

ORGANOMETALLIC STUDIES

XVI*. IRON π -COMPLEXES OF β -IONONE AND OTHER MODEL COMPOUNDS FOR VITAMIN A**.*.*.*

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INTRODUCTION

The reinvestigation by Hallam and Pauson³ of butadieneiron tricarbonyl has prompted a number of workers to investigate the generality of the reaction of dienes with iron carbonyls****. We have been particularly interested in studying the reaction between iron carbonyls and conjugated dienes substituted with various functional groups in order to assess the effect of such groups on the complexing properties of the dienes. This was to be the first stage in a wider program aimed at the eventual synthesis and characterization of metal π -complexes of suitably unsaturated natural products.

This communication reports the results of our investigation of the synthesis of iron complexes of substituted conjugated dienes and trienes which have been chosen as suitable model compounds for a study of Vitamin A metal complexes.

RESULTS AND DISCUSSION

At the start of this project, Stone and coworkers had reported⁵ that the reaction between iron dodecacarbonyl and several sorbic acid derivatives had produced, as expected, diene-Fe(CO)₃ complexes. However, those authors had failed to isolate the complex of the parent compound, sorbic acid, and no yields were reported for several of the other reactions⁵. It seemed appropriate to us to reinvestigate some of these reactions in particular since we had observed⁶ that the use of more polar solvents, such as di-*n*-butyl ether instead of hydrocarbon solvents has a beneficial effect on the yields of the reaction between dienes and iron pentacarbonyl. Thus we were able to obtain up to 59% yields of the sorbic acid complex (Ia), whereas Stone *et al.*⁵ had reported the formation of only polymeric material in the attempted preparation of this compound.

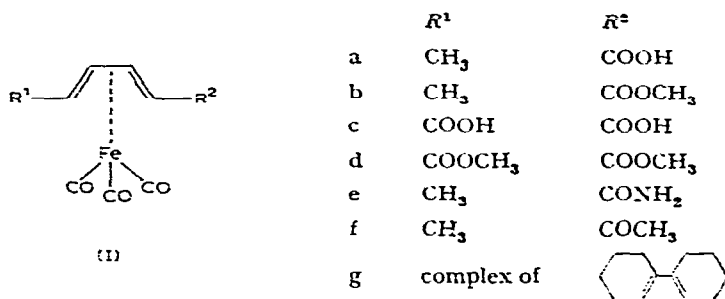
The yields for the other dieneiron tricarbonyl complexes (Ia)-(Ig) are given in Table I.

* Part XV, see ref. 1.

** A preliminary communication² has appeared.

*** This work has been supported by a P.L. 480 research grant, U.S.D.A. Project UR-A10-(40)-34.

**** For a recent review see ref. 4.

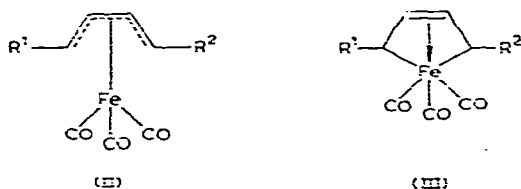


In an attempt to learn something about factors affecting the yields of these reactions a number of runs were carried out using Lewis acids such as boron trifluoride and anhydrous aluminum chlorides as catalysts. The reactions were carried out in sets of three, one reaction in the set without catalyst and the other two reactions, each with the addition of one of the Lewis acids mentioned. The three reactions in each set were carried out simultaneously under identical conditions of reflux time and temperature. Similarly the work up in isolating the reaction product was the same for each reaction. The results, summarized in Table 2, show that the yields of the reactions involving diene carboxylic esters are noticeably affected by the presence of Lewis acid catalysts. On the other hand the yields of diene carboxylic acid complexes are practically the same with or without catalysts.

It would be premature to speculate on the role, if any, of Lewis acid catalysts in these reactions. It is always dangerous to draw conclusions merely on the basis of reaction yields and further investigations are necessary to study these results.

The infrared and ultraviolet spectral data for the complexes (Ia)–(Ig) and their parent non-complexed conjugated dienes are compared in Table 3.

These data require several comments in connection with the controversy as to whether (II) or (III) is the best representation of dieneiron tricarbonyl complexes^{4,7-9}.



The suggestion by Wilkinson and coworkers⁷ that the NMR data are compatible with structure (III) has found support from other workers both on the basis of NMR⁸⁻⁹ and X-ray studies¹⁰⁻¹¹. Structure (II) has been found more compatible with infrared data⁷ as well as with the results of X-ray studies¹². A recent note¹³ on the ultraviolet spectra of two cobalt cyclopentadienyl complexes of cyclopentadienone derivatives states that even though there might be a small degree of localization in the metal-dienone interactions and partial rehybridization of the relevant carbon atoms, the combined effects of ring deformation and bond localization do not cause a sufficient loss of conjugation in the dienone ring as to justify the exclusive use of valence bond formulas such as depicted in (III).

TABLE I
 SUBSTITUTED BIENES - IRON TRICARBONYL COMPLEXES

Compound Formula	M. p. or (B. p./mm Hg) (°C)	Yield ^b (%)	Carbon (%)		Hydrogen (%)		Iron (%)		Mol. wt.	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found ^d
(1a) $(\text{CH}_3\text{C}_4\text{H}_4\text{COOH})\text{Fe}(\text{CO})_3$	18.2 (dec.)	59	42.89	43.20	3.20	3.31	22.16	22.06	252	252
(1b) $(\text{CH}_3\text{C}_4\text{H}_4\text{COOCH}_3)\text{Fe}(\text{CO})_3$	27	33	45.15	45.36	3.79	3.68			266	275
(1c) $(\text{COOH}\text{C}_4\text{H}_4\text{COOH})\text{Fe}(\text{CO})_3$	300 (dec.)	65	38.30	38.32	2.15	2.13	19.80	20.02	282	282
(1d) $(\text{COOCH}_3\text{C}_4\text{H}_4\text{COOCH}_3)\text{-Fe}(\text{CO})_3$	78 (dec.)	24	42.60	42.84	3.48	3.46	18.00	17.96	310	310
(1e) $(\text{CH}_3\text{C}_4\text{H}_4\text{CONH}_2)\text{Fe}(\text{CO})_3$	132-134 ^b	21							251	251
(1f) $(\text{CH}_3\text{C}_4\text{H}_4\text{COCH}_3)\text{Fe}(\text{CO})_3$	(80/o.1) ^c	53								
(1g) (Bicyclohexenyl) $\text{Fe}(\text{CO})_3$	(110/o.1)	66	59.58	59.77	6.00	6.09				

^a After chromatographic purification. ^b Lit.⁵ m.p. 132-134°. ^c Lit.⁵ m.p. 31-33°. ^d First column, cryoscopic method data; second column, mass spectrometry data.

TABLE 2

EFFECT OF CATALYSTS ON REACTION OF DIENES WITH IRON PENTACARBONYL^a

Reaction product	Reflux time (h)	Catalyst ^b	Yield (%)
(Ia) (CH ₃ C ₄ H ₄ COOH)Fe(CO) ₃	8	—	59.0
	8	A	61.0
	8	B	61.7
(Ib) (CH ₃ C ₄ H ₄ COOCH ₃)Fe(CO) ₃	8	—	42.6
	8	B	61.6
(Ic) (COOHC ₄ H ₄ COOH)Fe(CO) ₃	7	—	39.6
	7	A	42.7
	7	B	38.9
(Ic) (COOHC ₄ H ₄ COOH)Fe(CO) ₃	8	—	41.2
	8	A ^c	46.5
	8	B ^c	0
(Id) (COOCH ₃ C ₄ H ₄ COOCH ₃)Fe(CO) ₃	24	—	6.6
	24	A	32.4
	24	B	18.2
(Ie) (CH ₃ C ₄ H ₄ CONH ₂)Fe(CO) ₃	24	—	27
	24	A	27
(If) (CH ₃ C ₄ H ₄ COCH ₃)Fe(CO) ₃	24	—	44.3
	24	A	53.2
	24	B	49.2

^a The ratio diene: iron pentacarbonyl = 1:1.1 equiv. in di-*n*-butylether as solvent. ^b A = BF₃ etherate; B = AlCl₃ (anhydrous); each 5% by weight. ^c 1.1 equivalents.

TABLE 3

INFRARED AND ULTRAVIOLET SPECTRA OF CONJUGATED DIENES AND THEIR -Fe(CO)₃ COMPLEXES

Compound	$\nu_{C=O}$ (cm ⁻¹) ^a	$\nu_{C=O}$ (cm ⁻¹) ^a	λ_{max} (log ϵ) ^b (m μ)
Sorbic acid	—	1690	254 (4.40) ^c
(Ia)	2100 2050	1690	206 (4.26), 228 (4.23), 240 (4.11) ^d , 300 (3.38)
Methyl sorbate	—	1725	258 (4.50) ^c
(Ib)	2100 2050	1725	202 (4.31), 228 (4.19), 240 (4.11), 300 (3.27)
Muconic acid	—	1690	259 (4.43) ^c
(Ic)	2100 2050	1690	206 (4.27), 229 (4.29), 240 (4.20) ^d , 303 (3.54)
Dimethyl muconate	—	1725	259 (4.56), 265 (4.53) ^c
(Id)	2100 2050	1725	202 (4.39), 228 (4.40), 240 (4.31) ^d , 303 (3.52)
Sorbamide	—	1660	251 (4.44), 257 (4.44) ^c
(Ie)	2070 1970	1660	207 (4.34), 234 (4.19), 300 (3.31)
Sorbyl ketone	—	1660	270 (4.40) ^c
(If)	2070 1970	1660	202 (4.41), 225 (4.27), 250 (4.16), 310 (3.53)
Bicyclohexenyl	—	—	238 (4.26) ^c
(Ig)	2050 2000	—	202 (4.25), 229 (4.13), 240 (4.07) ^d , 290 (3.25) ^d

^a All spectra were measured in CHCl₃ solution [except (Ic), in KBr pellets] on Perkin-Elmer Infracord 137 spectrophotometer. ^b All spectra were measured in C₂H₅OH solution on Carry Model 14 recording spectrophotometer. ^c See ref. 18. ^d Inflexion points.

We should like to come out in support of this latter statement on the basis of the infrared and ultraviolet spectral data presented in Table 3.

The position of the carboxyl, carboxylate or ketonic carbonyl absorption in the infrared spectrum remains the same in both the parent diene and the $\text{Fe}(\text{CO})_3$ complex. It is hard to explain why formation of a Diels-Alder type adduct, as depicted in (III), which would take these carbonyl groups out of conjugation with the carbon-carbon double bonds should leave the position of the carbonyl absorption unchanged.

In a study of the ultraviolet spectra of organometallic compounds several years ago, Lundquist and Cais¹⁴ observed that all compounds containing a metal carbonyl moiety exhibit a highly intense end absorption at about 214 $m\mu$ (the limit of the instrument used). In the present study the spectra were measured down to 195 $m\mu$ and highly intense well defined maxima were observed for all the dieneiron tricarbonyl derivatives in the region 202-206 $m\mu$. The nature of these bands, together with that of the relatively lower intensity bands observed in the region 300-310 $m\mu$ could be described as metal-to-ligand charge transfer bands. This assignment is made by analogy to the assignment by Gray and Beach¹⁵, of the bands at 225 and 280 $m\mu$ of chromium hexacarbonyl to charge transfer bands of the metal-to-ligand type. Qualitatively, it would appear that the two additional absorption bands at 228 and 240 $m\mu$ observed for the dieneiron tricarbonyl derivatives are of the type of π - π^* transitions of the conjugated diene system (which in the free dienes absorb around 259 $m\mu$ with an intensity of about $\epsilon = 25,000$). This hypsochromic shift, and in particular the hypsochromic change in intensity ($\epsilon = 12,000$ -15,000) observed in the dieneiron tricarbonyl complexes might be due to a change from the *s-trans* conformation in the free diene to the *s-cis* conformation (and accompanying skewing effects, *vide infra*) in the metal complexes.

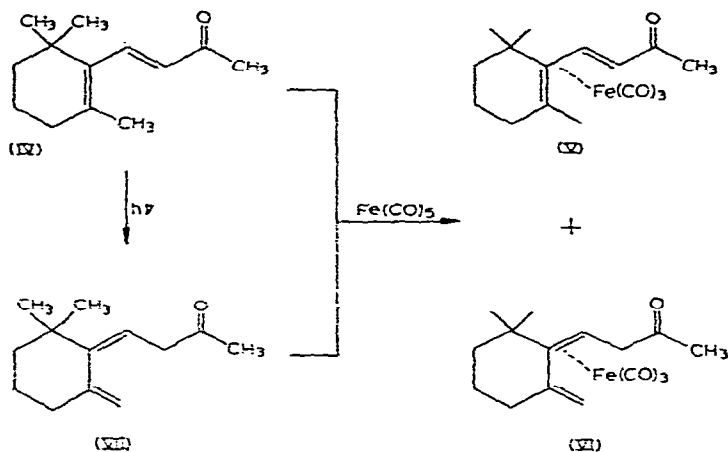
On the basis of this interpretation we suggest that the π -electron systems of the diene moiety in the $\text{Fe}(\text{CO})_3$ complexes do not appear to be changed in the manner that would be required by a structure such as (III). In this connection, it is noteworthy that from a recent study¹⁷ of the electronic absorption spectra of complexes of the types $\text{LM}(\text{C}_5\text{H}_5)$ and $\text{LM}(\text{CO})_2$, with L being a derivative of a quinone, cyclopentadienone or thiophene dioxide and $\text{M} = \text{Co}$, Fe or Ni , the authors¹⁷ conclude that the π -electron systems of the above ligands are only weakly perturbed by the interactions of the metals and they find that the number and position of the bands observed are in accord with the qualitative predictions which can be made by applying simple LCAO-MO theory to the bonding in these complexes.

The next reaction to be investigated was that between β -ionone, (IV), and iron carbonyls. From the reaction of (IV) with $\text{Fe}(\text{CO})_5$, in di-*n*-butylether as solvent two iron complexes could be isolated, to which structures (V) and (VI) were assigned on the basis of their ultraviolet, infrared and NMR spectra.

If the crude reaction product was chromatographed immediately, the complex (V) was the main, and sometimes only, π -iron tricarbonyl derivatives. If the crude reaction product was allowed to stand overnight at room temperature, before chromatography, complex (VI) was isolated in addition to (V), the ratio between the two isomers varying according to the conditions of the work up.

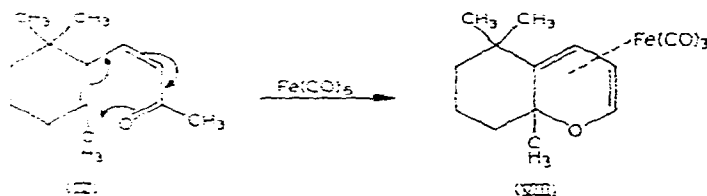
The known fact¹⁹⁻²² that upon irradiation, β -ionone rearranges to the isomer (VII), (hereafter called *exo*-ionone) enabled us to seek an independent proof for the structure of complex (VI). From the reaction of *exo*-ionone (VII) with $\text{Fe}(\text{CO})_5$, under

conditions similar to those used for β -ionone, the same two complexes (V) and (VI) could be isolated.



In addition to the complexes (V) and (VI), which showed ketonic carbonyl absorption bands at 1670 and 1720 cm^{-1} respectively, a third complex was isolated in these reactions which displayed terminal carbonyl absorption bands in the 2000 cm^{-1} region but no ketonic carbonyl bands in the region $1720\text{--}1670\text{ cm}^{-1}$.

This could be the iron tricarbonyl complex (VIII) of the cyclic ether arising from cyclization of β -ionone¹⁹⁻²².

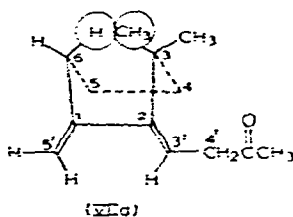
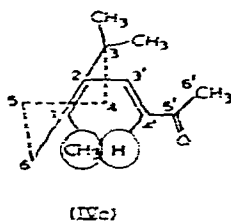


In view of the reported^{4, 23-24} ability of iron pentacarbonyl to cause both geometric and positional isomerization of double bonds, the isomerization $(\text{IV}) \rightleftharpoons (\text{VII})$ caused by $\text{Fe}(\text{CO})_5$ may not be entirely surprising even though formation of complex (VI) means taking the diene system of (IV) out of conjugation with the ketonic carbonyl of the side chain of β -ionone. However, a few structural considerations about β -ionone, (IV) and its isomer (VII), may lead to some doubts as to the ease of formation of the two complexes (V) and (VI) and to their likely stability once formed.

It has become rather well accepted that in order to form a dieneiron tricarbonyl complex, the diene system must be capable of conversion into the coplanar, *s-cis* conformation⁴.

Furthermore, the planarity of the cisoid butadiene ligand in butadieneiron tricarbonyl has been confirmed by X-rays¹² studies. On the other hand in the fully planar *s-cis*-butadiene, the H atoms at C-1 and C-4 are in bad steric interaction and since the diene system can be skewed away from the planar *s-cis* conformation by a considerable angle without there being an excessive loss of conjugation, it has been

questioned²⁵, whether the *s-cis* rather than a skew arrangement corresponds to the metastable energy minimum for the cisoid conformer. A simple MO Hückel calculation* for butadiene shows that for a twist angle $\gamma = 20^\circ$ around the $C_{(2)}-C_{(3)}$ bond there is a loss of only about 9% in π -electrons delocalization energy. Even for $\gamma = 40^\circ$ the loss in delocalization energy is less than 35%. With this in mind, one might perhaps inquire to what extent, if any, is there twisting around the essential single bond in butadieneiron tricarbonyl and analogous compounds? Or, to put the question in a different way, what is the maximum possible angle of deviation (twist) from the planar *s-cis* conformation, which would still allow for the formation and existence of stable dieneiron tricarbonyl complexes?



We would like to suggest that the varying degrees of twisting around the essential single bond, due to molecular overcrowding, which may be present in butadieneiron tricarbonyl and analogous compounds, could be one of the important factors governing the stability of such complexes.

Dreiding models of (IV) show that in the *s-cis* conformation, (IVa), full coplanarity of carbon atoms C-1, C-2, C-3' and C-4' would bring the H atoms of the methyl group on C-1 and the H-atom on C-4' into very close proximity ($\sim 0.77 \text{ \AA}$), much nearer than the sum of the van der Waals radii of two hydrogens ($\sim 2.4 \text{ \AA}$).

It is hard to envisage that such a situation, namely full coplanarity of carbon atoms 1, 2, 3' and 4', would prevail in the corresponding $\text{Fe}(\text{CO})_3$ complex, (V).

Molecular overcrowding and the implicit tendency to release the steric strain through twisting around the essential single bond, and thus deviation from coplanarity would account for the instability of the complex (V).

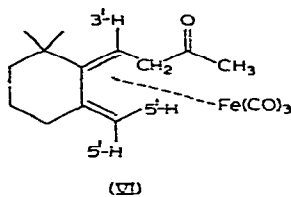
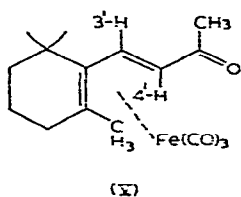
Dreiding models of *exo*-ionone, (VII), show that full coplanarity for the two exocyclic double bonds is possible only with the cyclohexane ring in the boat conformation, (VIIa). Some release from the 1-4 interactions between the CH_3 -group at C-3 and the H-atom at C-6 can be arrived at by changing the conformation to a twisted boat, though this is followed by some deviation from planarity of the diene system. The chair conformation, though preferable for the cyclohexane ring, appears to cause a rather large deviation from the coplanarity of the two exocyclic double bonds. For this reason, the twisted boat might be the required conformation of the cyclohexane ring in the $\text{Fe}(\text{CO})_3$ complex, (VI), though the other conformations cannot be excluded. However, since all these three possible conformations for (VI) would exhibit various degrees of intramolecular steric hindrance or twisting of bonds, one would expect an unstable complex which easily reverts back to the metal-free organic parent compound.

This is indeed the case and both (V) and (VI) are stable for longer periods of time *only* if kept at temperatures below 5° .

* Details for this and other MO calculations will be given in a future publication.

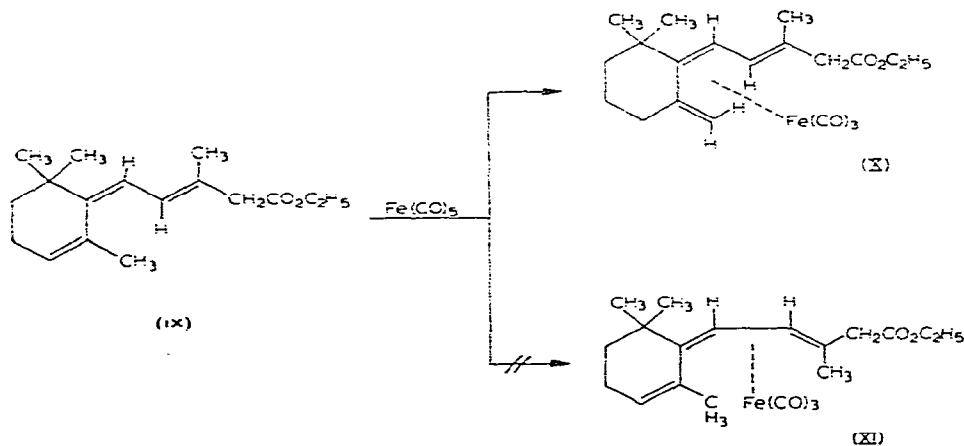
The NMR spectrum supports the assignment of structures (V) and (VI), respectively, to the two complexes. Assignments could be made by consideration only of the vinyl protons region between τ 2-4.

The two vinyl protons of β -ionone appear at τ 2.61 (4'-H) and 3.75 (3'-H). The remaining eighteen protons appear in the region τ 7.75-9.12 and the rather complicated spectrum makes it difficult to attempt a detailed assignment. In the complex (V) the vinyl hydrogen 4'-H becomes a "terminal" proton and would be expected to be shifted to higher fields, in the alkyl region⁴. Indeed, the NMR spectrum of (V) shows



only the "central" vinyl proton 3'-H as a doublet centred at τ 3.76. All other proton signals appear in the region τ 7.78-9.12, with an absorption pattern very similar to that in β -ionone. On the other hand, in complex (VI), all three vinyl protons, one 3'-H and two 5'-H are "terminal" hydrogens and would be expected to absorb in the high field region. Indeed, the NMR spectrum of (VI) shows no proton signals in the region τ 2-4 and all the absorption bands appear between τ 7.5-9.1. The absorption pattern in this region is quite different from that of either β -ionone, (IV), or the complex (V).

The next reaction to be investigated was that between *retro*-ionylidene acetate, (IX)²⁶⁻²⁷, and iron pentacarbonyl. Repeated chromatography of the reaction product allowed for the isolation of only one metal complex to which we assign structure (X).



The alternative possible structure, (XI), is not compatible with the spectral data.

The ultraviolet absorption band of (IX) (λ_{max} 284 $m\mu$, $\epsilon \sim 13,000$), which is typical of an all-*trans*-conjugated triene, undergoes a strong hypsochromic shift in the metal complex (λ_{max} 240 $m\mu$, $\epsilon \sim 15,000$). Although this shift to shorter wavelength could be explained as due to the formation of the *cis*-isomer as depicted in

(XI), the observed hyperchromic change in intensity would not be expected for such a structural change. This result would be more compatible with structure (X) in which the conjugation of the diene system of the *exo*-ionone complex, (VI), (λ_{max} 225, $\epsilon \sim 7900$) has been extended by the addition of a third double bond, and hence both the bathochromic and hyperchromic changes [compared to (VI)].

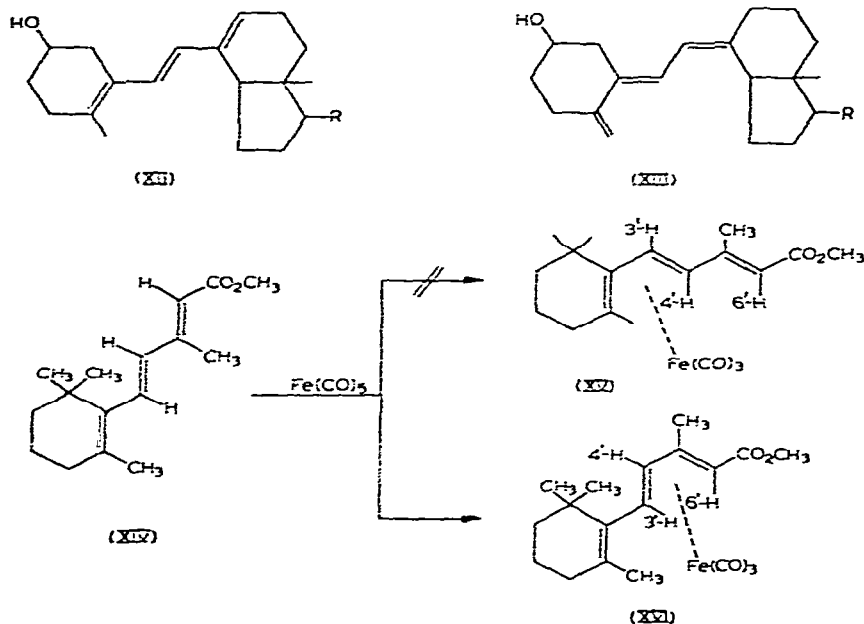
The NMR spectrum of the metal complex provides additional evidence in favour of structure (X). In the spectrum of the parent compound, (IX), it is possible to distinguish in the complex of bands in the region τ 7.5–9.3, two singlets at τ 7.96 and 8.15 due to the two CH_3 groups on the vinyl carbon atoms. In addition, the spectrum exhibits a quartet centred at τ 5.92, assigned to the CH_2 of the ester ethyl group, and a doublet at τ 6.97 assigned to the CH_2 in the α -position to the carboxylate group. The three vinyl protons are observed as doublets at τ 3.50, 3.83 and 4.38.

The spectrum of the metal complex shows the disappearance of the singlet vinyl-substituted CH_3 group at τ 8.15 and the second vinyl-substituted CH_3 group shifted slightly to lower field, at τ 7.80. The quartet of the CH_2 group of the ester ethyl group is practically unchanged (at τ 5.96) and of the vinyl protons the ones at τ 3.83 and τ 3.50 are absent. Only one vinyl proton appears to be present at τ 4.75.

In structure (X) all three vinyl hydrogens on the metal complex diene system are "terminal" protons and would be expected to absorb in the high-field alkyl region. There would be only one vinyl substituted CH_3 group and trans to it one vinyl hydrogen.

The relative intensities of the region τ 4–6 and τ 7–9.5 should be 2:23 in structure (X) and 5:21 in structure (XI). The experimental ratio observed was 2:22.5.

Final evidence for structure (X) was obtained when the complex was decomposed with a saturated alcoholic ferric chloride solution²⁴. The ultraviolet spectrum of the decomposition product exhibited the longest wavelength absorption at 269 $m\mu$ (log



ϵ 3.93). This is a large hypsochromic shift compared to the maximum (284 $m\mu$) of the starting material (IX). Furthermore this shift is what one would expect changing from the all-transoid triene system (IX) to the cisoid-transoid triene system present in (X) by analogy to the reported^{16,28} hypsochromic shift on going from tachysterol, (XII), (λ_{max} 280 $m\mu$) to vitamin D₂, (XIII) (λ_{max} 265 $m\mu$).

The next compound to be studied as model for Vitamin A, was β -ionylidene acetate²⁹, (XIV). From the reaction of the latter with iron pentacarbonyl only one metal complex could be isolated in 46% yield. Decomposition of this complex with FeCl₃ gave back the starting material (XIV) and on the basis of this evidence that no isomerization of the double bonds had taken place during the reaction with Fe(CO)₅ only structures (XV) and (XVI) had to be considered for the metal complex isolated in the reaction. The spectroscopic evidence seems to favour structure (XVI) for the following reasons: The NMR spectrum of the complex shows, in addition to the high field (τ 7.2-9.7) absorptions, two signals at 4.3 (vinyl H) and 6.4 (CH₃O) with relative intensities in the ratio 1:3. Structure (XV) has one "terminal" vinyl proton (4'-H which should absorb at high fields) one "central" vinyl proton, 3'-H and a third vinyl proton 6'-H. Therefore the absorption intensity ratio of the vinyl protons ($\tau \sim 4$) relative to the -OCH₃ protons (τ 6.4) should be 2:3. On the other hand structure (XVI) would have two "terminal" vinyl protons (3'-H and 6'-H) absorbing at high fields and only one "central" vinyl proton (4'-H) absorbing in the τ 4 region. In other words, the relative intensity ratio of the absorption at τ 4: τ 6 should be 1:3. As stated above, this is what has been observed experimentally.

The changes in the ultraviolet spectrum from λ_{max} 260 and 304 $m\mu$ (log ϵ 4.08 and 4.09 respectively) in the metal-free compound (XIV) to λ_{max} 245 and 320 $m\mu$ (log ϵ 4.23 and 3.82 respectively) in the complex are similar to the changes observed in going from methyl sorbate to its complex (Ib) (*vide supra*).

The same analogy between (XIV) and (XVI) on one hand and methyl sorbate and (Ib) on the other applies to various structural features observed in the respective infrared spectra, which is further evidence in support of structure (XVI). The mass spectra of all the complexes reported in this communication showed the expected³⁰ stepwise loss of the carbon monoxide groups. A detailed analysis of these spectra will be presented in a separate communication³¹. Similarly, the results of the reaction between vitamin A and iron carbonyls will be presented in a forthcoming publication.

EXPERIMENTAL

The infrared spectra were measured in chloroform solution on a Perkin-Elmer Infracord Model 137 spectrophotometer. The ultraviolet spectra were measured in ethanol solution on a Carry Model 14 recording spectrophotometer. The NMR spectra were measured on Varian Model A 60 spectrometer with tetramethylsilane as internal standard. The mass spectra were recorded on a type Atlas CH 4 mass spectrometer. Ionisation energy was maintained at 70 eV and the ionisation current at 20 μ A.

(1) Synthesis of the dieneiron tricarbonyl complexes (Ia)-(Ig)

The general procedure for the synthesis of the metal complexes collected in Table I consisted in refluxing together the diene (1 mole) and iron pentacarbonyl (1.1-1.5 moles) in peroxide-free di-*n*-butyl ether in an inert atmosphere for 8-12 h. After

removing the solvent by distillation in vacuum, the crude reaction products were purified by chromatography on either alumina or silica gel. The purity of the compounds was determined by means of thin-layer chromatography (t.l.c.) on at least two different adsorbents (usually silica and alumina).

(2) *Reaction of β -ionone with $Fe(CO)_5$*

Commercial β -ionone was purified by several methods as described in the literature³²⁻³³ and the purity tested by t.l.c. Even after repeated purifications it was never possible to obtain a sample of β -ionone which showed a single spot in t.l.c. Preparation of the pure semicarbazone (single spot in t.l.c.) followed by hydrolysis of the latter with oxalic acid³², and subsequent vacuum distillation (64.5°/0.05 mm) gave the purest sample of β -ionone, which still showed (t.l.c.) traces of two other compounds in addition to β -ionone. A solution of β -ionone (1 g) and iron pentacarbonyl (1.1 g) in di-*n*-butyl ether was refluxed for 8 h. in a nitrogen atmosphere. After filtration, the solvent was removed in vacuum (water pump) and the crude yellow oil (which had been allowed to stand at room temperature overnight), showed in the infrared spectrum terminal carbonyl bands in the region of 2000 cm^{-1} and ketonic carbonyl bands at 1720 and 1670 cm^{-1} . The crude oil was chromatographed on neutral alumina (50 g). Elution was with petroleum ether (150 ml) followed by petroleum ether/methylene chloride (2:1) (400 ml) and then methylene chloride (200 ml). The 50 fractions of 15 ml each which were collected were then combined into 6 major fractions (a-f) on the basis of t.l.c. behaviour. Fraction (a) (78 mg) which showed infrared bands of terminal carbonyls but no ketonic carbonyls, was not investigated further in the present work. Fraction (b) (270 mg) a yellow oil (oven temperature $\sim 100^\circ/0.1$ mm Hg) (single spot t.l.c.) showed infrared bands of terminal carbonyls (2060, 1980 cm^{-1}) and ketonic carbonyl (1720 cm^{-1}). The ultraviolet spectrum: λ_{max} (log ϵ): 205 (4.07), 225 (3.90), 300 (3.32) $m\mu$. This complex was assigned structure (VI). [Found: C, 57.00; H, 6.31; mol. wt., 332 (mass spectrometry), 300 (cryoscopic). $C_{16}H_{20}FeO_4$ calcd.: C, 57.85; H, 6.08%; mol. wt., 332.] Major fragments in the mass spectrum had *m/e* values: 332 $[C_{13}H_{20}OFe(CO)_3]^+$, 304 $[C_{13}H_{20}OFe(CO)_2]^+$, 276 $[C_{13}H_{20}OFe(CO)]^+$, 248 $[C_{13}H_{20}OFe]^+$, 192 $[C_{13}H_{20}O]^+$, 177, 149, 136, 121, 109, 93. The NMR spectrum showed bands only in the region τ 7.5-9.5 with no bands at lower fields. Fraction (c) (53 mg) showed two spots in t.l.c., corresponding to a mixture of fractions (b) and (d). Fraction (d) (110 mg) a yellow oil (oven temperature $\sim 100^\circ/0.1$ mm Hg) (single spot in t.l.c.) showed infrared bands of terminal carbonyls (2060, 1980 cm^{-1}) and ketonic carbonyl (1670 cm^{-1}). The ultraviolet spectrum: λ_{max} (log ϵ): 205 (4.23, terminal absorption), 220 (4.23), 296 (3.85) $m\mu$. This complex was assigned structure (V). [Found: mol. wt., 332 (mass spectrometer). $C_{16}H_{20}FeO_4$ calcd.: mol. wt. 332. Due to the lack of stability of the complex the elemental analyses consistently gave too high values for C, H and too low values for Fe.] The major fragments in the mass spectrum had identical *m/e* values with those obtained from isomer of fraction (b) but with completely different relative abundances. The NMR spectrum showed in addition to the bands in the region τ 7.5-9.5, a doublet centered at τ 3.76, in the ratio high field bands: low field bands 19:1. Fraction (e) (70 mg) was found to contain only β -ionone. Fraction (f) (230 mg) was also free of iron carbonyl complexes and showed infrared bands of ketonic carbonyls at 1720 and 1670 cm^{-1} . If the crude reaction product was chromatographed immediately, or was kept in the refrigerator (under nitrogen)

until chromatography, the amount of complex with $\nu_{C=O} = 1720 \text{ cm}^{-1}$ was greatly decreased.

When a solution of β -ionone in di-*n*-butyl ether, without $\text{Fe}(\text{CO})_5$, was refluxed for 8 h, no rearranged β -ionone was found in the reaction product.

(3) *Reaction of α -ionone with $\text{Fe}(\text{CO})_5$*

α -ionone, (VII), was prepared by irradiation of β -ionone¹⁹⁻²². A solution of α -ionone (1 g) and iron pentacarbonyl (1 g) in di-*n*-butyl ether was refluxed for 6 h in a nitrogen atmosphere. The work up was the same as described in the previous reaction. The crude reaction product had the same infrared spectrum as obtained from the reaction with β -ionone, namely there were two ketonic carbonyl bands at 1720 and 1670 cm^{-1} . Chromatography of the crude product was as for the previous experiment and the following fractions were separated: fraction (a), 480 mg; fraction (b), 120 mg; fraction (c), 140 mg; fraction (d), 280 mg; and fraction (f), 650 mg. (The designation a-f refers to the equivalent fractions of the previous experiment.) The two complexes of fractions (b) and (d) were identical with those obtained in the equivalent fractions from the experiment with β -ionone as starting material.

(4) *Reaction of β -ionone with $\text{Fe}(\text{CO})_5$ in the presence of BF_3 catalyst*

β -ionone (1 g) was reacted with iron pentacarbonyl (1.1 g) under exactly the same conditions as in experiment (2) except that a catalytic amount of boron trifluoride etherate was added to the reaction mixture. After identical work up and chromatography, the following fractions were separated: fraction (a), 200 mg; fraction (b), 345 mg; fraction (d), only traces; fraction (e), 190 mg; fraction (f), 180 mg. Thus, only the α -iononeiron tricarbonyl complex was obtained in this reaction.

When a solution of β -ionone in di-*n*-butyl ether with a catalytic amount of boron trifluoride etherate, but with no $\text{Fe}(\text{CO})_5$, was refluxed for 8 h, the reaction product consisted of a mixture of β -ionone and the rearranged isomer α -ionone ($\nu_{C=O} 1720 \text{ cm}^{-1}$), with predomination of the latter. When the α -ionone was refluxed in di-*n*-butyl ether in the presence of boron trifluoride etherate, but without $\text{Fe}(\text{CO})_5$, the infrared spectrum of the reaction product showed a ketonic carbonyl band at 1720 cm^{-1} and none at 1670 cm^{-1} ; i.e. no isomerization to β -ionone had taken place.

(5) *Reaction of β -ionone with $\text{Fe}_2(\text{CO})_9$*

β -ionone (0.95 g) and iron nonacarbonyl (1.82 g) in 50 ml petroleum ether (40-60°) were stirred at room temperature, under nitrogen, for 24 h. After evaporation of the solvent (water pump vacuum) the crude reaction product (1.2 g) was chromatographed on neutral alumina, as in the previous experiment. The fractions containing the metal complex (0.42 g) consisted only of the β -iononeiron tricarbonyl derivative, and none of the rearranged α -ionone complex.

(6) *Reaction of retro-ionylidene acetate, (IX), with $\text{Fe}(\text{CO})_5$*

A solution containing retro-ionylidene acetate^{26, 27}, (2 g) iron pentacarbonyl (1.7 g) and di-*n*-butyl ether (100 ml) was kept at 140° for 7 h. After filtration and removal of the solvent in vacuum, the residue, a dark-red oil, was chromatographed on neutral alumina (50 g). Elution was with petroleum ether (200 ml), petroleum ether/methylene chloride (4:1) (250 ml), methylene chloride (300 ml) and finally with chloroform (450

ml). The fractions containing the metal complex (t.l.c. and infrared spectrum) added to about 1.4 g, the remainder (~ 0.6 g) being a metal-free compound. Re-chromatography of 0.5 g of the fraction containing the metal complex yielded 0.2 g of pure material, (single spot on t.l.c.) b.p. $\sim 125^\circ/0.1$ mm Hg. The infrared spectrum showed absorption bands at 2070 and 200 cm^{-1} (terminal carbonyls), 1710 cm^{-1} (ester carbonyl) as well as strong bands at 1440 and 1150 cm^{-1} . The ultraviolet spectrum: λ_{max} ($\log \epsilon$): 209 (4.50), 240 (4.18), 310 (3.55) $\text{m}\mu$. This spectrum is radically different from that of the parent compound, *retro*-ionylidene acetate, (IX), which has λ_{max} ($\log \epsilon$): 284 (4.11), 330 (3.43) $\text{m}\mu$. This complex was assigned structure (X). [Found: mol. wt., 402 (mass spectrometer). $\text{C}_{20}\text{H}_{26}\text{FeO}_5$ calcd.: mol. wt., 402.] The major fragments in the mass spectrum had m/e values: 402 [$\text{C}_{17}\text{H}_{26}\text{O}_2\text{Fe}(\text{CO})_3$] $^{+}$, 374 [$\text{C}_{17}\text{H}_{26}\text{O}_2\text{Fe}(\text{CO})_2$] $^{+}$, 346 [$\text{C}_{17}\text{H}_{26}\text{O}_2\text{Fe}(\text{CO})$] $^{+}$, 318 [$\text{C}_{17}\text{H}_{26}\text{O}_2\text{Fe}$] $^{+}$, 262 [$\text{C}_{17}\text{H}_{26}\text{O}_2$] $^{+}$, 247, 206, 189, 133. The NMR spectrum showed bands in the region τ 4–5.95 (relative intensity 3) and τ 7.4–9.1 (relative intensity 22.5).

(7) Reaction of β -ionylidene acetate, (XIV), with $\text{Fe}(\text{CO})_5$

β -ionylidene acetate, (XIV), (prepared by esterifying β -ionylidene acetic acid²⁹ with diazomethane) (0.50 g) was refluxed for 7 h under nitrogen with iron pentacarbonyl (0.44 g) in di-*n*-butyl ether (50 ml). Work up and chromatography as in the previous reaction afforded 0.36 g (46%) of a pure compound (t.l.c.) which upon crystallization from methanol at -70° yielded yellow needles, m.p. 83 – 84° . The infrared spectrum exhibited very strong bands at 2070 and 1970 cm^{-1} (terminal C=O), a strong band at 1710 cm^{-1} (ketonic CO) and a weak band at 1600 cm^{-1} (C=C). The ultraviolet spectrum (in methanol) showed λ_{max} ($\log \epsilon$) at 245 (4.23) and 320 (3.82 $\text{m}\mu$). The NMR spectrum (in CCl_4) showed a doublet at τ 4.3 (vinyl H), a singlet at τ 6.4 (OCH_3) and a complex of bands in the range τ 7.3–9.1. The major fragments in the mass spectrum had m/e values: 388 [$\text{C}_{16}\text{H}_{24}\text{O}_2\text{Fe}(\text{CO})_3$] $^{+}$, 360 [$\text{C}_{16}\text{H}_{24}\text{O}_2\text{Fe}(\text{CO})_2$] $^{+}$, 357 [$\text{C}_{15}\text{H}_{21}\text{OFe}(\text{CO})_3$] $^{+}$, 332 [$\text{C}_{16}\text{H}_{24}\text{O}_2\text{Fe}(\text{CO})$] $^{+}$, 304 [$\text{C}_{16}\text{H}_{24}\text{O}_2\text{Fe}$] $^{+}$, 248 [$\text{C}_{16}\text{H}_{24}\text{O}_2$] $^{+}$, 87 [FeOCH_3] $^{+}$.

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SUMMARY

The products from the reaction of iron carbonyls with β -ionone and analogous conjugated dienes and trienes have been isolated and characterized. The suggestion has been made that the degree of twisting around the essential single bond in diene-iron tricarbonyl complexes may play a significant part in determining the properties of these compounds.

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SHORT COMMUNICATION

Some infrared studies of organometallic pseudohalogen*

As part of a detailed investigation into the structure, bonding, and chemical properties of pseudohalogen groups attached to organometallics, we have prepared the series of compounds $(\text{CH}_3)_3\text{MX}$ ($\text{M} = \text{Si, Ge, Sn, Pb}$; $\text{X} = \text{NCO, NCS, N}_3$), and studied their infrared spectra from 4000 to 300 cm^{-1} . While many of these compounds have been previously prepared, detailed infrared spectra have been reported only for the azides¹. The compounds studied in this investigation are listed in Table I.

Investigation concentrated on the three vibrational modes internal to the pseudohalogen group (two stretching, one bending) and the metal-pseudohalogen

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