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STEREOSPECIFIC GENERATION AND QUENCHING OF ACYCLIC DIENYLIRON TRICARBONYL CATIONS

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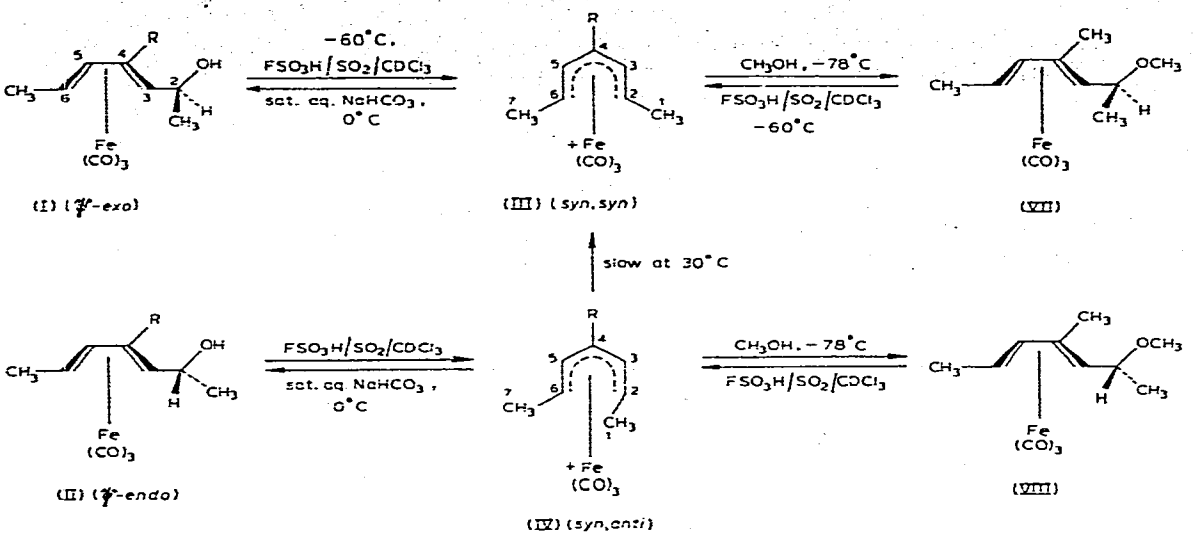
Summary

ψ-*exo*-*trans*-Dienoliron tricarbonyl complexes yield *syn*, *syn*-dienyliron tricarbonyl cations and ψ-*endo*-*trans*-dienoliron tricarbonyl complexes yield *syn*, *anti*-dienyliron tricarbonyl cations with $\geqslant$97% stereospecificity in fluorosulfonic acid at —60°C and with lower stereospecificity of 0°C. Aqueous or methanol quenching of these cations at 0°C or below proceeds in the above sense with $\geqslant$97% stereospecificity. However, aqueous quenching of *syn*, *anti* cations at 23°C produces up to ca. 30% ψ-*exo* alcohol which is not the result of acid catalyzed isomerization of ψ-*endo* alcohol subsequent to quenching. Sodium borohydride reduction of tricarbonyl(*cis*, *trans*-4-methyl-3,5-heptadienone)iron(V) gives a single *cis*-dienol complex which ionizes non-stereospecifically under all conditions. *syn*, *anti*-Tricarbonyl(4-methyl-3,5-heptadien-2-yl)iron cation (IV) is configurationally stable in FSO_3H and H_2SO_4 for hours at room temperature. The rate of slow isomerization of IV to its *syn*, *syn*-isomer is independent of bisulfate ion concentration and is unaccompanied by deuterium incorporation in D_2SO_4.

Stereospecific ionization of dienoliron tricarbonyl complexes in the presence of fluorosulfonic acid to produce *cis*-dienyliron tricarbonyl cations has been the subject of two brief reports [1,2]. Little is known about the configurational stability of the *anti*-substituted cations produced from ψ-*endo*-dienols (see Scheme 1) or of their reactions with nucleophiles. We report here a more thorough investigation of the ionization reactions and of the properties of the *cis*-dienyliron tricarbonyl cations produced.

Cation generation

The ψ-*exo*- and ψ-*endo*-tricarbonyl(*trans*,*trans*-4-methyl-3,5-heptadien-2-ol)-irons I (R = CH_3) and II (R = CH_3) ionized cleanly in $FSO_3H/SO_2/CDCl_3$ at —60°C to give the *syn*,*syn* and *syn*,*anti* cations III (R = CH_3) and IV (R = CH_3) respectively (Scheme 1). ^1H NMR spectra of cations III (R = CH_3) and IV (R = CH_3) (see experimental) clearly establish their structures [1,2,3]. They have



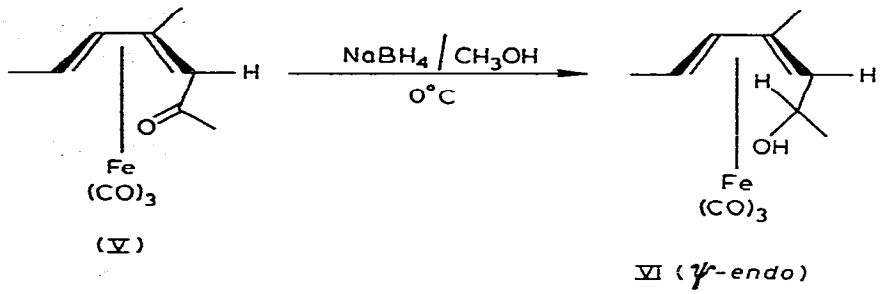
SCHEME 1. Low temperature ionization and quench.

been characterized further using ^{13}C NMR spectroscopy [4]. Production of III (R = CH_3) from I (R = CH_3) is completely stereospecific within the limits of NMR analysis, while samples of the *syn, anti* cation IV (R = CH_3) produced from II show NMR signals for a small amount, <5% in every case, of *syn,syn* cation III (R = CH_3). Parallel experiments with the *ψ-exo* and *ψ-endo* alcohol pair I (R = H) and III (R = H) gave results identical to those for the 4-methyl compounds *. The isomeric dienyliron tricarbonyl cations were identified by their characteristic ^1H NMR spectra [1].

Ionization stereospecificity for the *ψ-endo* dienols only is temperature dependent. Extraction of the dienol complexes from $CDCl_3$ into neat FSO_3H at −60°C gave results identical to those above, however at 0°C ionization of the *ψ-endo* dienols was only stereoselective. Ionization of II (R = H) at 0°C produced a ca. 2/1 mixture of *syn,anti* and *syn,syn* cations while II (R = CH_3) gave 3/1 mixture of *syn,anti* and *syn,syn* cations. Repeated NMR analysis showed that the composition of these mixtures did not change (see below). Thus, the observed products are produced under conditions of kinetic control.

Sodium borohydride reduction of the *cis* dienone complex V produced VI, the first reported *cis*-dienoliron tricarbonyl complex, as the sole product. TLC showed a single component with an R_f value identical to that of the *trans, ψ-endo* alcohol II (R = H). Mixed melting point determinations showed that the product was not identical to II. Structure VI is consistent with IR, NMR, mass spectral data and elemental composition (see experimental section). Like reduction of *trans*-dienoneiron tricarbonyl complexes [5], this reduction is highly stereospecific. The *ψ-endo* alcohol VI is the result of attack of borohydride ion at the

* The results are identical to those reported by Sorensen and Jablonski for ionization in FSO_3H. While they did not make it explicit, their published spectrum of IV (R = H) is in accord with the presence of a small amount of III (R = H) [1].



(V)

VI (ψ-endo)

least hindered face of the carbonyl group of V *. In contrast to all other dienol-iron tricarbonyl complexes studied, VI ionizes non-stereospecifically even at —60°C. Ionization of VI in $FSO_3H/SO_2/CDCl_3$ medium at —60°C typically produced a 1/3 *syn,anti* to *syn,syn* cation mixture.

Cation quenching

Quenching of the cations proceeded in highly stereospecific fashion under most conditions. Addition of —78°C solutions containing III (R = CH_3) and IV (R = CH_3) to excess methanol at —78° produced high yields of the diasteriomeric methyl ethers VII and VIII respectively (Scheme 1). Only traces of the minor product ether were revealed by TLC analysis of the total crude product. The structures of VII and VIII are consistent with observed IR, NMR and mass spec-

TABLE 1

QUENCHING STEREOCHEMISTRY FOR *syn,anti*-SUBSTITUTED DIENYLIRON TRICARBONYL CATIONS (IV, R = H) and IV, R = CH_3) [a]

R	Conditions	ψ-*exo* Product (%) [b]
CH_3	dry MeOH, —78°C	trace [c]
H	dry MeOH, —78°C	trace [c,d]
CH_3	sat. aq. $NaHCO_3$, 0°C	≤3
H	sat. aq. $NaHCO_3$, 0°C	≤3
CH_3	80% aq. acetone, sat. with $NaHCO_3$, 0°C	≤3
H	80% aq. acetone, sat. with $NaHCO_3$, 0°C	≤3
CH_3	80% aq. acetone, 0°C	≤3
H	80% aq. acetone, 0°C	≤3
CH_3	80% aq. acetone, 23°C	11, 13, 8 [e], 25 [e], 23 [e]
H	80% aq. acetone, 23°C	23
CH_3	80% aq. acetone, sat. with $NAHCO_3$, 23°C	16

[a] Cation solutions in $SO_2/CDCl_3/FSO_3H$ were produced by ionization at —60°C and contained >5% *syn, syn*-cation. [b] Determined by liquid chromatography using a 10 μ silica column with acetonitrile/hexane as eluent. A UV detector operating at 254 nm was employed, and we assumed that ϵ_{254} was equal for each pair of diasteriomers. [c] TLC analysis. [d] TLC scale experiment only. Components with R_f values similar to those of VII and VIII were assumed to have analogous structures. [e] NMR analysis.

* V Represents the most stable conformation with oxygen, not methyl, in the more crowded environment, cf. ref. 6.

tral properties. Cations III (R = CH_3) and IV (R = CH_3) were regenerated stereospecifically by treatment of VII and VIII respectively with FSO_3H at —60°C (Scheme 1).

The *syn,anti* cations IV (R = H) and IV (R = CH_3) were quenched under a variety of conditions, and results are displayed in Table 1. Only at the highest temperature does considerable leakage to *ψ-exo* product occur. At 23°C results were not reproducible, but the leakage to *ψ-exo* product always exceeded that observed at 0 and —78°C. A control experiment showed that formation of *ψ-exo* alcohol under these conditions is not the consequence of acid-catalyzed isomerization of *ψ-endo* alcohol. Our previous report that the tricarbonyl(*syn,anti*-5-methyl-3,5-heptadien-2-yl)iron cation is quenched in saturated bicarbonate to give a *ψ-exo* alcohol [2] is inconsistent with these data. The new data are very clear cut and much more complete, thus the earlier report is probably incorrect.

Configurational stability of syn, anti cations

While decomposition at temperatures over —40°C prevented a study of IV (R = H), IV (R = CH_3) exhibited exceptional configurational stability in FSO_3H. After 0.5 h at 40°C and an additional 3.5 h at 25°C, no isomerization could be detected by NMR analysis. Analysis after an additional 16 h period at 25°C revealed some conversion (≤10%) of the *syn,anti* isomer to the *syn,syn* isomer. At a temperature of 58°C, considerable isomerization of *syn,anti* to *syn,syn* occurs over a 0.5 h period.

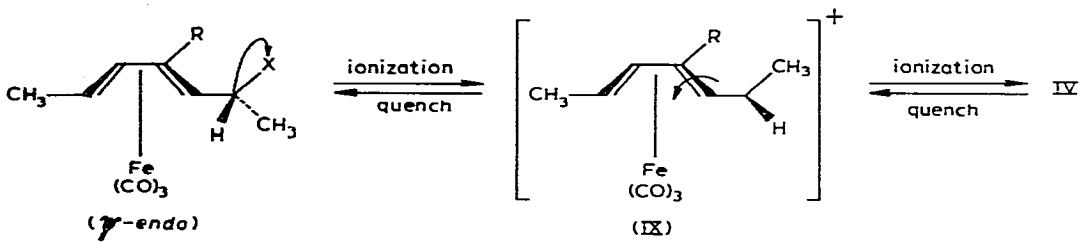
Cation IV (R = CH_3) exhibited a similar configurational stability in concentrated sulfuric acid. Isomerization was allowed to proceed in D_2SO_4 at room temperature for a period of one week (ca. 3 half lives). At the end of this time, NMR analyses revealed no deuterium incorporation in the resulting III (R = CH_3). The effect of an added base and nucleophile, bisulfate ion, was studied by establishing a first order rate for a given sample in sulfuric acid and then adding $NaHSO_4/H_2SO_4$ solution to bring about a known change in the bisulfate ion concentration. The rate of isomerization was independent of bisulfate concentration over the range 1.07—2.12 *M*

Discussion

The relative configuration of the *ψ-exo* diasteriomers produced by aqueous quenching of *syn,syn*-dienyliron tricarbonyl cations was originally proposed by Mahler and Pettit [3a] and was further supported by conformatical analysis and data of Clinton and Lillya [6]. Although questioned by Foreman [7] the original proposal has been vindicated recently by X-ray crystallography [8]. Thus, our results can be discussed in terms of absolutely reliable relative configurations.

At —60 to —65°C ionization of *trans*-dienoliron tricarbonyl complexes is nearly 100% stereospecific. The quenching experiments limit the sum of stereochemical leakage for ionization and subsequent quenching to less than 3%. *ψ-exo*-dienol complexes produce *syn*-substituted dienyliron tricarbonyl cations while *ψ-endo*-dienol complexes produce *anti*-substituted cations (Scheme 1). At 0°C ionization of *ψ-endo*-dienols proceeds by the above stereochemical pathways stereoselectively but is accompanied by up to ca. 33% leakage. Data on solvoly-

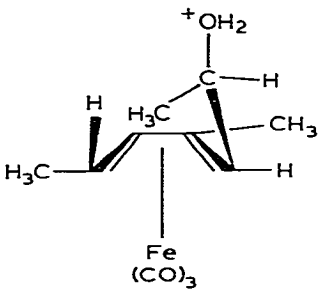
sis in 80% aqueous acetone show that leaving groups depart preferentially *exo* to iron to give *trans*-dienyliron tricarbonyl cation intermediates (e.g. IX) [5,9]. Stereospecific formation of *cis* cations can be understood as a consequence of *trans* to *cis* isomerization about the C(3)—C(4) bond with retention of configuration about the C(2)—C(3) bond (Scheme 2) [3a].



SCHEME 2. Stereospecific ionization and quenching.

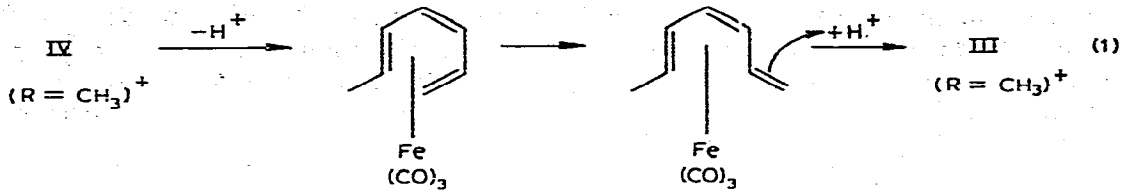
Stereospecific ionization of II (R = CH_3) and its derivatives must proceed via a transition state to a product, IX (R = CH_3) which are both destabilized by severe 1,3-methyl—methyl repulsions. The 3,5-dinitrobenzoate ester of II (R = CH_3) solvolyzes more slowly and less stereospecifically than any other dienyl dinitrobenzoate $Fe(CO)_3$ complex we have investigated [5]. It is remarkable then that II (R = CH_3) and II (R = H) which produces a relatively unstrained cation, IX (R = H) on stereospecific ionization behave identically within our limits of reproducibility. This suggests that leakage in the strong acid experiments involve not the *trans* cation IX but the *cis* cation IV in which the presence of a methyl group at C(4) should make no difference.

The *cis*-dienol complex VI ionizes non-stereospecifically even at —60°C. In this case it seems likely that non-bonded repulsions involving the α-methyl (C(1)) raise the energy of the transition state for *exo* ionization (VI′) sufficiently so that *endo* ionization, which is less favorable electronically but more favorable sterically, can compete.

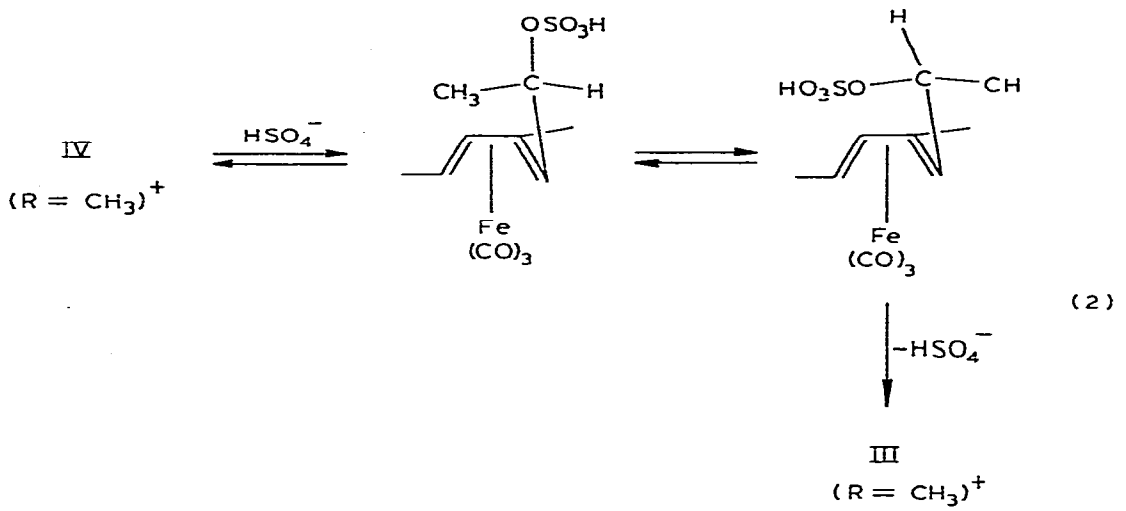


(VI′)

Our observations make it clear that anti substituted cations (e.g., IV (R = CH_3)) can be configurationally stable for long periods at room temperature in strong acids. Several initially attractive mechanisms for the slow *syn,anti* → *syn,syn* isomerization in sulfuric acid are eliminated by our data. Isomerization via an intermediate triene complex (eq. 1) is inconsistent with the lack of deturium incorporation and the independence of rate on bisulfate (base) concentration.



Exo [10] capture of IV (R = CH_3) at C(2) by bisulfate would produce the bisulfate ester of *cis*-dienol complex VI. Subsequent non-stereospecific ionization of this ester (as demonstrated for the alcohol) would provide an isomerization pathway (eq. 2). This mechanism is eliminated by independence of the isomerization of bisulfate concentration.



Elimination of these two mechanisms leaves a direct pathway involving rotation about the C(2)—C(3) bond to relieve steric strain as a possibility. If it occurs, this process is obviously too slow to account for the rapid stereochemical leakage which occurs when *syn,syn* cations are generated from *ψ-endo*-dienoliron tricarbonyl complexes in carboxylic anhydride/HBF_4 or $HClO_4$ mixtures [3].

Reactions of *cis*-dienyliron tricarbonyl cations with oxygen nucleophiles are highly stereospecific at temperatures up to 0°C. Only at 23°C did large amounts of non-stereospecific quenching occur. Products are in all cases complexes of *trans* not *cis* dienols. In contrast, quenching with amines gives either *cis*- or *trans*-dienylamine complexes, with high amine basicity favoring *cis* products [11]. *cis*-Dienol complexes are not formed reversibly during quench of the *syn,anti* cations IV (R = CH_3 or H). *Exo* attack [10] of water would produce a *cis*-dienol (e.g., VI) which would reionize non-stereospecifically (see above). Our data do not rule out reversible nucleophilic attack at C(3), C(4) or C(5), however. Indeed analogous attack of some cycloheptadienyliron cations by cyanide and borohydride ions has been documented [12].

The closely similar behavior of the cations IV (R = H) and IV (R = CH_3) on quenching is significant considering the expected differences between their corresponding *trans* isomers (IX) (see above). This and the similar stereochemistry

of ionization exhibited by *ψ-endo* alcohols II (R = H) and II (R = CH_3) stand in sharp contrast to the very different behavior observed when dinitrobenzoate esters of these alcohols solvolyzed in 80% aq. acetone at 25—45°C [5,9].

Experimental

Ionization and quenching experiments

Ionization in $CDCl_3/SO_2/FSO_3H$ mixtures were performed by a modification of Brookharts method [13] as described previously [4]. Ionization in $CDCl_3/FSO_3H$ was accomplished by addition of a freeze-pump-thaw degassed chloroform solution of the substrate to a chilled degassed sample of FSO_3H. After a short pause to allow the full sample to reach the desired temperature, the layers were mixed with a thin glass rod. All operations were carried out under nitrogen. Quenching was by pouring cold (ca. —78°C) strong acid samples into an excess of the quenching reagent at the given temperature with vigorous stirring. After 5 min, organic products were extracted using methylene chloride.

Tricarbonyl(syn,syn-4-methyl-3,5-heptadien-2-yl)iron fluorosulfonate (III, R = CH_3) and tricarbonyl(syn,anti-4-methyl-3,5-heptadien-2-yl)iron fluorosulfonate (IV, R = CH_3)

These salts were generated in $CDCl_3/SO_2/FSO_3H$ solutions and identified using ^1H NMR spectroscopy: III (R = CH_3): τ (ppm) 4.47 (d, 2, J_{23} 12 Hz, H(3,5)), 7.08 (sextet, 2, H(2,6)), 7.39 (s, 3, C(4)—CH_3), 8.28 (d, 6, J_{12} 6 Hz, 1 and 7-CH_3).

IV (R = CH_3): τ (ppm) 4.42 (d, 1, J_{23} 9 Hz, H(3)), 4.44 (d, 1, J_{56} 12 Hz, H(5)), 6.04 (m, 1, H(2)), 6.77 (sextet, 1, H(6)), 7.36 (s, 3, C(4)—CH_3), 8.18 (d, 3, J_{67} 6 Hz, 7-CH_3), 8.83 (d, 3, J_{12} 7 Hz, 1-CH_3).

ψ-exo-Tricarbonyl(trans,trans-2-methoxy-4-methyl-3,5-heptadiene)iron (VII)

A sample of III (R = CH_3) perchlorate was prepared by treating I (R = CH_3) with perchloric acid in acetic anhydride. Freshly prepared perchlorate salt (166 mg, 0.48 mmol) was added to 50 ml dry methanol and stirred at room temperature under nitrogen for two hours. The yellow solution was poured into 100 ml water and extracted with methylene chloride. The combined organic extracts were washed four times with 200-ml portions of water and dried over magnesium sulfate. Filtration and solvent removal under reduced pressure gave VII (171 mg, 83%) as a yellow oil which contained a trace of the *ψ-exo*-alcohol VI by TLC. The oil was purified by dry column chromatography (silica gel). IR (film): 2840, 2060, 1965, 1085 cm^{-1}; NMR ($CDCl_3$) τ (ppm) 5.08 (d, 2, J_{56} 8 Hz, H(5)), 6.73 (d, of q, 1, J_{12} 6 Hz, J_{23} 10 Hz, H(2)), 6.77 (s, 3, O$\underline{CH_3}$), 7.89 (s, 3, 4-$C\underline{H_3}$), 8.65 (d, 3, J_{67} 5.5 Hz, 7-CH_3), 8.75 (d, 3, J_{12} 6 Hz, 1-$C\underline{H_3}$), 9.0 (d of q, 1, J_{67} 5.5 Hz, J_{56} 8 Hz, H(6)), 9.32 (d, 1, J_{32} 10 Hz, H(3)). Mass spectrum (80 eV): *m/e* 280, 252, 224, 196, 164, 149.

ψ-endo-Tricarbonyl(trans,trans-2-methoxy-4-methyl-3,5-heptadiene)iron (VIII)

To a —78°C solution of IV (R = CH_3) prepared in a Schlenk tube under nitrogen in $CDCl_3/SO_2/FSO_3H$ from II (R = CH_3) (552 mg, 2.1 mmol) was added 5 ml of —78°C anhydrous methanol. The contents of the Schlenk tube were

then poured rapidly into 100 ml of cold (—78°C) stirring methanol; the solution was allowed to warm to room temperature, and was poured into saturated aqueous sodium bicarbonate. The solution was extracted with methylene chloride, the extracts washed with water, and dried ($MgSO_4$). Evaporation of solvent under reduced pressure left 527 mg (91%) of a yellow oil which contained a trace of the *ψ-endo* alcohol. The oil was purified by dry column chromatography (silica gel/benzene). The large yellow band gave 480 mg (83%) of a yellow oil that was pure according to TLC. The oil was crystallized by dissolving in a minimum volume of pentane and cooling to —78°C. The yellow crystals were collected at room temperature. An analytical sample was prepared by sublimation at 32—37°C (0.001 mmHg), m.p. 50—50.5°C, IR (film) 2840, 2060, 1965, 1105 cm^{-1}; NMR ($CDCl_3$) τ (ppm) 5.13 (d, 1, J_{56} 8 Hz, H_5), 6.20 (s, 3, OCH_3), 6.9 (d of q, 1, J_{23} 8 Hz, J_{12} 5.5 Hz, H(2)), 7.91 (s, 3, 4-CH_3), 8.61 (d, 3, J_{67} 6 Hz, 7-CH_3), 8.81 (d, 3, J_{12} 5,5 Hz, 1-CH_3), 9.15 (m, 1, H(6)), 9.28 (d, 1, J_{23} 8 Hz, H(3)); mass spectrum (80 eV) 280, 252, 224, 196, 164. (Found: C, 51.67; H, 5.89; Fe, 20.46. $C_{12}H_{16}O_4Fe$ calcd.: C, 51.46; H, 5.76; Fe, 19.94%).

ψ-endo-Tricarbonyl(cis,trans-4-methyl-3,5-heptadien-2-ol)iron (VI)

The *cis*-dienone complex V was prepared by acylation of tricarbonyl(*trans*-2-methylpentadiene)iron according to the method of Graf [14]. *cis*-Dienone (VII) (2.10 g, 8 mmol) was dissolved in 200 ml dry methanol in a 1-liter round bottom flask equipped with a magnetic stirrer. The solution was cooled to 0°C with an ice bath and then $NaBH_4$ (1.20 g, 32 mmol) was added slowly in small portions to the stirred solution. After the addition was complete, the solution was allowed to warm to room temperature and stirred for 2.5 h. Then 400 ml of water was added, and the mixture was stirred an additional 30 min. TLC (silica gel, CH_2Cl_2) showed the presence of some unreacted V. The solution was extracted with CH_2Cl_2 and the organic extracts were washed with water and dried ($MgSO_4$). Removal of solvent left a red oil (2.0 g) which was dissolved in a minimum amount of CH_2Cl_2. VI was crystallized by adding ca. 20% n-pentane and cooling to —78°C. Collection by suction filtration gave 1.0 g (47%) of bright yellow crystals, m.p. 92.0—93.5°C.

Recrystallization from 4/1 CH_2Cl_2/pentane at —78°C gave yellow crystals, m.p. 93—93.5°C. An analytical sample was prepared by sublimation at 45—55°C (0.001 mmHg), IR (film) 2060, 1965, 1100 cm^{-1}; NMR ($CDCl_3$): τ (ppm) 4.82 (q, 1, J_{56} 9.5 Hz, J_{35} ~ 15 Hz, H(5)), 6.82 (m, 1, H(2)), 7.47 (q, 1, J_{23} 9.5 Hz, J_{35} ~ 1.5 Hz, H(3)), 7.88 (s, 3, C(4)—CH_3), ca. 7.8—8.2 (m, 1, H(6)), 8.21 (d, 1, J 4 Hz, OH), 8.58 (d, 3, J_{76} 6 Hz, 7-CH_3), 8.85 (d, 3, J_{12} 6 Hz, 1-CH_3). Dilution shifted the OH doublet from τ 8.21 to 8.50 ppm. Addition of 2 drops D_2O and shaking caused disappearance of the OH doublet and simplification of the H_2 multiplet at τ 6.82 ppm. Mass spectrum (80 eV): 238 (M — CO), 210, 182, 164. (Found: C, 49.48; H, 5.14; Fe, 21.24. $C_{11}H_{14}O_4Fe$ calcd.: C, 49.66; H, 5.30; Fe, 20.99%).

Isomerization of IV (R = CH_3) in sulfuric acid

ψ-endo-Dienol II (R = CH_3) (284 mg) was dissolved in 98% sulfuric acid at 0°C, and the solution was diluted to a final volume of 2.00 ml (dienyliron tricarbonyl concentration 0.534 M, bisulfate ion concentration 1.07 M). Five portions of

this solution, measuring 0.40 or 0.30 ml, were transferred to separate NMR tubes and sealed with plastic caps and Parafilm. The tubes were allowed to stand at room temperature (ca. 23°C), and periodic NMR analysis was used to establish a first order rate for each sample. One sample was left as a control while measured amounts of 3.17 *M* sodium bisulfite in 98% sulfuric acid were added to the other four tubes to give final bisulfate concentration of 1.77 or 2.12 *M*. Rates were monitored as before to 2 to 5 half lives. Rearrangement was clearly first order and in no sample was a change in rate greater that our estimated 6% experimental error detected upon an increase in bisulfate ion concentration.

Acknowledgment

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