

## Isomerisation and Addition Reactions of some Monoterpene-Tricarbonyliron Complexes

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Reactions of myrcene, *cis*-ocimene, *cis*- and *trans*-allo-ocimene, and  $\alpha$ -phellandrene with iron carbonyls gave dienetricarbonyliron adducts, the structures of which were deduced from n.m.r. spectra and from identification of the olefins recovered after decomposition of the complexes.

The *cis*-ocimene and *cis*-allo-ocimene adducts were isomerised on heating, on treatment with alumina, or on reaction with triphenylmethyl tetrafluoroborate followed by sodium borohydride to give tricarbonyliron complexes in which the ligand had undergone both skeletal and double-bond rearrangement. The mechanism of the thermal isomerisation was delineated by tracer studies using carbon-14 and hydrogen-3.

Hydroboration of the adducts formed by myrcene and *cis*- or *trans*-allo-ocimene gave derivatives that could be decomposed under exceptionally mild conditions to give excellent yields of novel dihydromonoterpenes in which the isopropylidene double bond had been reduced. The iron-containing portion of the myrcene complex similarly acted as a protecting group during reduction with di-imide, and during hydroacetoxylation and hydration. The products of the last two additions were pyrolysed to give good yields of  $\alpha$ -myrcene.

THE reactivity of the organic system in complexes of conjugated dienes with tricarbonyliron is well established to differ from that in the uncomplexed ligand in a way that can sometimes be exploited in reactions of synthetic potential.<sup>1-4</sup> Although a few such complexes of monoterpenes have been prepared,<sup>5,6</sup> little is known about their chemistry:<sup>7</sup> on the other hand, detailed investigations have been made of the palladium and platinum complexes of several monoterpenes.<sup>8-11</sup>

We here report the preparation, together with some reactions, of five monoterpene-tricarbonyliron com-

plexes prepared by treatment of myrcene (I) (7-methyl-3-methylenecyclohexa-1,6-diene), *trans*-allo-ocimene (II) (3,7-dimethyl-2,6-octadiene-2,4,6-triene), *cis*-allo-ocimene (III) (3,7-dimethyl-2,6-octadiene-2,4,6-triene), *cis*-ocimene (IV) (3,7-dimethyl-2,6-octadiene-2,4,6-triene), and  $\alpha$ -phellandrene (V) (4-isopropyl-1-methylcyclohexa-1,5-diene) with pentacarbonyliron, with nonacarbonyldi-iron, and with dodecacarbonyltri-iron. Yields were 8–83% and the purified products were usually yellow-red viscous oils that could not be crystallised. The best preparative routes and the physical properties and elemental analyses are collected in Table 1, which also lists the products of certain isomerisations

TABLE 1  
Preparation and properties of monoterpene-tricarbonyliron complexes

Product <sup>a</sup>	Reactants	Yield (%)	B.p. <sup>b</sup> [m.p.] (°C)	Analysis <sup>c</sup> (%)			M <sup>+</sup> <sup>d</sup>	Olefin
				C	H	Fe		
(VI)	(I) + Fe(CO) <sub>5</sub>	80	75 at 0.05 mmHg	56.7	5.3	20.8	276	(I)
(VII)	[(II) + (III)] <sup>f</sup> + Fe <sub>3</sub> (CO) <sub>12</sub>	65	56 at 0.01 mmHg [37]	56.2	5.3	20.3	276	(III)
(X)	(IV) + Fe(CO) <sub>5</sub>	83	71 at 0.01 mmHg [−2]	57.2	6.1	20.0	276	(IV)
(XI) + (XII)	(V) + Fe <sub>3</sub> (CO) <sub>12</sub>	75 (68:32 w/w)	80 at 0.01 mmHg <sup>g</sup>	56.5	5.7	20.5 <sup>g</sup>	276 <sup>g</sup>	(V)
(VIII)	} (VII); heat <sup>h</sup> or (X)	55	68° at 0.01 mmHg	56.5	5.8	19.8	276	(XIV)
(IX)		15		[45]	56.3	5.6	20.1	276
(IX)	(VII) Al <sub>2</sub> O <sub>3</sub> <sup>h</sup>	99 <sup>h</sup>	[45] <sup>i</sup>	56.9	4.9	20.0	276	(II)
(XIII)	(XI) + (XII) Ph <sub>3</sub> C <sup>+</sup> BF <sub>4</sub> <sup>−</sup> <sup>h</sup>	5 <sup>i</sup>	[103] <sup>j</sup>	26.9	2.5	9.8 <sup>i</sup>		

<sup>a</sup> See text. In diagrams M represents Fe(CO)<sub>3</sub>. The orientation of this group with respect to the cisoid diene system is presumably as in (VI); sometimes for reasons of clarity, it is drawn in the opposite direction. <sup>b</sup> Bath temperature. <sup>c</sup> Calc. for C<sub>13</sub>H<sub>16</sub>FeO<sub>3</sub>: C, 56.5; H, 5.9; Fe, 20.3%. <sup>d</sup> Molecular ion. Other peaks always occurred at *m/e* 246, 220, 192, 162. <sup>e</sup> Olefin recovered on decomposition of adduct. <sup>f</sup> Mixture of (II) and (III) (70:30 w/w). <sup>g</sup> Of mixture, see text. <sup>h</sup> See text. <sup>i</sup> Isolated as the platinum hexafluoride salt (Calc. for C<sub>13</sub>H<sub>15</sub>FePtF<sub>6</sub>O<sub>3</sub>: C, 26.7, H, 2.6; Fe, 9.6%).

plexes. Some of the products can be utilised in routes to new monoterpene derivatives or in novel routes to known compounds.

### RESULTS

(a) *Preparation and Isomerisation of Monoterpene-tricarbonyliron Complexes.*—Complexes could be readily

<sup>1</sup> A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.*, 1968, 332.

<sup>2</sup> A. J. Birch and H. Fitton, *Austral. J. Chem.*, 1969, 22, 971.

<sup>3</sup> E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, 8, 117.

<sup>4</sup> H. W. Quinn and J. H. Tsai, *Adv. Inorg. Chem. Radiochem.*, 1969, 12, 217.

<sup>5</sup> R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, 16, 233.

and modifications. Thus: (a) when either the adduct (VII) derived from the allo-ocimenes or that (X) from *cis*-ocimene was refluxed in di-*n*-butyl ether for prolonged periods, a mixture of easily separable isomers (VIII) and (IX) was formed; (b) the adduct (VII) was partly converted into (IX) on chromatography on alumina, and on recycling six times yielded essentially (>98%) pure product; and (c) treatment of the adducts (XI) and (XII)

<sup>6</sup> D. Dell, N. Maoz, and M. Cais, *Israel J. Chem.*, 1969, 7, 783.

<sup>7</sup> H. Kappeler and J. Wild, Ger.P. 1801661/1969 (*Chem. Abs.*, 1969, 71, 61600).

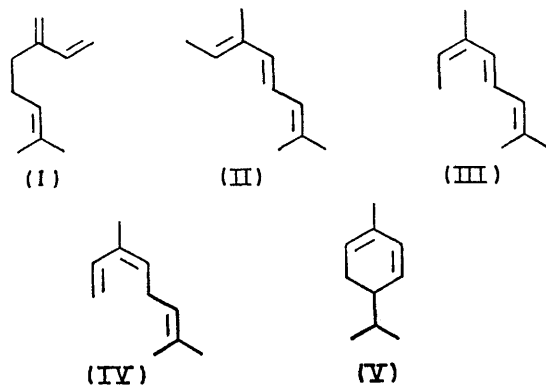
<sup>8</sup> S. Watanabe, K. Suga, and K. Hijikata, *Israel J. Chem.*, 1971, 9, 273.

<sup>9</sup> K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2196.

<sup>10</sup> K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2200.

<sup>11</sup> K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2203.

formed from  $\alpha$ -phellandrene with triphenylmethyl tetrafluoroborate gave a product that could be isolated as its platinum hexafluoride salt (XIII). Similar treatment of either (X) or (VII) followed by reaction with sodium



borohydride gave identical proportions (50 : 5 : 31 : 14) of compounds (VIII), (VII), (IX), and (X).

All the complexes were decomposed by treatment with cerium(IV) ammonium nitrate and the olefinic portion was isolated and identified: the free ligands are recorded in Table 1 and in all cases were obtained essentially (>98%) pure. Recoveries of these olefins were good (>90%) and controls showed isomerisation to be negligible (<2%, if any). Use of manganese dioxide,<sup>12</sup> triphenylphosphine,<sup>5</sup> or iron(III) chloride<sup>13</sup> in each case caused extensive rearrangement. All the free ligands are well characterised compounds for which standards were available except (XIV): this had b.p. 103°;  $M^+$  136;  $\tau$  9.10 (t,  $J$  6 Hz,  $H_a$ ), 8.42 (6H, s,  $H_b$ ), 7.61 (q,  $J$  6 Hz,  $H_c$ ) and 4.10–5.52br (5H,  $H_{c-f}$ ). Ozonolysis of this and oxidative work-up gave formic acid, acetone, oxalic acid, and 2-oxobutyric acid in yields of 30–80% of the theoretical.

Some attempts were made to isomerise *cis*-ocimene *via* the intermediacy of other metal complexes. The most successful involved refluxing with dichlorotetracarbonyl-rhodium: no complex could be isolated, although the solution became dark red, but under conditions where the substrate was thermally stable in the absence of the metal, a mixture (53 : 40 : 7 w/w) of the starting material with *trans*- and *cis*-allo-ocimenes was obtained. Longer reaction times gave tars and side products that were probably oligomers of the starting material and its isomers.

(b) <sup>1</sup>H N.m.r. Spectra of Complexes.—Assignments *a–j* refer to protons so designated in formulae (VI)–(XIII). Coupling constants are given where unambiguous measurements could be made.

(VI)  $\tau$  9.85 (1H, dd,  $J$  9 and 2 Hz, *b*), 9.78 (1H, d,  $J$  2 Hz, *d*), 8.35 (6H, d, *h*), 8.31–8.20 (2H, m, *a + e*), 7.65 (4H, m, *f*), 4.61 (2H, m, *c + g*).

(VII)  $\tau$  8.81 (3H, d,  $J$  5 Hz, *a*), 8.32 (6H, d, *g*), 7.87 (3H, s, *c*), 7.34 (1H, q, *b*), 7.00 (1H, t, *e*), 4.82 (2H, d,  $J$  9 Hz, *d + f*); irradiation at  $\tau$  8.81 caused the quartet centred at  $\tau$  7.34 to collapse to a singlet.

(VIII)  $\tau$  9.52 (1H, d,  $J$  2 Hz, *d*), 8.75 (3H, t,  $J$  6 Hz, *a*), 8.32 (6H, d, *h*), 8.20 (1H, d,  $J$  2 Hz, *c*), 7.74 (2H, q,  $J$  6 Hz, *b*), 6.99 (1H, dd,  $J$  9 and 7 Hz, *f*), 4.80 (2H, m, *e + g*).

(IX)  $\tau$  9.81 (1H, q, *b*), 8.56 (3H, d,  $J$  6 Hz, *a*), 8.34

(6H, d, *g*), 7.90 (3H, s, *c*), 6.99 (1H, dd,  $J$  8 and 9 Hz, *e*), 4.75 (2H, d,  $J$  10 Hz, *d + f*).

(X)  $\tau$  9.21 (1H, d,  $J$  2 Hz, *b*), 8.81 and 8.57 (total 2H, *d* and *m*, *f*), 8.36 (6H, s, *h*), 7.91 (3H, s, *d*), 7.38 (1H, m, *e*), 6.98 (1H, t, *a*), 4.85 (2H, m, *c + g*); irradiation at  $\tau$  4.85 decoupled the triplet at  $\tau$  6.98 to form a singlet; similar irradiation at  $\tau$  7.38 decoupled the doublet at  $\tau$  8.81.

(XI) and (XII)  $\tau$  9.20 (d,  $J$  6 Hz) and 9.25 (d,  $J$  6 Hz) (6H total, *f + f'*), 8.06(s) and 8.02(s) (3H total, *a + a'*), 7.61–8.60 (4H total, *c + d + e + c' + d' + e'*), 7.04–7.20 (total 2H, *b + g + b' + g'*), 4.84 (1H, d,  $J$  9 Hz, *h + h'*).

(XIII)  $\tau$  8.97 (6H, d,  $J$  7 Hz, *f*), 8.19 (1H, d,  $J$  6 Hz, *d*), 7.69 (1H, m, *e*), 7.11 (3H, s, *a*), 5.69 (2H, d,  $J$  3 Hz, *c*), 3.83 (2H, d,  $J$  5 Hz, *b*).

(c) Mössbauer Spectra.—The <sup>57</sup>Fe spectra of some of these complexes and a 7-acetoxy-derivative (see next section) yielded the parameters in Table 2.

TABLE 2

Mössbauer parameters for some dienetricarbonyliron complexes

Complex	$\delta(\text{Fe})/\text{mm s}^{-1}$ <sup>a</sup>	$\Delta/\text{mm s}^{-1}$ <sup>b</sup>	$\Gamma/\text{mm s}^{-1}$ <sup>c</sup>
(XV)	+0.04 <sub>5</sub>	1.46 <sub>1</sub>	0.27; 0.27
(XXI)	+0.02 <sub>7</sub>	1.45 <sub>7</sub>	0.26; 0.26
(X)	+0.04 <sub>4</sub>	1.43 <sub>7</sub>	0.29; 0.24
(VII)	+0.04 <sub>3</sub>	1.43 <sub>3</sub>	0.26; 0.27

<sup>a</sup> Chemical isomer shift. <sup>b</sup> Quadrupole splitting. <sup>c</sup> Width of resonance line(s) at half height.

(d) Tracer Studies of the Isomerisation (VII)  $\rightarrow$  (VIII).—A mixture of *cis*- and *trans*-allo-ocimenes labelled in the 3-methyl group with carbon-14 and hydrogen-3 was converted into (VII): the latter had specific activity  $5.2 \times 10^6$  disint. min<sup>-1</sup> mmol<sup>-1</sup>; <sup>3</sup>H/<sup>14</sup>C, 2.31  $\pm$  0.05. Isomerisation to (VIII) was effected and the complex was rigorously purified, after which the organic ligand was recovered, purified, and assayed for radioactivity. This compound had an isotope ratio (<sup>3</sup>H/<sup>14</sup>C) of 2.25  $\pm$  0.05, and after ozonolysis and oxidative work-up, essentially all the <sup>14</sup>C-tracer (>95%) was recovered in formic acid.

(e) Hydroboration of Diene Complexes and Related Reactions.—Hydroboration of the myrcene adduct (VI) and treatment with methanol gave a yellow oil (XV) (80%), b.p. 43° at 0.06 mmHg;  $M^+$  350;  $\tau$  9.75 (2H, m, *b + d*), 9.05 (6H, d,  $J$  7 Hz, *i*), 8.30 (2H, m, *a + e*), 8.15 (4H, m, *f*), 7.80–7.61 (2H, m, *g + h*), 6.44 (6H, d, *j*), and 4.60 (1H, t, *c*). On treatment with acetic acid at room temperature this yielded an iron-containing complex from which boron had been removed ( $M^+$  278); and further treatment with cerium(IV) ammonium nitrate gave 7-methyl-3-methyleneoct-1-ene (XVI) (43% from myrcene), b.p. 176° (Found: C, 87.3; H, 12.9%;  $M^+$ , 138. C<sub>10</sub>H<sub>18</sub> requires C, 86.9; H, 13.1%;  $M$ , 138); *m/e* 95, 81, 67, and 53. The structure of (XVI) was confirmed by ozonolysis followed by oxidative work-up to give formic acid and 5-methyl-1-oxohexanoic acid (yields 80 and 53% of theoretical). The olefin readily polymerised unless hydroquinone (1%) was added.

Hydroboration of the adduct from *cis*-allo-ocimene (VII), followed by treatment with methanol gave a viscous oil (70%),  $M^+$  350; b.p. 51° at 0.01 mmHg, which on stirring with alumina at room temperature gave a mixture of

<sup>12</sup> R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, 7, 1.

<sup>13</sup> L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, 87, 3253.

two tricarbonyliron complexes [(XVII) and (XVIII)],  $M^+$  278, which could easily be separated;  $\tau$  (XVIII) 9.10 (7H, d  $J$  6 Hz,  $h + e$ ), 8.93 (3H, d,  $J$  5 Hz,  $a$ ), 8.50 (1H, m,  $g$ ), 7.94 (3H, s,  $c$ ), 7.71 (2H, m,  $f$ ), 7.42 (1H, q,  $J$  6 Hz,  $b$ ), and 4.89 (1H, d,  $J$  12 Hz,  $d$ );  $\tau$  (XVII) 9.15 [8H, d,  $h + b, e$  (masked)], 8.59 (3H, d,  $a$ ), 8.51 (1H, m,  $g$ ), 7.91 (3H, s,  $c$ ), 7.68 (2H, m,  $f$ ), and 5.12 (1H, d,  $J$  11 Hz,  $d$ ).

Similar treatment of the complex formed by *trans*-allo-ocimene (IX) gave the single product (XVIII) (73%).

Treatment of (XVII) or (XVIII) with cerium(IV) ammonium nitrate gave the olefins (XIX) and (XX), isolated in 50 and 45% yields (based on the original starting material), respectively (Found: C, 87.2; H, 13.0; and C, 86.5; H, 13.1%, respectively.  $C_{10}H_{18}$  requires C, 86.9; H, 13.1%), which had virtually identical mass spectra ( $M^+$  138) and n.m.r. spectra [ $\tau$  9.08 (6H, d,  $J$  6 Hz), 8.51 (1H, m), 7.80–7.61 (8H), and 4.45–3.70 (3H)]. Ozonolysis with oxidative work-up yielded acetic acid, pyruvic acid, and 3-methylbutyric acid in 20–70% yields in either case.

When the *cis*-ocimene adduct (X) was hydroboronated and treated with alumina and methanol, isomerisation occurred to give a mixture (51 : 49) of (XVII) and (XVIII).

(f) *Other Additions to Tricarbonyliron Complexes.*—Hydrogenation of (VI) with Adams catalyst was unsuccessful under a variety of conditions as was reduction with hydrazine hydrate over asbestos wool. However, refluxing the complex with an excess of anthracene-9,10-di-imine gave an acceptable conversion (23%) into a complex that yielded (XVI) on treatment with cerium(IV) ion.

Treatment of (VI) with acetic acid and boron trifluoride gave a tricarbonyliron complex (XXI), b.p. 120–125° at 0.01 mmHg. Removal of the iron gave 7-acetoxy-7-methyl-3-methyleneoct-1-ene (XXII), b.p. 90° at 11 mmHg, identical (i.r. spectrum) with an authentic sample.<sup>14</sup> Addition of water to (VI), catalysed by sulphuric acid, gave a product, b.p. 60° at 0.01 mmHg, which could be converted into 2-methyl-6-methyleneoct-7-en-2-ol (XXIII), identical with a sample prepared by a previously described route.<sup>15</sup>

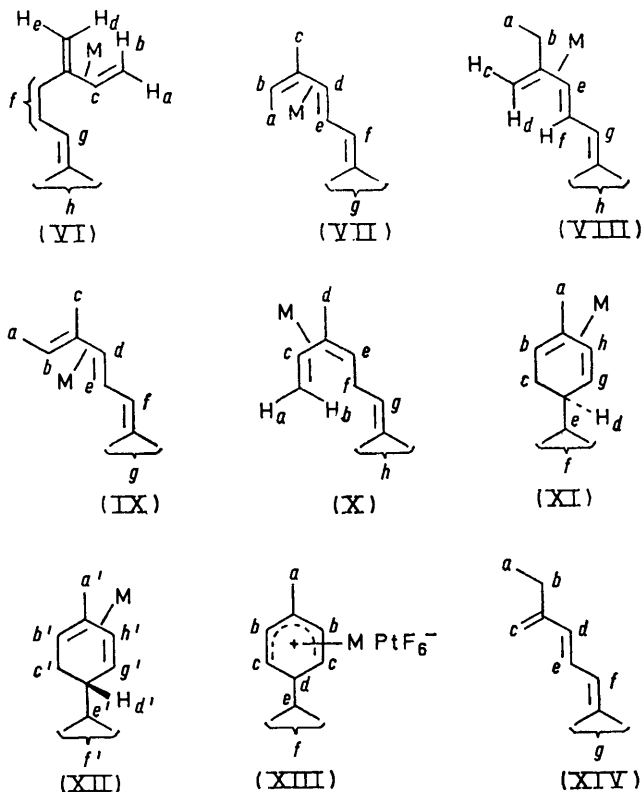
Pyrolysis of (XXI) and treatment of the product with cerium(IV) ammonium nitrate gave a high yield (ca. 90% conversion per cycle) of  $\alpha$ -myrcene (XXIV) and  $\beta$ -myrcene [commercial 'myrcene' (I)] (66 : 34). Similar treatment of the tricarbonyliron complex of (XXIII) gave a lower (ca. 20% per cycle) recovery of the same olefins in the proportions 51 : 49.

## DISCUSSION

It was virtually certain<sup>3,4</sup> that conjugated diene-tricarbonyliron complexes would be formed in these reactions; all complexes indeed gave satisfactory elemental analyses for 1 : 1 adducts and formed the expected molecular ion under electron impact (Table I).

The position of attachment of metal and also the skeleton of the olefinic ligand were assigned by n.m.r. spectroscopy. This procedure was based on correlations obtained<sup>12</sup> for butadienetricarbonyliron (XXV). For this compound, signals at  $\tau$  9.5–9.8 were attributable

to the 'inner' protons ( $H_b$ ) whereas signals at  $\tau$  8.2–8.4 were assigned to the 'outer' protons ( $H_a$ ), these signals being shifted from the region for those for the corresponding protons in uncomplexed dienes by the presence of the iron-containing group. Methyl-substitution at the terminal carbon atoms resulted in the 'inner' and 'outer' protons giving signals at  $\tau$  8.9–9.4 and ca. 7.3, respectively, and the methyl signals were shifted upfield when the methyl groups were in an 'inner' position, and less so displaced when in 'outer' positions. The protons  $H_c$  in (XXV) gave peaks in the region  $\tau$  4.6–4.9, that is, in the normal region for the corresponding protons in the uncomplexed diene. Thus, the terminal protons of the conjugated diene systems in our complexes should give signals at  $\tau$  values very different from those of uncomplexed dienes if no isomerisation (skeletal or double-bond) occurred during complex formation at the diene group. Most of the n.m.r. signals due to the remaining protons should, in contrast, remain unaffected when the olefin becomes part of a complex.



By using this approach, a consistent set of assignments of the n.m.r. spectra with structures (VI)–(XIV) \* could be achieved in all cases if the reasonable assumption was made that 'inner' protons of conjugated and complexed diene groups that were adjacent

<sup>14</sup> G. Ohloff, J. Seibl, and E. Sz. Kovats, *Annalen*, 1964, **675**, 83.

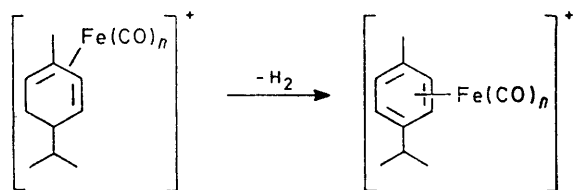
<sup>15</sup> J. H. Blumenthal, U.S.P. 3176022/1965 (*Chem. Abs.*, 1965, **62**, 16310).

\* See footnote a, Table I, concerning the representation of these structures.

to double bonds, *i.e.*  $H_e$  in (VII),  $H_f$  in (VIII) and  $H_g$  in (IX), gave resonances in the region  $\tau$  6.90–7.00. Often the spectrum of the monoterpene was considerably simplified when it was involved in complex formation. Thus  $H_{a-e}$  of myrcene (XXVI) formed an ABC system that transformed to an AMX system. Also signals for the methylene protons  $H_f$  of (X) were shifted upfield to  $\tau$  8.57 and 8.81 from their usual positions ( $\tau$  *ca.* 7.6), presumably owing to their proximity to the metal.

The retention, or otherwise, of the skeleton of the diene in the complex was also determined by the recovery and characterisation of the organic ligand after decomposition of the complex by cerium(IV) ammonium nitrate, a method shown not to cause skeletal rearrangement of monoterpenes under these conditions. In all the cases investigated, the structure deduced from the n.m.r. spectrum was thus confirmed.

The mass spectra of the complexes possessed peaks due to the molecular ion and to successive loss of carbonyl groups in a pattern that is general<sup>6</sup> for dienetricarbonyliron compounds and analogous  $\pi$ -bonded organometallics. However, some fragmentation of the organic system always occurred before loss of the iron atom, *e.g.* there was always a prominent peak at  $m/e$  162 due to  $[M - 3(CO) - 2(CH_3)]^+$ . The spectrum of [(XI) + (XII)] was of particular interest in that losses of two hydrogen atoms from the molecular and fragment ions were apparent. These probably resulted from the sequence shown in Scheme 1 ( $n = 0, 1, 2, \text{ or } 3$ ); such a pattern has been noted for complexes of cyclohexadienes.<sup>16</sup>



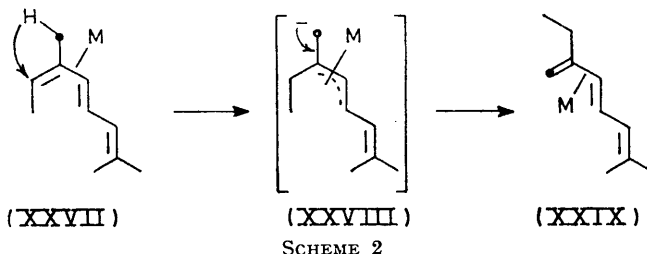
SCHEME 1

In common with most other iron complexes, the Mössbauer spectra showed two absorption lines of equal intensity. Values of  $\delta$  and  $\Delta$  closely resembled those of several other dienetricarbonyliron complexes.<sup>17</sup>

The tricarbonyliron adduct (VI) formed by myrcene had physical properties similar to those previously reported<sup>6</sup> and contained an unrearranged olefinic ligand. Previous workers<sup>6</sup> claimed that reaction of a mixture of *trans*- and *cis*-allo-ocimene [(II) and (III)]; the isomers can be separated with difficulty] with pentacarbonyliron gave two complexes: one (named Complex A) was shown to be (VIII), but the other (Complex B) was uncharacterised and was believed to be (VII) or (IX) or a mixture of these. We found that reaction of the allo-ocimenes with dodecacarbonyltri-iron gave a single product with an n.m.r. spectrum different from those of either Complex A or B. We assign this new product the structure (VII). When (VII) was heated

a mixture of two compounds was obtained which had n.m.r. spectra identical with those of the previously reported Complexes A and B: we assign these the structures (VIII) and (IX).

It has been suggested<sup>6</sup> that the skeletal rearrangement to form (VIII) occurs by means of an intramolecular shift of hydrogen as in Scheme 2 [where (XXVIII)



SCHEME 2

is a formal intermediate]. This mechanism is supported by the experiments using [<sup>14</sup>C,<sup>3</sup>H]-labelled (VII); *viz.* the maintenance of the <sup>14</sup>C/<sup>3</sup>H ratio from (XXVII) to (XXIX) was demonstrated and the location of tracer at the indicated position in product was demonstrated when substrate labelled with <sup>14</sup>C at C-3 was used.

An analogous rearrangement of the complex (X) formed from *cis*-ocimene could possibly generate myrcene and so would result in a monoterpene of industrial importance<sup>18</sup> being derived from one that is readily available but is of much less significance. In the event, reaction of *cis*-ocimene with all three iron carbonyls yielded (X), in which the skeleton of the olefin was unaltered. However, heating either (X) or (VII) or treatment of either with triphenylmethyl tetrafluoroborate followed by sodium borohydride led to formation of identical proportions of (VIII), (VII), (IX), and (X). It is well established<sup>3,4</sup> that the ligand in dienetricarbonyliron complexes is readily attacked by electrophiles, and the carbonium ion in the second method presumably extracts a hydride ion from either substrate to form (XXX), which takes up hydride ion from sodium borohydride to give a product mixture containing both rearranged and unrearranged ligand in which the comparatively stable (VIII) and (IX), predominate.

$\alpha$ -Phellandrene reacted with dodecacarbonyltri-iron to give a mixture of products that could not be separated by chromatographic methods. The n.m.r. spectra of these compounds were very similar (but not identical: see previous section) and could not be fully interpreted owing to the multiplicity and overlap of the signals. However, as removal of the iron-containing group regenerated  $\alpha$ -phellandrene (93%; >98% pure) the complexes are considered to be (XI) and (XII). Treatment of the mixture of products with triphenylmethyl tetrafluoroborate gave a complex that could be isolated as its platinum hexafluoride salt (XIII) in low yield;

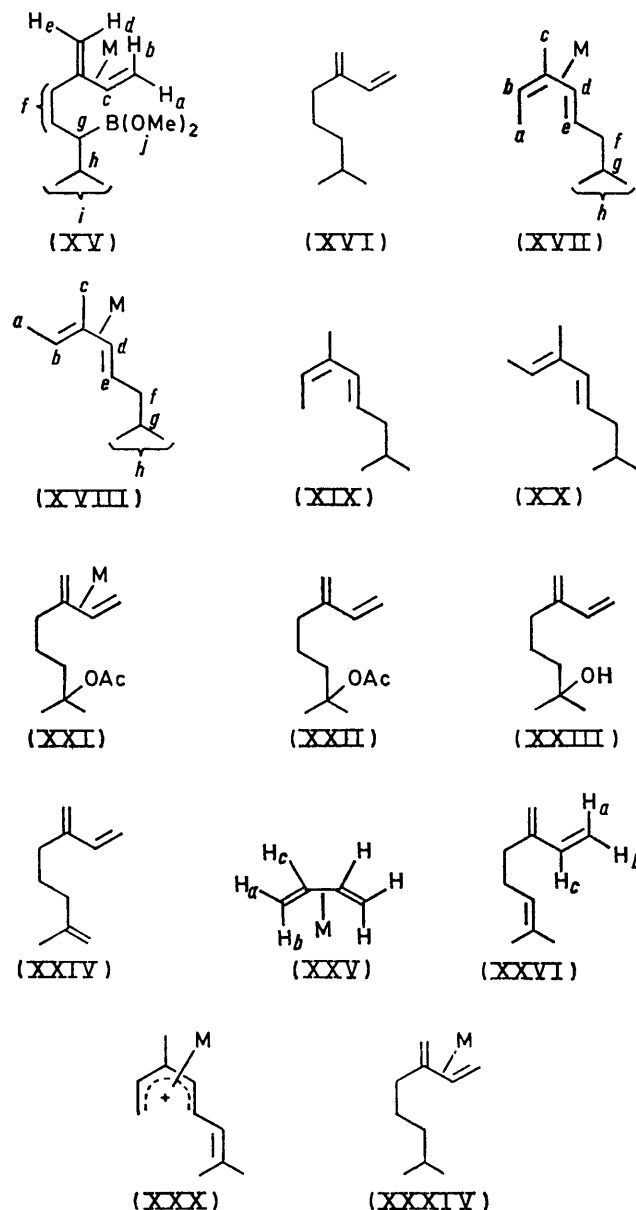
<sup>16</sup> J. Müller, *Angew. Chem. Internat. Edn.*, 1972, **11**, 653.

<sup>17</sup> R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 2332.

<sup>18</sup> R. Ansari, *Flav. Ind.*, 1970, **1**, 252.

$H_e$  and the iron-containing group may be *cis*-oriented as this proton is considerably shielded, as indicated by the n.m.r. spectrum.

Some of the above experiments indicate that pure samples of *cis*- and *trans*-allo-ocimene may be readily prepared in >90% yield from the commercially available



mixture of isomers, which is very difficult to separate, by conversion into (VII) and (IX) followed by recovery of the pure olefins.

Hydroboration of (VI) and methanolysis of the product led to isolation and characterisation of (XV), and similar, although uncharacterised, products resulted from analogous treatment of (VII) and (IX). The boron group could be removed from all three complexes

<sup>19</sup> M. A. Bennett, *Chem. Rev.*, 1962, **62**, 611.

<sup>20</sup> W. J. Houlihan, J. Levy, and J. Mayer, *J. Amer. Chem. Soc.*, 1959, **81**, 4692.

by treatment with acetic acid or alumina at room temperature. These are exceptionally mild conditions for the reaction; a typical procedure to decompose a boron adduct is treatment with propionic acid at reflux. The resulting products (XVI), (XIX), and (XX) are members of a novel class of dihydromonoterpenes in which the isopropylidene double bond has been reduced.

A few other reactions of tricarbonyliron complexes were explored in which the iron-containing system acted as a protecting group for the diene. Attempted catalytic hydrogenation of (VI) was unsuccessful, as has been found for reduction of other ligands complexed to iron,<sup>19</sup> but reduction with di-imide gave an acceptable (*ca.* 23%) yield of a complex (XXXIV) containing a reduced isopropylidene group. The routes to (XXII) and (XXIII) by hydroacetoxylation and hydration of (VI) were more convenient than those previously reported,<sup>15,20</sup> as also was the route to the uncommon  $\alpha$ -isomer (XXIV) of myrcene (*cf.* refs. 14 and 21). Presumably the last reaction would be general for the preparation of the  $\alpha$ -series of acyclic monoterpene hydrocarbons.

#### EXPERIMENTAL

(a) *Materials and Methods.*—The monoterpenes (typically >90% pure by g.l.c.) were obtained from Bush Boake Allen and Co. Ltd. (London) and were fractionally distilled under nitrogen to give a heart cut that was then gas chromatographed (if necessary) on a column (3 cm o.d.  $\times$  5 m) of Carbowax 20M (15% w/w on 80–100 mesh acid-alkali washed G-cel) at 100° with a flow rate of 7 l h<sup>-1</sup> to obtain pure material (>99% by g.l.c. on capillary columns; 0.5 mm  $\times$  50 m, Carbowax 20M and Apiezon L).

All n.m.r. spectra were measured for 10% solutions in deuteriochloroform with a Varian 100 MHz spectrometer, usually with tetramethylsilane as internal standard. Certain complexes had resonances near  $\tau$  10; for these, chloroform ( $\tau$  2.75) was used as standard. Mass spectra were measured with a Metrovick MS9 instrument at 70 eV bombarding potential.

(b) *Preparation of Dienetricarbonyliron Complexes.*—Each monoterpene (10 g) was refluxed with nonacarbonyl-di-iron (1.2 molar proportions) in benzene (200 ml) under nitrogen for 12 h. Work-up gave low (8–40%) yields of tricarbonyl complexes. Better yields usually were obtained on similar treatment with dodecacarbonyltri-iron or pentacarbonyliron in di-*n*-butyl ether. The reaction mixture was filtered and the solvent was removed under vacuum to give a brown oil. This was passed through a column of alumina (1 cm o.d.  $\times$  6 cm; Brockmann grade III) with pentane as eluant and the products were then distilled at low pressure to give yellow oils that were further purified either by preparative t.l.c. on alumina or silica gel with di-*n*-butyl ether–benzene mixtures as eluants, or by preparative g.l.c. on Carbowax 20M (1 cm o.d.  $\times$  3 m) at 175° with flow rate 6 l h<sup>-1</sup>. Generally the products defied attempts at crystallisation at normal or low temperatures.

Isomerisations of the complexes were carried out by refluxing a solution (10%) in di-*n*-butyl ether for 150 h;

<sup>21</sup> B. M. Mitzner, E. T. Theimer, L. Steinbach, and J. Wolt, *J. Org. Chem.*, 1965, **30**, 646.

by passing through an alumina column (2 cm o.d.  $\times$  30 cm; Brockmann grade III) with pentane as solvent; or by shaking the complex (2 g) with triphenylmethyl tetrafluoroborate (2.6 g) in methylene chloride-chloroform (20 ml; 75 : 25 v/v) for 3 h at 25°, followed by similar treatment with a solution of sodium borohydride (3 g) in ether (100 ml) at 25°.

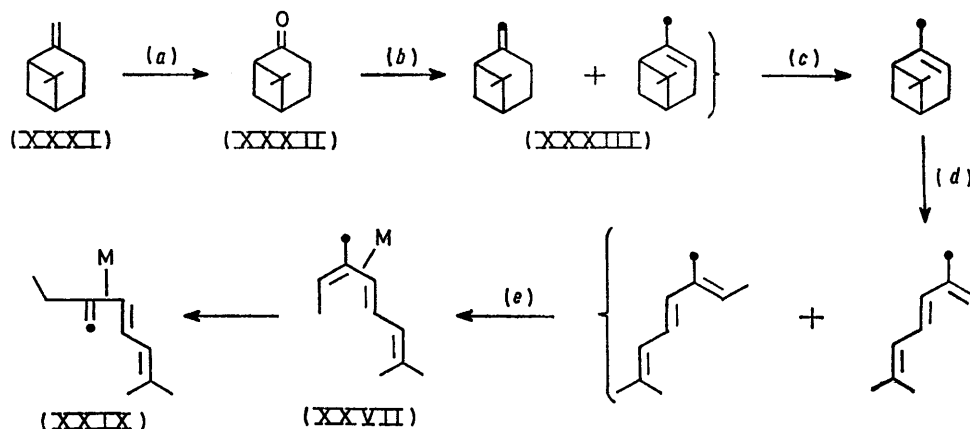
Attempts were made to isomerise *cis*-ocimene (1 g) by refluxing with tetracarbonyldichlorodirrhodium (2 g; prepared as in ref. 22) in benzene (100 ml) for 5 min; longer periods resulted in formation of much tar and high-boiling materials.

(c) *Structure of the Organic Ligand in the Adduct (VIII) and Tracer Studies on the Formation of the Latter*.—The olefin was recovered from (VIII) and purified by g.l.c on

min<sup>-1</sup> and <sup>3</sup>H/<sup>14</sup>C, 2.31. It was then converted into (XXIX). The latter was assayed for <sup>14</sup>C and <sup>3</sup>H; a portion was ozonised and the formic acid produced was isolated and also assayed for <sup>14</sup>C.

(d) *Radiochemical Methods*.—The technique of counting radioactive samples followed that previously outlined.<sup>23</sup> Assays were made on the free ligands rather than on the complexes to avoid difficulties due to lack of solubility in the counting medium and to quenching. Each counting period accumulated  $4 \times 10^4$  scintillations; this ensured that  $2 \sigma$  was  $\pm 1\%$ . Combined errors in weighing and counting were estimated at  $\pm 5\%$ .

(e) *Recovery of Organic Ligands*.—The best method was found to be shaking the complex (1 g) in ether (30 ml) with aqueous cerium(IV) ammonium nitrate (1M; 40 ml)



SCHEME 3

Carbowax 20M at 80°. The product (0.2 g) was ozonised in methanol (20 ml) at  $-10^\circ$  by use of a Nuair model 15-69K ozoniser, and the crude product was decomposed by treatment for 3 days at 20° with a mixture of formic acid (98% w/w; 3 ml) and hydrogen peroxide (30 vol; 2.5 ml), after which the peroxides were destroyed by treatment with manganese dioxide (10 mg) for 3 h at 0°. Acetone was distilled out of the mixture and collected as its 2,4-dinitrophenylhydrazone; the remaining acids were separated by methods previously described<sup>23</sup> and identified by their i.r. spectra.

The labelled adduct [<sup>14</sup>C,<sup>3</sup>H]-(VIII) was synthesised by the sequence of reactions in Scheme 3. Most of these steps are well known. Ozonolysis of  $\beta$ -pinene (XXXI) (10 g) in methanol at  $-10^\circ$  yielded nopinone (XXXII) (8 g), b.p. 78° at 8 mmHg. This was treated with [<sup>3</sup>H,<sup>14</sup>C]-methyl iodide in a Grignard reaction and was worked up with dilute hydrochloric acid to give a mixture of  $\alpha$ -pinene (XXXIII) and  $\beta$ -pinene: the mixture was then converted into  $\alpha$ -pinene by treatment with pentacarbonyliron.<sup>24</sup> On pyrolysis, [<sup>14</sup>C,<sup>3</sup>H]- $\alpha$ -pinene gave a mixture of labelled allo-ocimenes<sup>25,26</sup> (step d; 40% yield) and the crude product was converted into (XXVII) as previously described. After purification by g.l.c. and t.l.c., (XXVII) (60 mg) had a total radioactivity of  $1.2 \times 10^6$  disint.

<sup>22</sup> J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 212.

<sup>23</sup> D. V. Banthorpe, G. N. J. LePatourel, and M. J. O. Francis, *Biochem. J.*, 1972, **130**, 1045.

<sup>24</sup> P. A. Spaninger and J. L. von Rosenberg, *J. Org. Chem.*, 1969, **34**, 3658.

until the evolution of carbon monoxide had ceased. Recoveries were usually greater than 90%.

(f) *Hydroboration Experiments*.—Diborane generated by the addition of sodium borohydride (5.6 g) in bis-(2-methoxyethyl) ether (200 ml) to boron trifluoride-ether complex (28 ml) was passed into a solution of the appropriate complex (8 g) in tetrahydrofuran (130 ml), and the mixture was stirred under nitrogen at 20° for 12 h. The excess of borohydride was then destroyed by cautious addition of methanol at  $-78^\circ$  and the solution was worked up and concentrated under reduced pressure, sometimes to isolate the boron adduct. The boron was removed either by treatment of the complex (5 g) with glacial acetic acid (200 ml) at 25° for 12 h or by stirring at 25° for 48 h with a suspension of alumina (20 g.; Brockmann grade III) in methanol (200 ml).

(g) *Other Reactions*. The adduct (VI) (2 g) was reduced to (XXXIV) by refluxing under nitrogen for 5 h in ethanol (200 ml) with anthracene-9,10-di-imine (16 g).<sup>27</sup> Hydroacetoxylation of (VI) (3 g) was effected by treatment with acetic acid (20 ml) and 30% boron trifluoride-ether complex (500 ml) for 12 h at 15°, followed by the usual work-up. Hydration was carried out by heating the complex (3 g) in dioxan (15 ml) with 50% aqueous sulphuric acid (3 ml) at 2° for 7 h.

<sup>25</sup> J. E. Hawkins and H. G. Hunt, *J. Amer. Chem. Soc.*, 1951, **73**, 5379.

<sup>26</sup> J. E. Hawkins and W. A. Burris, *J. Org. Chem.*, 1959, **24**, 1507.

<sup>27</sup> E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, 1962, **84**, 685.

The tricarbonyliron complexes of (XXII) and (XXIII) were pyrolysed in a flow of nitrogen over glass wool in a well seasoned Pyrex tube at 475° and 500°, respectively with a throughput of 1.5 ml min<sup>-1</sup>.

(h) *Mössbauer Spectra*.—These were measured by Dr. R. Parish (Manchester). Curve-fitting was performed by

<sup>28</sup> N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971, p. 221.

computer<sup>28</sup> using independent Lorentzian curves for the two bands with 353 degrees of freedom for the error function.

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