

## A Series of Tricarbonyl(polyene aldehyde)iron Complexes

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The reaction of a series of  $\omega$ -phenylpolyenals with dodecacarbonyltri-iron affords isomeric mixtures of compounds of the general stoichiometry  $[\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}]\text{Fe}(\text{CO})_3$ ;  $n = 2-5$ . The major product is always the isomer in which the  $\text{Fe}(\text{CO})_3$  moiety is bonded to the butadiene fragment adjacent to the aldehyde function. The u.v. absorption spectra of the complexes indicate that the tricarbonyl(diene)iron unit considerably interrupts the transmission of conjugative effects along the polyene chain. The occurrence of the lowest energy absorption band at  $25\,400 \pm 400 \text{ cm}^{-1}$  ( $394 \pm 4 \text{ nm}$ ) in the spectra of the 2,4-dinitrophenylhydrazone derivatives of the above and related aldehyde and ketone complexes is evidence for the  $\text{Fe}(\text{CO})_3$  and  $>\text{C}=\text{O}$  functions being immediately adjacent.

It is well established that the co-ordination of organic 1,3-dienes to transition metal ions considerably modifies both the geometry<sup>1</sup> and reactivity<sup>2</sup> of the diene. The electronic structure of such complexes can be represented by the two extreme valence bond formulations (I) and (II). The formal differences suggested by (I) and (II) should not be emphasised and in molecular orbital terms the transition between them can be related to an increasing involvement of the most stable anti-bonding ( $\pi^*$ ) orbital of the diene into the bonding

scheme.<sup>3</sup> There is some disagreement, however, over the extent of the charge transfer from the essentially non-bonding metal orbitals into the antibonding ( $\pi^*$ )



(I)



(II)

ligand orbitals, or in valence bond terms, the importance of (II).<sup>4</sup> This formulation involves a rehybridisation towards  $sp^3$  at the terminal carbon atoms and implies a

<sup>1</sup> M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.

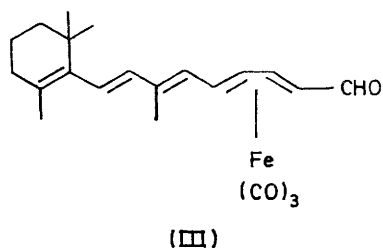
<sup>2</sup> B. F. G. Johnson, J. Lewis, A. W. Parkins, and G. L. Randall, *Chem. Comm.*, 1969, 595; M. L. H. Green, 'Organometallic Compounds,' vol. II, Methuen, London, 1968, p. 70.

<sup>3</sup> F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 731.

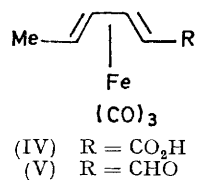
<sup>4</sup> R. Eiss, *Inorg. Chem.*, 1970, **9**, 1650, and references therein.

greater loss of conjugation in the co-ordinated butadiene unit.

Both the energy and the intensity of the first  $\pi \rightarrow \pi^*$  transition for a series of linear conjugated polyenes is a function of the number of double bonds.<sup>5</sup> Hence Birch and Fitton<sup>6</sup> have considered that for tricarbonyl-(vitamin-A aldehyde)iron (III) the u.v. absorption



spectrum indicated lower conjugation than in the original aldehyde, approximately equivalent to the loss of one double bond. However Cais and Moaz<sup>7</sup> have interpreted the differences in the u.v. spectra of sorbic acid and related compounds, and their iron tricarbonyl complexes (IV) as being mainly due to a change from the *s-trans* conformation in the free dienes to the *s-cis* conformation in the complexes. In contrast Gibson and Pettit<sup>8</sup> found that the 2,4-dinitrophenylhydrazone of tricarbonyl(sorbalddehyde)iron (V) has a u.v. absorption maximum at  $25\,500\text{ cm}^{-1}$ , a value characteristic of  $\alpha,\beta$ -unsaturated ketones. This was interpreted

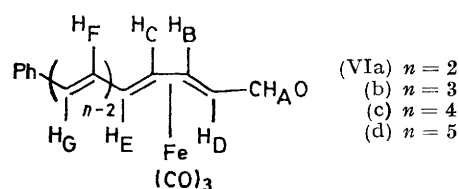


as indicating that the co-ordinated iron atom has little effect on the diene unit. In an attempt to clarify the nature of the electronic distribution in such diene metal complexes we have therefore systematically examined the effect the co-ordinated iron tricarbonyl group has on the electronic spectra, and hence on the transmission of conjugative effects in a series of  $\omega$ -phenylpolyenals, Ph(CH=CH)<sub>n</sub>CHO,  $n = 2-5$ , and their 2,4-dinitrophenylhydrazone derivatives.

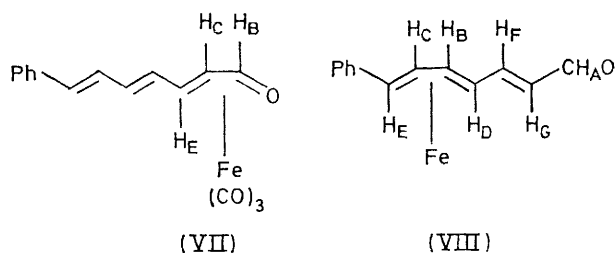
#### RESULTS AND DISCUSSION

**Synthesis.**—The reaction of the polyene aldehydes with Fe<sub>3</sub>(CO)<sub>12</sub> yields isomeric mixtures of complexes. The mass spectra of all the isolated products exhibit a parent molecular ion, and three other peaks due to the sequential loss of carbon monoxide, corresponding to the general molecular formula [Ph(CH=CH)<sub>n</sub>CHO]Fe(CO)<sub>3</sub>;  $n = 2-5$ . The location of the Fe(CO)<sub>3</sub> moiety in the polyene chain was determined from the <sup>1</sup>H n.m.r. and

i.r. spectra (Table 1). Including the aldehyde group, there are  $n$  sets of conjugated double bonds which can possibly co-ordinate to the iron atom, however the major product in each case is the complex (VI) in which the iron is bonded to the butadiene fragment adjacent to the aldehyde function. Thus the reaction of Ph(CH=CH)<sub>2</sub>CHO with Fe<sub>3</sub>(CO)<sub>12</sub> or Fe<sub>2</sub>(CO)<sub>9</sub> gave only one product which is readily identified as (VIa) and the reaction of Ph(CH=CH)<sub>3</sub>CHO and Fe<sub>3</sub>(CO)<sub>12</sub> yielded three crystalline compounds which were separated by chromatography on alumina and identified as (VII) (4%), (VIb) (27%), and (VIII) (7%). During the reactions of Ph(CH=CH)<sub>4</sub>CHO and Ph(CH=CH)<sub>5</sub>CHO with the iron carbonyl considerable decomposition of the ligand was apparent, however chromatography on alumina allowed the isolation of (VIc) and (VI d) as



pure compounds. The i.r. spectra of the crude reaction mixtures in the  $\nu(\text{C}\equiv\text{O})$  region indicated the presence of smaller amounts of other isomers but the similarity of their  $R_F$  values prevented their separation although a trace amount of a compound (IX), probably a heterodiene adduct similar to (VII) was isolated. All the above polyene aldehyde complexes, except the heterodiene adducts, (VII) and (IX), formed 2,4-dinitrophenylhydrazone derivatives in the usual manner and u.v. irradiation of (VIa) in the presence of triethylphosphine yielded the monosubstituted product (X). After the completion of this work Whitlock and co-workers<sup>9</sup> independently reported the isolation of (VIb) and (VIII) and showed (VIb) was the experimentally favoured isomer ( $K_{\text{eq}} = 2.88$ ).



**<sup>1</sup>H N.m.r. and I.r. Spectra.**—The n.m.r. spectra of the major products (VI), in which the co-ordinated butadiene unit is adjacent to the aldehyde group, are given in Table 1, the assignments being confirmed by double irradiation experiments. The olefin protons bonded to the co-ordinated butadiene unit show upfield shifts on co-ordination consistent with those previously observed

<sup>5</sup> H. H. Jaffe and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 228.

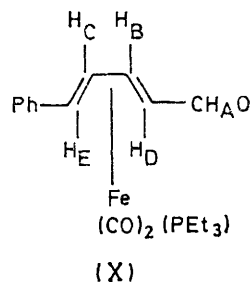
<sup>6</sup> A. J. Birch and H. Fritton, *J. Chem. Soc. (C)*, 1966, 2060.

<sup>7</sup> M. Cais and N. Moaz, *J. Organometallic Chem.*, 1966, **5**, 370.

<sup>8</sup> D. H. Gibson and R. Pettit, quoted in ref. 10.

<sup>9</sup> H. W. Whitlock, C. Reich, and W. D. Woessner, *J. Amer. Chem. Soc.*, 1971, **93**, 2483.

for other tricarbonyl(diene)iron compounds<sup>10</sup> and the aldehyde protons resonate as single doublets at  $\tau$  0.6–0.7



( $J$  4.0 Hz) compared with  $\tau$  0.4 ( $J$  8.0 Hz) for the free aldehydes. In contrast for (VIII) in which the aldehyde group and the co-ordinated diene unit are separated by

that the related ketones (XI) exhibit only one  $\nu(\text{C}=\text{O})$  absorption, at  $1682\text{ cm}^{-1}$ , interpreting this to indicate that the complexes show a strong preference for the single conformation in which the steric interactions of the ketone methyl group with the diene residue and the carbonyl groups are minimised. For the aldehyde complexes (VI) such steric interactions are not expected to be important and indeed the n.m.r. spectrum (Table 1) shows that the two conformers exist in equilibrium, the time averaged spectrum being observed. However, in the dicarbonyl compound, (X), where a carbonyl group has been replaced by the more 'bulky' triethylphosphine, and in (VII), where the aldehyde group is separated from the  $\text{Fe}(\text{CO})_3$  group by a free double bond, the i.r. data (Table 1) indicate that in each case, only one conformer is present in solution.

The large upfield shift of the single inner proton in the

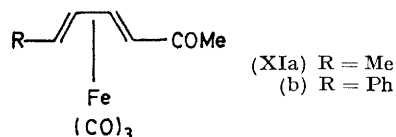
TABLE I  
Spectroscopic data for the complexes

Compound	<sup>1</sup> H N.m.r. spectral data ( $\tau$ ) <sup>a</sup>					H (other olefin)	Electronic spectral data/ $\text{cm}^{-1}$ <sup>b</sup>			Infrared spectral data/ $\text{cm}^{-1}$	
	H <sub>A</sub>	H <sub>B</sub>	H <sub>G</sub>	H <sub>D</sub>	H <sub>E</sub>		Complex <sup>c</sup>	Free polyal <sup>d</sup>		$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{O})$
(VIa)	0.61(d)	4.04(m)		8.42(q)	7.41(d)		37 900 (22.7)	31 800 (7.9)	30 900 (34.0)	2062, 2005, 1995, 1990	1703, 1686 <sup>e</sup>
(VIb)	0.69(d)	4.19(q)	4.46(q)	8.44(q)	7.44(t)	3.78(q) <sup>f</sup> 3.29(d) <sup>g</sup>	35 000 (22.3)	29 800 (18.8)	28 300 (40.0)	2060, 2005, 1990, 1987	1703, 1686
(VIc)	0.69(d)	4.20(m) <sup>h</sup> 4.53(q)		8.46(q)	7.49(t)	3.2–3.7	32 000 (24.5)	27 600 (33.6)	26 300 (50.0)	2060, 2004, 1991, 1987	1703, 1686
(VI d)	0.71(d)	4.23(m) <sup>h</sup> 4.55(q)		8.46(q)	7.49(t)	3.2–3.9	29 900 (23.0)	26 200 (42.5)	24 600 (63.5)	2059, 2004, 1991, 1987	1703, 1687
(VII)		<i>i</i>	<i>i</i>		7.78(q)	3.5–5.0				2047, 1986, 1977	
(VIII)	0.56(d)	4.40(q)	4.10(q)	8.00(t)	7.41(d)	3.34(q) <sup>f</sup> 3.77(q) <sup>g</sup>	34 400 (28.6)	29 000 (10.8)		2054, 1997, 1984	1693
(IX)										2046, 1986, 1974	
(X)	0.95(d)	4.86(t)	4.17(q)	7.43(m)	6.99(d)		39 200 (20.6)	32 500 (9.2)		1992, 1936	1657

<sup>a</sup> Assignments confirmed by spin decoupling; all signals of correct intensity; H(Ph), 2.7–2.8; coupling constants except for (VII) and (X),  $J_{AD}$  4 (8 for VIII),  $J_{BD} = J_{CE} = 9$ ,  $J_{BO}$  5,  $J_{FG}$  16 Hz. <sup>b</sup> Molar extinction coefficients ( $\times 10^{-3}$ ) in parentheses. <sup>c</sup> In  $\text{CH}_2\text{Cl}_2$ . <sup>d</sup> In  $\text{CHCl}_3$  from ref. 13. <sup>e</sup>  $\nu(\text{C}=\text{O})$  for the free aldehyde,  $1695\text{ cm}^{-1}$ . <sup>f</sup> H<sub>F</sub>. <sup>g</sup> H<sub>G</sub>. <sup>h</sup> Includes H<sub>F</sub>. <sup>i</sup> Obscured by olefin and phenyl resonances.

a free double bond this coupling constant remains as 8.0 Hz, the free ligand value (Table 1).

The i.r. spectra of the complexes (VI) in cyclohexane (Table 1) show three  $\nu(\text{C}=\text{O})$  bands ca. 2060, 2005, and  $1990\text{ cm}^{-1}$ , characteristic of tricarbonyl(diene)iron compounds, but with an additional shoulder appearing on the low frequency side of the  $1990\text{ cm}^{-1}$  band. Two  $\nu(\text{C}=\text{O})$  bands ca. 1703 and  $1686\text{ cm}^{-1}$  indicate that the aldehyde group is not directly involved in bonding to the metal. The i.r. data however, do indicate that the



complexed aldehyde must exist as two different conformers in solution. Clinton and Lillya<sup>11</sup> have shown

<sup>10</sup> R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 10.

<sup>11</sup> N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, 1970, **92**, 3058.

n.m.r. on co-ordination and the absence of a band between  $1900\text{--}1600\text{ cm}^{-1}$  assignable to the aldehyde stretching mode in the i.r. indicate that (VII) is a  $\pi$ -heterodiene adduct, the metal-ligand bonding being similar to that proposed for tricarbonyl(cinnamaldehyde)-iron and related complexes.<sup>12</sup> Insufficient of (IX) was obtained for an n.m.r. spectrum, however the i.r. spectrum is similar to that observed for (VII).

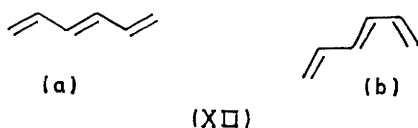
*Electronic Spectra.*—(i) *Polyene aldehyde complexes.* The u.v. absorption spectra of the free polyene aldehydes  $\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}$ ,  $n = 2\text{--}5$  (Table 1), are typical of linear conjugated polyenes;<sup>5</sup> that is the energy of the absorption assigned to the first  $\pi \rightarrow \pi^*$  transition progressively decreases and its intensity increases, as the number of double bonds increases. In contrast the iron tricarbonyl complexes (VI) show absorption maxima (Table 1) at higher energies than observed for the corresponding free aldehydes. These are assigned to essentially  $\pi \rightarrow \pi^*$  transitions of the co-ordinated polyenal, although the possibility of metal-diene

<sup>12</sup> A. M. Brodie, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J.C.S. Dalton*, 1972, 2031.

<sup>13</sup> W. Krauss and J. Grund, *Z. Elektrochemie*, 1954, **58**, 767.

( $d \rightarrow \pi^*$ ) type charge-transfer bands occurring in this region should be considered. For a series of sorbic acid complexes (IV), Cais and Moaz<sup>7</sup> have assigned bands *ca.*  $30\,000\text{ cm}^{-1}$  ( $\epsilon$  *ca.* 3000) to such transitions. However in the present series of compounds the replacement of a co-ordinated carbon monoxide group, by triethylphosphine, to give (X), causes the u.v. maxima to move to higher energies, whereas metal-ligand (*i.e.*  $M \rightarrow CO$ ) transitions have been shown to move to lower energies on phosphine substitution.<sup>14</sup> Moreover, as expected for  $\pi \rightarrow \pi^*$  transitions<sup>15</sup> the maxima undergo slight blue shifts ( $100\text{--}300\text{ cm}^{-1}$ ) on going to a less polar solvent (cyclohexane).

Calculations, assuming coplanarity of the conjugated chain, show that on going from (XIIa) to a conformation containing an *s-cis* double bond (XIIb) the energy of the first  $\pi \rightarrow \pi^*$  absorption band should decrease in both energy and intensity.<sup>16</sup> In the absence of steric hindrance effects it is found that *s-cis* conformers of dienes



absorb less strongly and at lower energy than the related *s-trans* forms.<sup>17</sup> However, although co-ordination of an iron tricarbonyl moiety perturbs the fully *s-trans* conformation of the free polyene aldehydes by introducing an *s-cis* butadiene unit, the considerable effect on the electronic spectra cannot be considered simply in structural terms. Figures 1 and 2 focus

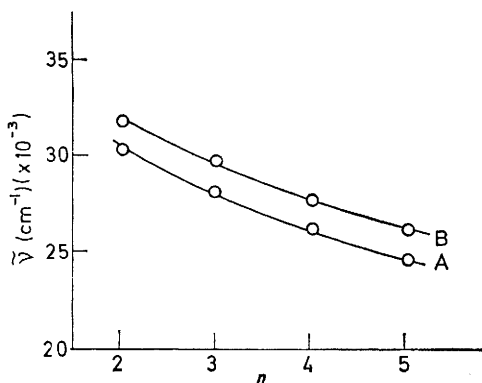


FIGURE 1 Frequency of the lowest energy absorption band for  $\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}$  (A) and the complexes (VIIa-d) (B) as a function of  $n$

attention on the lowest energy absorption and demonstrate that its energy and intensity can be correlated with the chainlength but that co-ordination has reduced

<sup>14</sup> P. S. Braterman and A. P. Walker, *Discuss. Faraday Soc.*, 1969, **47**, 121.

<sup>15</sup> Ref. 5, p. 186.

<sup>16</sup> N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 2811.

<sup>17</sup> E. S. Stern and C. J. Timmons, 'Electronic Absorption Spectroscopy in Organic Chemistry,' 3rd edn., Arnold, London, 1970, p. 38.

conjugation in the  $\pi$ -system. The X-ray crystal structure of tricarbonyl(vitamin-A aldehyde)iron (III) (and therefore presumably in the present series of compounds) shows that the bonding requirements of the metal atom causes the atoms in the polyene chain to

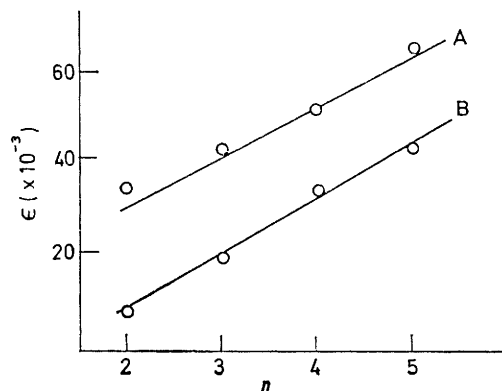


FIGURE 2 Intensity of the lowest energy absorption band for  $\text{Ph}(\text{CH}=\text{CH})_n\text{CHO}$  (A) and the complexes (VIa-d) (B) as a function of  $n$

deviate from the mean plane defined by the *s-cis* butadiene unit.<sup>18</sup> The subsequent loss of conjugation can be related to overlap between the lowest antibonding orbital on the ligand and the filled nonbonding metal orbitals, or in valence bond terms a tendency towards structure (II). Similarly the ability of the  $\text{Fe}(\text{CO})_3$  group to localise aromatic  $\pi$ -electrons has been demonstrated by Davis and Pettit<sup>19</sup> for a series of vinylbenzene complexes. The somewhat similar spectra of the two isomers (VIb) and (VIII) show that the localisation of electrons is not as complete as the formulation (II) would suggest. The higher energies ( $600\text{--}800\text{ cm}^{-1}$ ) of the bands observed for (VIb), where the co-ordinated metal is adjacent to the electron withdrawing aldehyde group, can be related to a greater back donation of electrons. This in turn is reflected in the positions of the  $\nu(\text{C}=\text{O})$  bands in the i.r. spectra. The higher frequencies observed for (VIb) than for (VIII) being a result of a diminished availability of electron density for transfer into the antibonding orbitals of the metal-carbonyl groups. The introduction of a phosphine group will result in a build up of electron density in the antibonding diene orbitals causing the absorption maxima to move to higher energies as the conjugation is reduced.

Two other results are relevant to the present discussion. The spectra of the all-*trans* conformers of 1-phenylbutadiene and 1,4-diphenylbutadiene show absorption maxima at  $35\,500$  and  $30\,500\text{ cm}^{-1}$  respectively, a difference of  $5000\text{ cm}^{-1}$ ,<sup>20</sup> however the difference is reduced to less than  $1500\text{ cm}^{-1}$  in the corresponding iron

<sup>18</sup> R. Mason and G. B. Robertson, *J. Chem. Soc. (A)*, 1970, 1229.

<sup>19</sup> R. E. Davis and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 716.

<sup>20</sup> H. M. Walborsky and J. F. Pendleton, *J. Amer. Chem. Soc.*, 1960, **82**, 1405; J. H. Pinckard, B. Willie, and H. Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938.

tricarbonyl complexes.<sup>11,21</sup> Reduction of the ketonic carbonyl group in the dienone complex (XIa) to the alcohol causes only small changes in the u.v. spectrum when compared to the changes observed for the free ligands.<sup>11</sup>

(ii) *2,4-Dinitrophenylhydrazone derivatives*. The lowest energy or principal band in the absorption spectra of the 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones is sensitive to changes in the structures of the parent compounds and its position is used for diagnostic purposes.<sup>22</sup> Thus for the polyenal derivatives the band moves to lower energy and becomes more intense as the chainlength increases (Table 2). The

production of a free double bond between the co-ordinated diene fragment and the phenylhydrazone group, as in the derivatives of (VIII) and (XV), causes a decrease in energy of the absorption by at least 1000 cm<sup>-1</sup>. The

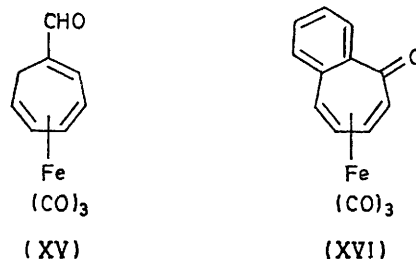


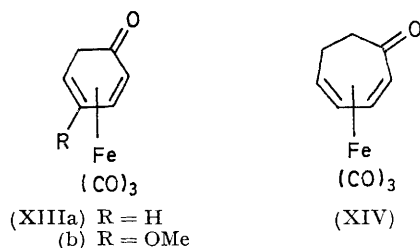
TABLE 2

Electronic spectral data (cm<sup>-1</sup>) for 2,4-dinitrophenylhydrazone derivatives <sup>a</sup>

(i) Fe(CO) <sub>3</sub> group adjacent to 2,4-dinitrophenylhydrazone chromophore			
(III)	25 600 <sup>b,e</sup>	(VIId)	25 100(57.6) <sup>e</sup>
(V)	25 500 <sup>e,d</sup>	(XIIIa)	25 600(23.5) <sup>e,g</sup>
(VIa)	25 400(29.9) <sup>e,f</sup>	(XIIIb)	25 600(24.0) <sup>e,g</sup>
(VIb)	25 400(33.1) <sup>e</sup>	(XIV)	25 100(23.7) <sup>e</sup>
(VIc)	25 400(42.2) <sup>e</sup>		
(ii) Other derivatives			
(VIII)	24 400(35.7) <sup>e</sup>	(XV)	23 800(28.8) <sup>e</sup>
(X)	24 400(25.9) <sup>e</sup>	(XVI)	24 300(26.6) <sup>e</sup>

<sup>a</sup> Lowest energy absorption, molar extinction coefficients ( $\times 10^{-3}$ ) in parentheses. <sup>b</sup> From ref. 6. <sup>c</sup> In EtOH. <sup>d</sup> From ref. 8. <sup>e</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup> Free derivative values: (VIa) 24 800 (49.8), (VIb) 24 000(52.5), (VIc) 23 200(63.1), (VIId) 22 600(71.0). <sup>g</sup> From ref. 23.

spectra of the 2,4-dinitrophenylhydrazone derivatives of the complexes (VI), in which the co-ordinated iron tricarbonyl moiety and aldehyde group are adjacent, contain a number of bands, but in contrast they are all dominated by the occurrence, in the narrow range 25 400—25 100 cm<sup>-1</sup> (Table 2), of the lowest energy absorption. Moreover the 2,4-dinitrophenylhydrazones of the iron tricarbonyl complexes (III), (V), (XIII), and (XIV) exhibit the lowest energy absorption in the same



region (Table 2). However in the 2,4-dinitrophenylhydrazone of the phosphine complex (X) the band decreases in energy by 1100 cm<sup>-1</sup> indicating that it must be a metal-ligand type charge transfer transition. The acceptor orbital must be essentially associated with the 2,4-dinitrophenylhydrazone chromophore since the in-

phenylhydrazone derivative of (XVI) also shows a peak at lower energies (Table 2). It is apparent therefore, that the spectra of the 2,4-dinitrophenylhydrazone derivatives can be used to provide structural information. Although the lowest energy band may vary somewhat in intensity, its occurrence in the 25 100—25 600 cm<sup>-1</sup> (398—390 nm) region does serve to identify the presence of adjacent Fe(CO)<sub>3</sub> and aldehyde or ketone carbonyl functions, providing of course, that the 1-substituent of the ketone does not form part of the conjugated system.

#### EXPERIMENTAL

I.r. spectra were measured as cyclohexane solutions on a Perkin-Elmer 257 instrument and u.v. absorption spectra on a Unicam SP 800 machine. <sup>1</sup>H N.m.r. spectra were obtained in CDCl<sub>3</sub> using a Varian HA 100 MHz spectrometer, with tetramethylsilane as internal standard, and mass spectra were measured on an A.E.I. MS 12 mass spectrometer at 70 eV.

All reactions were carried out under nitrogen, although the complexes are moderately stable in air. Elemental analyses were performed by the Microanalytical Laboratory, University College, London.

*Tricarbonyl[2-5-η-(5-phenylpenta-2,4-dienal)]iron (VIa)*.—A mixture of the dienal (1.85 g), dodecacarbonyltri-iron (6.04 g) and benzene (50 ml) was refluxed for 2.5 h. The solution was cooled and filtered through Kieselguhr. After solvent removal, the residue was chromatographed on 'H' grade alumina eluting with 10% ethyl acetate-toluene. Recrystallisation from a benzene-hexane solution gave the product (2.37 g; 68%) as yellow crystals, m.p. 154—155° (Found: C, 56.4; H, 3.7. Calc. for C<sub>14</sub>H<sub>10</sub>FeO<sub>4</sub>: C, 56.4; H, 3.4%). The complex was also prepared from the reaction of enneacarbonyldi-iron with the dienal (37% yield) and has previously been prepared from the reaction with iron pentacarbonyl.<sup>24</sup> The complex gives a scarlet 2,4-dinitrophenylhydrazone, m.p. 194° (decomp.) (Found: C, 50.2; H, 3.2; N, 11.7. Calc. for C<sub>20</sub>H<sub>14</sub>FeN<sub>4</sub>O<sub>7</sub>: C, 50.2; H, 3.0; N, 11.7%).

*Reaction of 7-Phenylhepta-2,4,6-trienal with Dodecacarbonyltri-iron*.—A mixture of the trienal (1.02 g) and the iron carbonyl (2.80 g) were refluxed in benzene (30 ml) for 2.5 h. After filtering through Kieselguhr, the residue was chromatographed on 'H' grade alumina eluting with

<sup>21</sup> A. M. Brodie, unpublished results.

<sup>22</sup> Ref. 17., p. 196.

<sup>23</sup> A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

<sup>24</sup> H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, 1965, **87**, 3605.

toluene and then recrystallised from a benzene-pentane solution to yield *tricarbonyl[(O,1-3)- $\eta$ -(7-phenylhepta-2,4,6-trienal)]iron* (VII) (0.08 g; 4%) as a yellow solid, m.p. 59–60° (Found: C, 59.3; H, 4.2. Calc. for  $C_{16}H_{12}FeO_4$ : C, 59.3; H, 3.7%). This complex did not form a 2,4-dinitrophenylhydrazone derivative. Elution with 10% ethyl acetate-toluene afforded a mixture of two compounds. These were separated on alumina using a 5% ethyl acetate-toluene solution. The first fraction, after recrystallisation from benzene-hexane yielded *tricarbonyl[2-5- $\eta$ -(7-phenylhepta-2,4,6-trienal)]iron* (VIb) (0.49 g; 27%) as yellow crystals, m.p. 104–105° (Found: C, 59.7; H, 4.0%). Similarly the second fraction gave *tricarbonyl[4-7- $\eta$ -(7-phenylhepta-2,4,6-trienal)]iron* (VII) (0.13 g; 7%), m.p. 169–170° (Found: C, 58.6; H, 3.7%). Both complexes gave scarlet 2,4-dinitrophenylhydrazones, m.p. 181° (decomp.) (VIb) and 188–189° (decomp.) (VII) (Found: C, 52.9; H, 3.5; N, 10.6 and C, 52.4; H, 3.3; N, 11.1 respectively. Calc. for  $C_{22}H_{16}FeN_4O_7$ , C, 52.4; H, 3.2; N, 11.1%).

*Reaction of 9-Phenylnona-2,4,6,8-tetraenal with Dodecacarbonyltri-iron.*—As described above the tetraenal (3.01 g) and the carbonyl (7.40 g) were refluxed in benzene (50 ml).

Chromatography using toluene, yielded as the first fraction, a yellow compound (0.01 g) probably (IX) (see text). Elution with 10% ethyl acetate-toluene gave a mixture of compounds, however repeated chromatography and recrystallisation from benzene-hexane yielded orange crystals (0.51 g; 10%) of *tricarbonyl[2-5- $\eta$ -(9-phenylnona-2,4,6,8-tetraenal)]iron* (VIc), m.p. 115–116° (Found: C, 61.6; H, 4.2. Calc. for  $C_{13}H_{14}FeO_4$ : C, 61.75; H, 4.0%). The 2,4-dinitrophenylhydrazone derivative formed as red crystals, m.p. 189° (decomp.) (Found: C, 54.8; H, 3.65;

N, 10.8. Calc. for  $C_{24}H_{18}FeN_4O_7$ : C, 54.3; H, 3.4; N, 10.6%).

*Reaction of 11-Phenylundeca-2,4,6,8,10-pentaenal with Dodecacarbonyltri-iron.*—Using the above method the pentaenal (2.02 g) and the carbonyl (4.21 g) afforded, after repeated chromatography and recrystallisation, orange crystals (0.26 g; 8%) of *tricarbonyl[2-5- $\eta$ -(11-phenylundeca-2,4,6,8,10-pentaenal)]iron* (VIId), m.p. 154–156° (Found: C, 64.1; H, 4.6. Calc. for  $C_{20}H_{16}FeO_4$ : C, 63.9; H, 4.3%). The complex gave a 2,4-dinitrophenylhydrazone derivative, m.p. 191° (decomp.) (Found: C, 56.7; H, 4.0; N, 10.3. Calc. for  $C_{26}H_{20}FeN_4O_7$ : C, 56.1; H, 3.6; N, 10.1%).

*Dicarbonyl(triethylphosphine)[2-5- $\eta$ -(5-phenylpenta-2,4-dienal)]iron* (X).—A mixture of triethylphosphine (0.34 g), the tricarbonyl (VIa) (0.88 g), and benzene (70 ml) were irradiated in a water-cooled annular apparatus using u.v. light from an 80 W mercury lamp. After 15 h the solution was filtered through Kieselguhr, the solvent removed and the residue chromatographed on 'O' grade alumina. Elution with 5% ethyl acetate-toluene gave the starting material (VIa) (0.31 g). The second fraction was eluted using 20% ethyl acetate-toluene. Recrystallisation yielded yellow crystals (0.25 g; 22%) of the *product*, m.p. 94° (Found: C, 59.1; H, 6.7. Calc. for  $C_{19}H_{25}FeO_3P$ : C, 58.8; H, 6.5%). The 2,4-dinitrophenylhydrazone derivative was obtained as red crystals, m.p. 165° (decomp.) (Found: C, 52.8; H, 5.4; N, 10.3. Calc. for  $C_{25}H_{25}FeN_4O_7P$ : C, 52.8; H, 5.1; N, 9.9%).

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