

ASSESSMENT OF BUTENE-1,4-DIOLS AS STARTING MATERIALS FOR THE PREPARATION OF π -ALLYLTRICARBONYLIRON COMPLEXES

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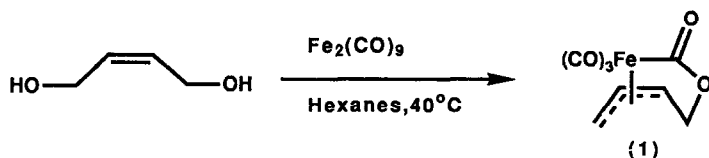
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Abstract: *This work assesses the use of butene-1,4-diols as starting materials for the synthesis of π -allyltricarbonyliron lactone complexes. It has been shown that substituents, and the use of Lewis acids, mainly $ZnBr_2$, in reactions with $Fe_2(CO)_9$ in benzene under ultrasonic conditions or in THF, greatly influence the yield and the product distribution.*

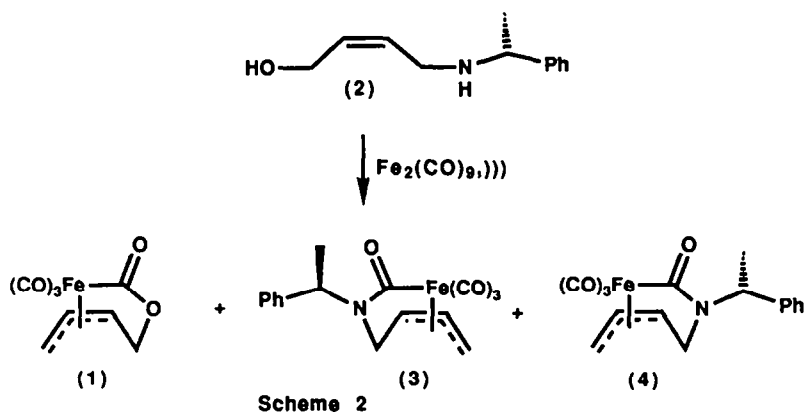
π -Allyltricarbonyl iron lactone complexes have been shown to be useful precursors for the preparation of lactones^{1,2,3} and lactams.⁴ These easily handled, air-stable complexes are usually obtained from vinyl epoxides by treatment with coordinatively unsaturated iron carbonyl species under a variety of conditions.^{1,3,5} There are also reports of generation of these complexes from *Z*-butene-1,4-diols⁶ or substituted derivatives such as 1,2-oxazines⁷ and amino-^{7,8} or halo-⁹ butenols. We have had occasion to re-investigate some of these reactions and to assess butene-1,4-diols as acid-stable, non-volatile precursors for π -allyltricarbonyliron lactone complexes under modified reaction conditions. These studies are reported below.

Heck and Boss first reported the iron lactone complex (1), obtained from *Z*-4-chloro-2-butenol in 5% yield by treatment with $Fe(CO)_5$ under photochemical conditions.⁹ Murdoch obtained a 25% yield by reaction with $Fe_2(CO)_9$ in petroleum ether at 40°C.⁶ However the use of *Z*-butene-1,4-diol as a starting material afforded (1) in an excellent 80% yield (Scheme 1).⁶

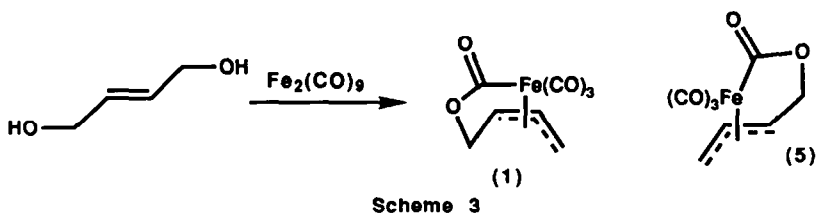


Scheme 1

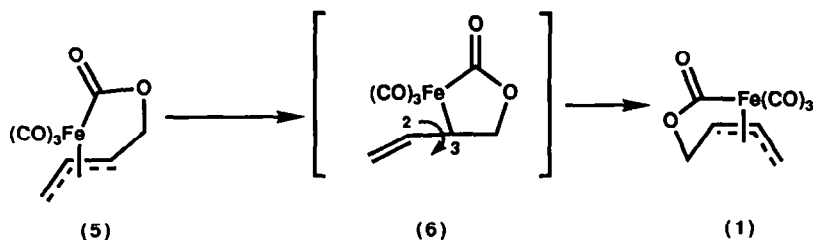
In our laboratories we have developed room temperature procedures for complex formation from vinyl epoxides.¹ Application of these methods to *Z*-butene-1,4-diol afforded (1) in 73% yield using $Fe_2(CO)_9$ in THF and in 55% yield with ultrasonication¹⁰ in benzene. Interestingly, the chiral amino butenol (2) reacted with $Fe_2(CO)_9$ in benzene with ultrasonication to give (1) together with the diastereoisomeric lactam complexes (3) and (4) in a ratio of 1:2:1 in 86% combined yield (Scheme 2). These optically pure lactam complexes may be useful for the preparation of homochiral β -lactams.



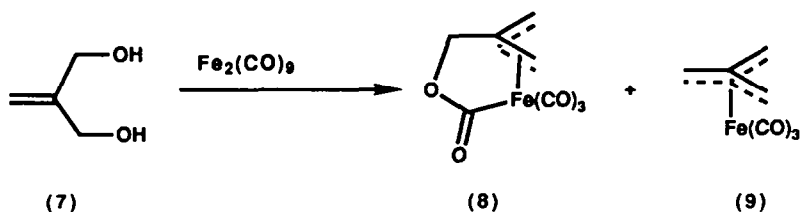
Treatment of *E*-2-buten-1,4-diol with $\text{Fe}_2(\text{CO})_9$ in THF or with ultrasound in benzene afforded (1) in 33 and 11% yields respectively. The low yields here may be attributed to formation of the unstable *trans*-ferrilactone complex (5) which could not be isolated in this example (Scheme 3).



We also presume that (1) in this reaction arises from (5) *via* isomerisation through a η^1 -intermediate (6) and rotation around the C2-C3 bond according to the mechanism previously proposed by Aumann.³



We have also re-investigated the reactions of the isobutene diol (7) with iron carbonyl species, previously studied by Murdoch⁶ and Shvo^{7,8}. Here we found a surprising difference between the preparation procedures. Reaction of (7) with $\text{Fe}_2(\text{CO})_9$ in THF lead to the tricarbonyliron lactone complex (8) as the minor product, in 12% yield, together with the trimethylenemethane complex (9)^{11,12} in 63% yield (Scheme 5).



Scheme 5

In strong contrast, the ultrasonic conditions afforded (8) as the major product (58%) accompanied by only trace amounts (5%) of the trimethylenemethane species. We attribute this to the influence of the reaction medium on the Lewis acidity of tetracarbonyliron. This species should be more Lewis acidic in the less coordinating benzene solvent than in THF. This effect was supported by addition of a Lewis acid, $\text{ZnCl}_2 \cdot \text{TMEDA}$, to the THF reaction mixture, resulting in an enhancement of the yield of ferralactone (8) to 40% with only traces of the trimethylenemethane complex being formed. Owing to these observations we have undertaken a more systematic study of the reactions of some substituted butene diols (10)-(17) with $\text{Fe}_2(\text{CO})_9$ (Tables 1-4).

Table 1: Reactions of 1-Phenylbut-2-ene-1,4-diols with $\text{Fe}_2(\text{CO})_9$

Conditions	Time/hrs	product/yield			
(10)		(18)	(19)	(20)	(21)
A	3	16	0	30	18
B	3.5	38	0	16	4
C	3	38	0	26	7
D	6	32	0	32	16
E	4	49	0	17	8
F	4	50	0	0	0
(11)		(18)	(19)	(20)	(21)
A	5	16	16	40	6
C	3	32	47	0	0
D	4	20	31	6	0
F	3	22	37	0	0

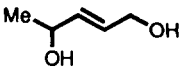
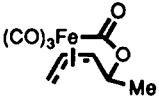
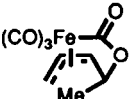
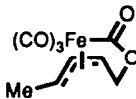
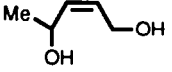
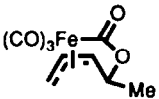
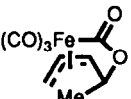
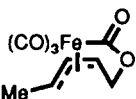
Table 2: Reactions of Non-2-ene-1,4-diols with $\text{Fe}_2(\text{CO})_9$

Conditions	Time/hrs	product/yield			
		(22)	(23)	(24)	(25)
A	4	0	4	0	42
C	6	0	9	0	17
D	4	0	20	14	20
F	4	17	6	0	0
		(22)	(23)	(24)	(25)
A	3	0	8	1	48
C	3	0	15	0	10
D	3	3	30	15	11
F	4	28	28	3	0

Table 3: Reactions of 5,5-dimethylhex-2-ene-1,4-diols with $\text{Fe}_2(\text{CO})_9$

Conditions	Time/hrs	product/yield		
		(26)	(27)	(28)
A	3.5	1	12	40
C	4	8	4	4
D	3.5	7	12	30
F	3.5	8	11	0
		(26)	(29)	(30)
A	4	5	0	0
C	3	64	1	0
D	4	22	0	0
F	3	61	0	3

Table 4: Reactions of Pent-2-ene-1,4-diols with $\text{Fe}_2(\text{CO})_9$

Conditions	Time/hrs	product/yield		
 (16)		 (31)	 (32)	 (33)
A	6	8	1	8
C	1.5	13	1	3
D	5.5	12	2	11
F	5	10	1	14
 (17)		 (31)	 (32)	 (33)
A	3	38	5	15
C	2	43	6	13
D	3	40	13	10
F	2.5	51	4	17

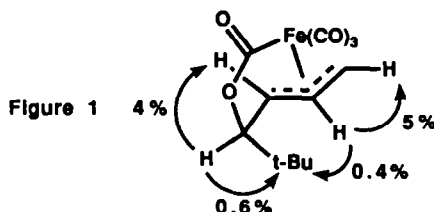
All reactions run at room temperature. (A) 2eq. $\text{Fe}_2(\text{CO})_9$, THF. (B) 2eq. $\text{Fe}_2(\text{CO})_9$, THF, ZnCl_2 .TMEDA. (C) 2eq. $\text{Fe}_2(\text{CO})_9$, THF, ZnBr_2 . (D) 2.2eq. $\text{Fe}_2(\text{CO})_9$, C_6H_6 ,))) (E) 2.2eq. $\text{Fe}_2(\text{CO})_9$, C_6H_6 ,))) ZnCl_2 .TMEDA. (F) 2.2eq. $\text{Fe}_2(\text{CO})_9$, C_6H_6 ,))) ZnBr_2 (1 M in THF).

Although these extensive results provide a complicated picture some general comments and conclusions can be drawn. Firstly it will be noticed that the mass balance in many reactions was poor. This is due to the fact that there was often substantial product decomposition and/or production of other non-iron containing materials which were not always isolated or characterised. Nevertheless, care was taken to obtain all iron carbonyl containing products even though some of these were fairly unstable. The reaction conditions have been chosen to cover experiments in THF with and without Lewis acids, and reactions in benzene under ultrasonication, also with and without Lewis acids present.

While we investigated a very wide range of Lewis acids, including magnesium bromide, diethylaluminium chloride, aluminium trichloride, and aluminium tri-*t*-butoxide, to assist the loss of the hydroxyl group during the formation of the complexes, we found that one equivalent of zinc bromide gave the best results. The use of larger amounts of Lewis acid resulted in no enhancement of the yield. The moderate to low yields of complexes were, in general, increased on addition of Lewis acids to the reaction mixture. In particular the addition of Lewis acids substantially reduced and sometimes eliminated the formation of lactol and carbonyl by-products produced by carbon carbon double bond migration reactions. It should also be noted that the yields from the *cis* diols were usually greater than from the *trans* diols. The use of alternative leaving groups such as halide, acetate,

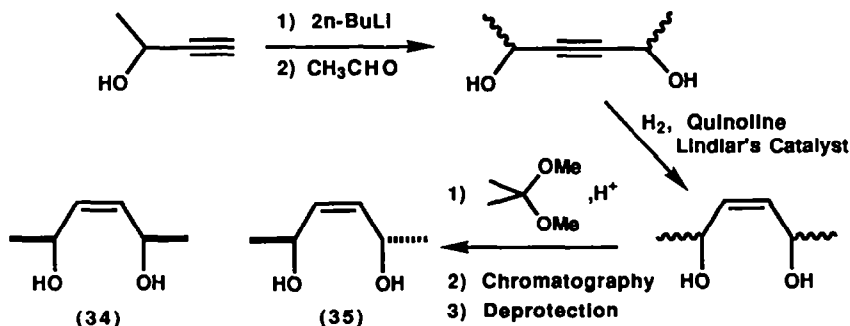
tosylate *etc.* was investigated briefly but all were found to be inferior to the free hydroxyl group.

The steric bulk of the substituents ($t\text{-Bu} > \text{Ph} > n\text{-C}_5\text{H}_{11} > \text{Me}$) also noticeably influenced the reactions. For example, when substituted by the large *t*-butyl group, as in the diol (14), the *trans* iron complex (27) could be isolated and characterised. Only one other example of a *trans* complex is known in the literature, also heavily substituted.³ Significantly, in the *trans* complex, the *t*-butyl group was determined by n.O.e. experiments to be in the *endo* position (figure 1). Clearly this acts to block rotation around the C2-C3 bond in the postulated η^1 -intermediate.



Further, the results suggest that without Lewis acids present the least hindered hydroxyl group leaves to give the complexes with the substituent, R, α to the oxygen as the major product. On the other hand, the yields of the other regioisomer are enhanced when Lewis acids are present. This may reflect some stabilization of developing positive charge in an intermediate species. In the cases of the phenyl substituted diols (10) and (11), where such charge stabilization should be most effective, the complex (18) with the substituent in the 4-position became the major product. It seems that, in general, steric factors are more important than charge stabilisation in determining the course of the reaction.

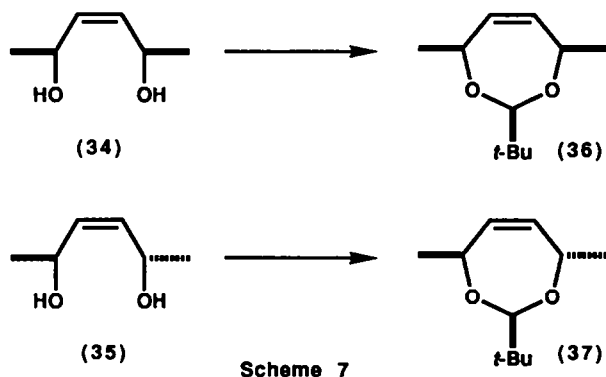
In order to probe the stereochemical consequences of complex formation in more detail we prepared two very specifically substituted diols (34) and (35). These were obtained by reaction of the dianion of butyn-2-ol with excess acetaldehyde followed by hydrogenation in the presence of Lindlar's catalyst and quinoline. Separation was achieved by selective conversion of one isomer to its acetonide with 2,2-dimethoxypropane. Separation of the remaining diol from the acetonide and hydrolysis of the latter furnished the two isomeric diols (scheme 6).



Scheme 6

Before proceeding with the preparation of iron carbonyl complexes, the diols(34) and (35) had to be

properly and fully characterised. In accord with previous studies by Cazaux¹³ they were separately reacted with pivalaldehyde to afford the cyclic acetals¹⁴ (36) and (37) (Scheme 7) which could be clearly differentiated by NMR.



As expected, each diol (34) and (35) gave a different ferrilactone complex. Treatment of the *dl*-diol (35) with $\text{Fe}_2(\text{CO})_9$ in benzene under ultrasonication or in THF gave the complex (38) in 55% and 31% yields respectively. Complex (38) was readily characterized by NMR and was in accord with all our previous studies and work by Moriarty.⁵ Similarly, the *meso*-diol (34) gave (39) in 4% and 25% yields. These complexes were additionally characterised by n.o.e. experiments the summaries of which are presented in figures 2 and 3.

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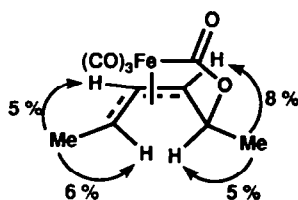


Figure 2

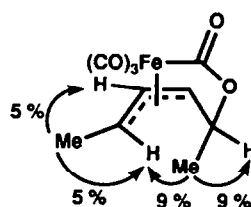
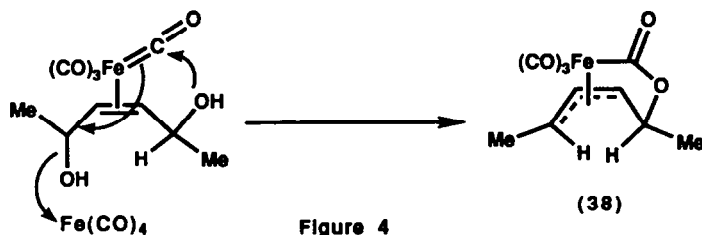


Figure 3

The results of these studies are consistent with Aumann's previously proposed mechanism for the conversion of ferrilactones to ferrilactams³ and implies that formation of the bridging lactone occurs *anti* to displacement of the Lewis acid complexed hydroxyl group. In these particular experiments presumably the coordinatively unsaturated $\text{Fe}(\text{CO})_4$ species is acting as the complexing Lewis acid (fig.4).



While the above studies are not exhaustive we believe that we have shown that butenediols may function as starting materials for π -allyl tricarbonyliron lactone complexes. Further, it has been shown that by varying the reaction conditions, most noticeably by addition of Lewis acids, changes in product ratio ensue. In some examples the use of $\text{Fe}_2(\text{CO})_9$ in THF can be dramatically different from reactions in benzene using ultrasound.

Since the π -allyltricarbonyliron lactone complexes are useful templates for further transformations, the above studies provide an additional guide to the choice of starting materials for this area of chemistry.

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Experimental:

Solutions were dried over anhydrous sodium sulphate, anhydrous potassium carbonate, or anhydrous magnesium sulphate. Diethyl ether and THF solvents were distilled from sodium-benzophenone ketyl, dichloromethane from phosphorus pentoxide, and toluene from sodium. Petrol refers to petroleum ether b.p. 40-60°C which was distilled prior to use. Other solvents and reagents were purified by standard procedures as necessary. The products were purified by flash column chromatography on Merck silica gel 60 (Art. 9385, 230-400 mesh) using petrol / diethyl ether as the solvent unless otherwise stated. Analytical thin layer chromatography was performed using pre-coated glass plates (Merck Kieselgel 60 F_{254}) and visualised by ultra-violet light, acidic ammonium molybdate (IV), aqueous potassium permanganate solution or iodine as appropriate. Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Sonication was carried out using a Semat 80W, 55KHz ultrasonic cleaning bath. Large scale sonication was carried out using a Heat Systems-Ultrasonics Processor Sonicator[®] Probe W-380. IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer as liquid films or dichloromethane solutions. Mass spectra were recorded under EI conditions unless otherwise stated, using VG-7070B, VG 12-253 and VG ZAB-E instruments. Microanalyses were performed in the Imperial College Chemistry Department microanalytical laboratory. ^1H NMR spectra were recorded in CDCl_3 or C_6D_6 using a Bruker WM 250, Jeol GSX 270 or Bruker AM-500 spectrometer. ^{13}C NMR spectra were recorded in C_6D_6 at 67.94 MHz on a Jeol GSX 270 or at 125.8 MHz on a Bruker AM-500 spectrometer. Chemical shifts are measured in p.p.m. downfield from TMS and coupling constants are measured in Hertz.

Z-(1'R)-4-(1'-methylbenzylamino)-2-butene-1-ol.(2).-A solution of Z-4-chloro-2-butenol¹⁵ (143 mg, 1.3 mmol) and (R)-(+)- α -methylbenzylamine (520 μ l, 4 mmol) in dry dichloromethane (2 ml) was stirred at room temperature for twelve hours, poured into water and extracted with dichloromethane. The combined organic layers were dried and evaporated to give an oil which was purified by flash chromatography on silica gel, eluting with 20-60% acetone/petrol to give the *amino alcohol* (2) as a pale brown solid, mp 50-52°C; δ_{H} (CDCl₃): 7.2-7.4 (5H, m, Ph), 5.82 (1H, m, CHCH₂OH), 5.75 (1H, m, CHCH₂N), 4.11 (2H, d, J=5.9 Hz, CH₂OH), 3.79 (1H, q, J=6.3 Hz, PhCHN), 3.12 (2H, d, J=5.9 Hz, CH₂N), 2.93 (2H, br. s, OH and NH), 1.39 (3H, d, J=6.3 Hz, CH₃); ν_{max} (CH₂Cl₂): 3603, 3200, 3030-2850 and 1603 cm⁻¹; m/z: 191 (M⁺), 176 (M⁺-CH₃), 173 (M⁺-H₂O), and 105 (PhCH⁺CH₃); [a]_D²⁹=+33.5° (c=0.46, CH₂Cl₂); (Found: C, 75.05; H, 9.05; N, 7.22. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%).

Preparation of 2-butene-1,4-diols:

1-Phenyl-2-butyne-1,4-diol.¹⁶ n-Butyl lithium (88 ml of a 2.5 M solution in hexanes, 220 mmol,) was added dropwise to a stirred solution of freshly distilled propargyl alcohol (5.9 ml, 100 mmol) in dry THF (100 ml) at -20°C under nitrogen. The mixture was stirred at -20°C for 10 minutes then cooled to -78°C and freshly distilled benzaldehyde (10.2 ml, 100 mmol) was added dropwise keeping the temperature below -70°C. The mixture was stirred at -78°C for 45 minutes then allowed to warm to 0°C over 30 minutes where it was stirred for 2 hours, quenched with saturated ammonium chloride solution and purified by silica gel chromatography and recrystallisation (ether/petrol) to give 1-phenyl-2-butyne-1,4-diol (12.9 g, 80%) as an off-white solid, m.p. 83-85°C (lit.¹⁶ 83-85°C); ν_{max} (CH₂Cl₂) 3590, 3048, 2872, 2300, 1491, 1450, 1377, 1257, 1192, 1123, 1076, 1019, 919, 692, and 637 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 1.99 (1H, br. s, -OH), 4.33 (2H, br. s, 4-H), 5.50 (1H, br. s, 1-H), 7.26-7.42 and 7.48-7.56 (5H, 2x m, Ph)

1-Phenyl-E-2-butene-1,4-diol (10).- Red-A1® (2.65 ml of a 3.4M solution in toluene, 9 mmol) was added dropwise to a stirred solution of 1-phenyl-2-butyne-1,4-diol (810 mg, 5 mmol) in dry THF (50 ml) at room temperature under argon. The mixture was stirred at room temperature for 30 minutes then quenched with water resulting in a purple coloured solution and gum formation. This mixture was then stirred with NaHCO₃ for 30 minutes and filtered with the filter residues being exhaustively washed with ethyl acetate. The product was then purified by silica gel chromatography to give the *E-olefin* (10) (764 mg, 93%) as a white solid, m.p. 83-84°C; ν_{max} (CH₂Cl₂) 3595, 3048, 2980, 2871, 1491, 1450, 1419, 1380, 1255, 1188, 1086, 974, 764, and 691 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 1.53 (1H, br. s, OH), 2.08 (1H, br. s, OH), 4.17 (2H, d, J_{4,3}=2.2Hz, 4-H), 5.24 (1H, t, J_{1,2}=J_{1,3}=2.3Hz, 1-H), 5.93 (2H, sept., 2-H, 3-H), and 7.27-7.39 (5H, m, Ar-H); m/z 164 (M⁺), 133 (M⁺-CH₂OH⁺), 105 (PhCHO⁺), 77 (Ph⁺), and 55 (C₃H₃O⁺); (Found: C, 72.87; H, 7.10. C₁₀H₁₂O₂ requires C, 73.14; H, 7.37%).

1-Phenyl-Z-2-butene-1,4-diol (11).¹⁶ A solution of 1-phenyl-2-butyne-1,4-diol (744 mg, 4.59 mmol) in dry THF (7 ml) was cooled to -78°C under argon and Lindlar's catalyst (93 mg) was added. The flask was then flushed with hydrogen, the solution warmed to -20°C and stirred under a hydrogen atmosphere for 3 hours. Filtration and purification by silica gel chromatography gave the Z-olefin (11) (750 mg, quantitative) as a yellow solid, m.p. 72-74°C (lit.¹⁶ 73-75°C); ν_{max} (CH₂Cl₂) 3246, 2927, 2857, and 1457 cm⁻¹; δ_{H} (250 MHz, CDCl₃) 2.16 (1H, br. s, OH), 2.66 (1H, br. s, OH), 4.21 (1H, br. d, J=13 Hz, 4-H), 4.41 (1H, br. d, J=13 Hz, 4-H), 5.54 (1H, br. d, J=5 Hz, 1-H), 5.73-5.80 (2H, m, 2-H, 3-H), and 7.24-7.40 (5H, m, Ph).

2-Nonyne-1,4-diol.- n-Butyl lithium (88 ml of a 2.5M solution in hexanes, 220 mmol) was added dropwise to a solution of freshly distilled propargyl alcohol (5.8 ml, 100 mmol) in dry THF (100 ml) at -22°C under nitrogen. This solution was stirred at -20°C for 10 minutes then cooled to -78°C. Freshly distilled n-hexanal (12.1 ml, 100 mmol) was added dropwise to the mixture, keeping the temperature below -60°C, and

the resulting mixture stirred at -70°C for 1 hour, warmed to 0°C over 30 minutes and stirred for another 1.5 hours. The reaction was quenched with ammonium chloride solution and the product purified by silica gel chromatography to give *2-nonyne-1,4-diol* (8.23 g, 53%) as a clear oil, ν_{max} (CH_2Cl_2) 3597, 3048, 2930, 2861, 2155, 1463, 1379, 1255, 1139, 1102, 1015, 910, 756 and 708 cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.89 (3H, t, $J_{8,9} = 6.8\text{ Hz}$, CH_3), 1.26-1.49 (6H, m, $\text{HOCHCH}_2(\text{CH}_2)_3$), 1.65-1.75 (2H, m, 5-H), 2.08 (1H, t, $J = 4.5\text{ Hz}$, 1-OH), 2.21 (1H, d, $J = 5.4\text{ Hz}$, 4-OH), 4.30 (2H, d, $J = 4.5\text{ Hz}$, 1-H), and 4.36-4.40 (1H, m, 4-H); m/z 155 ($\text{M}^+\text{-H}$), 138 ($\text{M}^+\text{-H}_2\text{O}$), 137 ($\text{M}^+\text{-H}_3\text{O}$), and 85; m/z (A.C.E. NH_3) 174 ($\text{M}^+\text{+NH}_4$), 125 ($\text{M}^+\text{-CH}_2\text{OH}$), 109 ($\text{M}^+\text{-C}_2\text{H}_2\text{OH}$), 85 ($\text{M}^+\text{-C}_5\text{H}_{11}$), 71 ($\text{C}_5\text{H}_{11}^+$), and 57 (C_4H_9^+); (A.C.E. NH_3 observed $\text{M}^+\text{+NH}_4$, 174.1494. $\text{C}_9\text{H}_{20}\text{NO}_2$ requires M, 174.1494); (Found: C, 72.87; H, 7.10. $\text{C}_{10}\text{H}_{12}\text{O}_2$ requires C, 73.14; H, 7.37%).

E-2-Nonene-1,4-diol (12).- Red-Al® (5.3 ml of a 3.4M solution in toluene, 18 mmol) was added dropwise to a stirred solution of 2-nonyne-1,4-diol (1.56 g, 10 mmol) in dry THF (50ml) at room temperature under argon. The mixture was stirred at room temperature for 1 hour then quenched with water resulting in the formation of a small amount of a white gum. This mixture was then stirred with NaHCO_3 for 30 minutes and filtered with the filter residues being exhaustively washed with ethyl acetate. The 2-methoxyethanol was removed under vacuum overnight. The product was then purified by silica gel chromatography to give the *E-olefin* (12) (1.51 g, 96%) as a clear, viscous oil which solidified to a white solid on standing in the refrigerator overnight, m.p. $42\text{-}43^{\circ}\text{C}$; ν_{max} (CH_2Cl_2) 3599, 3373, 2956, 2930, 2859, 1463, 1379, 1260, 1122, 1084, 1009, 974, 911, 828, and 696 cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.89 (3H, t, $J_{8,9} = 6.8\text{ Hz}$, CH_3), 1.23-1.64 (10H, m, $\text{HOCH}(\text{CH}_2)_4$, 2x OH), 4.10-4.21 (3H, m, 1-H, 4-H), and 5.69-5.89 (2H, m, 2-H, 3-H); m/z 157 ($\text{M}^+\text{-H}$), 140 ($\text{M}^+\text{-H}_2\text{O}$), 127 ($\text{M}^+\text{-CH}_2\text{OH}$), 99 ($\text{C}_5\text{H}_{11}\text{CO}^+$), 87 ($\text{M}^+\text{-C}_5\text{H}_{11}$), 71 ($\text{C}_5\text{H}_{11}^+$), and 31 (CH_2OH^+);

Z-2-Nonene-1,4-diol (13).- A solution of 2-nonyne-1,4-diol (3.12 g, 20 mmol) and dry THF (40 ml) was cooled to -78°C under argon and Lindlar's catalyst (585 mg) was added. The flask was then flushed with hydrogen, the solution warmed to -27°C and stirred under a hydrogen atmosphere for 23 hours. Filtration and purification by silica gel chromatography gave the *Z-olefin* (13) (1.96 g, 62%) as a viscous oil; ν_{max} (film) 3325, 3010, 2929, 2858, 1465, 1312, and 1019 cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.92 (3H, t, $J = 7\text{ Hz}$, CH_3), 1.23-1.80 (8H, br. m, $\text{HOCH}(\text{CH}_2)_4$), 2.26 (2H, br s, 2x OH), 4.13 (1H, ddd, $J_{1,3} = 1.2\text{ Hz}$, $J_{1,2} = 5.9\text{ Hz}$, $J_{1,1} = 12.9\text{ Hz}$, 1-H), 4.31 (1H, ddd, $J_{1,3} = 1.2\text{ Hz}$, $J_{1,2} = 7.3\text{ Hz}$, $J_{1,1} = 12.9\text{ Hz}$, 1-H), 4.38-4.46 (1H, m, 4-H), 5.55 (1H, dddd, $J_{3,1} = 1.2\text{ Hz}$, $J_{3,4} = 8.1\text{ Hz}$, $J_{3,2} = 11.3\text{ Hz}$, 3-H), and 5.72 (1H, dddd, $J_{2,4} = 1.0\text{ Hz}$, $J_{2,1} = 5.9\text{ Hz}$, $J_{2,1} = 7.3\text{ Hz}$, $J_{2,3} = 11.3\text{ Hz}$, 2-H); m/z 140 ($\text{M}^+\text{-H}_2\text{O}$), 127 ($\text{M}^+\text{-CH}_2\text{OH}$), 87 ($\text{M}^+\text{-C}_5\text{H}_{11}$), and 69 ($\text{M}^+\text{-H}_2\text{O-C}_5\text{H}_{11}$); (Found: C, 68.10; H, 11.29. $\text{C}_9\text{H}_{18}\text{O}_2$ requires C, 68.31; H, 11.46%).

5,5-Dimethyl-2-hexyne-1,4-diol.- *n*-Butyl lithium (26 ml of a 2.5M solution in hexanes, 66 mmol) was added dropwise to a stirred solution of freshly distilled propargyl alcohol (1.74 ml, 30 mmol) in dry THF (50 ml) at -20°C under nitrogen. The mixture was stirred at -20°C for 10 minutes then cooled to -78°C and trimethylacetaldehyde (3.36 ml., 30 mmol) was added dropwise keeping the temperature below -60°C . The mixture was stirred at -78°C for 45 minutes then allowed to warm to 0°C over 30 minutes where it was stirred for 2 hours, quenched with ammonium chloride solution and purified by silica gel chromatography to give *5,5-dimethyl-2-hexyne-1,4-diol* (2.35g, 55%) as an off-white solid, m.p. $52\text{-}54^{\circ}\text{C}$; ν_{max} (CH_2Cl_2) 3599, 3047, 2964, 2870, 2155, 1478, 1364, 1258, 1126, 1041, 1007, 893, and 732 cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.99 (9H, s, 3x CH_3), 2.29 (2H, br. s, 2x OH), 4.06 (1H, br. s, 4-H), and 4.31 (2H, br. s, 1-H); m/z 109 ($\text{M}^+\text{-H}_2\text{O-CH}_3$), 68 ($\text{M}^+\text{-(CH}_3)_3\text{C-CHO}$), and 57 ($(\text{CH}_3)_3\text{C}^+$); (Found: C, 67.37; H, 10.18. $\text{C}_8\text{H}_{14}\text{O}_2$ requires C, 67.57; H, 9.92%).

5,5-Dimethyl-*E*-2-hexene-1,4-diol (14).- Red-Al® (1.6 ml of a 3.4M solution in toluene, 5.4 mmol) was added dropwise to a stirred solution of 5,5-dimethyl-2-hexyne-1,4-diol (426 mg, 3 mmol) in dry THF (30 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 4 hours then quenched with water resulting in a small amount of gum formation. This mixture was then stirred with NaHCO₃ for 30 minutes and filtered with the filter residues being exhaustively washed with ethyl acetate. The product was then purified by silica gel chromatography to give the *E*-olefin (14) (310 mg, 72%) as a white solid, m.p. 33-34°C; ν_{\max} (CH₂Cl₂) 3602, 3440, 3051, 2960, 2869, 1477, 1398, 1382, 1363, 1258, 1088, 1037, 995, 976, and 697 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.87 (9H, s, 3x CH₃), 2.69 (1H, br. s, OH), 3.19 (1H, br. s, OH), 3.72 (1H, d, J = 5.4 Hz, 4-H), 4.09 (2H, d, J = 3.4 Hz, 1-H), and 5.68-5.77 (2H, m, 2-H & 3-H); m/z 126 (M⁺-H₂O), 113 (M⁺-CH₂OH), 87 ((CH₃)₃CCH₂O⁺), 70 (M⁺-(CH₃)₃C-CHO) and 57 (C₃H₅O⁺); (Found: C, 66.77; H, 11.08. C₈H₁₆O₂ requires C, 66.62; H, 11.18%).

5,5-Dimethyl-*Z*-2-hexene-1,4-diol (15).- A solution of 5,5-dimethyl-2-hexyne-1,4-diol (426 mg, 3 mmol) in dry THF (5 ml) was cooled to -78°C under argon and Lindlar's catalyst (53 mg) was added. The flask was then flushed with hydrogen, the solution warmed to -20°C and stirred under a hydrogen atmosphere for 14 hours. Filtration and purification by silica gel chromatography gave the *Z*-olefin (15) (296mg, 69%) as a white solid, m.p. 53-54°C; ν_{\max} (CH₂Cl₂) 3602, 3437, 3050, 3030, 2959, 2871, 1477, 1363, 1256, 1050, 1030, 1000, 935, and 742 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.90 (9H, s, 3x CH₃), 2.21 and 2.27 (2H, 2x br. s, 2x OH), 4.07 (1H, d, J_{4,3} = 8.8 Hz, 4-H), 4.10 (1H, br. dd, J_{1,2} = 5.6 Hz, J_{1,1} = 12.8 Hz, 1-H), 4.33 (1H, br. dd, J_{1,2} = 7.6 Hz, J_{1,1} = 12.8 Hz, 1-H), 5.62 (1H, ddt, J_{3,1} = 1.3 Hz, J_{3,4} = 8.8 Hz, J_{3,2} = 11.5 Hz, 3-H), and 5.78 (1H, dddd, J_{2,4} = 1.0 Hz, J_{2,1} = 5.6 Hz, J_{2,1} = 7.6 Hz, J_{2,3} = 11.5 Hz, 2-H); m/z 143 (M⁺-H), 113 (M⁺-CH₂OH), 87 ((CH₃)₃CCH₂O⁺), 70 (M⁺-(CH₃)₃C-CHO), and 57 (C₃H₅O⁺); (Found: C, 66.76; H, 11.41. C₈H₁₆O₂ requires C, 66.62; H, 11.18%).

Tetrahydro-2-(2-propynyloxy)-2H-pyran.¹⁷ Propargyl alcohol (5.8 ml, 100 mmol) was added dropwise to a stirred solution of 3,4-dihydro-2H-pyran (10.95 ml, 120 mmol) and *p*-toluene-sulphonic acid monohydrate (5 mg) under argon, keeping the temperature below 60°C. The mixture was allowed to stir for 30 minutes, basified with 5% aqueous potassium hydroxide (3 ml), and the product purified by Kugelrohr distillation (oven temperature 140-150°C) to give tetrahydro-2-(2-propynyloxy)-2H-pyran (13.6 g, 97%) as a clear oil; δ_{H} (270 MHz, CDCl₃) 1.49-1.87 (6H, m, (CH₂)₃), 2.40 (1H, t, J = 2.4 Hz, HC), 3.49-3.57 (1H, m, HCO), 3.79-3.87 (1H, m, CHO), 4.24 (1H, dd, J = 2.4, 15.6 Hz, one of CCH₂O), 4.27 (1H, dd, J = 2.4, 15.6 Hz, one of CCH₂O), and 4.81 (1H, t, J = 3.1 Hz, OCHO).

5-[(Tetrahydro-2H-pyran-2-yl)oxy]-3-pentyn-2-ol.¹⁸ n-Butyl lithium (21 ml of a 1.6M solution in hexanes, 33 mmol) was added dropwise to a stirred solution of tetrahydro-2-(2-propynyloxy)-2H-pyran (4.2 g, 30 mmol) in dry THF (100 ml) at -30°C under argon. The mixture was stirred at -30°C for 15 minutes then cooled to -70°C and acetaldehyde (9.5 ml of a 3.49M solution in THF, 33 mmol) was added dropwise keeping the temperature below -65°C. The mixture was stirred at -70°C for 30 minutes then allowed to warm to -45°C where it was stirred for 30 minutes, quenched with saturated aqueous ammonium chloride solution and purified by Kugelrohr distillation (oven temperature 120-150°C / 0.04 mm Hg) to give 5-[(tetrahydro-2H-pyran-2-yl)oxy]-3-pentyn-2-ol (5.28 g, 95%) as a clear, viscous oil; δ_{H} (500 MHz, CDCl₃) 1.45 (3H, d, J_{1,2} = 6.6 Hz, CH₃), 1.51-1.65 (4H, m, (CH₂)₂), 1.70-1.86 (2H, m, CH₂), 2.12 (1H, br. s, OH), 3.51-3.55 (1H, m, OCH_{eq}), 3.83 (1H, ddd, J = 3.0, 9.25, 11.7 Hz, OCH_{ax}), 4.24 (0.5H, dd, J_{5,2} = 1.5 Hz, J_{5,5} = 15.6 Hz, 5-H), 4.24 (0.5H, dd, J_{5,2} = 1.8 Hz, J_{5,5} = 15.6 Hz, 5-H), 4.31 (1H, dd, J_{5,2} = 1.8 Hz, J_{5,5} = 15.6 Hz, 5-H), 4.56 (1H, q, J_{2,1} = 6.6 Hz, 2-H), and 4.80 (1H, t, J = 3.4 Hz, OCHO).

2-Pentyne-1,4-diol.^{18,19} A solution of 5-[(tetrahydro-2H-pyran-2-yl)oxy]-3-pentyn-2-ol (4.61 g, 25 mmol) and *p*-toluene-sulphonic acid monohydrate (40 mg) in methanol (25 ml) was stirred at room temperature for 1.5 hours, basified to pH 8 by careful addition of a few drops of 10% aqueous potassium hydroxide, concentrated *in vacuo*, and the potassium *p*-toluene sulphonate precipitated out by the addition of ether (10 ml) and filtered off. The product was purified by silica gel chromatography to give 2-pentyne-1,4-diol (2.19 g, 88%) as a clear viscous oil; δ_{H} (500 MHz, CDCl_3) 1.45 (3H, d, $J_{5,4}$ = 6.7 Hz, 5-H), 2.70 (1H, br. s, 4-OH), 2.84 (1H, br. d, J = 3.5 Hz, 1-OH), 4.29 (2H, d, J = 3.5 Hz, 1-H), and 4.56-4.58 (1H, m, 4-H).

***E*-2-Pentene-1,4-diol (16).**²⁰ Red-Al® (4.0 ml of a 3.4M solution in toluene, 13.5 mmol) was added dropwise to a stirred solution of 2-pentyne-1,4-diol (751 mg, 7.5 mmol) in dry THF (50 ml) at room temperature under argon. The mixture was stirred at room temperature for 30 minutes then quenched with water resulting in a small amount of gum formation. This mixture was then stirred with NaHCO_3 for 30 minutes and filtered with the filter residues being exhaustively washed with ethyl acetate. The product was then purified by pumping overnight under vacuum, to remove the methoxyethanol, then by Kugelrohr distillation (oven temperature 110-130°C / 0.06 mm Hg) to give the *E*-olefin (16) (737 mg, 96%) as a viscous oil; δ_{H} (500 MHz, CDCl_3) 1.28 (3H, d, $J_{5,4}$ = 6.4 Hz, CH_3), 1.72 (2H, br. s, 1-H), 4.34 (1H, pent, $J_{4,5} \sim J_{4,3} \sim 6.3$ Hz, 4-H), 5.78 (1H, ddd, $J_{3,1}$ = 1.1 Hz, $J_{3,4}$ = 5.5 Hz, $J_{3,2}$ = 15.5 Hz, 3-H), and 5.83 (1H, dt, $J_{2,1}$ = 4.7 Hz, $J_{2,3}$ = 15.5 Hz, 2-H).

***Z*-2-Pentene-1,4-diol (17).**²¹ A solution of 2-pentyne-1,4-diol (751 mg, 7.5 mmol) and dry THF (20 ml) was cooled to -70°C under argon and Lindlar's catalyst (100 mg) was added. The flask was then flushed with hydrogen, the solution warmed to -40°C and stirred under a hydrogen atmosphere for 14 hours. Filtration and purification by silica gel chromatography (ethyl acetate) gave the *Z*-olefin (17) (681 mg, 89%) as a clear oil contaminated with 8% of the fully saturated diol [CH_3 at δ_{H} (250 MHz, CDCl_3) 1.19 (d)]; δ_{H} (250 MHz, CDCl_3) 1.25 (3H, d, $J_{5,4}$ = Hz, 5-H), 3.23 (2H, br. s, 2x OH), 4.08 (1H, dd, $J_{1,2}$ = 5.0 Hz, $J_{1,1}$ = 12.9 Hz, 1-H), 4.29 (1H, dd, $J_{1,2}$ = 6.5 Hz, $J_{1,1}$ = 12.9 Hz, 1-H), 4.63 (1H, pent, J = 6.5 Hz, 4-H), and 5.52-5.79 (2H, m, 2-H & 3-H).

3-Hexyn-2,5-diol. A solution of 1-butyne-3-ol (601 mg, 8.6 mmol) in THF (50 ml) under argon was cooled to -78°C and treated dropwise with *n*-butyl lithium (9.6 ml of a 2.5 M solution in hexanes, 24 mmol). The mixture was stirred at -78°C for fifteen minutes and at -20 to -30°C for one hour. The mixture was recooled to -78°C and treated with acetaldehyde (0.7 ml, 12.9 mmol) and allowed to warm to room temperature. Saturated aqueous ammonium chloride solution was added and the mixture was extracted with ether. The combined organic layers were dried, evaporated and purified by flash chromatography to give the diol (691 mg, 71%) as an oil, δ_{H} (270 MHz, CDCl_3) 4.55 (2H, q, J = 8 Hz, CHOH), 3.26 (2H, br. s, OH), and 1.43 (6H, 2x d, J = 8 Hz, $\text{CH}(\text{OH})\text{CH}_3$); ν_{max} (film) 3326 and 2930-3000 cm^{-1} ; m/z 114 (M^+), 99 ($\text{M}^+ - \text{Me}$), 96 ($\text{M}^+ - \text{H}_2\text{O}$), and 43 (CH_3CO^+).

***Z*-3-Hexen-2,5-diol.** A slurry of Lindlar's catalyst (60 mg) in dry THF (20 ml) containing 3-hexyn-2,5-diol (516 mg, 4.53 mmol) and quinoline (0.8 ml) was vigorously stirred under an atmosphere of hydrogen gas for three hours at room temperature. The flask was then flushed with argon and the contents were filtered through celite, evaporated and purified by flash chromatography on silica gel (15 g) eluting with 50% and 100% ether/petrol to give the diols as a 1:1 mixture: ν_{max} (film) 3345, 3000-2920, and 1095 cm^{-1} ; m/z 101 (M^+), 98 ($\text{M}^+ - \text{H}_2\text{O}$), 83 ($\text{M}^+ - \text{Me} - \text{H}_2\text{O}$), and 43 (CH_3CO^+); (Found: C, 61.74; H, 10.50. $\text{C}_6\text{H}_{12}\text{O}_2$ requires C, 62.04, H, 10.41%). The diols were taken up in dichloromethane (20 ml), cooled to 0°C and treated with camphor sulphonic acid (1 mg) and 2,2-dimethoxypropane (350 μl , 2.9 mmol). After four hours, the mixture was basified with anhydrous potassium carbonate, filtered and concentrated. The residue was purified by flash chromatography to give the volatile acetonide and the *meso*-diol (194 mg, 37%), δ_{H} (270 MHz, CDCl_3) 5.5

(2H, dd, $J_{3,2}=5$ Hz, $J_{3,5}=2$ Hz, 2x C=CH), 4.68 (2H, m, 2x CHOH), 2.5 (2H, br. s, 2x OH), and 1.28 (6H, d, $J=4$ Hz, 2x CH₃). The acetonide fractions were carefully concentrated, taken up in THF and treated with aqueous hydrochloric acid (0.5 ml of a 3 M solution). After one hour, anhydrous potassium carbonate was added, the mixture was filtered and the solvent was evaporated to give the *dl*-diol as a white solid, m.p. 92-94°C; $\delta_{\text{H}}(\text{CDCl}_3)$ 5.47 (2H, dd, $J_{3,2}=5$ Hz, $J_{3,5}=2$ Hz, 2x C=CH), 4.68 (2H, m, 2x CHOH), 2.05 (2H, br. s, 2x OH), and 1.29 (6H, d, $J=4$ Hz, 2x CH₃)

General Procedures for Iron Lactone Complex Formation. Method A.- The butenediol (1 mol. equiv.) was added as a solution in dry THF (10 ml/mmol) to diiron nonacarbonyl (2 mol. equiv.) under argon and the mixture stirred until no butenediol could be detected by t.l.c. (50 minutes-6 hours). The flask was then opened, toluene (approx. 2 ml/mmol) added, and the solution filtered through a pad of talc. The residues were washed with ether, the filtrate was concentrated *in vacuo* to the toluene phase and loaded onto a silica gel column. The majority of the organometallic impurities were eluted from the column using 10% ether in petrol and the ferrilactone and other products eluted with a more polar ether/petrol mixture. The filtration and evaporation during the work-up should be carried out in an efficient hood to avoid any contact with toxic organoiron by-products especially the volatile iron pentacarbonyl.

Method B.- The butenediol (1 mol. equiv.) was added as a solution in dry THF (10 ml/mmol) to diiron nonacarbonyl (2 mol. equiv.) and zinc chloride.TMEDA (1 mole equiv.) under argon and the solution stirred until no butenediol could be detected by t.l.c. The reaction was worked up and purified in identical fashion to Method A.

Method C.- The butenediol (1 mol. equiv.) was added as a solution in dry THF (10 ml/mmol) to diiron nonacarbonyl (2 mol. equiv.) under argon followed rapidly by ZnBr₂ (1M solution in THF, 1 mol. equiv.) and the solution was stirred until no butenediol could be detected by t.l.c. The reaction was worked up and purified in identical fashion to Method A.

Method D.- Diiron nonacarbonyl (2.2 mol. equiv.) was added from a side-arm addition tube to a stirred solution of the butenediol (1 mol. equiv.) in dry benzene (20 ml/mmol) under argon and the mixture was sonicated until no further butenediol could be detected by t.l.c. The reaction was worked up and purified in identical fashion to Method A.

Method E.- Diiron nonacarbonyl (2.2 mol. equiv.) was added from a side-arm addition tube to a stirred solution of the butenediol (1 mol. equiv.) and zinc chloride.TMEDA (1 mole equiv.) in dry benzene (20 ml/mmol) under argon and the mixture was sonicated until no further butenediol could be detected by t.l.c. The reaction was worked up and purified in identical fashion to Method A.

Method F.- Diiron nonacarbonyl (2.2 mol. equiv.) was added from a side-arm addition tube to a stirred solution of the butenediol (1 mol. equiv.), ZnBr₂ (1M solution in THF, 1 mol. equiv.) and dry benzene (20 ml/mmol) under argon and the mixture was sonicated until no further butenediol could be detected by t.l.c. The reaction was worked up and purified in identical fashion to Method A.

Reaction of Z-2-butene-1,4-diol with diiron nonacarbonyl. Method A.-Reaction of Z-2-butene-1,4-diol (49 mg, 0.56 mmol) with diiron nonacarbonyl (246 mg, 0.73 mmol) in THF (6 ml) for three hours gave 2-4- η^3 -(1-formyloxybut-3-en-2-ylato)tricarbonyliron (1)^{6,9} (97 mg, 73%) as a white solid, $\delta(\text{C}_6\text{D}_6)$ 3.78 (1H, dt, $J_{3,2}=J_{3,4\text{exo}}=8$ Hz, $J_{3,4\text{endo}}=13$ Hz, 3-H), 3.63 (1H, ddd, $J_{2,3}=8$ Hz, $J_{2,1\text{exo}}=5$ Hz, $J_{2,1\text{endo}}=2$ Hz, 2-H), 3.38 (1H, dd, $J_{1,1}=12$ Hz, $J_{1,2}=2$ Hz, 1-H_{endo}), 3.28 (1H, dd, $J_{1,1}=12$ Hz, $J_{1,2}=5$ Hz, 1-H_{exo}), 2.69 (1H, dd, $J_{4,3}=8$ Hz, $J_{4,4}=1.5$ Hz, 4-H_{exo}), and 2.55 (1H, dd, $J_{4,3}=13$ Hz, $J_{4,4}=1.5$ Hz, 4-H_{endo}).

Reaction of *Z*-2-butene-1,4-diol with diiron nonacarbonyl. Method D.-Reaction of *Z*-2-butene-1,4-diol (36 mg, 0.41 mmol) with diiron nonacarbonyl (224 mg, 0.62 mmol) in benzene (6 ml) for three hours gave the complex (1) (53 mg, 55%).

Reaction of *E*-2-butene-1,4-diol with diiron nonacarbonyl. Method A.-Reaction of *E*-2-butene-1,4-diol (73 mg, 0.83 mmol) with diiron nonacarbonyl (454 mg, 1.25 mmol) in THF (6 ml) for three hours gave the complex (1) (66 mg, 33%).

Reaction of *E*-2-butene-1,4-diol with diiron nonacarbonyl. Method D.-Reaction of *E*-2-butene-1,4-diol (57 mg, 0.64 mmol) with diiron nonacarbonyl (352 mg, 0.97 mmol) in benzene (6 ml) for 1.5 hours gave the complex (1) (17 mg, 11%).

Reaction of *Z*-(1'*R*)-4-(1'-methylbenzylamino)but-2-en-1-ol (2) with diiron nonacarbonyl.-Reaction of the aminoalcohol (2) (49 mg, 0.26 mmol) with diiron nonacarbonyl (186 mg, 0.5 mmol) in benzene (3 ml) according to method D and purification by flash chromatography on silica gel (5 g) eluting with 10-100% ether/petrol gave 2-4- η^3 -(1-[formyl-(1'*R*)-methylbenzylamino]but-3-en-2-ylato)tricarbonyliron (4) (18 mg, 21%) as an oil, $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 7.1 (5H, m, Ph), 5.63 (1H, q, $J=7$ Hz, NCHMe), 3.94 (1H, ddd, $J_{3,4\text{endo}}=13$ Hz, $J_{3,4\text{exo}}=8$ Hz, $J_{3,2}=7$ Hz, 3-H), 3.56 (1H, dt, $J_{2,1\text{endo}}=1$ Hz, $J_{2,3}=J_{2,1\text{exo}}=7$ Hz, 2-H), 3.01 (1H, d, $J_{4,3}=8$ Hz, 4- H_{exo}), 2.85 (1H, dd, $J_{1,1}=12$ Hz, $J_{1,2}=7$ Hz, 1- H_{exo}), 2.54 (1H, d, $J_{4,3}=13$ Hz, 4- H_{endo}), 2.46 (1H, dd, $J_{1,1}=12$ Hz, $J_{1,2}=1$ Hz, 1- H_{endo}), and 1.1 (3H, d, $J=7$ Hz, CH_3); $\nu_{\text{max}}(\text{CHCl}_3)$ 2950-3050, 1993, 2067, 1579, and 1491 cm^{-1} ; m/z 341 (M^+), 313 (M^+-CO), 285 (M^+-2CO), 257 (M^+-3CO), 201 ($\text{M}^+-\text{Fe}(\text{CO})_3$), 173 ($\text{M}^+-\text{Fe}(\text{CO})_4$), and 105 (PhCH^+CH_3), and its diastereoisomer (3) (38 mg, 42%) as needles, m.p. 92-93°C, $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 7.2 (5H, m, Ph), 5.7 (1H, q, $J=6$ Hz, NCHMe), 3.99 (1H, dt, $J_{3,4\text{endo}}=13$ Hz, $J_{3,4\text{exo}}=J_{3,2}=8$ Hz, 3-H), 3.48 (1H, m, 2-H), 3.0 (1H, dd, $J_{4,3}=8$ Hz, $J_{4,4}=2.5$ Hz, 4- H_{exo}), 2.55 (3H, m, 4- H_{endo} , 1- H_{exo} and 1- H_{endo}), and 0.95 (3H, d, $J=6$ Hz, CH_3); ν_{max} 3000-2850, 2072, 1988, and 1579 cm^{-1} ; m/z 341 (M^+), 313 (M^+-CO), 285 (M^+-2CO), 257 (M^+-3CO), 201 ($\text{M}^+-\text{Fe}(\text{CO})_3$), 173 ($\text{M}^+-\text{Fe}(\text{CO})_4$), and 105 (PhCH^+CH_3); and the complex (1) (14 mg, 23%).

Reaction of 2-hydroxymethylprop-2-en-1-ol (7) with diiron nonacarbonyl. Method A.-Reaction of the diol²² (7) (59 mg, 0.67 mmol) with diiron nonacarbonyl (559 mg, 1.54 mmol) in THF according to method A and purification by flash chromatography eluting with 0-100% ether/petrol gave trimethylenemethane-irontricarbonyl^{11,12} (9) (82 mg, 63%) followed by the complex (8)^{6,8} (19 mg, 12%) as a yellow solid, $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 3.36 (2H, s, CH_2O), 2.97 (2H, d, $J=0.7$ Hz, H_{exo}), 1.63 (2H, d, $J=0.7$ Hz, H_{endo}); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 3050-2900, 2086, 2019, and 1663 cm^{-1} ; m/z 238 (M^+), 210 (M^+-CO), 194 (M^+-CO_2), 182 (M^+-2CO), 166 ($\text{M}^+-\text{CO}-\text{CO}_2$), 154 (M^+-3CO), 138 ($\text{M}^+-2\text{CO}-\text{CO}_2$), 126 (M^+-4CO), and 110 ($\text{M}^+-3\text{CO}-\text{CO}_2$).

Reaction of 2-hydroxymethylprop-2-en-1-ol (7) with diiron nonacarbonyl. Method B.-Reaction of the diol (7) (58 mg, 0.66 mmol) with diiron nonacarbonyl (360 mg, 0.99 mmol) and zinc chloride.TMEDA (166 mg, 0.66 mmol) in THF (3.5 ml) gave the complex (8) (62 mg, 40%).

Reaction of 2-hydroxymethylprop-2-en-1-ol (7) with diiron nonacarbonyl. Method D.-Reaction of the diol (7) (100 mg, 1.1 mmol) with diiron nonacarbonyl (618 mg, 1.7 mmol) in benzene (8 ml) gave trimethylenemethaneirontricarbonyl (9) (11 mg, 5%) and the complex (8) (151 mg, 58%).

Reaction of 1-phenyl-*E*-2-butene-1,4-diol (10) with diiron nonacarbonyl. Method A.-Reaction of 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) for 3 hours gave a mixture of 4-*exo*-2-4- η^3 -(1-formyloxy-4-phenylbut-3-en-2-ylato)tricarbonyliron

(18)²³ (25 mg, 16%) as a yellow solid, m.p. 120°C (decomp.); ν_{\max} (CH₂Cl₂) 3063, 2082, 2029, 1668, 1599, 1491, 1450, 1377, 1280, 1156, 1061, 1028, 983, 756, 703, 675, 653, and 611 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 3.45 (1H, dd, $J_{1,1}=12.0$ Hz, $J_{1\text{exo},2}=5.1$ Hz, 1-H_{exo}), 3.57 (1H, dd, $J_{1,1}=12.0$ Hz, $J_{1\text{endo},2}=1.7$ Hz, 1-H_{endo}), 3.72 (1H, ddd, $J_{2,3}=7.5$ Hz, $J_{2,1\text{exo}}=5.1$ Hz, $J_{2,1\text{endo}}=1.7$ Hz, 2-H), 4.67 (1H, d, $J_{4,3}=12.5$ Hz, 4-H), 4.78 (1H, dd, $J_{3,4}=12.5$ Hz, $J_{3,2}=7.5$ Hz, 3-H), and 6.89-7.03 (5H, m, Ph); m/z 314 (M⁺), 286 (M⁺-CO), 258 (M⁺-2CO), 230 (M⁺-3CO), 202 (M⁺-4CO), 174 (M⁺-Fe(CO)₃), and 146 (M⁺-Fe(CO)₄); (Found: C, 53.50; H, 3.21. C₁₄H₁₀FeO₅ requires C, 53.54; H, 3.21%), tetrahydro-5-phenyl-2-furanol (20)²⁴ (25 mg, 30%), m.p. 50°C; ν_{\max} (CH₂Cl₂) 3590, 3417, 3025, 2947, 1492, 1453, 1349, 1227, 1212, 1186, 1046, 972, and 930 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 1.70-2.00 (2H, m, 4-H_{A+B}), 2.09-2.23 (1H, m, 3-H_{A+B}), 2.24-2.28 (0.55, m, 3-H_A), 2.36-2.39 (0.45H, m, 3-H_B), 4.82 (0.45H, dd, $J=8.5$ Hz, 6.5 Hz, 5-H_B) 5.18 (0.55H, dd, $J=6.9$, 7.0 Hz, 5-H_A), 5.34-5.38 (0.45H, m, 2-H_B), 5.48 (0.55H, dd, $J=3.2$, 7.3 Hz, 2-H_A), and 7.03-7.50 (5H, m, Ph); m/z 164 (M⁺), 146 (M⁺-H₂O), 107 (M⁺-C₂H₅CO), and 77 (C₆H₅⁺); (Found: C, 73.14; H, 7.37. C₁₀H₁₂O₂ requires C, 73.14; H, 7.37%), and 4-hydroxy-1-phenyl-1-butanone (21)²⁵ (15 mg, 18%); ν_{\max} (CH₂Cl₂) 3614, 3048, 2936, 1681, 1597, 1580, 1448, 1368, 1255, 1028, 770, and 687 cm⁻¹; δ_{H} (250 MHz, CDCl₃) 1.72-1.85 (1H, m, OH), 2.00 (2H, br. quin, $J\sim 6.5$ Hz, 3-H), 2.13 (2H, t, $J=7$ Hz, 4-H), 3.73 (2H, t, $J=6$ Hz, 4-H), 7.39-7.60 (3H, m, H-Ar), and 7.91-7.81 (2H, m, H-Ar).

Method B.- To a mixture of diiron nonacarbonyl (364 mg, 1 mmol) and ZnCl₂-TMEDA (126 mg, 0.5 mmol) under argon was added 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol) as a solution in dry THF (5 ml). This mixture was stirred at room temperature for 3.5 hours then worked-up as laid out in method A to give complex (18) (60 mg, 38%), lactol (20) (13 mg, 16%), and hydroxy ketone (21) (3 mg, 4%).

Method C.- Reaction of 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 4 hours gave a mixture of complex (18) (59 mg, 38%), lactol (20) (21 mg, 26%), and hydroxy ketone (21) (6 mg, 7%).

Method D.- Reaction of 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) for 6 hours gave a mixture of complex (18) (50 mg, 32%), lactol (20) (26 mg, 32%), and hydroxy ketone (21) (13 mg, 16%).

Method E.- Diiron nonacarbonyl (400 mg, 1.1 mmol) was added from a side-arm inlet tube to a mixture of 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol), ZnCl₂-TMEDA (126 mg, 0.5 mmol), and dry benzene (10 ml), the mixture was sealed under argon and sonicated for 4 hours then worked-up as laid out in method A to give complex (18) (77 mg, 49%), lactol (20) (14 mg, 17%) and hydroxy ketone (21) (7 mg 8%).

Method F.- Reaction of 1-phenyl-*E*-2-butene-1,4-diol (10) (82 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 4 hours gave complex 18 (78 mg, 50%), along with a trace of lactol (20).

Reaction of 1-phenyl-*Z*-2-butene-1,4-diol (11) with diiron nonacarbonyl. Method A.-

Reaction of 1-phenyl-*Z*-2-butene-1,4-diol (11) (82 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) for 5 hours gave a mixture of 1-*exo*-2-4- η^3 -(1-formyloxy-1-phenylbut-3-en-2-ylato)tricarbonyliron (19) (25 mg, 16%) as a yellow solid, m.p.120°C (decomp.); ν_{\max} (CH₂Cl₂) 3051, 2981, 2086, 2022, 1671, 1283, 1059, 990, 962, 938, 747, 731, 707, 682, 654, and 608 cm⁻¹; δ_{H} (250 MHz, C₆D₆) 2.67 (1H, dd, $J_{4\text{endo},3}=12.5$ Hz, $J_{4,4}=1.5$ Hz, 4-H_{endo}), 2.79 (1H, dt, $J_{4\text{exo},3}=7.8$ Hz, $J_{4,4}=J_{4\text{exo},2}=1.5$ Hz, 4-H_{exo}), 3.92 (1H, dt, $J_{3,4\text{endo}}=12.5$ Hz, $J_{3,4\text{exo}}=J_{3,2}=7.8$ Hz, 3-H), 4.03 (1H, d, $J_{2,3}=7.8$ Hz, 2-H), 4.71 (1H, br. s, 1-H), and 7.10-7.30 (5H, m, Ph); m/z 314 (M⁺), 286 (M⁺-CO), 258 (M⁺-2CO), 242 (M⁺-

CO-CO₂), 230 (M⁺-3CO), 214 (M⁺-2CO-CO₂), and 202 (M⁺-4CO); (Observed: M⁺-CO, 285.9928. C₁₃H₁₀FeO₄ requires M, 285.9928), complex (18) (25 mg, 16%), lactol (20) (33 mg, 40%), and hydroxy ketone (21) (5 mg, 6%).

Method C.- Reaction of 1-phenyl-Z-2-butene-1,4-diol (11) (82 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 3 hours gave a mixture of complex (18) (50 mg, 32%) and complex (19) (74 mg, 47%).

Method D.- Reaction of 1-phenyl-Z-2-butene-1,4-diol (11) (82 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) for 4 hours gave a mixture of complex (18) (32 mg, 20%), complex (19) (49 mg, 31%) and lactol (20) (5 mg, 6%).

Method F.- Reaction of 1-phenyl-Z-2-butene-1,4-diol (11) (82 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 3 hours gave complex (18) (35 mg, 22%) and complex (19) (58 mg, 37%).

Reaction of E-2-nonene-1,4-diol (12) with diiron nonacarbonyl. Method A.- Reaction of E-2-nonene-1,4-diol (12) (79 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) for 6 hours gave a mixture of 4-*exo*-1-3- η^3 -(4-formyloxynon-1-en-3-ylato)tricarbonyliron (23)²⁶ (5.5 mg, 3.5%); ν_{\max} (CH₂Cl₂) 3046, 2930, 2861, 2082, 2019, 1654, 1499, 1466, 1419, 1395, 1379, 1342, 1327, 1303, 1247, 1161, 1131, 1112, 1068, 1042, 998, 949, 919, 872, 771, and 706 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 0.95 (3H, t, J = 7.0 Hz, CH₃), 1.05-1.55 (8H, m, (CH₂)₄), 2.66 (1H, dd, $J_{4\text{endo},3}$ = 13.1 Hz, $J_{4\text{endo},4\text{exo}}$ = 1.5 Hz, 4-*H*_{endo}), 2.86 (1H, ddd, $J_{4\text{exo},3}$ = 8.1 Hz, $J_{4\text{exo},2}$ = 1.7 Hz, $J_{4\text{exo},4\text{endo}}$ = 1.5 Hz, 4-*H*_{exo}), 3.58 (1H, dddd, J_{1,CH_2} = 8.0 Hz, J_{1,CH_2} = 3.6 Hz, $J_{1,2}$ = 1.6 Hz, $J_{1,3}$ = 1.0 Hz, 1-H), 3.86 (1H, ddd, $J_{2,3}$ = 7.8 Hz, $J_{2,4\text{exo}}$ = 1.7 Hz, $J_{2,1}$ = 1.6 Hz, 2-H), and 4.04 (1H, dddd, $J_{3,4\text{endo}}$ = 13.1 Hz, $J_{3,4\text{exo}}$ = 8.1 Hz, $J_{3,2}$ = 7.8 Hz, $J_{3,1}$ = 1.0 Hz, 3-H); m/z 280 (M⁺-CO), 252 (M⁺-2CO), 224 (M⁺-3CO), 196 (M⁺-4CO), 140 (M⁺-Fe(CO)₄), and 124 (M⁺-Fe(CO)₃-CO₂) and tetrahydro-5-pentyl-2-furanol (25)²⁷ (33 mg, 42%); ν_{\max} (CH₂Cl₂) 3394, 2955, 2929, 2858, 1463, 1378, 1356, 1288, 1193, 1123, and 1027 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.91 (3H, t, J = 7.0 Hz, CH₃), 1.20-1.55 (8H, m, (CH₂)₄), 1.60-2.20 (3H, m, 3-H, 2x 4-H), 3.82-3.90 (0.4H, m, 3-H), 3.91-3.98 (1H, m, 5-H & 3-H), 4.11-4.22 (0.6H, m, 5-H), 5.41-5.44 (0.4H, m, 2-H), and 5.48-5.56 (0.6H, m, 2-H); δ_{H} (270 MHz, C₆D₆) 0.94 (3H, m, CH₃), 1.05-2.00 (12H, m, (CH₂)₄, 4-H, 3-H), 2.75 & 2.80 (1H, 2xbr. s, 2x OH), 3.81-3.93 (0.4H, m, 5-H), 4.14-4.25 (0.6H, m, 5-H), 5.36-5.41 (0.4H, m, 2-H), 5.43-5.48 (0.6H, m, 2-H); m/z 158 (M⁺), 140 (M⁺-H₂O), 112 (M⁺-CH₂O₂), 101 (M⁺-C₂H₅CO), and 87 (M⁺-C₃H₉); (Found: C, 68.56; H, 11.76. C₉H₁₈O₂ requires C, 68.31; H, 11.46%).

Method C.- Reaction of E-2-nonene-1,4-diol (12) (79 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 6 hours gave a mixture of complex (23) (13 mg, 8.5%) and lactol (25) (13.5 mg, 17%).

Method D.- Reaction of E-2-nonene-1,4-diol (12) (79 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) for 4 hours gave a mixture of complex (23) (31 mg, 20%), 4-*endo*-1-3- η^3 -(4-formyloxynon-1-en-3-ylato)tricarbonyliron (24)²⁶ (21 mg, 14%); ν_{\max} (CH₂Cl₂) 3047, 2981, 2930, 2873, 2084, 2026, 2014, 1663, 1381, 1113, 1072, 1016, 737, 684, 656, and 609 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 0.86 (3H, t, J = 7.5 Hz, CH₃), 1.00-1.39 (8H, m, (CH₂)₄), 2.83 (1H, dd, $J_{4\text{endo},3}$ = 13.0 Hz, $J_{4,4}$ = 1.7 Hz, 4-*H*_{endo}), 2.90 (1H, ddd, $J_{4\text{exo},3}$ = 8.0 Hz, $J_{4,4}$ = 1.7 Hz, $J_{4\text{exo},2}$ = 1.5 Hz, 4-*H*_{exo}), 3.75 (1H, dddd, $J_{3,4\text{endo}}$ = 13.0 Hz, $J_{3,2}$ = 8.4 Hz, $J_{3,4\text{exo}}$ = 8.0 Hz, $J_{3,1}$ = 1.4 Hz, 3-H), 3.84 (1H, ddd, $J_{2,3}$ = 8.4 Hz, $J_{2,1}$ = 6.4 Hz, $J_{2,4\text{exo}}$ =

1.5 Hz, 2-H), and 3.85 (1H, ddt, J_{1,CH_2} = 7.0 Hz, $J_{1,2}$ = 6.4 Hz, $J_{1,3}$ = 1.4 Hz, 1-H); m/z 308 (M^+), 280 (M^+ -CO), 252 (M^+ -2CO), 224 (M^+ -3CO), 196 (M^+ -4CO), 140 (M^+ -Fe(CO)₄), and 124 (M^+ -Fe(CO)₃-CO₂), and lactol (**25**) (16 mg, 20%).

Method F.- Reaction of *E*-2-nonene-1,4-diol (**12**) (79 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 4 hours gave a mixture of complex (**23**) (9 mg, 6%) and 4-*exo*-2-4- η^3 -(1-formyloxynon-2-en-4-ylato)tricarbonyliron (**22**)²⁸ (26 mg, 17%); ν_{max} (CH₂Cl₂) 3074, 2953, 2931, 2858, 2082, 2014, 1662, 1466, 1377, 1341, 1241, 1166, 1076, 1044, 984, 779, 740, 677, 656, and 612 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 0.85 (3H, br. t, $J \sim 7$ Hz, CH₃), 0.95-1.85 (8H, m, (CH₂)₄), 3.37 (1H, dd, $J_{1,1}$ = 12.1 Hz, $J_{1\text{exo},2}$ = 5.3 Hz, 1-*H*_{exo}), 3.48 (1H, dd, $J_{1,1}$ = 12.1 Hz, $J_{1\text{endo},2}$ = 1.7 Hz, 1-*H*_{endo}), 3.59 (1H, ddd, $J_{2,3}$ = 7.8 Hz, $J_{2,1\text{exo}}$ = 5.3 Hz, $J_{2,1\text{endo}}$ = 1.7 Hz, 2-H), 3.81 (1H, ddd, $J_{4,3}$ = 12.1 Hz, J_{4,CH_2} = 7.3 Hz, J_{4,CH_2} = 5.0 Hz, 4-H), and 3.87 (1H, dd, $J_{3,4}$ = 12.1 Hz, $J_{3,2}$ = 7.8 Hz, 3-H); m/z 280 (M^+ -CO), 252 (M^+ -2CO), 224 (M^+ -3CO), 196 (M^+ -4CO), 140 (M^+ -Fe(CO)₄), and 124 (M^+ -Fe(CO)₃-CO₂).

Reaction of Z-2-nonene-1,4-diol (13) with diiron nonacarbonyl. Method A.- Reaction of *Z*-2-nonene-1,4-diol (**13**) (79 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) for 3 hours gave a mixture of complex (**23**) (12 mg, 8%), complex (**24**) (1.5 mg, 1%), and lactol (**25**) (38 mg, 48%).

Method C.- Reaction of *Z*-2-nonene-1,4-diol (**13**) (79 mg, 0.5 mmol) with diiron nonacarbonyl (364mg, 1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 3 hours gave a mixture of complex (**23**) (23 mg, 15%) and lactol (**25**) (8 mg, 10%).

Method D.- Reaction of *Z*-2-nonene-1,4-diol (**13**) (79 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) for 3 hours gave a mixture of complex (**22**) (5 mg, 3%), complex (**23**) (46 mg, 30%), complex (**24**) (23 mg, 15%), and lactol (**25**) (9 mg, 11%).

Method F.- Reaction of *Z*-2-nonene-1,4-diol (**13**) (79 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 4 hours gave a mixture of complex (**22**) (43 mg, 28%), complex (**23**) (43 mg, 28%), and complex (**24**) (5.5 mg, 3.5%).

Reaction of 5,5-dimethyl-E-2-hexene-1,4-diol (14) with diiron nonacarbonyl. Method A.- Reaction of 5,5-dimethyl-*E*-2-hexene-1,4-diol (**14**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (182 mg, 0.5 mmol) for 3.5 hours gave a mixture of 3-*exo*-4-6- η^3 -(3-formyloxy-2,2-dimethylhex-5-en-4-ylato)tricarbonyliron (**26**) (1 mg, 1%); ν_{max} (CH₂Cl₂) 2962, 2084, 2026, 1654, 1367, 1038, 1004, 725, 660, and 607 cm⁻¹; δ_{H} (500 MHz, C₆D₆) 0.82 (9H, s, (CH₃)₃C), 2.43-2.46 (1H, m, J_{d} = 12.0 Hz, 4-*H*_{endo}), 2.62-2.64 (1H, m, J_{d} = 6.0 Hz, 4-*H*_{exo}), 3.06 (1H, d, $J_{1,2}$ = 2.0 Hz, 1-H), and 4.04-4.08 (2H, m, 2-H & 3-H); m/z 294 (M^+), 266 (M^+ -CO), 250 (M^+ -CO₂), 238 (M^+ -2CO), and 110 (C₈H₁₄⁺); (Observed: M^+ -CO, 266.0240. C₁₁H₁₄FeO₄ requires M , 266.0241), and *trans*-3-*endo*-4-6- η^3 -(3-formyloxy-2,2-dimethylhex-5-en-4-ylato)tricarbonyliron (**27**) (9 mg, 12%); ν_{max} (CH₂Cl₂) 2959, 2079, 2016, 1675, 1365, 970, and 727 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 0.98 (9H, s, (CH₃)₃C), 1.87 (1H, $J_{4\text{endo},3}$ = 13.0 Hz, 4-*H*_{endo}), 2.64 (1H, dd, $J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 9.0 Hz, 2-H), 2.73 (1H, d, $J_{4\text{exo},3}$ = 7.5 Hz, 4-*H*_{exo}), 3.85 (1H, d, $J_{1,2}$ = 2.7 Hz, 1-H), and 4.38 (1H, ddd, $J_{3,4\text{exo}}$ = 7.5 Hz, $J_{3,2}$ = 9 Hz, $J_{3,4\text{endo}}$ = 13.0 Hz, 3-H); m/z 294 (M^+), 266 (M^+ -CO), 237 (M^+ -(CH₃)₃C), and 57 ((CH₃)₃C⁺); (Observed: M^+ -CO, 266.0240. C₁₁H₁₄FeO₄ requires M , 266.0241), and a non-iron containing product, tentatively assigned as the lactol tetrahydro-5-(1,1-dimethylethyl)-2-furanol (**28**) (14.5 mg, 40%).

Method C.- Reaction of 5,5-dimethyl-*E*-2-hexene-1,4-diol (**14**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (182 mg, 0.5 mmol) and ZnBr₂ (0.25 ml of a 1M solution in THF, 0.25 mmol) for 4 hours gave a very low yield of a mixture of complexes (**26**) and (**27**) and lactol (**28**) (12 mg total, unresolved).

Method D.- Reaction of 5,5-dimethyl-*E*-2-hexene-1,4-diol (**14**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (200 mg, 0.55 mmol) for 3.5 hours gave a mixture of complex (**26**) (5 mg, 7%), complex (**27**) (9 mg, 12%), and a non-iron product tentatively assigned as the lactol (**28**) (11 mg, 30%).

Method F.- Reaction of 5,5-dimethyl-*E*-2-hexene-1,4-diol (**14**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (200 mg, 0.55 mmole) and ZnBr₂ (0.25 ml of a 1M solution in THF, 0.25 mmol) for 3.5 hours gave a mixture of complex (**26**) (6 mg, 8%) and complex (**27**) (8 mg, 11%).

Reaction of 5,5-dimethyl-*Z*-2-hexene-1,4-diol (15**) with diiron nonacarbonyl. Method A.-** Reaction of 5,5-dimethyl-*Z*-2-hexene-1,4-diol (**15**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (182 mg, 0.5 mmol) for 4 hours gave complex (**26**) (3.5 mg, 5%).

Method C.- Reaction of 5,5-dimethyl-*Z*-2-hexene-1,4-diol (**15**) (33 mg, 0.23 mmol) with diiron nonacarbonyl (182 mg, 0.5 mmol) and ZnBr₂ (0.23 ml of a 1M solution in THF, 0.23 mmol) for 3 hours gave a mixture of the complex (**26**) (43 mg, 64%) and a complex tentatively assigned as 3-*endo*-4-6- η^3 -(3-formyloxy-2,2-dimethylhex-5-en-4-ylato)tricarbonyliron (**29**) (0.7 mg, 1%); ν_{\max} (CH₂Cl₂) 3050, 2984, 2083, 2026, 1669, 1051, 1026, 1002, and 721 cm⁻¹; δ_{H} (250 MHz, C₆D₆) 0.74 (9H, s, (CH₃)₃C), 2.70 (1H, dd, $J_{4,4}$ = 1.9 Hz, $J_{4\text{endo},3}$ = 12.2 Hz, 4-H_{endo}), 2.83 (1H, ddd, $J_{4,4}$ = 1.9 Hz, $J_{4\text{exo},2}$ ~ 2.5 Hz, $J_{4\text{exo},3}$ = 6.3 Hz, 4-H_{exo}), and 3.55-3.72 (3H, m, 1-H, 2-H, 3-H).

Method D.- Reaction of 5,5-dimethyl-*Z*-2-hexene-1,4-diol (**15**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (200 mg, 0.55 mmol) for 4 hours gave complex (**26**) (16 mg, 22%) as the sole product.

Method F.- Reaction of 5,5-dimethyl-*Z*-2-hexene-1,4-diol (**15**) (36 mg, 0.25 mmol) with diiron nonacarbonyl (200 mg, 0.55 mmol) and ZnBr₂ (0.25 ml of a 1M solution in THF, 0.25 mmol) for 3 hours gave a mixture of complex (**26**) (45 mg, 61%) and 4-*exo*-2-4- η^3 -(1-formyloxy-5,5-dimethylhex-3-en-2-ylato)tricarbonyliron (**30**) (2.5 mg, 3%); ν_{\max} (CH₂Cl₂) 2079, 2018, 1662, 982, 811, and 723 cm⁻¹; δ_{H} (270 MHz, C₆D₆) 0.81 (9H, s, (CH₃)₃C), 3.43 (1H, dd, $J_{1,1}$ = 12.0 Hz, 1-H_{exo}), 3.49-3.52 (2H, m, 1-H_{endo}, 2-H), 3.89 (1H, ddd, $J_{3,1\text{endo}}$ = 0.5 Hz, $J_{3,2}$ = 6.9 Hz, $J_{3,4}$ = 12.9 Hz, 3-H), and 4.04 (1H, d, $J_{4,3}$ = 12.9 Hz, 4-H); m/z 294 (M⁺), 266 (M⁺-CO), 250 (M⁺-CO₂), 238 (M⁺-2CO), 222 (M⁺-CO₂-CO), 210 (M⁺-3CO), 194 (M⁺-CO₂-2CO), 182 (M⁺-4CO), 166 (M⁺-3CO-CO₂), and 110 (C₈H₁₄⁺); (Observed: M⁺-CO, 266.0240. C₁₁H₁₄FeO₄ requires M, 266.0241).

Reaction of *Z*-2-pentene-1,4-diol (17**) with diiron nonacarbonyl. Method A.-** Reaction of *Z*-2-pentene-1,4-diol (**17**) (126 mg, 1.2 mmol) with diiron nonacarbonyl (1010 mg, 2.8 mmol) for 3 hours gave a mixture of 2-*exo*-3-5- η^3 -(2-formyloxypent-4-en-3-ylato)tricarbonyliron (**31**)³ (118 mg, 38%); δ_{H} (270 MHz, C₆D₆) 0.95 (3H, d, $J_{\text{CH}_3,1}$ = 6.4 Hz, CH₃), 2.61 (1H, dd, $J_{4\text{endo},3}$ = 12.8 Hz, $J_{4,4}$ = 1.4 Hz, 4-H_{endo}), 2.78 (1H, dt, $J_{4\text{exo},3}$ = 8.1 Hz, $J_{4\text{exo},2}$ = $J_{4,4}$ = 1.4 Hz, 4-H_{exo}), 3.55 (1H, d, $J_{2,3}$ = 8.1 Hz, 2-H), 3.68 (1H, q, J_{1,CH_3} = 6.4 Hz, 1-H), and 3.85 (1H, dt, $J_{3,4\text{exo}}$ = $J_{3,2}$ = 8.1 Hz, $J_{3,4\text{endo}}$ = 12.8 Hz, 3-H), 2-*endo*-3-5- η^3 -(2-formyloxypent-4-en-3-ylato)tricarbonyliron (**32**)³ (16 mg, 5%); δ_{H} (270 MHz, C₆D₆) 0.93 (3H, d, $J_{\text{CH}_3,1}$ = 6.4 Hz, CH₃), 2.72-2.84 (2H, m, 4-H_{endo}, 4-H_{exo}), 3.56-3.67 (2H, m, 2-H, 3-H), and 3.80 (1H, br. pent., J_{1,CH_3} = 6.4 Hz, $J_{1,2}$ ~ 5.5 Hz, 1-H) and 4-*exo*-2-4- η^3 -(1-formyloxypent-3-en-2-

ylato)tricarbonyliron (**33**)³ (47 mg, 15%); δ_{H} (270 MHz, C₆D₆) 1.05 (3H, d, $J_{\text{CH}_3,4}$ = 6.0 Hz, CH₃), 3.27 (1H, dd, $J_{1,exo,2}$ = 5.4 Hz, $J_{1,1}$ = 11.8 Hz, 1-H_{exo}), 3.36 (1H, d, $J_{1,1}$ = 11.8 Hz, 1-H_{endo}), 3.45 (1H, dd, $J_{2,1,exo}$ = 5.4 Hz, $J_{2,3}$ = 7.6 Hz, 2-H), 3.56 (1H, dq, $J_{4,3}$ = 12.1 Hz, J_{4,CH_3} = 6.0 Hz, 4-H), and 3.67 (1H, dd, $J_{3,2}$ = 7.6 Hz, $J_{3,4}$ = 12.1 Hz, 3-H).

Method C.- Reaction of *Z*-2-pentene-1,4-diol (**17**) (55.5 mg, 0.5 mmol) with diiron nonacarbonyl (364 mg, 1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 2 hours gave a mixture of the complex **31** (54 mg, 43%), the complex (**32**) (8 mg, 6%), and the complex (**33**) (16 mg, 12.5%).

Method D.- Reaction of *Z*-2-pentene-1,4-diol (**17**) (102 mg, 0.92 mmol) with diiron nonacarbonyl (800 mg, 2.2 mmol) for 3 hours gave a mixture of complex (**31**) (93 mg, 40%), complex (**32**) (29 mg, 12.5%) and complex (**33**) (23 mg, 10%).

Method F.- Reaction of *Z*-2-pentene-1,4-diol (**17**) (55.5 mg, 0.5 mmol) with diiron nonacarbonyl (400 mg, 1.1 mmol) and ZnBr₂ (0.5 ml of a 1M solution in THF, 0.5 mmol) for 2.5 hours gave a mixture of complex (**31**) (64 mg, 51%), complex (**32**) (5 mg, 4%), and complex (**33**) (21 mg, 17%).

Reaction of *E*-2-pentene-1,4-diol (17**) with diiron nonacarbonyl.** **Method A.**- Reaction of *E*-2-pentene-1,4-diol (**17**) (53 mg, 0.5 mmol) with diiron nonacarbonyl (440 mg, 1.2 mmol) for 6 hours gave a mixture of complex (**31**) (10 mg, 8%), complex (**32**) (1 mg, 1%), and complex (**33**) (11 mg, 8%).

Method C.- Reaction of *E*-2-pentene-1,4-diol (**17**) (55 mg, 0.5 mmol) with diiron nonacarbonyl (430 mg, 1.2 mmol) and ZnBr₂ (1.1 ml of a 1M solution in THF, 1.1 mmol) for 1.5 hours gave a mixture of the complex (**31**) (16 mg, 12%), the complex (**32**) (1.5 mg, 1%), and the complex (**33**) (3 mg, 2%).

Method D.- Reaction of *E*-2-pentene-1,4-diol (**17**) (113 mg, 1.1 mmol) with diiron nonacarbonyl (639 mg, 1.8 mmol) for 6 hours gave a mixture of complex (**31**) (34 mg, 12%), complex (**32**) (6 mg, 2%), and complex (**33**) (31 mg, 11%).

Method F.- Reaction of *E*-2-pentene-1,4-diol (**17**) (50 mg, 0.5 mmol, 92%) with diiron nonacarbonyl (440 mg, 1.2 mmol) and ZnBr₂ (1.1 ml of a 1M solution in THF, 1.1 mmol) for 5 hours gave a mixture of the complex (**31**) (13 mg, 11%), the complex (**32**) (1 mg, 1%), and the complex (**33**) (17 mg, 14%).

Reaction of *dl*-*Z*-3-hexen-2,5-diol (35**) with diiron nonacarbonyl.** **Method A.**- Reaction of the *dl*-diol (**35**) (57 mg, 0.49 mmol) with diiron nonacarbonyl (358 mg, 0.98 mmol) in THF (4 ml) according to method A and purification by flash chromatography on silica gel (1.5 g) eluting with 5-30% ether/petrol gave the complex (**38**)⁵ as a white solid (40 mg, 31%), δ_{H} (C₆D₆) 3.78 (1H, dd, J = 7, 11 Hz, 3-H), 3.74 (1H, dq, J = 1.5, 7 Hz, 1-H), 3.66 (1H, dq, J = 11, 5 Hz, 4-H), 3.43 (1H, dd, J = 7, 1.5 Hz, 2-H), 1.14 (3H, d, J = 5 Hz, 4-Me), 0.98 (3H, d, J = 7 Hz, 1-Me).

Method D.-Reaction of the *dl*-diol (**35**) (43 mg, 0.37 mmol) with diiron nonacarbonyl (404 mg, 1.11 mmol) in benzene (3 ml) according to method D gave the complex (**38**) (54 mg, 55%).

Reaction of *meso*-*Z*-3-hexen-2,5-diol (34**) with diiron nonacarbonyl.** **Method A.**- Reaction of the *meso*-diol (**34**) (30 mg, 0.25 mmol) with diiron nonacarbonyl (188 mg, 0.52 mmol) in THF (2 ml) according to method A and purification by flash chromatography on silica gel (1 g) eluting with 5-25% ether/petrol gave the complex (**39**)⁵ as a white solid (17 mg, 25%), δ_{H} (C₆D₆) 3.86 (1H, dq, J = 11, 6 Hz, 4-H), 3.81 (1H, dq, J = 5, 7 Hz, 1-H), 3.57 (1H, dd, J = 8, 11 Hz, 3-H), 3.52 (1H, dd, J = 8, 5 Hz, 2-H), 1.16 (3H, d, J = 6 Hz, 4-Me), 0.95 (3H, d, J = 7 Hz, 1-Me).

Method D.- Reaction of the *meso*-diol (34) (41 mg, 0.35 mmol) with diiron nonacarbonyl (386 mg, 1.06 mmol) in benzene (3 ml) according to Method D gave the complex (39) (4 mg, 4%).

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