

Figure 1. Plot of  $\log k$  vs.  $\Delta$  strain. Data from Table I. Slope:  $-0.3$ . Correlation coefficient 0.92. Points not included in the correlation are indicated with open circles.

parametrization was used in order to have a consistent set of parameters (see below). For the evaluation of the strain in the transition state we accept the hypothesis of a product-like transition state, and we assume that its energy should be related to that of the ketone. Calculations of ketone strain were made in the same way as the hydrocarbons with the Allinger force-field, which is also parametrized for carbonyl compounds.<sup>6b</sup> The calculations of 37 hydrocarbons and ketones, together with the oxidation rates of the respective alcohols are summarized in Table I. Figure 1 shows a plot of the oxidation rates ( $\log k$ ) against the strain difference ketone-alcohol ( $\Delta$  strain). The straight line has a slope of  $-0.3$  and a correlation coefficient of 0.92. The compounds 5, 6, and 8, which deviate by more than 2 standard deviations ( $S_y = 0.37$ ) from the straight line are not included in the correlation (see below).

The plot covers a rate range of 1 to 15000. The correlation coefficient of 0.92 is surprisingly high, and it seems to justify both our hypotheses, namely that alcohol strain reflects methyl strain, and that the properties of the ketone are reflected in the transition state. However, it is interesting to note that a difference of 15 kcal/mol in  $\Delta$  strain corresponds only to a variation of 15000 in rates or ca. 5.7 kcal in enthalpies of activation. This could in part be due to a systematic overestimation of the alcohol strain by our use of the methyl analogues for the calculations. The more important part must, however, be due to the fact that either the strain of the alcohol has not fully disappeared or the strain of the ketone is not fully developed in the transition state.<sup>12</sup> There is good reason to believe that the nonbonded interactions of the alcohol are mostly, if not entirely, re-

lieved.<sup>9</sup> The structure of the transition state must be such that this strain relief can occur, while the (angle-) strain in the ketone is only partially built up. Our approach does not allow more detailed conclusions concerning the structure of the transition state.

The exclusion of the compounds 5, 6, and 8 from the correlation can in part be justified. The entropies of activation for oxidation of tetramethylcyclobutanol (8) and di-*tert*-butylmethanol (6) differ considerably from the average value obtained for unhindered alcohols.<sup>3</sup> This indicates that other factors might contribute in these cases. Kwart suggested that sterically hindered alcohols such as 6 are oxidized by another mechanism than the unhindered ones.<sup>15</sup> Our calculations lead to a similar conclusion. In the case of isopropyl alcohol (5) it is likely that the ketone model does not sufficiently reflect the polar substituent effects operating in the reaction ( $\rho^* = -1^1$ ). If an appropriate correction for the different alkyl substitution is applied, isopropyl alcohol falls within the limits of 2 standard deviations.

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Paul Müller,\* Jean-Claude Perlbeger

Département de Chimie Organique, Université de Genève  
1211 Geneva 4, Switzerland

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## Formation of Ethyl Ketones through Sequential Insertion Reactions of Alkyl Tetracarbonylferrates

Sir:

We previously demonstrated the utility of  $\text{Na}_2\text{Fe}(\text{CO})_4$  in the preparation of anionic alkyl and acyl iron complexes.<sup>1</sup> These complexes have been shown to be useful intermediates for the preparation of aldehydes,<sup>1</sup> ketones,<sup>2</sup> and other carbonyl derivatives<sup>3</sup> from common alkylating agents. We now wish to describe a facile conversion of alkyl halides and tosylates to ethyl ketones through the alkylation of  $\text{Na}_2\text{Fe}(\text{CO})_4$  in the presence of ethylene (eq 1). Examples of this

Table I. Preparation of Ethyl Ketones<sup>a</sup>

RX	Temp (°C)	Ketone <sup>b</sup>	% yield <sup>c</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub> Br	25	C <sub>5</sub> H <sub>11</sub> COC <sub>2</sub> H <sub>5</sub>	95
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	25	C <sub>4</sub> H <sub>9</sub> COC <sub>2</sub> H <sub>5</sub>	89 (71 <sup>d</sup> )
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	25	C <sub>4</sub> H <sub>9</sub> COC <sub>2</sub> H <sub>5</sub>	89
PhCH <sub>2</sub> CH <sub>2</sub> Br	5 <sup>e</sup>	PhCH <sub>2</sub> CH <sub>2</sub> COC <sub>2</sub> H <sub>5</sub>	83 <sup>f</sup>
C <sub>6</sub> H <sub>13</sub> Br	5 <sup>e</sup>	C <sub>6</sub> H <sub>13</sub> COC <sub>2</sub> H <sub>5</sub>	93 (83 <sup>d</sup> )
<i>sec</i> -C <sub>5</sub> H <sub>11</sub> OTs	25 <sup>g</sup>	<i>sec</i> -C <sub>5</sub> H <sub>11</sub> COC <sub>2</sub> H <sub>5</sub>	90
Br(CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	5 <sup>e</sup>	C <sub>2</sub> H <sub>5</sub> CO(CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	63 <sup>d</sup>

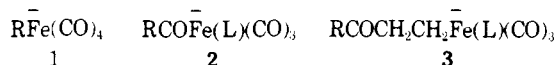
<sup>a</sup>Unless otherwise stated, reactions employed 1.0 mmol of RX and Na<sub>2</sub>Fe(CO)<sub>4</sub> derived from 1.33 mmol of Fe(CO)<sub>5</sub>.<sup>4</sup> All alkylations were conducted under ethylene at 1 atm. <sup>b</sup>Each product was identified through spectra, comparison with an authentic sample, and through its semicarbazone derivative. <sup>c</sup>Determined by GLPC.

<sup>d</sup>Isolated yield, 4 mmol scale. <sup>e</sup>Initial reaction at 5° for 2 hr then 25° for 2 hr. <sup>f</sup>Isolated yield as the semicarbazone derivative. <sup>g</sup>With 1.0 ml of HMPA added.



single-flask ambient pressure conversion are shown in Table I. The preparation of 3-dodecanone from 1-bromononane illustrates a typical procedure. A slurry of Na<sub>2</sub>Fe(CO)<sub>4</sub> in 35 ml of dry THF was prepared by the reduction of 0.74 ml (5.32 mmol) of Fe(CO)<sub>5</sub> with 5 ml of 1% Na(Hg) as previously described.<sup>1,4</sup> The vessel was purged with ethylene to remove carbon monoxide, cooled to 5°, and treated with 0.78 ml (4.0 mmol) of 1-bromononane. The ethylene atmosphere was maintained throughout. The mixture was stirred for 2 hr at 5° and then 2 hr at 25° whereupon it was treated with 0.5 ml of HOAc, stirred for 5 min, poured into H<sub>2</sub>O, and extracted twice with ether. The concentrated extracts were filtered through a short plug of alumina to remove iron-containing residues. Distillation gave 0.61 g (83%) of 3-dodecanone, semicarbazone mp 90°.

The conversion is believed to proceed in the following manner. Alkylation of Na<sub>2</sub>Fe(CO)<sub>4</sub> with an electrophile gives rise to alkyl tetracarbonylferrate complex **1**<sup>5</sup> which is converted in the presence of ethylene to anionic acyl iron complex **2** (L = C<sub>2</sub>H<sub>4</sub>). This process is analogous to the mi-

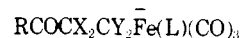


gratory insertion reactions observed when **1** is treated with other good ligands.<sup>6</sup> Unlike the stable acyl complexes found in the presence of CO and phosphines,<sup>1,5</sup> **2** (L = C<sub>2</sub>H<sub>4</sub>) undergoes yet another insertion reaction in which the acyl group migrates to the coordinated ethylene<sup>7</sup> giving β-acyl-ethyl iron complex **3**. The net uptake of 2 equiv of ethylene suggests that the coordination site vacated by acyl migration is filled by another ethylene to give **3** (L = C<sub>2</sub>H<sub>4</sub>). The possibility that metal saturation is achieved through intramolecular ketocarbonyl involvement cannot be excluded, however. Coordination of this type has been observed in a stable iridium complex.<sup>11</sup>

While we anticipated that termination of the process would occur by reductive elimination of the ethyl ketone from an iron(II) hydride formed upon protonation of **3**, we have found that addition of DOAc to the reaction mixture prior to work-up gives ketone containing no deuterium at C<sub>1</sub>,<sup>12</sup> indicating that the hydrogen atom which replaces iron in **3** is not derived from the added proton source. Alkylation of Na<sub>2</sub>Fe(CO)<sub>4</sub> with 1-bromononane in the presence of ethylene-*d*<sub>4</sub>, acidification with HOAc and base catalyzed removal of exchangeable α-methylene deuterium<sup>12</sup> gave 3-dodecanone containing >92% C<sub>1</sub>-*d*<sub>3</sub>. Thus the hydrogen atom replacing iron in **3** comes ultimately either from a C<sub>2</sub> methylene group or from another molecule of ethylene. A reasonable process involving a second ethylene is the oxida-

tive addition of the coordinated ethylene in **3** (L = C<sub>2</sub>H<sub>4</sub>) to give an intermediate vinyl hydride which could undergo reductive elimination of ketone now containing a hydrogen atom derived from the second ethylene. Oxidative addition of ethylene has been implicated in other systems.<sup>13</sup>

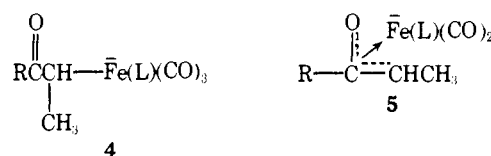
Differentiation between these two possibilities was achieved through the use of partially deuterated ethylene. Alkylation of Na<sub>2</sub>Fe(CO)<sub>4</sub> as above in the presence of ethylene-*1,1-d*<sub>2</sub> gave after removal of exchangeable deuterium 3-dodecanone containing 12% *d*<sub>0</sub>, 48% *d*<sub>1</sub>, 38% *d*<sub>2</sub>, and 1% *d*<sub>3</sub> at C<sub>1</sub>. In the absence of a large secondary isotope effect, comparable amounts of **3a** and **3b** should result from **2** (L = CH<sub>2</sub>CD<sub>2</sub>). If the hydrogen replacing iron in **3** is obtained from C<sub>2</sub>, the resulting product should be composed of comparable amounts of ketones *d*<sub>1</sub> and *d*<sub>2</sub> at C<sub>1</sub> from **3a** and **3b**, respectively. On the other hand, if this hydrogen is obtained from another molecule of ethylene-*d*<sub>2</sub>, the product would be expected to be composed of species *d*<sub>0</sub> and *d*<sub>1</sub> at C<sub>1</sub> from **3a** and *d*<sub>2</sub> and *d*<sub>3</sub> at C<sub>1</sub> from **3b**.<sup>14</sup> The absence of appreciable *d*<sub>0</sub> and *d*<sub>3</sub> species<sup>15</sup> and the presence of comparable amounts of species *d*<sub>1</sub> and *d*<sub>2</sub> at C<sub>1</sub> strongly supports the notion that complex **3** rearranges in a manner which results in transfer of a hydrogen from C<sub>2</sub> to C<sub>1</sub>.<sup>16</sup>



**3a**, X = D; Y = H

**3b**, X = H; Y = D

**3c**, X = Y = D



The complex generated upon rearrangement of **3** is thought to be an "enolate" complex either of the σ-type, represented as **4**, or a π-oxaalkenyl structure such as **5**. Structures of the latter type have been previously proposed as intermediates.<sup>17</sup> The net uptake of 2 equiv of ethylene and the absence of CO evolution would seem to favor a σ-type structure, however. While we have been unable to isolate this final complex, evidence of its presence has been found in a strong infrared band at 1585 cm<sup>-1</sup> which is replaced by the normal ketone band (1718 cm<sup>-1</sup>) upon acid quench. Careful removal of all volatiles under high vacuum prior to acidification gives a residue which liberates ketone upon addition of HOAc. Some free ketone could be detected in the vapors above unquenched reaction mixture likely owing to adventitious protonation of the "enolate" on the small scale employed. In addition, this intermediate has been intercepted through the addition of methyl iodide whereupon predominately C<sub>2</sub> methylated ketone is obtained.

Several kinetic features of this transformation are noteworthy. Following the rapid consumption of *n*-butyl iodide at 25° (<5 min) only butane from **1** and increasing amounts of ketone are observed in quenched samples. Significantly, pentanal from **2** is not observed suggesting the rapid conversion of **2** to **3**. The absence of any appreciable amount of ketone which is *d*<sub>2</sub> at C<sub>1</sub> from the previously described alkylation under C<sub>2</sub>D<sub>4</sub> further suggests that intermediate **3** is short-lived. The presence of any unrearranged **3c** would give ketone *d*<sub>2</sub> at C<sub>1</sub> upon HOAc quench. These observations make it likely that the rearrangement of **1** is the rate-limiting step in cases where initial alkylation is rapid.

Unfortunately, this process does not appear useful for the preparation of ketones from higher alkenes. Alkylation of Na<sub>2</sub>Fe(CO)<sub>4</sub> with *n*-pentyl bromide in the presence of pro-

pylene (3 atm) gave mainly hexanal in 70% yield and only a low yield (10–15%) of 4-nonanone. The same alkylation in the presence of excess 1-hexene gave only hexanal in 94% yield. The high yields of aldehyde reflect the presence of complex **2** and suggest that while higher alkenes may serve as ligands for the carbonyl insertion process subsequent acyl transfer is inhibited. We have found, however, that a number of olefins which are Michael acceptors readily participate in this process forming the basis of a versatile method for the conjugate addition of acyl anion equivalents. These results will be reported shortly.

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- The presence of a small amount of undeuterated ketone may be a result of incomplete  $\alpha$ -methylene exchange,<sup>12</sup> unequal formation of **3a** and **3b** through a small secondary isotope effect or an isotope effect in the suggested  $\beta \rightarrow \alpha$  rearrangement operating on the small amount (4%) of ethylene- $d_1$  contaminating our sample of ethylene- $d_2$ , or a combination of any of these factors.
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Manning P. Cooke, Jr.,\* Robert M. Parlman

Department of Chemistry, Washington State University  
Pullman, Washington 99163

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## Bis(1-substituted-borabenzene)iron Complexes

Sir:

The borabenzene anion **2** like the long known cyclopentadienide **1** is an anionic  $6\pi$ -electron aromatic ring. Herberich et al. found that **3** could be produced via ring expansion of cobaltocene with boron halides.<sup>1</sup> Recently **3** has been elegantly converted to other transition metal complexes.<sup>2,3</sup>

Following our synthesis of the free 1-phenylborabenzene anion **2a**,<sup>4</sup> we undertook to prepare transition metal complexes directly from the ligand. Specifically we now wish to report on the general synthesis of bis(1-substituted-borabenzene)iron complexes **4**.<sup>5,6</sup> These materials exhibit properties and show reactions which find a close parallel in the well-known chemistry of ferrocene.

Diene **6a** is readily available from the exchange reaction of 1,1-dibutyl-1,4-dihydrostannabenzene (**5**) with phenylboron dibromide.<sup>4</sup> Treatment with *tert*-butyllithium produces **2a**<sup>4</sup> which yields air-stable red-orange crystals of bis(1-phenylborabenzene)iron (**4a**) on treatment with ferrous chloride in an overall yield of 31%: mp 156–157.5°; mass spectral  $m/e$ , 362 ( $\text{M}^+$ ,  $\text{C}_{22}\text{H}_{20}^{11}\text{B}_2^{56}\text{Fe}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\tau$  5.21 (d,  $J = 9.5$  Hz, 4 H), 4.41–4.66 (m, 6 H), 2.61 (m, 6 H), 2.18 (m, 4 H);  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -14.4; uv ( $\text{C}_2\text{H}_5\text{OH}$ )  $\lambda_{\text{max}}^{\text{nm}}$  234 (28000), 270 (15400), 362 (1500). Since the  $^1\text{H}$  NMR spectrum of bis(1-phenyl- $d_5$ -borabenzene)iron, available ultimately from the reaction of **5** with phenyl- $d_5$ -boron dibromide, showed signals only at  $\tau$  5.21 and 4.41–4.66, the low field signals of **4a** were due to the uncomplexed phenyl protons. The borabenzene ring protons of **4a** are shifted upfield approximately 1.5 ppm relative to **2a**. This upfield shift on complexation is similar to that between ferrocene ( $\tau$  6.0) and sodium cyclopentadienide ( $\tau$  4.7). Similarly the reaction of methylboron dibromide with **5** gave **6b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\tau$  9.2 (s, 3 H) 6.9 (m, 2 H); 3.3 (dt,  $J = 13$ , 2 Hz, 2 H); 2.8 (brd,  $J = 13$  Hz, 2 H);  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -52.8. On deprotonation by *tert*-butyllithium in tetrahydrofuran-pentane, followed by reaction with ferrous chloride, **6b** afforded bis(1-methylborabenzene)iron **4b**. The yield from **5** is 34%: mp 44–45°;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\tau$  9.31 (s, 6 H), 5.70 (brd,  $J = 10$  Hz, 4 H), 4.7 (m, 6 H); mass spectral  $m/e$ , 238 ( $\text{M}^+$ ,  $\text{C}_{12}\text{H}_{16}^{11}\text{B}_2^{56}\text{Fe}$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  -20.5, uv ( $\text{C}_2\text{H}_5\text{OH}$ )  $\lambda_{\text{max}}^{\text{nm}}$  214 (35000), 274 (2170), 312 (1320), 362 (660).

In a variation of this procedure, **5** is treated directly with boron tribromide at  $-78^\circ$ , giving dibutyltin dibromide and 1-bromo-1,4-dihydroborabenzene (**6d**), which is easily separated by distillation:  $^1\text{H}$  NMR ( $\text{CHCl}_3$ ),  $\tau$  7.15 (m, 2 H),

