Synthesis of Substituted Hydroxybutadiene Tricarbonyliron Complexes

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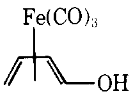
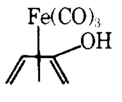
Abstract: The reaction of 2-pyrone tricarbonyliron with various alkoxy or alkyl- and aryllithium reagents was found to be a high-yield pathway to numerous 1,4-disubstituted butadiene tricarbonyliron complexes. The reaction conditions used allow for the isolation of only one geometric isomer (Z,E), but conversion to the E,E isomer is accomplished by isomerization in benzene. 2-Pyrone tricarbonyliron reacts with excess $LiAlH_4$ to yield, as a major product, (2,3,4,5η)-(2Z)-2,4-pentadienal tricarbonyliron. The mechanism of this reaction was studied in detail using $LiAlD_4$ and analyzing the deuterium label distribution in the products. Spectral and experimental data for the enolate anion are reported and provide unequivocal evidence for the intervention of a symmetrical π-allyl anion intermediate in the reaction pathway.

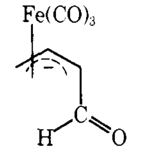
Although many organic dienes have been complexed to transition metals, in only a relatively few cases has a functional group been attached to the organic ligand. In the traditional methods of organic chemistry, functional groups have been used to probe into the reactivity and electronic structure of new organic systems, and we felt that a similar approach might be fruitful in the field of organometallic chemistry. Among the functional groups which might prove useful for this purpose, the hydroxyl and amino groups appeared most promising, for not only do these groups interact strongly with unsaturated systems, but a sensitive measure of this interaction is available in the pK_a of the former and pK_b of the latter. Some time ago[1] we reported that 1- and 2-hydroxybutadiene tricarbonyliron (I, II) complexes may be prepared and are stable in the absence of air, and we also showed that the enolate salt of I is best represented[2] as a complex of the rare[3] π-allyl anion complex of tricarbonyliron (III). Further work with compounds of this type was handicapped by the lack of a general synthesis which would lead to a variety of substituted derivatives. We have now developed such a synthesis for derivatives of I, and in this paper we report on some properties and transformations of these novel compounds.[4]



I



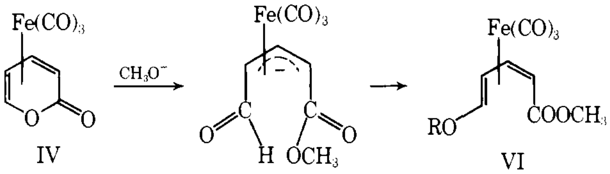
II



III

Results and Discussion

Our syntheses begin with the easily obtained complex 2-pyrone tricarbonyliron (IV) which arises in 80–89% yield when 2-pyrone[5] is heated with diiron ennacarbonyl in benzene for 1–2 h.[6] The complex is extremely stable and not at all sensitive to air.



IV

V

VI

a, R = H

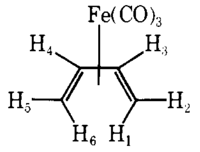
b, R = CH_3

c, R = $COCH_3$

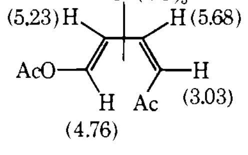
(1)

The 2-pyrone complex, IV, reacts readily with bases to form salts of the π-allyl anion complex. For example, reaction of the yellow IV with 1 molar equiv of sodium methoxide in methanol at room temperature gives immediately a blood-red solution of the anion V. A solution of this anion is indefinitely stable, but solutions of the corresponding enol, formed upon acidification, decompose slowly, especially in the presence of air. However, reaction of V with acetic anhydride gives the acetoxy ester (methyl(2,3,4,5η)-(2Z,4E)-5-acetoxy-2,4-pentadienoate tricarbonyliron) VIc in high yield. The π-allyl anion V was also found to react with methyl iodide or dimethyl sulfate to form, in moderate yields, the methoxy ester VIb and with H^+ the enol ester VIa.

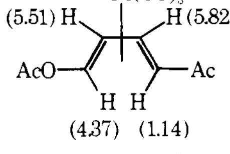
The NMR spectra of compounds like VI are reasonably definitive as to structure, especially when E and Z isomers are available for comparison. Because many of our structural conclusions will depend upon NMR analysis, it appears worthwhile to summarize briefly the main types of absorption in these complexes. The parent complex, butadiene tricarbonyliron (VII), exhibits three distinct sets of proton resonances. Those at highest field (δ 0.22) are H_1 and H_6 (anti), which are most shielded by the iron, those at intermediate field (δ 1.73) are H_2 and H_5 (syn), and those at lowest field (δ 5.37) are assigned to H_3 and H_4. The large chemical shift difference between the syn protons (δ 1.8–1.6) and the anti protons (δ 0.2–0.5) in the butadiene moiety has now been observed in numerous dieneiron complexes.[7] Substitution on the terminal carbons of a diene system with unsaturated or electronegative substituents like carbomethoxy, acetoxy, or keto functions shifts the neighboring protons to lower fields, but the 1.5–2.0 ppm difference between syn and anti protons is still observed. A comparison of the NMR of (3,4,5,6η)-(3Z,5E)-6-acetoxy-3,5-hexadien-2-one tricarbonyliron (VIII) to that of the 3E,5E isomer (IX) shows the large shift observed (3.03–1.14 ppm) for the Z to E isomerization. The NMR spectrum thus provides an unequivocal method for ascertaining the orienta-



VII

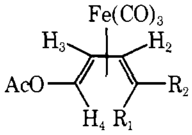


VIII (3Z,5E)



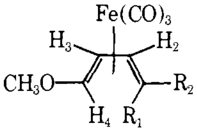
IX (3E,5E)

Table I. Chemical Shifts (δ) of Protons in Substituted Acetoxy Diene Tricarbonyliron Complexes



	OAc	H_4	H_3	H_2	R_1	R_2
$R_1 = O{=}CCH_3$ $R_2 = H$	2.12	4.76	5.23	5.68	2.04	3.03
$R_1 = H$ $R_2 = O{=}CCH_3$	2.13	4.37	5.51	5.82	1.14	2.08
$R_1 = O{=}CPh$ $R_2 = H$	2.08	4.98	5.54	5.75	7.49, 7.94	3.80
$R_1 = H$ $R_2 = O{=}CPh$	2.09	4.54	5.58	6.04	1.75	7.45, 7.92
$R_1 = O{=}COCH_3$ $R_2 = H$	2.06	5.26	5.29	5.71	3.64	2.81
$R_1 = O{=}CCH{=}CH_2$ $R_2 = H$	2.07	4.74	5.32	5.70	6.28, 5.62	3.17
$R_1 = O{=}CH$ $R_2 = H$	2.06	4.79	5.35	5.60	9.03	2.92
$R_1 = H$ $R_2 = O{=}CH$	2.13	4.52	5.55	5.95	1.21	9.47
$R_1 = O{=}CN(C_2H_5)_2$ $R_2 = H$	2.06	5.40	5.29	5.77	3.00, 3.61 1.10, 1.18	2.85
$R_1 = O{=}COH$ $R_2 = H$	2.08	5.35	5.32	5.65	10.12	2.87

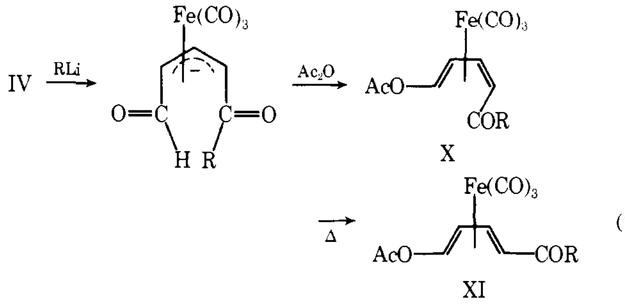
Table II. Chemical Shifts (δ) of Protons in Substituted Methoxy Diene Tricarbonyliron Complexes



	OCH_3	H_4	H_3	H_2	R_1	R_2
$R_1 = O{=}COCH_3$ $R_2 = H$	3.54	4.71	5.22	5.54	3.61	2.67
$R_1 = O{=}CCH_3$ $R_2 = H$	3.50	4.19	5.21	5.53	2.07	2.94
$R_1 = H$ $R_2 = O{=}CCH_3$	3.53	3.67	5.38	5.71	0.96	2.08

tion of substituents on the diene termini. Tables I and II summarize the NMR data obtained for some of the numerous complexes derivable from 2-pyrone tricarbonyliron.

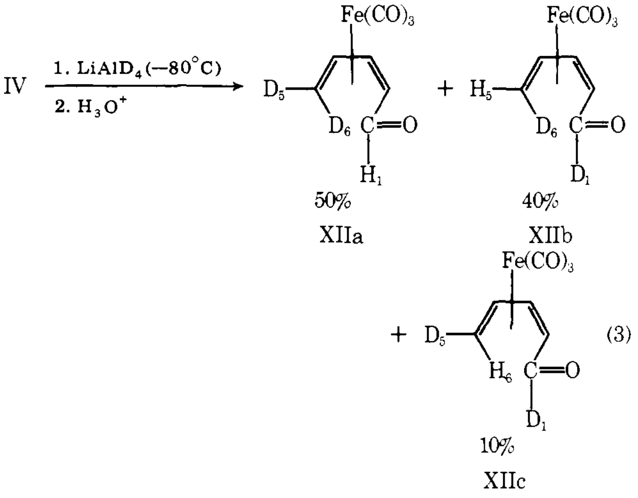
Reaction of IV with 1 equiv of alkyl- or aryllithium compounds at low temperature also gives a deep red solution of a π-allyl anion complex which can be trapped by acetic anhydride to furnish 4-acetoxy-1-acylbutadiene tricarbonyliron complexes (eq 2). Yields in this sequence are nearly quantitative. If the opening and trapping are carried out at relatively low temperature (below room temperature) the acyl group is found exclusively in the anti position (X), but isomerization from the anti to the syn position (X → XI) (eq 2) occurs on heating,[8] especially in the presence of Fe_2CO_9.[13] For this reason it is possible to obtain pure samples of both the *Z,E* and *E,E* isomers. We have never found any trace of the acetoxy substituent in the anti position, and consider the equilibrium constant for the isomerization to the syn position to be quite large.



(2)

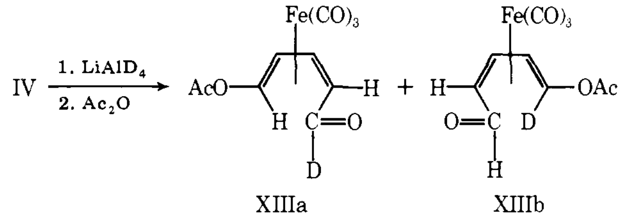
$R = CH_3, C_6H_5, CH{=}CH_2, H, N(C_2H_5)_2$

Reduction of IV with $LiAlH_4$, even at low temperature (−80 °C), formed as the major product, 25–30% yield, (2,3,4,5η)-(2*Z*)-2,4-pentadienal tricarbonyliron complex (XII). When the reduction was carried out with an excess of $LiAlD_4$, the products had the deuterium label distributed as shown in eq 3. This distribution could be determined in the following manner. The mass spectrum showed that each aldehyde molecule contained two deuterium atoms. Secondly, the ^1H NMR showed that the aldehyde proton (H_1) and H_5 were both reduced to about one-half of their initial values, and that H_6 was nearly completely missing from the spectrum. However, the deuterium magnetic resonance (^2H NMR) spectrum of the mixture of labeled isomers was most definitive. It showed three singlets, corresponding in position (ppm) to the aldehyde deuteron (D_1), D_5, and D_6 in the ratio of 5:6:9, thus indicating the product composition shown in eq 3. Stereospecific reduction from the side away from the metal and loss of the hydroxyl group from this same side accounts for the predominance of anti over syn deuterium (XIIb:XIIc = 4:1).[4,9,10]



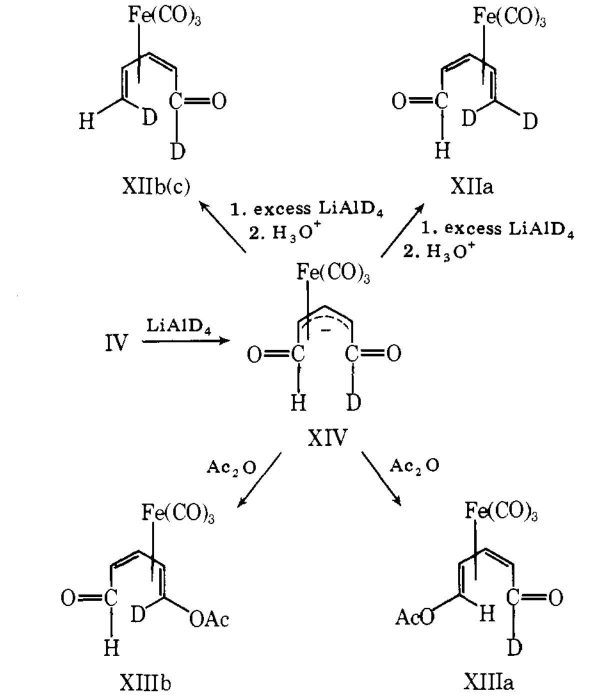
(3)

If reduction with $LiAlD_4$ is not carried to completion, and the resulting anion is trapped at 0 °C by reaction with acetic anhydride, an acetoxy aldehyde (XIII) is obtained in 10% yield. ^2H and ^1H NMR analysis showed that the deuterium label is distributed as shown in eq 4, half in the aldehyde group and half on the diene. This product distribution, as well as that of eq 3, suggests the intervention of a symmetrical intermediate in the reduction, namely the 1,3-diformyl-π-allyl anion tricarbonyliron complex (XIV). The results of the deuterium labeling experiments are best accounted for by the pathway shown in Scheme I. The symmetrical dialdehyde XIV is formed by deuteride addition, and trapping by acetic anhydride to form the acetates XIIIb or XIIIa or further reduction by excess $LiAlD_4$ can occur at either aldehyde with equal probability. To investigate this possibility a better synthesis of



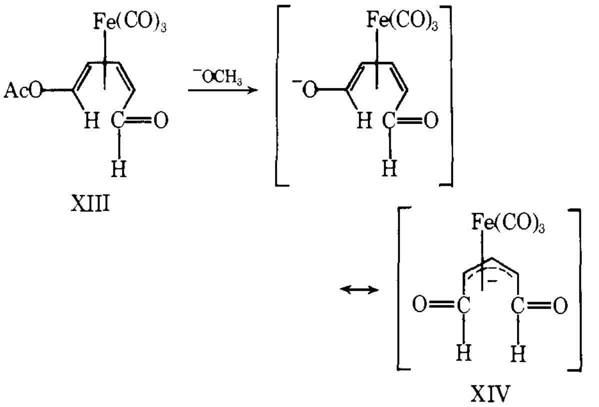
(4)

Scheme I



(2,3,4,5η)-(2*Z*,4*E*)-5-acetoxy-2,3-pentadienal tricarbonyliron (XIII) was sought. Complex XIII was found to be produced in 40-50% yield by the reaction of 2-pyrone tricarbonyliron (IV) with diborane at 0 °C, followed by trapping with acetic anhydride. Its spectral properties were in full accord with its structure and the formyl group could be isomerized to the syn position upon refluxing in benzene for 10 h.

Reaction of XIII with sodium methoxide in methanol rapidly generates a deep red solution of a salt, to the anion of which we assign the symmetrical structure XIV. Evaporation of the methanol gives a red solid which is stable indefinitely under argon, but which slowly decomposes when exposed to air.



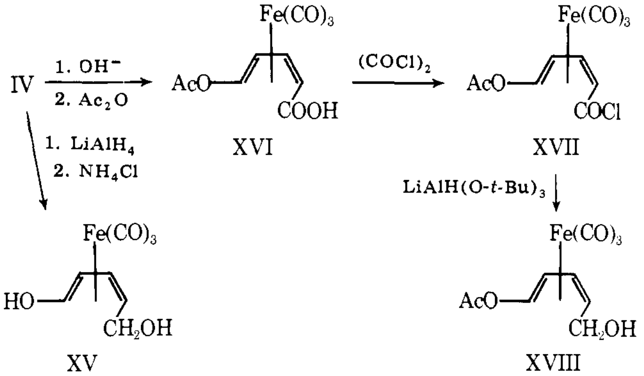
(5)

The NMR spectrum of XIV is consistent with a symmetric 1,3-diformyl-π-allyl anion complex. There are only three absorptions in the spectrum and these integrate in the ratio of 2:1:2. The aldehyde protons (H_1) absorb at δ 7.90 and are doublets coupled to proton H_2, $J_{12} = 8.3$ Hz. Proton H_2 is an overlapping set of doublets centered at δ 5.83 coupled to protons H_1 and H_3, $J_{23} = 7.2$ Hz. Proton H_3 is a triplet (δ 3.85) since it is coupled to two equivalent protons.

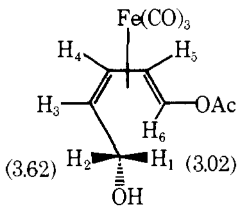
The IR spectrum of XIV shows absorptions for the carbonyl ligands at 2040, 1990, and 1905 cm^{-1} characteristic of π-allyl anion complexes. In addition there is an absorption at 1600 cm^{-1} which can be assigned to the aldehyde carbonyl groups. This low value for the carbonyl stretch may indicate that the aldehyde oxygen bears some of the negative charge.

When 2-pyrone tricarbonyliron (IV) is allowed to react with an excess of $LiAlH_4$ at −80 °C and the reaction mixture is poured into an ammonium chloride solution instead of the stronger acid used earlier (eq 3) the aldehyde complex, pentadienal tricarbonyliron (XII), is not obtained, but instead an air-sensitive complex which, upon treatment with acid or base, generates XII. We suspected this compound to be the enol carbinol XV. In order to test this hypothesis we decided to synthesize this alcohol and see if it would rearrange to XII. Reduction of the acetoxy aldehyde XIII without cleavage of the ester group did not prove possible, despite several attempts. However, the pathway outlined in Scheme II did prove successful. Hydrolysis of IV and trapping with acetic anhydride gives the acid XVI (pK_a = 5.75 in 50% of ethanol-water) in 51% yield. This could be converted to its acid chloride (XVII) and reduced by lithium tri-*tert*-butoxyaluminum hydride without attack at the acetoxyl group.

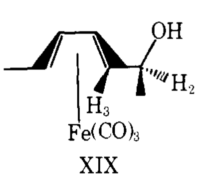
Scheme II



Alcohol XVIII is a stable yellow liquid. The most likely conformation for XVIII is that with the hydroxyl group occupying the least crowded position. Protons H_1 and H_2 differ in chemical shift by 0.60 ppm owing to the influence of the tricarbonyliron. The geminal coupling constant (J_{12} = 11.6 Hz) can be measured directly from the NMR spectrum. Lillya[11] has reported the NMR spectra of tricarbonyliron complexes of some secondary dienols in which the carbinol hydrogen is forced to occupy the sterically most crowded position (XIX, iron below plane of diene). The vicinal coupling constants for the resulting anti-periplanar relationship between H_2 and H_3 varied from 8 to 9 Hz. In agreement with these observations the NMR of XVIII shows that H_1 is coupled to H_3 by 9.5 Hz. Proton H_2 is coupled to H_3 by 5.5 Hz. This smaller coupling constant is consistent with a syn-periplanar orientation.



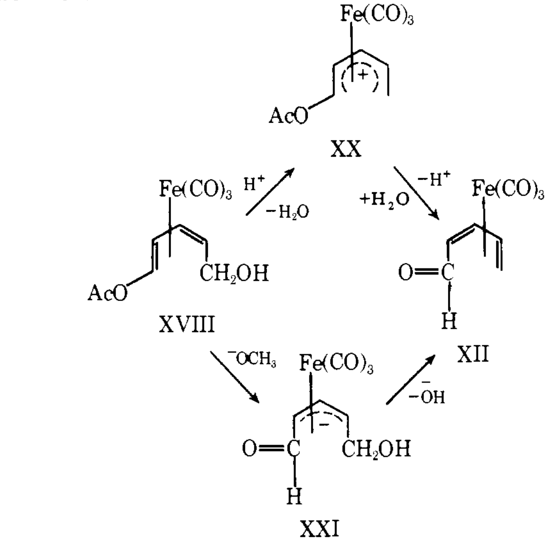
XVIII



XIX

The acetoxyl alcohol XVIII proved to be extremely reactive. Column chromatography of XVIII on silica gel sufficed to convert it to the aldehyde XII. Brief treatment with 0.1 N HCl in THF-water also produced XII, presumably by way of the pentadienyl cation XX. But XVIII is also converted (Scheme III) rapidly to XII by loss of hydroxide from the π-allyl anion XXI.

Scheme III



2-Pyrone tricarbonyliron has proved to be an ideal precursor for numerous substituted diene tricarbonyliron complexes. The cisoid nature of the 2-pyrone ligand greatly facilitates complexation to iron tricarbonyl, and eliminates the need for elaborate synthetic pathways to substituted dienes followed all too often by low yield complexations. We feel that starting with a complexed pyrone and doing the chemical transformations necessary to generate the desired product in both high yield and controlled stereochemistry will prove to be a valuable synthetic procedure.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-10 instrument and were calibrated against a polystyrene film. NMR spectra were recorded on Varian Associates Model A-60A, Model EM-360, or Model HA-100 NMR spectrometer or JEOL PFT-100 NMR spectrometer with a Nicolet 1083 data system. NMR spectra were calibrated with internal tetramethylsilane (δ 0.00). Mass spectra were obtained at 70 eV on a Varian MAT CH-5 or CH-7 spectrometer.

2-Pyrone Tricarbonyliron (IV). To a slurry of 700 mL of anhydrous benzene and 75.0 g (0.208 mol) of diiron enneacarbonyl (Fe_2CO_9) was added 13.5 g (0.414 mol) of 2-pyrone.[5,12] After warming at 45-50 °C for 1-2 h, the solution was filtered and the solvent removed at reduced pressure. The dark residue was purified by dry column chromatography using silica gel and eluting with hexanes and CH_2Cl_2. The yellow crystalline complex[6] resulting from removal of the CH_2Cl_2 at reduced pressure and recrystallization from hexane-ether was obtained in 80-89% (26.0-29.5 g) yield: mp 140-142 °C; IR (CH_2Cl_2) 2070, 1995 ($C\equiv O$), 1745 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 3.02 (dd, 1 H), 5.65 (m, 2 H), 6.32 ppm (m, 1 H); mass spectrum *m/e* 236, 208, 180, 152.

(3,4,5,6η)-(3*Z*,5*E*)-6-Acetoxy-3,5-hexadien-2-one Tricarbonyliron. To a mixture of 1.00 g (4.24 mmol) of 2-pyrone tricarbonyliron in 200 mL of anhydrous ether cooled to −78 °C was added dropwise 8.50 mmol of a methyllithium-ether solution. After stirring for 15 min the bright red π-allyl anion was trapped with 10 mmol of acetic anhydride and the solution was allowed to warm to room temperature. The organic solution was washed with 50-mL portions of NH_4Cl and H_2O and dried over $MgSO_4$. Filtration, removal of solvent, and recrystallization from hexane-ether yielded 1.05 g (86%) of the yellow crystalline complex: mp 95.5-96.5 °C; IR (CH_2Cl_2) 2060, 1995 ($C\equiv O$), 1755, 1640 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.04 (s, 3 H), 2.12 (s, 3 H), 3.03 (d, 1 H), 4.76 (d, 1 H), 5.23 (t, 1 H), 5.68 ppm (t, 1 H); mass spectrum *m/e* 294, 266, 238, 210, 95.

Anal. ($C_{16}H_{12}O_6Fe$) C, H.

(3,4,5,6η)-(3*E*,5*E*)-6-Acetoxy-3,5-hexadien-2-one Tricarbonyliron. Thermal isomerization of the 3*Z*,5*E* isomer was accomplished by refluxing in benzene for 12 h or by refluxing for 1 h in benzene containing a catalytic amount of diiron enneacarbonyl. Filtration and removal of the solvent followed by recrystallization from benzene-hexane gave quantitative conversion to the 3*E*,5*E* complex: mp 68-69 °C; IR (CH_2Cl_2) 2060, 1990 ($C\equiv O$), 1760, 1650 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 1.14 (d, 1 H), 2.08 (s, 3 H), 2.13 (s, 3 H), 4.37 (d, 1 H), 5.51 (t, 1 H), 5.82 ppm (t, 1 H); mass spectrum *m/e* 294, 266, 238, 210.

Reaction of 2-Pyrone Tricarbonyliron with Aryl- and Vinyllithium Reagents. Using conditions and procedures identical with those outlined in the preparation of the (3,4,5,6η)-(3*Z*,5*E*)-6-acetoxy-3,5-hexadien-2-one tricarbonyliron complex substituting phenyl- or vinyllithium reagents for the methyllithium, high yields of the substituted butadiene tricarbonyliron complexes were obtained.

(2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienophenone Tricarbonyliron: 79% yield; mp 123.5-125.0 °C; IR (CH_2Cl_2) 2060, 1990 ($C\equiv O$), 1755, 1640 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.08 (s, 3 H), 3.80 (d, 1 H), 4.98 (d, 1 H), 5.54 (t, 1 H), 5.75 (5, 1 H), 7.49 (m, 3 H), 7.94 ppm (m, 2 H); mass spectrum *m/e* 356, 328, 300, 272, 157, 56.

(2,3,4,5η)-(2*E*,4*E*)-5-Acetoxy-2,4-pentadienophenone Tricarbonyliron: mp 133.0-134.0 °C; IR (CH_2Cl_2) 2060, 1995 ($C\equiv O$), 1760, 1650 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 1.75 (d, 1 H), 2.09 (s, 3 H), 4.54 (d, 1 H), 5.58 (t, 1 H), 6.04 (t, 1 H), 7.45 (m, 3 H), 7.92 ppm (m, 2 H); mass spectrum *m/e* 356, 328, 300, 272, 184, 157, 56, 28. Anal. ($C_{16}H_{12}O_6Fe$) C, H.

(4,5,6,7η)-(4*Z*,6*E*)-7-Acetoxy-1,4,6-heptatrien-3-one Tricarbonyliron: mp 108-109.5 °C; IR (CH_2Cl_2) 2060, 1995 ($C\equiv O$), 1760, 1660 ($C=O$), 1610 cm^{-1} ($C=C$); NMR ($CDCl_3$) δ 2.07 (s, 3 H), 3.17 (d, 1 H), 4.74 (d, 1 H), 5.32 (t, 1 H), 5.62 (m, 2 H), 6.28 ppm (m, 2 H); mass spectrum *m/e* 306, 278, 250, 222, 107, 56, 28. Anal. ($C_{12}H_{10}O_6Fe$) C, H.

Methyl (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienoate Tricarbonyliron (VIc). To a solution of 1.00 g (4.24 mmol) of 2-pyrone tricarbonyliron in 80 mL of ether-20 mL of methanol, stirred at room temperature, was added 0.50 g of metallic sodium. After 15 min, acetic anhydride was added dropwise until the red solution turns yellow. The organic layer was washed with 50-mL portions of 0.1 N HCl, ammonium chloride, and water, dried over magnesium sulfate, and chromatographed on silica gel. Removal of the elution solvent yielded 1.27 g (96%) of the crystalline yellow complex: mp 113.5-114.0 °C; IR (CH_2Cl_2) 3050, 2990, 2060, 1990 ($C\equiv O$), 1755, 1705 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.81 (d, 1 H), 3.64 (s, 3 H), 5.26 (d, 1 H), 5.29 (t, 1 H), 5.71 ppm (t, 1 H); mass spectrum *m/e* 282 ($M^+ - 28$), 254, 226, 56. Anal. ($C_{11}H_{10}O_7Fe$) C, H.

***N,N*-Diethyl-(2,3,4,5η)-(2*Z*,4*E*)-5-acetoxy-2,4-pentadienamide Tricarbonyliron.** A 250-mL three-necked round-bottom flask equipped with a magnetic stirrer, gas inlet (argon), and addition funnel was charged with 0.55 g (2.32 mmol) of 2-pyrone tricarbonyliron in 150 mL of anhydrous ether and cooled to 0 °C. To a cooled solution of 1.00 g (13.7 mmol) of diethylamine in 15 mL of ether was added 4.8 mmol of *n*-butyllithium. The freshly generated diethyllithium amide was then added slowly to the cooled solution of 2-pyrone tricarbonyliron. After 15 min an excess of acetic anhydride was added and the solution allowed to warm to room temperature. The organic layer was washed with 50-mL portions of water, 0.1 N HCl, 0.1 N KOH, water, and NH_4Cl and dried over $MgSO_4$. Chromatography on silica gel and collecting the fraction eluting with ethyl ether yielded 0.418 g (72% based on 0.39 g of starting material (0.160 g recovered unreacted)) of crystalline yellow complex: mp 134.5-135.5 °C; IR (CH_2Cl_2) 2045, 1985 ($C\equiv O$), 1755, 1610 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 1.10 (t, 3 H), 1.18 (t, 3 H), 2.08 (s, 3 H), 2.85 (d, 1 H), 3.00 (m, 2 H), 3.61 (m, 2 H), 5.29 (t, 1 H), 5.40 (d, 1 H), 5.77 ppm (t, 1 H); mass spectrum *m/e* 323 ($M^+ - 28$), 295, 267, 224, 152, 56, 28. Anal. ($C_{14}H_{17}O_6NFe$) C, H.

(3,4,5,6η)-(3*Z*,5*E*)-6-Methoxy-3,5-hexadien-2-one Tricarbonyliron. To 1.00 g (4.23 mmol) of 2-pyrone tricarbonyliron in 200 mL of anhydrous ethyl ether cooled to −80 °C was added dropwise 6 mmol of CH_3Li-ether solution. After 15 min the cooling bath was removed and 5 mL of dimethyl sulfate was added. Heat was applied and the reaction mixture was refluxed for 16 h. The reaction was quenched with 50 mL of 1 N HCl and the yellow ether layer was separated and washed with two 50-mL portions of 0.1 N KOH. The aqueous extracts (red) were treated with acetic anhydride and extracted with benzene and the solvent was removed at reduced pressure to yield 0.210 g (16.7%) of the (3*Z*,5*E*)- and (3*E*,5*E*)-6-acetoxy-3,5-hexadien-2-one tricarbonyliron complexes. The original layer (ether) was washed with 100-mL portions of water, 0.1 N HCl, water, and NH_4Cl, dried over $MgSO_4$, and absorbed onto silica gel for dry column chromatography. Elution with CH_2Cl_2–ether produced, after removal of solvent, 0.923 g (82%) of the 3*Z*,5*E* complex: IR (CH_2Cl_2) 3050, 2985, 2040 ($C\equiv O$), 1990 ($C\equiv O$), 1660 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.94 (d, 1 H), 3.50 (s, 3 H), 4.19 (d, 1 H), 5.21 (t, 1 H), 5.53 ppm (t, 1 H); mass spectrum *m/e* 266 (M^+), 238, 210, 182, 95, 56.

(3,4,5,6η)-(3*E*,5*E*)-6-Methoxy-3,5-hexadien-2-one Tricarbonyliron. Quantitative conversion of the 3*Z*,5*E* isomer was accmplished by refluxing for 15 min in benzene with 1.0 g of Fe_2CO_9 for catalyst. Purification by column chromatography (silica gel) produced the 3*E*,5*E* isomer as a stable yellow oil: IR (CH_2Cl_2) 3050, 2990, 2045 ($C\equiv O$), 1990 ($C\equiv O$), 1678 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 0.96 (d, 1 H), 2.08 (s, 3 H), 3.53 (s, 3 H), 3.67 (d, 1 H), 5.38 (t, 1 H), 5.71 ppm (dd, 1 H); mass spectrum *m/e* 266 (M^+), 238, 210, 182, 152, 150, 124, 95, 82, 56. Anal. ($C_{10}H_{10}O_5Fe$) C, H.

Methyl (2,3,4,5η)-(2*Z*,4*E*)-5-Methoxy-2,4-pentadienoate Tricarbonyliron (VIb). To a solution of 1.00 g (4.24 mmol) of 2-pyrone tricarbonyliron in 80 mL of ether–20 mL of methanol, stirred at room temperature, was added 0.50 g of metallic sodium. After 15 min, TLC showed that all of the starting material had been opened to the π-allyl anion. Dimethyl sulfate (4 mL) was added and the solution was warmed for 2 h. The reaction mixture was treated with 50 mL of 1 N HCl and the organic layer was separated, washed with 0.1 N KOH, water, and saturated NH_4Cl, dried ($MgSO_4$), absorbed onto silica gel, and chromatographed with CH_2Cl_2. Two major fractions were isolated. The second fraction yielded 0.448 g of 2-pyrone tricarbonyliron. The faster eluting component was the methyl (2,3,4,5η)-(2*Z*,4*E*)-5-methoxy-2,4-pentadienoate tricarbonyliron complex. Product crystallizes from hexane at 0 °C but melts on warming to room temperature: IR (CH_2Cl_2) 2040 ($C\equiv O$), 1985 ($C\equiv O$), 1705 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.57 (d, 1 H), 3.44 (s, 3 H), 3.52 (s, 3 H), 4.59 (d, 1 H), 5.10 (t, 1 H), 5.43 ppm (t, 1 H); mass spectrum *m/e* 282 ($M^+ - 28$), 254, 226, 198, 56, 28.

Reaction of 2-Pyrone Tricarbonyliron with Lithium Aluminum Hydride. A 250-mL three-necked round-bottom flask equipped with an overhead stirrer and argon flow was charged with 150 mL of anhydrous ether and 0.850 g (3.6 mmol) of 2-pyrone tricarbonyliron. The solution was deaerated with argon and cooled to −78 °C. Lithium aluminum hydride (0.300 g, 7.9 mmol) which had been refluxed in 30 mL of ether was added to the rapidly stirred solution over a 15-min interval. After an additional 30 min, the reaction was quenched with 30 mL of 3 N H_2SO_4 and the solution was allowed to warm to 0 °C. The yellow ether layer was separated and washed with water and extracted with three 30-mL portions of 5% KOH. The aqueous layer was blood red. The organic layer was washed once with water and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The NMR spectrum indicated the presence of starting material (IV), (2,3,4,5η)-(2*Z*)-2,4-pentadienal tricarbonyliron (XII), and a small amount of the 2*E* isomer. The aldehyde complexes were purified by dry column chromatography using silica gel and eluting with methylene chloride. A yellow oil was obtained in 28% yield (0.225 g): IR ($CHCl_3$) 3020, 2830, 2730, 2060 ($C\equiv O$), 1980 ($C\equiv O$), 1660 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 1.42 (dd, 1 H), 2.20 (m, 1 H), 3.95 (dd, 1 H), 5.52 (m, 2 H), 9.20 ppm (dd, 1 H); mass spectrum *m/e* 222 (M^+), 194, 166, 138, 116, 83, 56. A small amount of (2*E*)-pentadienal tricarbonyliron was also obtained (0.040 g, 5% yield): IR ($CHCl_3$) 3000, 2820, 2730, 2075 ($C\equiv O$), 1980 ($C\equiv O$), 1670 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 0.85 (dd, 1 H), 1.25 (dd, 1 H), 2.12 (m, 1 H), 5.60 (m, 1 H), 6.00 (m, 1 H), 9.27 ppm (d, 1 H); mass spectrum *m/e* 222 (M^+), 194, 166, 138, 110, 84, 56.

The red aqueous extracts were combined in a 125-mL Erlenmeyer flask and cooled to 0 °C. Acetic anhydride was added (8 mL) until the red color disappeared and the solution was yellow. Extraction with benzene gave a yellow organic layer which was washed with five 100-mL portions of water and dried ($MgSO_4$) and the solvent was removed under vacuum. The yellow oil was purified by dry column chromatography, eluted with methylene chloride, to give 0.100 g (10%) of the (2,3,4,5η)-(2*Z*,4*E*)-5-acetoxy-2,4-pentadienal tricarbonyliron complex (XIII): mp 80.5–81.5 °C; IR ($CHCl_3$) 3020, 2830, 2730, 2080 ($C\equiv O$), 1990 ($C\equiv O$), 1755 ($C=O$), 1665 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.92 (dd, 1 H), 4.79 (d, 1 H), 5.35 (m, 1 H), 5.60 (m, 1 H), 9.03 ppm (dd, 1 H); mass spectrum *m/e* 280 (M^+), 252, 224, 196, 81, 56. Anal. ($C_{10}H_8O_6Fe$) C, H.

A small amount of the 2*E*,4*E* isomer was present (50 mg, 5%). Refluxing in benzene for a few minutes with Fe_2CO_9 rapidly converts the 2*Z*,4*E* isomer into the (2,3,4,5η)-(2*E*,4*E*)-5-acetoxy-2,4-pentadienal tricarbonyliron isomer:[13] mp 86.0–86.5 °C; IR ($CHCl_3$) 3050, 2960, 2050 ($C\equiv O$), 1980 ($C\equiv O$), 1755 ($C=O$), 1655 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 1.21 (dd, 1 H), 2.13 (s, 3 H), 4.52 (d, 1 H), 5.55 (m, 1 H), 5.95 (m, 1 H), 9.47 ppm (d, 1 H); mass spectrum *m/e* 280 (M^+), 252, 224, 196, 168, 126, 81, 56.

Reaction of 2-Pyrone Tricarbonyliron with Lithium Aluminum Deuteride. The same general procedure reported for the opening of 2-pyrone tricarbonyliron with lithium aluminum hydride was followed. The lithium aluminum deuteride (0.300 g, 7.9 mmol) was dissolved in hot ether and added with rapid stirring over a 15-min interval to 0.850 g (3.6 mmol) of 2-pyrone complex in 150 mL of ether that had been cooled in a dry ice–acetone bath. After the usual workup, the products were purified by dry column chromatography on silica gel adsorbent and elution with methylene chloride. 2-Pyrone tricarbonyliron (0.60 g) was recovered. The (2*Z*)-pentadienal tricarbonyliron (0.190 g) with a small amount of the 2*E* isomer present was obtained as a yellow oil in 26% yield. 5-Acetoxypentadienal tricarbonyliron (XIII), 0.10 g (10% yield), was obtained by trapping with acetic anhydride in the manner previously described.

In order to simplify further analysis the mixture was taken up in benzene and refluxed overnight under argon to cause a complete thermal isomerization of the formyl group to the syn position. The resulting (2*E*)-pentadienal tricarbonyliron was purified by dry column chromatography using silica gel adsorbent and eluting with methylene chloride: IR ($CHCl_3$) 3000, 2820, 2730, 2075 ($C\equiv O$), 1980 ($C\equiv O$), 1670 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 0.85 (m, 0.12 H), 1.30 (m, 1 H), 2.14 (m, 0.38 H), 5.62 (m, 1 H), 6.02 (m, 1 H), 9.42 ppm (d, 0.50 H); mass spectrum *m/e* 224 (M^+), 196, 180, 168, 152, 141, 140, 124, 56 (base peak); ^3H NMR ($CHCl_3$, Freon-11 lock) 21.4 (s, 0.5 D), 14.1 (s, 0.6 D), 12.8 ppm (0.9 D). (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienal tricarbonyliron complex was also analyzed by NMR after it was purified by dry column chromatography (silica gel, methylene chloride eluent): IR ($CHCl_3$) 3050, 2960, 2830, 2720, 2050 ($C\equiv O$), 1980 ($C\equiv O$), 1755 ($C=O$), 1655 cm^{-1} ($C=O$); NMR ($CDCl_3$) δ 2.03 (s, 3 H), 2.88 (dd, 1 H), 4.80 (d, 0.50 H), 5.37 (t, 1 H), 5.70 (m, 1 H), 9.18 ppm (dd, 0.50 H); mass spectrum *m/e* 280, 252, 224, 196, 168, 82, 56. A small amount of the 5-acetoxy-(2*E*,4*E*)-pentadienal tricarbonyliron was also present: NMR ($CDCl_3$) δ 1.15 (dd, 1 H), 4.45 (d, 0.50 H), 5.25–5.90 (m, 2 H), 9.33 ppm (d, 0.50 H).

Reaction of 2-Pyrone Tricarbonyliron with Lithium Aluminum Hydride. Workup with Weak Acid. 2-Pyrone tricarbonyliron (0.900 g, 3.8 mmol) was reacted with lithium aluminum hydride (0.350 g, 9.2 mmol) using the procedure previously described. After stirring for 30 min at −78 °C the reaction mixture was quenched with 20 mL of saturated ammonium chloride and stirred for an additional 15 min. It was then allowed to warm to 0 °C. The yellow-red ether layer was separated and washed with water. Decomposition was apparent and it appeared that an air-sensitive product was present. Extraction with 5% potassium hydroxide solution gave red aqueous extracts which slowly turned yellow.

The organic layer was washed with water, filtered through Celite, and dried ($MgSO_4$). The yellow solid obtained after removal of solvent was analyzed by NMR and was identified as 2-pyrone tricarbonyliron. The pentadienal complexes were not present.

The red aqueous extracts were combined and treated with acetic anhydride in the manner previously described. The aqueous solution was extracted with benzene three times. The yellow benzene extracts were washed with three 100-mL portions of water and dried ($MgSO_4$). After purification by dry column chromatography (silica gel, methylene chloride eluent) the NMR indicated that pentadienal tricarbonyliron and a small amount of 5-acetoxypentadienal tricarbonyliron complex XIII were present. A total of 0.100 g of material was isolated.

Reaction of 2-Pyrone Tricarbonyliron with Diborane. 2-Pyrone tricarbonyliron (1.0 g, 4.25 mmol) was placed in a 125-mL Erlenmeyer flask and 50 mL of THF (distilled from $LiAlH_4$) was added. Argon was bubbled through the solution and the flask was cooled to 0 °C with an ice bath. Over a 5-min period, 10 mL of a 1 M THF solution of borane (Ventron) was added. The solution was stirred for 2.5 h at 0 °C. Benzene was added and the solution was extracted once with 50 mL of water and then with five 50-mL portions of saturated sodium carbonate solution until the aqueous extracts were no longer red.

The benzene layer was washed with water and dried ($MgSO_4$).

Evaporation of the solvent under vacuum gave 0.66 g of recovered 2-pyrone.

A small amount of acetic anhydride (2 mL) was added to the red aqueous extracts, with stirring, until the solution turned yellow. The aqueous layer was extracted with three 50-mL portions of benzene. The yellow benzene extracts were combined, washed with four 100-mL portions of water and dried ($MgSO_4$) and the solvent was removed. The product, (2,3,4,5η)-(2*Z*,4*E*)-5-acetoxy-2,4-pentadienal tricarbonyliron (XIII), was obtained in 40% yield (based on starting material consumed).

Isolation of 1,3-Diformyl-π-allyl Anion Tricarbonyliron (XIV). (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienal tricarbonyliron (XIII) (0.180 g, 0.64 mmol) was dissolved in 20 mL of methanol and placed in a 75-mL Schlenk tube with a stirring bar and argon flow. The solution was deaerated with argon and cooled to 0 °C with an ice bath. All operations were carried out under argon. Sodium methoxide (0.053 g, 0.98 mmol) dissolved in 10 mL of methanol was added and the solution was stirred for 45 min.

The methanol was removed under vacuum and 20 mL of deaerated water was added. The red aqueous solution was extracted with two 20-mL portions of ether. The water was evaporated under high vacuum and the red solid that remained was dissolved in acetonitrile (d_3) in a glove box and filtered through Celite into an NMR tube: IR (CH_3CN) 2980, 2040 ($C{\equiv}O$), 1990 ($C{\equiv}O$), 1920 ($C{\equiv}O$), 1600 cm^{-1} ($C{=}O$); NMR (CD_3CN) δ 3.85 (dd, 2 H), 5.23 (t, 1 H), 7.90 ppm (d, 2 H).

(2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienoic Acid Tricarbonyliron (XVI). 2-Pyrone tricarbonyliron (3.0 g, 13 mmol) and 190 mL of THF-water (50-50 v %) solution were placed in a 250-mL Erlenmeyer flask with a stirring bar. The solution was deaerated and covered with argon. With rapid stirring 45 mL of 5% potassium hydroxide solution was added over a 5-min period. After 0.5 h acetic anhydride (6 mL) was added until the red color disappeared and the solution became yellow.

Water and 100 mL of benzene were added and the yellow organic layer was separated. The aqueous layer was extracted with two 50-mL portions of benzene. The benzene extracts were combined and extracted with four 100-mL portions of saturated sodium carbonate solution.

The yellow aqueous extracts were combined and 6 N hydrochloric acid was added until the solution was acidic. The aqueous solution was extracted with three 50-mL portions of benzene. The yellow organic extracts were combined, washed with water, and dried ($MgSO_4$). Removal of the solvent and recrystallization from hexane–ether afforded 2.03 g (51% yield) of acid which decomposes without melting at 125 °C. The pK_a, measured potentiometrically, was 5.75 in 50–50 v % ethanol: IR ($CHCl_3$) 3060–2680, 2080 ($C{\equiv}O$), 2000 ($C{\equiv}O$), 1775 ($C{=}O$), 1670 ($C{=}O$), 1440 cm^{-1} (m); NMR ($CDCl_3$) δ 2.98 (s, 3 H), 2.87 (d, 1 H, J_{HH} = 6.5 Hz), 5.32 (t, 1, H), 5.35 (d, 1 H, J_{HH} = 5.0 Hz), 5.65 (q, 1 H), 10.12 ppm (s, 1 H); mass spectrum *m/e* 268, 240, 212, 184, 169, 64, 56, 28.

(2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienoyl Chloride Tricarbonyliron (XVII). (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienoic acid tricarbonyliron (1.6 g, 5.4 mmol), 20 mL of benzene (dried over calcium hydride), and 3 drops of pyridine were placed in a 75-mL flame-dried Schlenk tube with a stirring bar. Oxalyl chloride (1.43 g, 12 mmol) in benzene was added to the rapidly stirring solution over a 10-min period. Gas evolution began immediately. The solution was warmed to 40 °C and stirred for 25 min until gas evolution ceased.

The solvent was evaporated and the product was recrystallized from hexane–benzene, giving 1.5 g of acid chloride (88% yield): mp 93–95 °C; IR ($CHCl_3$) 3005, 2055 ($C{\equiv}O$), 1990 ($C{\equiv}O$), 1755 ($C{=}O$), 1700 ($C{=}O$), 1445 cm^{-1}; NMR ($CDCl_3$) δ 2.13 (s, 3 H), 2.97 (d, 1 H), 5.06 (d, 1 H), 5.44 (m, 1 H), 5.74 ppm (m, 1 H); mass spectrum *m/e* 260, 258, 232, 223, 212, 177, 115, 56.

(2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienol Tricarbonyliron (XVIII). (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienoyl chloride tricarbonyliron (1.00 g, 3.18 mmol) and 20 mL of THF (dried over $LiAlH_4$) were placed in a 75-mL Schlenk tube and cooled to 0 °C with an ice bath. Over a 10-min period 1.70 g (6.36 mmol) of lithium tri-*tert*-butoxyaluminum hydride was added. The yellow solution gradually turned red. After stirring for 1 h the reaction was quenched with saturated ammonium chloride solution. Ether and water were then added and the organic layer was separated. The aqueous layer was washed with two additional 50-mL portions of ether. The ether extracts were combined, washed with water, and dried ($MgSO_4$). The solvent was removed under vacuum and 0.480 g of product (54% yield), a yellow oil, was obtained: IR (thin film) 3400 (OH), 2980, 2040 ($C{\equiv}O$), 1980 ($C{\equiv}O$), 1750 ($C{=}O$), 1365, 1210 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (s, 3 H), 2.67 (m, 1 H), 3.02 (q, 1 H), 3.62 (q, 1 H), 3.65 (broad, 1 H), 5.08 (d, 1 H), 5.20 (dd, 1 H), 5.57 ppm (m, 1 H); mass spectrum *m/e* 254, 226, 198, 138 (base peak), 116, 56, 43.

Reaction of (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienol Tricarbonyliron (XVIII) with Hydrochloric Acid. XVIII (0.10 g, 0.35 mmol) was dissolved in 15 mL of THF and placed in a 50-mL Erlenmeyer flask. The solution was deaerated and 8.0 mL of 0.1 N hydrochloric acid was added to the rapidly stirring solution over a period of 30 min. Ether was added and the organic layer washed with water and dried over $MgSO_4$. The solvent was removed and the NMR spectrum indicated that (2,3,4,5η)-(2*Z*)-2,4-pentadienal tricarbonyliron (XII) had been formed in 42% yield.

Reaction of (2,3,4,5η)-(2*Z*,4*E*)-5-Acetoxy-2,4-pentadienol Tricarbonyliron (XVIII) with Sodium Methoxide. Complex XVIII (0.10 g, 0.35 mmol) was stirred with excess sodium methoxide (0.100 g, 1.9 mmol) in 40 mL of methanol at 0 °C for 45 min. Ether was added and the organic layer washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded 0.040 g (56%) of the (2,3,4,5η)-(2*Z*)-2,4-pentadienal tricarbonyliron (XII) complex.

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