Electron-transfer Reduction of Fluorenone with n-Butyl-lithium Mediated by an Iron–Sulphur Cluster

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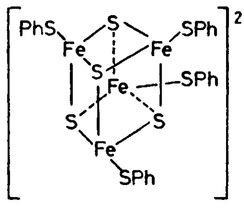
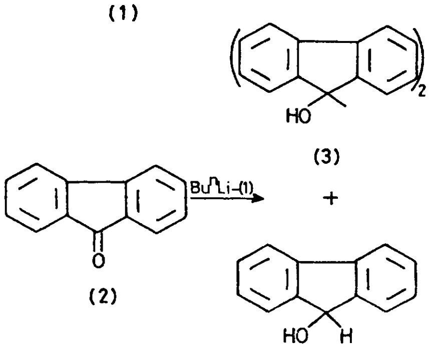
Summary The iron–sulphur cluster (**1**) functions as an electron-transfer agent in the reduction of fluorenone with n-butyl-lithium to form bifluoren-9-yl-9,9′-diol and/or fluoren-9-ol.

Recently, a ferredoxin model compound, a tetra(mercapto-μ_3-sulphido-iron) cluster, has been synthesized.[1] It catalyses the transfer of electrons from external reductants to molybdenum complexes in nitrogenase model systems,[1,2] and has been used for the fixation of carbon dioxide in amino-acid synthesis.[3] We have studied the possibility of carrying out electron-transfer reactions with $[Fe_4S_4(SPh)_4](Bu^n{}_4N)_2$ (**1**) in a simple organic redox system and now report the first example of such a reaction, the reduction of fluorenone (**2**) with n-butyl-lithium in the presence of (**1**), giving rise either to the bifluorenyl diol (**3**) together with octane as the major products, or to the fluorenol (**4**) and butane and butenes in the optimal n-butyl-lithium–(**1**) reducing system.

The complex (**1**) was prepared by Holm's method[1] and the reactions were carried out as follows: complex (**1**) was added to a frozen solution of n-butyl-lithium in degassed hexane–diethyl ether. The solution, after melting, was stirred under helium at 0 °C for 0·5 h. Compound (**2**) was



(1)



(2)

(3)

(4)

then added, and the mixture was allowed to warm to room temperature and stirred vigorously for 20 h. The reaction was stopped by adding water or benzenethiol. The product distribution is shown in Table.

TABLE[a]

Iron complex	Molar ratio $\mathrm{Bu^nLi}$: Fe ion	Yield, %[b]				Unchanged (**2**), %
		(**3**)	(**4**)	(**5**)	Bu–Bu[c]	
(**1**)	2 : 1	62	9	4	36	20
(**1**)	4 : 1	6	63	10	0	13
$FeCl_3$	3 : 1	93	0	0	2	0
$FeCl_3$	6 : 1	8	2	76	0	1
FeS	2 : 1	0	0	94	0	1

[a] (**2**) : Fe ion molar ratio 1 : 1. Amounts of (**2**) : 0·55—1·4 mmol in hexane (0·4—3 ml)–ether (5 ml). [b] Isolated yield except for octane. [c] Determined by g.l.c. and based on (**2**).

In the absence of (**1**), 9-butylfluorenol (**5**) was obtained in 87 and 98% yield with molar ratios of n-butyl-lithium : (**2**) of 2 : 1 and 4 : 1, respectively. In the presence of (**1**), however, (**3**) and (**4**) were produced together with small amounts of (**5**). The yields of (**3**) and (**4**) depended on the amount of n-butyl-lithium added. For a $\mathrm{Bu^nLi}$: (**2**) molar ratio of 2 : 1, (**3**) was formed predominantly along with octane. The formation of (**3**) constitutes an overall two-electron reductive dimerization of (**2**). Compound (**4**) was formed predominantly for a $\mathrm{Bu^nLi}$: (**2**) ratio of 4 : 1. The product resulting from the n-butyl-lithium in this case was not octane, but was composed of butane, but-1-ene, and *cis*- and *trans*-but-2-enes (by g.l.c.). When D_2O was added to the mixtures after the reaction [$\mathrm{Bu^nLi}$: (**2**) = 4 : 1] fluoren[^{2}H]ol (67%) was obtained in amounts similar to the amounts in the case of undeuteriated fluorenol from H_2O (63%). This demonstrates that two electrons are transferred from the reduced (**1**) to (**2**). However, (**1**) was regenerated in $>$ 97% purity on addition of benzenethiol to the mixtures after the reaction. We have also compared the function of (**1**) with that of iron(III) chloride and iron(II) sulphide (Table). In the n-butyl-lithium–iron(III) chloride (3 : 1) system, (**3**) was produced along with butane and butenes, but octane was not formed. This phenomenon indicates that the function of (**1**) in these systems is essentially different from that of iron(III) chloride. For a $\mathrm{Bu^nLi}$: $FeCl_3$ ratio of 6 : 1 (**5**) was the major product. Thus, iron(III) chloride was ineffective for the formation of (**4**) by two-electron reduction.

The above results constitute evidence for the function of the iron-sulphur cluster in transferring electrons from n-butyl-lithium to (**2**) and suppressing the addition of n-butyl-lithium to (**2**). It is probable that such behaviour occurs in other organic oxidation–reduction systems.

(*Received*, 21*st March* 1977; *Com.* 270.)

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