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NEW METHODOLOGY FOR THE INTRODUCTION OF SULFUR INTO ORGANIC MOLECULES

SYNTHESIS OF ANHYDROUS Li_2S, Li_2S_2 AND LiSR SPECIES BY LITHIUM TRIETHYLBOROHYDRIDE REDUCTION OF ELEMENTAL SULFUR AND DISULFIDES

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Abstract—Anhydrous THF solutions of Li_2S or Li_2S_2 (or chemically equivalent species) are rapidly and quantitatively formed by the reaction of common yellow sulfur with appropriate stoichiometries of commercially available $LiEt_3BH$. Only volatile by-products H_2 and Et_3B are produced; however, the Et_3B probably associates with the anionic sulfur species generated. Subsequent reaction with electrophiles (alkylating agents or acylating agents) affords sulfide or disulfide derivatives in high yields. In several cases, literature procedures are substantially improved. Disulfides are cleaved to lithium mercaptides by $LiEt_3BH$. Subsequent addition of electrophiles affords unsymmetrical sulfides. Trisulfides and tetrasulfides can also be prepared by $LiEt_3BH$ reduction of S_8, but only in low yield.

Organosulfur compounds feature prominently in organic chemistry and biochemistry.[1,2] Important naturally occurring sulfides and disulfides include penicillins, cephalosporins, biotin, gliotoxin and lipoic acid.[1] Numerous sulfur containing reagents have been developed for C–C bond forming reactions.[1-3]

Despite a plethora of methods and techniques, research continues on the development of new reagents for the introduction of sulfur into organic molecules.[4-7] In previous studies, we discovered that trialkylborohydrides such as $LiEt_3BH$ are able to cleave polymeric Se_x to Li_2Se or Li_2Se_2 depending upon reaction stoichiometry (eqns i and ii).[8]

$$Se + 2LiEt_3BH \longrightarrow Li_2Se + 2Et_3B + H_2 \quad (i)$$

$$2Se + 2LiEt_3BH \longrightarrow Li_2Se_2 + 2Et_3B + H_2. \quad (ii)$$

These results indicated that it might be possible to generate nucleophilic S anions by the action of $LiEt_3BH$ on common yellow sulfur, S_8. Accordingly, we report in this paper that anhydrous THF solutions of Li_2S and Li_2S_2 (or chemically equivalent species) can be prepared in a convenient one flask operation as illustrated in eqns (iii) and (iv).[9] Organodisulfides can be similarly cleaved to lithium mercaptides. We also detail the synthesis of a variety of organosulfur compounds via the addition of electrophiles to these reaction mixtures; in several cases, our methodology offers considerable improvement over the literature procedures.

$$S + 2LiEt_3BH \longrightarrow Li_2S + 2Et_3B + H_2 \quad (iii)$$

$$2S + 2LiEt_3BH \longrightarrow Li_2S_2 + 2Et_3B + H_2. \quad (iv)$$

RESULTS

The addition of 2.0 equivalents of $LiEt_3BH$ (1.0 M in THF) to 1.0 equivalent of powdered sulfur under dry N_2 resulted in the instantaneous formation of a homogeneous yellow solution and the evolution of gas over the course of 2 min. Reactions were conducted on 2–10 mmol scales and without cooling.

A variety of alkylating agents and acylating agents were added to solutions prepared as described above. After appropriate reaction times, high yields of sulfide derivatives could be obtained, as summarized in Table 1. These results indicate that Li_2S, or a chemically equivalent species, is cleanly formed when sulfur is reacted with 2 equivalents of $LiEt_3BH$ (eqn iii).

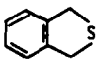
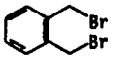
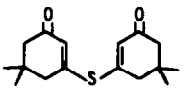
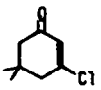
Commercial anhydrous Li_2S did not dissolve in THF. Furthermore, 2.86 mmol of commercial Li_2S failed to dissolve in 5.72 ml of 1.0 M Et_3B in THF. These conditions mimic the product stoichiometry in eqn (iii) (2:1 molar ratio Et_3B:Li_2S). Thus our Li_2S solutions are supersaturated. Upon 2–24 hr standing, we usually observed that a cream colored precipitate formed.

The addition of 1.0 equivalent of $LiEt_3BH$ to 1.0 equivalent of powdered sulfur under dry N_2 also immediately afforded a homogeneous yellow solution. A variety of alkylating agents and acylating agents were added to this preparation. As depicted in Table 2, high yields of disulfide derivatives were obtained after appropriate reaction times. These results indicate that Li_2S_2, or a chemically equivalent species, is cleanly formed when sulfur is reacted with one equivalent of $LiEt_3BH$ (eqn iv).

The formation of Li_2S and Li_2S_2 occurred equally well if the yellow sulfur was suspended in THF prior to reaction with $LiEt_3BH$. Attempts to prepare N,N'-thiobissuccinimide and N,N'-dithiobissuccinimide[4] by reacting Li_2S and Li_2S_2 with N-bromosuccinimide unequivocally failed.

A THF solution of dibenzyl disulfide (one equivalent) reacted with 2.0 equivalents of $LiEt_3BH$ over the course of 2 min. This solution was then treated with three representative electrophiles as depicted in entries 1–3 in Table 3. Good to high yields of unsymmetrical sulfides

Table 1. Symmetrical organosulfides prepared

entry	Product[a]	Electrophile	Yield(%)[b]	Reaction Conditions[c]
(1)	$(C_6H_5CH_2)_2S$	$C_6H_5CH_2Cl$	(94)	3 hr
(2)	$(\underline{n}\text{-}C_3H_7)_2S$	$\underline{n}\text{-}C_3H_7Br$	69	3.5 hr
(3)	$(\underline{n}\text{-}C_4H_9)_2S$	$\underline{n}\text{-}C_4H_9I$	71	5 hr
(4)	$(\underline{n}\text{-}C_5H_{11})_2S$	$\underline{n}\text{-}C_5H_{11}Br$	71	5 hr
(5)	$(\underline{sec}\text{-}C_4H_9)_2S$	$\underline{sec}\text{-}C_4H_9I$	63	12 hr reflux
(6)			(63)	1.5 hr
(7)	$(CH_3CO)_2S$	CH_3COCl	87	2 hr
(8)	$(C_2H_5OCO)_2S$	C_2H_5OCOCl	51	2.5 hr
(9)			(55)	12 hr reflux

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[a]Identified by comparison to authentic samples or literature spectral data.

[b]Yields are based upon starting sulfur. Bracketed values are ^1H NMR yields relative to 1,2,4,5-tetrachlorobenzene or 1,4-di(t-butyl)-benzene internal standard.

[c]Room temperature unless noted

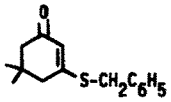
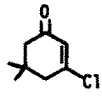
Table 2. Symmetrical organodisulfides prepared

entry	Product[a]	Electrophile	Yield(%)[b]	Reaction Conditions
(1)	$(C_6H_5CH_2)_2S_2$	$C_6H_5CH_2Br$	(89) 85	5 hr, 25°C
(2)	$(\underline{n}\text{-}C_3H_7)_2S_2$	$\underline{n}\text{-}C_3H_7I$	(83) 64	4 hr, 25°C
(3)	$(H_2C{=}CHCH_2)_2S_2$	$H_2C{=}CHCH_2Cl$	(75)	1 hr, 25°C+ 0.5 hr reflux
(4)	$(H_2C{=}CHCH_2)_2S_2$	$H_2C{=}CHCH_2Br$	(93) 66	2 hr reflux 12 hr, 25°C
(5)	$(\underline{n}\text{-}C_4H_9)_2S_2$	$\underline{n}\text{-}C_4H_9I$	(87) 78	1 hr reflux
(6)	$(\underline{n}\text{-}C_5H_{11})_2S_2$	$\underline{n}\text{-}C_5H_{11}Br$	99	2 hr reflux
(7)	$(\underline{sec}\text{-}C_4H_9)_2S_2$	$\underline{sec}\text{-}C_4H_9I$	(73)	2 hr reflux
(8)	$(C_6H_5CO)_2S_2$	C_6H_5COCl	85	1 hr, 25°C
(9)	$(CH_3CO)_2S_2$	CH_3COCl	(82)	0.5 hr, 25°C

[a]Identified by comparison to authentic samples or literature spectral data

[b]Yields are based upon starting sulfur. Bracketed values are ^1H NMR yields relative 1,2,4,5-tetrachlorobenzene or 1,4-di(t-butyl)benzene internal standard.

Table 3. Unsymmetrical organosulfides prepared

entry	Product[a]	Starting Disulfide	Electrophile	Yield(%)[b]	Reaction Conditions
(1)	CH_3-S-$CH_2C_6H_5$	$(C_6H_5CH_2)_2S_2$	CH_3I	(75) 54	2-4 hr, 25°C
(2)	(CH_3CO)-S-$CH_2C_6H_5$	$(C_6H_5CH_2)_2S_2$	CH_3COCl	(100)	4 hr, 25°C
(3)		$(C_6H_5CH_2)_2S_2$		(63)	3 hr reflux
(4)	$C_6H_5CH_2CH_2$-S-CH_3	$(CH_3)_2S_2$	$C_6H_5CH_2CH_2I$	90	16 hr, 25°C

[a]Identified by spectral and physical data

[b]Yields are based upon starting disulfide. Bracketed values were determined by ^1H NMR relative 1,4-di(t-butyl)benzene or 1,2,4,5-tetrachlorobenzene internal standard

were obtained indicating the formation of benzyl mercaptide under the reaction condition (eqn v).

$$RS\text{–}SR + 2LiEt_3BH \longrightarrow 2RS\text{–}Li + 2Et_3B + H_2 \quad (v)$$

$$R = CH_2C_6H_5, CH_3$$

Immediate gas evolution occurred when a THF solution of dimethyl disulfide (one equivalent) was treated with $LiEt_3BH$ (two equivs). The subsequent addition of 2-phenylethyl iodide afforded 2-phenylethyl methyl sulfide (entry 4, Table 3), indicating the clean formation of methyl mercaptide according to eqn (v).

Sulfur was reacted with lower stoichiometries of $LiEt_3BH$, since it was felt that symmetrical trisulfides and tetrasulfides might be available via eqns (vi) and (vii).

$$3S + 2LiEt_3BH \longrightarrow Li_2S_3 + 2Et_3B + H_2 \quad (vi)$$

$$4S + 2LiEt_3BH \longrightarrow Li_2S_4 + 2Et_3B + H_2. \quad (vii)$$

A homogeneous solution resulted from the reaction of 3 equivs of sulfur with 2 equivs of $LiEt_3BH$ (eqn vi). Benzhydryl bromide (2 equivs) was subsequently added. This electrophile was chosen because distinct methine proton ^1H NMR resonances have been observed for most species of the formula $(C_6H_5)_2CH$–$(S)_x$–$CH(C_6H_5)_2$:[10] dibenzhydryl pentasulfide, (δ, $CHCl_3$) 5.60 ppm; dibenzhydryl tetrasulfide, 5.55 ppm; dibenzhydryl trisulfide, 5.21 ppm; dibenzhydryl disulfide, 4.73 ppm. The reaction mixture was analyzed by ^1H NMR and found to contain all of the above species. Dibenzhydryl trisulfide constituted 40% of the products. The attempted preparation of dibenzyl trisulfide afforded similar results.

Trialkylborohydrides $NaEt_3BH$, KEt_3BH and K(sec-$C_4H_9)_3BH$ all rapidly reacted with sulfur with gas evolution. However, the resulting reaction mixtures were heterogeneous. The sequential treatment of sulfur with 2 equivs of KEt_3BH and 2 equivs of benzyl bromide afforded dibenzyl sulfide in only 16% yield. Better yields of organosulfur compounds were obtained with $NaEt_3BH$. However, dibenzyl sulfide and di-n-butyl sulfide (prepared from sulfur via two equivalents of $NaEt_3BH$ followed by 2 equivs of alkylating agent) were accompanied by significant amounts of disulfide by-products.

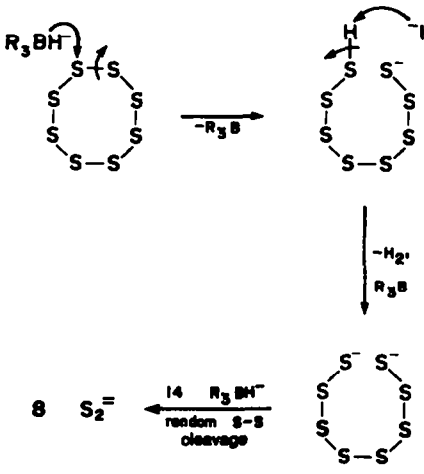
DISCUSSION

The methodology described herein enables the high-yield synthesis of a variety of symmetrical dialkyl and diacylsulfides and disulfides in a simple one flask procedure from non-sulfur containing precursors. Only volatile by-products (H_2 and Et_3B) are produced. Probably the major drawback is the moderate expense[11] of $LiEt_3BH$.

A variety of nucleophilic reagents such as CN^-, SO_3H^- and carbanions (acetylides, Grignard reagents) have been observed to cleave S_8 rings.[2] Sodium borohydride reacts with sulfur to yield the synthetically useful hydride reductant $NaBH_2S_3$,[12] and $LiAlH_4$ and sulfur react to yield an undefined sulfide which liberates H_2S upon acidification.[13] Our report constitutes the first example of alkali metal sulfide synthesis via action of a hydride reagent upon sulfur. Equation (viii) depicts the probable S–S bond cleavage-deprotonation sequence responsible for deoligomerization. Complete reduction to S^{2-} or S_2^{2-}, as opposed to the reaction course with $NaBH_4$, is likely a consequence of the enhanced nucleophilicity of $LiEt_3BH$ relative to other boron and aluminum hydride reductants.[14]

Although the synthesis of numerous organosulfur compounds is adequately served by inexpensive commercially available $Na_2S{\cdot}9H_2O$, this reagent is of course incompatible with electrophiles requiring strictly anhydrous conditions. Anhydrous alkali metal sulfides are commerically available, but they are exceedingly hygroscopic and insoluble in non-polar organic solvents. Thus our one flask *in situ* synthesis offers obvious advantages. Alkali metal disulfides are not commercially available. Methods for their preparation, such as Li/NH_3,[15] are cumbersome and sometimes afford mixtures of polysulfide salts.[2,16]

The role of the by-product Et_3B in our reaction mixtures is unclear but probably of consequence. As a Lewis acid,



(VIII)

it is certainly capable of associating with anionic sulfur species. Since trialkylboranes and their corresponding ate adducts (R_3BX^-) exhibit large ^{11}B NMR chemical shift differences,[14f,g] a probe exists for the degree of association. In preliminary experiments,[17] we have observed that our reaction mixtures exhibit ^{11}B chemical shifts 12–36 ppm upfield from Et_3B (78.0 δ, ppm *vs* $BF_3{\cdot}OEt_2$).[14g] The ^{11}B NMR chemical shift for $LiEt_3BH$ is reported as −12.3 (δ,ppm *vs* $BF_3{\cdot}OEt_2$).[14f] Thus it is clear that the Et_3B by-product depicted in eqns (iii)–(v) is not completely in the free state. However, any association is certainly not a key factor in the ensuing chemistry. Nonetheless, it may be partly responsible for the apparent supersaturation noted in the results section. Boron containing by-products have recently been observed to play important roles in other reactions: Marked differences were demonstrated in the solubility and reactivity of $Na^+C_6H_5Se^-$ depending upon whether it was prepared by $NaBH_4$ or Na reduction of diphenyl diselenide.[18]

Upon workup, the Et_3B by-product volatilizes when the THF is removed. We have handled all product workups detailed herein and elsewhere[8,19] without special precaution and without incident. However, other researchers have recommended that rotary evaporatory vacuums be broken with N_2 when Et_3B is among the volatiles.[20]

Several of the organosulfur components we have made (or failed to make) deserve comment. The first four entries in Table 1 establish that benzylic halides and primary alkyl iodides and bromides readily react with the Li_2S preparation at room temperature. Not unexpectedly, sec-C_4H_9I (entry five) required a reflux period. Considering the availability of $Na_2S{\cdot}9H_2O$, the preparation of the first five compounds in the table must be regarded as unexceptional.

The cyclic sulfide, 1,3-dihydroisothianaphthene, was prepared in higher yield than is normally obtained[21,22] as depicted in entry 6. While other cyclic sulfides should be similarly available, yields will be a function of the dihalide employed and the dilution conditions. We obtained variable spectroscopic yields of 2,11-dithia[3.3]-metacyclophane from α,α'-dibromo-*m*-xylene, although in principle our methodology should be as good as that recently reported by Vögtle.[6]

Examples of the acylation of our Li_2S preparation are provided by entries 7 and 8 in Table 1. These reactions would proceed in much lower yield, if at all, under protic conditions or with $Na_2S{\cdot}9H_2O$. Diacyl sulfides (monothioanhydrides) have not heretofore been available in a single step procedure from non-sulfur containing precursors. In most instances, they have been prepared by the acylation of monothioacids or their anions.[23] The compound $(EtOCO)_2S$ (entry 8) represents a functionality class for which no other convenient entry is currently (to our knowledge) available.[24]

β-Chlorovinyl ketones are also known to react with sulfur nucleophiles.[25] The reaction of the Li_2S preparation with 3-chloro-5,5-dimethyl-cyclohex-2-enone afforded a reasonable spectroscopic yield of sulfide 1, but the isolated yield was always much lower. The sulfide 1 had been prepared previously in 5% yield with $Na_2S{\cdot}9H_2O$.[26] Our melting point differed, so we undertook a complete characterization of this compound (Experimental).

The reactivity of the Li_2S_2 preparation towards electrophiles (Table 2) generally parallels that observed with Li_2S. Previously, the better preparative methods for dibenzoyl disulfide (entry 8) have involved oxidation of thiobenzoic acid or its conjugate base.[27] Such procedures have also been employed for diacetyl disulfide.[28] Disulfides have been observed to undergo oxygen and light initiated chain reactions with trialkylboranes.[29] We routinely conducted our reactions under N_2 and never observed any competition from this potential side reaction.

Although there are many routes to unsymmetrical dialkyl sulfides, the $LiEt_3BH$ disulfide cleavage (eqn v) should be of utility. Entries 1–3 in Table 3 demonstrate the reactivity of benzyl mercaptide thus prepared in an alkylation, an acylation, and a conjugate addition reaction. The preparation of benzyl methyl sulfide (entry 1) could also be executed in a single flask from sulfur by the sequential addition of $LiEt_3BH$, benzyl chloride, $LiEt_3BH$, and methyl iodide. However, the spectroscopic yield dropped to 45%.

Lithium methyl mercaptide has seen use as a reagent for the cleavage of lactones and ethers,[30] and can be easily generated from dimethyl disulfide and $LiEt_3BH$ *in situ*. The 2-phenylethyl methyl sulfide[31] subsequently prepared (entry 4) is in part responsible for the characteristic "skunky odor" of fox urine.[32]

Although we have not attempted to optimize conditions for the formation of symmetric trisulfides or tetrasulfides (eqns vi and vii), it is clear from the results of our exploratory reactions that they will be available only in modest yield. It appears that Li_2S_3 undergoes disproportionation before reaction. In our Li_2S and Li_2S_2 alkylations, sulfur containing by-products were never observed.

Trialkylborohydrides can in most cases be prepared by reaction of an alkali metal hydride MH with a trialkylborane R_3B.[14a,b,d,f] Hence Li_2S or Li_2S_2 might be available by reaction of S_8 with a stoichiometric amount of LiH and a catalytic amount of Et_3B; the Et_3B would be continually regenerated according to eqns (ii) and (iv). However, in work directed at metal CO anion synthesis,[19b] we have found such modifications to require longer reaction and set-up times. Furthermore, the LiH–Et_3B reaction is somewhat slow at room temperature.[14f] Nonetheless, we call these possible modifications to the attention of researchers who may be interested in cost minimization.

From the organic synthesis standpoint, $LiEt_3BH$ seems uniquely suited among trialkylborohydrides for

sulfur reduction. The use of $NaEt_3BH$, KEt_3BH, or $K(sec\text{-}Bu)_3BH$ afforded heterogeneous reactions mixtures which were less effective in subsequent reactions. Salts such as Na_2S, K_2S and K_2S_2 would be expected to be much less soluble (or less prone to supersaturation) in THF. However, these reactions may find use among inorganic chemists as facile means of preparing various sulfide and disulfide salts.

OVERVIEW

This work and our previous study with selenium[8] has demonstrated the utility of $LiEt_3BH$ for the reductive cleavage of heteroatom–heteroatom bonds. Trialkylborohydrides are also able to effect net cleavage of a number of transition metal–metal bonds. Thus metal carbonyl anions can be prepared from metal CO dimers in a rapid one flask procedure according to eqn (ix).[19]

$$L_n(CO)_xM\text{—}M(CO)_xL_n + 2LiEt_3BH \longrightarrow \longrightarrow 2Li[L_n(CO)_xM] + 2Et_3B + H_2 \quad \text{(ix)}$$

Although this is our final full paper in a series[8,19b] on applications of trialkylborohydrides to synthetic problems in organic and organometallic chemistry, additional related uses for R_3BH^- reagents are certain to be discovered. For instance, P–P or Sn–Sn bonds might be subject to similar cleavage reactions. We hope that the procedures and discussion contained herein will not only aid in the preparation of certain organosulfur compounds, but help stimulate the exploration of these new areas as well.

EXPERIMENTAL

General. All experiments were carried out under dry N_2. Commercial yellow sublimed sulfur (J. T. Baker) was used without further purification. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl.

$LiEt_3BH$ (Super Hydride) and $K(sec\text{-}Bu)_3BH$ (K-Selectride) were obtained from Aldrich as 1.0 M and 0.5 M THF solns, respectively, and used without further standardization. Literature procedures were employed for the preparation of $NaEt_3BH$[14f] and KEt_3BH,[14e,19b] which were standardized prior to use.

Most of the organic compounds used to prepare sulfide and disulfide derivatives were common commercially available materials which were (unless noted) used without purification. 3-Chloro-5,5-dimethylcyclohex-2-enone was prepared by the method of Clark and Heathcock.[33]

IR spectra were recorded on a Perkin–Elmer Model 521 Spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained using Varian T-60 and CFT-20 spectrometers, respectively, with Me_4Si internal standard. Mass spectra were taken on an AEI MS-9 instrument. Elemental analyses were conducted by Galbraith. M.pts were taken on a Büchi Schmeltzpunktbestimmungsapparat, and are uncorrected.

Preparation of Li_2S in THF. To 1.0 equiv (2–10 mmol) powdered yellow sulfur under N_2 in a Schlenk flask was added 2.0–2.1 equiv 1.0 M $LiEt_3BH$ in THF. Although a reaction occurred immediately, the solution was allowed to stir 15 min before the addition of any organic compound.

Preparation of Li_2S_2 in THF. To 1.0 equiv (2–10 mmol) powdered yellow sulfur under N_2 in a Schlenk flask (in some reactions the sulfur was suspended in THF) was added 1–1.05 equiv 1.0 M $LiEt_3BH$ in THF. Although reaction occurred immediately, the solution was allowed to stir 15 min before the addition of any organic compound.

Dibenzyl sulfide. To 2.73 mmol Li_2S prepared as described above was added 0.629 ml (5.48 mmol) of benzyl chloride dropwise. After 3 hr stirring, the solvent was removed and the residue extracted with $CDCl_3$. Addition of 1,2,4,5-tetrachlorobenzene and ^1H NMR analysis (δ, $CDCl_3$: 3.56 (s, 4 H), 7.30 (s, 10 H); lit.[34] 3.57, 7.30) indicated a 94% yield.

Di-n-propyl sulfide. To 2.84 mmol Li_2S prepared as described above was added 0.516 ml (5.68 mmol) of 1-bromopropane. After 3.5 hr stirring, the solvent was removed and residue chromatographed on a silica gel column in 5% EtOAc in hexane. Thus isolated was 0.232 g (69.1%) of product, ^1H NMR (δ, $CDCl_3$): 0.97 (t, 6 H), 1.58 (m, 4 H), 2.46 (t, 4 H) (lit. (δ, CCl_4):[35] 0.98, 1.59, 2.44).

Di-n-butyl sulfide. To 2.28 mmol Li_2S prepared as described above was added 0.530 ml (4.65 mmol) of *n*-iodobutane dropwise. After 5 hr stirring, the solvent was removed and the residue chromatographed on a silica gel column in 5% EtOAc in hexane. Thus obtained was 0.231 g (1.61 mmol, 70.6%) of product, ^1H NMR (δ, $CDCl_3$): 0.97 (3 H), 1.50 (m, 4 H), 2.50 (lit.[34] 0.96, 1.52, 2.51).

Di-sec-butyl sulfide. To 2.49 mmol Li_2S prepared as described above was added 0.577 ml (4.98 mmol) of sec-BuI. The reaction was then refluxed under N_2 overnight. The solvent was then removed and the residue column chromatographed on silica gel using 5% EtOAc in hexane. Thus obtained was 0.244 g (1.56 mmol, 62.7%) of product, ^1H NMR (δ, $CDCl_3$): 0.70–1.88 (m), 2.75 (sextet) (lit.[34] 0.70–1.90 (m), 2.75 (sextet)).

Di-n-pentyl sulfide. To 3.56 mmol Li_2S prepared as described above was added dropwise 0.882 ml (7.12 mmol) of 1-bromopentane. After 5 hr stirring, the solvent was removed and the residue chromatographed on silica gel using 5% EtOAc in hexanes. Thus obtained was 0.442 g of product (2.54 mmol, 71.3%), ^1H NMR (δ, $CDCl_3$): 0.97 (3 H), 1.30 (m, 6 H), 2.47 (2 H).

1,3-Dihydroisothianaphthene. To 1.62 mmol of Li_2S prepared as described above was added dropwise a soln of 0.428 g (1.62 mmol) of α,α′-dibromo-*o*-xylene in 25 ml THF over a 1.5 hr period. 1,2,4,5-Tetrachlorobenzene internal standard was added and the solvent removed. ^1H NMR analysis of the residue indicated a 63% yield of 1,3-dihydroisothianaphthene (δ, $CDCl_3$): 4.22 (s, 4 H), 7.20 (s, 4 H) (lit.[21b] 4.06, 7.02 in CCl_4). Because of this chemical shift discrepancy, a similar reaction was run and the product purified by preparative Vpc; an identical ^1H NMR spectrum was obtained, and the mass spectrum (10 eV, *m/e* (%): 136 (100), 104 (1.5), 91 (2.5) established the molecular formula as C_8H_8S and *not* $(C_8H_8S)_2$.

Diacetyl sulfide. To 3.68 mmol Li_2S prepared as described above was added 0.523 ml (7.37 mmol) acetyl chloride. A white milky suspension resulted. After 2 hr stirring, 30 ml $CHCl_3$ was added and the ppt removed by filtration. The solvent was removed to yield 0.377 g of product (86.8%) which was pure by ^1H NMR (δ, $CDCl_3$): 2.50 (s) (lit.[23a] 2.50).

Bis(ethoxycarbonyl) sulfide. To 4.94 mmol of Li_2S prepared as described above was added 0.945 ml (9.88 mmol) of ethyl chloroformate dropwise. After 2.5 hr stirring, the solvent was removed and residue chromatographed in hexanes on silica gel. Thus obtained was 0.445 g of product (50.6%). ^1H NMR (δ, $CDCl_3$): 1.32 (t, 3 H), 4.33 (q, 2 H); (lit.[36] 1.33, 4.32). IR (cm^{-1}, THF): 1782 (s), 1758 (m), 1720 (m) (lit.[36] 1785, 1760, 1720).

Bis(5,5-dimethyl-2-cyclohexen-1-on-3-yl) sulfide (1). To 1.96 mmol Li_2S prepared as described above was added 0.620 g. (3.91 mmol) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one. The mixture was then refluxed for 12 hr. The solvent was removed, and in several experiments it appeared as though a reasonable ^1H NMR yield of product was formed (internal standard method). However, column chromatography on silica gel in 10% EtOAc in hexane afforded 1 as a yellow oil in yields of around 10%. Crystllization could be achieved by dissolving 1 in hot hexane followed by storage in a freezer. Since our m.p. (82–83°) differed from that previously reported (176–7°),[26] we provide here our full characterization of this compound: ^1H NMR (δ, $CDCl_3$): 1.13 (s, 6 H), 2.33 (s, 2 H), 2.47 (d, 2 H), 6.23 (t, 1 H); ^{13}C NMR ($CDCl_3$): 196.5, 155.3, 129.3, 50.9, 44.8, 34.2, 28.0 ppm; IR (cm^{-1}, $CHCl_3$): 1660 (s, br), 1582 (s); MS *m/e* (%): 278 (100), 263 (54), 194 (46), 155 (38), 110 (40), 83 (47): Analysis. (Found: C, 69.19: H, 8.11; S, 11.74. Calc. for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96; S, 11.52%).

Dibenzyl disulfide. To 2.49 mmol of Li_2S_2 prepared as described above was added benzyl bromide (0.615 ml, 5.35 mmol) in 10 ml THF. After 5 hr stirring the solvent was removed and the

residue taken up in hexane/H_2O. The hexane layer was separated and the hexane evaporated. The residue was extracted with hot EtOH, which was then cooled to 0°. Water was added. White crystals of product formed, which was isolated by filtration and dried under vacuum. Yield: 0.518 g (85%), m.p. 64° (authentic sample: 66°).

Di-n-propyl disulfide. To 2.51 mmol of Li_2S_2 prepared as described above was added *n*-PrI (0.51 ml, 5.24 mmol) in 5 ml dry THF. After 4 hr stirring, the solvent was removed and the residue taken up in hexanes/H_2O. The organic layer was washed with H_2O and dried with $MgSO_4$. The solvent was removed on a rotary evaporator to give 0.240 g of product (1.60 mmol, 63.5%) which was pure by ^{1}H NMR (δ, CCl_4): 1.0 (t, 3H) 1.7 (m, 2 H), 2.67 (t, 3 H). (lit.[35] 0.93, 1.70, 2.69).

In a second identical reaction, *p*-di(*t*-butyl)benzene internal standard was added prior to workup. The yield as determined by ^{1}H NMR was 83%.

Diallyl disulfide. To 2.49 mmol of Li_2S_2 prepared as described above was added 5.8 mmol (0.50 ml) of allyl bromide (distilled and stored over sives) in 5 ml THF. The mixture was refluxed for 2 hr. An internal standard, *p*-di(*t*-butyl)benzene, was then added. The solvent was removed and the residue taken up in hexanes/H_2O. The hexane layer was washed and dried with $MgSO_4$. The hexane was removed and the product and standard taken up as $CDCl_3$. A 93% yield was indicated by ^{1}H NMR: (δ, $CDCl_3$): 3.27 (d, 2 H) 4.92–5.36 (m, 2H), 5.73 (m, 1 H). (lit.[35] (δ, CCl_4) 3.29, 4.90–5.28, 5.72)

In a separate reaction run for 12 hr at 25°, a 66% isolated yield was obtained.

Di-n-butyl disulfide. To 2.50 mmol Li_2S_2 prepared as described above was added 0.59 ml (5.18 mmol) of 1-iodobutane dissolved in 5 ml THF. After 1 hr reflux, the solvent was removed and the residue taken up in hexanes/H_2O. The organic layer was washed and dried over $MgSO_4$. The solvent was removed on a rotary evaporator with a hot water bath. 0.681 g (3.88 mmol, 78%) of product was obtained which was pure by ^{1}H NMR (δ, $CDCl_3$): 0.97 (t, 3 N) 1.57 (m, 4 H), 2.70 (t, 2 H) (lit.[34] 0.95, 1.57, 2.70). In a similar reaction, a 87% ^{1}H NMR yield of di-*n*-butyl disulfide was obtained.

Di-n-pentyl disulfide. To 2.50 mmol of Li_2S_2 prepared as described above was added 0.62 ml (5.0 mmol) of *n*-pentyl bromide in 10 ml THF. The reaction mixture was refluxed for 2 hr, after which the solvent was removed. The residue was taken up in hexane/H_2O. The hexane layer was washed and dried with $MgSO_4$. The hexane was removed, affording 0.511 g (2.48 mmol; 99%) of product which was pure by ^{1}H NMR (δ, $CDCl_3$): 0.97 (t, 3 H), 1.43 (m, 6 H), 2.73 (t, 2 H).

Di-sec-butyl disulfide. To 2.05 mmol Li_2S_2 prepared as described above was added 0.58 ml (5.01 mmol) of 2-iodobutane. The mixture was refluxed for 2 hr, after which the solvent was removed. The residue was taken up in Et_2O/H_2O. After washing and drying with $MgSO_4$, 1,2,4,5-tetrachlorobenzene internal standard was added and the solvent removed. The yield of product was 73% by ^{1}H NMR (δ, $CDCl_3$): 1.0 (t, 3 H), 1.27 (d, 3 H), 1.60 (m, 2 H), 2.71 (m, 1H). (lit.[34] 1.0, 1.30, 1.59, 2.73)

Dibenzoyl disulfide. To 2.53 mmol Li_2S_2 prepared as described above was added 0.67 ml of benzoyl chloride (5.76 mmol) in 5 ml THF. After 1 hr reaction, the solvent was removed and the residue extracted with $CHCl_3$. The chloroform was removed, leaving behind product as a yellow solid which was washed with cold EtOH until colorless. Hexane was added to the EtOH washings, causing an additional amount of product to crystallize. The combined weight of dibenzoyl disulfide was 0.587 g (85%), m.p. 134–135° (lit.[27] 136°).

Diacetyl disulfide. To 2.53 mmol Li_2S_2 prepared as described above was added 0.4 ml acetyl chloride (5.60 mmol) in 10 ml THF. The reaction mixture was stirred for 0.5 hr, after which 1,4-di(*t*-butyl)benzene internal standard was added. The solvent was then removed and the product and standard taken up in $CDCl_3$. ^{1}H NMR analysis indicated 82% yield of diacetyl disulfide (δ, $CDCl_3$): 2.53 (s, 3 H).

Benzyl methyl sulfide. To dibenzyl disulfide (0.615 g, 2.49 mmol) in THF was added 5 ml of a 1.0 M THF soln of $LiEt_3BH$. After 15 min, CH_3I (0.8 ml, 12.8 mmol) in THF was added. Following 2 hr stirring, 1,4-di(*t*-butyl)benzene internal standard was added. The solvent was removed and the residue extracted with $CDCl_3$. ^{1}H NMR analysis indicated a 75% yield of product (δ, $CDCl_3$): 1.88 (s, 3 H), 3.60 (s, 2 H), 7.25 (s, 5 H). When a similar reaction was subjected to an ether/H_2O workup, a 54.3% yield of benzyl methyl sulfide was *isolated.*

Benzyl acetyl sulfide. To dibenzyl disulfide (0.616 g, 2.5 mmol) in THF was added 5.25 ml of a 1.0 M THF soln of $LiEt_3BH$. After 15 min, acetyl chloride (0.45 ml, 6.3 mmol) in THF was added. Following 4 hr stirring, 1,4-di(*t*-butyl)benzene was added and the solvent removed. The residue was extracted with $CDCl_3$. ^{1}H NMR analysis indicated a quantitative yield of product (δ, $CDCl_3$): 2.14 (s, 3 H), 4.02 (s, 2 H), 7.17 (s, 5 H).

3-Benzylthio-5,5-dimethylcyclohex-2-enone. To 3.84 mmol benzyl mercaptide prepared as described in the previous two preparations was added 0.621 g (4.04 mmol) of 3-chloro-5,5-dimethylcyclohex-2-enone. The yellow mixture was refluxed 3 hr. After cooling, 1,2,4,5-tetrachlorobenzene internal standard was added. The solvent was removed and the residue taken up in Et_2O/H_2O. The ether layer was washed and dried over $MgSO_4$. The ether was removed and the residue taken up in CCl_4. A 62.5% yield was indicated by ^{1}H NMR (δ, CCl_4): 1.03 (s, 6H), 2.13 (s, 2 H), 2.24 (d, 2 H), 4.00 (s, 2 H), 5.81 (t, 1 H), 7.28 (s, 5 H) (lit.[26] 1.02, 2.12, 2.24, 3.94, 5.82, 7.28). Product from a second experiment was purified on a silica gel column using 5% EtOAc in hexanes and found to melt at 84.5–85.5 (lit.[26] 84–85)°.

2-Phenylethyl methyl sulfide. To a stirred soln of 0.20 ml (2.2 mmol) of dimethyl disulfide in 5 ml of THF was added 4.4 ml of a 1.0 M THF soln of $LiEt_3BH$. After 10 min, 1.0 g (4.4 mmol) of 2-phenylethyl iodide was added dropwise to the homogeneous soln. After 16 hr, the solvent was removed and the residue chromatographed on a silica gel column in 5% EtOAc in hexane. The product was obtained as a translucent liquid (0.603 g, 90%).[31] ^{1}H NMR (δ, $CDCl_3$): 2.12(s), 2.84(m, A_2B_2), 7.34(s). ^{13}C NMR ($CDCl_3$): 140.6, 128.5, 126.3, 35.9 (2C), 15.6 ppm. ms, *m/e* (%): 152(90), 104(69), 91(38), 61(100).

Attempted preparation of dibenzhydryl trisulfide. To 0.089 g of sulfur (2.78 mmol) was added 1.85 ml of a 1.0 M THF soln of $LiEt_3BH$. Gas evolution (*ca.* 3 min) was followed by stirring (15 min). Benzhydryl bromide (0.457 g; 1.85 mmol) was then added. After 3.5 hr stirring, the solvent was removed and the residue dissolved in $CDCl_3$. ^{1}H NMR analysis (see results section) indicated a 1.0:1.5:1.0 ratio of disulfide: trisulfide: (tetra + penta) sulfide products.

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