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Preliminary communication

PREPARATION AND PROPERTIES OF IRON CARBONYL COMPLEXES OF 2,5-DIHYDROTHIOPHENE-1 OXIDE

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Summary

On reaction with diironnonacarbonyl in refluxing ether, 2,5-dihydrothiophene-1-oxide forms an iron tricarbonyl complex in which the ligand has not undergone rearrangement. The iron tricarbonyl complex is formed from an intermediate that appears to be a tetracarbonyl complex in which the iron is bonded to the sulfoxide, but not to the double bond of 2,5-dihydrothiophene-1-oxide. Some reactions of the tricarbonyl complex have been examined.

The synthetic potential of the thiophene ring system [1] would be much enhanced were there available methods of reversibly modifying the relative distribution of electron density about the ring. One approach to this end would be to change the valency about the sulfur atoms as in thiophenium salts, oxides, and dioxides. (We have made previously efforts in this area [2]). However, all attempts at a conceptually different reaction, namely complexation of the diene segments of the thiophene ring to a metal carbonyl have failed*. We report here the results of our initial efforts towards achieving such complexation using an indirect route wherein 2,5-dihydrothiophene-1-oxide (I), a "thiophene hydrate", is used as a latent synthetic equivalent. The projected dehydration of I is a transformation known to be general [4].

Birch reduction of thiophene gave the known 2,5-dihydrothiophene [5], which was oxidized to I in 86% yield by t-butylhypochlorite in methanol at −80°C [6]. Hydrogen peroxide [5a], *meta*-chloroperbenzoic acid [7], or sodium metaperiodate [8] were not satisfactory as oxidizing agents. On refluxing I and diiron nonacarbonyl (1 : 2 ratio) in ether for 2.5 h under nitrogen, followed by filtration and sublimation, there was obtained in 76% yield an analytically pure product (III) of molecular composition corresponding to an iron tricarbonyl

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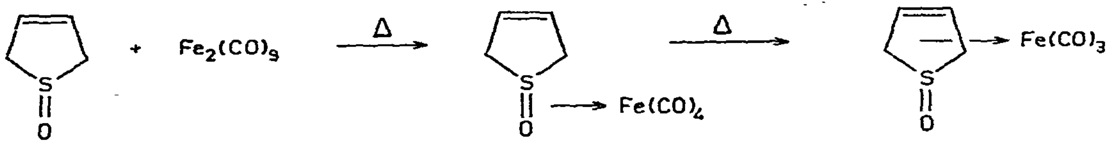
*With thiophene itself desulfurization occurs [3a, b]; chromium carbonyl complexes and an iron complex bonded to the aromatic sextet of thiophene derivatives are known [3c].

complex of I (eq. 1). When the reaction was monitored by ^{1}H NMR spectroscopy, it became clear that III was formed quantitatively, but that it was preceded by an unstable intermediate, which we formulate (see below) as the tetracarbonyl complex (II).



(I) (II) (III)

Spectral data* establish clearly that in the end-product III both the sulfoxide moiety and double bond are complexed. Full details of the crystal structure were elucidated by X-ray diffraction techniques. Some crystallographic data are given in Fig. 1 and Table 1; the details of the structure will appear separately [9]. In accord with literature precedent [10] the iron atom is bonded to the oxygen of the sulfoxide, which occupies an axial position of the trigonal bipyramid whereas the double bond is in equatorial position. ESCA measurements reveal the sulfur atom of III to be more electropositive than in uncomplexed sulfoxides [11].

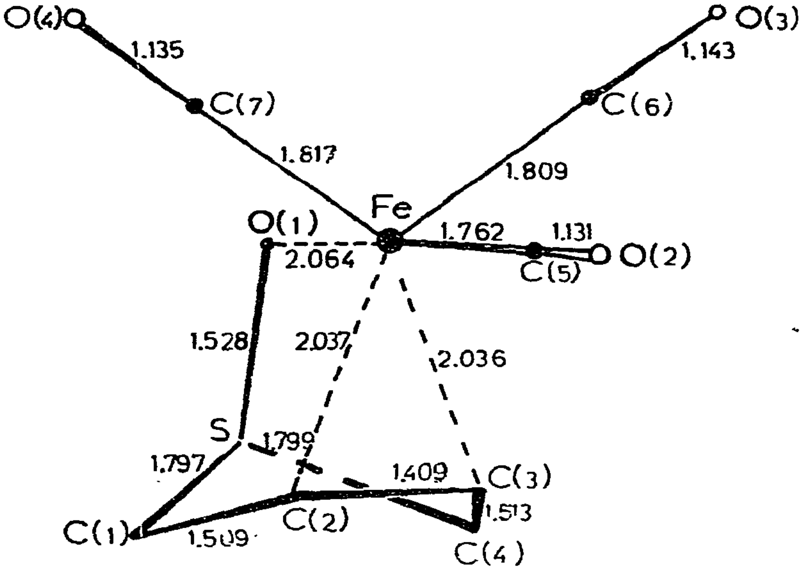


Fig. 1. Structure and bond lengths of compound III.

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*^{1}H NMR (C_3D_6O, 40°C): δ (ppm) 3.82 (d, 2, J_{vic} 2 Hz, vinyl), δ 2.69 (d, 2, J_{gem} 14.5 Hz, J_{vic} 2 Hz, CH_2) and δ 3.17 (d, 2, J_{gem} 14.5 Hz, J_{vic} 2 Hz, CH_2); ^{13}C NMR (CH_2Cl_2, 37°C, δ (ppm) relative to TMS, noise decoupled): δ 46.85 (sp^3 C), δ 57.01 (sp^2 C) and δ 213.80 ($C\equiv O$). (This absorption on cooling splits reversibly to two absorptions δ 213.00 and 214.50 ppm, ratio 2 : 1, corresponding to respectively the equatorial and axial carbonyls of the trigonal bipyramid). IR (KBr): 2963, 2910, 2037, 1950-1915 (br), 1100, 1070, 1020 cm^{-1}; microanalytical data were satisfactory.

TABLE 1

CRYSTAL DATA

(The crystals are monoclinic, space group $P2_1/c$ with unit-cell parameters a 7.997, b 10.086, c 13.534 Å and β 124.64°. The unit cell contains four molecular units, $Z = 4$)

	Bond angles (°)	Non-bonding distances (Å)	
Fe—C(7)—O(4)	176	Fe—S	2.956
Fe—C(6)—O(3)	176	C(5)—C(2)	2.717
Fe—C(5)—O(2)	179	C(5)—C(3)	2.792
C(7)—Fe—C(6)	109		
C(7)—Fe—C(5)	91		
C(6)—Fe—C(5)	93		
Fe—O(1)—S	110		
C(1)—S—C(4)	90		
C(1)—S—O(1)	100		
C(4)—S—O(1)	101		

On allowing a 1 : 1 mixture of diiron nonacarbonyl and I to react briefly in ether, followed by recrystallization from the same solvent at −35°C, the intermediate II was isolated in good yield, but it was contaminated with about one equivalent of free ligand (I), which also crystallizes under these conditions. No compound III is present but on warming to room temperature II spontaneously is transformed to this product. By tedious recrystallizations a sample of unstable II was obtained containing only about 10% of free I and no other contaminants. Both the ^{1}H NMR and ^{13}C NMR spectra[*] reveal that the double bond of I is not complexed since chemical shifts in II for the vinylic protons are scarcely shifted form those of pure I[**]. The mass spectrum contains no parent peak but exhibits four successive losses of CO and resembles closely that of III. We formulate II as the tetracarbonyl complex bonded to the sulfoxide. There is little precedent for this selective complexation at the heteroatom rather than at the alkene moiety in the case of iron carbonyl complexes[***]. Indeed the opposite order of reactivity is found in the reactions of α,β unsaturated ketones [13] (For a demonstration that tetracarbonyl complexes are intermediates in the reactions of conjugated dienes see Ref. 14.) A distant analogy may exist in observations with some conjugated nitriles [3b].

In contrast to experience with III, pseudorotation in II was not frozen out even at −97°C [16, 15]; we tentatively suggest that the ligand may be equatorial rather than axial [15].

Although I is cleanly converted into thiophene on treatment with acetic anhydride [4] at 40°C neither this reagent nor any other tried dehydrates the organic ligand into III. The failure to achieve dehydration is likely a result of the

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[*] ^{1}H NMR (C_3D_6O, −41°C): δ (ppm) 4.45 (s, 4, CH_2) and δ 6.22 (s, 2, vinyl-H); ^{13}C NMR (C_3D_6O, −34°C, noise decoupled, δ (ppm) relative to TMS): δ 71.95 (sp^3 C), δ 126.74 (sp^2 C), and δ 212.65 (C≡O). Even at −90°C the carbonyl absorption remains a singlet but new absorptions begin to appear at δ 60.39 and 126.08 ppm; this process is reversible and may possibly indicate reversible σ and π bonding of the sulfoxide although other explanations are not eliminated. IR (KBr): 3060, 2960, 2912, 2070, 1970-1915 (broad), 1135, 1080, 1030 cm^{-1}.

[**] ^{13}C NMR ($CDCl_3$, 40°C, δ (ppm) relative to TMS, noise decoupled): δ 123.66 (sp^2 C) δ 58.78, (sp^3 C); ^{1}H NMR (C_3D_6O, −40°C, δ (ppm) related to TMS): δ 6.12 (s, 2, vinyl), δ 3.94 (d, 2, J_{gem} 17 Hz, CH_2) and δ 3.40 (d, 2, J_{gem} 17 Hz, CH_2).

[***] Selective complexation at an heteroatom is known for some other metals [12].

direct bonding of the sulfoxide oxygen to the iron atom. It is possible to release the unisomerized ligand (I) in at least 75% yield from III by either irradiation in THF [18] or treatment with excess trimethylamine oxide in benzene [19]. The good yield from the complexation reaction, the simplicity of method, and absence of isomerizationiin the organic ligand (this last item contrasting sharply with results from other systems [20-23][*]) portend well for the synthetic potential of complexed allylic sulfoxides. Attempts to introduce functionalities at the methylene group in III are being pursued.

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[*] Absence of isomerisation in the organic ligand is observed in some other metal complexes [23].