Transition-metal Mediated Asymmetric Synthesis. Part 3.[1] Preparation and Stereospecific Alkylation of Unsymmetrically Substituted Tricarbonyl(cyclohexadienyl)iron(1+) Salts: an Organometallic Approach to the Synthesis of Carvone, Cryptomerion, and Bilobanone

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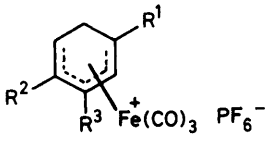
Tricarbonyl(η^5-3-methoxy-2-methylcyclohexa-2,4-dienyl)iron(1+)hexafluorophosphate(1−) has been prepared by a novel method based on thallium(III) oxidation. The opposite substitution pattern is obtained by hydride abstraction. Alkylation by bis(1-methylethenyl)cadmium, to introduce an olefinic side-chain, has been shown to be stereospecific for the α-face, and removal of the metal affords the expected enones. (±)-Carvone and -sylvecarvone have been prepared by this means. The results indicate the importance of regiocontrol of alkylation if chiral salts are to be employed in synthesis.

STEREOSPECIFIC reactions typical of transition-metal π-complexes can be used to direct the formation of resolved centres at carbon if chiral complexes are employed. The concept is general to any unsymmetrically substituted π-olefin complex, provided that the complex is sufficiently stable to allow synthetic application. Appropriate choice of the metal and ligand system should permit the method to encompass a wide variety of co-ordination modes and reaction types. The initial investigation concentrated on η^4 and η^5 tricarbonyliron complexes and demonstrated that stereospecific alkylation at a molecular chiral centre and subsequent removal of the metal can lead[2] without racemisation to a resolved chiral centre at carbon. I have recently reported[1] the preparation, in fully resolved form, of the synthetically useful salt (1a) which can be regarded as a convenient source of resolved 4-methylcyclohex-2-enone rings in synthesis design.



(1)

a; R^1 = Me, R^2 = OMe, R^3 = H
b; R^1 = R^2 = H, R^3 = OMe
c; R^1 = H, R^2 = Me, R^3 = OMe
d; R^1 = R^3 = H, R^2 = Me
e; R^1 = H, R^2 = OMe, R^3 = Me
f; R^1 = R^3 = H, R^2 = OMe
g; R^1 = R^2 = R^3 = H

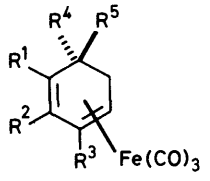
To develop further the application of chiral transition-metal π-complexes in asymmetric organic synthesis, progress must be made in several areas. First, key organometallic intermediates must be identified and prepared, and their synthetic value proven with racemic material. Secondly, to be of use in a practical asymmetric synthesis, the complexes must be obtained in fully resolved form, and the synthetic steps must be checked to ensure racemisation does not occur. Thirdly, the absolute configuration of the intermediates must be determined to permit the prediction of the absolute configurations of the chiral centres produced by alkylation. Progress towards the first of these objectives has been made, and an investigation of the fairly simple problem of the creation of a single chiral centre, such as is found in the terpenes carvone, cryptomerion, and bilobanone, is reported in this paper. These natural products have in common a 2-methylcyclohex-2-enone ring with an unsaturated side-chain at C-5. Attention has already been drawn[3,4] to the value of the tricarbonyl(η^5-3-methoxycyclohexadienyl)iron(1+) salt (1b) as a synthetic equivalent of the C-5 cation of cyclohexenone. In general, a 1,3-relationship between the reactive terminus of the dienyl complex and a methoxy-substituent should lead to 5-substituted cyclohexenones since, after alkylation and removal of the metal, hydrolysis of the unmasked enol ether gives rise to a carbonyl group at the carbon which carried the methoxy-substituent in the original complex. Furthermore, the stereochemical consequence of this sequence is unambiguous once the stereochemistry of alkylation is determined. Thus the chiral salt (1c) should serve as a precursor to resolved 5-substituted 2-methylcyclohex-2-enone rings provided alkylation of the highly activated dienyl ligand occurs, in preference to elimination to form a trimethylenemethane linkage. Elimination from 1-alkyl substituents to give triene complexes is common.[5] Although the 2-methyl-substituted salt (1d) does not undergo elimination,[6] the more reactive salt (1c) may behave differently.

Studies on racemic samples, described here, have confirmed the utility of the approach, which leads to the stereospecific formation of the chiral centre at C-5 in the desired manner.

RESULTS AND DISCUSSION

Synthesis of the salt (1c) by hydride abstraction appeared to be impractical since reaction is expected to occur either at the less sterically hindered methylene group or at a position *para* to a methoxy-substituent (see below). An alternative is to employ the elimination of a

labile substituent to form the dienyl system. A 1,3-relationship between methoxy-substituents should lead to the desired result. Of the two possible substitution patterns, 1,3-dimethoxy-2-methyl and 2,4-dimethoxy-1-methyl, the former is more attractive since reversible protonation at C-4 cannot result in rearrangement of the position of co-ordination.* Thus treatment of diene complex (2a) with acid should result in elimination of methanol from C-1 to give the required salt (1c); this was indeed found to be the case.



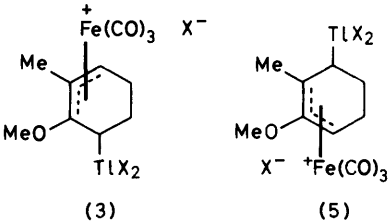
(2)

a; $R^1 = R^3 = OMe$, $R^2 = Me$, $R^4 = R^5 = H$
b; $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Me$
c; $R^1 = R^4 = R^5 = H$, $R^2 = OMe$, $R^3 = Me$
d; $R^1 = Me$, $R^2 = OMe$, $R^3 = R^4 = R^5 = H$
e; $R^1 = OMe$, $R^2 = Me$, $R^3 = R^4 = R^5 = H$
f; $R^1 = OMe$, $R^2 = R^3 = R^4 = H$, $R^5 = Me$
g; $R^1 = OMe$, $R^2 = R^3 = R^5 = H$, $R^4 = Me$
h; $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = COMe$
i; $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = COMe$
j; $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = CN$

Reduction of 2,6-dimethoxytoluene with lithium in liquid ammonia [8] gave 2,4-dimethoxy-3-methylcyclohexa-1,4-diene. The reaction was slow, requiring prolonged exposure to the reducing conditions to achieve a satisfactory conversion. Direct complexation with $Fe(CO)_5$ in dibutyl ether under reflux gave a mixture of complexes as expected. The required complex (2a) was obtained in low yield together with products arising from demethoxylation. After distillation the mixture was separated by column chromatography on silica. Elution with hexane gave first the 5β-methyl complex (2b). Monomethoxy-complexes were eluted next in the order (2c), the major product (2d), (2e), and then the epimers (2f) and (2g) which were eluted together. Finally the desired product (2a) was washed from the column with benzene. Identification of these complexes was based primarily on their ^1H n.m.r. spectra. The doublet (7 Hz) at δ 0.88 in the spectrum of complex (2b) indicated a methyl substituent attached to an sp^3 carbon. Coupling of adjacent protons was typical of β-substituents and the spectrum was quite distinct from that of the known 5α-complex. The complexes (2f) and (2g) gave similar doublets at δ 0.95 and 1.01 and resonances at δ 3.37 and 3.44 typical of 1-methoxy-substituents. The spectrum of compound (2e) similarly included a singlet at δ 3.49 indicating a 1-methoxy-substituent. In this case the methyl resonance appeared as a singlet at δ 2.11, corresponding to substitution at C-2. Reversal of the substituents at C-1 and -2 was revealed by the positions of the two singlets in the spectrum of complex (2d) at δ 1.66 and 3.67. The complex (2c) has both substituents on inner carbons at the diene and showed singlet resonances at δ 2.06 and 3.54. The spectrum of compound (2a) included singlets at δ 3.49 and 3.53, indicating the presence of methoxy-substituents at C-1 and -3, and a methyl singlet at δ 2.15 corresponding to substitution at C-2. A single olefinic resonance was apparent at δ 3.19. In addition, protons at inner and outer positions on the diene gave characteristic resonances, and an analysis of the coupling between these signals confirmed the positions of the pairs of substituents on the diene. Typical positions for methyl resonances are δ 1.6 (1-Me) and 2.1 (2-Me), while methoxy-resonances occur at δ 3.5 (1-OMe) and 3.6 (2-OMe).

Conversion of complex (2a) into the salt (1c) was initially examined under the conditions used by Birch and Hass.[9] Treatment of (2a) with concentrated sulphuric acid and precipitation with ammonium hexafluorophosphate gave a 4 : 1 mixture of complexes (1c) and (1e), indicating that 1,2-demethoxylation [10] had occurred to a small extent. A modification [3] using trifluoroacetic acid (TFA) gave a single salt which was identified as (1c) by the downfield position of the methoxy-proton resonance (4.26 p.p.m.). This occurs at a similar position to that in the 3-methoxy-salt (1b).[3] While this method provided a sufficient quantity of compound (1c) for a study of its alkylation, the difficulty experienced with the preparation of the neutral precursor (2a) was a severe limitation. Preconjugation of the diene before complexation should suppress [3] the undesirable demethoxylation, but a number of reagents were employed for this purpose without success.

A more satisfactory route to the salt (1c) was postulated which involved the introduction of an additional alkoxy-substituent into a more readily available disubstituted complex. Thallium(III) oxidation in ethanol has been shown [11] to produce a 5-ethoxy-substituted complex. The mechanism proposed involves addition of thallium(III) at a terminus of the co-ordinated diene to form a η^3-allyl intermediate [*e.g.* (3) or (5)]. If the reaction were performed with complex

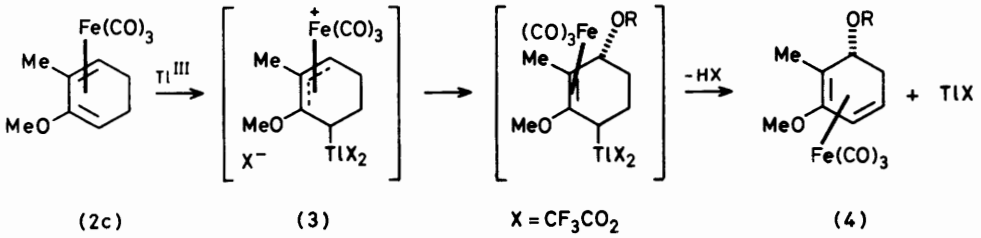


(3) (5)

(2c), preferential formation of the 1-methoxy-allyl intermediate (3) would be expected to result in the introduction of the alkoxy-group at the position required for the preparation of the salt (1c). Unfortunately, treatment of the complex (2c) with thallium tristrifluoroacetate (TTFA) in ethanol–triethyl orthoformate

* Such a process will racemise an optically active complex. This suggests that resolution of the salt, not its precursor, should be attempted. Similar racemisations have been observed for other complexes (ref. 2, 7).

was unsuccessful. When the less reactive triacetate salt was used, starting material was recovered. Problems experienced in the isolation of the required 5-alkoxy-complex from the reaction with TTFA seemed to be the main limitation. This difficulty was overcome by performing the oxythallation, and the elimination to give the salt, in one step. When the complex (2c) and

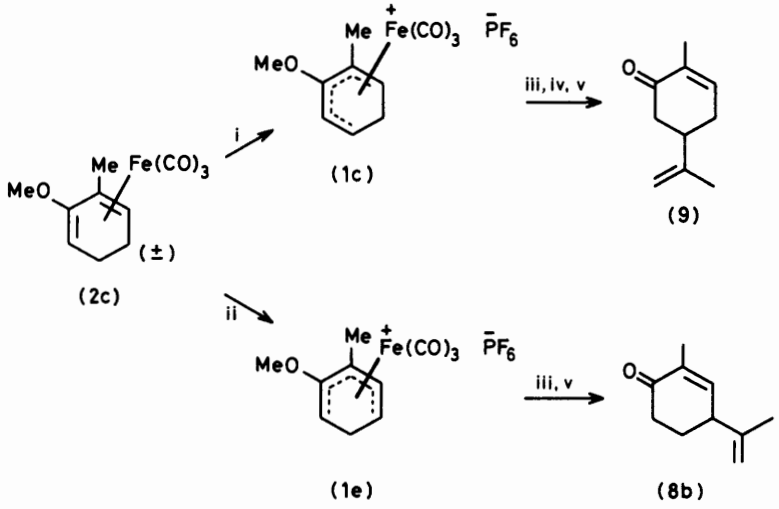


(2c) (3) X = CF_3CO_2 (4)

SCHEME 1

TTFA were ground together in a dry-bag under argon, a vigorous reaction occurred. Addition of saturated aqueous ammonium hexafluorophosphate gave direct access to the salt (1c), obtained as a 10 : 1 mixture with its isomer (1e); presumably this occurred by elimination of a 5-TFA substituent from the complex (4; R = $COCF_3$). The predominance of isomer (1c) in the product mixture must reflect the preferential formation of intermediate (3) over (5), and gives support to the mechanism shown in Scheme 1. Previously η^5 tricarbonyliron salts have been prepared by hydride abstraction,[12] protonation of trienes,[13] or by elimination reactions.[9,14] The success of the novel procedure described above indicates that thallium(III) oxidation can offer an alternative means of preparation, and shows promise as a convenient route to the salt (1c), which is not readily accessible by conventional methods. Further work, however, is required to determine satisfactory reaction conditions.

The 2-methoxy-3-methyl salt (1e), a by-product of the above reaction, should be the major product of hydride abstraction from complex (2c), for the reasons indicated above. Treatment of the complex (2c) with triphenylmethylium tetrafluoroborate gave a 1 : 4 mixture of the cations (1c) and (1e) as tetrafluoroborate salts. Recrystallisation from water gave pure complex (1e) which was converted into the hexafluorophosphate salt with aqueous ammonium hexafluorophosphate. Thus, oxythallation and hydride abstraction are complementary procedures, affording preferentially the salt (1c) or (1e) from the common precursor (2c) (see Scheme 2).



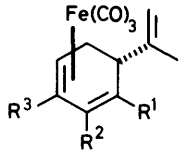
(2c) (1c) (9) (1e) (8b)

SCHEME 2 *Reagents*: i, $Tl(TFA)_3$, $NH_4^+PF_6^-$; ii, $Ph_3C^+BF_4^-$, $NH_4^+PF_6^-$; iii, $(CH_2{=}CCH_3)_2Cd$; iv, chromatography; v, pyridinium chlorochromate

Before the alkylation of these salts could be investigated, a satisfactory method for the introduction of the 1-ethenyl side-chains, needed for synthetic purposes, was required. Organocadmium reagents are known [15] to react well with η^5-tricarbonyliron salts, and di-isopropylcadmium was successfully employed [7,16] in the chemical correlation of the salts (1d) and (1f) with α-phellandrene

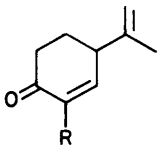
and cryptone, respectively. Accordingly, bis(1-methylethenyl)cadmium (6) was prepared, *via* the Grignard reagent, from 2-bromopropene; the regioselectivity and stereospecificity of the reaction of compound (6) with salts of the type (1) have been examined in detail.

Alkylation of complex (1f) with the cadmium reagent (6) gave a single product (7a). Removal of the tricarbonyliron group by oxidation with pyridinium chlorochromate (PCC) has been shown [17] to lead directly from methoxydiene complexes to enones. In this case,



(7)

a; $R^1 = R^2 = H$, $R^3 = OMe$
b; $R^1 = R^2 = H$, $R^3 = Me$
c; $R^1 = Me$, $R^2 = R^3 = H$
d; $R^1 = H$, $R^2 = OMe$, $R^3 = Me$
e; $R^1 = Me$, $R^2 = OMe$, $R^3 = H$
f; $R^1 = H$, $R^2 = Me$, $R^3 = OMe$
g; $R^1 = R^2 = R^3 = H$



(8)

a; R = H
b; R = Me

compound (8a) was obtained in good yield from the iron complex (7a). No rearrangement to the isomeric phenol was observed, confirming the viability of the alkylation-decomplexation process as a route to enones containing olefinic side-chains with unsaturation adjacent to the ring. Alkylation of the salt (1d) with the reagent (6) gave two products (7b) and (7c), which could be separated analytically by g.l.c. The ^1H n.m.r. spectrum of the mixture indicated that the major product was compound (7b). A similar mixture of products has been obtained from the alkylation of the salt (1d) with other organocadmium reagents.[15,16] The effect of varying the reaction temperature on the product distribution was examined. In contrast to results obtained from hydride reductions,[6] alkylation of complex (1d) by the reagent (6) was most regioselective at low temperature (see Experimental section). Poor yields at low temperature may be due to inadequate solubility of the reagents. Better results were obtained by simultaneous addition of compounds (1d) and (6) from separate syringes to dry dichloromethane at −95 °C. A 4 : 1 mixture of the isomers (7b) and (7c) was obtained in 51% yield. Reaction of the salt (1c) with the cadmium reagent (6), performed in this way, was less regioselective, giving a 2 : 1 mixture of products (7d) and (7e) in similar yield. The major isomer corresponded to alkylation at C-5. In both these cases, alkylation of the 2-methyl-substituted salts (1c) and (1d) was only moderately regioselective. The required isomer (7d) was separated from compound (7e) by chromatography and converted into (±)-carvone (9) by treatment with PCC. Chemical correlation of the salt (1c) with carvone, achieved by this method, provides a way of determining the absolute configuration of the former compound if it can be obtained in an optically active form. Alkylation of the salt (1e) with the reagent (6) was regiospecific; a single product (7f) was obtained. Decomplexation with PCC gave (±)-sylvecarvone (8b) as expected.

Inspection of the n.m.r. spectra of the alkylation products (7a—f) confirmed that single stereoisomers are produced. Since the controlled formation of a chiral centre in this way forms the basis for the application of resolved salts in asymmetric organic synthesis, it is essential to prove the relative stereochemistry between the alkyl side-chain and the metal centre. This was achieved in this case by the alkylation of the unsubstituted salt (1g). Alkylation by the reagent (6) at −25 °C gave a single product (7g) which was identical with a sample obtained [13] from the 5α-acetyl complex (2h) by a Wittig reaction. Base-catalysed epimerisation of compound (2h) under the Wittig conditions can be discounted since it can be recovered unchanged if conversion into compound (7g) is incomplete. The 5β-isomer (2i) is known [18] to be the thermodynamically less stable form. Assignment of the relative stereochemistry in complex (2h) was deduced from its preparation [19] from the cyanide adduct (2j) which has been shown [19] to be the 5α-isomer by *X*-ray crystallography. Thus, in common with a variety of other nucleophilic additions to tricarbonyliron salts, alkylation by the cadmium reagent (6) occurs exclusively on the α-face.

CONCLUSION

It is apparent from these preliminary investigations that the crucial challenge in the application of tricarbonyliron complexes in asymmetric synthesis lies not in control of stereochemistry, which is assured by the properties of the transition-metal π-complexes, but rather in regiocontrol of the alkylation. While the metal serves to distinguish the two faces of the complexed ring, the substituents on the ring at the molecular chiral centre are also important to differentiate between the reactive termini of the dienyl system. Some substituents at an unsymmetrical position are effective in directing nucleophiles to a single terminus, but others, for example a 2-methyl substituent, are not. Mixtures of regioisomers result, and regioselective nucleophiles are then required so that wasteful separation of products can be avoided. Current work is directed towards the resolution of the salt (1c), and towards the development of suitable regioselective nucleophiles, based on stabilised enolate additions, which are known [6] to be highly selective for the alkylation of the salt (1d) at C-5.

EXPERIMENTAL

All reactions of tricarbonyliron complexes were performed under a nitrogen atmosphere, unless otherwise indicated. ^1H N.m.r. spectra were recorded on a Varian Associates

H.A. 100 spectrometer, and ^{13}C n.m.r. spectra on a Jeol FT 60 spectrometer. I.r. spectra were measured on Perkin-Elmer 257, 683, or 225 instruments and mass spectra were obtained with an A.E.I. MS9 spectrometer. Ether refers to diethyl ether throughout. (−)-Carvone was purchased from Ega-chemie Gesellschaft.

1,3-*Dimethoxy*-2-*methylcyclohexa*-1,4-*diene*.[8]—A solution of 2,6-dimethoxytoluene (50 g, 0.33 mol) in tetrahydrofuran (THF) (112 ml) and t-butyl alcohol (188 ml) was added to liquid ammonia (1 l) in a flask fitted with a refrigerated condenser. Lithium wire (9.4 g, 1.40 mol) was added in short lengths during 30 min. The blue solution was stirred under reflux for 15 h. Solid ammonium chloride (10 g) was added and the ammonia evaporated. The residue was dissolved in cold water and extracted with ether (3 × 300 ml). The combined extracts were washed with water (200 ml) and brine (40 ml), and dried over magnesium sulphate. Evaporation gave the crude diene (42.9 g, 86%) which was contaminated by a small proportion of starting material. Fractional distillation through a spinning band column gave a sample of the pure diene (20 g), b.p. 46 °C at 0.5 mmHg (Found: C, 70.15; H, 8.9. $C_9H_{14}O_2$ requires C, 70.08; H, 9.17%); $\nu_{max.}$ (liquid film) 1 690, 1 660, 1 595, 968, 950, 820, 775, and 705 cm^{-1}; $\delta(CDCl_3)$ 1.23 (3 H, d, Me), 2.86 (3 H, m, 2-, 5-H), 3.55 (6 H, s, OMe), and 4.47 (2 H, m, 4-, 6-H); *m/z* 154 (M^+, 24%), 152 (21), 139 (60), 124 (100), 108 (24), 91 (22), 79 (22), and 77 (21). Other fractions included aromatic material.

Direct Complexation of 1,3-*Dimethoxy*-2-*methylcyclohexa*-1,4-*diene*.—The diene (20 g, 0.13 mol) was heated under reflux with an excess of $Fe(CO)_5$ (34 ml) in di-n-butyl ether (160 ml) which had been passed through a column of alumina before use. After 48 h the dark mixture was cooled, filtered through Celite, and evaporated. The residue was fractionally distilled at 30—50 °C (at 10^{-3} mmHg) to give starting material (5 g, 20% recovery), and a mixture of diene complexes (9.3 g). Chromatography with hexane on silica gel (400 g) in a 40-mm diameter column afforded the following compounds (in order of elution): *tricarbonyl*(1—4-η-5β-*methylcyclohexa*-1,3-*diene*)-*iron*(0) (2b) (0.31 g, 1%) was obtained by distillation at 35 °C (at 10^{-3} mmHg) as a golden oil [(Found: C, 51.65; H, 4.6. $C_{10}H_{10}FeO_3$ requires C, 51.32; H, 4.31%); $\nu_{max.}$ (cyclohexane) 2 040 and 1 971 cm^{-1}; $\nu_{max.}$ (liquid film) 1 375, 1 332, and 965 cm^{-1}; $\delta(CDCl_3)$ 0.88 (3 H, d, *J* 7 Hz, Me), 1.35—2.05 (3 H, m, 5α-, 6α-, 6β-H), 2.94 (1 H, dt, 4-H), 3.15 (1 H, m, 1-H), and 5.05—5.35 (2 H, m, 2-, 3-H); *m/z* 234 (M^+, 2%), 206 (25), 178 (14), 162 (10), 148 (16), and 134 (100)]; *tricarbonyl*(1—4-η-2-*methoxy*-3-*methylcyclohexa*-1,3-*diene*)*iron*(0) (2c) was obtained as a yellow solid (2.46 g, 10%); $\nu_{max.}$ (cyclohexane) 2 033, 1 964, and 1 955 cm^{-1}; $\nu_{max.}$ (Nujol mull) 1 213, 1 158, 1 040, 722, and 663 cm^{-1}; $\delta(CDCl_3)$ 1.55 (4 H, m, 5-, 6-H), 2.06 (3 H, s, Me), 2.85 (1 H, t, *J* 3 Hz, 4-H), 3.38 (1 H, t, *J* 3 Hz, 1-H), and 3.54 (3 H, s, OMe); *m/z* 264 (M^+, 3%) 236 (19), 208 (6), 206 (11), 178 (100), 176 (7), 162 (8), and 148 (15). A sample was crystallised from pentane at −78 °C for analysis, m.p. 63—64 °C (Found: C, 50.13; H, 4.64. $C_{11}H_{12}FeO_4$ requires C, 50.03; H, 4.58%). A 1 : 1 mixture (1.27 g, 5%) of complex (2c) and *tricarbonyl*(1—4-η-2-*methoxy*-1-*methylcyclohexa*-1,3-*diene*)*iron*(0) (2d) was eluted next. Further chromatography (silica gel–hexane) and crystallisation from pentane at −78 °C gave a sample of complex (2d) as a golden oil, b.p. 30 °C at 10^{-3} mmHg (Found: C, 49.9; H, 4.7. $C_{11}H_{12}FeO_4$ requires C, 50.03; H, 4.58%), $\nu_{max.}$ (cyclohexane) 2 035 and 1 968 cm^{-1}; $\nu_{max.}$ (liquid film) 1 252, 1 038, 1 020, 742, and 722 cm^{-1}; $\delta(CDCl_3)$ 1.4—2.0 (m) and 1.66 (s) (integrated for 7 H, 5-, 6-H, Me), 2.64 (1 H, m, 4-H), 3.67 (3 H, s, OMe), and 4.95 (1 H, d, *J* 6.5 Hz, 3-H); *m/z* 264 (M^+, 2%), 236 (21), 234 (2), 208 (5), 206 (15), 178 (100), 176 (7), 162 (7), and 148 (15). Separation of the mixture of products from the complexation reaction continued with the elution of *tricarbonyl*(1—4-η-1-*methoxy*-2-*methylcyclohexa*-1,3-*diene*)*iron*(0) (2e) which was crystallised from pentane at −78 °C and sublimed as a waxy yellow solid (0.27 g, 1%) at 30—40 °C (at 10^{-3} mmHg) (Found: C, 50.2; H, 4.5. $C_{11}H_{12}FeO_4$ requires C, 50.03; H, 4.58%); $\nu_{max.}$ (cyclohexane) 2 036 and 1 965 cm^{-1}; $\nu_{max.}$ (neat) 1 330, 1 208, 1 151, 1 035, 1 006, and 705 cm^{-1}; $\delta(CDCl_3)$ 1.4—1.9 (3 H, m, 6α-, 5-H), 2.11 (3 H, s, Me), 2.28 (1 H, m, 6β-H), 2.75 (1 H, m, 4-H), 3.49 (3 H, s, OMe), and 4.98 (1 H, d, *J* 6 Hz, 3-H); *m/z* 264 (M^+, 2%), 236 (20), 208 (6), 206 (14), 178 (100), 176 (6), 162 (9), and 148 (14). *Tricarbonyl*(1—4-η-1-*methoxy*-6-*methylcyclohexa*-1,3-*diene*)*iron*(0) was obtained as a 1 : 2 mixture of epimers (2f) and (2g) after distillation at 30—45 °C (at 10^{-3} mmHg) in the form of a golden oil (0.63 g, 2.5%) (Found: C, 50.05; H, 4.5. $C_{11}H_{12}FeO_4$ requires C, 50.03; H, 4.58%); $\nu_{max.}$ (cyclohexane) 2 039, 2 032, 1 965, and 1 955 cm^{-1}; $\nu_{max.}$ (liquid film) 1 201, 1 029, and 705 cm^{-1}; $\delta(CDCl_3)$ 0.95 and 1.01 (2 d, each *J* 6 Hz, α- and β-Me, integrated for 3 H), 1.1—2.6 (3 H, m, 5-, 6-H), 2.70 and 2.86 (1 H, m, 4-H), 3.37 and 3.44 (3 H, pair of singlets, OMe), 4.8—5.1 (1 H, m, 3-H), and 5.24 (1 H, d, *J* 4 Hz, 2-H); *m/z* 264 (M^+, 1%), 236 (27), 234 (2), 208 (11), 206 (15), 178 (100), 176 (6), 164 (31), 162 (10), 148 (14), and 134 (20). Prolonged elution afforded a sample of *tricarbonyl*(1—4-η-1,3-*dimethoxy*-2-*methylcyclohexa*-1,3-*diene*)*iron*(0) (2a) (0.579 g, 2%), contaminated with a small amount of 1,6-dimethoxytoluene which could not be removed by chromatography or crystallisation. The ^1H n.m.r. spectrum [$\delta(CDCl_3)$ 1.2—1.7 (4 H, m, 5-, 6-H), 2.15 (3 H, s, Me), 3.19 (1 H, m, 4-H), 3.49 (3 H, s, OMe), and 3.53 (3 H, s, OMe)]; mass spectrum [*m/z* 294 (M^+, 2%), 266 (16), 264 (4), 236 (53), 234 (4), 208 (55), 206 (18), 178 (100), 176 (9), 164 (30), 148 (19), and 134 (8)], and subsequent chemical reactions (see below) are consistent with the above formulation. The complex was comparatively unstable and no further attempt was made to obtain a pure sample. Finally the column was washed with benzene. This gave further complex (2a) (*ca.* 0.8 g, 3%) mixed with 1,6-dimethoxytoluene and di-n-butyl ether. The crude samples of the product (2a) were combined. The total yield of diene complexes after chromatography was 25% (based on consumed diene).

Tricarbonyl(1—5-η-3-*methoxy*-2-*methylcyclohexa*-2,4-*dien*-1-*yl*)*iron*(1+) *Hexafluorophosphate*(1−) (1c).—The crude samples of tricarbonyl(1—4-η-1,3-dimethoxy-2-methylcyclohexa-1,3-diene)iron(0), obtained as described above, were combined and cooled to −10 °C. Neat trifluoroacetic acid (5 ml) was added and the mixture was stirred for 1 h until the original, brown reaction mixture had lightened in colour to become a clear yellow solution. Ammonium hexafluorophosphate (2 g, *ca.* 3 equiv.) was added in water (20 ml), and the precipitate so formed was collected, washed with water and ether, and dried (KOH). This crude material was purified by precipitation from CH_2Cl_2–CH_3NO_2 by slow addition of ether to give the title salt as a yellow powder (1.04 g, 60%) (Found: C, 32.35; H, 2.9; P, 7.4. $C_{11}H_{11}F_6FeO_4P$ requires C, 32.38; H, 2.72; P, 7.59%); $\nu_{max.}$ (CH_3CN) 2 098 and 2 046 cm^{-1};

$\delta(CD_3NO_2)$ 1.88 (1 H, d, *J* 16 Hz, 6α-H), 2.23 (3 H, s, Me), 2.95 (1 H, dt, *J* 16, 6 Hz, 6β-H), 3.92 (1 H, m, 5-H), 4.06 (1 H, m, 1-H), 4.26 (3 H, s, OMe), and 6.13 (1 H, d, *J* 8 Hz, 4-H). Similar demethoxylation of the complex (2a) with concentrated sulphuric acid (1 ml) at 5 °C gave a 4 : 1 mixture of the salts (1c) and (1e).

Preparation of Complex (1c) *by Oxythallation and Elimination*.—Tricarbonyl(1—4-η-2-methoxy-3-methylcyclohexa-1,3-diene)iron(0) (2c) (0.596 g, 2.25 mmol) and thallium tristrifluoroacetate (1.23 g, 2.26 mmol) were ground together in small portions with a pestle and mortar in a dry-bag under an argon atmosphere. A vigorous exothermic reaction took place. Ammonium hexafluorophosphate (0.447 g, 2.67 mmol) was added in water (3 ml) and the suspension mixed thoroughly. After addition of six drops of concentrated sulphuric acid, the mixture was extracted first with ether (2 × 5 ml) and then with CH_2Cl_2 (5 × 10 ml) until the extracts were colourless. The CH_2Cl_2 extracts were combined and washed with water (5 ml), and the yellow aqueous washings extracted again with CH_2Cl_2 (2 × 5 ml). The CH_2Cl_2 fractions were dried over magnesium sulphate and evaporated to give the crude salt (0.198 g) which was purified by precipitation with ether from CH_2Cl_2–CH_3NO_2 to yield a 10 : 1 mixture of the salts (1c) and (1e) (0.166 g, 19%).

Tricarbonyl(1—5-η-2-*methoxy*-3-*methylcyclohexa*-2,4-*dienyl*)*iron*(1+) *Hexafluorophosphate*(1−) (1e).—Tricarbonyl(1—4-η-2-methoxy-3-methylcyclohexa-1,3-diene)-iron(0) (2c) (2.47 g, 9.4 mmol) was dissolved in CH_2Cl_2 (5 ml), and the solution added dropwise at 5 °C to a stirred solution of triphenylmethylium tetrafluoroborate (3.1 g, 9.4 mmol) in CH_2Cl_2 (100 ml). After 1 h the mixture was poured into ether (300 ml) and the precipitate was collected, washed with ether, and dried (KOH). The product, a yellow powder (2.58 g, 78%) was shown by ^1H n.m.r. to be a 4 : 1 mixture of tetrafluoroborate salts of complexes (1e) and (1c) (Found: C, 37.95; H, 3.3. $C_{11}H_{11}BF_4FeO_4$ requires C, 37.76; H, 3.17%). Recrystallisation from water (50 ml) gave the pure product which was redissolved in water and precipitated by addition of saturated aqueous ammonium hexafluorophosphate to give the title salt (1e) (1.65 g) (Found: C, 32.7; H, 2.95; P, 7.55. $C_{11}H_{11}F_6FeO_4P$ requires C, 32.38; H, 2.72; P, 7.59%); $\nu_{max.}$ (CH_3CN) 2 101 and 2 046 cm^{-1}; $\delta(CD_3NO_2)$ 2.12 (1 H, d, *J* 14 Hz, 6α-H), 2.78 (3 H, s, Me), 3.09 (1 H, dt, *J* 14, 6 Hz, 6β-H), 3.79 (3 H, s, OMe), 4.11 (1 H, dd, *J* 7, 2 Hz, 5-H), 4.18 (1 H, m, 1-H), and 6.14 (1 H, d, *J* 7 Hz, 4-H). Addition of ammonium hexafluorophosphate to the filtrate from the recrystallisation precipitated a mixture of the hexafluorophosphate salts (0.62 g).

Bis(1-*methylethenyl*)*cadmium* (6).—The *ca.* 0.17M solution of bis(1-methylethenyl)cadmium used in the alkylation reactions described below was prepared as follows: two drops of 1,2-dibromoethane, dry THF (5 ml), and magnesium turnings (0.7 g, 0.029 g-atom) were stirred together while 2-bromopropene (3 g, 25 mmol) and additional THF were added from separate syringes at such a rate as to maintain reflux. The total volume of THF was made up to 45 ml and the mixture was stirred at room temperature for 2 h. Anhydrous cadmium chloride (2.3 g, 12.6 mmol) was added in portions from a solids tube and washed in with THF (30 ml). Heat was evolved. The mixture was warmed gently for 15 min, stirred at room temperature for 2 h, and allowed to settle at 5 °C overnight. Aliquots were withdrawn from the clear supernatant when required; the solution could be stored at 5 °C for several days without deterioration.

Alkylation Reactions.—The tricarbonyl(cyclohexadienyl)-iron(1+) salt (*ca.* 0.9 mmol) was dissolved in acetonitrile (3 ml). The solution was cooled to −24 °C and 0.17M bis(1-methylethenyl)cadmium solution in THF (6 ml, 1 mmol) was added. After 7 min, hexane (10 ml) and 5% aqueous ammonium chloride (5 ml) were added and the mixture was stirred for 2 min at 5 °C. A white precipitate formed. The suspension was filtered through Celite and the residue was washed with hexane (10 ml). The filtrate was extracted with hexane (2 × 10 ml) and the extracts were washed with water (5 × 10 ml), dried over magnesium sulphate, and filtered through a small pad of silica [hexane–ether, 1 : 1 (v/v) as eluant]. The products were obtained by evaporation of the yellow washings and vacuum distillation.

The following compounds were obtained by the above procedure.

Tricarbonyl[1—4-η-2-*methoxy*-5α-(1-*methylethenyl*)-*cyclohexa*-1,3-*diene*]*iron*(0) (7a). Alkylation of tricarbonyl-(1—5-η-2-methoxycyclohexa-2,4-dien-1-yl)iron(1+) hexafluorophosphate(1−) (1f) gave the *product* (7a) in 70% yield as a yellow oil, b.p. 35—37 °C at 10^{-3} mmHg (Found: C, 53.9; H, 4.85. $C_{13}H_{14}FeO_4$ requires C, 53.82; H, 4.83%); $\nu_{max.}$ (cyclohexane) 2 045, 1 975, 1 640, 1 225, 1 172, 887, 768, and 675 cm^{-1}; $\delta(CDCl_3)$ 1.45 (1 H, dm, *J* 14 Hz, 6α-H), 1.56 (3 H, d, *J* 1 Hz, Me), 2.04 (1 H, dq, *J* 14, 11, 4 Hz, 6β-H), 2.54 (1 H, m, 4-H), 2.64 (1 H, dt, *J* 11, 3 Hz, 5β-H), 3.32 (1 H, m, 1-H), 3.63 (3 H, s, OMe), 4.61 (*J* 1 Hz) and 4.73 (2 H, both m, C=CH_2), and 5.18 (1 H, dd, *J* 6, 2 Hz, 3-H); *m/z* 290 (M^+, 4%), 262 (31), 234 (51), 232 (22), 206 (12), 205 (12), 204 (67), 188 (18), and 164 (100).

Tricarbonyl[1—4-η-2-*methyl*-5α-(1-*methylethenyl*)*cyclohexa*-1,3-*diene*]*iron*(0) (7b). Alkylation of tricarbonyl(1—5-η-2-methylcyclohexa-2,4-dien-1-yl)iron(1+) hexafluorophosphate(1−) (1d) gave the *product* (7b) as a 7 : 3 mixture with the isomer (7c), in 57% yield, b.p. 30—35 °C at 10^{-3} mmHg (Found: C, 57.2; H, 5.2. $C_{13}H_{14}FeO_3$ requires C, 57.00; H, 5.15%); $\nu_{max.}$ (cyclohexane) 2 041, 1 974, 1 971, 1 642, 887, and 754 cm^{-1}; $\delta(CDCl_3)$ 1.36 (1 H, dm, *J* 15 Hz, 6α-H), 1.53 (3 H, d, *J* 1 Hz, Me), 2.05 (1 H, dq, *J* 15, 11, 4 Hz, 6β-H), 2.08 (3 H, s, 2-Me), 2.6—2.9 (2 H, m, 5β-, 4-H), 3.05 (1 H, m, 1-H), 4.59 and 4.71 (2 H, both m, C=CH_2), and 5.31 (1 H, d, *J* 5 Hz, 3-H); *m/z* 274 (M^+, 3%), 246 (20), 218 (30), 216 (13), 190 (16), 189 (18), 188 (100), 172 (28), and 158 (30). The mixture could be separated by g.l.c. on 2% OV17 on Gas Chrome Q at 50—150 °C (4 °C min^{-1}). An injector temperature of 140 °C was used; at higher temperatures pyrolysis occurred during injection. Retention times of 25 min for (7b) and 26 min for (7c) were assigned by comparison with product ratios determined by ^1H n.m.r.

Tricarbonyl[1—4-η-2-*methoxy*-3-*methyl*-5α-(1-*methylethenyl*)*cyclohexa*-1,3-*diene*]*iron*(0) (7f). Alkylation of tricarbonyl(1—5-η-2-methoxy-3-methylcyclohexa-2,4-dien-1-yl)iron(1+) hexafluorophosphate(1−) (1e) gave the *product* (7f) as a yellow oil in 83% yield, b.p. 40 °C at 10^{-3} mmHg (Found: C, 55.55; H, 5.3. $C_{14}H_{16}FeO_4$ requires C, 55.29; H, 5.30%); $\nu_{max.}$ (cyclohexane) 2 040, 1 970, 1 962, 1 640, 1 213, 1 153, 886, 741, 720, and 668 cm^{-1}; $\delta(CDCl_3)$ 1.36 (1 H, dm, *J* 14 Hz, 6α-H), 1.52 (3 H, d, *J* 1 Hz, Me), 2.00 (1 H, dq, *J* 15, 12, 4 Hz, 6β-H), 2.14 (3 H, s, 3-Me), 2.55 (1 H, t, *J* 4 Hz, 5β-H), 2.66 (1 H, d, *J* 2.5 Hz, 5-H), 3.27 (1 H, q, *J* 4, 3 Hz, 1-H), 3.57 (3 H, s, OMe), and 4.61 (*J* 1 Hz) and 4.67 (2 H, both m, C=CH_2); *m/z* 304 (M^+, 304.0397. C_{14}-

$H_{16}FeO_4$ requires 304.0398, 4%), 276 (35), 248 (37), 246 (20), 220 (12), 219 (14), 218 (100), 216 (8), 202 (22), 198 (12), and 178 (80).

Tricarbonyl[1—4-η-5α-(1-*methylethenyl*)*cyclohexa*-1,3-*diene*]*iron*(0) (7g). Alkylation of tricarbonyl(1—5-η-cyclohexa-2,4-dien-1-yl)iron(1+) hexafluorophosphate(1−) (1g) gave the product (7g) as a yellow oil, in 68% yield, b.p. 35—40 °C at 10^{-3} mmHg), $\nu_{max.}$ (cyclohexane) 2 048, 1 980, and 1 976 cm^{81}; δ($CDCl_3$) 1.35 (1 H, dm, *J* 15 Hz, 6α-H), 1.55 (3 H, d, *J* 1 Hz, Me), 2.03 (1 H, dq, *J* 15, 10, 4 Hz, 6β-H), 2.78 (1 H, m, 5β-H), 2.92 (1 H, m, 4-H), 3.05 (1 H, m, 1-H), 4.61 (*J* 1 Hz) and 4.72 (2 H, both m, C=CH_2), and 5.38 (2 H, m, 2- and 3-H); δ(^{13}C) ($CDCl_3$) 19.4 (Me), 29.4 (C-6), 46.2 (C-5), 60.3 (C-1), 64.8 (C-4), 85.1 (C-2, -3), 110.3 (=CH_2), 149.1 (=*C*Me), and 212.1 (M-CO); *m/z* 260 (*M*$^+$, 260.0136. $C_{12}H_{12}FeO_3$ requires *M*, 260.0136, 5%), 232 (30), 230 (3), 204 (40), 202 (10), 176 (15), 174 (100), 172 (10), 168 (28), and 134 (40). The excellent agreement of the ^{13}C chemical shifts with the literature [13] values indicates that complex (7g) is the same stereoisomer as that prepared from the cyano-complex (2j), thus establishing the α stereochemistry of the side chain. A revised ^1H n.m.r. assignment was deduced by comparison of chemical shift data from the series of compounds (7a—g).

Alkylation of Tricarbonyl(1—5-η-3-*methoxy*-2-*methylcyclohexa*-2,4-*dienyl*)*iron*(1+) *Hexafluorophosphate*(1−) (1c) *at* −95 °C.—A solution of the salt (1c) (0.304 g, 0.77 mmol) in acetonitrile (3 ml) and 0.17M bis(1-methylethenyl)cadmium (6) (6 ml, 1 mmol) in THF were added simultaneously from separate syringes to dry dichloromethane at −95 °C (liquid nitrogen–ether slush bath). Precipitation occurred at once. After being stirred for 10 min the mixture was allowed to warm slowly until homogeneous (*ca.* −60 °C). Hexane (15 ml) and 5% aqueous ammonium chloride (5 ml) were added and the reaction was worked up as before. The complexes (7d) and (7e) were obtained as a 2 : 1 mixture (0.117 g, 52%). G.l.c. retention times on 2% OV17 were 29 and 30 min, respectively. The mixture was separated by preparative t.l.c. on silica with hexane–ether (3 : 1, v/v) as eluant, to give *tricarbonyl*[1—4-η-3-*methoxy*-2-*methyl*-5α-(1-*methylethenyl*)*cyclohexa*-1,3-*diene*]*iron*(0) (7d), b.p. 45 °C at 10^{-3} mmHg; $\nu_{max.}$ (cyclohexane) 2 040, 1 970, 1 961, 1 150, and 761 cm^{-1}; δ($CDCl_3$) 1.27 (1 H, dm, *J* 15 Hz, 6α-H), 1.52 (3 H, d, *J* 1 Hz, Me), 1.81 (1 H, dq, *J* 15, 11, 4 Hz, 6β-H), 2.11 (3 H, s, 2-Me), 2.37 (2 H, m, 5β-, 1-H), 3.12 (1 H, d, *J* 4 Hz, 4-H), and 4.59 (*J* 1 Hz) and 4.67 (2 H, both m, C=CH_2); *m/z* 304 (*M*$^+$, 304.0399. $C_{14}H_{16}FeO_4$ requires 304.0398, 5%), 276 (37), 274 (3), 246 (38), 244 (27), 220 (26), 218 (95), 202 (19), 178 (100), 172 (13), 148 (17), and 91 (10); R_F 0.58; and *tricarbonyl*[1—4-η-2-*methoxy*-1-*methyl*-6α-(1-*methylethenyl*)*cyclohexa*-1,3-*diene*]*iron*(0) (7e), b.p. 45 °C at 10^{-3} mmHg; $\nu_{max.}$ (cyclohexane) 2 041, 1 972, 1 966, 1 640, 1 248, 1 183, 1 168, 1 149, 1 120, 1 010, and 890 cm^{-1}; δ($CDCl_3$) 1.34 (1 H, dm, *J* 15 Hz, 5α-H), 1.42 (3 H, d, *J* 1 Hz, Me), 1.48 (3 H, s, 1-Me), 1.97 (1 H, dq, *J* 15, 11, 4 Hz, 5β-H), 2.50 (1 H, m, 4-H), 2.85 (1 H, dd, *J* 11, 4 Hz, 6β-H), 3.75 (3 H, s, OMe), 4.69 (2 H, m, C=CH_2), and 4.99 (1 H, d, *J* 6 Hz, 3-H); *m/z* 304 (*M*$^+$, 304.0399. $C_{14}H_{16}FeO_4$ requires *M*, 304.0398, 8%), 276 (27), 248 (42), 246 (8), 220 (19), 218 (47), 202 (12), 192 (12), 178 (100), 147 (12), and 91 (12); R_F 0.48.

Temperature Dependence of Alkylation of Tricarbonyl(1—5-η-2-*methylcyclohexa*-2,4-*dien*-1-*yl*)*iron*(1+) *Hexafluorophosphate*(1−) (1d).—Alkylations at −78, −40, −24, and +5 °C were performed using the general procedure described above. Alkylation at −95 °C was performed by the method employed for the alkylation of the salt (1c). The product ratio was determined by g.l.c. analysis as described previously. In all cases the major product was complex (7b). The results are indicated in the Table.

Ratio of products from the alkylation of complex (1d) at different temperatures

Temperature (°C)	−95	−78	−40	−24	+5
Ratio of (7b) : (7c)	80 : 20	78 : 22	76 : 24	71 : 29	74 : 26

Conversion of Methoxydiene Complexes into Enones with Pyridinium Chlorochromate.—Reaction of the 5α-(1-methylethenyl)-substituted complexes (7a, d, and f) with pyridinium chlorochromate (PCC) was comparatively slow. The normal procedure [17] was modified accordingly. The complex (*ca.* 0.6 mmol) was dissolved in CH_2Cl_2 (20 ml) and added to a suspension of PCC (500 mg, 2.3 mmol) in CH_2Cl_2 (40 ml) and the mixture was kept at 35 °C for 1.5 h. The brown suspension was allowed to cool and was stirred at room temperature overnight. After addition of ether (100 ml), the mixture was filtered, washed with water (4 × 20 ml), and dried ($MgSO_4$). The crude product was distilled.

The following compounds were obtained by the above procedure.

4-(1-*Methylethenyl*)*cyclohex*-2-*enone* (8a). Decomplexation of compound (7a) gave the *enone* (8a) as a clear oil in 58% yield, b.p. 40 °C at 1.5 mmHg (Found: C, 79.35; H, 8.85. $C_9H_{12}O$ requires C, 79.37; H, 8.88%), $\nu_{max.}$ (neat) 1 680, 1 360, 1 245, 1 210, 1 175, 895, 850, 840, and 735 cm^{-1}; δ($CDCl_3$) 1.79 (3 H, d, *J* 2 Hz, Me), 2.08 (2 H, m, 5-H), 2.46 (2 H, m, 6-H), 3.04 (1 H, m, 4-H), 4.78 and 4.90 (2 H, both m, C=CH_2), 6.03 (1 H, dd, *J* 10, 3 Hz, 2-H), and 6.84 (1 H, dd, *J* 10, 4 Hz, 3-H); *m/z* 136 (*M*$^+$, 85%), 121 (15), 108 (18), 94 (35), 93 (44), 80 (48), 79 (100), 77 (24), and 68 (10).

2-*Methyl*-4-(1-*methylethenyl*)*cyclohex*-2-*enone* (8b). Decomplexation of compound (7f) gave (±)-sylvecarvone [20] as a clear oil in 63% yield, b.p. 40 °C at 1 mmHg (lit.,[21] 138—140 °C at 10 mmHg); $\nu_{max.}$ (neat) 1 680, 1 650, 1 450, 1 420, 1 360, 1 100, 1 029, and 891 cm^{-1}; δ($CDCl_3$) 1.79 (3 H, s, 2-Me), 1.80 (3 H, d, *J* 2 Hz, Me), 2.06 (2 H, m, 5-H), 2.48 (2 H, m, 6-H), 3.05 (1 H, m, 4-H), 4.78 and 4.88 (2 H, both m, C=CH_2), and 6.61 (1 H, m, 3-H); *m/z* 150 (*M*$^+$, 100%), 135 (18), 122 (10), 108 (35), 107 (48), 93 (90), 91 (23), 79 (43), 77 (20), 69 (5), 67 (6), 65 (6), 53 (10), and 41 (17).

2-*Methyl*-5-(1-*methylethenyl*)*cyclohex*-2-*enone* (9). Decomplexation of compound (7d) gave (±)-carvone as a clear oil in 67% yield, b.p. 40 °C at 1 mmHg. The product was identical (^1H n.m.r., g.l.c.) with an authentic sample of (−)-carvone.

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