Enantiomeric Recognition during Cyclopentanone Formation with Iron(0)

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Abstract: In an effort to probe both the extent of stereospecificity and the reasons for stereospecificity in carbonylation reactions with iron(0), a series of norbornene substrates have been coupled to cyclopentanones with $Fe(CO)_5$. Even in the absence of potential chelation and strong polarization of the coupling centers, enantiomeric recognition is observed. This behavior is understood in terms of the olefin π^* acceptor orbital.

An important and yet frequently elusive goal of synthetic chemistry is the specific synthesis of a desired stereoisomer. Examples illustrating the importance of stereospecific syntheses are manifold, asymmetric reduction being one example while stereochemical specification during ring formation is another.

Although organometallic procedures which allow one to choose among a variety of stereochemical products are only now being carefully developed, organometallic chemistry does offer an increasing number of synthetically useful stereospecific reactions. In the following article, we report a coupling reaction which leads to exclusive formation of only one of 36 possible isomers and which takes place with enantiomeric recognition. That is, only enantiomers of like absolute configuration couple to one another.

The importance of configuration about a metal center in determining the stereochemical outcome of a reaction is amply illustrated by asymmetric induction during catalytic hydrogenation,[1] a process whose utility is illustrated by the Monsanto synthesis of L-Dopa. Stereospecific carbon–carbon bond formation is of equal importance, especially since carbon–carbon linkages are generally difficult to prepare. Processes which generate C–C bonds often yield a variety of stereoisomers, not only adding preparative difficulty, but also reducing the yield of desired material. Two additional goals of synthesis are the incorporation of functionality such as the highly versatile carbonyl group, and the formation of carbon rings. Organometallic chemistry offers novel routes to elusive materials. Carbonylation reactions based on transition metal chemistry are well known including such useful and well-known processes as the oxo reaction[2] and the use of the tetracarbonylferrate anion developed by Collman.[3]

We have recently investigated iron carbonyl induced formation of substituted cyclopentanones from strained olefins.[4] This reaction meets the synthetic goals identified above in that it is stereospecific, leads to rings, and incorporates functionality into the newly formed ring. Furthermore, product stereochemistry may be changed without loss of specificity by inclusion of lone-pair donors.[5] Iron pentacarbonyl is a remarkably stereo- and regiospecific reagent, often yielding only one product when numerous are possible. Thus, cyclopentanone formation from diene **1**, reaction 1, gives exclusively exo-trans-exo ketone **1a** in 80% yield, although six isomers might arise.[4] Efficient classical routes to this polycyclic material are difficult to envision. The lack of importance of the second double bond in this particular reaction is confirmed by the equivalent reactivity of olefin **2.** While yields are reduced as ring strain decreases, norbornadiene and norbornene undergo similar conversions to the corresponding exo-trans-exo cyclopentanones.

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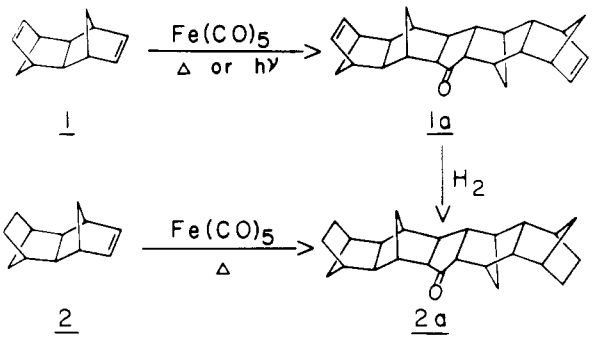
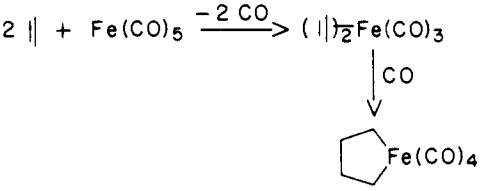
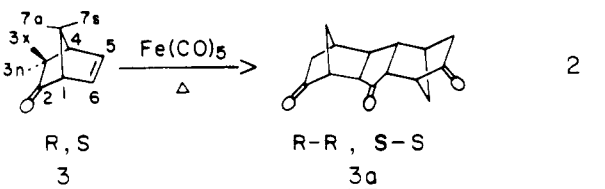


In the absence of a Lewis base at the 7 position and syn to the reactive double bond, all norbonyl systems thus far considered form exo-trans-exo products while a 7-syn alkoxy group leads to exo-trans-endo stereochemistry. Present evidence suggests that in those systems containing a 7-syn alkoxy group, a second double bond may be important in facilitating stereospecificity.[5b] Analysis of the reaction pathway leading to exo-trans-exo products indicates a series of organometallic intermediates, including a bis olefin iron tricarbonyl species followed, as a consequence of oxidative coupling, by a five-membered metallocycle, as illustrated in Scheme I.[4c,6]

Scheme I

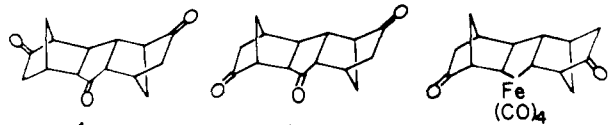


Cyclopentanone formation from identical, achiral norbonyl olefins may lead to a maximum of six stereoisomers. When the coupling olefins are identical and chiral, a more complex situation arises.[7] As has been discussed,[7,8] cyclopentanone formation from racemic 2-ketonorborn-5-ene (**3**) may lead to 36 isomers. Four of these isomers are meso, eight are dissymmetric, containing a C_2 axis and represent four enantiomeric pairs, and 24 are asymmetric, representing 12 enantiomeric pairs. Remarkably, when racemic norbornenone is treated with iron pentacarbonyl, only one racemic product is formed.[8] As illustrated in reaction 2, this product is dissymmetric, containing



a C_2 symmetry axis, and is once again the exo-trans-exo product. Compared to norbornene coupling, stereospecificity has been maintained about the newly formed ring but with the added feature of enantiomeric recognition. That is, coupling only proceeds between identical enantiomers.

Iron complexes to simple norbornyl olefins preferentially from the exo face. Thus it is understandable that exo,exo products are formed.[4c,7] The trans arrangement about the bond opposite the CO function arises from the two olefins in the bis olefin complex and/or in the activated complex leading to oxidative coupling being antiparallel to one another.[4c] Observation of enantiomeric recognition is striking. Indeed, even with enantiomeric recognition, two products might be formed, the observed fully syn isomer, **3a,** and the fully anti isomer, **4a.** Cyclopentanone **4b,** the isomer having exo-trans-exo stereo-



4a 4b 5

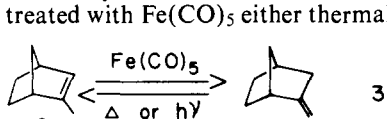
chemistry about the ketone ring in which the norbornyl residues are of opposite absolute configuration, is also not formed. Exclusive coupling of like enantiomers *and* the exclusive observation of the fully syn product must both be understood in order to extend the utility of this reaction.

The highly electronegative ketone oxygen strongly polarizes the reactive double bond of **3,** a feature which might be expected to influence enantiomeric recognition. The proximal end of the double bond is far more negative than the distal end, as illustrated by the 12.2-ppm chemical shift difference observed between these carbons in the ^{13}C spectrum.[8] The observed product implies metallocycle formation such that the iron binds at the proximal end, to C_6 and C_6' (see structure **5**) with C-C bond formation between C_5 and C_5'. This situation might be the result of double bond polarization and/or lone-pair interaction with the iron center during or prior to metallocycle formation. An alternative appreciation of the observed product formation lies in the nature of the olefin π^* orbital and does not rely on either the occupied π orbital or oxygen lone pairs.

Results

In order to study the extent to which iron(0) is an enantiospecific reagent, we have investigated cyclopentanone formation from norbornyl systems containing exocyclic double bonds. Highly electronegative, lone-pair bearing substituents have been excluded. In these experiments, the relative importance of the occupied ligand π orbital and the unoccupied π^* orbital in determining the outcome of enantiomeric recognition has been probed, facilitating an understanding of both enantiomeric recognition *and* the exclusive formation of fully syn product. Once again the remarkable specificity of iron(0) has been demonstrated.

When pure 2-methylnorbornene (**6**) or 2-methylenenorborane (**6a**) is treated with $Fe(CO)_5$ either thermally or photo-



6 6a 3

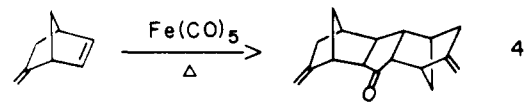
chemically, an equilibrium is established favoring exocyclic isomer **6a.** This is in contrast to conversion of β-pinene of α-pinene,[9] a preferential exocyclic to endocyclic conversion. Double bond isomerizations catalyzed by iron(0) are well known. When possible, unconjugated dienes rearrange to conjugated 1,3-diene iron tricarbonyl complexes[10] and several examples of conversion of unsaturated primary alcohols to aldehydes are now known.[11] Cyclopentanone formation from **6, 6a,** or the equilibrium mixture does not occur under standard conditions.

The absence of cyclopentanone formation, a process which goes in only moderate yield with norbornene itself, may be largely a consequence of the low equilibrium concentration of endocyclic olefin **6.** That coupling did not occur when pure **6** was used indicates that the 1,3-proton shift is faster than cyclopentanone formation since norbornene readily couples to the exo-trans-exo cyclopentanone. exocyclic olefin **6a** is not sufficiently strained to suffer coupling under our reaction conditions. Of course, the methyl group may also serve to deactivate the double bond to coupling. Thermolysis of $Fe(CO)_5$ and 1-methylnorborn-2-ene (**7**) at 145 °C for 72 h

7

produces less than 1% ketonic product while norbornene yields 10% isolated product when heated with $Fe(CO)_5$ at 125 °C for 48 h.

Diene **8** contains both an exocyclic and an endocyclic double bond and is isoelectronic with norbornenone **3.** Incorporation of this endocyclic double bond further increases the ring strain of **8** with respect to **6a** by straining the norbornyl skeleton. Consequently, the thermodynamically unfavorable isomerization of **8** to the fully endocyclic form is even less favorable than the **6a-6** equilibrium. This is illustrated by the observed equilibrium which lies greater than 99% toward **8.**[12] Thus olefin **8** is an ideal test for our understanding of iron(0) induced



R, S R-R, S-S

8 8a

cyclopentanone formation. Heating racemic 2-methylenenorborn-5-ene (**8**) with $Fe(CO)_5$ at 125 °C for 48 h led to an isolated 10% yield of cyclopentanone **8a.** In spite of the absence of a highly electronegative function, only one of 36 possible isomers was formed, this being the same as that from the isoelectronic ketone. Identification of this isomer, and its enantiomer, was carried out by ^{13}C and ^1H NMR, spectral assignments being reported in Tables I and II.

Although compound stoichiometry is $C_{17}H_{20}O$, only nine carbon resonances are observed, indicating the presence of either a C_2 molecular axis or a mirror plane with one of the carbon atoms lying on the symmetry element. This immediately reduces the complexity of the stereochemical assignment from a choice among 20 structures to one among eight structures. Comparison of the ^{13}C spectrum of **8** and **8a** shows significant changes only at C_5 and C_6, the carbons being coupled. Carbon assignments are straightforward, compare favorably with those reported for the corresponding triketone, and were confirmed by off-resonance proton decoupling. Selection of the observed product from among the eight possible was accomplished by ^1H NMR. As has been observed for all of the cyclopentanones formed in this manner from reagents containing no 7-syn-lone-pair donors, the proton spectrum of **8a** is quite simple, a consequence of molecular symmetry. The resonances at 2.92 and 2.40 ppm are assigned to the bridgehead protons H_1 and H_4, respectively. The resonance at 2.40 ppm is significantly broadened with respect to that at 2.92 ppm, as the 2.40-ppm resonance contains coupling to an exo ring proton, and is thus assigned to the bridgehead proton adjacent to the two carbon bridge methylene group. Differentiation be-

Table I. Carbon NMR Spectral Assignments[a]

Carbon	Olefin **8**[b]	Ketone **8a**[b]
1	51.1 (50.2)	50.7 (47.9, 45.4)
2	151.2	151.8
3	42.2 (33.6)	37.2 (35.7)
4	50.2 (51.1)	49.9 (50.7, 45.4)
5	136.6 (134.4)	45.4 (50.7, 49.9)
6	134.4 (136.6)	58.9
7	33.6 (42.2)	35.7 (37.2)
8	103.8	103.9
CO		224.0

[a]Chemical shifts in parts per million (δ) from internal Me_4Si. [b]The numbering system is illustrated on compound **3**.

Table II. Proton NMR Spectral Assignments[a]

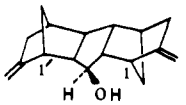
Proton	Olefin **8**	Ketone **8a**	Alcohol **8b**
1	3.11 $J_{1,7} \sim 0.5$	2.92	1:2.80
2			1′:2.26
3x	2.23 $J_{3x,3n} = 15.5$	2.21[c] $J_{3x,3n} = 16.0$	
3n	1.79	1.91	
4	2.93 $J_{3x,4} \sim 4$	2.40 $J_{3x,4} \sim 4$	4:2.25 $J_{3x,4} \sim 4$
5	6.07	1.94 $J_{5,6} = 7.5$	4′:2.20
6	6.07	2.23	
7a	1.39 $J_{7a,7s} = 8.0$	1.30[c] $J_{7a,7s} = 10.5$	7:1.28
7s	1.59	1.15	7′:1.15
8a	4.95[c]	4.95	4.86
8s	4.67	4.64	4.57
9			4.01 $J_{6,9} = 10.0$, $J_{6,9} = 4.5$

[a]Chemical shifts in parts per million (δ) from internal Me_4Si, J (hertz). [b]The numbering system is illustrated on compound **8b**. [c]Assignment uncertain.

tween H_1 and H_4 was accomplished by determining the relative sensitivities of the resonances at 2.92 and 2.40 ppm to the shift reagent $Eu(fod)_3$.[13] The resonance at 2.92 ppm is the second most sensitive in the spectrum and consequently is assigned to the bridgehead proton nearest to the carbonyl function. The observation that the bridgehead proton nearest the carbonyl group and that adjacent to the exocyclic double bond are the same is consistent with the fully syn isomer.

The AB pattern uncoupled resonances showing a coupling constant of 7.5 Hz at 1.94 and 2.23 ppm are assigned respectively to protons H_5 and H_6, the cyclopentanone ring protons. The relative assignment of these two resonances is based on the expectation that the proton nearest to the electronegative carbonyl oxygen will be deshielded with respect to that further away and on the observation that the resonance at 2.23 ppm is the most sensitive resonance in the spectrum to shift reagent. This behavior and the magnitude of $J_{5,6}$ is similar to those reported for analogous materials.[4,5a,8] Resonances assigned to H_5 and H_6 are relatively sharp, indicative of minimal coupling to bridgehead protons H_4 and H_1, respectively. Consequently, H_5 and H_6 must be endo relative to the norbornyl system giving the compound the exo,exo structure.

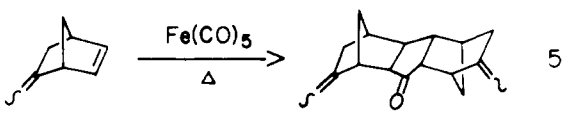
Choice between the C_2 symmetric isomer having a trans structure and the C_s symmetric isomer having a cis structure was based on the spectrum of the single alcohol derived from the ketone upon $LiAlH_4$ reduction. The carbinol methine proton of the alcohol product appears as a doublet of doublets moving as a single unit with shift reagent and displaying coupling constants of 4.5 and 10.0 Hz. The trans ketone may lead to but one alcohol, **8b.** This alcohol will have a cis and trans



8b

proton adjacent to the methine proton resulting in observation of a doublet of doublets while the cis ketone could lead to two alcohols, each of which would display the carbinol methine proton as a triplet resonance. Thus, the syn-exo-trans-exo-syn stereochemistry is confirmed. Loss of molecular symmetry as a consequence of alcohol formation is confirmed by loss of equivalency of protons H_1 and H_1' as well as H_7 and H_7'. If perchance the ketone had been cis and only one of the two possible alcohols formed, not only would the carbinol methine proton have appeared as a triplet, but also the mirror plane present in the hypothetical ketone would have been preserved.

A mixture of (*Z*)- and (*E*)-2-ethylidenenorborn-5-ene (**9**) was treated with $Fe(CO)_5$ leading to an unseparated mixture of cyclopentanones. Once again, the syn-exo-trans-exo-syn stereochemistry with two different ethylidene functions is observed. This implies the presence of three products, one



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R,S — **9**

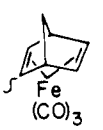
R–R, S–S — **9a,b,c**

having both ethylidene methyl groups *Z*, one with both *E*, and one containing both types of methyl groups. One would not expect NMR to differentiate between the symmetric pair on the one hand and the asymmetric product on the other. The distribution of *Z* and *E* methyl groups in the ketone mixture may be compared to that in the reagent hydrocarbon as a test of our thesis that double bond isomerization does not occur. The necessary, although insufficient, observation of equivalent distributions is consistent with no exocyclic-endocyclic isomerization. For this to be fully valid, there must be a thermodynamic distribution change for the methyl location between the reagents and the cyclopentanones produced. Once again, coupling took place at the double bond which may only be internal.

Discussion

Isomerization of **8** into endocyclic 2-methylnorbornadiene lies further toward structure **8** than the **6–6a** equilibrium lies toward **6a.** Indeed, there is no indication of coupling of double bonds bearing a methyl group, and the observed product contains only exocyclic double bonds. Furthermore, if 2-methylnorbornadiene were formed in significant quantity, one would anticipate the formation of the corresponding 2-methylnorbornadiene iron tricarbonyl complex analogous to that formed from norbornadiene. When norbornadiene is treated with $Fe(CO)_5$ this complex is the principal product.[14] We must, therefore, conclude that the exocyclic-endocyclic double bond equilibrium which one might write for **8** is not disturbed by the iron system. Similar arguments apply to **9.**

Complex formation would be expected to be sufficiently favorable to influence the observed distribution between free **8** and bound 2-methylnorbornadiene (**10**). However, for **10** to



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form, free ligand must be trapped, two iron centers must be simultaneously bound to a transient norbornadiene moiety, or a bimolecular substitution of endo-bound iron(0) for exo-bound

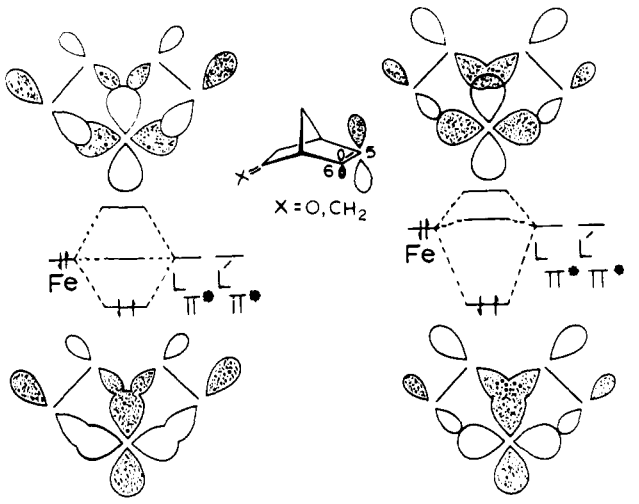

Figure 1. Qualitative MO diagram of the bisolefin intermediate.

iron(0) must occur. Each of these cases is unlikely, the first because the equilibrium between **8** and the free ligand from **10** lies toward **8**, and the second two because of the need for two reactive iron(0) centers, these being present only in small quantity. The only likely route to **10** would be direct formation by a 1,3-proton shift from the endo face of the norbornyl moiety. The lack of observation of **10** is further circumstantial evidence for isomerization from the exo face.

The relative lack of polarization of the reactive double bond of **8** compared to **3** is indicated by the small ^{13}C chemical shift difference observed for C_5 and C_6 of 2.2 ppm, only 18% of the difference observed for norbornenone. The difference between these materials is as expected and is a consequence of the low electronegativity of CH_2 relative to oxygen. In addition, there are no lone pairs on CH_2 with which the iron center may interact. Thus, neither a chelation effect utilizing lone pairs nor polarization of the occupied π orbital are suitable for explanation of enantiomeric recognition or the stereochemical outcome of the reaction.

While approximate, INDO calculations performed on norbornenone and methylenenorbornene do permit an appreciation of observed enantiospecificity. In each case, the respective LUMO's of the reactive double bonds have coefficients larger at C_5 than at C_6. The HOMO and LUMO coefficients listed in Table III are not to be taken as exact values but are intended to indicate gross differences only. It is this acceptor orbital, π_3^*, which is important in stabilizing olefin-iron complexation through back-bonding. Further, the combination of π^* orbitals of the two ligands which is fully bonding to the metal is the combination orbital which correlates with the newly formed C-C σ orbital of the metallocycle. This is not to imply orbital symmetry arguments to explain cyclopentanone formation but only suggests a low energy route from bis olefin complex to metallocycle.

As illustrated, maximum bis olefin iron tricarbonyl stability is achieved when the C_5 carbons are adjacent to one another as this leads to significant C-C interaction in the bis olefin intermediate (Figure 1).[7] The resultant product of this intermediate is fully syn cyclopentanone **8a**. Switching the bis olefin complex geometry so that the C_6 carbons are adjacent will, to a first approximation, not change olefin-iron bonding but will decrease complex stability through a strong decrease in C-C interaction. Because the same metal and olefin orbitals are used in either case, the extent of C-C interaction is the controlling factor. Placing the C_6 carbons adjacent to one another would generate the unobserved anti,anti isomer. A similar although not so drastic loss of intermediate stability via loss of C-C interaction without change in the Fe-C interactions would occur if different enantiomers were present on the same iron center, a situation which would lead to the syn,anti isomer.

Table III. Coefficients of the HOMO and LUMO Orbitals for the Reactive Double Bonds

Compd	HOMO (π_2)		LUMO (π_3^*)	
	C_5	C_6	C_5	C_6
Norbornenone	0.3232	0.3816	0.2771	−0.2081
5-Methylenenorbornene	0.4977	0.4624	0.4196	−0.3678

The kinetic barrier which must be surmounted in proceeding from bis olefin complex to metallocycle is lowest from the complex wherein the C_5 carbons are adjacent to one another. In this intermediate, C-C interaction along the route to C-C bond formation is already well established. The other two possible arrangements for this intermediate would require higher activation energies for oxidative coupling as C-C interaction would not be so well developed at an early stage. Thus, enantiomeric recognition and the specific product observed are consequences of the same phenomenon. Intermediate stability, and thus concentration, is maximized when the C_5 carbons are adjacent and this same intermediate has the lowest activation energy to carbon-carbon bond formation. Each of these contributes to a maximum rate for formation of the fully syn enantiomeric recognition product. Since formation of the bis olefin intermediate is an equilibrium process, there is no difficulty in exclusive selection of one stereochemical product.

The factors which control carbon-carbon bond formation are important but poorly understood. It is our expectation that ligand acceptor orbitals will be found dominant in governing the details of oxidative coupling in a wide variety of systems wherein the metal has a large complement of occupied levels.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in CCl_4. NMR spectra were obtained in $CDCl_3$ and chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane standard. Proton spectra were obtained on both Varian A-60A and Varian HA-100 spectrometers. Carbon spectra were obtained on a Bruker 90-MHz spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6L spectrometer while microanalyses were determined by Galbraith Laboratories, Knoxville, Tenn.

General Procedure for Cyclopentanone Ring Formation with Fe(0). As a general procedure, a mixture of the olefin and $Fe(CO)_5$ (2:1 mole ratio) was heated in a deaerated Pyrex pressure bottle (Fisher and Porter) at 125 °C for 48 h. After cooling, unreacted $Fe(CO)_5$ was removed under vacuum, and the crude product dissolved in chloroform, filtered through Celite, chromatographed, and recrystallized. The iron-rich residue is mildly pyrophoric and should be treated with care.

Preparation of Ketone 8a. 2-Methylene-5-norbornene (42.5 g, 400 mmol) (Aldrich) was treated according to the general procedure in a 250-ml pressure bottle. After deareation with nitrogen, 39.2 g (200 mmol) of $Fe(CO)_5$ was added. The pressure bottle was fitted with a pressure gauge and sealed, and the mixture heated with stirring at 125 °C for 48 h. After cooling to room temperature, excess $Fe(CO)_5$ and unreacted diene were removed under vacuum. The crude reaction mixture was slurried in $CHCl_3$ and filtered through Celite. The filtrate was concentrated under vacuum, taken up in a minimum of $CHCl_3$, and chromatographed on a 4 × 40 cm silica gel column (100–200 mesh). Elution with 50:50 $CHCl_3$/hexanes gave unreacted diene, ketone, and unidentified polymeric material. There was no evidence of olefin iron tricarbonyl complex. Recrystallization from hexanes followed by vacuum sublimation gave white crystals, 2.80 g (6%), of

pure ketone: mp 111-112 °C; IR (CCl_4) 1725 cm^{-1} (carbonyl); mass spectrum *m/e* (parent) 240 (calcd 240). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39; O, 6.66. Found: C, 85.06; H, 8.35.

Preparation of Alcohol 8b. A solution of 373 mg (1.55 mmol) of ketone **8a** in 25 ml of THF was added to 147 mg (7.75 mmol) of $LiAlH_4$ in 10 ml of THF. The reaction mixture was refluxed with stirring for 24 h. After $LiAlH_4$ destruction, the crude reaction mixture was filtered and the filtrate reduced under vacuum. Chromatography of the residue on a 2 × 20 cm silica gel column (100-200 mesh) with 50:50 benzene/dichloromethane followed by recrystallization from hexanes gave white crystals, 286 mg (79%), of pure alcohol: mp 115-116 °C; mass spectrum *m/e* (parent) 242 (calcd 242). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15; O, 6.60. Found: C, 84.40; H, 9.20.

Preparation of Ketones 9a-c. Ketones **9** were prepared by the same procedure employed for ketone **8a.** 2-Ethylidene-5-norbornene (47.2 g, 390 mmol) (Aldrich) and 38.5 g (196 mmol) of $Fe(CO)_5$ were used. Elution with $CHCl_3$ gave unreacted diene and ketones. The ketones were recrystallized from pentane and vacuum sublimed. White, crystalline solid (5.95 g, 11.4%) was obtained; mp 81-83 °C; IR (CCl_4) 1725 cm^{-1} (carbonyl); mass spectrum *m/e* (parent) 268 (calcd 268). Anal. Calcd for $C_{19}H_{24}O$: C, 85.08; H, 9.01; O, 5.96. Found: C, 85.20; H, 9.46.

Reaction of 1-Methyl-2-norborene with $Fe(CO)_5$ (7). A reaction mixture containing a 2:1 mole ratio of 1-methyl-2-norbornene to $Fe(CO)_5$ was treated according to the general procedure. There was no evidence of cyclopentanone formation after heating for 48 h at 125 °C. 1-Methyl-2-norbornene was recovered unchanged. Cyclopentanone formation also did not occur at temperatures up to 160 °C and time periods to 7 days.

Reaction of 2-Methyl-2-norbornene (6) with $Fe(CO)_5$. A reaction mixture containing a 2:1 mole ratio of 2-methyl-2-norbornene to $Fe(CO)_5$ was treated according to the general procedure. There was no evidence of olefin iron tricarbonyl complex or cyclopentanone formation after heating for 48 h at 125 °C. However, 2-methyl-2-norbornene underwent equilibration to 2-methylenenorbornane. Product distribution: 82% 2-methylene, **6a;** 18% 2-methyl, **6.** The distribution of isomers was ascertained by comparison of integrated NMR resonances at δ 5.47 (olefin, 2-methyl) and 4.72, 4.47 (olefin, 2-methylene).

Reaction of 2-Methylenenorbornane (6a) with $Fe(CO)_5$. A reaction mixture containing 2:1 mole ratio of 2-methylenenorbornane to $Fe(CO)_5$ was treated according to the general procedure. Once again, no cyclopentanone was formed during heating for 48 h at 125 °C although 2-methyl-2-norbornene was formed. Product distribution: 85% 2-methylene, **6a;** 15% 2-methyl, **6.**

Preparation of 1-Methyl-2-norbornene (7) and 2-Methyl-2-norbornene (6). The synthesis of 1-methyl-2-norbornene and 2-methyl-2-norbornene was carried out in a 1500-ml Aminico high-pressure reaction vessel according to a literature preparation.[15] Methyl cyclopentadiene dimer (340 g) (Aldrich) and 10.0 g of anhydrous sodium carbonate were placed in the reaction vessel. The vessel was pressurized to 900 psi with ethylene and heated with shaking for 7 h at 190 °C. Upon cooling, the reaction mixture was filtered through Celite and distilled at atmospheric pressure. Initial cuts were made at 111-115, 116-118, and 119-121 °C. Each cut was, then distilled on a Nester/Faust annular Teflon spinning band column (h = 61 cm, bore = 8 mm). Purity of the fractions was ascertained by GLC on a 0.25 in. × 5 ft 20% SF 96 (Firebrick) column and ^1H NMR spectral analysis: yield 66.5% overall; 115.8 g (40.2%) of 1-methyl-2-norbornene, bp 100 °C (lit. 104-105 °C); IR (CCl_4) 3040 (olefinic CH), 1620 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.92-1.25 (m, 2, bridge), 1.11-1.95 (m, 4), 1.32 (s, 3, methyl), 2.75 (m, 1, bridgehead), 5.72 (d, 1, J = 5.5 Hz, olefin), 5.95 (dd, 1, J = 5.5, 3.0 Hz, olefin). 2-Methyl-2-norbornene (171.9 g, 59.7%), bp 114 °C (lit. 118-119 °C); IR (CCl_4) 3060 (olefinic CH), 1630 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.85-1.58 (m, 4), 1.09 (m, 2, bridge), 1.68 (d, 1, J = 2.0 Hz, methyl), 2.42 (m, 1, bridgehead), 2.70 (m, 1, bridgehead), 5.47 (m, 1, olefin).

Preparation of 2-Methylenenorbornane (6a). 1-Methylenenorbornane was prepared via a Wittig synthesis[16] from 2-norbornanone (norcamphor) (Aldrich). Methyltriphenylphosphonium bromide (321 g, 0.90 mol) was treated with 57.6 g (0.90 mol) of *n*-butyllithium in 780 ml of diethyl ether with stirring for 3 h. 2-Norbornanone (33 g, 0.30 mol) was added and the solution allowed to reflux for 15 h. The reaction mixture was washed with water, and the organic phase dried over $MgSO_4$. Vacuum removal of solvent followed by distillation gave 22.8 g (19%) of product: bp 123 °C; IR CCl_4 3080 (olefinic GH), 1670 cm^{-1} (exocyclic olefinic CC); NMR ($CDCl_3$) δ 1.38 (m, 2, bridge), 1.42-1.95 (m, 2), 1.13-1.72 (m, 4), 2.28 (m, 1, bridgehead), 2.62 (m, 1, bridgehead), 4.47 (d, 1, vinyl), 4.72 (d, 1, vinyl).

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