Reactivity of Co-ordinated Ligands. Part XI.[1] The Relative Reactivity of Tricarbonyliron–Cyclohexadienone and –Cycloheptadienone

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The tricarbonyliron complexes of cyclohexa-2,4-dienone and cyclohepta-2,4-dienone undergo the Reformatskii reaction with methyl α-bromoacetate and zinc to give the expected hydroxy-esters. Both esters lose the hydroxy-group on reaction with trityl tetrafluoroborate to give dienyl salts. The salts are readily deprotonated to give neutral complexes with a substituted exocyclic double bond. Tricarbonyl(cyclohexa-2,4-dienone)iron shows no enol reactivity, but tricarbonyl(cyclohepta-2,4-dienone)iron undergoes the Mannich reaction with dimethylammonium chloride and paraformaldehyde to give the expected α-dimethylaminomethyl derivative.

In earlier papers in this series we have shown that varying patterns of ligand reactivity can be brought about by several factors. In this study we show the way in which the chemistry is affected by a change in the ring size of the co-ordinated ligand.

In our preliminary communication of this work[2] we reported the ketonic and enolic reactions of the title compounds. On the basis of n.m.r. evidence we suggested that ring expansion reactions occurred on deprotonation of the complexes (III) and (VIII) to give complexes with seven- and eight-membered rings respectively. *X*-Ray structure determinations[3] have disproved this and shown that the complexes produced contain exocyclic double bonds.

Preparation of the Dienone Complexes.—The six-membered ring ketone (I) was prepared on a large scale by the procedure published earlier.[4] Weiss and Hübel have reported[5] the cycloheptadienone complex (VI) as a

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[1] Misnumbering of this Series has occurred and Parts VIII, IX, and X are considered to be, respectively, *J. Chem. Soc.* (*A*), 1971, 2699; *J.C.S. Dalton*, 1972, 456; *ibid.*, p. 463.

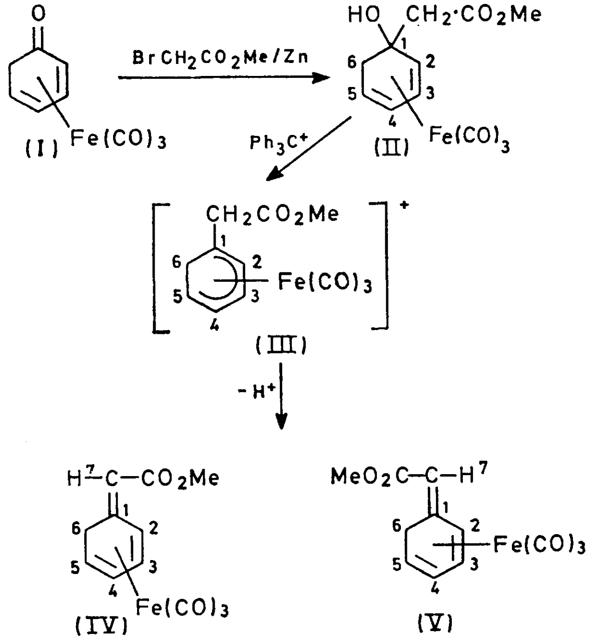
[2] J. Lewis and A. W. Parkins, *Chem. Comm.*, 1968, 1194.

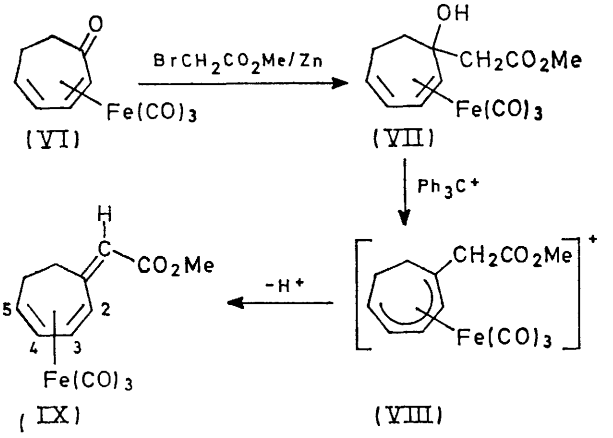
[3] R. Mason, personal communication.

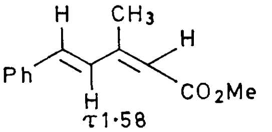
[4] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[5] E. Weiss and W. Hübel, *Chem. Ber.*, 1962, **95**, 1179.

constituent of the complex mixture of products obtained by hydrogenation of tricarbonyl(tropone)iron. The report[6] that the iron carbonyl complex of homotropone can be made by oxidation of its alcohol precursor, suggested that a similar procedure might provide a more attractive route to the cycloheptadienone complex (VI). Thus nucleophilic attack by hydroxide ion on tricarbonyl(cycloheptadienyl)iron fluoroborate[7,8] followed by oxidation with chromium trioxide in pyridine gave the ketone in 14% yield. The oxidation method may also be used to prepare the six-membered ketone (I) from tricarbonyl(cyclohexadienyl)iron tetrafluoroborate.[9]

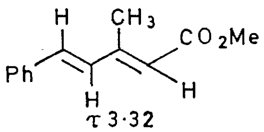






τ1·58

(Xa)



τ 3·32

(Xb)

Nucleophilic Attack on the Dienone Complexes.—The ketones (I) and (VI) both undergo the normal ketone characterisation reactions. The preparation of the oxime of the six-membered ring ketone required careful control of pH. We were not able to induce the oxime to undergo the Beckmann rearrangement, but have made no studies of oxime formation in the case of the seven-membered ring ketone (VI).

Pettit and his co-workers[10] have successfully carried out reactions of Grignard reagents with aldehyde groups attached to diene fragments bonded to the tricarbonyliron residue. However, our attempts to accomplish similar reactions with the tricarbonyliron complexes of cyclohexa-2,4-dienone and cyclohepta-2,4-dienone have been unsuccessful. The reactions of these complexes with organo-lithium reagents or isopropylmagnesium bromide give brown solutions, but we were not able to isolate or characterise the products. A deep red solution is obtained when the six-membered ring homologue is treated with methylenetriphenylphosphorane; but again we failed to obtain a stable product. With carbanions of lower reactivity we have obtained normal ketone reactions.

(a) *Six-membered ketone.* When tricarbonyl(cyclohexa-2,4-dienone)iron (I) is refluxed with activated zinc dust and methyl α-bromoacetate in dry benzene, the expected Reformatskii reaction[11] occurs to give, after hydrolysis and chromatography, the hydroxy ester (II) as pale yellow crystals m.p. 59—60°. The spectroscopic data for the ester is given in Table 1. The n.m.r. spectra of cyclic diene fragments bonded to the iron carbonyl residue may be divided[12] into ' inner ' protons which occur between τ 4·6 and 4·9, and ' outer ' protons which occur between τ 6·6 and 7·3. The assignments given in Table 1 have been made using these criteria. A comparison of the relative intensities before and after the addition of D_2O shows that the hydroxyl proton coincides in chemical shift with the methyl group. Both protons on C(6) of the ester (II) have the same chemical shift and occur as a well defined doublet at τ 8·1.

The hydroxy-ester (II) reacts with triphenylmethyl tetrafluoroborate in dichloromethane to give a salt of composition $C_{12}H_{11}BF_4FeO_5$. The organic product from the reaction is triphenylmethanol. The ^{1}H n.m.r. spectrum of the salt is given in Table 2 and is assigned in terms of structure (III). This assignment has been confirmed by spin decoupling and agrees well with the

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[6] J. D. Holmes and R. Pettit, *J. Amer. Chem. Soc.*, 1961, **83**, 2531.

[7] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497.

[8] M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc.* (*A*), 1967, 240.

[9] M. Haas, personal communication.

[10] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955.

[11] R. L. Shriner, *Org. Reactions*, 1942, **1**, 1; K. A. Kocheshkov and L. V. Abrama in ' The Organic Compounds of Zinc and Cadmium,' North Holland Publishing Company, Amsterdam, 1967, p. 121.

[12] R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 1.

shifts observed for cyclohexadienylirontricarbonyl.[13] In water, the salt (III) undergoes deprotonation to give the neutral complex $C_{12}H_{10}FeO_5$ (IV). The structure of this complex was initially considered to be (XVIII). This suggestion was based on the ^1H n.m.r. spectrum which showed five resonances at τ 4·3 (2H, m), 4·8 (2H, m), 6·3 (3H, s), 6·8 (m), and 7·5 (2H). However, the structure of this derivative has now been established by *X*-ray crystallography as (IV). Because of several inconsistencies of the ^1H n.m.r. spectrum with this structure [2] we shall discuss it in detail. From normal chemical-shift correlations the resonance at τ 6·3 is assigned to the ester protons and the resonance at τ 7·5 to the methylene protons. It seems reasonable to assume that 5-H will behave as a normal outer proton and on this basis the multiplet at τ 6·8 is assigned to this proton. The assignments of the other resonances was made with the aid of double irradiation experiments. Irradiation at τ 6·8 affects only the resonances at τ 7·5 and 4·3 and so part of the resonance at τ 4·3 is assigned to 4-H. Irradiation at τ 7·5 causes a sharpening of the τ 4·8 and 6·8 resonances. Thus the acrylic proton 7-H must make up part of the absorption at τ 4·8 and be coupled to one of the methylene protons by allylic coupling. Assignment of 2-H and 3-H cannot be made with absolute certainty as the spectrum is complicated by two pairs of protons each coincidentally having the same chemical shifts, and also by allylic coupling. However, it seems preferable to assign part of the resonance at τ 4·8 to 2-H and part of the peak at τ 4·3 to 3-H as shown in Table 3. If this assignment is reversed it does not affect the argument which follows. The spectrum is consistent with the *X*-ray structure provided that 2-H and 7-H both occur at τ 4·8, as the other chemical shifts are within the expected ranges. In methyl acrylate the CH resonance occurs at τ 3·8 but this resonance is sensitive to the *trans*-group and in methyl 3-aminobut-2-enoate, where there is a *trans*-amino-group, the proton absorbs at τ 5·4.[14] Thus the assignment of part of the resonance at τ 4·8 to 7-H in (IV) is reasonable.

TABLE 1

	Chemical-shift position in $CDCl_3$ (τ units)						I.r. frequency in Nujol (cm^{-1})	
Compound	OH	α-CH_2	CO_2Me	2-H + 5-H	3-H + 4-H	Ring methylene protons	C=O ester	OH
(II)	6·3	7·6	6·3	6·9	4·7	8·1	1705	3500
(VII)	6·5	7·5	6·3	7·0	4·7	7·5—9·0	1710	3480

TABLE 2

Chemical-shift position in liq.SO_2 (τ units)

Compound	CO_2Me	3-H	2-H + 4-H	5-H	Methylene protons
(III)	6·2	2·7	4·1	5·6	6·8—7·9
(VIII)	6·2	2·9	4·0	5·0	7·0—8·5

TABLE 3

	Chemical-shift position (τ units)						I.r. frequency in Nujol (cm^{-1})	
Compound	2-H	3-H + 4-H	5-H	Methylene protons	7-H	CO_2Me	C=O ester	C=C of exocyclic double bond
(IV) (in $CDCl_3$)	4·8	4·3	6·8	7·5	4·8	6·3	1700	1610
(V) [in $(CD_3)_2CO$]	6·3	4·1	6·9	7·5 and 6·5	4·4	6·4	1700	1610
(IX) (in $CDCl_3$)	5·3	4·5	6·8	7·5—8·3	4·5	6·3	1705	1608

Since there is no report of an outer proton such as 2-H absorbing as low as τ 4·8 this lowering of the chemical shift by τ 1·5 can only be attributed to the effect of the methoxycarbonyl group; this led us to suggest previously that a ring expansion had occurred. The n.m.r. spectrum of the compound was run using deuterioacetone as solvent in the hope of producing solvent shifts which would simplify the spectrum. The multiplet at τ 4·8 changed considerably but the absorption did not move sufficiently to determine the multiplicity of each.

We assign the strong band at 1610 cm^{-1} in the i.r. spectrum of (IV) to the stretching vibration of the uncoordinated double bond and the band at 1700 cm^{-1} to the stretching vibration of the carbonyl group of the ester.

The hydroxy ester (II) can be dehydrated on slow passage down a silica-gel chromatography column to give another compound (m.p. 86—88 °C) shown by its analysis and mass spectrum to be an isomer of (IV). The i.r. spectra of both isomers are very similar and only differ in small details. The n.m.r. of the compound (m.p. 86—88 °C) in deuteriochloroform has a multiplet at τ 4·5 (3H), a sharp singlet at τ 6·4 (3H), and a complicated region τ 6·5—6·9 containing several resonances (3H) together with a complex doublet centred on τ 7·5 (1H). This spectrum is consistent with structure (V) and in an attempt to confirm this, the spectrum was rerun using deuterioacetone as solvent. This fortunately produced solvent shifts which simplified the spectrum considerably. The low-field resonance was modified to give a multiplet at τ 4·1 (2H) and a singlet at τ 4·4 (1H). These resonances can be assigned to the inner protons (3-H and 4-H) and the acrylic proton (7-H) respectively.

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[13] D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.

[14] N. S. Bhacca, L. J. Johnson, and J. N. Schoolery, ' N.m.r. Spectra Catalogue,' Varian Associates, Palo Alto, California, 1963. Spectra 64 and 442.

Multiplets at τ 6·3 (1H) and τ 6·9 (1H) are assigned to the outer protons (2-H and 5-H) respectively. A complex doublet at τ 7·5 is attributed to one of the methylene protons (6-H), the other proton giving rise to a similar doublet at τ 6·5 which is partly obscured by the singlet at τ 6·4 (3H) which is due to the methyl group. These assignments as shown in Table **3** were confirmed by spin-decoupling experiments. The structure of (V) has been confirmed by *X*-ray studies[3] and it is interesting to note that the absorption due to 2-H occurs at τ 6·3 in this isomer compared with τ 4·8 in the other isomer (IV). A similar difference in chemical shift has been observed for the protons on C-4 of the compounds (Xa) and (Xb).[15]

If either (IV) or (V) is dissolved in concentrated sulphuric acid the n.m.r. spectrum indicates that the cation (III) is produced in each case. If these sulphuric acid solutions are diluted with water and extracted with ether a mixture of (IV) and (V) is obtained. The proportions of each isomer were found to be variable and dependent on the pH at which the extraction is carried out. Thus deprotonation of the cation (III) in acidic media produces isomer (V) whereas deprotonation in neutral media gives isomer (IV). The reason for the stereospecific nature of this deprotonation is not apparent, but it may be associated with the nature of the nucleophile in the different media. Thus in acidic media a water molecule is the most probable nucleophile whilst in neutral media hydroxide ion could act as the nucleophile. The reaction may proceed by different mechanisms—a bimolecular mechanism in the case of the more nucleophilic hydroxide ion, and a unimolecular mechanism in the case of deprotonation by water molecules.

If isomer (IV) is passed down a silica-gel column the complex undergoes isomerisation to the other isomer (V). This is presumably associated with the acidic nature of silica gel and the formation of the cation (III) as an intermediate.

(b) *Seven-membered ketone*. Tricarbonyl(cyclohepta-2,4-dienone)iron (VI) undergoes the Reformatskii reaction to give the expected hydroxy-ester (VII). The spectroscopic data for the ester are given in Table 1. This hydroxy-ester reacts with trityl tetrafluoroborate in dichloromethane to give a salt of composition $C_{13}H_{13}BF_4FeO_5$, and the organic product is again triphenylmethanol. The n.m.r. spectrum of $C_{13}H_{13}BF_4FeO_5$ is summarised in Table 2 and shows that the compound has structure (VIII). Deprotonation of this salt in water produces a compound (IX) of composition $C_{13}H_{12}FeO_5$. The spectroscopic data of this complex is given in Table 3. The n.m.r. absorption due to 2-H at τ 5·3 and the methylene proton absorptions at τ 7·5—8·3 suggest that the complex has structure (IX). Attempts to produce the geometrical isomer of (IX) were unsuccessful.

Reactivity of the Complexes (IV) *and* (V).—As described above, protonation of the complexes (IV) and (V) gives the cation (III). It is interesting to note that no protonation of C-5 to give a transoid dienyl system takes place. Treatment of the cation (III) with amines or sodium methoxide results in deprotonation to give (IV) rather than nucleophilic addition to the dienyl system. Thus this cation is much more acidic than other dienyl iron tricarbonyl cations (see for example ref. 4). This is due to the combined electron-withdrawing effects of the methoxycarbonyl and cyclohexadienyl systems. With the more nucleophilic borohydride ion, addition of a hydride ion to the dienyl system takes place to give a yellow oil. This complex was shown to be tricarbonyl-(methoxycarbonylmethylcyclohexa-1,3-diene)iron (XI), indicating that addition of the hydride ion takes place at the unsubstituted end of the dienyl system.

Reaction of the complexes (IV) and (V) with ceric ammonium nitrate resulted in oxidation of the iron atom and displacement of the diene ligand. The organic product from this reaction was isolated and identified as methyl phenylacetate. Thus the iron tricarbonyl group stabilises the ligand in the exocyclic double-bond form but on displacement the ligand undergoes a 1,3-hydride shift to produce a benzene ring. Reaction of the complexes (IV) and (V) with acetyl chloride–aluminium chloride produced unstable products which could not be characterised.

Several reactions typical of olefins were attempted with the complexes (IV) and (V) to find out if the exocyclic double-bond reacts as a normal olefin. Reactions with hydrogen chloride, mercuric acetate, ozone, and carbene (produced from di-iodomethane and a zinc–copper couple) all lead to extensive decomposition of the diene complexes. These reagents probably attack the iron atom rather than the free double bond. Reaction of the complexes (IV) and (V) with *N*-bromosuccinimide did produce a small amount of material which was shown by mass spectroscopy to be a monobromo-substituted derivative. Unfortunately insufficient of this material was produced to determine the position of bromination.

Reaction of the cyclohexadienone complex with methyl α-bromopropionate and zinc gives the substituted hydroxy-ester (XII). Assuming that the nucleophile approaches the ketone group from the *exo*-side of the ring the alcohol (XII) will have an *endo*-hydroxy-group. This hydroxy-ester has two asymmetric centres and as non-optically active starting materials were used the product will contain two diastereoisomers.[16] The n.m.r. spectrum shows that two isomers are present in equal proportions. These alcohols could not be separated by chromatography but careful crystallisation from light petroleum gave a pure sample of one of the diastereoisomers.

Reaction of this diastereoisomer with trityl tetrafluoroborate gave the salt (XIII), which was shown by n.m.r. spectroscopy to be a single diastereoisomer. Deprotonation of this salt in water gave the complex (XIV) as a single isomer. If the mixture of diastereoisomers

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[15] R. H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, 1962, **27**, 1535.

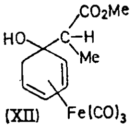
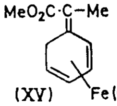
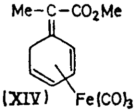
[16] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 20.

of the hydroxy-ester is used in these series of reactions both diastereoisomers of the salt (XIII) and both isomers (XV) and (XIV) are produced. N.m.r. data for these complexes are given in Tables 4 and 5.

In Tables 4 and 5, A and B refer to the two series of diastereoisomers; only the isomers marked B were isolated as pure compounds. The other compounds were made as mixtures of diastereoisomers

TABLE 4

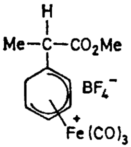
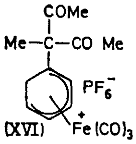
N.m.r. spectra in $CDCl_3$ at 60 MHz

Compound	Isomer	Inner protons	Outer protons	Methylene protons	Methyl protons	Ester protons	Tertiary hydrogen	OH
				Assignments *				
 (XII)	A	τ 4·65m	τ 7·10m	τ 8·20m	τ 8·83d J = 6 Hz	τ 6·35s	τ 7·80q J = 6 Hz	τ 6·75s
	B	τ 4·65m	τ 7·10m	τ 8·20m	τ 8·88d J = 7 Hz	τ 6·30s	τ 7·78q J = 7 Hz	τ 6·62s
 (XV)	A	τ 4·42m	τ 6·68m	τ 7·67m τ 7·32m	τ 8·16s	τ 6·40s		
 (XIV)	B	τ 4·42m	τ 4·95m τ 6·78m	τ 7·46m τ 7·68m	τ 8·32s	τ 6·33s		

* s = Singlet, m = multiplet, d = doublet, q = quartet, t = triplet.

TABLE 5

N.m.r. spectra at 60 MHz

Compound	Isomer	Dienyl protons	Methylene protons	Ester protons	Methyl protons	Tertiary hydrogen	COMe protons
				Assignments			
 (XIII) in SO_2	A	2·75m (1H) 4·10m (2H) 5·67m (1H)	7·52m 7·80m	6·23s	8·60d J = 7 Hz	6·82q J = 7 Hz	
	B	As above	As above	6·18s	8·71d J = 7 Hz	6·85q J = 7 Hz	
 (XVI) in $(CO_3)_2CO$	A	2·47t (1H) J = 5 Hz 3·80m (2H) 5·52m (1H)	7·90m *	6·06s	8·42s		7·75s
	B	As above	As above	6·18	8·14s		7·75s

* Partially obscured by solvent absorption.

Protonation of the complexes (XV) and (XIV) gives only the diastereoisomer of the salt from which the neutral complex was originally formed. This shows that the protonation and deprotonation reactions are stereospecific processes and that (XIV) and (XV) cannot be interconverted by protonation.

In contrast to the behaviour reported above for complexes (IV) and (V), treatment of the complexes (XIV) and (XV) with aluminium chloride and acetyl chloride in dichloromethane produced a yellow tetrachloroaluminate salt which was purified by dissolution in water and reprecipitation of the cation (XVI) as the pale yellow hexafluorophosphate. The i.r. spectrum of this complex has strong bands at 1756 and 1708 cm^{-1} which are assigned respectively to the ester and ketone carbonyl stretching frequencies. The instability of the related product from reactions of complexes (IV) and (V) may be correlated with the presence of electron-withdrawing acyl and ester groups and no compensating Me group.

Enol Reactions.—Although the six and seven-membered ring dienone complexes show similar behaviour with nucleophilic reagents, a study of the enol reactions of the complexes indicates a fundamental difference in their reactivity. Thus, tricarbonyl(cyclohepta-2,4-dienone)iron(VI) undergoes the Mannich reaction[17] with dimethylammonium chloride and paraformaldehyde to

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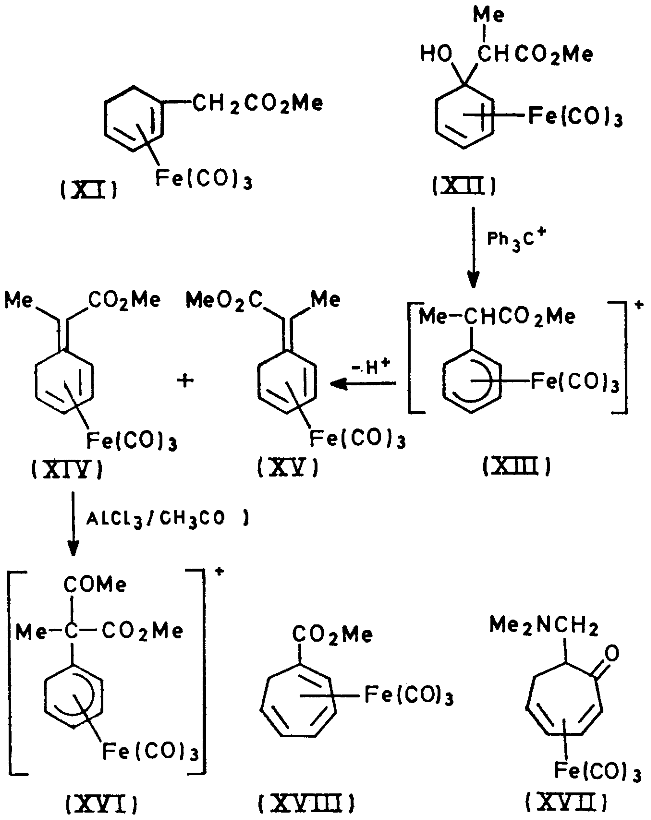
[17] F. F. Blicke, *Org. Reactions*, 1942, **1**, 303.

give the expected α-dimethylaminomethyl derivative (XVII), but we were unable to induce the six-membered ketone to undergo α-amino methylation. Several variations in the reaction conditions were tried in an attempt to force the cyclohexadienone complex to undergo the Mannich reaction, but without success. Under conditions which gave an 88% conversion with the seven-membered ring extensive decomposition occurred when the six-membered complex was used and we recovered only 20% of the starting material with no detectable α-aminomethylation.



(XI) (XII) (XIV) (XV) (XIII) (XVI) (XVIII) (XVII)

The Mannich base (XVII) can be sublimed *in vacuo*, and its n.m.r. spectrum shows a peak at τ 7·9 corresponding to the amine protons. The stretching frequency of the ketone is 1638 cm^{-1} compared with 1655 cm^{-1} in the starting material.

The Mannich reaction is generally considered to proceed by electrophilic attack on the enol of the ketone. We propose that the difference in reactivity is a consequence of the relative stabilities of the enol intermediates.

Formation of the enol of the six-membered complex would require a planar six-carbon-ring system. The hexadienone complex has been shown by *X*-ray crystallography [18] to have a folded ring system with the ketone group bent away from the iron atom. Thus enol formation with a planar ring conformation, would involve considerable rearrangement of the ring system; in contrast the co-ordinated seven-membered ring is much more flexible and enol formation may be attained without significant modification of the co-ordinated ring system. This change would thus not necessarily involve as much steric strain. In addition the enolic form of a seven-membered ring would be a cycloheptatriene complex and these compounds are well established.[19]

The ruthenium analogue of (I) has been prepared by a method similar to that used for the iron compound. The reaction of triruthenium dodecacarbonyl with 1-methoxycyclohexa-1,4-diene [20] was reinvestigated and the product found to contain a small amount (5%) of tricarbonyl (1-methoxycyclohexa-1,3-diene) ruthenium as well as the 2-substituted isomer. Reaction of the carbonyl with 1-methoxycyclohexa-1,3-diene produced the isomers in the same proportions. The reason why ruthenium preferentially reacts to give the 2-substituted isomer as the major product is not known. Reaction of the product with trityl tetrafluoroborate and subsequent hydrolysis of the tetrafluoroborate salt gave a low yield of tricarbonyl ruthenium cyclohexa-2,4-dienone.

EXPERIMENTAL

Tricarbonyl(cyclohepta-2,4-dienone)iron(0) (VI).—Tricarbonyl(cycloheptadienyl)iron fluoroborate [8] (10 g) was shaken with water (500 ml), 10% aqueous potassium hydrogen carbonate solution (50 ml), and ether (500 ml). The ethereal layer was separated and the aqueous phase was extracted with ether (3 × 150 ml). Concentration of the combined ethereal extracts gave an orange oil which was dissolved in pyridine (50 ml) and added to a mixture of chromium trioxide (5 g) in pyridine (50 ml). The mixture was stirred at room temperature for 15 h, and then diluted with ethyl acetate (200 ml). The solution was filtered through alumina, and washed with 2N-hydrochloric acid (4 × 200 ml) and then water (2 × 200 ml). The organic layer was dried ($MgSO_4$) and evaporated to give the *product*. Sublimation (60°/0·6 mmHg) gave analytically pure material (1·05 g, 14% from fluoroborate salt) [Found: C, 48·7; H, 3·4%; *M* (mass spectrometry), 248. Calc. for $C_{10}H_8FeO_4$: C, 48·8; H, 3·3%; *M*, 248]. After three sublimations the melting point of the ketone was 103—106° (sealed tube under nitrogen) (lit.,[5] 108—110°). The *dinitrophenylhydrazone* had m.p. 189—191° (lit., 190—192°) (Found: C, 44·8; H, 3·1; N, 13·0. Calc. for $C_{12}H_{12}FeN_4O_7$: C, 44·9; H, 2·8; N, 13·1%).

Tricarbonyl(1-*hydroxy*-1-*methoxycarbonylmethylcyclohexa*-2,4-*diene*)*iron*(0) (II).—Tricarbonyl(cyclohexa-2,4-dienone)iron (10 g, 43 mmol) was refluxed under nitrogen with activated zinc dust (12 g, 183 mmol) and methyl α-bromoacetate (10 ml, 109 mmol) in dry benzene (400 ml) for 4 h. The mixture was cooled to 0° and hydrolysed with 2N-sulphuric acid (200 ml). The benzene layer was dried ($MgSO_4$) and evaporated *in vacuo* to remove solvent and

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[18] O. S. Mills, personal communication.

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unchanged ester. The dark oil was transferred to a 85 × 3·5 cm column of silica (Whatman S. G. 31) made up in benzene. 6% Ethyl acetate–benzene (3 l) eluted the *product* (6·15 g, 74% yield, 62% conversion) during 2 h. Starting material (2·5 g) was recovered by elution with 20% ethyl acetate–benzene. Tricarbonyl(1-hydroxy-1-methoxycarbonylmethylcyclohexa-2,4-diene)iron forms pale yellow crystals, m.p. 59—60° (Found: C, 46·8; H, 3·9. $C_{12}H_{12}FeO_6$ requires C, 46·8; H, 3·9%). The mass spectrum shows a prominent peak at *m*/*e* 280, 28 below the molecular ion.

Tricarbonyl(1-*methoxycarbonylmethylcyclohexa*-2,4-*dienyl*)-*iron*(II) *Fluoroborate* (III).—Tricarbonyl(1-hydroxy-1-methoxycarbonylmethylcyclohexa-2,4-diene)iron (576 mg, 1·87 mmol) in dichloromethane (5 ml) was treated with trityl fluoroborate (621 mg, 1·88 mmol) in the same volume of solvent. The yellow precipitate of the *product* (503 mg, 71%) which formed with time was filtered off and washed with dichloromethane (Found: C, 37·8; H, 2·5. $C_{12}H_{11}BF_4FeO_5$ requires C, 38·1; H, 2·9%). The organic product from this reaction was identified as triphenylmethanol.

Tricarbonyl(cis-1-*methoxycarbonylmethylenecyclohexa*-2,4-*dienylidene*)*iron*(0) (IV).—Tricarbonyl(1-methoxycarbonylmethylcyclohexa-2,4-dienyl)iron(II) fluoroborate (204 mg) was warmed for 3 min on a steam-bath with water (25 ml). After cooling to room temperature, the solution was extracted with ether (25 ml) and the ether layer was washed with water (25 ml). Evaporation of the solvent *in vacuo* gave the *product* (153 mg, 98%) which was recrystallised from pentane to give orange-yellow crystals, m.p. 130—132° (Found: C, 49·8; H, 3·8. $C_{12}H_{10}FeO_5$ requires C, 49·7; H, 3·5%). The mass spectrum shows a prominent peak at *m*/*e* 234, 56 below the molecular ion.

Tricarbonyl(trans-1-*methoxycarbonylmethylenecyclohexa*-2,4-*dienylidene*)*iron*(0) (V).—Tricarbonyl(1-hydroxy-1-methoxycarbonylmethylcyclohexa-2,4-diene)iron(0) (430 mg) was dissolved in a small volume of toluene and the solution was run down a (2·5 × 40 cm) column of silica gel made up in toluene. The complex was eluted slowly with toluene, and two yellow bands were produced. The first fraction gave the *product* (190 mg) on evaporation and the second fraction yielded starting material (186 mg). The yield of dehydrated product is 47%, conversion 83%. The product was recrystallised from pentane to give lemon-yellow crystals (0·155 g), m.p. 86—88° (Found: C, 49·7; H, 3·45. $C_{12}H_{10}FeO_5$ requires C, 49·7; H, 3·5%). The mass spectrum shows a parent molecular ion at *m*/*e* 290 and the stepwise loss of three carbonyl groups.

Tricarbonyl(cis-1-*methoxycarbonylmethylenecyclohepta*-2,4-*dienylidene*)*iron*(0) (IX).—Tricarbonyl(1-methoxycarbonylmethylcyclohepta-2,4-dienyl)iron fluoroborate (0·5 g) was warmed with water (50 ml) on a steam-bath. On cooling to room temperature the solution was extracted with ether (50 ml) and the ether extract was dried and evaporated to give the *product* (354 mg, 91%) as a yellow oil, which gave crystals, m.p. 62—64° from pentane at −78° (Found: C, 51·0; H, 4·2. $C_{13}H_{12}FeO_5$ requires C, 51·3; H, 4·0%). The mass spectrum shows a strong molecular ion at *m*/*e* 304.

Tricarbonyl(1-*hydroxy*-1-*methoxycarbonylmethylcyclohepta*-2,4-*diene*)*iron*(0) (VII).—This compound was prepared using the same conditions as described above for tricarbonyl(1-hydroxy-1-methoxycarbonylmethylcyclohexa-2,4-diene)iron; it formed pale yellow crystals, m.p. 73·5—75° (Found: C, 48·7; H, 4·5. $C_{13}H_{14}FeO_6$ requires C, 48·5; H, 4·4%). The mass spectrum shows a prominent peak at *m*/*e* 294, 28 below the molecular ion.

Tricarbonyl(1-*methoxycarbonylmethylcyclohepta*-2,4-*dienyl*)*iron*(II) *Fluoroborate* (VIII).—This compound was prepared in a manner similar to that used for tricarbonyl-1-methoxycarbonylmethylcyclohexa-2,4-dienyl)iron fluoroborate (Found: C, 40·0; H, 3·4. $C_{13}H_{13}BF_4FeO_5$ requires C, 39·8; H, 3·3%).

Tricarbonyl(1-*methoxycarbonylmethylcyclohexa*-1,3-*diene*)-*iron*(0).—Tricarbonyl(1-methoxycarbonylmethylcyclohexa-2,4-dienyl)iron(II) fluoroborate (330 mg) was added to a solution of sodium borohydride (200 mg) in water (15 ml) at 0 °C and the mixture was stirred for 15 min. The resultant suspension was extracted with ether (2 × 20 ml) and the ether extracts were dried ($MgSO_4$). Evaporation to dryness gave a yellow oil which darkened on exposure to the air. The oil was distilled *in vacuo* (0·01 mmHg at 60 °C) to give the *product* (194 mg, 76%) as a pale yellow liquid (Found: C, 49·5; H, 4·14. $C_{12}H_{12}FeO_5$ requires C, 49·3; H, 4·11%). The mass spectrum shows a parent molecular ion at *m*/*e* 292, the stepwise loss of three carbonyl groups and fragments of the ester group.

Displacement of Organic Ligand from either cis- *or* trans-*Isomers of Tricarbonyl*(1-*methoxycarbonylmethylenecyclohexa*-2,4-*dienylidene*)*iron*(0).—The complex (355 mg) in ethanol (10 ml) was treated with an excess of ceric ammonium nitrate in ethanol–water. The mixture was stirred for 1 h at room temperature and then diluted with water (100 ml). The solution was then extracted with ether (2 × 25 ml). The ether extracts were washed with water, dried ($MgSO_4$) and evaporated to give a colourless oil (136 mg, 70%) which was identified as methyl phenyl acetate by comparison of its i.r., n.m.r., and mass spectra with those of an authentic sample.

Tricarbonyl-1-*hydroxy*-1-(α-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dieneiron*(0) (XII).—Tricarbonylcyclohexa-2,4-dienoneiron (2 g) was heated under reflux with zinc powder (2·4 g) and methyl α-bromopropionate (2 ml) in benzene (70 ml) for 4 h with stirring. The mixture was cooled to 0 °C and sulphuric acid (40 ml; 2N) was then added to it. The organic layer was separated, dried ($MgSO_4$) and evaporated to give a brown oil. Chromatography on a silica-gel column using toluene–ethyl acetate (16 : 1) as eluant gave the *product* as a yellow oil (1·79 g, 65%). The i.r. spectrum has ν(OH) 3480 cm^{-1} and a band at 1720 cm^{-1} due to the ester carbonyl group. Pale yellow crystals (m.p. 88—89°) of one of the diastereoisomers were obtained by crystallisation of the oil from light petroleum (b.p. 40—60°) in a refrigerator (Found: C, 48·7; H, 4·55. $C_{13}H_{14}FeO_6$ requires C, 48·5; H, 4·35%). The mass spectrum shows a prominent peak at *m*/*e* 294 due to the loss of carbon monoxide from the parent molecular ion.

Tricarbonyl-1-(α-*methoxycarbonylethyl*)*cyclohexadienyliron*(II) *Tetrafluoroborate* (XIII).—Tricarbonyl-1-hydroxy-1-(α-methoxycarbonylethyl)cyclohexa-2,4-dieneiron(0) (1·76 g) was dissolved in dichloromethane (10 ml) and trityl tetrafluoroborate (1·9 g, 1·1 molar equiv.) in 10 ml of the same solvent was added. The mixture was shaken for 0·5 h and ether (100 ml) was then added to precipitate the yellow solid; this was filtered off and washed with ether and dried to give the *product* (1·98 g, 93%) (Found: C, 39·8; H, 3·4. $C_{13}H_{13}FeO_5BF_4$ requires C, 39·8; H, 3·32%).

Tricarbonyl-cis- *and* trans-1-(α-*methoxycarbonylethylidene*)-*cyclohexa*-2,4-*dienylideneiron*(0) (XIV) and (XV).—Tricarbonyl-1-(α-methoxycarbonylethyl)cyclohexadienyliron-

(II) tetrafluoroborate (1·6 g) was suspended in water (150 ml) and heated on a steam-bath for 5 min. The mixture was cooled to room temperature and extracted with ether (3 × 40 ml); the ether extracts were dried ($MgSO_4$). Evaporation and recrystallisation of the residue from light petroleum (b.p. 60—80) gave the *product* as a yellow solid (m.p. 65—75°) (0·94 g, 76%). These two isomers could not be separated by chromatography or recrystallisation (Found: C, 51·3; H, 4·15. $C_{13}H_{12}FeO_5$ requires C, 51·3; H, 3·95%). If the crystals of one diastereoisomer of the hydroxy-ester are used in the last two reactions the *cis*-isomer (m.p. 67—70°) of the above product is obtained.

Tricarbonyl-1-(*α-acetyl-α-methoxycarbonylethyl*)*cyclohexadienyliron*(II) *Hexafluorophosphate* (XVI).—Tricarbonyl-1-(α-methoxycarbonylethylidene)cyclohexa-2,4-dienylideneiron(0) (400 mg) was dissolved in dichloromethane (10 ml) and added dropwise to a stirred solution of aluminium chloride (1·5 g) and acetyl chloride (1 ml) in the same solvent (15 ml) at 0°. The mixture was stirred for 0·5 h at 0°; the yellow precipitate was filtered off and dissolved in water (50 ml). The aqueous solution was washed with ether and 15% ammonium hexafluorophosphate solution (10 ml) was added to it. The precipitate was stirred for 5 min and was then filtered off and washed with water and ether to give the *product* as a pale yellow solid (401 mg, 63%) (Found: C, 36·6; H, 3·21. $C_{15}H_{15}FeO_6PF_6$ requires C, 36·6; H, 3·06%).

Tricarbonyl(*7-dimethylaminomethylcyclohepta*-2,4-*dienone*)-*iron*(0) (XVII).—Tricarbonyl(cyclohepta-2,4-dienone)iron (496 mg, 2 mmol) was refluxed with dimethylammonium chloride (1·3 g, 16 mmol) and paraformaldehyde (500 mg, 17 mmol) in ethanol (25 ml) for 15 h under nitrogen. After cooling to 0° water (50 ml) was added to the solution which was then extracted with ether (4 × 50 ml). The ether extracts were combined, dried, and evaporated to give the starting material (347 mg); the aqueous layer was basified with sodium hydroxide and again extracted with ether (3 × 50 ml). The extracts were evaporated to give the *product* (162 mg, 27% yield, 88% conversion) which was sublimed twice (60°/0·5 mmHg) to give yellow crystals, m.p. 109—112° (Found: C, 51·3; H, 5·0; N, 4·7. $C_{13}H_{15}FeNO_4$ requires C, 51·2; H, 5·0; N, 4·6%). The mass spectrum shows a prominent peak at *m/e* 267, 28 below the molecular ion.

Reactions of Ketones (I) *and* (VI) *with Organo-lithium and Grignard Reagents*.—The ketone (I) (2 mmol) was stirred for 1 h with the appropriate alkyl-lithium (1 or 4 mmol) or Grignard reagent (RMgX) (1 or 4 mmol) in ether at 0°. After hydrolysis of the solution no identifiable products were obtained.

Tricarbonylcyclohexa-2,4-*dienoneruthenium*(0).—A solution of 1-methoxycyclohexa-1,3-diene (6 ml) and triruthenium dodecacarbonyl (1·0 g) in benzene (60 ml) was heated under reflux for 19 h. The resultant brown solution was filtered through alumina and evaporated *in vacuo* to give a brown oil. Chromatography on silica gel did not completely separate the isomers but the first part of the eluate gave a yellow oil (0·185 g) which was shown to be a mixture of the 1- and 2-methoxy-complexes in the ratio of 1 : 2. The total yield of diene complexes was 1·062 g (70%). Treatment of the mixture of 1- and 2-methoxy-complexes in dichloromethane (2 ml) with trityl tetrafluoroborate (0·205 g, 1 molar quantity) in 3 ml of the same solvent gave a white dienyl salt which was precipitated by addition of ether (10 ml). The salt was filtered off, suspended in water (10 ml) and the solution was heated on a steam-bath for 10 min. The resultant mixture was extracted with ether (2 × 5 ml) and the combined ether extracts were dried to give a white solid. Sublimation of this solid (30° at 0·01 mmHg) gave the cyclohexadienone complex (0·012 g) [0·8% overall from $Ru_3(CO)_{12}$] (Found: C, 38·5; H, 2·45. $C_9H_6RuO_4$ requires C, 38·80; H, 2·15%). The mass spectrum shows a parent molecular ion at *m/e* 280 (^{102}Ru) with the expected Ru isotope pattern, and peaks due to the stepwise loss of three carbonyl groups. The i.r. spectrum (in Nujol) is very similar to that of the iron compound and has metal carbonyl bands at 2075 and 1995 cm^{-1} and a ketone stretching frequency at 1652 cm^{-1}.

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