SHORT COMMUNICATION

The reaction of 1,4-dithiins with iron carbonyls

The reported[1] formation of the complex (I) from the reaction of thiophene with tri-iron dodecacarbonyl prompted us to investigate similar reactions with other sulphur heterocycles as a possible route to iron heterocycles. Although 2,6- and 3,5-diphenylthiopyran-4-ones failed to give appreciable quantities of products, the reactions with 1,4-dithiins were more successful. The 1,4-dithiin system is of particular interest in that it can be regarded as being π-isoelectronic with cyclooctatetraene, whose reactions with metal carbonyls have been extensively investigated[2]. Alternatively, if both lone pairs of each sulphur atom are utilised it may be compared with the aromatic cyclooctatetraene dianion.

The principle product of the reaction of tetraphenyl-1,4-dithiin with either di-iron nonacarbonyl or tri-iron dodecacarbonyl was a red diamagnetic complex, m.p. 140°, with the composition $(C_{14}H_{10}S_2)Fe_2(CO)_6$. An analogous complex $(C_8H_6S_2)$-$Fe_2(CO)_6$, m.p. 95°, was obtained from 2,5-diphenyl-1,4-dithiin. The infrared spectra of these complexes show bands at 2080, 2040 and 2000 cm^{-1} characteristic of terminal carbonyl ligands. This leads us to formulate these complexes as (IIa) and (IIb) by analogy with those formed by iron carbonyls with other 1,2-dithiolato ligands[3]. The fate of the remainder of the dithiin molecule has been clarified in the tetraphenyl series where, in addition to (IIa), it was possible to isolate diphenylacetylene and the complex(III)[4]. The latter compound is a major product of the reaction of diphenylacetylene with di-iron nonacarbonyl under these conditions[5]. Several examples of the cleavage of a vinyl–sulphur bond have been reported previously[1,6]. Not surprisingly an analogous reaction did not occur with thianthrene; instead, at room temperature it catalysed the conversion of di-iron nonacarbonyl into tri-iron dodecacarbonyl. A similar catalytic effect was observed with the afore-mentioned thiopyranones, diphenyl sulphide and thiophene, which does not give (I) under these conditions.

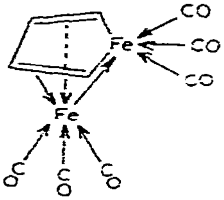
Experimental

Infrared spectra were recorded for nujol mulls using a Perkin-Elmer model 137E spectrophotometer. Molecular weights were measured osmometrically in benzene.

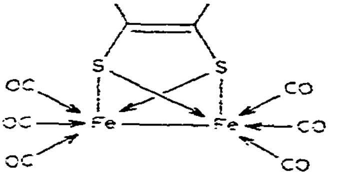
Reaction of tetraphenyl-1,4-dithiin with $Fe_2(CO)_9$. Tetraphenyl-1,4-dithiin[7] (1.8 g) dissolved in dry dioxane (250 ml) was stirred for several hours with di-iron nonacarbonyl (8 g) at room temperature and under nitrogen. The resulting mixture was filtered and the residue extracted with toluene to give unreacted dithiin (0.5 g). The filtrate was evaporated *in vacuo*, the residue taken up in 60–80° petroleum ether and chromatographed on silica gel. Two dark red fractions (*i*) and (*ii*) were eluted. Rechromatography of fraction (*i*) gave successively diphenylacetylene (70 mg, m.p. 61.5°, from aqueous alcohol), a small quantity of tri-iron dodecacarbonyl and finally a bright red complex, (IIa), (145 mg, m.p. 140–145° decomp.), which crystallised as needles from aqueous methanol. (Found C, 46.2; H, 1.8; Fe, 22.2; O, 18.3; S, 12.2; mol. wt., 513. $C_{20}H_{10}Fe_2O_6S_2$ calcd.: C, 46.0; H, 1.9; Fe, 21.4; O, 18.4; S, 12.3%; mol.

wt., 522.) Fraction (*ii*) on rechromatography gave traces of a black and a yellow complex on elution with petroleum ether. Petroleum ether–benzene (1:1) eluted the red complex, $(PhC{\equiv}CPh)_2Fe_2(CO)_7$, (III), (10 mg, m.p. 161–163° decomp., from petroleum ether); ν_{max} 2090, 2060, 2010 and 1665 cm^{-1}, identical with an authentic sample[4].

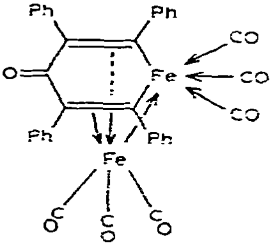
Reaction of 2,5-diphenyl-1,4-dithiin with iron carbonyls. (*a*) 2,5-Diphenyl-1,4-dithiin[8] (1 g) in dry benzene (80 ml) was stirred for several hours with di-iron nonacarbonyl (2.8 g) at room temperature under nitrogen. The filtered red solution was evaporated *in vacuo* and chromatographed on silica gel in 60–80° petroleum ether. Elution with petroleum ether gave the complex(IIb) (70 mg, m.p. 95–97° decomp. as red plates from aqueous methanol). (Found: C, 37.9; H, 1.7; Fe, 25.7; O, 21.7; S, 14.2; mol. wt., 442. $C_{14}H_8Fe_2O_6S_2$ calcd.: C, 37.7; H, 1.3; Fe, 25.0; O, 21.5; S, 14.4%; mol. wt., 446.)



(I)



(II) a R = R' = Ph
b R = H, R' = Ph



(III)

Petroleum ether–benzene (9:1) eluted unreacted dithiin (0.55 g). Traces of unstable complexes were eluted by more polar eluants but could not be characterised.

(*b*) 2,5-Diphenyl-1,4-dithiin (2.7 g) in benzene (100 ml) was refluxed under nitrogen in a flask fitted with a Soxhlet extractor, the thimble of which contained tri-iron dodecacarbonyl (10 g). After refluxing overnight the benzene solution was filtered, evaporated and worked up as above to give the complex(IIb) (180 mg) and unreacted dithiin (1 g).

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Department of Chemistry, Queen Elizabeth College, London, W. 8 (England)

C. W. Bird
E. M. Hollins

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