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$Fe_2(CO)_9$ IN TETRAHYDROFURAN OR UNDER SONOCHEMICAL CONDITIONS AS CONVENIENT PRACTICAL ROUTES TO π-ALLYLTRICARBONYLIRON LACTONE COMPLEXES

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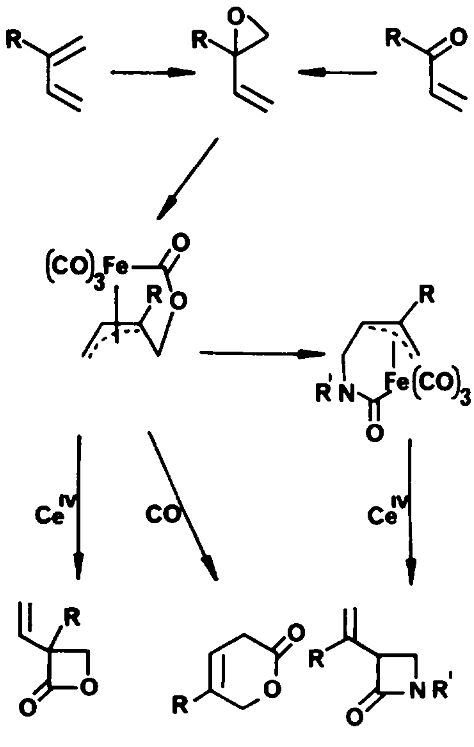
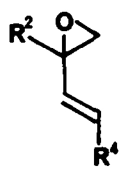
Abstract:- A series of alkenyl epoxides were converted into their corresponding π-allyltricarbonyliron lactone complexes by either treatment with tetrahydrofuran solutions of $Fe_2(CO)_9$ at room temperature, or in hydrocarbon solvents with $Fe_2(CO)_9$ under ultrasonification conditions. The new routes constitute convenient practical alternatives to presently existing methodology.

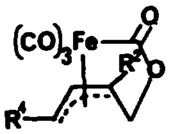
π-Allyltricarbonyliron lactone complexes have been shown to be useful precursors for the synthesis of lactones and lactams. For example, oxidation of these species with ceric ammonium nitrate leads predominantly to alkenyl substituted β-lactones,[1] whilst exhaustive carbonylation affords δ-lactones.[2] Treatment of these lactone complexes with amines in the presence of Lewis acids, gives the corresponding lactam complexes by an S_N' like mechanism. These upon oxidation with Ce(IV) provide a novel route to β-lactams,[3] a structural unit common to many important antibiotics (Scheme).

π-Allyltricarbonyliron lactone complexes are prepared by treatment of alkenyl epoxides with coordinatively unsaturated iron carbonyl species, generated under thermal or photochemical conditions.[4] The thermal reactions however, are not amenable to more sensitive or complex substrates,[2b] while the photochemical route inevitably involves high dilutions and use of the volatile and toxic pentacarbonyliron ($Fe(CO)_5$).

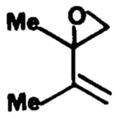


Scheme





(1)	R^2 = Me	R^4 = H	(11)
(2)	R^2 = H	R^4 = Ph	(12)
(3)	R^2 = Me	R^4 = Ph	(13)
(4)	R^2 = Ph	R^4 = 1'-Napth	(14)
(5)	R^2 = Me	R^4 = $^nC_6H_{13}$	(15)



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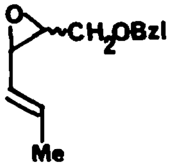

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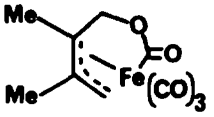

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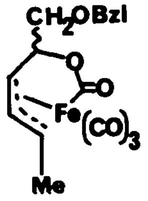

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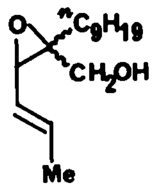

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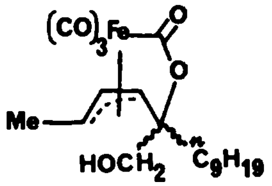

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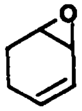

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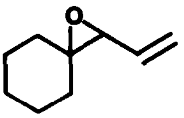

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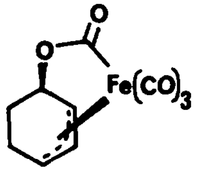

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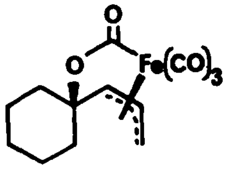

(20)

Alternatively these complexes can be prepared by a less general method and in low yield from 1,4-dihydroxybut-2-enes, 1,4-hydroxyaminobut-2-enes or oxazines.[5] Clearly these reaction conditions are unsatisfactory for large scale synthesis, therefore new and convenient methods of preparation are required if these complexes are to find more general synthetic use. Here we report upon two new methods which we believe satisfy these criteria.

The first of these involves the use of nonacarbonyl diiron ($Fe_2(CO)_9$), an orange crystalline and easily handled solid, in tetrahydrofuran solution. Dissolution of $Fe_2(CO)_9$ in tetrahydrofuran is known[6] to produce solutions which are thought to contain the carbonyl complex, $Fe(CO)_4 \cdot THF$. It is not unreasonable to expect that these solutions would react with alkenyl epoxides to give the corresponding π-allyltricarbonyliron lactone complexes. This indeed was found to be the case. The alkenyl epoxides

(1) to (8) were smoothly converted to the iron complexes (11) to (18) in moderate to excellent yields upon reaction at room temperature (Table).

Table: *Reaction of Alkenyl Epoxides with $Fe_2(CO)_9$.*

Epoxide	Product	Method[a]	Reaction time h	Yield %
(1)	(11)	A	0.75	94[d]
		B	5	76[d]
(2)	(12)	A	0.5	100 [d]
		B	0.6	68
(3)	(13)	A	2	64
		B	0.6	63
(4)	(14)	A	2	59
		B	5	65
(5)	(15)	A	0.75	56
		B	1.2	66
(6)	(16)	A	2	42
		B	1	44
(7)	(17)	A	2	34
		B	5	79
(8)[b]	(18)	A	0.5	71
(9)[c]	(19)	B	1.5	34
(10)[c]	(20)	B	1.5	50

a) Method A: $Fe_2(CO)_9$ in THF; Method B: $Fe_2(CO)_9$ in benzene or ether under ultrasonification

b) This epoxide failed to react using method B.

c) This epoxide was not studied under method A conditions.

d) Yield based on $Fe_2(CO)_9$.

During these reactions it was noticed that the initially red coloured solutions turned green on completion of reaction, presumably due to formation of $Fe_3(CO)_{12}$. Attempted reaction with $Fe_3(CO)_{12}$ or $Fe(CO)_5$ in THF, failed to afford the complexes with alkenyl epoxides. The starting alkenyl epoxides can be prepared by a variety of methods involving selective epoxidation of dienes,[7] methylenation of enones or enals using dimethylsulphonium methylide[8], or from carbonyl compounds using arsonium ylides.[9]

The reaction conditions using $Fe_2(CO)_9$/THF were satisfactory for most substrates, however a complimentary process was also investigated which would allow reaction at room temperature in hydrocarbon solvents such as benzene, hexane, petroleum ether etc., but still using $Fe_2(CO)_9$ as the convenient source of carbonyliron species. As the alkenyl epoxides failed to react with $Fe_2(CO)_9$ alone in these solvents (over a period of up to two weeks), we subjected the reaction mixtures to ultrasonification using a Semat 80 Watt, 50 kHz ultrasonic bath. Under these conditions it was now possible to readily convert the alkenyl epoxides (1) - (7) and (9) - (10) to the corresponding complexes (11) - (17) and (19)-(20) in a synthetically acceptable fashion (Table). The use of ultrasonification methods in chemistry is of considerable current interest[10] and reactions of metal carbonyls under these conditions has proved particularly topical.[11,12]

The reaction is carried out in suba-sealed round bottomed flask immersed in the ultrasonic bath, until disappearance of $Fe_2(CO)_9$, or t.l.c. indicates the reaction to be complete. The product was isolated by filtration using a 'Celite' pad, followed by chromatography on a silica gel column or recrystallisation. With volatile alkenyl epoxides, it was expedient to use an excess of the epoxide over $Fe_2(CO)_9$ in order to ensure high yields of complex.

In control reactions, neither $Fe(CO)_5$ nor $Fe_3(CO)_{12}$ in hydrocarbon solvents were found to react with alkenyl epoxides under sonochemical conditions. Exposure of $Fe_2(CO)_9$ alone to ultrasonification gave $Fe(CO)_5$, precipitated elemental iron and carbon monoxide. Dienes in the presence of $Fe_2(CO)_9$ failed to afford complexes under similar reaction conditions, though in a separate experiment, tricarbonyliron diene complexes were shown to be stable to the sonochemical method. On the other hand the π-allyltricarbonyliron lactone complexes were slowly decomposed in benzene solution under prolonged ultrasonification (≈ 25% decomposition after 18 h).

These results strongly suggest that the conclusions presented by Suslick[12] on related systems are highly debatable, and that alternative pathways could be operating during these sonochemical procedures. Clearly more work is required to properly define possible reactive intermediates and the effect of varying reaction conditions.

Nevertheless, we believe that above procedures constitute practically useful methods for the preparation of π-allyltricarbonyliron lactone complexes, further uses of which will be reported in detail later.

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrometer for solutions in $CHCl_3$ unless otherwise stated. ^1H NMR spectra were recorded at 60 MHz using a Varian EM 360A, or at 250 MHz using a Bruker WH250 spectrometer, for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were obtained using a V.G. Micromass 7070 B spectrometer. Solvents were dried using standard methods. Chromatography was performed on MN-Silica gel 60 (230-400 mesh) under pressure.

General Procedure for the Preparation of π-Allyltricarbonyliron Lactone Complexes using $Fe_2(CO)_9$ in Tetrahydrofuran. $Fe_2(CO)_9$ was added to a stirred solution of the alkenyl epoxide in THF. Upon formation of a green solution (or complete dissolution of $Fe_2(CO)_9$), solvent was removed under reduced pressure. The residue was dissolved in the minimum quantity of benzene and eluted through a short column of silica gel with benzene-ether to afford the pure ferrilactone complex.

2-4-η^3-(1-Formyloxy-2-methylbut-3-en-2-ylato) tricarbonyliron (11). To a solution of (1) (2.5g, 0.03mol) in THF (75ml) was added $Fe_2(CO)_9$ (9.2g, 0.03mol). Work up after 0.75 h as above and elution of the column with 20% ether-benzene gave the complex (11) (7.0g, 94%) m.p. 101°C, identical to the previously prepared compound.[2a]

2-4-η^3-(1-Formyloxy-4-phenylbut-3-en-2-ylato) tricarbonyliron (12). To a solution of (2) (0.29g, 2.0mmol) in THF (30ml) was added $Fe_2(CO)_9$ (0.62g, 1.7mmol). After 0.5 h, work up in the usual manner and elution of the column with 25% ether-benzene gave the complex (12) (0.53g, 100%), m.p. >120°C (decomp.); IR 2080, 2030, 1665 and 984 cm^{-1}; NMR δ4.05 (1H, dd, J = 12.5, 5.5 Hz, H-1), 4.17 (1H, dd, J = 12.5, 1.5 Hz, H-1), 4.78 (1H, ddd, J = 7.5, 5.5, 1.5 Hz, H-2), 4.82 (1H, d, J = 12.5 Hz, H-4), 5.62 (1H, dd, J = 12.5, 7.5 Hz, H-3), and 7.28-7.42 (5H, m, Ph) (Found: C, 53.76; H, 3.21%. $C_{14}H_{10}FeO_5$ requires C, 53.54; H, 3.21%).

2-4-η^3-(1-Formyloxy-2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (13). To the epoxide (3) (100mg, 0.62mmol) in THF (20ml) was added $Fe_2(CO)_9$ (350mg, 0.96mmol). After 2 h, work up as above gave the complex (13) (130mg, 64%), m.p. 150°C; IR 3020, 2920, 2070, 2000, 1710, 1655, 1595, 1440 and 970 cm^{-1}; NMR δ1.45 (3H, s, Me), 3.38 (1H, d, J_{AB} = 12.4Hz, H-1), 3.57 (1H, d, J_{AB} = 12.4Hz, H-1) 4.67 (1H, d, J = 12.4 Hz, H-3), 4.98 (1H, d, J = 12.4 Hz, H-4), and 7.08 (5H, s, Ph) (Found: C, 55.03; H, 3.46%. $C_{15}H_{12}O_5Fe$ requires C, 54.91; H, 3.69%).

2-4-η^3-(1-Formyloxy-2-phenyl-4-napthylbut-3-en-2-ylato)tricarbonyliron (14). To a solution of (4) (100mg, 0.37mmol) in THF (20ml) was added $Fe_2(CO)_9$ (200mg, 0.56mmol). After 2 h, work up as above gave the complex (14) (96mg, 59%), m.p. 146-9°C (decomp.); IR 3060, 2930, 2080, 2020, 1720, 1690 and 1600 cm^{-1}; NMR δ4.40 (1H, d, J_{AB} = 10 Hz, H-1), 4.48 (1H, d, J_{AB} = 10 Hz, H-1), 5.12 (1H, d, J = 12 Hz, H-4), 6.35 (1H, d, J = 12 Hz, H-3), 7.25 (5H, s, Ph), and 7.30-8.05 (7H, m, napth).

2-4-η^3-(1-Formyloxy-2-methyldec-3-en-2-ylato) tricarbonyliron (15). A solution of (5) (195mg, 1.16mmol) in THF (22ml) with $Fe_2(CO)_9$ (0.43g, 1.2mmol) was stirred for 0.75 h. Work up as above and elution with 15% ether-benzene gave the complex (15) (211mg, 56%) as an oil, IR 2930, 2860, 2080, 2030, 2010, 1665, 1460, 1385 and 985 cm^{-1}; NMR δ0.98 (3H, t, J = 6.7 Hz, 10-Me), 1.20-1.78 (9H, m), 1.97 (3H, s, 2-Me), 2.22 (1H, ddd, J = 13.2, 8.4, 4.8 Hz, H-5), 3.75 (1H, ddd, J = 11.9, 8.4, 4.8 Hz, H-4), 3.85 (1H, dd, J = 12.0, 1.1 Hz, H-1), 4.08 (1H, d, J = 12.0 Hz, H-1), and 4.71 (1H, d, J = 11.9 Hz, H-3) (Found: C, 52.05; H, 5.94%. $C_{14}H_{20}FeO_5$ requires C, 51.87; H, 6.22%).

2-4-η^3-(2,3-Dimethyl-1-formyloxybut-3-en-2-ylato)tricarbonyliron (16). To the alkenyl epoxide (6) (50mg, 0.51mmol) in THF (20ml) was added $Fe_2(CO)_9$ (278mg, 0.76mmol). Work up as above after 2 h gave the complex (16) (54mg, 42%), m.p. 104°C, identical to the previous prepared compound.[1]

2-4-η^3-(1-Benzyloxymethyl-1-formyloxypent-3-en-2-ylato)tricarbonyliron (17). To the epoxide (7) (50mg, 0.25mmol) in THF (20ml) was added $Fe_2(CO)_9$ (135mg, 0.37mmol). After 2 h, work up as above gave the complexes (17) (31mg, 34%) as a mixture of isomers at C-1, m.p. 64-65°C; IR 3020, 2950, 2850, 2070, 2005 and 1667 cm^{-1}; NMR δ1.83 (3H, d, J = 5.6 Hz, 4-Me), 3.53 (2H, m, $C\underline{H_2}OBn$), 4.07 (1H, m, H-4), 4.40 (1H, dd, J = 10.3, 4.5 Hz, H-3), 4.57 (4H, m, $PhC\underline{H_2}$, H-2, H-1) and 7.34 (5H, s, Ph) (Found: C, 55.10; H 4.35%. $C_{17}H_{16}FeO_6$ requires C, 54.87; H, 4.34%).

Preparation of 2-4-η^3-(5-Formyloxy-5-hydroxymethyltetradec-3-en-4-ylato)tricarbonyliron (18). To a solution of (8) (100mg, 0.47mmol) in THF (20ml) was added $Fe_2(CO)_9$ (227mg, (0.63mmol). After 0.5 h, work up as above gave the complexes (18) as a mixture of isomers at C-5, (100mg, 71%), m.p. 95 - 99°C; IR 2960, 2940, 2875, 2860, 2090, 2030 and 1655 cm^{-1}; NMR δ0.87 (3H, br t, J = 7.6 Hz, 15-Me), 1.15-1.80 (17H, m), 1.56 (1H, br s, OH), 1.87 (3H, d, J = 6.4 Hz, 1-Me) 3.64 (2H, m, 6-$C\underline{H_2}$) 4.10 (1H, dq, J = 11.9, 6.4 Hz, H-2), 4.58 (1H, d, J = 7.6 Hz, H-4), and 4.67 (1H, dd, J = 11.9, 7.6 Hz, H-3) (Found: C, 55.54; H, 6.94%. $C_{19}H_{28}O_6Fe$ requires C, 55.90; H, 6.91%).

General Procedure for the Preparation of π-Allyltricarbonyliron Lactone Complexes using Ultrasonification. A solution of the alkenyl epoxide in an inert solvent (usually benzene) with $Fe_2(CO)_9$ was subjected to ultrasonification until dissolution of the iron carbonyl occured (0.5 - 5 h). Filtration of the mixture through a pad of 'Celite' and removal of the solvent under reduced pressure (taking care not to heat the solution above room temperature), gave a residue which was purified by column chromatography and/or recrystallisation to give the ferrilactone complex.

2-4-η^3-(1-Formyloxy-2-methylbut-3-en-2-ylato) tricarbonyliron (11). A solution of isoprene epoxide (1) (2g, 23.6mmol) in benzene (800ml) containing $Fe_2(CO)_9$ (2.9g, 7.9mmol) was reacted ultrasonically for 5 h. Work up gave the complex (11) (1.5g, 76%) (based on $Fe_2(CO)_9$) identical in all respects to the previously prepared material. Conducting the reaction on a smaller scale gave an improved (90%) yield.

2-4-η^3-(1-Formyloxy-4-phenyl-but-3-en-2-ylato)tricarbonyliron (12). The epoxide (2) (0.67g, 4.6mmol) in ether (50ml) containing $Fe_2(CO)_9$ (1.66g, 4.6mmol) was reacted ultrasonically for 0.6 h. Work up gave the complex (12) (0.98g, 68%) identical to the material prepared above.

2-4-η^3-(1-Formyloxy-2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (13). A solution of the epoxide (3) (100mg, 0.62mmol) in benzene (20ml) containing Fe$_2$(CO)$_9$ (350mg, 0.96mmol) was reacted ultrasonically for 0.6 h. Work up gave the complex (13) (128mg, 63%) identical to the material prepared above.

2-4-η^3-(1-Formyloxy-2-phenyl-4-napthylbut-3-en-2-ylato)tricarbonyliron (14). A solution of the epoxide (4) (100mg, 0.37mmol) in benzene (20ml) containing Fe$_2$(CO)$_9$ (200mg, 0.56mmol) was reacted ultrasonically for 5 h. Work up gave the complex (14) (108mg, 65%), identical to the material prepared above.

2-4-η^3-(1-Formyloxy-2-methyldec-3-en-2-ylato)tricarbonyliron (15). A solution of the epoxide (5) (131mg, 0.78mmol) in benzene (35ml) containing Fe$_2$(CO)$_9$ (0.28g, 0.8mmol) was reacted ultrasonically for 1.2 h. Work up gave the complex (15) (166mg, 66%) identical to that prepared above.

2-4-η^3-(2,3-Dimethyl-1-formyloxy-but-3-en-2-ylato)tricarbonyliron (16). A solution of the epoxide (6) (150mg, 0.51mmol) in benzene (20ml) containing Fe$_2$(CO)$_9$ (278mg, 0.76mmol) was reacted ultrasonically for 1 h. Work up gave the complex (16) (56mg, 44%), identical to that prepared previously.

2-4-η^3-(1-Benzyloxymethyl-1-formyloxypent-3-en-2-ylato)tricarbonyliron (17). A solution of the epoxide (7) (50mg, 0.25mmol) in benzene (20ml) containing Fe$_2$(CO)$_9$ (135mg, 0.36mmol) was reacted ultrasonically for 5 h. Work up gave the complex (17) (73mg, 79%) identical to the previously prepared material.

2-4-η^3-(Cyclohex-3-en-2-ylato)-1-oxycarbonyltricarbonyliron (19). The epoxide (9) (438mg, 5.0mmol) in benzene (60ml) with Fe$_2$(CO)$_9$ (1.82g, 5.0mmol) was reacted ultrasonically for 1.5 h. Work up gave the complex (19) (448mg, 34%), m.p. 74°C (decomp.) (Lit.[3c] 80°C); IR 2900, 2100, 1990, 1650, 1460, 1375, 1340, 1325, 1060, 1010, 995 and and 975 cm^{-1}; NMR δ1.10-1.37 (1H, m), 1.48-1.73 (1H, m); 2.18 (1H, ddd, J = 18, 11.5, 5.5 Hz, H-5β), 2.44 (1H, dddd, J = 18, 6.5, 6.5, 1 Hz, H-5α), 4.52 (1H, dm, J = 7 Hz, H-1), 4.70 (1H, ddd, J = 6.5, 5.5, 2 Hz, H-4), 5.44 (1H, dd, J = 6.5, 6.5 Hz, H-3), and 5.75 (1H, ddd, J = 7, 6.5, 2 Hz, H-2).

2-4-η^3-Spiro(cyclohexane-1,1'-but-3-en-2-ylato)-1-oxycarbonyltricarbonyliron (20). A solution of the epoxide (10) (293mg, 2.2mmol) in benzene (80ml) containing Fe$_2$(CO)$_9$ (0.86g, 2.4mmol) was reacted ultrasonically for 1.5 h. Work up gave the complex (20) (333mg, 50%) m.p. 96°C (decomp.) identical to the previously prepared material.[1]

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