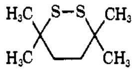
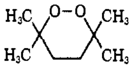
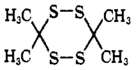
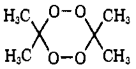
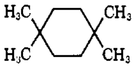
Table V. Activation Parameters for Ring Inversion in Tetramethyl 6-Rings

Compound	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mole
	15.6[a,e]	6.7	13.8 (−2°)
	17.9[a,e]	14.4	14.6 (12°)
	15.9[b,f]	1.2	15.6 (14°)
	11.7[c,g]	−10.7	15.0 (30°)
			11.6 (−53°)[d,e]

[a] F. Claeson, F. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961). [b] This work. [c] R. W. Murray, P. R. Story, and M. L. Kaplan, *ibid.*, **88**, 526 (1966). [d] H. Friebolin, W. Faisst, and H. F. Schmid, *Tetrahedron Letters*, 1317 (1966). [e] For the chair-to-chair process. [f] For the chair-to-twist process. [g] For the chair to assumed boat process.

which avoids the *cis* configuration for the C–S–S–C moiety (*e.g.*, II), *i.e.*, that which avoids maximized vicinal lone pair–lone pair repulsions across the S–S bond. Such interactions would seem to be better minimized in I or III than in II and we favor the semiplanar transition state (I). If it is reasonable to assume that the entropy of activation may be estimated from $\Delta S^{\ddagger} = R \ln (n)$ in which n = number of reaction pathways,[7c] $\Delta S^{\ddagger} = R \ln 2 = +1.4$ eu is in qualitative agreement with the entropy of activation for the chair-to-twist process (+1.2 eu) in duplodithioacetone. The twist-to-chair process is apparently more complicated.

The presence of adjacent atoms possessing lone pairs of electrons leads to substantial enhancements in the barriers to ring inversion in a number of tetramethyl six-membered heterocycles as compared to the cyclohexane analog. The data are summarized in Table V. Although differing force constants for bond angle deformation in the transition state must account for some of the barrier increase, lone pair–lone pair repulsions cannot be ruled out as a significant contributor.[9]

A recent paper reported activation parameters for the twist-to-chair process in duplodithioacetone ($\Delta H^{\ddagger} = 22.2 \pm 2$ kcal/mole, $\Delta S^{\ddagger} = 21.0 \pm 7$ eu, $\Delta G^{\ddagger} = 16.1 \pm 0.2$ at 20°)[10] at significant variance with the values reported here. However, the kinetic parameters were obtained *only* by the line shape method and no comparison to equilibration data was performed.[11]

Experimental Section

The nmr spectra were recorded on a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.

Temperature was measured using a calibrated copper–constantan thermocouple placed about 1 in. below the sample. Temperature readings were taken simultaneously with the recording of the spectrum and are accurate to ±0.1° at the sample.

Computer calculations were performed on an RCA Spectra 70-46 computer.

Acknowledgment. We are grateful to Professor M. Saunders for supplying the computer programs used and for invaluable advice and assistance. We thank the Worcester Area College Computation Center for many hours of donated computer time as well as Research Corporation and the National Science Foundation (COSIP Grant) for financial support.

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(10) B. Magnusson, B. Rodman, and S. Rodmar, *Arkiv Kemi*, **31** (7), 65 (1969).

(11) In a personal communication, Professor Magnusson indicated that temperature stability was not of a high order in his equipment providing a source for the discrepancy in $\Delta S^{\ddagger}$.

Conformational Analysis of Tricarbonyl(diene)iron Compounds

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Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received October 6, 1969*

Abstract: Tricarbonyl(diene)iron complexes bearing terminal 1-hydroxyethyl groups have been prepared by sodium borohydride reduction of complexed dienones and direct complexation of dienols. Conformational analysis allows firm predictions of preferred conformations which have been used as a basis for assigning *R*,*R* and *S*,*S* relative stereochemistry to compounds **1** and **11** and *R*,*S* and *S*,*R* relative stereochemistry to **2** and **12**. Compounds **1** and **11** in which the hydroxy group prefers to be *exo* to iron are designated *ψ-exo* and **2** and **12** in which hydroxy is *endo* with respect to iron are designated as *ψ-endo* compounds. Uncomplexed dienones exist as mixtures of *s-cis* and *s-trans* enones; however the complexed dienones appear to prefer the *s-cis* conformation of the enone unit. Reduction of complexed dienones with sodium borohydride is highly stereospecific, producing 95% or more of the *ψ-endo* diastereomer in agreement with the transition state model developed by Karabatsos.

Tricarbonyl(diene)iron compounds which contain one additional asymmetric carbon exist as two diastereomeric forms, *e.g.*, **1** and **2**, owing to the asymmetry of the complexed diene moiety.[2] Diastereomeric tricarbonyl(*trans*,*trans*-3,5-heptadien-2-ol) iron complexes **1** and **2** have been prepared in pure

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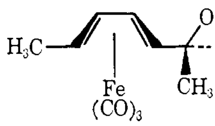
(1) (a) Texaco Research Fellow 1965–1966; (b) Alfred P. Sloan Foundation Fellow 1969–1971.

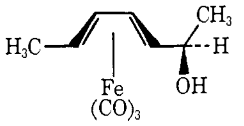
(2) Compound **1** is a mixture of *R*,*R*, and *S*,*S* enantiomers and **2** a mixture of *R*,*S*, and *S*,*R* enantiomers. For the purpose of assigning configuration, each carbon of the diene is considered to be bonded to iron.[3]

(3) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

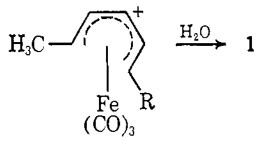
form by Mahler and Pettit,[3] who have suggested relative configurations **1** (mp 85°) and **2** (mp 70°) on the basis of a proposed mechanism for hydrolysis of **3**, R = CH_3.



1

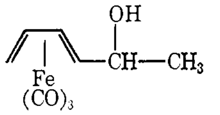


2



3

Hydrolysis of **3**, R = H, also gives only one diastereomer of dienol complex **4**.[4]



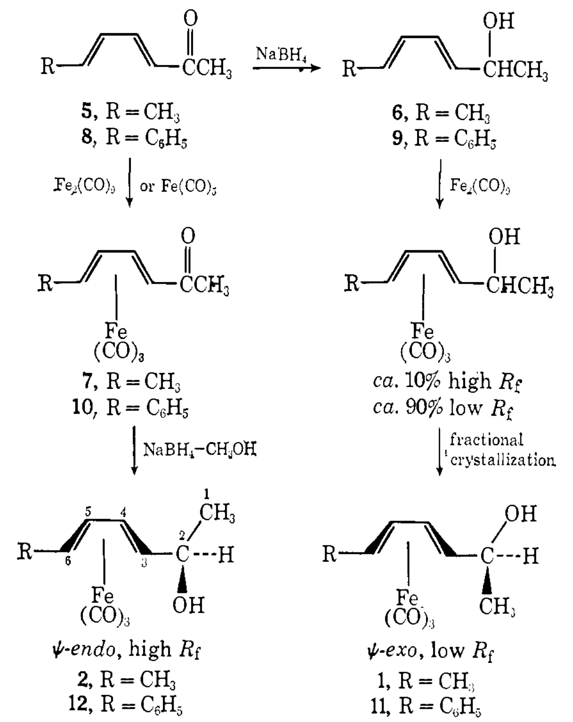
4

We have prepared two pairs of diastereomeric tricarbonyl(dienol)iron compounds (**1** and **2**, **11** and **12**) in the course of a study of solvolysis of their esters.[5] In order to determine the preferred stereochemistry of the solvolysis reactions, conformational analysis of and determination of relative stereochemistry for these compounds was necessary.

Steric interactions involving carbon monoxide ligands in tricarbonyl(arene)chromium complexes have been proposed to account for slow ring rotation and nmr chemical shifts of ring hydrogens[6a] and Friedel–Crafts acylation patterns in substituted tricarbonyl(arene)-chromiums.[6b] Price and Sorensen have pointed out that these data are consistent with an alternative explanation;[7] however, steric effects in acylation have been unequivocally demonstrated in a subsequent case.[6c] The stereochemistry of protonated tricarbonyl(norbornadiene)iron is consistent with the existence of steric interactions between the carbon monoxide and norbornadiene ligands as well.[8]

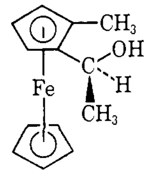
Synthesis. Preparation of the two pairs of diastereomeric dienol complexes is outlined in Scheme I. Sodium borohydride reduction of the complexed dienones, **7** and **10**, is strikingly stereospecific giving almost exclusively the diastereomers which have higher R_f values on silica gel and alumina thin layers. In the methyl series the low-R_f diastereomer is formed to the extent of *ca.* 5% while only a trace of the low-R_f diastereomer was formed in the reduction of **10** in the phenyl series.[9] Conversely, treatment of dienols **6** and **9** with diiron enneacarbonyl gave mixtures rich in the low-R_f diastereomers from which they were isolated by crystallization. Our dienol complex **2** melted at 41° compared to the reported value of 70–71.5°.[3] Repetition of the original synthesis gave a mixture of two alcohols which were chromatographically identical with our **1** and **2**, and the nmr spectrum of **2** is consistent with that reported previously.[3] Oxidation of our 41° alcohol with chromium trioxide in pyridine gave the starting ketone **7**. Thus, the 71 and 41° alcohols must be dimorphs.

Scheme I. Preparation of Diastereomeric Tricarbonyl(dienol)iron Compounds[a]



[a] The numbering system used for these compounds is given on structures **2–12**.

Relative Stereochemistry of the Dienol Complexes. In contrast to ferrocenyl carbinols[10,11] and several other organotransition metal alcohols,[12] the tricarbonyl(dienol)iron compounds exhibit no intramolecular hydrogen bonding between the hydroxy group and iron. Thus, Hill and Richards[10] infrared method of assigning relative configurations to ferrocenyl carbinols such as **13** was not available to us. Application of the principles of conformational analysis to the dienols and their precursors, however, has made it possible to interpret their physical and chemical properties in terms of relative configuration with considerable confidence.



13

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(4) J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, 85, 3959 (1963).

(5) (a) N. A. Clinton and C. P. Lillya, *Chem. Commun.*, 579 (1968); (b) N. A. Clinton and C. P. Lillya, *J. Am. Chem. Soc.*, 93, 3065 (1970).

(6) (a) D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. S. Robinson, and R. Spratt, *Chem. Commun.*, 231 (1966); (b) W. R. Jackson and W. B. Jennings, *ibid.*, 824 (1966); (c) D. E. F. Gracey, W. R. Jackson, and W. B. Jennings, *ibid.*, 366 (1968).

(7) J. T. Price and T. S. Sorensen, *Can. J. Chem.*, 46, 515 (1968).

(8) D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Am. Chem. Soc.*, 89, 6387 (1967).

(9) Owing to the close similarity of the ir and nmr spectra of the diastereomers, a spectroscopic estimate of composition was not feasible. Our estimates are based on comparison of the crude product with synthetic mixtures using tlc and appear to be accurate to ±2%.

(10) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, 83, 4216 (1961).

(11) D. S. Trifan, J. L. Weinmann, and L. P. Kuhn, *ibid.*, 79, 6566 (1957); D. S. Trifan and R. Bacskai, *ibid.*, 82, 5010 (1960); and H. Falk and R. Schlögl, *Monatsh. Chem.*, 96, 1065 (1965).

(12) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, 83, 3840 (1961); W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, 1170 (1965); and S. G. Cottis, H. Falk, and K. Schlögl, *Tetrahedron Lett.*, 2875 (1965).

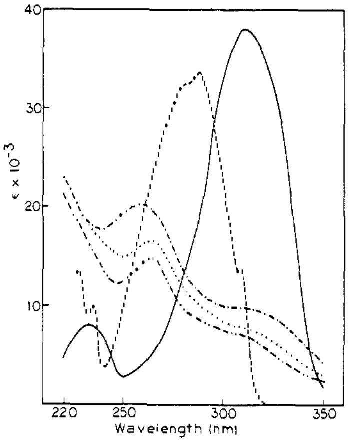
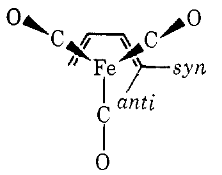
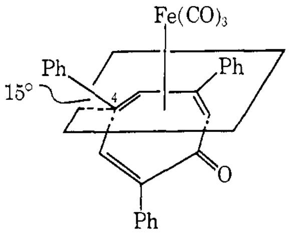


Figure 1. Ultraviolet spectra of diene–Fe(CO)$_3$ complexes and free dienes: ———, 6-phenyl-3,5-hexadien-2-one (**8**); -----, 6-phenyl-3,5-hexadien-2-ol (**9**); -·-·-·-, 6-phenyl-3,5-hexadien-2-one–Fe(CO)$_3$ (**10**); ···········, ψ-*exo*-6-phenyl-3,5-hexadien-2-ol–Fe(CO)$_3$ (**11**); -·-··-·, 1-phenylbutadiene–Fe(CO)$_3$.

X-Ray crystallography has afforded detailed knowledge of the geometry of the tricarbonyliron complexes of 12 structurally diverse dienes.[13] The 4-carbon diene unit is planar or nearly so; and when the complexes are viewed along the normal dropped from iron to the diene plane, two carbonyl ligands are always eclipsed with the two formal double bonds of the diene (**14**). It is highly unlikely that this conformation of the Fe(CO)$_3$ group is an artifact of crystal packing forces since all 12 compounds exhibit this preference. We can conclude, therefore, that it is a molecular property which will persist in solution. *anti* substituents (see **14**), which are ring residues in all of the cases in which their geometry is known, are displaced from the diene plane away from iron.[13b–g,i–k] *syn* substituents appear to be bent toward iron slightly[13b,f] as in the case of tricarbonyl(2,4,6-triphenyltropone)iron (**15**) in which the C$_4$-phenyl bond makes an angle of 15° with the diene plane.[13f,14] Corresponding bond lengths and angles in the tricarbonyl(diene)iron unit of all these compounds are strikingly similar. As an aid in conformational analysis, we have constructed a scale model of a *syn*-substituted tricarbonyl(diene)iron complex using typical bond lengths and angles.[13,15]

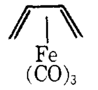


14

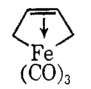


15

We have begun our analysis of steric effects in the dienol complexes by assuming that staggered conformations about the carbinol carbon–diene bond represent energy minima. While this is in contrast to simple uncomplexed olefins like propene[16a] and 1-butene[16b] in which alkyl groups or hydrogens are eclipsed with the double bond, we feel it is reasonable on two counts. First, our model shows that staggered conformations minimize steric interactions between substituents on the carbinol carbon and the bulky Fe(CO)$_3$ group. Second, the complexed diene has considerable saturated character which favors a staggered conformation. The electronic structure of conjugated diene–transition metal complexes can be represented as a hybrid of structures **16a** and **16b**.[17] Green has summarized the evidence for Fe(CO)$_3$ complexes and has concluded that structure **16b**, involving σ-bonds and some rehybridization at the terminal carbons, is the more important contributer.[17b] Cais and Maoz have emphasized that the uv spectra of these complexes are not in accord with the localized structure **16b** alone.[18] Uv absorption of our compounds (Figure 1) are even less in accord with the delocalized structure of **16a** alone. Complexation of a diene with conjugating terminal substituents reduces absorption in the π–π^* region dramatically.[19] Reduction of the carbonyl group of cinnamylidene acetone (**6**) results in a shift of the π–π^* band of 22 nm to the blue; however, reduction of the carbonyl group in the complexed dienone (**10**) results in only small changes in uv absorption. Similar observations have been made in the methyl series. This loss of conjugation between diene π orbitals and terminal substituents has been mentioned by others[13h,20] and is in accord with some saturated character at the terminal carbons. Terminal phenyl substituents on uncomplexed dienes appear as nmr multiplets; but on complexation of the diene they collapse, without fail, to sharp singlets[21] characteristic of nonconjugated



16a



16b

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(13) (a) O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963); (b) N. A. Bailey and R. Mason, *ibid.*, **21**, 652 (1966); (c) M. Churchill and R. Mason, *Proc. Chem. Soc.*, 226 (1964); (d) A. Robson and M. R. Truter, *Tetrahedron Lett.*, 3079 (1964); (e) R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964); (f) D. L. Smith and L. F. Dahl, *ibid.*, **84**, 1743 (1962); (g) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); (h) A. J. Birch, H. Fitton, R. Mason, G. B. Robertson, and J. E. Strangroom, *Chem. Commun.*, 613 (1966); (i) A. J. Birch, H. Fitton, M. McPartlin, and R. Mason, *ibid.*, 531 (1968); (j) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961); (k) I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Am. Chem. Soc.*, 90, 5023 (1968).

(14) We would like to thank Professor Dahl for supplying us with detailed structural data for this compound and for calculating the angle quoted here.

(15) Details about the model are given in the Experimental Section.

(16) (a) D. R. Hershbach and L. C. Kirschner, *J. Chem. Phys.*, **28**, 728 (1958); (b) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(17) (a) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 100 (1967). (b) M. L. H. Green, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen, London, 1968, pp 70–74.

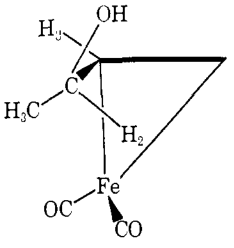
(18) M. Cais and N. Maoz, *J. Organometal. Chem.*, **5**, 370 (1966).

(19) Cais and Maoz have assigned the maxima at 260–270 nm as π–π^* and the weaker shoulders at *ca.* 310 nm as d–π^* in analogy with some π-cyclopentadienonecobalt complexes. Reassignment of the π–π^* transition as the 310-nm band requires a drastic decrease in π–π^* intensity on complexation and reassignment to a band at lower wavelength requires a drastic shift to the blue on complexation. Both are consistent with reduced conjugation in the π system of the ligand.

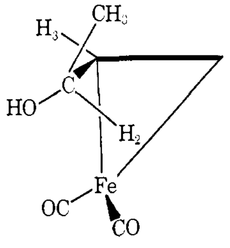
(20) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. Wild, *J. Chem. Soc., A*, 332 (1968).

phenyl groups.[22] Furthermore, C_4 in **15** is displaced from the plane of its 3-bonded carbons by 0.22 Å which is nearly half the distance for tetrahedral geometry.[13f]

Examination of our scale model shows that the three distinct positions which substituents on the carbinol carbon occupy in an idealized staggered conformation can be classified according to steric crowding as shown in Figure 2.[15] Position c is severely crowded by terminal carbonyl 2 and the diene residue while a group in position b suffers less severe crowding from terminal carbonyls 1 and 2. The sterically preferred conformations of the diastereomeric dienol complexes will be those with the largest groups in the two relatively uncrowded positions, **17** and **18**. The diastereomers are designated *ψ-exo* and *ψ-endo* according to the preferred conformation of hydroxy group relative to iron.[10]



17, *ψ-exo*



18, *ψ-endo*

The contrasting behavior of the diastereomeric dienol complexes on alumina and silica gel thin layers is striking. The isomers produced by reduction of the complexed dienones, **2** and **12**, have high R_f values which are similar to those of the complexed dienones (**7** and **10**) themselves. However, the other complexed dienol isomers, **1** and **11**, exhibit low R_f values which are nearly identical with those of the uncomplexed dienols and are significantly less soluble in nonpolar solvents than are **2** and **12**. The exposed hydroxy group of the *ψ-exo* diastereomers accounts for the polar behavior of **1** and **11** while the unusual nonpolar behavior of **2** and **12** is in good agreement with *ψ-endo* stereochemistry and a sterically shielded hydroxy group. Hill and Richards *ψ-exo* and *ψ-endo* ferrocenyl carbinols exhibit differential chromatographic behavior in the same sense, *i.e.*, R_f (*ψ-exo*) < R_f (*ψ-endo*),[10] and the chromatographic behavior of the semirigid isomeric dienols **19** and **20**[23] is in agreement with the above conclusions as well.

Diastereomeric pairs of complexed dienols and pairs of the corresponding 3,5-dinitrobenzoate esters[24] exhibit consistent but small chemical shift differences in their nmr spectra. Significantly, the vicinal coupling constants J_{23} (see **17** and **18**) are large, falling within a range of *ca.* 8–9 Hz, and are identical within experimental error for diastereomeric pairs. This is in accord with our proposal that **17** and **18** which make H_2 and H_3 *anti-periplanar* are the most stable conformations of the complexed dienols.[25,26] These assignments of relative configuration confirm Mahler and Pettit's original stereochemical assignments for **1** and **2** and define the stereochemistry of hydrolysis of **3**, R = CH_3.[3]

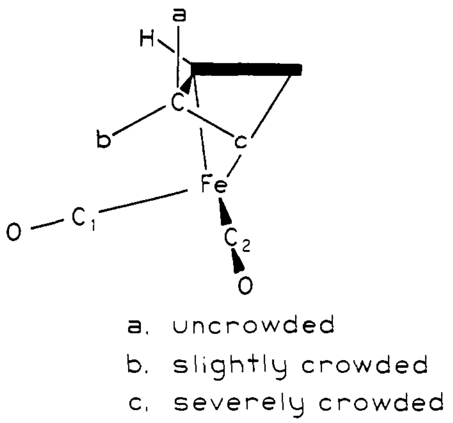
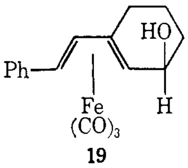
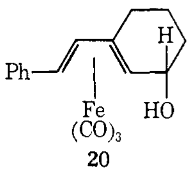


Figure 2. The staggered conformation of a *syn*-substituted tricarbonyl(diene)iron complex. The diene is viewed "edge on" looking from the *syn* substituent toward the diene.



19



20

The *ψ-exo* dienols are the more stable isomers. Rearrangement of the *ψ-endo* isomer in the methyl series to its *ψ-exo* isomer on an alumina column has been described.[3] We have equilibrated the isomeric phenyl dienol complexes in ethyl ether using aluminum isopropoxide and acetone as well as aluminum *t*-butoxide and quinone. Concomitant decomposition reduces the accuracy of our experiments, but we are able to assign a minimum value of 9 to K_{eq} for conversion of the *ψ-endo* isomer to *ψ-exo*. This requires the larger methyl group to occupy the slightly crowded position in the more stable isomer instead of hydroxy and cannot be explained on the basis of steric interactions alone. The observed order of stability could be caused by destabilization of the *ψ-endo* isomers owing to repulsion of the C–O and diene–iron dipoles[27] in its preferred conformation (**18**).

Conformation of Complexed Dienones. The infrared spectra of dienones **5** and **8** undergo striking changes in the carbonyl region upon complex formation. The uncomplexed dienones exhibit multiple bands in the carbonyl region (Table I) owing to the existence of *s-cis* and *s-trans* conformations of the enone moiety.[28,29] In

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(21) *Cf.* this and other work in these laboratories and H. W. Whitlock and Y. N. Chuah, *Inorg. Chem.*, **4**, 424 (1965).

(22) (a) *Cf.* High Resolution NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, spectra 505 ethylbenzene (phenyl on saturated carbon singlet), 305 *cis*-stilbene (phenyl twisted out of conjugation singlet). 306 *trans*-stilbene (conjugated phenyl multiplet). (b) Phenyl ferrocene exhibits a phenyl multiplet in the nmr (personal communication from M. D. Rausch). (c) Examination of our scale model shows clearly that the conformation in which phenyl is roughly coplanar with the diene moiety is favored. Thus, steric factors do not prevent conjugation.

(23) Compounds **19** and **20** were prepared in a stereospecific fashion and will be described in a subsequent paper: unpublished work of D. E. Kuhn.

(24) See ref 5 and the accompanying paper.

(25) *Cf.* A. A. Bothner-By in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965.

(26) Esterification does not increase the effective size of an hydroxy group. *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 44.

(27) For tricarbonyl(butadiene)iron $\mu(C_6H_6)$ = 2.15 ± 0.05 D with the diene probably the positive end. *Cf.* H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1156 (1962): **46**, 1588 (1963).

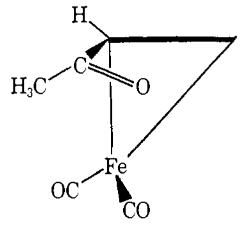
(28) This is common for α,β-unsaturated ketones. *Cf.* R. S. Erskine

contrast, the complexed dienones, **7** and **10**, exhibit single carbonyl stretching frequencies. Either the complexed ketones have a strong preference for a single conformation or, as is the case for saturated ketones, the different conformers do not exhibit significantly different carbonyl stretching frequencies.

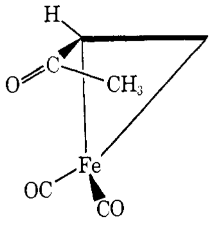
Table I. Carbonyl Ir Frequencies of Dienones and Their $Fe(CO)_3$ Complexes in CCl_4

Compound	Frequency, cm^{-1}
$CH_3(CH{=}CH)_2COCH_3$	1690, 1670
$[CH_3(CH{=}CH)_2COCH_3]Fe(CO)_3$	1682
$Ph(CH{=}CH)_2COCH_3$	1692, 1672
$[Ph(CH{=}CH)_2COCH_3]Fe(CO)_3$	1682

We favor the former explanation for several reasons. Examination of our model reveals only two sterically reasonable conformations **21** and **22** which will also be favored by any residual conjugation in the dienone ligand. Conformation **21** should be favored owing to destabilization of **22** by steric interactions of the ketone methyl group with the diene residue and the proximate terminal carbonyl group. A consequence of the partially saturated character of the complexed diene will be to make the carbonyl eclipsed conformation **21** more favorable energetically than in the uncomplexed dienones. Saturated aldehydes and ketones normally exist in carbonyl eclipsed conformations.[30,31] Relative to the hydrogen-carbonyl interaction the alkyl-carbonyl interaction is stabilizing for groups smaller than *t*-butyl.[31] Finally, the high stereospecificity of reduction of the dienone complexes is consistent with strong conformational preference.

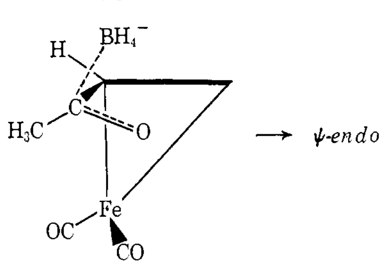


21

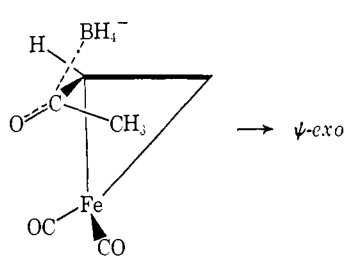


22

Interconversion of Dienols and Dienones. The stereochemistry of sodium borohydride reduction of the complexed dienones in methanol is in good agreement with our assignment of relative stereochemistry. Using the model of Karabatsos[32] for carbonyl addition transition states in which carbonyl is eclipsed with the group of medium size on an asymmetric α carbon and the incoming reagent approaches on the side of the small group (**23**), we can predict that the *ψ-endo* isomer should predominate in the reduction products.[33] In fact, reduction of **7** and **10** gives product mixtures which are more than 95% *ψ-endo*. The striking stereospecificity of these reactions requires a free energy difference between **23** and **24** of *ca.* 1.8 kcal/mol and, to our knowledge, exceeds that observed for addition to any other acyclic ketone.[32,34] This is consistent with strong conformational preference in the ketone which the transition states for reduction resemble.[32]



23



24

Oxidation of the diastereomeric dienol complexes **11** and **12** with chromic anhydride in pyridine proceeds at significantly different rates to give ketone **10**. Oxidation of the *ψ-endo* alcohol (**12**) approached completion after 24 hr at *ca.* 25°; however, the *ψ-exo* isomer (**11**) gave only a trace of ketone after a similar period. *Axial* alcohols are oxidized more rapidly than their *equatorial* epimers in the cyclohexane and steroid series owing to relief of steric interactions during fragmentation of the intermediate chromium esters.[35] Wilcox, *et al.*, have estimated that 75% of the steric strain which is absent in the ketone has been lost at the transition state.[36] Prediction of the relative oxidation rates of our acyclic alcohols is somewhat complicated by the possibility that oxidation could lead to different initial conformations of the ketone. However, since in terms of steric strain the transition states resemble the product ketone[36] and conformers of the chromium esters and the ketone will be interconverted rapidly, we need consider only the ground state energies of the alcohols and diastereomeric transition states leading to the most stable conformation of the ketone. This leads to the prediction that the less stable diastereomer should be oxidized more rapidly, in agreement with observation.

Summary. Conformational analysis of tricarbonyl (dienol)iron π complexes provides a detailed, self-consistent explanation of the unusual difference in properties of pairs of diastereomeric compounds as well as the stereochemistry of their formation by ketone

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and E. S. Waight, *J. Chem. Soc.*, 3425 (1960); and K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

(29) Fermi resonance involving the overtone of the $C\alpha$–H out-of-plane bending absorption has been ruled out as a cause of the multiple bands by means of deuterium labeling experiments. Unpublished work of A. F. Kluge.

(30) Reference 25, pp 19–21.

(31) G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965), and references therein.

(32) G. J. Karabatsos, *ibid.*, **89**, 1367 (1967).

(33) Consideration of torsional interactions in the transition state for reduction as suggested by M. Chérest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2199 (1968), also leads to the conclusion that a transition state closely related to **23** should be preferred.

(34) When polar groups are present on $C\alpha$, similar high stereospecificity is sometimes observed. This is thought to arise because of coordination of the polar group with the attacking reagent: D. J. Cram and D. R. Wilson, *J. Am. Chem. Soc.*, **85**, 1245 (1963).

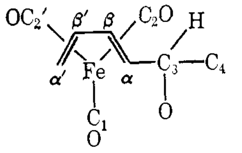
(35) Reference 26, pp 81–84 and 271–273, and K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 164–166.

(36) C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

reduction. Our considerations suggest that steric interactions involving the dienol ligand and terminal carbonyl groups on iron are of primary importance in determining conformation. The major assumptions in the work about conformational preference of the $Fe(CO)_3$ group and the existence of staggered conformations about the carbinol carbon–diene bond are shown to be reasonable. The conclusions presented here account well for the solvolytic behavior of the complexed dienol esters reported earlier,[5] and their further testing is in progress.

Experimental Section

Scale Model of Tricarbonyl(dienol)iron Complexes. The model was constructed using a scale of 2 in. = 1 Å. Bond distances and angles used are listed. The angle between the C_α—C_3 bond and the

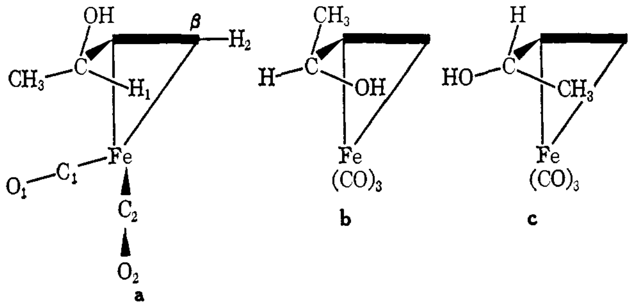


Bond distances, Å	
Fe—CO	1.75
Fe—C_α	2.12
Fe—C_β	2.05
C_α—C_β	1.45
C_β—$C_{\beta'}$	1.40
C≡O	1.17
C_α—C_3	1.51
C_3—C_4	1.54
C_β—H	1.08
C_3—O	1.43

Bond angles, deg	
$\alpha\beta\beta'$	120
$\alpha\beta C_3$	118
C_1FeC_2	100
C_2FeC_2'	92
FeC_1O	180
FeC_2O	180
At C_3	109.5

diene plane was 15°.[14] To define the positions of the terminal carbonyl groups, the following extra criteria were used. Carbons α and α' are displaced *ca.* 0.5 Å from the plane which contains Fe, C_2≡O, and C_2'≡O; and the plane which contains C_1, C_2, and C_2' is inclined at an angle of 30° to the diene plane.[13a] The location of C_3 with respect to the $Fe(CO)_3$ group is a crucial factor in determining steric interactions in the different conformations. Thus, the C_3—Fe and C_3—C_2 distances as determined by measurement of the model were compared to the corresponding distances in the 2,4,6-triphenyltropone complex[37] and found to correspond within 0.03 Å. A total of 11 other nonbonded distances from the model including C_α—C_2, C_β—C_2, C_α—C_1 and $C_{\beta'}$—C_2 were checked against values reported for the 2,4,6-triphenyltropone,[37,38] cyclooctatetraene,[13g] and butadiene[13a] complexes. In each case the values agreed within 0.1 Å and in all but 3 agreed within 0.05 Å. A typical set of measurements made on idealized staggered conformations are listed in Table II.

Table II. Steric Interactions in ψ-*exo*-Tricarbonyl(dienol)iron Complexes **1** and **11**



Interatomic distances less than the sum of van der Waals radii[a]					
Conformer **a**		Conformer **b**		Conformer **c**	
Atoms	R^b	Atoms	R^b	Atoms	R^b
CH_3—C_1	0.36	HO—C_2	0.62	CH_3—H_2	0.39
CH_3—C_2	0.48	HO—O_2	0.52	CH_3—C_2	1.13
CH_3—O_2	0.10	HO—C	0.64	CH_3—O_2	1.13
H_1—C_2	0.25	CH_3—C	0.26	CH_3—C	0.82
H_1—C	0.07			HO—C_2	0.09

[a] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964). The value of 1.0 Å for aromatic hydrogens was used for H_2 and the value for perpendicular approach to doubly bonded oxygen, 1.60 Å, was used for terminal carbonyl oxygen. [b] Sum of van der Waals radii minus interatomic distance on model in ångström units.

General. Infrared spectra were recorded on Beckman IR-10 and Perkin-Elmer 237-B instruments and were calibrated with the 1603 cm^{-1} polystyrene band. Nmr data were obtained on a Varian Associates A-60 instrument using tetramethylsilane as an internal standard. Nmr samples in deuteriochloroform were passed through a fine filter (Metricel-Alpha 8, pore size 0.2 μ) to remove any paramagnetic particles caused by autoxidation of the organoiron compounds. Determination of uv spectra was done with a Cary-14 spectrometer. Melting points were determined on a Mel Temp apparatus and are uncorrected, and elemental analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

3,5-Heptadien-2-ol (6). A slurry of 7.5 g (0.20 mol) of sodium borohydride in water was added to a solution of 15 g of 3,5-heptadien-2-one[39] (0.14 mol) in 70 ml of methanol. The reaction mixture was stirred overnight at room temperature and then diluted with 400 ml of water. The products were extracted into four 50-ml portions of ether, and the combined extracts were dried ($MgSO_4$). Filtration and subsequent evaporation of the filtrate under reduced pressure left a thick oil which was distilled under vacuum. 3,5-Heptadien-2-ol was collected at 78–80° (20 mm) [lit.[40] bp 78° (20 mm)] as 11.4 g (76%) of a colorless oil: ir (CCl_4) 3610 and 3400 cm^{-1} (broad) (OH); uv max (C_6H_{12}) 230 nm (ϵ 18,000); nmr ($CDCl_3$) τ 8.8 (d, 3, J_{12} = 7 Hz, 1-CH_3), 8.25 (d, 3, J_{67} = 6 Hz, 7-CH_3), 6.15 (s, 1, OH), 5.7 (m, 1, H_2), 3.7–4.6 (m, 4, H_{3-6}).

6-Phenyl-3,5-hexadien-2-ol (9). A slurry of 10 g (0.26 mol) of sodium borohydride in 220 ml water was added to a solution of 18 g (0.10 mol) of 6-phenyl-3,5-hexadien-2-one[41] in 220 ml of methanol. The reaction mixture was stirred for 2 hr and then diluted with 400 ml of water. Organic products were extracted into five 100-ml portions of ethyl ether, and the combined extracts were dried ($MgSO_4$). Filtration and evaporation of the dried extract gave **9** as a white solid, 13.5 g (75%): mp 66.5–67.5° (lit.[42] 65–66°); ir (CCl_4) 3610, 3550–3100 cm^{-1} (OH); uv max (C_6H_{12}) 308 (13,600), 287 (33,400), 278 nm (sh, ϵ 31,900); nmr (CCl_4) τ 8.8 (d, 3, J_{12} = 6.5 Hz, -CH_3); 7.2 (s, 1, OH), 5.75 (m, 1, C*H*-OH), 3.4–4.5 (m, 4, =CH-), 2.85 (narrow m, 5, -Ph).

Tricarbonyl(3,5-heptadien-2-one)iron (7). 3,5-Heptadienone[39] (55.5 g, 0.50 mol) and 200 ml (1.5 mol) of iron pentacarbonyl in 200 ml of methylcyclohexane were heated at reflux under nitrogen for 42 hr. The mixture was filtered twice to give a clear red solution which, on evaporation, left a thick, red oil. Vacuum distillation of this oil gave, after a low boiling forerun, 33 g (26%) of **7** as a clear red oil which crystallized slowly on standing. Repeated recrystallization of a small sample from Skellysolve F at −78° gave a light yellow solid: mp 38.5–39.5° (lit.[43] mp 31–33°); ir (CCl_4) 2060, 1970 cm^{-1} (C≡O), 1682 (C=O); uv max (95% C_2H_5OH) 310 (3200), 245 nm (sh, ϵ 14,100) (lit. values in ref 18); nmr ($CDCl_3$) τ 8.75 (d, 1, J = 8.5 Hz, H_3), 8.30–8.65 (m, 4, H_6, 7-CH_3), 4.8 (m, 1, H_4), 4.3 (m, 1, H_5).

Tricarbonyl(6-phenyl-3,5-hexadien-2-one)iron (10). Diiron enneacarbonyl (75 g, 0.21 mol) was added to a solution of 18 g (0.10 mol) of 6-phenyl-3,5-hexadien-2-one[41] in 400 ml of dry ethyl ether and the suspension was stirred and heated at reflux under nitrogen for 90 min. Filtration of the reaction mixture and evaporation of the filtrate gave a green solid which was triturated with a few milliliters of Skellysolve F and collected by filtration as a yellow solid. Continued washing with small portions of Skellysolve F removed the last traces of green material and left 12.35 g (37%) of

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(37) Douglas L. Smith, Ph.D. Thesis, University of Wisconsin.

(38) In cases where the desired distance was not quoted it was calculated from the atomic coordinates and unit cell dimensions.

(39) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(40) E. A. Braude and J. A. Cales, *ibid.*, 2085 (1951).

(41) L. Diehl and A. Einhorm, *Ber.*, **18**, 2320 (1885), and T. Plati, W. H. Strain, and S. L. Warren, *J. Am. Chem. Soc.*, **65**, 1273 (1943).

(42) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 2646 (1949).

(43) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1960).

10 as a light yellow solid, mp 112–113°. Sublimation at 80° (0.01 mm) gave analytically pure material: mp 114–114.5°; ir (CCl_4) 2060, 1980 ($C\equiv O$), 1682 cm^{-1} ($C=O$); uv (Figure 1) nmr (CCl_4) τ 8.65 (d, 1, J_{34} = 7 Hz, H_3), 8.90 (s, 3, CH_3), 7.80 (d, 1, J_{56} = 8 Hz, H_6), 4.20 (q, 2, H_4 and H_5), 2.95 (s, 5, Ph).

Anal. Calcd for $C_{15}H_{12}O_4Fe$: C, 57.72; H, 3.88; Fe, 17.89. Found: C, 57.94; H, 3.92; Fe, 17.90.

***ψ-endo*-Tricarbonyl(3,5-heptadien-2-ol)iron (2).** A slurry of 6 g (100 mmol) of sodium borohydride in 100 ml of water was added to a solution of 6 g (23.8 mmol) of tricarbonyl(3,5-heptadien-2-one)iron (**7**) in 100 ml of methanol, and the reaction mixture was stirred at room temperature for 2 hr. Dilution with 400 ml of water and extraction with five 50-ml portions of ethyl ether gave red ether extracts which were dried ($MgSO_4$). Evaporation of the dry extract under vacuum and vacuum distillation of the remaining red oil gave 5.05 g (84%) of crude product, bp 100° (0.3 mm). Tlc analysis (silica gel–$CHCl_3$) showed the presence of *ca.* 5% of the *ψ-exo* isomer. Crystallization and recrystallization from Skellysolve C gave 2 g of a yellow solid which was recrystallized from 100 ml of Skellysolve F to give 0.8 g (13%) of light yellow crystals: mp 41° (lit.[3] mp 70–71.5°). Tlc analysis showed no trace of *ψ-exo* isomer: ir ($CHCl_3$) 3600, 3500–3400 (OH), 2010, 1990–1940 cm^{-1} ($C\equiv O$); uv max (C_6H_{12}) 290 (2800), 220 nm (end abs, ϵ 21,000); nmr ($CDCl_3$) τ 8.5–9.1 [m, 8, analyzed as 9.03 (t, 1, J_{23} = J_{34} = 7.5 Hz, H_3), 8.8 (m, 1, H_6), 8.70 (d, 3, J_{12} = 7 Hz, 1-CH_3), 8.61 (d, 3, J_{67} = 6 Hz, 7-CH_3)], 7.95 (d, 1, J = 3.5 Hz, OH), 6.30 (m, 1, H_2), 4.75–5.10 (m, 2, H_4 and H_5).

Anal. Calcd for $C_{10}H_{12}O_4Fe$: C, 47.65; H, 4.80; Fe, 22.12. Found: C, 47.45; H, 4.80; Fe, 21.92.

***ψ-endo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-ol)iron (12).** A slurry of 12 g (0.32 mol) of sodium borohydride in 220 ml of water was added to a solution of 10 g (0.032 mol) of tricarbonyl(6-phenyl-3,5-hexadien-2-one)iron (**10**) in 220 ml of methanol and the mixture was stirred under nitrogen at room temperature for 2 hr. The reaction mixture was diluted with 400 ml of water and extracted with five 100-ml portions of ethyl ether. The combined dark-yellow extracts were dried ($MgSO_4$) and evaporated to give a brown solid. Tlc analysis (silica gel–$CHCl_3$) revealed the presence of less than 5% of the *ψ-exo* isomer in this crude product. Washing with 10 ml of cold Skellysolve F followed by recrystallization from 100 ml of Skellysolve B gave 4.25 g (41%) of light yellow crystals, mp 97.5–98.5°, which tlc analysis showed to be pure. Repeated recrystallization from Skellysolve F gave analytically pure **12**: mp 98–98.5°; ir ($CHCl_3$) 3605, 3550–3350 (broad, OH) 2020, 2000–1960 cm^{-1} ($C\equiv O$); nmr ($CDCl_3$) τ 8.62 (d, 3, J_{12} = 6.5 Hz, –CH_3), 8.6 (t or q, 1, J_{23} = 8 Hz, J_{34} = 7 Hz, H_3), 8.38 (s, 1, OH), 7.95 (d, 1, J_{56} = 9 Hz, H_6), 6.2 (m, 1, H_2), 4.68 (q, 1, J_{34} = 7 Hz, J_{45} = 6 Hz, H_4), 4.22 (q, 1, J_{45} = 6, J_{56} = 9 Hz, H_5), 2.78 (s, 5, C_6H_5).

***ψ-exo*-Tricarbonyl(3,5-heptadien-2-ol)iron (1).** A suspension of 75 g (0.21 mol) of diiron enneacarbonyl in a solution of 13 g (0.12 mol) of 3,5-heptadien-2-ol in 100 ml of dry ethyl ether was stirred and heated at reflux under nitrogen for 2 hr. Filtration of the reaction mixture and subsequent evaporation left a red oil which was vacuum distilled, the fraction of bp 95–100° (0.3 mm) being collected. This crude product solidified on standing and was shown by tlc analysis (silica gel–$CHCl_3$) to contain *ca.* 10% of the *ψ-endo* isomer. Three recrystallizations from Skellysolve C gave tlc-pure **1** as 4.55 g (16%) of light yellow crystals: mp 84–85° (lit.[3] mp 85–86°); ir ($CHCl_3$) 3610, 3550–3300 (broad, OH), 2040, 2000–1960 cm^{-1} ($C\equiv O$), nmr ($CDCl_3$) τ 9.08 (t, 1, J_{23} = J_{34} = 8 Hz, H_3), 8.5–8.75 [m, 7, analyzed as 8.71 (d, J_{12} = 7 Hz, 1-CH_3), *ca.* 8.6 (m, H_6), and 8.54 (d, J_{67} = 6 Hz, 7-CH_3)], 8.20 (s, 1, OH), 6.43 (m, 1, H_2), 4.8 (m, 2, H_4 and H_5).

***ψ-exo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-ol)iron (11).** A suspension of 75 g (0.21 mol) of diiron enneacarbonyl in a solution of 20 g (0.073 mol) of 6-phenyl-3,5-hexadien-2-ol in 400 ml of dry ethyl ether was stirred and heated at reflux under nitrogen for 90 min. The reaction mixture was filtered twice and evaporated under vacuum to give a green solid. Trituration with five 2-ml portions of Skellysolve F gave 9 g (39%) of a crude yellow solid. Tlc analysis (silica gel–$CHCl_3$) showed *ca.* 10% *ψ-endo* isomer in the crude product. Three recrystallizations from 200-ml portions of Skellysolve C gave **11** as 2.25 g (10%) of yellow crystals which were homogeneous on tlc: mp 135–135.5°; ir ($CHCl_3$) 3600, 3500–3350 (broad, OH), 2040, 1980–1960 cm^{-1} ($C\equiv O$); uv max (C_6H_{12}, Figure 1) nmr ($CDCl_3$) τ 8.5–8.8 [q, 4, analyzed as 8.73 (t, 1, J_{23} = J_{34} = 8 Hz, H_3), 8.60 (d, 3, J_{12} = 7.5 Hz, CH_3)] 8.15 (s, 1, OH), 7.83 (d, 1, J_{56} = 9 Hz, H_6), 6.32 (m, 1, H_2), 4.61 (q, 1, J_{34} = 8, J_{45} = 5 Hz, H_4), 4.22 (q, 1, J_{45} = 5, J_{56} = 9 Hz, H_5).

Equilibration of *ψ,exo*- and *ψ-endo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-ol)iron Complexes (11 and 12). A sample of each alcohol in ether containing aluminum isopropoxide was deaerated by bubbling nitrogen through the solution for 30 min. A trace of acetone was added and the samples were sealed and heated for 18 hr at 125°. Tlc analysis (silica gel–$CHCl_3$) demonstrated the *ψ-endo* alcohol had been largely converted to the *ψ-exo* while the *ψ-exo* alcohol gave only traces of the *ψ-endo* isomer. Repetition of this experiment using aluminum *t*-butoxide and quinone in ether for 36 hr at 125° showed that the *ψ-endo* isomer was converted to a mixture with *ca.* 5% or less *ψ-endo* content while the *ψ-exo* isomer gave only a trace of the *ψ-endo*. Concurrent decomposition of the dienol complexes occurs in the equilibrations. Thus, though the apparent equilibrium mixture contains <5% of the *ψ-endo* isomer we have made a conservative estimate of a minimum *ψ-exo* to *ψ-endo* ratio of 9:1 to allow for possible selective destruction of the *ψ-endo* isomer.

Oxidation of *ψ-exo*- and *ψ-endo*-Tricarbonyl(6-phenyl-3,5-hexadienol)iron (11 and 12). To a solution of 0.1 g (0.32 mmol) in 8 ml of pyridine and 2 ml of benzene was added 0.1 g (1 mmol) of chromium trioxide. The solutions were stirred under nitrogen at *ca.* 25° for 24 hr. The reaction mixtures were then poured into water and the organic materials extracted into ethyl ether. The ether extracts were dried ($MgSO_4$), and the ether was evaporated. The crude products were spotted on tlc plates (silica gel) along with authentic alcohols and the expected product, ketone **10**. After drying in an oven to remove traces of pyridine the plates were developed in chloroform showing that the *ψ-endo* isomer had been almost completely oxidized to **10** while the *ψ-exo* isomer had given only traces of ketone. Another plate was spotted with the crude products and ketone **10** and after drying was respotted (coincident with the original spots) with 2,4-dinitrophenylhydrazine reagent. Oven drying and development ($CHCl_3$) showed that the 2,4-dinitrophenylhydrazones were chromatographically identical.

Oxidation of *ψ-endo*-Tricarbonyl(3,5-heptadien-2-ol)iron (2). Chromium trioxide (0.1 g, 1 mmol) was added to a solution of 0.1 g (0.39 mmol) of *ψ-endo*-tricarbonyl(3,5-heptadien-2-ol) iron in 15 ml of pyridine and 5 ml of benzene, and the reaction mixture was stirred under nitrogen for 24 hr at room temperature. Dilution of the reaction mixture with water, and extraction of the organic materials into ethyl ether followed by drying ($MgSO_4$) and evaporation gave a crude product. The product was shown to be identical with the expected ketone **7** by tlc comparison with an authentic sample.

Thin Layer Chromatographic Analysis. All tlc was performed using Camag silica gel and alumina containing 5% $CaSO_4$ binder and fluorescent indicator. Spots were visualized using ultraviolet light and iodine vapor. Quantitative analysis of mixtures was performed by spotting equal weights (delivered volumetrically from a microliter syringe) of unknown and standard (prepared by mixing known amounts of authentic materials) alongside of one another and developing. The method is quite sensitive when used to estimate components present in small amounts, and we feel our estimates are accurate to at least ±2% in the 1–10% range.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in partial support of this work.