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Metal Assisted Ring Expansions. The Stereospecific Expansion of Pinene Induced by $Fe(CO)_5$

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Abstract: Iron pentacarbonyl induced carbonyl insertions into the cyclobutane rings of α- and β-pinene are described and are the first metal induced ring expansions of monovinylcyclobutane derivatives. Under experimental conditions employed, the location of cyclobutane ring opening is governed by the entering iron species and not by the simple thermally controlled ring opening process generally observed. Expansion is thought to proceed via σ–π-allyl metal and acyl–π-allyl intermediates. The two ketonic products formed in synthetically useful quantities are skeletally enantiomeric and are formed stereospecifically.

Since the observation that metals frequently induce formal symmetry-forbidden molecular rearrangements,[2] the interest in the versatility and pathways available to such systems has blossomed. Much elegant work has been described of the opening of cyclopropyl rings as in bicyclo[1.1.0]butanes,[3] quadricyclene,[4] unsaturated bicyclic systems such as hexamethyl(Dewar benzene),[5] and four-membered rings as in cubane.[6] Both stoichiometric and catalytic reactions have been considered, and product sensitivity to the electronic properties of the metal has been noted.[6,7] Controversy still rages[8] as to whether these systems are best described as concerted, symmetry-allowed processes taking advantage of the metal orbital structure to become allowed, or as sequential processes which take advantage of formal radical or ionic pathways made low in energy by the metal system.

Metal induced ring opening with metal retention has been demonstrated for numerous polycyclic three-membered rings,[2] the four-membered ring system of cubane,[6a] and a divinylcyclobutane system[6b] reported by Cotton. Reports have appeared describing ring opening of vinylcyclopropyl systems which retain the metal simultaneously bound to the resultant π-allyl function and the linkage deficient carbon. Semibullvalene,[9a] bullvalene,[9b] and bicyclo[3.1.0]hexene[10] undergo such reactions with $Fe_2(CO)_9$ forming the chelated $Fe(CO)_3$ product. Related ring openings of polycyclic ketones containing three-membered rings have also been reported; barbaralone[11] may be opened with $Fe_2(CO)_9$.

Expansion of carbon skeletons via introduction of the highly versatile carbonyl function is frequently difficult but is of major synthetic importance. Metal catalyzed or assisted carbonyl insertion reactions are becoming increasingly frequent as exemplified by use of the well-known oxo process to extend olefins and the use of tetracarbonylferr(−II)ate[12] to extend organic halides. Vinylcyclopropane may be ring-expanded with rearrangement[13] to the corresponding cyclohexenone using $Fe(CO)_5$ or $Fe_2(CO)_9$ under photolytic conditions; intermediates present in this expansion reaction[14] have been characterized at low temperatures. Carbon monoxide insertion into a chelated σ-π-allyl metal complex to give the acyl-π-allyl metal intermediate is indicated.[11,14] Reaction products containing σ-π-allyl metal chelates and carbonyl inserted acyl-π-allyl metal chelates have been reported from tricarbonyl(cycloocta-1,5-diene)metal(0) complexes with iron, ruthenium, and osmium.[15] Nevertheless, metal assisted chain extension and ring expansion reactions must still be viewed as unusual reactions of major synthetic potential. One purpose of the following discussion will be to further elucidate the synthetic range of ring expansion reactions.

Stereospecific olefin coupling reactions[16] brought about both thermally and photochemically by iron carbonyls have been reported along with reaction pathway considerations.[17] In such systems, product stereochemistry is exceedingly sensitive to the possibility of metal chelation between a double bond and a near-by alkoxy oxygen.[18,19] Benzonorbornadiene[16] couples exclusively to the corresponding exo-trans-exo cyclopentanone product, while 7,7-dimethoxybenzonorbornadiene[18] couples to the exo-trans-endo product. Carbonyl additions carried out by Reppe[20] have been known for many years and include a wide variety of substrates.

Catalytic olefin isomerization reactions have been extensively studied and are now both well understood and frequently employed in the laboratory. The active pathway appears to involve hydride extraction forming the π-allyl metal hydride intermediate followed by hydride introduction to the previously unsaturated carbon center and catalyst departure,[21] although a concerted mechanism has been suggested.[22] Stereospecific isomerizations have been employed as routes to otherwise expensive materials. Illustrative of such a case is the isomerization of (−)-β-pinene to (−)-α-pinene[23] with 97% optical retention brought about by $Fe(CO)_5$. A product yield of 45% was reported, the remaining 55% being present as residue. No δ-pinene was observed.

In the following report, we discuss a four-membered carbon ring being opened and expanded via a π-allyl pathway using as our vehicle the heretofore unobserved ring expansions of α- and β-pinene. This remarkable iron carbonyl induced reaction takes place stereospecifically to form two ketonic products whose skeletal structures are related as an enantiomeric pair. We show that opening of the four-membered ring occurs in a fashion totally different[24] from the extensively studied thermal rearrangements of pinene and substituted pinenes.

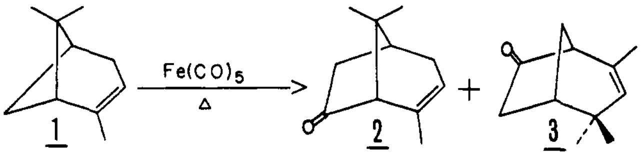
Results

When either α-pinene or β-pinene is heated neat with an equimolar quantity of $Fe(CO)_5$ in a sealed glass container, the pressure slowly increases with deposition of a black, mildly pyrophoric solid. Filtration of the resultant liquid phase followed by vacuum distillation of the filtrate gives two components, the first being α-pinene containing no ^{1}H NMR observable β-pinene and the second being a mixture of two ketonic products. Reaction 1 shows the main net chemical change being observed with product structures illustrated from (−)-α-pinene.[25]

Table I. The 60-MHz Proton Magnetic Resonance Assignments of Ketones 2 and 3[a]

Ketone 2		Ketone 3	
Proton	Chemical shift, τ ppm ($J_{2,3}$, Hz)	Proton	Chemical shift, τ ppm ($J_{2,3}$, Hz)
2	8.33 1.5	2	8.32 1.5
3	4.59	3	4.87
8a	9.04	4a[b]	9.02
8s	9.01	4s[b]	8.88

[a] Copies of the spectra of these ketones are incorporated in the microfilm edition of the journal. See paragraph at end of paper. [b] Differentiation between 4a and 4s is uncertain.



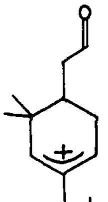
Products 2 and 3 are isomeric ketones with enantiomeric carbon skeletons. Structural assignments are based upon the observed ^{1}H NMR spectra, compiled in Table I, and chiroptic properties. Of significance is the observation that the olefinic proton of **2** is subject to additional coupling in comparison to that of **3**. The olefinic protons of **2** and **3** are coupled to their respective vinyl methyl groups and long range to the two bridgehead protons; that of **2** is further coupled to the adjacent methylene group not present in **3**.

Observed resonances of the *gem*-methyl protons are consistent with these assignments. Ketone **3** has two distinct *gem*-methyl groups with a chemical-shift difference of 0.14 ppm, similar to the difference of 0.12 ppm reported for dihydrocamphene.[26a] While analogy to differentiation between geminal protons in the [2.2.1] system[26b] taken together with the possibility of shielding of 7a by the carbonyl double bond suggests that 7a resonates at higher field than does 7s, an unequivocal differential assignment has not yet been made.

In contrast to the clear difference in magnetic environments of the geminal methyl groups of **3**, the *gem*-methyl protons of **2** are nearly identical. The observed resonances at τ 9.01 and 9.04 are at slightly higher field than is the corresponding *syn*-methyl resonance of pinane (τ 8.99).[27] The *gem*-methyl groups of **2** are deshielded with respect to the *syn*-methyl groups of both α- and β-pinene[27] which resonate at τ 9.15 and 9.28, respectively. With respect to pinane, introduction of the double bond of α- and β-pinene significantly shields the *syn*-methyl group while slightly deshielding the *anti*-methyl group. A similar effect would be expected in ketone **2** with the initial anticipation of nonequivalent methyl groups. The carbonyl group of **2** might be expected to have a similar but oppositely signed effect on the 7a and 7s protons. Thus the magnetic equivalency of 7a and 7s in **2** results from two compensating interactions. Chemical shifts observed for the vinyl methyl groups of **2** and **3** are in keeping with that observed for α-pinene at τ 8.37.

Differentiation between the resonances assigned to the *gem*-methyl groups of **2** was accomplished by noting chemical-shift difference changes with successive additions of $Eu(fod)_3$.[28] Upon the addition of a small quantity of this paramagnetic reagent, the chemical-shift difference decreased with coalescence upon further addition of the reagent; finally, an increasingly large difference developed with still further additions. As the 7a methyl group of **2** is closer to the europium coordination site than is the 7s group, it has been assigned to the higher field resonance.

The mass spectra of **2** and **3** show parent ions at m/e^+ = 164 with intensities relative to the base fragment at m/e^+ = 107 of 59 and 35%, respectively. Product **3** might be expected to lose a methyl group to form the corresponding π-allyl cation of mass 149. A fragment of this mass is observed (27%); no fragment of mass 163 (P − 1) is observed. On the other hand, preliminary consideration of **2** might lead one to expect a mass fragment at 163 corresponding to formation of the π-allyl cation analogous to the proposed 149 fragment from **3**. Only a minor fragment at $m/e^+ = 163$ (<1%) is observed with the $m/e^+ = 149$ fragment being 29% of the base fragment. In fact, the mass spectra of **2** and **3** are quite similar. Rupture of the linkage from the carbonyl carbon to the adjacent bridgehead position of either ketone leads to the identical π-allyl fragment of $m/e^+ = 164$, illustrated as **4**. Loss of one of the *gem*-methyl groups of this fragment extends the π system and accounts for the mass 149 fragment and for the base peak fragment of mass 107. The similarity of the two mass spectra is supportive of the assigned skeletal similarity of **2** and **3**.

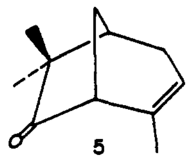


$m/e^+ = 164$

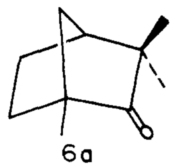
4

Ketones **2** and **3** are chiral and are formed stereospecifically. As is seen later, the similarity of the n-π^* chromophores of these two products is illustrated in both their uv and chiroptic spectra, all of which are typical of β,γ-unsaturated ketones.[29,30] The Cotton effects of **2** and **3** are oppositely signed and of nearly the same value, confirming the skeletal enantiomeric character of these two ketones.

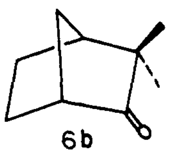
An alternative bicyclo[3.2.1] structure having the requisite skeleton and whose olefinic ^{1}H NMR spectrum might be expected to be similar to that of **2** is shown as **5**. Related α-*gem*-dimethyl ketones[31] **6a** (fenchone) and **6b** display magnetically similar *gem*-methyl groups as does camphene.[26] Thus the ^{1}H NMR spectrum assigned to **2** is not inconsistent with that of **5**. Considerable evidence allows us to exclude **5**, however. *gem*-Methyl resonances observed at τ 9.01 and 9.04 are slightly higher than those which one would expect for **5** based on the observed resonances of **6a** and **6b**. Mass spectral loss of dimethyl ketene from **5** or from the parent − 1 fragment derived from **5** would generate fragments of mass 94 and 93, respectively, and the mass spectra of **5** and **3** would be clearly different in this region. Only a moderately important fragment for **2** (**5**) is observed at mass 93 (23%) with a minor fragment at 94 (4%); furthermore, the two ketones are identical in this region. Finally, the chiroptic properties of the compound assigned to structure **2** are inconsistent with those of **5**. If **5** were present, it would have been formed either as a racemic mixture or with the same absolute configuration as **3**, both of these possibilities being opposed to observations.



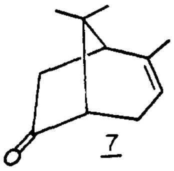
5



6a



6b



7

Ketone **7**, which might obtain from δ-pinene, is inconsistent with the observed Cotton effects and uv spectra of the observed ketones as it is skeletally enantiomeric with neither **2** nor **3**, nor is it a β,γ-unsaturated ketone. Furthermore, **7** would be expected to display a mass spectrum substantially different from that of **2** or **3**.

Ring expansion with its requisite opening of a carbon-carbon σ bond is kinetically unfavorable with respect to double-bond isomerization. Thus at 100° isomerization takes place slowly, while ketone formation does not occur.

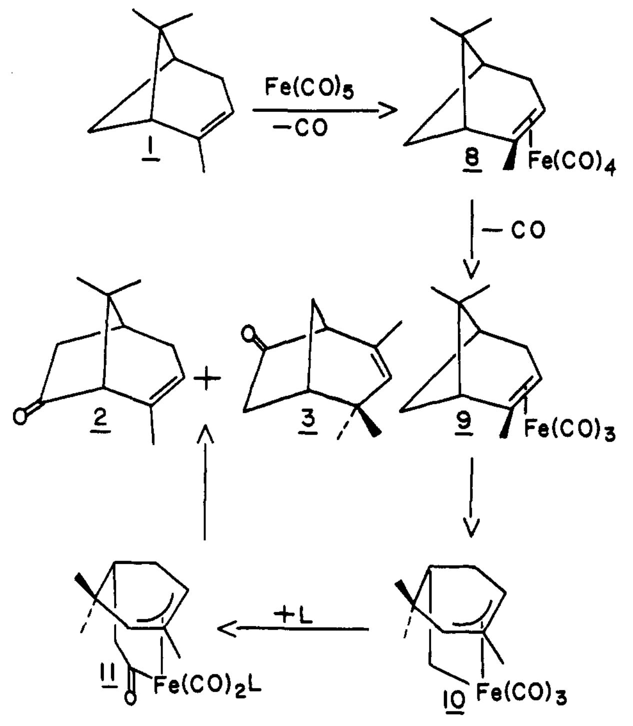
Discussion

An extensive literature exists describing thermal rearrangements of α- and β-pinene, pinene protonation reactions which occur with skeletal rearrangement, and solvolysis reactions from the pinene bicyclo[3.1.1] system.[24] In general, these rearrangements give product distributions consistent with opening of the carbon-carbon bond bearing the *gem*-methyl groups. When closure takes place from such intermediates, the C_s symmetry of the π-allyl structure requires racemization and resultant loss of optical activity. Products **2** and **3** are both optically active and skeletally enantiomeric, as demonstrated by their Cotton effects of opposite sign, observations which preclude the existence of achiral intermediates. Thus iron carbonyl induced ring expansion of the pinenes cannot proceed via trapping of thermally generated ring opened species. Furthermore, the observed products are inconsistent with ring opening adjacent to the *gem*-methyl groups. Were the carbonyl group to be inserted into this linkage, ketone **5** would be formed exclusively and, in all likelihood, it would be racemic as reasonable intermediates would contain a symmetry plane.

Ring expansion via carbonyl insertion into the one-carbon methylene bridge with maintenance of the *gem*-dimethyl group system as part of an undisturbed cyclic structure obviates the formation of an achiral intermediate and leads to the formation of optically active products. Substantial preferred ring opening does not occur under the experimental conditions, requiring that bond breakage be directly induced by the active iron species. Under thermal and photolytic conditions, tetracarbonyliron(0) is known to be the preliminary reactive species[17,32] generated from $Fe(CO)_5$. In the presence of olefins, this highly reactive intermediate is trapped forming a (monoolefin)tetracarbonyliron(0) species, as illustrated in reaction Scheme I. Formation of this complex is highly sensitive to bulky substituents situated above the trapping double bond,[16b,17a] and indeed attack syn to a substituent as large as a methyl group is extremely improbable. Thus iron attack on the α-pinene double bond must occur from the side endo to the bridge bearing the *gem*-methyl groups. Once the iron system is attached to the least hindered side of the double bond, direct involvement in ring opening must rupture the thermally inaccessible bond.

Ring openings of vinylcyclopropanes yielding intermediates and/or stable complexes containing the iron tricarbonyl nucleus simultaneously bound σ to the liberated carbon

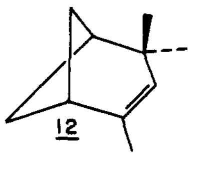
Scheme I



center and to the generated π-allyl system are well known.[9-11,13,14] Similar cleavage in the α-pinene system will generate intermediate **10** after loss of an additional molecule of carbon monoxide. As clear evidence to the contrary is not presently available, the usual 16–18 electron rule[33] has been applied in developing reaction Scheme I, although we hasten to point out that paramagnetic species may be present during the course of the reaction.

Migratory insertion of a carbonyl group to form acyl-π-allyl intermediate **11** carries the sequence to within one step of product. Closure adjacent to the *gem*-methyl groups results in retention of configuration and formation of product **2**, while closure to the opposite side of the π-allyl group generates the skeletal enantiomer of **2**, ketone **3**. No evidence for closure to the central carbon of the π-allyl system has been found.

Two potential equilibria must be considered in this scheme. It is reasonable to expect that closure of **11** either adjacent to the carbon bearing the *gem*-methyl groups or adjacent to the methylene group might be kinetically preferred. The observation of a product distribution of 46% **2** and 54% **3** could indicate kinetic selectivity to be minimal under the experimental conditions or it could arise from the establishment of a thermodynamic equilibrium between **2** and **3**. Thermal isomerization of **3** in the absence of iron carbonyl does proceed but at a rate far too slow to account for the observed product distribution. In the presence of $Fe(CO)_5$, ketone **2** does not isomerize, although considerable decomposition occurs. Thus the observed product distribution must be due to minimal kinetic selectivity for closure of **11**. Closure from intermediate **10** to α-pinene may be ruled out as in all likelihood this would result in generation of olefin **12**, a species which neither Spanninger[23] nor we have observed.



12

Experimental Section

^{1}H NMR spectra were obtained on a Varian A-60A instrument and chemical shifts reported in parts per million (τ) downfield from an internal tetramethylsilane (Me_4Si) standard. Routine mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6L spectrometer, high resolution mass spectra using a Du Pont Model 21-110B instrument, and infrared spectra using Perkin-Elmer 437 and 621 spectrophotometers. Circular dichroic spectra were obtained using a Cary 60 spectropolarimeter.

Ketone separation proved to be of considerable difficulty and was accomplished using high-pressure liquid chromatography (Waters Associates, Milford, Mass.); three injection sequences were necessary. Porasil A/60 served as the solid phase, and chloroform (Mallincodt AR) was used as the eluting solvent in all cases. The first injection of 0.8 ml of ketone mixture onto two 2 ft × $\frac{3}{8}$ in. lengths of column efficiently separated the ketone mixture from other minor components with a single pass. This mixture was collected and reinjected onto four column lengths, 8 ft, and recycled for a total column length of 80 ft. At this time the separation was approximately 96% complete. Collection of the two 96% pure ketones was followed by yet a third injection and recycling to a total of 80 ft once again. In this manner complete separation was accomplished. Flow rates of 5 ml/min were used in all cases with 80 ft of column requiring 4.5 hr.

Reactions were carried out in annealed Pyrex pressure bottles (Fisher and Porter) fitted with a pressure gauge; reaction temperatures were maintained at 160 ± 0.5° for 68 hr. Typical experimental procedures involved reacting equimolar amounts of $Fe(CO)_5$ and pinene, from Aldrich and used directly, followed by product filtration through Celite and vacuum distillation. The ketone mixture distilled between 56 and 57° (0.7 Torr). Highest ketone yields were obtained from β-pinene with an initial pressure of 30 psi CO. In all cases, α-pinene was isolated.

Under the reaction conditions employed, small changes took place when the pinenes were heated neat in the absence of $Fe(CO)_5$. The specific rotation of (+)-α-pinene decreased from $[\alpha]^{24}\text{D}$ +53.9 ± 0.2° (*c* 19.24, $CHCl_3$) to $[\alpha]^{24}\text{D}$ +53.0 ± 0.3° (*c* 19.32, $CHCl_3$). Sample discoloration was noted, although no difference was observed between the ^{1}H NMR spectra obtained before and after heating. The behavior of (−)-β-pinene was somewhat different when treated in an identical manner. In this case, the liquid remained colorless but a small quantity of a white, chloroform-insoluble, high-melting solid formed. The remaining liquid displayed a specific rotation which had increased from $[\alpha]^{24}\text{D}$ −18.9 ± 0.2° (*c* 19.90, $CHCl_3$) [lit.[34c] $[\alpha]^{22}\text{D}$ −22.7°, (neat)] to $[\alpha]^{24}\text{D}$ −19.7 ± 0.2° (*c* 19.89, $CHCl_3$), while once again no difference was observed between the two ^{1}H NMR spectra.

Data for Ketones from (+)-α-pinene: $[\alpha]^{24}\text{D}$ +47.2° (neat) (lit.[34a,b] $[\alpha]\text{D}$ +51.1°). **Ketone 2:** uv λ_{max} 292 cm^{-1} (ϵ 267, cyclohexane); $[\phi]^{24}\text{D}$ −659 ± 3° (*c* 3.90, cyclohexane); CD λ_{max} 292 cm^{-1} (θ −4.2 × 10^4, MeOH); ir (neat) 1744 cm^{-1} (ν_{CO}); mass spectrum m/e^+ (parent) (calcd for $C_{11}H_{16}O$, 164.1200) 164.1192; yield from β-pinene under CO 29%. **Ketone 3:** uv λ_{max} 292 cm^{-1} (ϵ 314, cyclohexane); $[\phi]^{24}\text{D}$ +637 ± 3° (*c* 3.27, cyclohexane); CD λ_{max} 292 cm^{-1} (θ +4.3 × 10^4, MeOH); ir (neat) 1742 cm^{-1} (ν_{CO}); mass spectrum m/e^+ (parent) (calcd for $C_{11}H_{16}$, 164.1200) 164.1198; yield from β-pinene under CO 34%.

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Supplementary Material Available. A copy of the 60-MHz ^{1}H NMR spectra of ketonic products will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number *JACS-75-4288*.

References and Notes

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Rotational Isomerism in the Compounds η^5-$C_5H_5FeCOLCH_2R$

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Abstract: A series of compounds η^5-$C_5H_5Fe(CO)_2CH_2R$ and η^5-$C_5H_5FeCOLCH_2R$ (L = phosphorus donor; R = Ph, $SiMe_3$, 1-naphthyl) have been prepared and characterized. Ir spectra in the carbonyl stretching region indicate rotational isomerism about the iron-alkyl bonds in both types of compounds, while ^1H NMR spectra show that interconversion between rotamers in both systems is rapid on the NMR time scale. Variable-temperature NMR studies of the tertiary phosphine derivatives suggest that steric considerations determine the rotamer preferences, and that the stablest rotamer is that in which the bulky η^5-C_5H_5 is gauche to both methylene hydrogen atoms.

In recent years, there has been a number of reports of conformational isomerism resulting from restricted rotation about single bonds in organotransition metal chemistry. Among the earliest of these were suggestions that compounds of the type η^5-$C_5H_5Fe(CO)_2MX_2R$ (M = Si, Ge; X = Cl, Br, I; R = alkyl) exist in solution as mixtures of rotational isomers with respect to the iron–M bond.[1-4] Conclusions were based on the observations of four strong carbonyl stretching bands in the ir spectra of the compounds. Similar behavior has been observed for series of methylthio-bridged[5] and metal–metal bonded[6] bimetallic carbonyl complexes.

Nuclear magnetic resonance evidence has been presented for restricted rotation about phosphorus–metal[7-9] and phosphorus–carbon[10] bonds in complexes of tertiary phosphines containing the bulky *tert*-butyl group, although similar claims for the compounds *trans*-$PdCl_2[PPh(CH_2Ph)_2]_2$[11] and $M(CO)_3[\eta^6$-o-$MeC_6H_4)P(o$-$tolyl)_2]$[12] (M = Cr, Mo) are open to alternative interpretations. In the former case, although the observation of a quartet of triplets for the benzylic methylene resonance was taken as evidence for restricted rotation about the phosphorus–methylene bonds,[11] it has been pointed out that the methylene protons are magnetically nonequivalent even if rotation about the phospho-