Absolute Configuration of some Tricarbonyl(cyclohexadiene)iron Complexes

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Summary The absolute configurations of the complexes (**1**) and (**6**), obtained by chiral transfer of $Fe(CO)_3$ to the dienes, have been determined by transformation into the known terpenes cryptone and phellandrene.

UNSYMMETRICAL dienes yield chiral complexes with organometallic ligands such as $Fe(CO)_3$. The chirality can be transferred to new centres generated by completely stereospecific reactions using such complexes, or more particularly the derived dienylium salts.[1] Removal of $Fe(CO)_3$ then eliminates the inducing chirality. The method can therefore result in resolution at a new centre to the extent that the original complex is resolved.

As the first step to utilisation it is necessary to determine absolute configurations in some key complexes, and, if possible, to relate o.r.d. curves† to the nature of substitution to enable assignment in unknown cases. For this purpose it is not necessary to have fully resolved complexes. The synthetically important 2-OMe and 2-Me tricarbonylcyclohexadienyliumiron cations are the subject of the present work.

Optically active complexes can be obtained in some cases by classical resolution,[2] or in a state of partial resolution by asymmetric induction in complexation by transfer of $Fe(CO)_3$ from a chiral α,β-unsaturated ketone complex.[3] Elucidation of the mechanism of this complexation also

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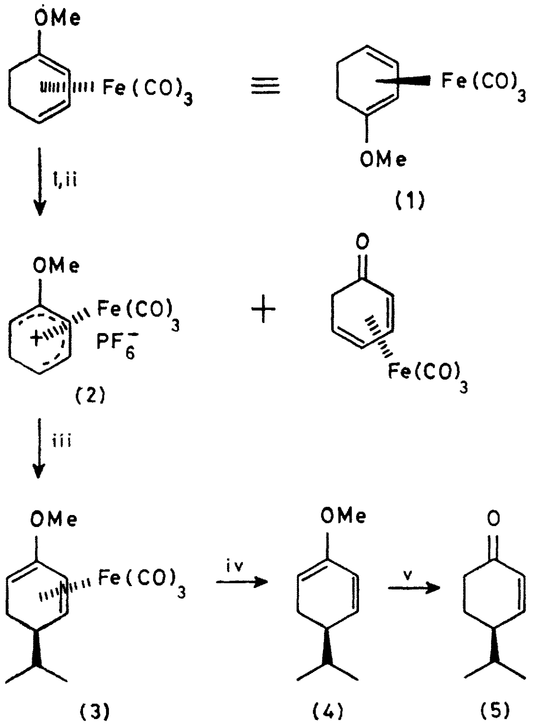
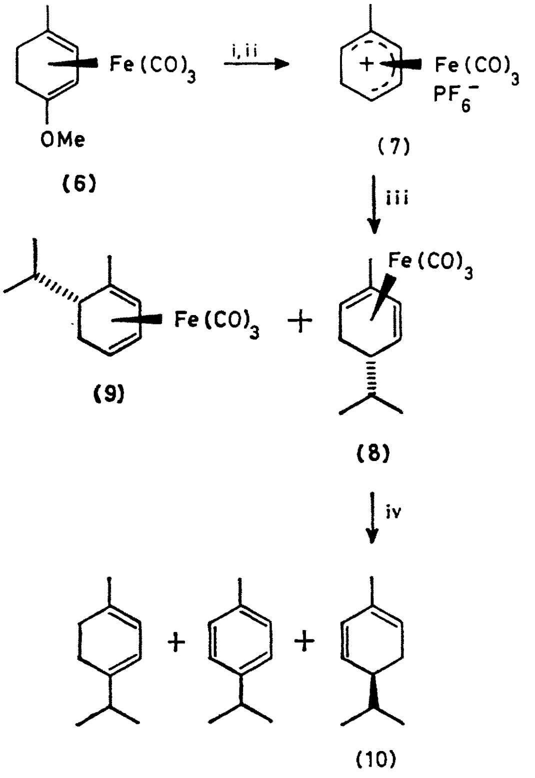
† O.r.d. spectra reported take the form of simple curves between 650 and 480 nm, indicating only the sign of rotation. Observation of the o.r.d. curve below 480 nm is prevented by the u.v. absorption of the complexes.

requires the definition of the absolute configurations of some key compounds so obtained. Transfer of $Fe(CO)_3$ to two methoxycyclohexa-1,3-dienes from the complex of (+)-pulegone, conversion of the products into tricarbonylcyclohexadienyliumiron salts, and nucleophilic additions have enabled configurations to be determined by conversion into known terpenes. The conclusions are based on α-nucleophilic attack [opposite to the $Fe(CO)_3$ group]; further evidence for the total stereospecificity of this reaction is given.



SCHEME 1. i, $Ph_3C^+BF_4^-$, CH_2Cl_2, 15 °C, then hydrolysis at 90 °C, ii, sat. NH_4PF_6 (aq.), iii, Pr^i_2Cd, tetrahydrofuran, MeCN, −24 °C, iv, $Me_3NO{\cdot}2H_2O$, Me_2NCOMe, 60 °C, v, $(CO_2H)_2$, SiO_2, H_2O, 15 °C.

The (+)-tricarbonyl-(2-methoxycyclohexadienylium)iron hexafluorophosphate (**2**) ($[\alpha]_D$ + 4·8°, *c* 6, MeCN), obtained by hydride abstraction[1] from (+)-tricarbonyl-(1-methoxycyclohexadiene)iron,[3] was alkylated[4] with di-isopropylcadmium in 53% yield to (−)-tricarbonyl-(5α-isopropyl-2-methoxycyclohexa-1,3-diene)iron (**3**) ($[\alpha]_D$ −5·1°, *c* 9, $CHCl_3$), from which the metal was removed by $Me_3NO{\cdot}2H_2O$ in dimethylacetamide. The crude enol–ether (**4**) was hydrolysed by mild acid treatment to (*R*)-(−)-cryptone (**5**) in 49% yield from (**3**) ($[\alpha]_D$ −2·9°, *c* 6, EtOH), semicarbazone m.p. 196—197 °C (lit.[5] 196—195 °C, *R*,*S*). Comparison of the o.r.d. spectrum with that of an authentic specimen of (*R*)-(−)-cryptone indicated the absolute configurations shown in Scheme 1. The enantiomeric excess is low {(*R*)-(−)-cryptone[6] $[\alpha]_D$ −119·3°} but some racemisation may have occurred during hydrolysis. However, the enantiomeric excess in the original process[3] is clearly inadequate to form the basis of syntheses.



SCHEME 2. i, H_2SO_4, 5 °C, ii, sat. NH_4PF_6 (aq.), iii, Pr^i_2Cd, tetrahydrofuran, MeCN, −24 °C, iv, $Me_3NO{\cdot}2H_2O$, Me_2NCOMe, 60 °C.

Reaction of (+)-tricarbonyl-(1-methoxy-4-methylcyclohexadiene)iron (**6**) with H_2SO_4[7] gave (−)-tricarbonyl-(2-methylcyclohexadienylium)iron hexafluorophosphate[3] (**7**) ($[\alpha]_D$ −2·5°, *c* 9, MeCN), converted by di-isopropylcadmium into (−)-tricarbonyl-(5α-isopropyl-2-methylcyclohexa-1,3-diene)iron (**8**) ($[\alpha]_D$ −1·2°, *c* 13, $CHCl_3$) (2 parts) and the 6α-isomer (**9**) (1 part) which were separated by chromatography on silver nitrate-impregnated silica. The combined yield was 78%. The enantiomer of (**8**) ($[\alpha]_D$ + 11·9°, *c* 3, $CHCl_3$) has been prepared[8] by direct complexation of (*R*)-(−)-α-phellandrene ($[\alpha]_D$ −223°, *c* 1·5, $CHCl_3$). Comparison of the o.r.d. spectra† of the two antipodes of (**8**) indicates the absolute configurations drawn (Scheme 2). The enantiomeric excess is again low. No evidence of the other known[8] β-isopropyl stereoisomer [which would result from β-alkylation of the salt (**7**)] was observed from the alkylation, again confirming the stereospecificity of the reaction.

Removal of $Fe(CO)_3$ from (−)-tricarbonyl-(5α-isopropyl-2-methylcyclohexa-1,3-diene)iron (**8**) gave a product containing (*S*)-(+)-α-phellandrene (**10**), α-terpinene, and *p*-cymene, of which the first is the only chiral constituent. O.r.d. of this mixture agreed with the absolute configurations reported above. All compounds provided satisfactory n.m.r. spectra, and were compared by g.c. with known compounds when appropriate.

The use of the $Fe(CO)_3$ complex of (−)-3β-acetyloxypregna-5,16-dien-20-one in transfer of $Fe(CO)_3$ yielded diene complexes of the opposite absolute configurations to those derived from (+)-pulegone with a higher enantiomeric excess.[3]

We thank Mr. I. A. Southwell (Museum of Applied Arts and Sciences, Sydney) for an authentic specimen of (*R*)-(−)-cryptone.

(*Received*, 31*st March* 1980; *Com.* 334.)

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