexane as the eluent.

Benzo[b]naphtho[2,1-d]thiophene (**6**): colourless leaflets (hexane): m.p. 183.5–184.5 °C (lit[15b] 185 °C); ^{1}H NMR: δ 8.24–8.14 (m, 3H), 8.00–7.96 (m, 2H), 7.88 (d, 1H, *J* = 8.3 Hz), 7.64–7.45 (m, 4H); ^{13}C NMR: δ 139.1, 137.3, 136.6, 132.65, 132.4, 129.0, 128.9, 126.7, 126.3, 126.2, 125.5, 124.55, 124.5, 123.0, 121.6, 119.7.

Dinaphtho[1,2-b:2′,1′-d]thiophene (**8**): colourless leaflets (chloroform): m.p. 253–254 ºC (lit[16b] 255–257 °C); ^{1}H NMR: δ *ca* 8.26 and 8.24 (2 overlapping d, 4H), 8.02 (d, 2H, *J* = 7.5 Hz), 7.92 (d, 2H, *J* = 8.5 Hz), 7.66–7.58 (2t, 2H, *J* = 8.5 Hz); ^{13}C NMR: δ 136.75, 133.8, 132.1, 129.1, 129.0, 126.9, 126.15, 125.7, 124.3, 119.8.

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