New Synthesis of Tetradentate Organosulphur Ligands by Organotin Reduction of Bis(dithiolanes)

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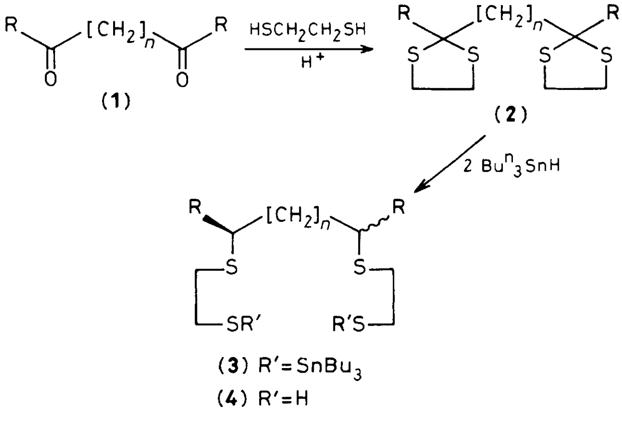
Tetradentate organosulphur ligands are efficiently prepared by the selective reduction of bis(dithiolanes) with two equivalents of tri-n-butyltin hydride.

The use of disulphide dithiols (**4**) as tetradentate ligands for a variety of metal ions is well established.[1,2] Compounds of this type, and ligands derived from them, have been used as models of the copper binding site of the 'blue' proteins,[3] and as precursors to polythiomacrocyclic compounds.[4] We report herein a convenient, high yield procedure for the preparation of a variety of disulphide dithiols (**4**) (Scheme 1).

Our earlier work[5] on the selective desulphurization of 2-alkyl(or aryl)-1,3-dithiolanes by one equivalent of tri-n-butyltin hydride to produce β-alkyl(or aryl)thioethyl tributyltin sulphides suggested that tetradentate organosulphur ligands (**3**) and (**4**) might be obtained from the selective reduction of bis(1,3-dithiolanes) (**2**) by Bu^n_3SnH. In turn, compounds (**2**) could be readily prepared from the reaction of ethane-1,2-dithiol with diketones or dialdehydes (**1**).

Several known bis(dithiolane) compounds (**2a**),[6] (**2b**),[6] (**2c**), and (**2d**)[7] were prepared and subsequently reduced with two equivalents of Bu^n_3SnH in refluxing benzene, using azoisobutyronitrile initiation. The yields of bis(tributyltin sulphides) (**3**) were excellent. These compounds were smoothly destannylated on silica gel to give the disulphide dithiols (**4**) in good isolated yields.[5] The dithiol product structures were confirmed by n.m.r. and i.r. spectroscopy and they exhibited the expected molecular ion in their mass spectra.

The reductions of (**2b**) and (**2c**) introduced two new chiral centres in the products. Consequently the dithiols (**4b**) and (**4c**) were each isolated as roughly 1 : 1 diastereoisomeric mixtures.



(**1**)

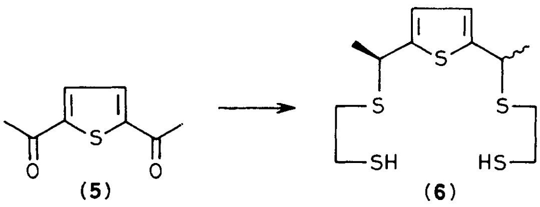
(**2**)

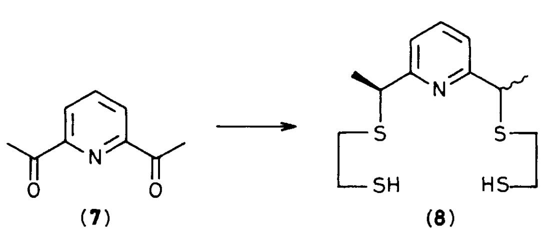
(**3**) $R'=SnBu_3$
(**4**) $R'=H$

	Compound (**2**)		% Yield	
	R	*n*	(**3**)	(**4**) [from (**3**)]
a;	H	1	96	69
b;	Me	1	98	84
c;	H	2	97	87
d;	Me	2	80	93

Scheme 1

The synthesis of 3,7-dithianonane-1,9-dithiol (**4a**) has been previously reported.[1] It was prepared by the dialkylation of propane-1,3-dithiol with 2-chloroethanol, and the intermed-


(5) **(6)**


(7) **(8)**

iate disulphide diol was converted into (**4a**) by reaction first with thiourea in refluxing concentrated HCl, then with KOH. The present method provides a superior overall yield of product under considerably milder conditions. Certainly for the synthesis of more substituted systems [*i.e.* R ≠H in (**4**)], we feel that the Bu^n_3SnH procedure is the method of choice.

To test the versatility of the method for incorporation of more complex structural features into polydentate organosulphur ligands (**4**), more structurally diverse diketones were used as starting materials. When 2,5-diacetylthiophene (**5**) was treated with ethanedithiol, we obtained the corresponding bis(ethylenedithioacetal). Subsequent reduction with two equivalents of Bu^n_3SnH, followed by destannylation on silica gel, gave a 55% yield [from (**5**)] of diastereoisomeric ligands (**6**) [i.r. (neat) 2540 cm^{-1}; ^1H n.m.r. (CCl_4) δ 6.70 (s, 2H), 3.15 (q, 2H), 2.34—2.75 (m, 8H), and 1.45—1.80 (s, 8H); M^+, calc. for $C_{12}H_{20}S_5$: *m/z* 324.0169, found: 324.0171]. In a similar manner, the use of 2,6-diacetylpyridine (**7**) resulted in a 64% yield of diastereoisomeric ligands (**8**) [i.r. (neat) 2550 cm^{-1}; ^1H n.m.r. (CCl_4) δ 7.02—7.28 (m, 3H), 4.02 (q, 2H), 2.35—2.80 (m, 8H), and 1.35—1.80 (m, 8H); M^+, calc. for $C_{13}N_{21}HS_4$: *m/z* 319.0557, found: 319.0553].

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