Introduction of Sulphur into Organic Molecules *via* Lithium Triethylborohydride Reduction of S_8

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Summary Solutions in tetrahydrofuran of Li_2S and Li_2S_2 (or chemically equivalent species) are rapidly formed by reaction of elemental sulphur with appropriate stoicheiometries of $LiEt_3BH$; subsequent addition of electrophiles affords sulphide or disulphide derivatives in high yields.

ALTHOUGH there exists a variety of means for the introduction of sulphur into organic molecules,[1] research continues on the development of new sulphur transfer reagents and methods.[2,3] In previous studies, we have demonstrated the utility of trialkylborohydrides such as $LiEt_3BH$ for the cleavage of metal carbonyl dimers to metal carbonyl anions[4] and the preparation of anhydrous Li_2Se and Li_2Se_2 from grey powdered Se_x.[5] Hence it was of interest to determine if $LiEt_3BH$ could be employed in the generation of nucleophilic sulphur anions from yellow sulphur, S_8.

We report now that anhydrous tetrahydrofuran (THF) solutions of Li_2S and Li_2S_2 (or chemically equivalent species) can be synthesized by the simple addition of appropriate stoicheiometries of $LiEt_3BH$[6] to powdered sulphur [equations (1) and (2)], and that these solutions can be used to prepare a variety of sulphide and disulphide derivatives in high yield. Although numerous syntheses of such compounds are available, the present method provides a substantial improvement over many of these preparations, and is limited only by the moderate expense of trialkylborohydride reagents.

$$S + 2LiEt_3BH \longrightarrow Li_2S + 2Et_3B + H_2 \qquad (1)$$

$$2S + 2LiEt_3BH \longrightarrow Li_2S_2 + 2Et_3B + H_2 \qquad (2)$$

Addition of $LiEt_3BH$[6] (2·0 equiv.; 1·0 M in THF) to powdered sulphur (1·0 equiv.) under dry N_2 resulted in the instantaneous formation of a homogeneous yellow solution and the evolution of gas during 2 min. Reactions were conducted on 2—10 mmol scales and without cooling. To these solutions were subsequently added a variety of electrophiles (2·0—2·2 equiv.) (Table, A). After the indicated reaction time, high yields of sulphide derivatives could be isolated, indicating that a species chemically equivalent to Li_2S had been cleanly formed.

Similarly, the addition of $LiEt_3BH$ (1·0 equiv.) to powdered sulphur (1·0 equiv.) resulted in a homogeneous yellow solution of Li_2S_2 (or an equivalent entity). A number of disulphide derivatives were analogously prepared (Table, B).

TABLE. Preparation of sulphides and disulphides

A: Sulphides R_2S

	Electrophile RX	% Yield of sulphide R_2S[a]	Reaction time/h and conditions[b]
(1)	$PhCH_2Cl$	(94)	3
(2)	Bu^nI	71	5
(3)	$n\text{-}C_5H_{11}Br$	71	5
(4)	Bu^sI	63	12 (reflux)
(5)	MeCOCl	87	2
(6)	EtOCOCl	51	2·5
(7)	3-Chloro-5,5-dimethylcyclohex-2-enone	(55)	12 (reflux)

B: Disulphides R_2S_2

	Electrophile RX	% Yield of disulphide R_2S_2[a]	Reaction time/h and conditions[b]
(8)	$PhCH_2Br$	(89) 85	5
(9)	$H_2C{=}CHCH_2Cl$	(75)	1 + 0·5 (reflux)
(10)	Bu^nI	(87)78	1
(11)	$n\text{-}C_5H_{11}Br$	64	12 + 0·2 (reflux)
(12)	Bu^sI	(73)	2 (reflux)
(13)	PhCOCl	85	1
(14)	MeCOCl	(82)	0·5

[a] Products were identified by comparison with authentic samples or literature spectral data. Isolation procedures were unexceptional (column chromatography, distillation, or recrystallization). Yields are based upon starting sulphur and are not optimized. Values in parentheses are based on ^1H n.m.r. spectroscopy relative to 1,2,4,5-tetrachlorobenzene or 1,4-di-(t-butyl)benzene internal standard. [b] Room temperature unless noted.

Although simple dialkyl sulphides can be synthesised by use of $Na_2S{\cdot}9H_2O$, this reagent is incompatible with electrophiles requiring strictly anhydrous conditions. It is noteworthy that the Li_2S preparation readily undergoes acylation (entries 5 and 6, Table, A), providing a distinct improvement over existing synthetic methods for diacyl sulphides.[7] β-Chlorovinyl ketones (entry 7) are other electrophiles from which sulphides are formed most effectively in aprotic media.[8] While anhydrous alkali metal sulphides are commercially available, they are exceedingly hygroscopic, and thus our one-flask, *in situ* synthesis offers obvious advantages.

Alkali metal disulphides are not commercially available. Methods for their preparation (*e.g.*, Li–NH_3)[9] are cumbersome and sometimes afford mixtures of polysulphide salts.[1b,10] Alkylation of Na_2S_2 has been reported to proceed only in fair yield.[1b,10] The Table shows that the unoptimized disulphide yields are uniformly high. Thus disulphides may be readily prepared from non-sulphur containing precursors. Particularly for the diacyl disulphides (entries 13 and 14), the procedures are markedly simpler than reported methods.[11]

$NaBH_4$ reacts with sulphur to yield the synthetically useful hydride reductant $NaBH_2S_3$,[12] and $LiAlH_4$ and sulphur react to yield an undefined sulphide which liberates H_2S upon acidification.[13] Our report constitutes the first synthesis of alkali metal sulphides *via* action of a hydride reagent upon sulphur. 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.[6]

The role of the by-product Et_3B [equations (1) and (2)], which is volatilized upon solvent removal during workup, is unclear but probably of relevance. Commercial anhydrous Li_2S is insoluble in THF, and 2·86 mmol of Li_2S failed to dissolve in 5·72 ml of 1·0 M Et_3B in THF, yet our reaction mixtures appear homogeneous. Marked differences have recently been demonstrated in the solubility and reactivity of Na^+PhSe^- depending upon whether it is prepared by $NaBH_4$ or Na reduction of diphenyl diselenide.[14]

Several useful extensions of our method are apparent. Disulphides are instantly cleaved to lithium thiolates by reaction with $LiEt_3BH$. Subsequent addition of an electrophile leads to a convenient synthesis of unsymmetric sulphides. Thus from dibenzyl disulphide were prepared benzyl methyl sulphide (75%; *via* MeI) and benzyl acetyl sulphide (100%; *via* AcCl). We have also had some success in the preparation of symmetric trisulphides by varying the sulphur–$LiEt_3BH$ stoicheiometry, and details will be reported in our paper.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

(*Received*, 21*st June* 1978; *Com.* 661.)

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