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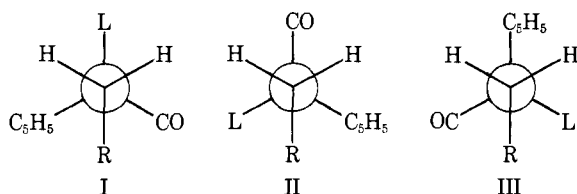
## A Comparative Study of the Chemistry of the Diastereomers of $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{O}Ph)_3]\text{CHPhSiMe}_3$

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**Abstract:** Reaction of racemic or resolved  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{O}Ph)_3]\text{I}$  with racemic  $\text{Me}_3\text{SiPhCHMgBr}$  gives a mixture of the two diastereomers of  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{O}Ph)_3]\text{CHPhSiMe}_3$  at low temperatures. Selective decomposition of the *RR,SS* diastereomer, predicted to be the more highly hindered, occurs above room temperature, however, leading to the isolation of the pure *RS,SR* isomer. Sulfonylation reactions of both diastereomers are reversible and provide a novel route, via the diastereomeric sulfinate complexes, to epimerization of the alkyl complexes. Kinetic and thermodynamic studies in  $\text{SO}_2\text{-CDCl}_3$  mixtures show that although (*RS,SR*)- $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{O}Ph)_3]\text{CHPhSiMe}_3$  (**1**) is the thermodynamically more stable diastereomer, (*RR,SS*)- $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{O}Ph)_3]\text{CHPhSiMe}_3$  (**2**) can be formed in disproportionate amounts by the interaction of **1** with  $\text{SO}_2$ .

We have recently shown that primary alkyl-iron complexes of the type  $\eta^5\text{-C}_5\text{H}_5\text{FeCOLCH}_2\text{R}$  (L = phosphorus donor; R = Ph,  $\text{SiMe}_3$ , 1-naphthyl) exist in solution as three staggered rotamers, I, II, and III.<sup>1</sup> On the apparently valid



assumption that vicinal coupling constants,  $^3J_{\text{PH}}$ , between the phosphorus and the protons on the  $\alpha$ -carbon atom of the alkyl group decrease in the order *trans*  $\gg$  *gauche*, it was concluded that interconversion between rotamers is rapid on the NMR time scale and that ligand steric requirements determine rotamer populations. Since the order of ligand steric requirements is  $\eta^5\text{-C}_5\text{H}_5 > \text{L} > \text{CO}$ , III was found to be the most stable rotamer.

In this paper we extend our investigations to secondary alkyl complexes of the types  $\eta^5\text{-C}_5\text{H}_5\text{FeCOLCHRR}'$ . These should exist as mixtures of diastereomers, the relative stabilities of which should be affected by the sizes of the ligands on the iron

and the  $\alpha$ -carbon atoms. The opportunity was thus presented to study the relationships between steric factors and degree of asymmetric induction, as reflected by relative ease of formation of diastereomers and/or their relative thermodynamic stabilities. We find indeed that the diastereomers of the compound  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{CHPhSiMe}_3$  do exhibit rather different properties, one being thermally stable at room temperature (**1**), the other quite labile (**2**). Some of this work has been communicated previously.<sup>2,3</sup>

## Experimental Section

All reactions were carried out under nitrogen or under vacuum, while organic solvents were dried and deoxygenated. Sulfur dioxide (anhydrous, Matheson) was used as purchased;  $\text{SO}_2$  reactions which were monitored by NMR spectroscopy were carried out in flame-sealed thick-walled 5-mm NMR tubes. NMR spectra were run on a Bruker HX60 spectrometer in CW and FT modes. Analyses were carried out by Microanalysis Laboratories Ltd., Toronto.

$\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{CHPhSiMe}_3$  (**1**). A solution of  $\text{Me}_3\text{-SiPhCHMgBr}$ , prepared in about 75% yield from 4 g (16 mmol) of  $\text{Me}_3\text{SiPhCHBr}^4$  and 0.4 g of magnesium turnings in 25 ml of ether, was added to a stirred solution of  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{I}$  (5 g, 8.5 mmol) in 25 ml of benzene. The mixture was stirred at 35 °C for about 20 min and allowed to cool, when the solvent was removed under reduced pressure. The oily residue was extracted with a mixture of 10 ml of methylene chloride and 150 ml of petroleum ether (bp 30–40 °C). The extract was then eluted through a deaerated alumina column (50 × 2.5 cm), first with 200 ml of petroleum ether, then a 60:40 mixture of petroleum ether–methylene chloride. The latter removed a yellow band of the product which was obtained as a yellow oil on removal of the solvent (yield 2.4 g, 45%). The compound slowly crystallizes on standing at –10 °C for several days. The solid is stable in air for several hours, but solutions decompose extensively after a few minutes exposure to air.

The infrared spectrum (cyclohexane solution) exhibited  $\nu_{\text{CO}}$  at 1950  $\text{cm}^{-1}$ , while the proton NMR spectrum ( $\text{C}_6\text{D}_6$  with  $\text{Me}_4\text{Si}$  lock) showed resonances at  $\delta$  2.24 (doublet, CH,  $^3J_{\text{PH}} = 10.2$  Hz), 4.05 (doublet,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.0$  Hz) 0.33 (singlet,  $\text{SiMe}_3$ ), and  $\sim 7.14$  (multiplet, Ph). The  $^{13}\text{C}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , D lock,  $\text{Me}_4\text{Si}$  internal reference) exhibited resonances at  $\delta$  2.9 (doublet,  $\alpha\text{-CH}$ ,  $J_{\text{PC}} \approx 18$  Hz), 2.27 (singlet,  $\text{SiMe}_3$ ), 82.8 (doublet,  $\text{C}_5\text{H}_5$ ,  $J_{\text{PC}} = 1.5$  Hz), 121–157 (Ph), and 219.5 (doublet, CO,  $J_{\text{PC}} = 50$  Hz). Anal. Calcd for  $\text{C}_{34}\text{H}_{35}\text{FeO}_4\text{PSi}$ : C, 65.58; H, 5.68. Found: C, 66.00; H, 6.10.

$\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{CHPhSiMe}_3$  (**1** + **2**). When the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{I}$  with the Grignard reagent was carried out at 0 °C for 1 h, the yellow product eluted from the alumina column contained **1** and **2** in an approximately 3:1 ratio. In addition to the resonances listed above, the proton NMR spectrum contained resonances at  $\delta$  2.13 (doublet, CH,  $^3J_{\text{PH}} = 10.5$  Hz), 4.30 (doublet,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.0$  Hz), and 0.35 (singlet,  $\text{SiMe}_3$ ) which may be assigned to **2** (see below). The  $^{13}\text{C}$  NMR spectrum exhibited resonances at  $\delta$  1.6 (doublet,  $\alpha\text{-CH}$ ,  $J_{\text{PC}} \approx 18$  Hz), 2.20 (singlet,  $\text{SiMe}_3$ ), 82.70 (doublet,  $\text{C}_5\text{H}_5$ ,  $J_{\text{PC}} = 1.4$  Hz), 121–157 (Ph), and 219.5 (doublet, CO,  $J_{\text{PC}} = 50$  Hz).

**2** is much less stable in solution than is **1**, and while separation of **1** and **2** may be accomplished by slow chromatography on alumina, extensive decomposition of **2** occurs. Although the nature of the products of decomposition of **2** was not investigated in detail, paramagnetic species are generated, as is shown by broadening of lines in the NMR spectrum and generation of a signal in the ESR spectrum when **2** is allowed to stand in solution for 30 min at room temperature. No nitroxide signal developed when **2** decomposed in the presence of nitrobenzene in  $\text{C}_6\text{D}_6$ .

$\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{CHPhSiMe}_3$ . This complex was prepared by treating  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{PPh}_3\text{I}$  with  $\text{Me}_3\text{SiPhCHMgBr}$  according to the procedure outlined above for **1**. The reaction had to be carried out at 35 °C because it did not proceed at lower temperatures. The product is sensitive to chlorinated solvents and purification by column chromatography and recrystallization was carried out using benzene–petroleum ether mixtures. The infrared spectrum (cyclohexane solution) exhibited  $\nu_{\text{CO}}$  at 1922  $\text{cm}^{-1}$ , while the  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) showed resonances at  $\delta$  1.40 (doublet, CH,  $^3J_{\text{PH}} = 7.7$  Hz), 4.77 (doublet,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 1.5$  Hz), 0.30 (singlet,  $\text{SiMe}_3$ ), and  $\sim 7.14$

(multiplet, Ph). Anal. Calcd for  $\text{C}_{34}\text{H}_{35}\text{FeO}_4\text{PSi}$ : C, 71.07; H, 5.68. Found: C, 71.64; H, 6.16.

**Reaction of 1 with  $\text{SO}_2$** . Initial attempts to insert  $\text{SO}_2$  into the iron–carbon bond of **1** by conventional methods,<sup>5</sup> i.e., by refluxing a solution of **1** in neat  $\text{SO}_2$ , followed by evaporation of the solvent and elution of the material from an alumina column, yielded no sulfinate complex, but rather mixtures of **1** and **2**. Analysis of a 50:50 mixture (C, 65.94; H, 5.92%) confirmed the isomeric relationship between **1** and **2**. Mixtures were also obtained by bubbling  $\text{SO}_2$  through solutions of **1**, in various solvents, the relative amounts of **1** and **2** obtained as products varying greatly as the experimental conditions were varied. Thus, in most solvents **1** was greatly favored at room temperature and above, while **2** was favored at lower temperatures, especially if the  $\text{SO}_2$  were removed rapidly. On the other hand, no epimerization was observed in petroleum ether.

The interaction of **1** and **2** with  $\text{SO}_2$  was best studied using NMR spectroscopy by following the reaction in neat  $\text{SO}_2$  in a sealed tube. Although **1** is stable in  $\text{SO}_2$  at –23 °C, it reacts slowly at –3 °C, rapidly at 17 °C, the two doublets at  $\delta$  4.08 ( $\text{C}_5\text{H}_5$ ) and 1.90 (CH) being replaced respectively by a doublet at  $\delta$  4.32 and a singlet at  $\delta$  4.89, which are attributed to a new *S*-sulfinate complex,  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P}(\text{OPh})_3]\text{SO}_2\text{CHPhSiMe}_3$ . **3**, **2** behaves similarly, its doublet resonances at  $\delta$  4.45 ( $\text{C}_5\text{H}_5$ ) and 1.80 (CH) being replaced by a doublet at  $\delta$  4.54 ( $\text{C}_5\text{H}_5$ ) and a singlet at  $\delta$  5.27 (CH) of a second *S*-sulfinate complex isomer, **4**. Changes in the  $\text{SiMe}_3$  and Ph resonances were relatively small in both cases. Equilibration between **3** and **4** also occurred, although at a rate much slower than those of the initial sulfonylation reactions.

**3** and mixtures of **3** and **4** could be isolated as orange-red solids if kept cold (–10 °C) as the  $\text{SO}_2$  solvent was removed under reduced pressure. Both readily lose  $\text{SO}_2$ , both in the solid state and in solution in organic solvents, at room temperature and satisfactory analytical and infrared data could not be obtained.

Loss of  $\text{SO}_2$  in solutions in organic solvents is sufficiently slow at low temperatures, however, that NMR spectra of **3** and **4** can be obtained. Chemical shifts and coupling constants ( $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ ) at 0 °C of **3** and **4** respectively are  $\delta$  5.07, 5.25 (CH), 4.43, 4.65 ( $\eta^5\text{-C}_5\text{H}_5$ ), 0.15, 0.31 ( $\text{SiMe}_3$ ), and  $\sim 7.2$ , 7.2 (Ph).

**Kinetic Studies.** Kinetic runs were carried out in both neat  $\text{SO}_2$  and in  $\text{SO}_2\text{-CDCl}_3$  mixtures. Known amounts of alkyl compound (**1**, **2**) were transferred to an NMR tube in cold degassed methylene chloride solution; the solvent was then removed under reduced pressure. Known amounts of  $\text{SO}_2$  and, where appropriate, degassed cold  $\text{CDCl}_3$  were then added to the cooled sample, and the tube was flame-sealed under vacuum. Sample solutions prepared in this way could be kept at –10 °C with no apparent decomposition or reaction. They were normally transferred directly to a cooled probe (–10 °C), whereupon the probe was raised to the desired temperature (approximately 45 s to reach thermal equilibrium) and the reaction was monitored by measuring the relative intensities of the cyclopentadienyl resonances of **1**, **2**, **3**, and **4**. The NMR spectrometer was locked on 0.05 ml of hexamethyldisiloxane in the case of runs in neat  $\text{SO}_2$ , on the deuterium in the case of runs in  $\text{CDCl}_3$ .

When neat  $\text{SO}_2$  was used as solvent, pseudo-first-order rate constants were obtained. The reactions went essentially to completion and linear first-order plots could be obtained for at least two half-lives. The rate constants for the **3** → **4** and **4** → **3** isomerizations were obtained by treating the data as first-order approaches to equilibrium<sup>6</sup> after **1** and **2** were no longer present in solution. The expression used was

$$\ln \frac{[A]_0 - [A]_e}{[A]_t - [A]_e} = (k_{\text{forward}} + k_{\text{back}})t \quad (1)$$

where  $[A]_t$ ,  $[A]_0$ , and  $[A]_e$  are the mole fractions of the decreasing species at time  $t$ , at time zero, and at equilibrium, respectively. Equilibrium for the reaction was achieved after about 8 h at 20 °C.

Second-order rate constants were obtained for the reactions in  $\text{CDCl}_3$  using the expression<sup>6</sup>

$$\frac{1}{[1 \text{ or } 2]_0 - [\text{SO}_2]_0} \ln \frac{[\text{SO}_2]_0 [1 \text{ or } 2]_t}{[1 \text{ or } 2]_0 [\text{SO}_2]_t} = kt \quad (2)$$

where the subscripts  $t$  and 0 represent times  $t$  and 0, respectively. Linear plots were obtained in all cases for at least half of the reaction, while equilibration between all four complexes was generally achieved after about 3 h.

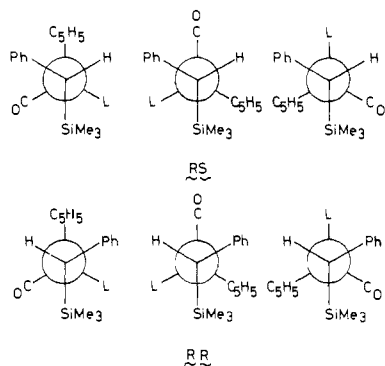


Figure 1. Staggered conformations of the *RS* and *RR* isomers.

Errors in rate constants are generally believed to be about 10%.

## Results and Discussion

As noted in the introductory section, compounds of the type  $\eta^5\text{-C}_5\text{H}_5\text{FeCOLCHPhSiMe}_3$  should exist as two diastereomerically related pairs of enantiomers, *RS,SR* and *RR,SS*.<sup>7</sup> The *RS* and *RR* enantiomers and their staggered conformations are illustrated in Figure 1. On the basis of relative ligand steric requirements, i.e.,  $\eta^5\text{-C}_5\text{H}_5 > \text{L} > \text{CO}$ , and  $\text{SiMe}_3 > \text{Ph} > \text{H}$ ,<sup>1</sup> the stablest rotamer of each should be that in which the  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{SiMe}_3$  groups are mutually trans. Similarly, the stablest rotamer of the *RS* enantiomer should be less crowded, and therefore more stable, than that of the *RR* enantiomer.

In spite of the above considerations, however, reactions of racemic  $\eta^5\text{-C}_5\text{H}_5\text{FeCOLI}$  ( $\text{L} = \text{PPh}_3, \text{P(OPh)}_3$ ) with racemic  $\text{Me}_3\text{SiPhCHMgBr}$  at 35 °C gave materials which appeared from their proton NMR spectra to contain, in both cases, only one of the two possible diastereomers. Since the second diastereomer of  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P(OPh)}_3]\text{CHPhSiMe}_3$  (**2**) was later isolated at lower temperatures, the observed asymmetric induction was clearly not a result of kinetic control of the reaction of the Grignard. It seems rather that the decreasing yield of **2** with increasing reaction temperature was a result of its low thermal stability even at room temperature (see Experimental Section); the compound decomposed, either during the course of the reaction or during workup. No attempt was made to isolate products of the decomposition process, but homolysis to give radicals does not seem to be a likely mechanism. Decomposition in  $\text{C}_6\text{D}_6$  in the presence of the spin trap, phenyl *tert*-butyl nitron,<sup>8</sup> did not lead to the formation of a nitroxide. Only rather broad lines attributable to iron-containing species were observed in the ESR spectrum.

Identification of **1** and **2** as the *RS,SR* and *RR,SS* diastereomers, respectively, was made by the temperature dependence of their vicinal coupling constants,  $^3J_{\text{PH}}$  (Figure 2). Both coupling constants vary smoothly with temperature, that of **1** decreasing, that of **2** increasing as the temperature is lowered. Thus barriers to rotation about the iron-carbon bonds are sufficiently low that rotation about the iron-carbon bonds is rapid on the NMR time scale and weighted, time-averaged NMR spectra are being observed. It can be seen that  $^3J_{\text{PH}}$  of the limiting, low temperature spectra of **1** and **2** are clearly small and large, respectively, consistent with their stablest rotamers being those in which the  $\alpha$ -hydrogen is gauche and trans, respectively, to the phosphorus. The temperature dependence of  $\eta^5\text{-C}_5\text{H}_5\text{FeCOPPh}_3\text{CHPhSiMe}_3$  was consistent with its also having the *RS,SR* configuration.

The relative ease of preparation of the two diastereomers, **1** and **2** may be compared only cursorily with analogous information on similar complexes in the literature, as decomposition of **2** during workup procedures made it impossible to estimate the importance of kinetic effects on the relative

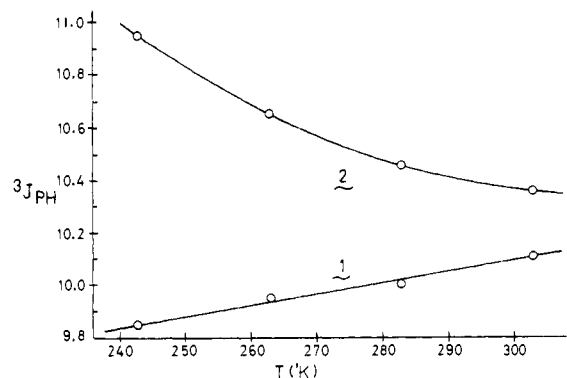


Figure 2. Temperature variations of  $^3J_{\text{PH}}$  of **1** and **2**.

amounts of **1** and **2** formed. Not surprisingly, perhaps, the compounds  $\eta^5\text{-C}_5\text{H}_5\text{FeCOPPh}_3\text{R}$  ( $\text{R} = \textit{threo}\text{-CHDCHDPh}$ ,<sup>9</sup> *threo*-CHDCHDCMe<sub>3</sub>,<sup>10</sup> CH<sub>2</sub>CHMePh,<sup>11</sup> and CH(OEt)Me<sup>12</sup>) all form the respective diastereomers as 50:50 mixtures; with the possible exception of the last-mentioned, the differences in degrees of crowding in the pairs of diastereomers should be slight. We note that the complex  $\eta^5\text{-C}_5\text{H}_5\text{FeCOPPh}_3\text{CHMeEt}$ ,<sup>13</sup> prepared in only 32% yield by a method analogous to that used for the preparation of **1** and **2**, exhibits only one set of resonances in both its <sup>1</sup>H and <sup>13</sup>C NMR spectra. Although the authors do not comment on the possibility of asymmetric induction during the synthesis of this compound, the reported procedure would also appear to yield only a single diastereomer.

Sulfonylation, or insertion of SO<sub>2</sub> into the iron-carbon bond of **1**, was initially attempted because <sup>13</sup>C NMR facilities were not to be available for a few months and there was concern that **1** might actually be a mixture of diastereomers with coincident proton NMR spectra (**2** had not, at that time, been prepared by the Grignard method). Sulfur dioxide insertion into metal-carbon bonds had been shown to be highly stereospecific,<sup>5</sup> proceeding with inversion of configuration at the  $\alpha$ -carbon<sup>10</sup> and with retention at the iron.<sup>14</sup> Reaction of SO<sub>2</sub> with **1** was thus expected to be stereospecific and rapid,<sup>5</sup> and it seemed unlikely that the proton NMR spectra of diastereomeric sulfinates would also be coincident.

Treatment of **1** with SO<sub>2</sub> under a variety of conditions expected to yield a sulfinate, however, resulted only in partial epimerization to the *RR,SS* diastereomer, **2**. Ratios of **1**:**2** varied from 4:1 to 1:4, implying kinetic control of product distribution on the one hand, thermodynamic control on the other. Following the reactions of both **1** and **2** in liquid SO<sub>2</sub> by proton NMR spectroscopy, however, showed that both appear to react to give single products, **3** and **4**, respectively. Although these were too thermally unstable in the absence of SO<sub>2</sub> to be characterized properly, their proton NMR spectral parameters suggest that they are the expected diastereomeric *S*-sulfinates,  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}[\text{P(OPh)}_3]\text{SO}_2\text{CHPhSiMe}_3$ , rather than the *O*-bonded isomers. Thus the resonances of the  $\alpha$ -protons of **1** and **2** are shifted downfield about 3 ppm on SO<sub>2</sub> insertion; in other cases the *S*-sulfinates are generally shifted downfield about 1.5–2 ppm, *O*-sulfinates < 1 ppm.<sup>15</sup> In addition, the introduction of a chiral sulfur atom in an *O*-bonded sulfinate complex would give a molecule with three chiral centers<sup>15</sup> and a potentially much more complicated NMR spectrum.

The sulfonylation reactions in liquid SO<sub>2</sub> appeared to be stereospecific, and indeed pumping on a sample of solid **3** (prepared by removing SO<sub>2</sub> under reduced pressure from a solution of **1** in SO<sub>2</sub> at 0 °C) at 55 °C yielded only **1**. In addition, when a sample of **3** was dissolved in CD<sub>2</sub>Cl<sub>2</sub> at a sufficiently low temperature (–10 °C) that its desulfonylation could be followed by NMR spectroscopy, it was found that only

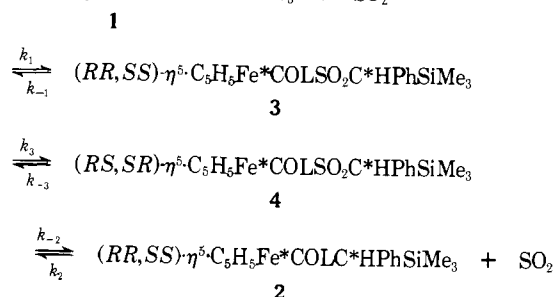
**Table I.** Pseudo-First-Order Rate Constants for the Sulfonylation of **1** and **2** in Liquid SO<sub>2</sub>

Temp (°C)	$k_1$ (s <sup>-1</sup> ) <sup>a</sup>	$k_2$ (s <sup>-1</sup> ) <sup>a</sup>
-8	$1.3 \times 10^{-4}$	$2.4 \times 10^{-4}$
-3	$3.4 \times 10^{-4}$	$5.8 \times 10^{-4}$
+2	$6.8 \times 10^{-4}$	$9.7 \times 10^{-4}$
+7	$12.3 \times 10^{-4}$	$19.5 \times 10^{-4}$

<sup>a</sup> Errors  $\pm 10\%$ .

**1** was formed initially as the temperature was slowly raised. This was followed, however, by a period ( $\sim 50\%$  of the total reaction) during which **2** was actually formed faster and in larger quantities, than was **1**, although eventually, as the system approached equilibrium, the ratio of **1**:**2** became approximately 6:1. Since **1** and **2** do not equilibrate in the absence of SO<sub>2</sub>, it seems reasonable to suppose that the epimerization occurs between **3** and **4**. A reasonable scheme for the system is shown in Scheme I.

Scheme I. Scheme for the reactions of **1** and **2** with SO<sub>2</sub> in CDCl<sub>3</sub>  
 (RS,SR)- $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe\*COLC\*HPhSiMe<sub>3</sub> + SO<sub>2</sub>



A study was made of the kinetic and thermodynamic parameters for each of the above steps in order to better understand the widely differing distribution of products under various conditions. The relatively strong, quite distinct cyclopentadienyl resonances in the proton NMR spectra made concentration measurements quite straightforward. Pseudo-first-order rate constants ( $k_1$  and  $k_2$ ) for the sulfonylation reactions in liquid SO<sub>2</sub> (SO<sub>2</sub> in  $\sim 140$  molar excess) are shown in Table I. At 22 °C,  $k_3$  and  $k_{-3}$  were  $6 \times 10^{-5}$  and  $24 \times 10^{-5}$  s<sup>-1</sup>, respectively, much smaller than  $k_1$  and  $k_2$ .

Second-order rate constants,  $k_1$  and  $k_2$ , in CDCl<sub>3</sub> ( $[1]_0 \approx [2]_0 \approx 0.3$  M,  $[\text{SO}_2]_0 \approx 0.4\text{--}2$  M) at 22 °C were found to be  $2.1 \times 10^{-4}$  and  $35 \times 10^{-4}$  s<sup>-1</sup> M<sup>-1</sup>, respectively. Values of  $k_3$  and  $k_{-3}$  in CDCl<sub>3</sub> could not be determined because, in contrast to the situation in liquid SO<sub>2</sub>, **3**  $\rightleftharpoons$  **4** equilibration occurred much more rapidly in CDCl<sub>3</sub> than did the sulfonylation reactions. Equilibrium constants for the system in CDCl<sub>3</sub> as a function of total SO<sub>2</sub> concentration at 22 °C are listed in Table II; it is seen that they are rather dependent on the SO<sub>2</sub> concentration.

Calculations of free energies of activation were carried out using the expression<sup>16</sup>

$$\Delta F^\ddagger = -RT \ln \left( \frac{h(\text{rate constant})}{kT} \right) \quad (3)$$

while free energies were calculated using the expression

$$\Delta F = -RT \ln (\text{equilibrium constant}) \quad (4)$$

Values of both parameters in the two solvents used are listed in Table III. As can be seen, **1** is more stable than its diastereomer, **2**, by about 1.1 kcal, qualitatively consistent with the predictions based on the expected relative degrees of crowding in the molecules. Differences between the alkyl compounds and

**Table II.** Equilibrium Constants in CDCl<sub>3</sub> at 22 °C<sup>a</sup>

[SO <sub>2</sub> ] <sub>0</sub>	$K_1$ ( $=k_1/k_{-1}$ ) <sup>b</sup>	$K_2$ ( $=k_2/k_{-2}$ ) <sup>b</sup>	$K_3$ ( $=k_3/k_{-3}$ )	$K_4$ ( $1 \rightleftharpoons 2$ )	$K_5$ ( $2 \rightleftharpoons 3$ ) <sup>b</sup>
2	1.5		0.34		
0.9	1.3	2.8	0.27	0.13	10.0
0.5	1.2	2.3	0.24	0.14	9.2
0.25	1.0	1.1	0.17	0.15	6.7

<sup>a</sup> [Total iron]  $\approx 0.7$  M. Errors  $\pm 10\%$ . <sup>b</sup> M<sup>-1</sup>.**Table III.** Values of  $\Delta F^\ddagger$  and  $\Delta F$  (kcal mol<sup>-1</sup>,  $\pm 0.1$ )<sup>a</sup>

Solvent	$\Delta F^\ddagger$ ( <b>1</b> $\rightarrow$ <b>3</b> )	$\Delta F^\ddagger$ ( <b>2</b> $\rightarrow$ <b>4</b> )	$\Delta F^\ddagger$ ( <b>3</b> $\rightarrow$ <b>4</b> )	$\Delta F^\ddagger$ ( <b>4</b> $\rightarrow$ <b>3</b> )
SO <sub>2</sub>	20.1	19.9	23.0	22.2
CDCl <sub>3</sub>	22.4	20.6		

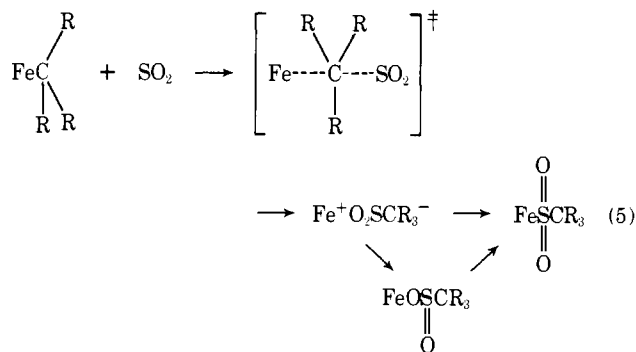
Solvent	$\Delta F$ ( <b>1</b> $\rightarrow$ <b>3</b> ) <sup>b</sup>	$\Delta F$ ( <b>2</b> $\rightarrow$ <b>4</b> ) <sup>b</sup>	$\Delta F$ ( <b>3</b> $\rightarrow$ <b>4</b> ) <sup>b</sup>	$\Delta F$ ( <b>1</b> $\rightarrow$ <b>2</b> ) <sup>b</sup>	$\Delta F$ ( <b>2</b> $\rightarrow$ <b>3</b> ) <sup>b</sup>
SO <sub>2</sub>			0.9		
CDCl <sub>3</sub>	0	-0.1	1.0	1.1	-1.1

<sup>a</sup> [SO<sub>2</sub>] = 0.25 M, 22 °C. <sup>b</sup> 22 °C.

the corresponding sulfinates, on the other hand, are rather small.

Although the original intentions of the present work did not include an examination of the mechanism of the sulfonylation of iron alkyl complexes, the compounds described here are unique in that they appear to be the only ones described in the literature for which the sulfonylation is both readily reversible and, on occasion, nonstereospecific. A discussion of the possible reasons for the differences would, therefore, seem proper. Pseudo-first-order rate constants for the sulfonylation of **1** and **2** in liquid SO<sub>2</sub> as a function of temperature are listed in Table I. Arrhenius plots of the data yield  $\Delta H^\ddagger$  (**1**  $\rightarrow$  **3**) and  $\Delta H^\ddagger$  (**2**  $\rightarrow$  **4**) of  $22.2 \pm 1$  and  $20.4 \pm 1$  kcal, respectively, and knowing values of  $\Delta F^\ddagger$  (Table III), it is possible to calculate  $\Delta S^\ddagger$  values of  $+7 \pm 3$  and  $+2 \pm 4$  eu, for the **1**  $\rightarrow$  **3** and **2**  $\rightarrow$  **4** conversions, respectively.

These values are all considerably more positive than those reported previously for other iron compounds<sup>5,17,18</sup> ( $\Delta H^\ddagger \approx 3\text{--}9$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger \approx -62$  to  $-43$  eu), for which a mechanism involving backside electrophilic attack on the  $\alpha$ -carbon atom has been proposed, i.e.



It has been suggested that the large, negative entropies of activation are consistent with the bimolecular nature of the reaction coupled with developing charges in the possibly extensively solvated transition state.<sup>17</sup>

In spite of the differences in activation parameters between our system and others,<sup>17,18</sup> however, there seems little need to involve a different mechanism for sulfonylation of the second-

dary alkyl complexes; the reactions are second order and can occur stereospecifically, as has been observed previously for other, similar iron alkyl complexes.<sup>5</sup> The higher, positive values of  $\Delta H^\ddagger$  observed for our system may reflect a greater degree of iron-carbon bond breaking in forming the transition state in eq 5, a reasonable supposition if the R groups are sufficiently bulky that the incoming SO<sub>2</sub> molecule cannot approach the  $\alpha$ -carbon atom as closely as in the case of methyl or primary alkyl compounds. Similarly the almost negligibly small values of  $\Delta S^\ddagger$  may reflect a release of strain and a concomitant increase in internal molecular motions on going from **1** and **2**, which are undoubtedly highly crowded, to the transition state in eq 5. This effect would be relatively unimportant in the other compounds previously studied<sup>5,17,18</sup> and could serve to offset those factors, noted above, causing a decrease in the entropy of activation. On the other hand, we cannot explain the absence of detectable *O*-sulfinato intermediates.

We have considered the suggestion, made by Jacobson and Wojcicki,<sup>18</sup> that sulfonylation in organic solvents in the absence of an excess of SO<sub>2</sub> may proceed by a different mechanism than in liquid SO<sub>2</sub>, possibly with retention of configuration at the  $\alpha$ -carbon atom. Following their suggestion, we have reacted *threo*-PhCHDCHDFe(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sup>19,20</sup> with a deficiency of SO<sub>2</sub> (<0.5 M) in chloroform at room temperature. Although the sulfonylation proceeded rather slowly, it was every bit as stereospecific as is the sulfonylation of the same compound in liquid SO<sub>2</sub>, yielding *erythro*-PhCHDCHDSO<sub>2</sub>Fe(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) exclusively.

Attempts to confirm the mechanism of the epimerization reactions have met with little success. In an effort to learn whether the change in configuration occurred at iron or at carbon, we reacted resolved (+)- $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeCO[P(OPh)<sub>3</sub>]<sub>2</sub> with the racemic Grignard reagent. Unfortunately, both the iron alkyl product and the iron iodide obtained from its subsequent iodine cleavage were racemic. By analogy with work by Brunner,<sup>24</sup> it seems possible that magnesium salts may well induce racemization at iron.

Consistent with the principle of microscopic reversibility, the desulfonylation of **3** in the solid state and, initially at least, in CD<sub>2</sub>Cl<sub>2</sub> solution at low temperature, gives only **1**. Under conditions which we have not been able to clearly define, however, but which seem to be met better in chloroform or methylene chloride solutions than in neat SO<sub>2</sub> or in petroleum ether, a kinetically preferred conversion of **3** to **2** occurs, presumably via **4**.<sup>25</sup> The key to this behavior, which is not known to occur with primary alkyl iron compounds, probably lies in the nature of the secondary alkyl group and/or in the degree of crowding in the sulfinato complexes. A reasonable reaction, consistent with the principle of microscopic reversibility, would be the partial reversal of eq 5. If, because of steric hindrance, the ion pair [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeCOP(OPh)<sub>3</sub>]<sup>+</sup>[O<sub>2</sub>SCHPhSiMe<sub>3</sub>]<sup>-</sup> were stabilized under proper conditions of solvation, temperature, etc., it is possible that the sulfinato anion could either dissociate SO<sub>2</sub> or be susceptible to repeated backside electrophilic attacks on the central carbon atom by other molecules of SO<sub>2</sub>, resulting in epimerization at the carbon atom.<sup>3</sup> The suggestion is consistent with observations that epimerization during desulfonylation in CD<sub>2</sub>Cl<sub>2</sub> did not occur initially, but only after some free SO<sub>2</sub> had been generated.

A second possibility would involve dissociation of the sulfinato complexes in just the opposite sense, i.e., to give [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeCOP(OPh)<sub>3</sub>]<sup>-</sup> and [SO<sub>2</sub>CHPhSiMe<sub>3</sub>]<sup>+</sup>. The latter could then dissociate to give SO<sub>2</sub> and a planar carbonium ion, leading to the observed racemization; a similar mechanism has been proposed for the desulfonylation of alkanesulfonyl chlorides in cases where a relatively stable carbonium ion can be formed.<sup>26</sup> Although such a mode of dissociation of **3** and **4** would generate a relatively stable carbonium ion, it does not seem likely because of the expectedly high basicity and nucleophilicity of the [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeCOP(OPh)<sub>3</sub>]<sup>-</sup> anion. Furthermore, the reaction might also be expected to proceed with *erythro*-PhCHDCHDFe(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) (see above), which would generate a relatively stable deuterated phenonium ion.<sup>25</sup> Radical mechanisms generating either  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeCOP(OPh)<sub>3</sub> or CHPhSiMe<sub>3</sub> also seem unlikely, as none of the expected products of reactions of these species with CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> was observed.

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