

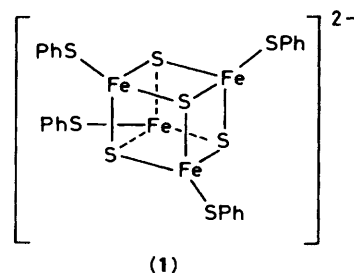
## Electron-transfer Reduction of Esters with Carbanions mediated by an Iron–Sulphur Cluster

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The iron–sulphur cluster (1) acts as an electron-transfer agent in the reduction of *S*-phenyl thiobenzoate and phenyl benzoate with *n*-butyl-lithium and phenyl-lithium to give benzil and benzoin.

The iron–sulphur cluster,  $(\text{Bu}^n_4\text{N})_2\text{Fe}_4\text{S}_4(\text{SPh})_4$  (1), is attractive as a model compound of ferredoxin which catalyses electron-transfer reactions in biological systems. Previously we have reported that the cluster (1) mediates the transfer of electrons from *n*-butyl-lithium to aromatic ketones and aldehydes to give the corresponding pinacols<sup>1</sup> and from phenyl-lithium to protons to give hydrogen.<sup>2</sup> Furthermore, we have shown recently that the phenyl-lithium activated  $\text{Fe}_4\text{S}_4\text{Cl}_4^{2-}$  cluster acts as a hydride transfer agent in substrate selective hydrogenation of carbonyl compounds with

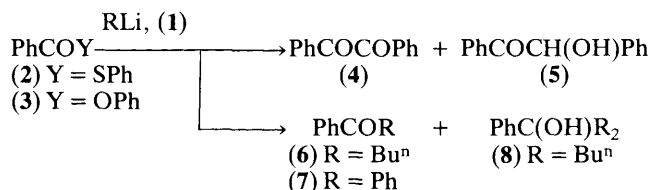


**Table 1.** Reduction of (2) and (3) with the RLi-(1) system.<sup>a</sup>

Substrate	RLi	Molar ratio RLi:Subst.:(1)	Yield, % <sup>b</sup>			
			(4)	(5)	(6) or (7)	(8)
(2)	Bu <sup>n</sup> Li	16:2:1	0	42	6	15
		16:4:1	6	34	0	31
	PhLi	12:2:1	33	16	14	—
		12:4:1	28	21	32	—
(3)	Bu <sup>n</sup> Li	16:2:1	0	32	3	23
		16:4:1	0	31	9	42
	PhLi	12:2:1	2	44	46	—
		12:4:1	8	28	30	—

<sup>a</sup> (1): 0.125 mmol in Et<sub>2</sub>O (5 ml)-hexane (1.7 ml) (for Bu<sup>n</sup>Li) and Et<sub>2</sub>O (6.8 ml) (for PhLi); Ar, room temp., 20 h. <sup>b</sup> Isolated yield based on substrate. Ph<sub>3</sub>COH was not obtained.

hydrogen gas.<sup>3</sup> We now report the novel function of the cluster (1) which mediates the transfer of electrons from n-butyl-lithium and phenyl-lithium to *S*-phenyl thiobenzoate (2) and phenyl benzoate (3) in homogeneous system to give benzil (4) and benzoin (5) by bimolecular reduction.



The cluster (1) was added to a frozen solution of n-butyl-lithium or phenyl-lithium in degassed hexane-diethyl ether or diethyl ether respectively. The mixture, after melting, was stirred under argon at 0°C for 30 min. The resulting black solution was frozen again and the ester (2) or (3) was added under argon. The mixture, after melting, was stirred at room temperature for 20 h. The reactions were stopped by adding dilute hydrochloric acid.

The ether layer was concentrated by rotary evaporation and the resulting brown oil was chromatographed on silica gel. In the case of the Bu<sup>n</sup>Li-(1)-(2) system, elution with carbon tetrachloride gave diphenyl disulphide as a white solid as the first fraction, followed by (6) as a colourless oil. Subsequent elution with benzene gave (4) as a yellow solid, followed by (8) as a pale yellow oil. Elution with chloroform gave (5) as a white solid. In the case of the PhLi-(1)-(2) or (3) system, (7), (4), and phenol were eluted with benzene as fractions 1, 2, and 3 respectively. All products were identified by their i.r. and <sup>1</sup>H n.m.r. spectra and the yields were estimated by measuring the weight of the isolated substances. The results are summarized in Table 1.

The reactions of (2) and (3) with n-butyl-lithium and phenyl-lithium in the presence of the cluster (1) gave (4) by bimolecular reduction, followed by further reduction of (4) to (5), the ketones (6) and (7) and tertiary alcohol (8) being obtained as the by-products. Benzyl alcohol and benzophenone and butyrophenone pinacols were not produced in these reactions. The optimal molar ratios of n-butyl-lithium and phenyl-lithium to the cluster (1) giving the highest yield of (4) and (5) were 16:1 and 12:1, respectively, for an ester to

(1) molar ratio of 4:1. When the RLi to (1) molar ratio was higher than the optimal ratio, the yields of (4) and (5) decreased with increase in yields of (6), (7), and (8).

The formation of (4) constitutes an overall two-electron reductive dimerization of (2) or (3) by the reduced cluster (1), as shown in the reduction of aromatic ketones and aldehydes with the Bu<sup>n</sup>Li-(1) system giving their pinacols.<sup>1</sup> The electron-transferring function of the cluster (1) was compared with that of a mononuclear complex consisting of iron(III) chloride and n-butyl-lithium. The reaction of (2) with the (4:1) Bu<sup>n</sup>Li-FeCl<sub>3</sub> system [FeCl<sub>3</sub>: 0.5 mmol in Et<sub>2</sub>O (5 ml)-hexane (1.7 ml)] was found to give (4) and (5) in lower yields than those for the reducing system using the cluster (1); for a (2) to FeCl<sub>3</sub> molar ratio of 1:1, the yields of (4) and (5) based on (2) after 20 h were 0 and 27% respectively. The other reduction products were not obtained at all. In the (3:1) Bu<sup>n</sup>Li-FeCl<sub>3</sub> system, the reduction of (2) did not occur. For molar ratios higher than 4:1, (8) was obtained as the main product [53% yield for a (2) to FeCl<sub>3</sub> molar ratio of 1:1]. However (3) was reduced mainly to benzyl alcohol (9) by the (4:1) Bu<sup>n</sup>Li-FeCl<sub>3</sub> system under similar conditions; for (3) to FeCl<sub>3</sub> molar ratios of 0.5:1 and 1:1, the yields of (9) based on (3) after 20 h were 20 and 12% respectively. The yields of (4) and (5) were very low. The formation of (9) indicates that an intermediate iron-hydride species, which may be formed by β-hydrogen elimination from n-butyl-lithium,<sup>4</sup> acts as a reducing agent. Thus, it is apparent that there is a significant difference in reactivity between the reduced cluster (1) and mononuclear iron complexes.

The above results indicate characteristic behaviour of the cluster (1) which undergoes bimolecular reduction by transferring electrons from n-butyl-lithium and phenyl-lithium to (2) and (3).

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