Sulphinyl-controlled Formation of Diastereoisomerically Pure (Oxadiene)tricarbonyliron(o) Complexes

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The sulphonyl and sulphinyl substituted oxadienes $[RS(O)_nCH=CHC(Me)=O; R = Bu^t, Ph; n = 2,1]$ form stable tricarbonyliron(o) complexes; the sulphinyl complexes formed are diastereoisomerically pure and the relative stereochemistry of the tricarbonyliron(o) unit and the sulphinyl substituent in the products has been determined by an X-ray crystal structure analysis of $[Bu^tS(O)CH=CHC(Me)=O](CO)_3Fe^0$.

We have recently conducted extensive investigations into the reactivity of tricarbonyliron(o) complexes of α,β-unsaturated ketones. We have found that these complexes undergo a number of interesting reactions,[1,2] and that they may be converted into tricarbonyliron(o) complexes of vinyl-ketenes,[3,4] vinylketenimines[5,4] and vinylallenes,[6] which in turn possess diverse and novel reactivity. Almost all of our exploratory work has been based on tricarbonyliron(o) complexes of α,β-unsaturated ketones with a β-phenyl substituent, a class of complex which may be exemplified by compound 1. This is a reflection of the much greater stability of complexes of ligands bearing β-phenyl substituents compared to complexes of ligands bearing β-alkyl substituents. These latter complexes may be synthesised and used, but extreme care must be taken to exclude air from all manipulations involving them.

As part of a study designed to determine whether substituents other than aryl groups will confer stability on tricarbonyliron(o) complexes of α,β-unsaturated ketones, it was decided to examine the effect on complex stability of replacing the phenyl group of 1 with sulphonyl and sulphinyl groups. As a result of these investigations, we now report that not only do β-sulphonyl and β-sulphinyl substituted α,β-

unsaturated ketones form very stable tricarbonyliron(o) complexes, but also, and of more general significance, that the chirality of the sulphinyl substituent exerts good diastereoisomeric control over the complexation reaction.†

4-(tert-Butylsulphenyl)but-3-en-2-one 2a and 4-(phenyl-sulphenyl)but-3-en-2-one 2b were readily synthesised using literature procedures,[8] and subsequent oxidation of 2a and b with 2.2 equivalents of mCPBA proceeded smoothly to give the β-sulphonyl derivatives 3a[8] and b[8] (Scheme 1). The sulphones 3a and b were then stirred with 1.1 equivalents of (benzylideneacetone)tricarbonyliron(o) 1[4] at 35 °C for 14 h in a solvent mixture of pentane and toluene (1 : 1). Chromatography of the two product mixtures and crystallisation produced two sets of orange–yellow crystals which were

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† As far as we are aware, only one previous report of sulphinyl-substituted diene tricarbonyliron(o) complexes has appeared.[7] In this report, the conversion of 1-sulphinyl substituted buta-1,3-dienes into their tricarbonyliron(o) complexes is used to characterise the dienes. The complexation reaction [which uses $Fe(CO)_5$ as its source of the tricarbonyliron(o) unit] and its products are not described in any detail, and unfortunately the ratios of diastereoisomers produced are not presented.
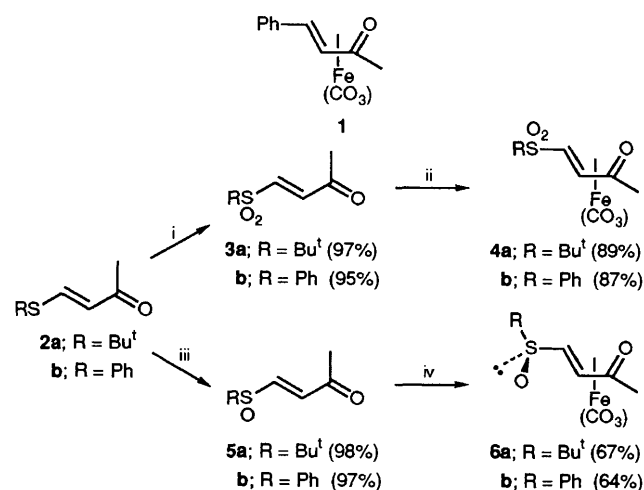
Scheme 1 *Reagents*: i, 2.2 equiv. *m*CPBA; ii, 1.1 equiv. 1; iii, 1 equiv. *m*CPBA; iv, 1.4 equiv. 1

identified as the new tricarbonyliron(o) complexes 4a and b.‡ Gratifyingly complexes 4a and b proved to be completely air-stable in the solid state and only very slightly air-sensitive in solution. Thus they are as stable and as easy to manipulate as complex 1 and other tricarbonyliron(o) complexes of β-phenyl-α,β-unsaturated ketones.

Attention then turned to the complexation of the novel sulphoxide 5a and sulphoxide 5b,[9] which are readily formed by addition of one equivalent of *m*CPBA to sulphides 2a and b. Complexation of 5a and b was initially examined under identical conditions to those used for the complexation of sulphones 3a and b. Accordingly compound 5a was stirred with 1.1 equivalents of (benzylideneacetone)tricarbonyliron(o) 1 at 35 °C for 14 h in a solvent mixture of pentane and toluene (1:1). Filtration of the product mixture through a short plug of alumina to remove iron residues and subsequent solvent evaporation gave a red oil which was examined by 270 MHz ¹H NMR spectroscopy. This revealed that the red oil contained benzylideneacetone, a novel complex, and (benzylideneacetone)tricarbonyliron(o) 1 in a ratio of 65:27:8. Column chromatography on silica led to the isolation of each of these components plus a minor fourth component which did not contain any protons.§ The yellow band containing the novel complex was evaporated to dryness, examined by 270 MHz ¹H NMR spectroscopy, and then crystallised from pentane. The crystalline air-stable product was fully characterised‡ and identified as a single diastereoisomer of [4-(*tert*-butylsulphinyl)but-3-en-2-one]tricarbonyliron(o) **6a** produced in 35% yield. Careful examination of the 270 MHz ¹H NMR spectra of the crude product and complex 6a prior to crystallisation indicated that only one diastereoisomer had been present in the product mixture. Similarly, when 4-(phenylsulphinyl)but-3-en-2-one **5b** was subjected to identical reaction conditions, work-up, and analysis, the novel diastereoisomerically pure complex **6b** was isolated in 32% yield. Examination of the data obtained again revealed that only one diastereoisomer of the sulphinyl complex was present in the product mixture. It is of note that subsequent optimised complexations of 5a and b using 1.4 equivalents of complex 1 gave diastereoisomerically pure **6a** and b in 67 and 64% yield, respectively.

The relative stereochemistry of the single diastereoisomer of 6a produced by transfer of the tricarbonyliron(o) unit from

‡ The new compounds 4a, 4b, 5a, 6a and 6b all gave satisfactory IR, ¹H NMR, ¹³C NMR, low resolution mass spectral and microanalytical data.

§ This minor component of the product mixture was tentatively assigned as a mixture of clusters containing iron atoms, sulphur atoms and carbonyl groups,[10,11] thus indicating the fate of some of the sulphinyl 5a during the course of the reaction.

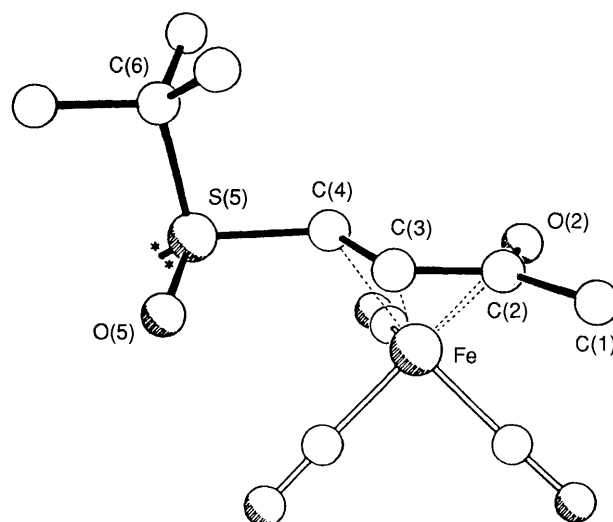Fig. 1 Molecular structure of [Bu^{t}S(O)CH=CHC(Me)=O](CO)$_3$Fe^0 **6a**. Selected bond lengths (Å) and bond and torsion angles (°): C(1)–C(2) 1.490(5), C(2)–C(3) 1.406(6), C(3)–C(4) 1.421(4), C(4)–S(5) 1.772(4), S(5)–C(6) 1.844(5), C(2)–O(2) 1.312(5), S(5)–O(5) 1.500(3), Fe–O(2) 2.024(3), Fe–C(2) 2.097(5), Fe–C(3) 2.054(5), Fe–C(4) 2.073(4); O(2)–C(2)–C(3) 115.2(3), C(2)–C(3)–C(4) 115.7(3), C(3)–C(4)–S(5) 118.8(3), C(4)–S(5)–C(6) 100.4(2), C(4)–S(5)–O(5) 106.2(2), O(5)–S(5)–C(6) 106.4(2), O(2)–C(2)–C(3)–C(4) 5.3(6), C(2)–C(3)–C(4)–S(5) −174.0(3), C(3)–C(4)–S(5)–C(6) −95.4(4), C(3)–C(4)–S(5)–O(5) 15.2(4).
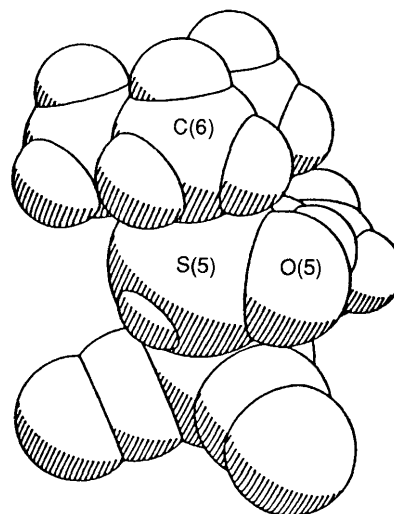

Fig. 2 Space filling model of [Bu^{t}S(O)CH=CHC(Me)=O](CO)$_3$Fe^0 **6a** viewed down S(5)–C(4) bond

the benzylideneacetone complex 1 to the sulphoxide 5a was determined by an X-ray crystal structure analysis (Fig. 1).¶ This revealed that in the diastereoisomer formed the oxygen of the sulphinyl group is placed surprisingly close to a metal carbonyl ligand whilst the sterically less demanding sulphinyl lone pair lies between two metal carbonyl ligands (Fig. 2). It may be significant that, in contrast to the single resonance

normally associated with the three fluxional carbonyl ligands in (diene)tricarbonyliron(o) complexes at room temperature,[12] the room temperature ^{13}C NMR spectra of sulphinyl complexes **6a** and **b** each contained three sharp signals corresponding to the metal-carbonyl carbons,|| thus revealing that in solution at room temperature interchange of the three metal carbonyl groups is restricted. Further studies are underway to determine whether the restricted interchange of metal carbonyl groups is due to the bulk of the sulphur atom or to a sulphinyl metal-carbonyl interaction, and to determine the origin of the diastereoisomeric control observed in the complexation reactions.

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|| The ^{13}C NMR spectra of complexes **6a** and **b** measured at 25 °C contained sharp signals at δ 202.2, 205.6 and 208.8, and δ 202.1, 206.1 and 207.3, respectively.

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