nmr (CCl_4, 60 MHz) δ 1.9 (quintet, J = 7.5 Hz, 2 H), 2.8 (m, 4 H), 4.6 (quintet, J = 5 Hz, 2 H); ir (neat) 3.27 (sh), 3.34 (s), 3.38 (s), 3.41 (s), 3.52 (sh), 5.1 (s), 5.88 (w), 6.92 (m), 7.03 (m), 9.55 (m), 11.8 μ (s); m/e 80.0600 (calcd for C_6H_8, 80.0626).

Control Experiments. (a) A 50:50 mol % mixture of the tetradeuterio diene **8a** (8 μl) and perprotio diene **3** (7.6 μl) was pyrolyzed at 275° for 2 hr in a 100-ml carefully neutralized tube sealed at −78° under nitrogen at 120 mm. The mass spectrum of the recovered volatile pyrolysate in the region of m/e 75–85 was examined indicating that little, if any, m/e 82 material ($C_6H_6D_2$) was present.

(b) A threefold change in the pressure of diene **8a** was found to have no influence on the observed fraction of isomerization.

(c) Allenylcyclobutane (**13**) was pyrolyzed at 278° for 3.25 hr under the same condition described for the pyrolysis of diene **8a**. The recovered pyrolysate was analyzed on a capillary DBTCP column and by nmr indicating only unchanged starting material. At 315°, pyrolysis of **13** for 2.5 hr under the same condition gave 10% of a product whose retention time on a capillary DBTCP column was identical with that of diene **3**.

Pyrolysis of 14, 15, 16, 18, and 19. All starting materials and products were characterized previously.[1b,21] Pyrolyses were performed in a static reactor whose construction has been published.[29]

Each run utilized 3 μl of diene with 15–20% of distilled n-octane as a standard in a 200-ml well-conditioned reactor at the indicated temperatures. After the indicated lengths of time, the material was removed, collected from the vacuum line by condensing in a liquid nitrogen trap, and analyzed on a DBTCP capillary column. No loss of material for each run was found relative to the internal standard. The results are summarized in Table II.

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

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[29] J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971).

Tricarbonyl(*trans*-π-pentadienyl)iron Cations. Solvolysis Stereochemistry

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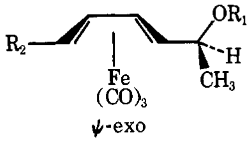
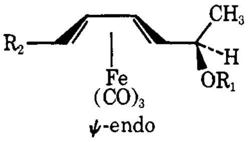
Abstract: The ψ-*exo*- and ψ-*endo*-tricarbonyl(*trans,trans*-4-methyl-3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron esters, **12b** and **11b**, respectively, were prepared and solvolyzed in 80% aqueous acetone. The ψ-exo/ψ-endo rate ratio was 2500 ± 1000. Sodium borohydride reduction of *trans,trans*-dienone tricarbonyliron complexes gives ψ-endo alcohols in a highly stereoselective fashion. These data along with nmr vicinal coupling constants in the complexed dienols support previous assignments of ψ-exo and ψ-endo configurations and demonstrate unambiguously that the leaving group departs exo to iron in the solvolyses. The *exo*- and *endo*-tricarbonyl(3-*trans*-β-styryl)-2-cyclohexen-1-yl 3,5-dinitrobenzoate)iron esters gave a low exo/endo solvolysis rate ratio of 6. This anomalous behavior is discussed in terms of steric and conformational effects.

Analysis of nonbonded interactions in syn-substituted tricarbonyl(diene)iron compounds based on many known crystal structures gave the conformational model shown in Figure 1.[3] Assumption that the larger groups will avoid the very crowded position (c) led to our conclusion that the most stable conformations of several diastereomeric dienol complexes and their esters were those shown here as **1** and **2**. The corresponding dinitrobenzoates underwent S$_N$1 type solvolysis with retention of configuration and gave ψ-exo/ψ-endo rate ratios of *ca.* 90. Based on this we concluded that the leaving group preferred to depart exo to (away from) iron.[4]



ψ-exo
1a, $R_2 = CH_3$
b, R_2 = Ph



ψ-endo
2a, $R_2 = CH_3$
b, R_2 = Ph

The conformational analysis and resulting assignments of relative configuration and conformational preference upon which our conclusions about solvolysis stereochemistry are based are entirely reasonable and self-consistent. Nevertheless, such a treatment of organotransition metal molecules has little precedent. Thus further tests of our assumptions and conclusions were in order. This paper describes such work.

Synthesis

Two cyclic dienol complexes were prepared in a fashion which allowed unambiguous assignment of their stereochemistry. Key reactions are shown in Scheme I. Owing to the large size of the tricarbonyliron group, borohydride reduction of the dienone complex **3** should proceed by addition of hydride exo to iron[4a,5] to give *endo* alcohol, **5a**. In fact, only one alcohol with a high R_f on silica gel thin layers, indicative of a sterically shielded hydroxy group,[4a,6,7] was produced. Complexation of **4a** was nonstereospecific, as expected, pro-

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[1] NDEA Fellow, 1965–1968.

[2] To whom correspondence regarding this work whould be addressed; Alfred P. Sloan Foundation Fellow, 1969–1971.

[3] N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3058 (1970).

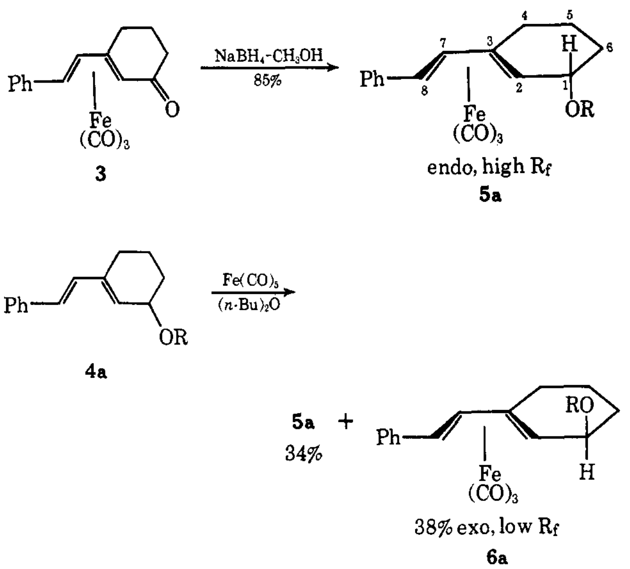
[4] (a) N. A. Clinton and C. P. Lillya, *ibid.*, **92**, 3065 (1970); (b) N. A. Clinton and C. P. Lillya, *Chem. Commun.*, 579 (1968).

[5] D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **72**, 5743 (1950); W. G. Dauben, G. J. Fonken, and D. S. Noyce, *ibid.*, **78**, 2579 (1956).

[6] D. H. R. Barton and G. A. Morrison, *Fortsch. Chem. Org. Naturst.*, **19**, 163 (1961).

[7] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

Scheme I. Synthesis of Cyclic Dienol Complexes

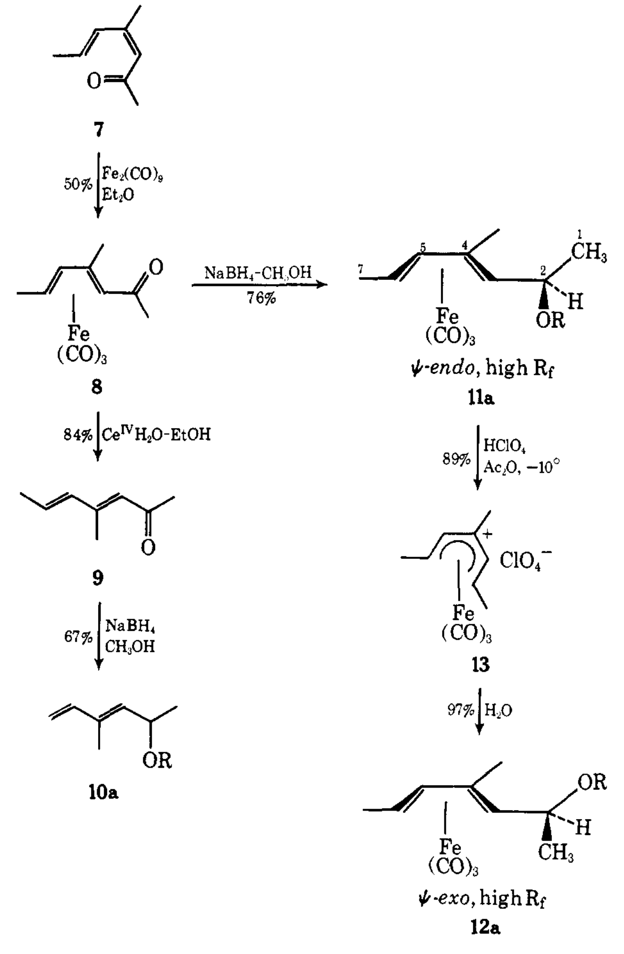


a, R = H
b, R = 3,5-dinitrobenzoyl

ducing the low R_f *exo*-dienol complex (**6a**) in addition to **5a**.

Synthesis of 4-methyl-3,5-heptadien-2-ol and its tricarbonyliron complexes is shown in Scheme II. Reduction of **8** gives ψ-endo (high R_f) alcohol (**11a**) contaminated by less than 1% of its ψ-exo (low R_f) diastereomer (**12a**).[8] Conversion of **11a** to **12a** *via* **13** exemplifies the hydrolysis of syn,syn substituted *cis*-π-pentadienyltricarbonyl-iron cations to give *ψ-exo*-dienol complexes exclusively.[4a,9–11] Direct complexation of dienol **10a** gave a mixture of **11a** and **12a**.

Scheme II. Synthesis of 4-Methyl-Substituted Dienols



a, R = H
b, R = 3,5-dinitrobenzoyl

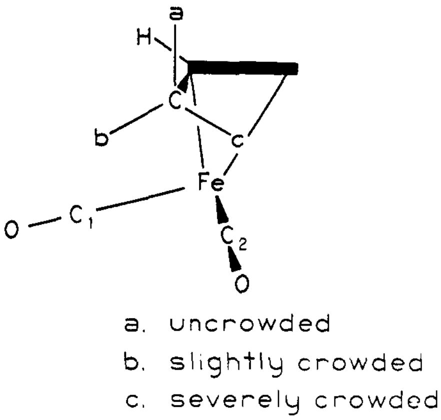


Figure 1. The staggered conformation of a syn-substituted tricarbonyl(diene)iron complex. The diene is viewed "edge on" looking from the syn substituent toward the diene. The third terminal $C \equiv O$ group is eclipsed by $C_2 \equiv O$.

Solvolysis Results

The 3,5-dinitrobenzoate esters were solvolyzed in 80% aqueous acetone under nitrogen, and the rates were followed titrimetrically. Rates were first order to at least two half-lives. Previous work has shown that the esters **1a** and **b** and **2a** and **b** (R_1 = 3,5-dinitrobenzoyl) solvolyze with alkyl oxygen fission under the same conditions.[4] Results are presented in Tables I and II.

Product studies showed that the complexed esters solvolyzed cleanly to give only complexed dienols with unrearranged carbon skeletons. Product ratios were estimated by tlc.[8] Major products were isolated and minor products were identified by tlc. All products were demonstrated to be stable under solvolysis and work-up conditions. Results are shown in Table III.

Discussion

We pointed out previously that the sodium borohydride reduction of tricarbonyliron complexes of acyclic dienones leads to ψ-endo alcohols in a highly stereoselective fashion, in accord with predictions based on the Karabatsos transition-state model[12] for carbonyl addition. This was one of several arguments used in the assignment of relative stereochemistry to ψ-exo and ψ-endo alcohols.[3] Our subsequent work has shown that the stereoselectivity is general. Amounts of ψ-endo alcohol[8] in the crude sodium borohydride reduction products of complexed dienones are **13**, R =

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(8) Based on analysis of the crude product by the tlc method described in ref 3.

(9) C. P. Lillya and R. A. Sahatjian, *J. Organometal. Chem.*, **25**, C67 (1970).

(10) In FSO_3H–SbF_5–SO_2 at −70° **11a** gives the syn,anti,cis cation exclusively which apparently equilibrates to the more stable **13** in $HClO_4$–Ac_2O at −10°; D. W. Garrett, unpublished work. See ref 9 and 11 for further examples.

(11) T. S. Sorensen and C. R. Jablonski, *J. Organometal. Chem.*, **25**, C62 (1970).

(12) G. J. Karabatsos, *J. Amer. Chem. Soc.*, **89**, 1367 (1967).

Table I. First-Order Solvolysis Rates in 80% Aqueous Acetone[a]

Compd	Temp, °C	k, min^{-1}	k_{rel}[d] at 30°
4b	15	$(5.15 \pm 0.07) \times 10^{-3}$	
	20	$(9.74 \pm 0.04) \times 10^{-3}$	
	25	$(1.91 \pm 0.03) \times 10^{-2}$	
	30	$3.47 \times 10^{-2\,b}$	56
6b	30	$3.70 \times 10^{-3\,b}$	6.0
	35	$(6.84 \pm 0.15) \times 10^{-3}$	
	40	$(1.41 \pm 0.06) \times 10^{-2}$	
	45	$(1.99 \pm 0.06) \times 10^{-2}$	
5b	30	$6.16 \times 10^{-4\,b}$	1.0
	35	$(1.13 \pm 0.04) \times 10^{-3}$	
	40	$(2.03 \pm 0.10) \times 10^{-3}$	
	45	$(3.62 \pm 0.06) \times 10^{-3}$	
12b	0	$(5.97 \pm 0.02) \times 10^{-3}$	
	5	$(1.21 \pm 0.02) \times 10^{-2}$	
	10	$(2.42 \times 0.06) \times 10^{-2}$	
	30	$2.90 \times 10^{-1\,b}$	2500
10b	15	$(2.89 \pm 0.01) \times 10^{-3}$	
	30	*Ca.* $2.2 \times 10^{-2\,b,c}$	*Ca.* 190
11b	30	$1.16 \times 10^{-4\,b}$	1.0
	40	$(4.57 \pm 0.03) \times 10^{-4}$	
	45	$(8.87 \pm 0.14) \times 10^{-4}$	
	50	$(1.66 \pm 0.01) \times 10^{-3}$	

[a] 80% acetone–20% water (v/v at 25°). [b] Extrapolated from measurements at other temperatures. [c] Extrapolated from 15° assuming $\Delta H^{\ddagger} = 22.7$ kcal/mol. [d] Cyclic (**4b**–**6b**) and 4-methyl (**10b**–**12b**) series are compared internally and not to each other.

Table II. Activation Parameters in 80% Aqueous Acetone at 30°

Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
4b	21.2 ± 1.2^{a}	4.9 ± 4.0^{a}
6b	22.7 ± 5.4	5.3 ± 18.0
5b	22.0 ± 2.4	-0.5 ± 8.0
12b	20.9 ± 1.7	8.1 ± 5.7
11b	25.2 ± 1.0	7.0 ± 3.4

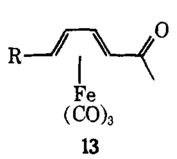
[a] Uncertainties are the maximum possible errors calculated by the method of R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961).

Table III. Solvolysis of Dienyl Dinitrobenzoate–$Fe(CO)_3$ Complexes in 80% Aqueous Acetone

Compound	Stereo-chemistry	k_{rel}, 30°	% product with retained configuration
12b	ψ-Exo	2500	>99
1a, R_1 = DNB[a]	ψ-Exo	540	>99
1b, R_1 = DNB	ψ-Exo	190	>99
6b	Exo	32	95
2a, R_1 = DNB	ψ-Endo	6.2	>99
5b	Endo	5.3	5
2b, R_1 = DNB	ψ-Endo	2.2	95
11b	ψ-Endo	1.0	55–60

[a] DNB = 3,5-dinitrobenzoyl.

CH_3, *ca.* 95%[3]; **13**, R = C_6H_5, 98%[3]; **14**, 95%[13]; and **8**, 99%. We have proposed that in tricarbonyliron complexes of secondary dienols and their derivatives, the carbinol hydrogen will always prefer to occupy the crowded position (c in Figure 1).[3] The resulting antiperiplanar relationship of the vicinal hydrogens H_2 and H_3 (see Table IV) predicts that the nmr coupling constants J_{23} will be large and independent of relative configuration. Table IV shows that this expectation has been realized.



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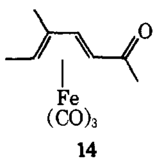

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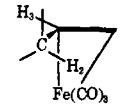
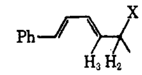
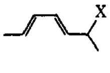
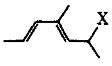
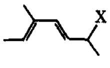
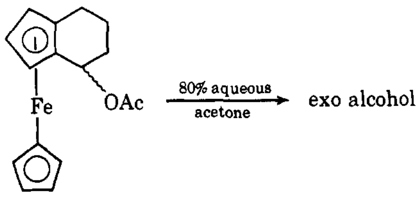
Table IV. Vicinal Coupling Constants, J_{23}, in $Fe(CO)_3$ Complexes of Dienols and Their Derivatives



Complex of	X	J_{23},[a] Hz ψ-exo	ψ-endo
	OH	8	*Ca.* 8
	ODNB	9	9
	OH	8	*Ca.* 7.5
	ODNB	8.5	8
	OCH_3	8	
	OAc	8.5	
	OH	9	8.5
	ODNB	10	10
	OH	8	8

[a] Uncertainty ±0.5 Hz.

While reduction stereochemistry and J_{23} values[14] are in accord with our conformational proposals, the solvolysis behavior of the cyclic esters was unexpected. The cyclic ferrocenyl acetates **15** solvolyze with an exo/endo rate ratio of 2500 and produce only exo alcohol.[7,15] In contrast to this and our earlier observations with dienyl ester–tricarbonyliron complexes,[4] both complexed cyclic esters solvolyzed more slowly than the uncomplexed ester (**4b**), and the exo/endo rate ratio is only 6.0. This unexpected behavior is probably caused primarily by steric interactions which make solvolysis of the exo ester (**6b**) abnormally slow. Examination of a molecular model[3] shows that **6b** should prefer the half-chair conformation in which the leaving group (ODNB) is *pseudoequatorial* (**16**). If the requirement for ODNB departure exo to iron is strict, solvolysis must be preceded by inversion of the "cyclohexene" ring and will proceed *via* transition state **17**. However, this transition state is destabilized relative to **16** by a severe steric interaction between the ring methylene and the terminal CO group which project toward the reader in drawing **17**. This is essentially the same in-



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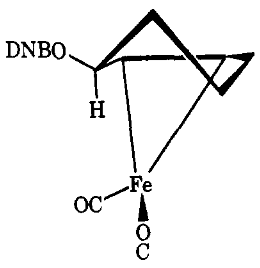
[13] R. A. Sahatjian, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1969.

[14] Values for the analogous coupling constants could not be extracted from nmr spectra of the cyclic alcohols and their derivatives.

[15] D. S. Trifan and R. Bacskai, *Tetrahedron Lett.*, No. 13, 1 (1960).



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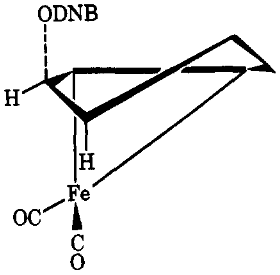

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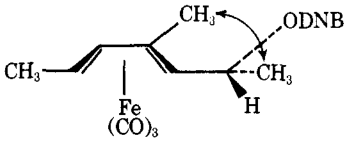
teraction which we propose retards solvolysis of the ψ-endo esters **2a** and **2b** (R = 3,5-dinitrobenzoyl).[4,16] The principle of microscopic reversibility virtually requires that a similar interaction be present in the transition state for exo capture of the intermediate cation by solvent. Thus, the 5% endo alcohol (**5a**) produced by solvolysis may be a consequence of abnormally slow exo capture rather than abnormally fast endo capture.

Detailed knowledge of the geometry of diene–tricarbonyliron compounds[3] allows some firm predictions about the behavior of the 4-methyl esters **11b** and **12b** relative to **1a** and **2a** (R = 3,5-dinitrobenzoyl). The steric effect of the 4-methyl group should make the already crowded position, c in Figure 1, more crowded, leaving the other positions (a and b) unaffected. The transition state for solvolysis of the ψ-endo isomer (**11b**) should be destabilized relative to that for **2a** (R = 3,5-dinitrobenzoyl) by the methyl–methyl interaction shown in **18**. The ψ-exo isomer (**12b**) should experience only a small rate enhancing inductive effect of the 4-methyl group. Thus, we expected an enhanced ψ-exo/ψ-endo rate ratio for **12b** and **11b**. In agreement with this, the ratio was 2500 ± 1000[17] *vs.* 90 for previous ψ-exo–ψ-endo pairs. Table III shows that **12b** is most reactive while **11b** is the least reactive of all the complexed dienyl dinitrobenzoates we have studied. This reactivity difference is reflected in the *ca.* 4 kcal/mol difference in $\Delta H^{\ddagger}$ for the two compounds (Table II). If either our assignments of relative configuration or our proposal that the leaving group departs exo to iron had been in error, addition of the 4-methyl group should have lowered the ψ-exo/ψ-endo rate ratio. Thus, these results constitute strong support for our original deductions.[18]



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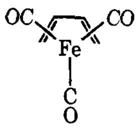
The collected data in Table III paint a consistent picture. All the ψ-exo esters solvolyze more rapidly than any ψ-endo ester. The low reactivity of the cyclic exo ester (**6b**) is caused by steric effects (see above). In the absence of complicating effects, the cyclic endo ester (**5b**) would be expected to be the least reactive of all these compounds. However, **5b** should suffer considerable steric destabilization. The conformer corresponding to formula **16** will be strained by interactions between the *endo*-dinitrobenzoate group and carbonyl ligands while that corresponding to formula **17** suffers from the ring methylene–carbonyl interaction discussed previously. Thus, the unexpected high solvolysis rate for **5b** could be caused by relief of steric strain in the transition state for ionization.[19,20] In agreement with this, equilibration of the two alcohols **5a** and **6a** in the presence of aluminum isopropoxide and *p*-benzoquinone showed that the exo isomer **6a** is the more stable. The acyclic esters exhibit a mechanistically suggestive trend of decreasing stereospecificity with decreasing solvolytic reactivity. Discussion will be reserved pending completion of a detailed study of stereochemical leakage in solvolysis of **11b**.

Clearly, virtually all of the chemistry discussed here is dependent on the geometry of tricarbonyl(diene)iron complexes in solution. For convenience we have used a "rigid" model (**19**) based on solid-state X-ray data. This is equivalent to assuming a significant energy barrier to rotation of the tricarbonyliron group relative to the diene. We have never suggested that the tricarbonyliron group cannot rotate, a process which would be unexceptional in light of many known dynamic changes undergone by organo-transition metal compounds.[21,22] The success of our analysis does not vindicate our model. The striking conformational effects we have observed would conceivably arise even if rotation of the tricarbonyliron group were completely free, because interactions with the diene residue alone could make position c (Figure 1) more crowded than position b. Our experiments would, however, seem to preclude a preferred geometry such as **20** which is significantly different from that in the solid state, **19**.



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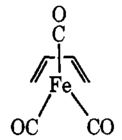

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Experimental Section

General. Infrared spectra were recorded on a Beckman IR-10 instrument and were calibrated with the 1601-cm⁻¹ polystyrene band. Nmr data were obtained on a Varian Associates A-60 instrument with tetramethylsilane (τ 10.00) as an internal standard. Nmr integration values have been rounded to the nearest whole number. Elemental analyses were performed by the Schwartzkopf

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[16] Owing to local C_s symmetry of the ferrocenyl moiety ($C_5H_5FeC_5H_4$), both cyclic (exo isomers) and acyclic secondary ferrocenyl esters will suffer almost identical steric interactions during exo departure of the carboxylate group. Thus solvolysis of *exo*-**15** is not expected to be abnormally slow.

[17] The uncertainty represents the maximum possible error of measurement and extrapolation. Thus the **12b**/**11b** rate ratio is significantly higher than 90.

[18] Our results also fit the case in which both of these deductions are in error, a possibility which we deem highly unlikely.

[19] *Cf.* A. Strietwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 92, and P. D. Bartlett and C. G. Swain, *J. Amer. Chem. Soc.*, 77, 2801 (1955).

[20] Richards and Hill (ref 7) have suggested that solvolysis of *endo*-**15** may be *retarded* by hindrance of acetate departure by the opposite ring and by an unfavorable electrostatic interaction between iron electrons and the charge on the developing acetate ion. This interpretation, which is just the opposite of what we propose for **5b**, is not demanded by Richards and Hill's data. For **5b** steric hindrance to 3,5-dinitrobenzoate departure does not appear likely when models are examined, and the data do strongly suggest that solvolysis of **5b** is accelerated by some factor which is absent in **2b**, R_1 = ODNB, and **11b**.

[21] *Cf.* F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

[22] In a distantly related case, time-averaged equivalence of ligands was observed for $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ at room temperature. Rotational motion was effectively frozen out at *ca.* −100°; see J. D. Warren and R. J. Clark, *Inorg. Chem.*, 9, 373 (1970), and references therein.

Microanalytical Laboratory, Woodside, N.Y., and by Mr. Charles Meade of the University of Massachusetts Analytical Services Laboratory. All tlc was performed on Camag silica gel which contained a fluorescent indicator. Visualization was accomplished using ultraviolet light, iodine vapor, and thiocyanate spray.[4a]

3-(*trans*-β-Styryl)-2-cyclohexenone. In a 1-l. three-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a pressure equalized addition funnel, 33.9 g (0.185 mol) of β-bromostyrene (92% trans by nmr) was converted to *trans*-β-styrylmagnesium bromide by the method of Seyferth, *et al.*[23] The resulting tetrahydrofuran solution was cooled to −5° and stirred while 3-isobutoxy-2-cyclohexenone[24] (24.4 g, 0.16 mol) in 200 ml of dry tetrahydrofuran was added over a period of 30 min. After the solution was stirred for 1 hr at 0° and subsequently allowed to warm to room temperature, 300 ml of a 10% hydrochloric acid solution was added. The mixture was extracted with ethyl ether. The organic layer was washed successively with 5% aqueous sodium thiosulfate, 5% aqueous sodium carbonate, 5% aqueous sodium hydroxide, and water, and then was dried ($MgSO_4$). The tacky, dirty-yellow solid obtained from reduced pressure evaporation of the solvent was dissolved in warm methanol, cooled (15°), and filtered to remove traces of *trans,trans*-1,4-diphenyl-1-3,-butadiene as a light yellow, flaky solid (4–5%): mp 150–151.5° (lit.[23,25] mp 147–149° and 150.5°). The infrared spectrum was identical with the literature spectrum.[26] Further cooling (0°) of the filtrate caused more crystals to form. They were collected by filtration and recrystallization from methanol to give 18.1 g (57%) of product: mp 64.5–65°; ir (CCl_4) 1675, 1665 ($C{=}O$), and 962 cm^{-1} (*trans*-$CH{=}CH$); nmr (CCl_4) τ 2.65 (m, 5, $-C_6H_5$), 3.10 (s, 2, H_7 and H_8[27]), 4.03 (s, 1, H_2), 7.2–8.2 (m, 6, CH_2's).

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from benzene giving dark red needles: mp 249–250°.

Anal. Calcd for $C_{20}H_{18}N_4O_4$: C, 63.43; H, 4.79; N, 14.83. Found: C, 63.59; H, 4.84; N, 14.83.

3-(*trans*-β-Styryl)-2-cyclohexenol (4a). Sodium borohydride (7.57 g, 0.20 mol), dissolved in 20 ml of water, was slowly added in small portions to a cooled (0°), stirring solution of 3-(*trans*-β-styryl)-2-cyclohexenone (9.92 g, 0.05 mol) in 400 ml of methanol, and the mixture was allowed to warm to room temperature. After 3 hr of stirring, the mixture was poured into about 1600 ml of water causing a fine white precipitate to form. After 15 min, the precipitate was collected by filtration and dried, yielding 9.4 g (94%) of crude alcohol. Recrystallization from hot Skellysolve B gave 8.5 g (85%) of **4a** as a white powder: mp 107–108°; ir (CCl_4) 3607 (free, CH), 3350 (broad, bonded, OH), 959 cm^{-1} (*trans*-$CH{=}CH$); nmr ($CDCl_3$) τ 2.73 (m, 5, C_6H_5), 3.3 and 3.55 (AB quartet, 2, J_{78} = 17 Hz, H_7 and H_8), 4.20 (d, 1, J_{12} = 3 Hz, H_2), 5.73 (s, broad, 1, H_1), 7.55–8.70 (m, 7, -OH and -CH_2's).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.96; H, 8.15.

3-(*trans*-β-Styryl)-2-cyclohexen-1-yl 3,5-Dinitrobenzoate (4b). Alcohol **4a** was treated with a 4–5 molar excess of bis(3,5-dinitrobenzoic) anhydride in dry pyridine for 30 min at room temperature. The pyridine solution was taken up in benzene and washed successively with 5% aqueous sodium carbonate, 10% hydrochloric acid, 5% aqueous sodium carbonate, and water. Drying (1:1 $MgSO_4$–$CaCl_2$) and evaporation of the benzene layer under reduced pressure left a tacky yellow solid. The crude product was purified by dissolving it in a minimum amount of methylene chloride and subsequently adding Skellysolve F to precipitate **4b** as 1.36 g (87%) of light yellow granules: mp 100° dec; ir (KBr) 3093 (Ar–H), 1725 (ester $C{=}O$), 1532, 1334 (NO_2), and 965 cm^{-1} (*trans*-$CH{=}CH$); nmr ($CDCl_3$) τ 0.91 (s, 3, dinitrobenzoate Ar-H), 2.72 (m, 5, C_6H_5), 3.35 (s, 2, H_7, H_8), 3.83–4.50 (m, 2, H_1, H_2), 7.33–8.42 (m, 6, CH_2's).

Anal. Calcd for $C_{21}H_{18}N_2O_6$: C, 63.96; H, 4.60; N, 7.10. Found: C, 63.89; H, 4.49; N, 7.22.

Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexenone)iron (3). 3-(*trans*-β-Styryl)-2-cyclohexenone (3.96 g, 0.02 mol), 250 ml of di-*n*-butyl ether (freshly distilled over calcium hydride), and several crystals of hydroquinone were mixed in a 500-ml flask equipped with a reflux condenser and protected with a nitrogen atmosphere. Iron pentacarbonyl (7.29 g, 0.037 mol; 5 ml), freshly distilled under nitrogen, was added, and the mixture was heated at reflux for 14.5 hr. The mixture was cooled and filtered several times through Filter Cel, and the solvent was removed under reduced pressure leaving orange crystals which, on recrystallization from Skellysolve C, gave 4.13 g (61%) of **3** as bright orange crystals: mp 162–163°; ir (CCl_4) 2058, 2000, 1980 ($C{\equiv}O$), and 1681 cm^{-1} ($C{=}O$); nmr ($CDCl_3$) τ 2.63 (s, 5, C_6H_5), 3.99 (d, 1, $J_{7,8}$ = 10 Hz, H_7), 7.09 (m, *ca.* 2, H_2, H_8), 7.36–8.18 (m, *ca.* 6, CH_2's).

Anal. Calcd for $C_{17}H_{14}FeO_4$: C, 60.38; H, 4.17; Fe, 16.52. Found: C, 60.34; H, 4.02; Fe, 16.52.

***endo*-Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexenol)iron (5a).** Sodium borohydride (1.15 g, 0.04 mol) dissolved in 30 ml of water was slowly added in small portions to a cooled (0°), stirring solution of **3** (3.38 g, 0.01 mol) in 350 ml of methanol, and the mixture was allowed to warm to room temperature. After 3 hr of stirring, the mixture was poured into about 900 ml of water causing a fine, light yellow precipitate to form. After 15 min the precipitate was collected by filtration and dried, yielding 3.23 g (95%) of crude reaction product. Tlc analysis showed none of the exo isomer alcohol present. Recrystallization from Skellysolve C gave 2.78 g (82%) of **5a** as a yellow powder: mp 114–115.5°; ir (CCl_4) 3615 (free, OH), 3460 (broad, bonded, OH), 2045, 1984, and 1967 cm^{-1} ($C{\equiv}O$); nmr ($CDCl_3$) τ 2.77 (s, 5, C_6H_5), 4.25 (d, 1, $J_{7,8}$ = 8.5 Hz, H_7), 5.70 (s, broad, 1, H_1), 7.14 (m, 2, H_2, H_8), 7.8–8.8 (m, 7, O*H* and -C*H*$_2$'s).

Anal. Calcd for $C_{17}H_{16}FeO_4$: C, 60.03; H, 4.74; Fe, 16.42. Found: C, 60.07; H, 4.92; Fe, 16.37.

***endo*-Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexen-1-yl 3,5-dinitro benzoate)iron (5b).** Ester **5b** was prepared from alcohol **5a** in the same way as **4b** (see above) except that the acylation reaction was allowed to run overnight. The product was isolated in 90% yield as fine orange-yellow granules: dec mp >90°; ir (KBr) 3126 (dinitrobenzoyl Ar–H), 2030, 1977, 1954 ($C{\equiv}O$), 1723 (ester $C{=}O$), 1545 and 1342 cm^{-1} ($—NO_2$); nmr ($CDCl_3$) τ 0.72 (s, 3, dinitrobenzoyl Ar–*H*), 2.77 (s, 5, $-C_6H_5$), 4.2 (m, 2, H_1, H_7), 7.0 (broad, 2, H_2H_8), 7.5–8.2 (m, 6, -C*H*$_2$'s).

Anal. Calcd for $C_{24}H_{18}FeN_2O_9$: C, 53.96; H, 3.40; Fe, 10.45; N, 5.24. Found: C, 54.05; H, 3.40; Fe, 10.5; N, 5.43.

***exo*-Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexenol)iron (6a).** 3-(*trans*-β-Styryl)-2-cyclohexenol (4.0 g, 0.02 mol), diiron enneacarbonyl[28] (21.8 g, 0.06 mol), and 200 ml of dry ethyl ether were added to a 500-ml, three-necked, round-bottomed flask equipped with a stirrer, reflux condenser, and rubber septum, and protected by a nitrogen atmosphere. The mixture was heated at reflux, and the disappearance of the uncomplexed alcohol was monitored by tlc (small amounts of reaction mixture were withdrawn by needle and syringe through the rubber septum). After 2 hr of refluxing (tlc analysis indicated the disappearance of 3-styrylcyclohex-2-enol and formation of three new compounds), the mixture was allowed to cool and was filtered. Evaporation of the solvent under reduced pressure left a dark green oil which was dissolved in methylene chloride and chromatographed on Ventron 507C-1 neutral alumina. Elution with methylene chloride gave first a small amount of a dark green liquid which was not characterized further. The second band gave a yellow solid which was purified by dissolving it first in a minimum amount of methylene chloride and then precipitating a solid by dropwise addition of Skellysolve F to give 2.33 g (34%) of the endo alcohol (**5a**). Purification in the above manner of the yellow solid obtained from the third band yielded 2.55 g (37%) of **6a** as yellow needles: mp 128–130°; ir (CCl_4) 3630 (free, OH), 3440 (broad, bonded, OH), 2040, 1985, and 1965 cm^{-1} ($C{\equiv}O$); nmr ($CDCl_3$) τ 2.8 (s, 5, $-C_6H_5$), 4.32 (d, 1, $J_{7,8}$ = 8.5 Hz, H_7), 5.90 (s, broad, 1, H_1), 7.22 (m, 2, H_2, H_8), 7.8–8.7 (m, 7, O*H* and -C*H*$_2$'s).

Anal. Calcd for $C_{17}H_{16}FeO_4$: C, 60.03; H, 4.74; Fe, 16.42. Found: C, 59.81; H, 4.64; Fe, 16.28.

***exo*-Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexen-1-yl 3,5-dinitrobenzoate)iron (6b).** Ester **6b** was prepared in the same fashion as **4b** (see above) except that the acylation reaction was allowed to run no longer than 15 min. The product was obtained in 87% yield as fine orange-yellow granules: dec mp >95°; ir (KBr) 3118 (dinitrobenzoyl Ar–H), 2037, 1979, 1950 ($C{\equiv}O$), 1728 (ester $C{=}O$), 1545 and 1340 cm^{-1} ($-NO_2$).

Anal. Calcd for $C_{24}H_{18}FeN_2O_9$: C, 53.96; H, 3.40; Fe, 10.45; N, 5.24. Found: C, 54.00; H, 3.33; Fe, 10.5; N, 5.25.

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(26) Sadtlers Standard Spectra, Vol. 3, The Sadtler Research Laboratories, Philadelphia, Pa., 1962, spectrum no. 3512.

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Tricarbonyl((*E*,*E*)[29]-4-methyl-3,5-heptadienone)iron (8). Diiron enneacarbonyl (48.5 g, 0.134 mol), (*Z*,*E*)-4-methyl-3,5-heptadien-2-one[30] (8.1 g, 0.055 mol), and 200 ml of dry ethyl ether were added to a 500-ml, round-bottomed flask equipped with a stirrer and reflux condenser. The mixture was heated at reflux for 17 hr, was allowed to cool, and was filtered several times through Filter Cel, and the solvent was removed under reduced pressure. The dark green oil obtained was chromatographed on Ventron 507C-1 neutral alumina. Elution with Skellysolve B, Skellysolve B–benzene (1:1), and benzene gave minor amounts of a dark green material and an unstable orange-yellow liquid which were not characterized further. Continued elution with benzene–methylene chloride (1:1) and finally methylene chloride gave the product which was obtained by evaporation as an amber oil: 8.47 g (49.4%); ir (film) 2043, 1990, 1975 ($C\equiv 0$), and 1678 cm^{-1} ($C=O$); nmr ($CDCl_3$) τ 4.95 (d, broad, 1, $J_{5,6} = 6$ Hz, H_5), 7.49 (s, 3, 4-CH_3), 7.89 (s, 3, -$COCH_3$), 8.53 [m, 4, analyzed as ~8.53 (d, 3, $J = 5.5$ Hz, 7-CH_3), ~8.53 (m, 1, H_6)], 9.12 (s, 1, H_3).

The brick red 2,4-dinitrophenylhydrazone derivative of **8**, recrystallized from a benzene–ethanol mixture, decomposed above 182°.

Anal. Calcd for $C_{17}H_{16}FeN_4O_7$: C, 45.97; H, 3.63; Fe, 12.58; N, 12.61. Found: C, 46.00; H, 3.52; Fe, 12.6; N, 12.50.

(*E*,*E*)-4-Methyl-3,5-heptadienone (9). Cerric ammonium nitrate (41.25 g, 75 mmol) was dissolved in 150 ml of distilled water, then 50 ml of ethanol was added. Tricarbonyl(4-methyl-3,5-heptadienone)iron (2.9 g, 11 mmol) was dissolved in 50 ml of ethanol, then slowly added over a period of 10 min to the stirring cerric ammonium nitrate solution. After stirring for 1 hr (tlc analysis indicated complete reaction), the reaction mixture was extracted several times with ethyl ether. The ethereal extracts were combined, washed with water, dried ($MgSO_4$), and filtered, and then the solvent was removed by reduced pressure evaporation to give 1.15 g (83.8%) of **9** as a yellow liquid. This material was shown to be identical with authentic *trans*,*trans*-4-methyl-3,5-heptadienone[31] by glpc and nmr and ir spectroscopy.

(*E*,*E*)-4-Methyl-3,5-heptadien-2-ol (10a). Sodium borohydride (1.89 g, 50 mmol) was slowly added in small portions to a cooled (0°), stirring solution of *trans*,*trans*-4-methyl-3,5-heptadienone (1.56 g, 12.5 mmol) in 100 ml of methanol, and the mixture was allowed to warm to room temperature. After 0.5 hr of stirring, 350 ml of water was added. The mixture was stirred for an additional 15 min and then extracted with ethyl ether. The organic layer was washed with water, dried ($MgSO_4$), and filtered. Reduced pressure evaporation of the solvent gave 1.05 g (66.8%) of pure **10a** (tlc analysis) as a light yellow oil: ir (film) 3350 (broad, OH) and 955 cm^{-1} (*trans*-$CH=CH$); nmr (CCl_4) τ 4.0 (d, 1, $J_{56} = 16$ Hz, H_5), 4.35 (2 q, some lines obscured, 1, $J_{56} = 16$ Hz and $J_{6,7} = 6$ Hz, H_6), 4.70 (d, broad, 1, $J_{2,3} = 7$ Hz and $J_{allylic} \sim 1$ Hz, H_3), 5.45 (2 q, 1, $J_{2,3} = 7$ Hz and $J_{1,2} = 6$ Hz, H_2), 5.90 (s, broad, 1, O*H*), 8.52 [m, 6, analyzed as 8.52 (d, 3, 7-CH_3), 8.52 (d, 3, 4-CH_3)], 8.83 (d, 3, $J_{1,2} = 6$ Hz, 1-CH_3). The alcohol was analyzed as its 3,5-dinitrobenzoate ester (see below).

(*E*,*E*)-4-Methyl-3,5-heptadien-2-yl 3,5-Dinitrobenzoate (10b). Ester **10b** was prepared in the same way as **4b** (see above). The crude oily product was purified by precipitation from methylene chloride at −78° by addition of Skellysolve F giving light yellow granules: mp 84–85°[32]; ir (film) 3105 (Ar–H), 1729 ($C=O$), 1545 and 1340 cm^{-1} (-NO_2); nmr ($CDCl_3$) τ 0.86 (s, 3, Ar-*H*), 3.75–4.83 (m, 4, H_2, H_3, H_5, and H_6), 8.0–9.3 (m, 9, 3 CH_3's).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.04; N, 8.75. Found: C, 56.20; H, 4.85; N, 8.72.

ψ-*endo*-Tricarbonyl((*E*,*E*)-4-methyl-3,5-heptadien-2-ol)iron (11a). Sodium borohydride (1.51 g, 0.04 mol) was added slowly in small portions to a cooled stirring solution of **8** (2.64 g, 0.01 mol) in 200 ml of methanol, and the mixture was allowed to warm to room temperature. After 2.5 hr of stirring, 400 ml of water was added. The mixture was stirred for an additional 15 min and then extracted with ethyl ether. The organic layer was washed with water, dried ($MgSO_4$), and filtered. Reduced pressure evaporation of the solvent gave 2.46 g (92.5%) of a dark yellow oil shown by tlc analysis to be **11a** which contained trace amounts of the ψ-exo isomer (<1%). Purification of the oil by dissolving it first in a minimum amount of methylene chloride, then adding Skellysolve F dropwise, gave 2.02 g (75.8%) of **11a** as bright yellow crystals: mp 64–65°; ir (CCl_4) 3622 (free, OH), 3490 (broad, bonded, OH), and 2035, 1998, 1983 cm^{-1} ($C\equiv O$); nmr ($CDCl_3$) τ 5.05 (d, 1, $J_{5,6} = 8$ Hz, H_5), 6.13 (2 q, 1, $J_{1,2} = 6$ Hz and $J_{2,3} = 8.5$ Hz, H_2), 7.88 (s, 3, 4-CH_3), 8.07 (s, 1, O*H*), 8.5–9.2 [m, 8, analyzed as 8.6 (d, 3, $J_{6,7} = 6$ Hz, 7-CH_3), 8.7 (d, 3, $J_{1,2} = 6$ Hz, 1-CH_3), *ca.* 8.8 (m, obscured, 1, H_6), 9.12 (d, 1, $J_{2,3} = 8.5$ Hz, H_3)].

Anal. Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30; Fe, 20.99. Found: C, 49.70; H, 5.28; Fe, 20.7.

ψ-*endo*-Tricarbonyl((*E*,*E*)-4-methyl-3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron (11b). Ester **11b** was prepared in the same way as **4b** (see above). Precipitation of the crude product from methylene chloride at 0° by addition of Skellysolve F gave a 75% yield of light yellow crystals: mp 108–109° dec; ir (film) 3108 (Ar–H), 2033, 1970 (broad) ($C\equiv O$), 1730 (ester $C=O$), 1544 and 1342 cm^{-1} (-NO_2); nmr ($CDCl_3$) τ 0.7 (s, 3, Ar–*H*), *ca.* 4.8 (m, 1, H_2), 4.91 (d, 1, $J_{5,6} = 8$ Hz, H_5), 7.70 (s, 3, 4-CH_3), 8.2–9.2 [m, 8, analyzed as 8.45 (d, 3, $J_{6,7} = 6$ Hz, 7-CH_3), 8.51 (d, 3, $J_{1,2} = 6$ Hz, 1-CH_3, *ca.* 8.6 (m, 1, H_6), 8.96 (d, 1, $J_{2,3} = 10$ Hz, H_3)].

Anal. Calcd for $C_{18}H_{16}FeN_2O_9$: C, 46.98; H, 3.51; Fe, 12.14; N, 6.09. Found: C, 46.75; H, 3.29; Fe, 11.9; N, 6.00

Tricarbonyl(*cis*-4-methyl-3,5-heptadien-2-yl)iron Perchlorate (13). A solution containing 60% perchloric acid (0.30 g, 1.8 mmol) in acetic anhydride, prepared by adding the acid dropwise to 5 ml of cooled (−10°) acetic anhydride, was added dropwise to ψ-endo alcohol (**11a**) (0.266 g, 1.0 mol) in 3 ml of acetic anhydride at −10°. When about half of the acid solution had been added, yellow crystals began to separate from the solution. After the mixture was stirred at −10° for 3 hr, ethyl ether was added which caused a large amount of yellow crystals to separate from the solution. The precipitate was collected by filtration, washed with ethyl ether, and dried yielding 0.309 g (88.7%) of **13** as light yellow crystals: mp 150° dec (sometimes explosively); ir (Nujol mull) 2097 and 2040 cm^{-1} ($C\equiv O$); nmr [$(CD_3)_2CO$] τ 3.77 (d, 2, $J_{2,3} = 12$ Hz, H_3, H_5), 6.42 (sextet, 2, $J_{1,2} = 6$ Hz and $J_{2,3} = 12$ Hz, H_2, H_6), 7.19 (s, 3, 4-CH_3), 8.19 (d, 6, $J_{1,2} = 6$ Hz, 1 and 7-CH_3's).

Anal. Calcd for $C_{11}H_{13}FeO_7Cl$: C, 37.92; H, 3.76; Cl, 10.18; O, 32.11. Found: C, 38.00; H, 3.82; Cl, 10.15; O, 32.08.

ψ-*exo*-Tricarbonyl((*E*,*E*)-4-methyl-3,5-heptadien-2-ol)iron (12a). Tricarbonyl(*cis*-4-methyl-3,5-heptadien-2-yl)iron perchlorate (1.44 g, 4.15 mmol) was added to 300 ml of distilled water and stirred at room temperature for 1 hr. The mixture was extracted with ethyl ether, and the organic layer was washed with water and dried ($MgSO_4$). Reduced pressure evaporation of the solvent gave 1.057 g (97%) of pure **12a** (tlc analysis) as a yellow oil which hardened on standing. Recrystallization of the tacky solid by first dissolving it in a minimum amount of methylene chloride and then precipitating a crystalline solid by dropwise addition of Skellysolve F gave 0.976 g (88%) of **12a**, as light yellow needles: mp 91–92°; ir (CCl_4) 3620 (free, OH), 3380 (broad, bonded, OH), 2033, 1997, and 1975 cm^{-1} ($C\equiv O$); nmr (CCl_4) τ 5.06 (d, 1, $J_{5,6} = 8$ Hz, H_5), 6.23 (m, 1, $J_{1,2} \sim 6$ Hz and $J_{2,3} \sim 9$ Hz, H_2), 7.78 (s, 3, 4-CH_3), 7.8 (s, broad, 1, OH), 8.6 [t, 6, analyzed as 8.6 (d, 3, $J_{6,7} = 5.5$ Hz, 7-CH_3), 8.67 (d, 3, $J_{1,2} = 6$ Hz, 1-CH_3)], *ca.* 9 (m, *ca.* 1 H_6), 9.34 (d, 1, $J_{2,3} = 9$ Hz, H_3).

Anal. Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30; O 24.05. Found: C, 49.65; H, 5.17; O, 24.00.

ψ-*exo*-Tricarbonyl((*E*,*E*)-4-methyl-3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron (12b). The preparation of **12b** was identical with that of **11b** (see above) in every detail. The product was obtained as yellow crystals in 75% yield: mp 111–112°; ir (film) 3108 (Ar–H), 2035, 1975 broad ($C\equiv O$), 1730 (ester $C=O$), 1548 and 1342 cm^{-1} (-NO_2); nmr ($CDCl_3$) τ 0.84 (s, 3, Ar–*H*), 4.5–6.0 (m, 2, H_2, H_5), 7.83 (s, 3, 4-CH_3), 8.2–8.8 (m, 7, analyzed as 8.40 (d, 3, 1-CH_3), 8.55 (s, broad, 4, H_6, 7-CH_3)], 9.03 (d, 1, $J_{2,3} = 10$ Hz, H_2).

Anal. Calcd for $C_{18}H_{16}FeN_2O_9$: C, 46.98; H, 3.51; Fe, 12.4; N, 6.09. Found: C, 47.10; H, 3.70; Fe, 12.1; N, 6.32.

Relative Stability of *exo*- and *endo*-Tricarbonyl(3-(*trans*-β-styryl)-2-cyclohexenol)iron (6a and 5a). A sample of each alcohol (10.0 mg) was added to aluminum isopropoxide (20.0 mg) and *p*-benzoquinone (7.0 mg) contained in a 7-in. pressure tube and the system was flushed with nitrogen. Dry ethyl ether (2 ml), degassed by bubbling nitrogen through it for 2 hr, was added and the tubes were sealed using standard bottle caps with Buna-N liners and heated at 105° for 23 hr. Tlc analysis of both crude reaction mixtures showed that some decomposition and isomerization of the alcohols had occurred and that the exo/endo ratio in both samples was *ca.*

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(32) This compound would not crystallize in subsequent preparations.

9:1. Each solution was washed successively with 5% hydrochloric acid, 5% aqueous sodium carbonate, and water, and then was dried ($MgSO_4$). The solvent was evaporated and the residues were analyzed by tlc.[3] Both iodine vapor and iodine–thiocyanate[4a] visualization showed that the two samples had identical 85:15 (±3) exo/endo ratios.

Kinetic Measurements. Experimental details of the kinetic measurements and the treatment of data were identical with those described previously[4a] with one exception. Initially we observed inconsistent and high infinity titers. The problem was traced to leaching of acidic substances from the red rubber serum caps used to seal our reaction flasks. Use of an all glass anaerobic sampling device[33] gave consistent infinity titers which were never outside the range 95–105% of theory.

Solvolysis Product Identification. Minor products were identified and the compositions of the crude solvolysis products were determined by the tlc method previously described.[3] Small samples of the dinitrobenzoate esters ($3 \times 10^{-3} M$ in 80% aqueous acetone) were heated in sealed tubes for at least 10 half-lives. After quenching and addition of 5% aqueous sodium carbonate to the solvolysis solution, the organic products were extracted into ethyl ether, dried ($MgSO_4$) for 10 min, and analyzed immediately. In cases where the similar R_f values of an uncomplexed dienol and the corresponding ψ-exo complexed dienol caused ambiguity, the iodine–thiocyanate visualization method which is specific for iron compounds[4a] was employed. Control experiments demonstrated that all product alcohols were stable under both solvolysis and work-up conditions.

Major products were isolated using a work-up identical with that described above followed by recrystallization and/or alumina chromatography as necessary. Isolated materials were shown to be identical with authentic samples. Results are listed below in the form: "ester solvolyzed → % yield product," **4b** → 50% **4a**, **5b** and/or **6b** → 45–50% **6a**, **10b** → 70% **10a**,[34] **11b** → 24% **11a** + 17% **12a**, **12b** → 71% **12a**.

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[33] See D. E. Kuhn, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1969, for details.

[34] Tlc showed traces of unsolvolyzed ester. Ir analysis suggests no major contamination by allylic isomers.

X-Ray Studies on Cyclopropenyl Cations.[1] II. Crystal and Molecular Structure of 1,2,3-Trisdimethylaminocyclopropenium Perchlorate

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Abstract: The crystal structure of 1,2,3-trisdimethylaminocyclopropenium perchlorate has been determined using 829 reflections recorded on a diffractometer. The crystals are orthorhombic with space group *Pnma*. The unit cell dimensions are $a = 14.232\ (4)$, $b = 10.304\ (3)$, and $c = 9.196\ (3)$ Å. The calculated and observed densities are consistent with the presence of four molecules in the unit cell. Therefore, the molecule is bisected by the crystallographic mirror plane reducing the asymmetric unit to half the molecule. The structure was determined by the heavy atom technique and refined by the method of full-matrix least squares to a final R value of 0.076. The cyclopropenium ring is symmetrical with a C–C bond length of 1.363 Å. This value is significantly shorter than the C–C bond in benzene and appears to be characteristic of cyclopropenyl cations. The average exocyclic C–N bond length is 1.333 Å which is considerably shorter than the normal C–N single bond and the cyclopropenyl C-C bond. The nitrogen atoms show small deviations from the plane of the cyclopropenium ring. Two of the nitrogen atoms are displaced on one side of the ring, while the other to the opposite side. All of the six methyl groups are displaced toward the same side of the cyclopropenium ring to a slightly larger extent than the nitrogen atoms. The planes of the symmetry related dimethylamino groups are twisted at angles of 20.8° to the plane of the cyclopropenium ring, while the plane of the third amino group makes a dihedral angle of 9.9°. The nonplanarity of the molecule as a whole is due to the hydrogen–hydrogen interactions between the methyl groups on adjacent nitrogen atoms.

The existence of carbonium ions as reaction intermediates has long been recognized, and there has been exhaustive studies in this area in the literature. Moreover, direct observations of carbonium ions in solution by nmr spectroscopy have been reported by a number of workers.[3] However, little X-ray structural studies on carbonium ions have been reported. Some of the carbonium ions whose structures have been determined by X-ray diffraction techniques are as follows: triphenylmethyl perchlorate,[4] *sym*-triphenylcyclopropenium perchlorate,[1] 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate,[5] methyloxocarbonium hexafluoroantimonate,[6] methyl-, ethyl-, and isopropyloxocarbonium hexachloroantimonate,[7] tetraanisyl-

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[1] For part I, see M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966); **85**, 3302 (1963).

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