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The reactions of α-phenyl- and α-ferrocenylcarbinols with diiron nonacarbonyl

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Abstract

Diiron nonacarbonyl oxidized a series of α-phenylcarbinols to their corresponding aldehydes and ketones. In addition, this reagent converted 4-methoxybenzyl alcohol to 4-methoxybenzyl ether, albeit in low yield. Under the same reaction conditions, oxidation was minor with a group of α-ferrocenylcarbinols as ether synthesis was the major reaction with those substrates which could not dehydrate; however, stereoselective olefin synthesis predominated when elimination was possible.

Introduction

The usual reaction of an allylic alcohol with an iron carbonyl reagent is the generation of a saturated aldehyde or ketone via the isomerization and tautomerization of its double bond. A classic example, the conversion of 2-propen-1-ol (**1**) to propanal (**6**), occurs through the action of iron pentacarbonyl [1]. The accepted mechanism for this rearrangement involves the intermediacy of an iron tricarbonyl hydride **4**, which provides access to **6** through loss of the iron tricarbonyl fragment and subsequent tautomerization (Scheme 1).

A report by Barborak, Watson, McPhail, and Miller [2] discussed the reaction of an allylic carbinol that behaved unpredictably when it was treated with iron pentacarbonyl. In the presence of that reagent [(6,7,8,9-*n*)-bicyclo[3.2.2]nona-2,6,8-trien-4-ol]iron tricarbonyl (**8**) was converted to [(2,3,6,7-*n*)-bicyclo[3.2.2]nona-2,6,8-trien-4-one]iron tricarbonyl (**9**) rather than the expected product, **7**. This apparent oxidation was considered anomalous; consequently, a search for other models that might exhibit similar behavior was not undertaken by these researchers. In this

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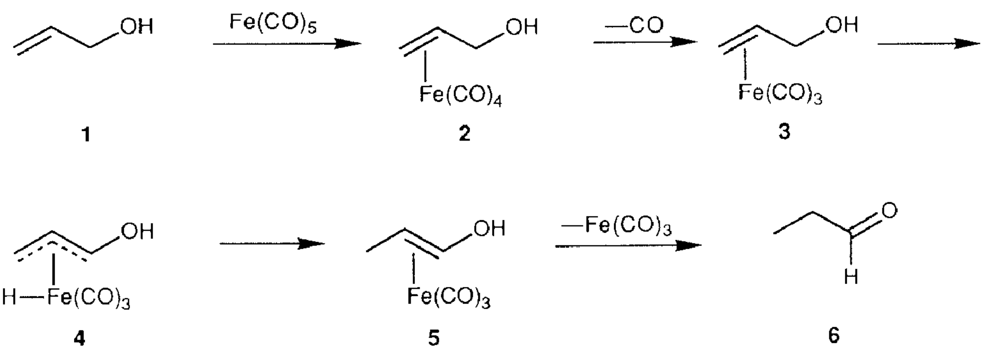
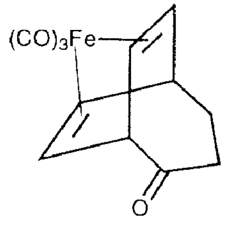


Scheme 1

report, the reactions of a series of α-phenylcarbinols and α-ferrocenylcarbinols with diiron nonacarbonyl ($Fe_2(CO)_9$) are discussed; results suggest that outcomes other than those brought about by double-bond isomerization are indeed possible and perhaps predictable.



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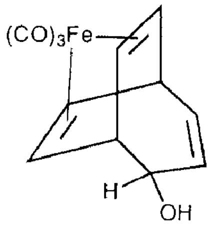

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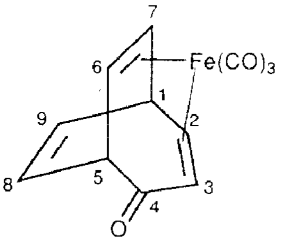

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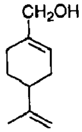
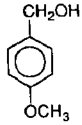
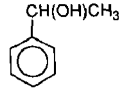
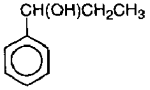
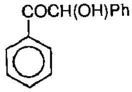
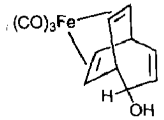
Results and discussion

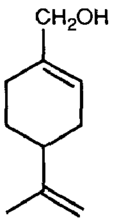
The recent discovery in this laboratory that diiron nonacarbonyl oxidized perillyl alcohol (**10**) to perillaldehyde (**13**) demonstrated that a class of unsaturated carbinol substrates exist that may be converted to aldehydes and ketones without the movement or loss of a double bond. This particular reaction was followed by IR spectroscopy, which indicated an iron tricarbonyl complex (**11**, ν(CO) 1940, 2037 cm^{-1}) was generated and eventually converted to (perillaldehyde)iron tricarbonyl (**12**, ν(CO) 1940, 2060 cm^{-1}). Complex **12** was isolated as an orange-red oil which was partially contaminated with free aldehyde. The identity of **12** was confirmed by the fact that only perillaldehyde (**13**) was recovered once the iron tricarbonyl complex totally decomposed in solution. The formation of **11**, a 1,5-dieneiron tricarbonyl, prevented olefin isomerization [1] and thus allowed an extramolecular iron carbonyl species to effect the observed oxidation. Although not recognized by Barborak and his co-workers, a similar event must have occurred during the reaction of the bicyclic nonatrienol, **8**. The fluxional behavior of the iron tricarbonyl fragment of that substrate allowed it to migrate from the 8,9-diene center so as to protect the 2,3-diene network from isomerization. Consequently, oxidation of the alcohol moiety to a ketone was permitted through the action of free iron carbonyl.

Table 1

Reactions ^{a} of unsaturated carbinols with $Fe_2(CO)_9$

Substrate	Reaction time	Carbonyl (%)	Ether (%)
	30 h ^{b}	70	–
	30 h ^{b}	35	–
	30 h ^{b}	45	27
	30 h ^{b}	72	–
	30 h ^{b}	78	–
	30 h ^{b}	77	–
	10 h ^{c}	70	–

[a] Each reaction was conducted under a nitrogen atmosphere. [b] Benzene solvent, reflux temperature. [c] Heptane solvent, reflux temperature [2].



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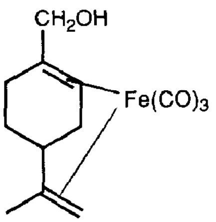

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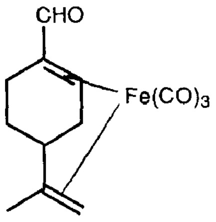

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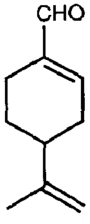

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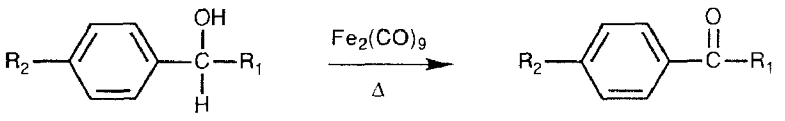
The oxidation of **8** and **10** led to the conclusion that unsaturated carbinols with restrained allylic centers could be oxidized by iron carbonyl reagents, and a series of benzylic alcohols appeared to be perfect models for testing this hypothesis. As expected, diiron nonacarbonyl oxidized benzyl alcohol (**14**), 4-methoxbenzyl alcohol



14: $R_1 = R_2 = H$

15: $R_1 = H$; $R_2 = OCH_3$

16: $R_1 = CH_3$; $R_2 = H$

17: $R_1 = C_2H_5$; $R_2 = H$

18: $R_1 = COPh$; $R_2 = H$

19: $R_1 = R_2 = H$

20: $R_1 = H$; $R_2 = OCH_3$

21: $R_1 = CH_3$; $R_2 = H$

22: $R_1 = C_2H_5$; $R_2 = H$

23: $R_1 = COPh$; $R_2 = H$

Scheme 2

(**15**), 1-phenyl-1-ethanol (**16**), 1-phenyl-1-propanol (**17**), and benzoin (**18**) to their corresponding aldehydes and ketones (Table 1, Scheme 2). In each case, the identity of the reaction product was confirmed by comparison to an authentic sample. Phenethyl alcohol (a β-phenylcarbinol), 1-(5-norbornene-2-yl)propan-1-ol, and 2-hydroxymethylnorbornane did not react in the presence of diiron nonacarbonyl, which supported the premise that only carbinols with restrained allylic centers could be oxidized by this reagent.

Reaction rates were dissimilar, but the results can be rationalized. For example, the high reaction rate of perillyl alcohol, as compared to benzyl alcohol, may be a consequence of a synergistic interaction [3,4] between the organic ligand and its iron tricarbonyl fragment. Iron carbonyl reagents do not coordinate with phenyl rings under normal conditions [5,6], and this may explain the sluggish conversion of **14**. Indeed a competitive study of these two carbinols showed that very little benzaldehyde formed during the reaction of equal portions of benzyl alcohol and perillyl alcohol in the presence of an equivalent amount of diiron nonacarbonyl. A synergistic interaction may also have accelerated the oxidation of benzoin to benzil, since the dark red color exhibited during this reaction indicated complex formation. The secondary carbinols, 1-phenyl-1-ethanol and 1-phenyl-1-propanol, oxidized much faster than benzyl alcohol, which suggested a carbocation intermediate as proposed by Barborak et al. [2]. TLC analysis of the reaction between benzyl alcohol and diiron nonacarbonyl after the introduction of bis(triphenylphosphine)iminium chloride indicated the presence of bis(triphenylphosphine)iminium hydrotetracarbonylferrate [7]. In addition, an IR (KBr) spectrum of this crude mixture possessed discernible absorptions at (ν(CO) 2001, 1910, and 1880 cm^{-1} which correlate well with those of pure bis(triphenylphosphine)iminium hydrotetracarbonylferrate (ν(CO) 2001, 1906, and 1879 cm^{-1}). Unfortunately, it was not possible to isolate this solid through chromatography, but the TLC and IR data do offer evidence for a carbocation intermediate during these reactions [8*]. Therefore, the following mechanism is suggested to rationalize the observed oxidations using benzyl alcohol (**14**) as a model. Hydride abstraction from **14** by iron tetracarbonyl could provide access to ion-pair **24**, and subsequent protonation of its counter anion, hydrotetra-

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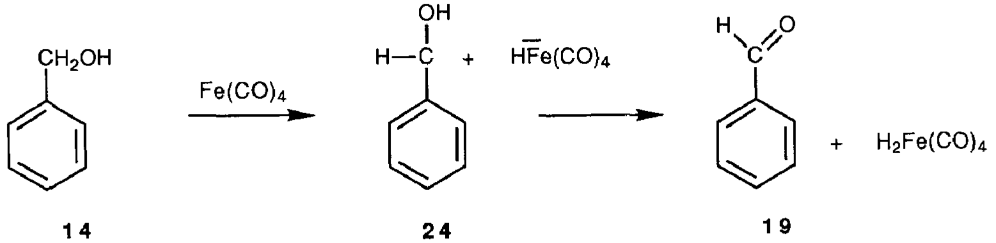
* Reference number with asterisk indicates a note in the list of references.

$$Fe_2(CO)_9 \xrightarrow[-CO]{\Delta} 2\ Fe(CO)_4$$



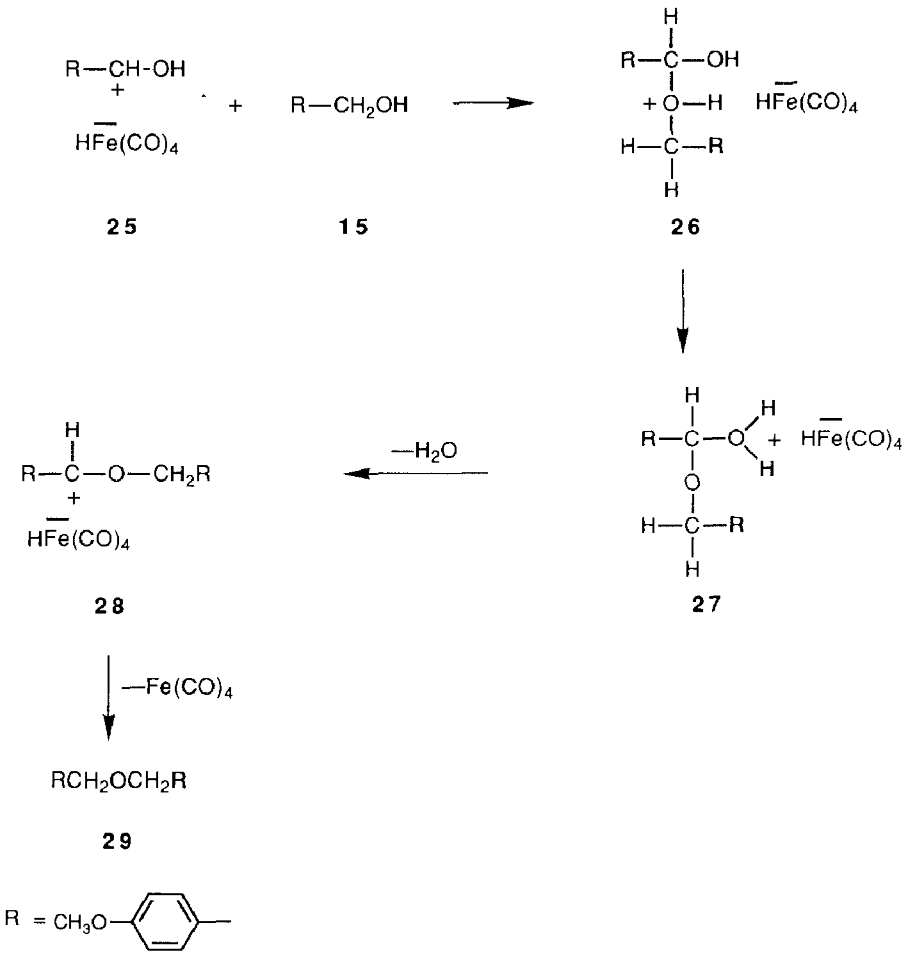
Scheme 3

carbonylferrate, followed by rearrangement, would then give benzaldehyde (**19**) and dihydroiron tetracarbonyl (Scheme 3). It has also been shown that the reaction of **19** with diiron nonacarbonyl in refluxing hexane provided benzyl benzoate in 54% yield after 96 h, and ester formation from an aldehyde substrate could conceivably follow a similar mechanistic route. However, the converison of aldehydes to esters in the presence of iron carbonyl is the subject of another paper [9].

The reaction of 4-methoxybenzyl alcohol (**15**) with diiron nonacarbonyl was complicated and at least four products were generated, although only two were characterized. The major species formed was 4-methoxybenzaldehyde (**20**), but this reaction gave rise to 4-methoxybenzyl ether (**29**) as well. The identity of **29** was established by its comparison to the ether prepared by the reaction of 4-methoxybenzyl iodide [10] with **15** in the presence of sodium hydride.

A possible mechanism for ether synthesis could conceivably involve carbocation intermediates too (Scheme 4). Once formed, ion-pair **25** would be susceptible to nucleophilic attack by free carbinol to yield the protonated adduct, **26**. An intramolecular proton transfer followed by loss of water would provide **28**, the precursor of **29**, which could then accept a hydride ion from the iron carbonyl anion to yield 4-methoxybenzyl ether (**29**).

Treatment of α-ferrocenylcarbinols with diiron nonacarbonyl gave quite unexpected results (Table 2, Schemes 5 and 6). For instance, carbinol **30**, hydroxymethylferrocene [11,12], was converted to ferrocenecarboxaldehyde (**32**) [13], and bis(ferrocenylmethyl) ether (**34**) [11], but the latter compound was synthesized in greater yield. Likewise, carbinol **31**, (hydroxyphenylmethyl)ferrocene [14], provided benzoylferrocene (**33**) [14], along with bis(phenylferrocenylmethyl) ether (**35**) [14], as the major product. Unlike their phenyl counterparts, the reactions of 1-ferrocenyl-1-ethanol (**36**) [15] and 1-ferrocenyl-1-propanol (**37**) [15,22], provided olefins vinylferrocene (**39**) [15,16], and *trans*-1-ferrocenyl-1-propene (**40**) [17,18] as the major products. Acetylferrocene (**42**) was also generated in low yield from the reaction of **36**, but a ketone was not isolated from the reaction of **37**. Elimination was the only observed outcome from the treatment of 2-ferrocenyl-2-propanol (**38**) [19], with diiron nonacarbonyl, which gave isopropenylferrocene (**41**) [17,20]. Heating a solution of **36** or **37** in benzene for 6 h did not effect an elimination; however, **38** did



Scheme 4

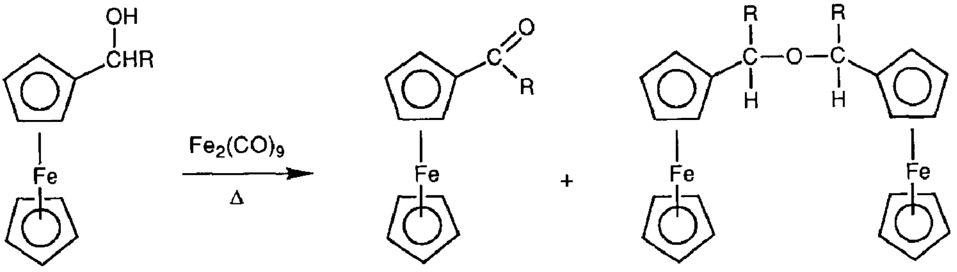
eliminate to a small extent in refluxing benzene, and this emphasized the lability of its hydroxyl group [21]. The fact that **38** is a tertiary alcohol obviated its oxidation, and its predisposition to eliminate may explain why no other products were generated from this reaction. Of paramount interest was the stereoselectivity that

Table 2

Reactions [a] of α-ferrocenylcarbinols with $Fe_2(CO)_9$

Substrate [b]	Reaction time	Carbonyl (%)	Ether (%)	Olefin (%)
$FcCH_2OH$	30 h	20	51	–
$FcCH(OH)CH_3$	5 h	8	–	49
$FcCH(OH)CH_2CH_3$	16 h	–	–	47
$FcC(OH)(CH_3)_2$	5 h	–	–	90
FcCH(OH)Ph	15 h	19	59	–

[a] Each reaction was conducted under nitrogen in benzene at the reflux temperature of that solvent. [b] Fc = ferrocenyl.



30: R = H
31: R = Ph

32: R = H
33: R = Ph

34: R = H
35: R = Ph

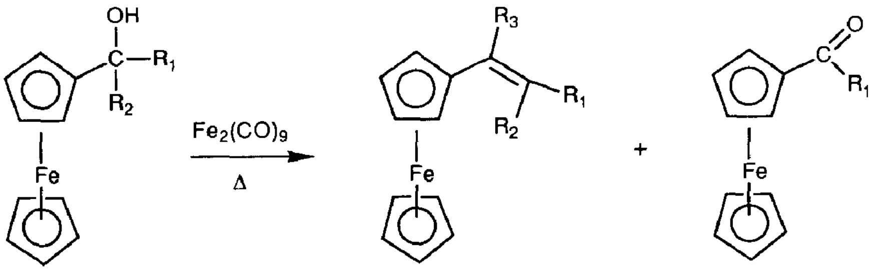
Scheme 5

accompanied the reaction of 1-ferrocenyl-1-propanol. The isolation of *trans*-1-ferrocenyl-1-propene in greater than 95% stereochemical yield reflected the high degree of stereocontrol imposed by the iron carbonyl reagent.

Ether generation from carbinols **30** and **31** probably adhered to the same mechanistic pathway as previously outlined for the formation of 4-methoxybenzyl ether (**29**).

The dehydration of carbinols **36**, **37**, and **38** is undoubtedly due to the unusual lability [21] of their hydroxyl functions, since similar outcomes were not observed with their phenyl counterparts.The faster reaction rates of the α-ferrocenylcarbinols, as compared to the benzylic alcohols, are probably a consequence of the stability of their intermediates, and the unusual stability of α-metallocenylcarbinols is well documented [19,21].

Finally, an unexpected difference in the reactions o the phenyl- versus the ferrocenyl carbinols was observed. Under the same reaction conditions employed with the α-phenylcarbinols, oxidation was minor among the ferrocene derivatives. Instead, ether synthesis became the major reaction with those ferrocene substrates which could not dehydrate and, when elimination was possible, stereoselective olefin synthesis predominated.



36: R_1 = CH_3; R_2 = H
37: R_1 = C_2H_5; R_2 = H
38: R_1 = R_2 = CH_3

39: R_1 = R_2 = R_3 = H
40: R_1 = CH_3; R_2 = R_3 = H
41: R_1 = R_2 = H; R_3 = CH_3

42: R_1 = CH_3

Scheme 6

Experimental

^{1}H NMR spectra were recorded on Varian EM-390 and Bruker WM-250 spectrometers, operating at 90 and 250 MHz, respectively. Infrared spectra were obtained from a Shimadzu 460 or a Perkin–Elmer 457 grating spectrometer. Mass spectra were recorded on an AEI MS-902 direct probe high resolution instrument. All solvents were dried over activated 3 Å molecular sieves or distilled over sodium benzophenone ketyl.The series of α-phenylcarbinols, authentic samples of their corresponding carbonyls, diiron nonacarbonyl, ferrocenecarboxaldehyde, vinylferrocene, and benzoylferrocene were purchased from commercial sources. The α-ferrocenylcarbinols, and any of the carbonyl precursors which could not be obtained commercially, were prepared by literature methods [11,12,14,15,18,19,22].

*Reaction of perillyl alcohol (**10**), benzyl alcohol (**14**), 4-methoxybenzyl alcohol (**15**), 1-phenyl-1-ethanol (**16**), 1-phenyl-1-propanol (**17**), and benzoin (**18**) with diiron nonacarbonyl*

A solution of each carbinol (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 30 h under nitrogen. Each reaction mixture was then filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2) to provide perillaldehyde (**13**, 70%) benzaldehyde (**19**, 35%), 4-methoxybenzaldehyde (**20**, 45%), acetophenone (**21**, 72%), propiophenone (**22**, 78%), and benzil (**23**, 77%), respectively. In addition, the reaction of **15** provided 4-methoxybenzyl ether (**29**, 27%). ^{1}H NMR ($CDCl_3$): δ 7.27, 6.88 (AA'BB', J_{AB} ~ 8.86, 8H), 4.45 (s, 4H), 3.80 (s, 6H). IR (thin film): 3000(w), 2955(m), 2835(m), 1613(s), 1587(m), 1512(s), 1463(m), 1443(m), 1360(m), 1302(m), 1247(s), 1172(m), 1079(s), 1034(s), 821(s) cm^{-1}. Mass spectrum (m/e): exact mass calculated for $C_{16}H_{18}O_3$ was 258.1256, found 258.1258. Anal. Found: C, 74.57; H, 7.29. $C_{16}H_{18}O_3$ calcd.: C, 74.40; H, 7.02%.

*Reaction of benzaldehyde (**19**) with diiron nonacarbonyl*

A solution of **19** (1.88 mmol) in 20 ml hexane was degassed by three consecutive freeze-pump-thaw cycles before it was refluxed in the presence of 2.19 mmol $Fe_2(CO0_9$ for 96 h. The reaction mixture was filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2) to provide benzyl benzoate (0.52 mmol, 55%). The identity of the liquid was confirmed by comparison with an authentic sample.

*Reaction of benzyl alcohol (**14**) with diiron nonacarbonyl in the presence of bis(triphenylphosphine)iminium chloride*

A solution of **14** (20.0 mmol) in 200 ml benzene was degassed with a 20 min nitrogen purge before it was heated to reflux in the presence of 40.0 mmol of $Fe_2(CO)_9$. After ~ 6 h, 5.0 mmol of bis(triphenylphosphine)iminium chloride was added to the flask and the reaction was continued. An aliquot was removed for TLC (silica gel 60, 50% $MeOH/CHCl_3$) and IR (KBr) analysis after a 10 min period. TLC was conducted under nitrogen, and iodine detection showed a spot (R_f = 0.16) which co-eluted with authentic bis(triphenylphosphine)iminium hydrotetracarbonylferrate [7]. The remaining aliquot was concentrated in vacuo and the oily mixture was used to obtain an IR spectrum (KBR): ν(CO) 2001, 1910, and 1880 cm^{-1}; authentic material provides a carbonyl profile at 2001, 1906, and 1879 cm^{-1}.

Reaction of α-phenylcarbinols in refluxing benzene

A solution of each carbinol (**14**, **15**, **16**, and **17**, 10.0 mmol each) in 100 ml benzene was heated to reflux under a nitrogen atmosphere for 30 h. Each solution was then rotary evaporated and analyzed by TLC (silic gel 60, CH_2Cl_2) and ^1H NMR spectroscopy. Very little, if any change was observed.

Reaction of hydroxymethylferrocene (30) with diiron nonacarbonyl

A solution of **30** (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 30 h. The mixture was then filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2) to provide ferrocenecarboxaldehyde (**32**, 20%), identified by its comparison with an authentic sample, and bis(ferrocenylmethyl)ether (**34**, 51%). ^1H NMR ($CDCl_3$): δ 4.27 (s, 4H), 4.18 (m, 18H); IR (CH_2Cl_2): 1102(s), 1058(s), 1044(s), 1000(s) cm^{-1}; mass spectrum: exact mass calculated for $C_{22}H_{22}Fe_2O$ 414.0369, found: 414.0363; m.p. 128–129.5 °C, lit. [11]: 129–130 °C.

Reaction of (hydroxyphenylmethyl)ferrocene (31) with diiron nonacarbonyl

A solution of **31** (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 15 h. The mixture was then filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2/hexane) to give benzoylferrocene (**33**, 19%), identified by its comparison with an authentic sample, and bis(phenylferrocenylmethyl) ether (**35**, 59%). ^1H NMR ($CDCl_3$): δ 7.18 (m, 10H), 4.05 (m, 8H), 3.90 (m, 2H), 3.68 (s, 10H). Anal. Found: C, 72.32; H, 5.46. $C_{34}H_{30}Fe_2O$ calcd.: C, 72.09; H, 5.29%; m.p. 59–61 °C, lit. [14]: 52–56 °C.

Reaction of 1-ferrocenyl-1-ethanol (36) with diiron nonacarbonyl

A solution of **36** (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 5 h. The mixture was then filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2/hexane) to give vinylferrocene (**39**, 49%) and acetylferrocene (**42**, 8%). The identity of each product was confirmed by comparisons with authentic samples.

Reaction of 1-ferrocenyl-1-propanol (37) with diiron nonacarbonyl

A solution of **37** (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 16 h. The mixture was then filtered over Celite, concentrated, and chromatographed (silica gel 60, CH_2Cl_2/hexane) to provide *trans*-1-ferrocenyl-1-propene (**40**, 47%), identical to the olefin prepared by a documented route [18].

Reaction of 2-ferrocenyl-2-propanol (38) with diiron nonacarbonyl

A solution of **38** (10.0 mmol) in 100 ml benzene was degassed with a 20 min nitrogen purge before it was refluxed in the presence of 20.0 mmol $Fe_2(CO)_9$ for 5 h. The mixture was then filtered over Celite and the filtrate was rotary evaporated to about half of its original volume. Upon cooling, isopropenylferrocene (**41**, 90%) crystallized as an orange-red solid, identical to the olefin prepared by documented routes [17,20].

Reaction of α-ferrocenylcarbinols in refluxing benzene

A solution of each carbinol (**30, 31, 36, 37**, and **38**, 5.0 mmol each) in 50 ml benzene was heated to reflux under a nitrogen atmosphere for 24 h. Each solution was then rotary evaporated and analyzed by ^1H NMR spectroscopy. No discernible change was observed with carbinols **30, 31, 36**, or **37**. However, 2-ferrocenyl-2-propanol (**38**) did eliminate to a small extent to provide isopropenylferrocene (**41**) in ~ 15% yield.

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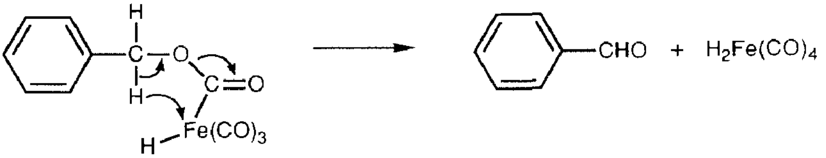
8 An alternative mechanism which was previously considered and also proposed by one of the reviewers involves nucleophilic addition of **14** to iron tetracarbonyl to generate intermediate **24A**. This intermediate could provide access to **19** and dihydroiron tetracarbonyl, but such an intermediate would not give an ether as observed during the reactions of 4-methoxybenzyl alcohol (**15**) and many of the α-ferrocenylcarbinols.



24A **19**

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