Tricarbonyl(*trans*-π-pentadienyl)iron Cations. Solvolysis of Complexed Dienyl Dinitrobenzoates[1a] and Protonation of Complexed Dienones[1b]

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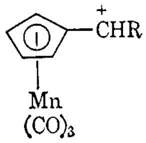
Abstract: Several dienyl 3,5-dinitrobenzoate esters and their tricarbonyliron complexes have been prepared and solvolyzed in 80% aqueous acetone. Solvolysis proceeds by an SN1, alkyl-oxygen fission mechanism with complete retention of configuration except in the case of **12b** which gives *ca.* 6% alcohol of inverted configuration. Relative solvolysis rates of diastereomeric pairs of secondary esters, **8b** and **9b**, **11b** and **12b**, show that the leaving group prefers to depart *exo* to iron. Estimated minimum rate factors for anchimeric assistance by the $Fe(CO)_3$ group range from 12 for **12b** to 8700 for **8b** though the actual values could be considerably larger. Product studies show that the intermediates in several of the solvolyses are tricarbonyl(*trans*-π-pentadienyl)iron cations (**7**) and not the *cis* isomers (**6**). The solvolysis data are consistent with direct nucleophilic participation by iron or iron–carbon hyperconjugation. Nmr data on protonated tricarbonyl(*trans,trans*-3,5-heptadien-2-one)iron (**34**) are difficult to interpret in terms of the latter mechanism, however. Results of a study of the isomerization of **34** to the *cis,trans* isomer **35** in sulfuric acid favor a mechanism involving nucleophilic attack of water at iron to catalyze the reaction.

Many carbonium ions are stabilized dramatically by π-bond formation to transition metal atoms. Examples of unusually stable organotransition metal cations have recently been summarized.[3] All known stable organotransition metal cations possess organic ligands with fully conjugated π-electron systems in which, at least conceivably, all carbons can be bonded directly to the metal atom. Presence of these structural features does not guaranty a highly stabilized cation. Cymmantrylcarbinyl cations (**1**), while they are more stable than the corresponding benzyl cations, appear to be much less stable than their ferrocenyl analogs.[4]



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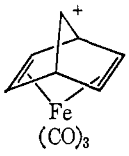

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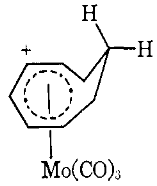
Absence of these structural features results in a less stable ion. Thus tricarbonyl(7-norbornadienyl)iron cation (**2**) is destabilized relative to 7-norbornyl cation because the requirements of iron carbon bonding prevent homoallylic delocalization of the charge at C_7.[3] Homoconjugation does occur in tricarbonyl(homotropylium)molybdenum cation (**3**).[5,6] Simple π-homoallylic structures (**4**), however, are now unknown. Thus tricarbonyl(norbornadiene)iron undergoes protonation at iron rather than at carbon which would give a complexed homoallylic cation,[7] and Friedel–Crafts acylation of tricarbonyl(diene)iron compounds occurs only at terminal diene carbons which suggests the absence of the homoallylic intermediate **5**.[8]



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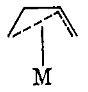

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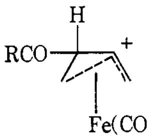

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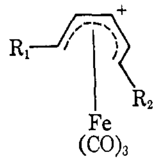
Stable tricarbonyl(π-pentadienyl)iron cations were first reported by Fischer and Fischer.[9] Mahler and Pettit showed that these isolable cations have the *cis* structure (**6**).[10] Attempts to prepare *trans* isomers (**7**) either gave no reaction or led to the more stable *cis* salts, and no firm evidence for or against existence of *trans* cations was found.[10]



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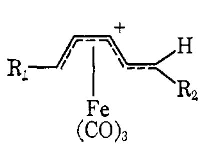

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As part of a continuing effort to elucidate the structural features associated with and the mechanisms responsible for stability in organotransition metal cations, we undertook a study of tricarbonyl(*trans*-π-pentadienyl)iron cations. These ions seem to

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[1] Part of this work has been the subject of preliminary communications. (a) N. A. Clinton and C. P. Lillya, *Chem. Commun.*, 579 (1968), and Abstract No. 190, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1–3, 1967. (b) Abstract No. 230, 1st Northeastern Regional Meeting of the American Chemical Society, Boston, Mass., Oct 13–15, 1968.

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

[3] D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, **90**, 2561 (1968).

[4] W. E. McEwen, J. A. Manning, and J. Kleinberg, *Tetrahedron Lett.*, 2195 (1964).

[5] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965).

[6] The possibility of homoconjugation in the tricarbonyl(bicyclo[3.2.1]octadienyl)iron cation has been pointed out; however, no clear evidence for it has been reported: T. N. Margulis, L. Schiff, and M. Rosenblum, *ibid.*, **87**, 3269 (1965).

[7] D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *ibid.*, **89**, 6387 (1967).

[8] R. E. Graf, unpublished work in this laboratory. An earlier report of 2-acylation of tricarbonyl(butadiene)iron (G. C. Ecke, U. S. Patent 3,149,135 (1964)) has been shown to be incorrect.

[9] E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).

[10] J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955 (1963).

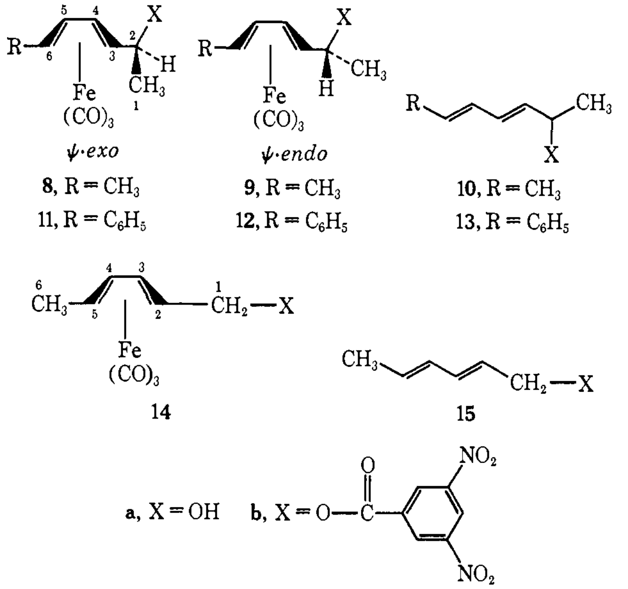

Figure 1. Structures of dienol derivatives (the numbering systems appear on structures 8-11 and 14).

possess all the structural features associated with stability. Furthermore, in a geometrical sense they are very closely related to the stable ferrocenyl carbinyl cations in which there has been so much recent interest.[11]

Solvolysis Studies

Results. The dienyl 3,5-dinitrobenzoate esters shown in Figure 1 were prepared by standard procedures which are described in the Experimental Section. Treatment of the complexed dienols[12] with 3,5-dinitrobenzoyl chloride in pyridine failed to give the desired esters cleanly; however, substitution of bis(3,5-dinitrobenzoic) anhydride for the acid chloride led to the complexed dienyl 3,5-dinitrobenzoates in satisfactory yields.

Solvolyses were carried out in 80% aqueous acetone (v/v), and the resulting kinetic data are presented in Tables I and II. The light-yellow solutions of the organoiron esters did become somewhat darker during the course of the solvolyses. However, oxidation which is so facile in the case of tricarbonyl(norbornadiene)iron compounds[3] was easily suppressed by use of deoxygenated solvents and anaerobic conditions. The solvolyses were initially first order with the first significant deviations usually coming near 2 half-lives. Rate data were always collected over the first half-life only. 3,5-Dinitrobenzoic acid is insufficiently dissociated in 80% aqueous acetone to allow accurate conductimetric rate measurements. Thus the liberated acid was titrated using standard alkali and bromothymol blue indicator.

Table I. Solvolysis Rates[a]

Compd	Temp, °C	k, min^{-1}
8b	7	$(2.57 \pm 0.05) \times 10^{-3}$
	14	$(8.0 \pm 0.05) \times 10^{-3}$
	20	$(1.56 \pm 0.05) \times 10^{-2}$
	30	6.3×10^{-2} [b]
	45	3.6×10^{-1} [b]
9b	30	$(7.2 \pm 0.3) \times 10^{-4}$
	45	$(4.53 \pm 0.1) \times 10^{-3}$
10b	30	$(1.02 \pm 0.1) \times 10^{-3}$
	45	$(6.58 \pm 0.5) \times 10^{-3}$
11b	7	$(9.25 \pm 1.5) \times 10^{-4}$
	20	$(5.89 \pm 0.1) \times 10^{-3}$
	25	$(1.16 \pm 0.2) \times 10^{-2}$
	30	2.2×10^{-2} [b]
12b	30	$(2.54 \pm 0.05) \times 10^{-4}$
	45	$(1.70 \pm 0.05) \times 10^{-3}$
13b	30	$(2.13 \pm 0.05) \times 10^{-3}$
	45	$(1.40 \pm 0.05) \times 10^{-2}$
14b	45	$(2.11 \pm 0.05) \times 10^{-3}$
15b	45	$(3.52 \pm 0.05) \times 10^{-4}$ [c]
	45	$(1.22 \pm 0.02) \times 10^{-4}$ [d]
	45	1.04×10^{-5} [e]
8-OAc	45	$(6.57 \pm 0.5) \times 10^{-4}$
Ferrocenyl-1-ethyl acetate	45	$(4.26 \pm 0.05) \times 10^{-2}$
	45	4.58×10^{-2} [f]

[a] The solvent is 80% acetone–20% water (v/v at 25°) unless otherwise noted. [b] Extrapolated from measurements at other temperatures. [c] In 50% aqueous acetone. [d] In 60% aqueous acetone. [e] Calculated using the mY equation (m = 0.743): E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948). [f] Extrapolated from data in E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

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

Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
8b	22.4 ± 1.3[a]	9.9 ± 4.2[a]
9b	22.8 ± 2.6	2.5 ± 8.4
10b	23.1 ± 3.3	4.3 ± 11.0
11b	22.7 ± 2.8	8.8 ± 9.1
12b	23.6 ± 1.3	3.1 ± 4.2
13b	23.4 ± 1.3	6.5 ± 4.2

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

Table III. Salt and Common Ion Effects

Compd	Temp, °C	Salt	k, min^{-1}
8b	7		$(2.57 \pm 0.1) \times 10^{-3}$
	7	0.0110 M $NaBF_4$	3.17×10^{-3}
	7	0.0113 M NaODNB[a]	$(1.35 \pm 0.22) \times 10^{-3}$
9b	45		$(4.53 \pm 0.1) \times 10^{-3}$
	45	0.0129 M NaODNB[a]	3.08×10^{-3}
10b	45		$(6.6 \pm 0.5) \times 10^{-3}$
	45	0.0133 M NaODNB[a]	5.72×10^{-3}

[a] ODNB = 3,5-dinitrobenzoate.

Salt and common ion effects for the three methyl-substituted secondary esters are listed in Table III. The neutral salt, sodium fluoroborate, increases the solvolysis rate of the ψ-*exo* ester (**8b**) while addition of sodium 3,5-dinitrobenzoate depressed the solvolysis rates of **8b** and **9b** and probably that of the uncomplexed ester (**10b**) as well. These observations are consistent with an SN1 mechanism for solvolysis.[13] The rate dependence on solvent polarity observed for the uncomplexed primary ester **15b** (m = 0.743) also supports an SN1-type mechanism. Since **15b** is the least reactive of the 3,5-dinitrobenzoate esters studied, it is not likely that alternative hydrolysis mechanisms can compete

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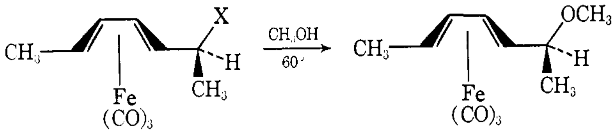
[11] (a) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967), and references therein. (b) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).

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

[13] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

effectively with the SN1 process for any of the others either. Alkyl-oxygen fission in the solvolysis of **8**-OAc and **8b** was demonstrated by methanolysis which gave the methyl ether **17**. The nmr spectrum of the red oily product was uniquely consistent with structure **17**. Thin layer chromatography (tlc) revealed the presence of only one isomer, and we have tentatively assigned *ψ-exo* stereochemistry to **17** in analogy with our results in aqueous acetone. Alcohol **8a** was shown to be stable under the methanolysis conditions proving that **17** is the initial solvolysis product.

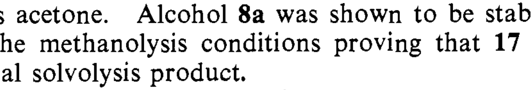


8-OAc, X = OCOCH$_3$
8b, X = ODNB
17

The solvolysis products of the uncomplexed esters (**10b**, **13b**, and **15b**) were examined using nmr and ir spectroscopy and tlc. Spectra and chromatograms of the crude products closely resembled those of the pure alcohols. Thus the amounts of allylic isomers and olefin formed are probably small. The relative areas under the nmr signals for olefinic and aliphatic hydrogens respectively ruled out cyclopentenols as major products. It seems reasonable that in aqueous acetone pentadienyl carbonium ions should be captured by the nucleophilic solvent before they can cyclize to cyclopentenyl ions as they do in highly acidic solvents where carbonium ion lifetimes are longer.[14]

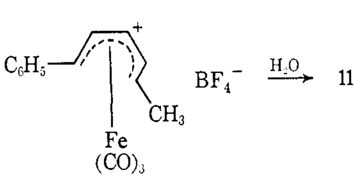
Examination of the crude solvolysis products from the complexed esters (**8b**, **9b**, **11b**, **12b**, and **14b**) by nmr and ir spectroscopy showed that the original carbon skeleton was retained in the product alcohols in every case. Formation of the complexed *cis*-π-pentadienyl cation **18** and subsequent hydrolysis gave rearranged alcohol **19**.[15] This alcohol was assigned *ψ-exo* stereochemistry because its R_f on silica gel thin layers was similar to those of the *ψ-exo* alcohols **8a** and **11a** and that of the primary alcohol **14a**.[12] Comparison of the crude solvolysis product from **14b** with **19** by tlc revealed no trace of the rearranged alcohol in the solvolysis products.[16] Hydrolysis of **20** appeared to give only the *ψ-exo* alcohol resulting from nucleophilic attack remote from the phenyl group.

14a



18
19

Since the *ψ-exo-ψ-endo* alcohol pairs have nearly identical nmr and ir spectra,[12] product stereochemistry was determined by characterization of isolated materials and by the tlc method previously described.[12]



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The solvolyses are exceptionally clean reactions. The only side products revealed by tlc are small amounts of uncomplexed alcohols which were not present when deoxygenated solvolysis solutions were analyzed directly. For the secondary esters of the methyl series, **8b** and **9b**, and the *ψ-exo* phenyl-substituted ester (**11b**) tlc revealed less than 1% alcohol of inverted configuration. The trace amounts of inverted alcohol present in each sample did not appear to exceed that present in the sample of alcohol used to prepare the dinitrobenzoate ester. Thus these reactions proceed with retention of configuration in a highly stereospecific manner.

Spectroscopic analysis and isolation showed the major product of solvolysis of the *ψ-endo*-phenyl-substituted ester (**12b**) to be the alcohol of retained configuration (**12a**). Tlc analysis of the crude product revealed the presence of a minor component with an R_f on silica gel which was identical with that of the *ψ-exo* alcohol **11a** and that of the uncomplexed alcohol **13a** which could have been formed by oxidation. This minor component was shown to be primarily an iron-containing compound by heating an iodine treated tlc plate at 100° to produce some ferric ion and subsequently spraying with aqueous ammonium thiocyanate to give a red spot. Comparison with standard mixtures of **11a** and **12a** both by simple iodine visualization[12] and by the thiocyanate method showed that the *ψ-exo* alcohol (**11a**) comprised between 5 and 7.5% of the solvolysis product.

Epimerization during the conversion of alcohol **12a** to its 3,5-dinitrobenzoate ester was eliminated as a source of **11a** in the solvolysis product by tlc analysis during the initial stages of solvolysis. Since the *ψ-exo* ester (**11b**) solvolyzes *ca.* 90 times faster than the *ψ-endo* isomer, the presence of *ψ-exo* ester impurity would cause the solvolysis product to be richer in *ψ-exo* alcohol during the early stages of solvolysis. No variation in the composition of the solvolysis product with time was found, however.

Discussion

Relative solvolysis rates and stereochemistry for the secondary esters are listed in Table IV. The *ψ-exo*/*ψ-endo* rate ratio is 87 in both the methyl and the

Table IV. Relative Rates and Stereochemistry for Solvolysis of Secondary 3,5-Dinitrobenzoates in 80% Aqueous Acetone at 30°

Compound			Retention of configuration,
Stereochem	Series	k_{rel}	%
ψ-exo	CH$_3$ (**8b**)	250	>99
ψ-exo	Ph (**11b**)	87	>99
Uncomplexed	Ph (**13b**)	8.4	
Uncomplexed	CH$_3$ (**10b**)	4.0	
ψ-endo	CH$_3$ (**9b**)	2.7	>99
ψ-endo	Ph (**12b**)	1.0	92.5–95

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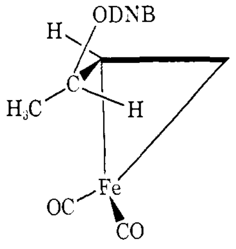
(14) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964); and N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Amer. Chem. Soc.*, 87, 2153 (1965).

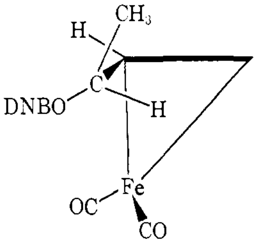
(15) J. E. Mahler, D. N. Gibson, and R. Pettit, *ibid.*, 85, 3959 (1963).

(16) Our experience with tlc of *ψ*-exo- and *ψ-endo*-dienol complexes makes us confident that the R_f of the *ψ-endo*-alcohol corresponding to **19** would have been much higher than that of the solvolysis product, **14a**. Since no second component was resolved, we conclude that it also is absent.

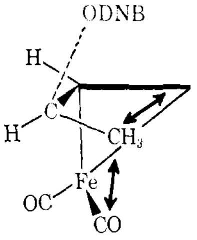
phenyl series. Owing to steric interactions the *ψ-exo* alcohols, **8a** and **11a**, prefer a conformation in which the hydroxy group is *exo* to iron while the *ψ-endo* alcohols, **9a** and **12a**, prefer a conformation in which hydroxy is *endo* with respect to iron.[12] Dinitrobenzoylation of the hydroxy oxygen should not change its effective size very much. The best $-\Delta G°_x$ values determined in cyclohexanes are OH (hydrogen donor solvents) 0.87, $OCOCH_3$ 0.60, and $OCOC_6H_4$-*p*-NO_2 0.98 kcal/mol.[17] Thus the preferred conformations of the 3,5-dinitrobenzoate esters should be **21** and **22** in which the diene is viewed edge-on looking down the C_2–C_3 bond. It is apparent that the leaving group prefers to depart *exo* to iron. The *ψ-endo* esters, in which the leaving group prefers to be *endo* to iron, solvolyze more slowly than their *ψ-exo* isomers in which the leaving group occupies the favorable *exo* position. The transition state for solvolysis of *ψ-endo* compounds is destabilized by interaction of the 1-methyl and the proximate terminal carbonyl as well as the diene residue (**23**).[12] *endo* departure of the leaving group in which solvolysis is slowed by "steric hindrance to ionization" (**24**) as proposed by Brown[18] for *endo*-2-norbornyl compounds is not consistent with the high degree of retention of configuration in these solvolyses.[19] Since the *ψ-exo* alcohols are significantly more stable than their *ψ-endo* isomers,[12] the high *ψ-exo*/*ψ-endo* rate ratios are not likely to be a consequence of ground-state energy differences between the dinitrobenzoate esters. A stereoelectronic preference caused by bonding changes involving iron during solvolysis is strongly implied.



21, *ψ-exo*



22, *ψ-endo*



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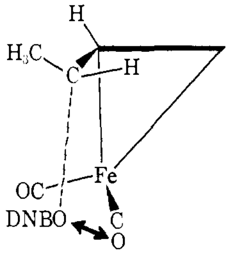

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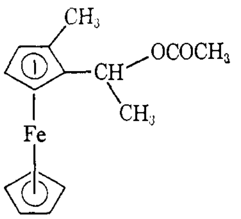
The high *ψ-exo*/*ψ-endo* rate ratios and high degree of retention of configuration make these solvolyses strikingly similar to those of ferrocenylcarbinyl compounds.[21,22] The *ψ-exo*/*ψ-endo* rate ratios observed in 80% aqueous acetone for acyclic ferrocenylcarbinyl compounds like **25** are about a factor of 7 smaller than those observed here.[21] Nucleophilic participation by neighboring iron[22,23] and hyperconjugation involving Fe–C bonds[24] have been proposed to account for the data on the ferrocenyl system.[25] These mechanisms are shown below for the dienyl esters.



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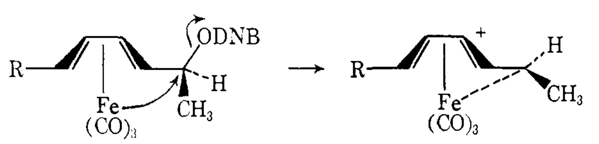
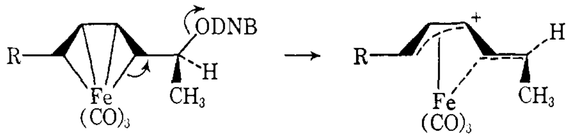
Iron participation



26 **27**

Hyperconjugation



28 **29**

The rate enhancement (anchimeric assistance[26]) due to participation of the $Fe(CO)_3$ group can be discussed in terms of Winstein's model of competing assisted ionization (k_Δ) and unassisted ionization (k_s).[27] Solvolysis stereochemistry can be used to estimate values of k_Δ/k_s. Unassisted S$_N$1 solvolyses proceed with a high degree of inversion.[28] Since the methyl compounds (**8b** and **9b**) and the *ψ-exo* phenyl compound **11b** solvolyze with >99% retention of configuration assisted solvolysis clearly proceeds with *ca.* 100% retention and these compounds must solvolyze almost exclusively by the assisted route. Thus, for these compounds k_Δ/k_s is at least 100. The *ψ-endo* phenyl compound (**12b**), however, solvolyzes with *ca.* 6% leakage to *ψ-exo* product. The *ψ-exo* product could arise *via* unassisted solvolysis or possibly *via* assisted ionization to give a "*ψ-endo*" ion (**30**, R = C_6H_5) which subsequently is converted to the "*ψ-exo*" ion (**31**) to the extent of 6%. The former mechanism is attractive because the relatively slow rate of assisted solvolysis of **12b** can be offered as an explanation for why only **12b** exhibits stereochemical leakage. There

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(17) J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 199.

(18) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 155.

(19) This path of ionization should lead eventually to the same intermediate ion derived from the *ψ-exo* compound and would require substantial inversion of configuration as is actually observed for *endo*-2-norbornyl compounds.[20]

(20) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2953 (1949).

(21) E. A. Hill and J. H. Richards, *ibid.*, 83, 4216 (1961).

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

(23) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc*,, 81, 3484 (1959).

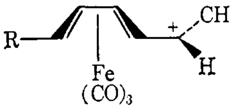
(24) T. G. Traylor and J. C. Ware, *Tetrahedron Lett.*, 1295 (1965).

(25) See ref 11a and b for discussions of the relative merits of these two mechanisms from different points of view.

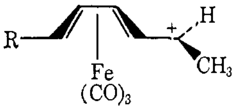
(26) We will use this term regardless of specific mechanism; *cf.* ref 11a.

(27) *Cf.* A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 6546 (1968).

(28) Reference 13, pp 72 and 73.



"*ψ-endo*"
30



"*ψ-exo*"
31

is no obvious reason why **30** should isomerize to **31** when R is phenyl but not when R is methyl. Nevertheless, the latter mechanism cannot be ruled out. Therefore, *ca.* 8% must be considered to be only a *maximum* estimate for unassisted solvolysis of **12b**.[29] This corresponds to a minimum k_Δ/k_s of 12. Since k_s should be similar for a pair of *ψ-exo,ψ-endo* isomers, k_s for the *ψ-endo* isomers can be used to estimate *minimum* anchimeric assistance factors of 8700 and 1100 for *ψ-exo* esters **8b** and **11b**, respectively.

Combination of our estimates of k_Δ/k_s for the *ψ-endo* esters with the data in Table IV shows that complexation to an $Fe(CO)_3$ group lowers the rate of unassisted solvolysis by factors of at least 100 and 150 in the phenyl and methyl series, respectively. Complexation to $Fe(CO)_3$ probably increases the ability of the diene to donate electrons inductively,[30] so changes in inductive effects cannot be responsible. Scale models[12] suggest that a slight twisting from **24** toward conformation **22** should eliminate any steric hindrance to ionization. The difference in diene conformation between the *s-cis* complexes and the *s-trans* uncomplexed esters may contribute to the rate decrease[31] and a substantial portion is probably caused by a decrease in π-electron delocalization through the complexed diene.[12]

Reference to Table V shows that the solvolysis rate enhancement caused by complex formation is four times larger in the primary series (200) than in the secondary (55). The increase for the phenyl-substituted secondary ester complex at 30° is only a factor of 10. The rate enhancement for addition of an α-methyl group is four times smaller in the complexed series (170) than in the uncomplexed (630).[27] Decreasing anchimeric assistance on going from primary to secondary systems and consequently low α-methyl effects are characteristic of systems in which nucleophilic participation by a neighboring group occurs.[32] The α-methyl effect for ferrocenyl carbinyl acetates is very low, $k[FcCH(OAc)CH_3]/k[FcCH_2OAc] = 10$ in 80% aqueous acetone.[23,33] More typical is $k[PhCH_2CH(OTs)CH_3]/k[PhCH_2CH_2OTs] = 76$ in formic acid.[34]

Table V. Relative Solvolysis Rates for Primary and Methyl-Substituted Secondary Dinitrobenzoates in 80% Aqueous Acetone at 45°

Compound	k_{rel}
ψ-exo-Secondary (**8b**)	35,000
Uncomplexed secondary (**10b**)	630
14b	200
$CH_3(CH{=}CH)_2CH_2ODNB$[a] (**15b**)	1

[a] ODNB = 3,5-dinitrobenzoate.

The relative effects of phenyl and methyl substituents on the solvolysis rates (Table IV) are unusual. In the uncomplexed esters phenyl enhances the solvolysis rate relative to methyl by a factor of 2.1. This is expected on the basis of the phenyl groups' ability to delocalize positive change.[35] However, in the *ψ-exo* and *ψ*-endo complexed esters phenyl is rate retarding with respect to methyl by a factor of 2.7–2.8. This is consistent with reduced π-electron delocalization through the complexed diene causing the electron-withdrawing inductive effect of phenyl[36] to dominate its overall substituent effect.

Several things about the nature of the organotransition metal cation intermediates in these reactions can be deduced. First, they are quite stable. The relative solvolysis rates of 1-ferrocenyl-1-ethyl acetate, trityl acetate,[23] and **8**-OAc in 80% aqueous acetone at 45° are 65:13:1. The cation from **8**-OAc and **8b** is highly discriminating in its reaction with nucleophiles: k_{ODNB}/k_{H_2O} is 1600 ± 600 in 80% aqueous acetone.[37] It is probably less discriminate than 1-ferrocenyl-1-ethyl cation[23] and possibly more discriminate than trityl cation for which $k_{OAc}/k_{H_2O} = 90$ in 80% aqueous dioxane.[23,38]

For several of these reactions product studies show unequivocally that the intermediates are tricarbonyl(*trans*-π-pentadienyl)iron cations (**7**) and not the previously described *cis* isomers (**6**). Hydrolysis of the *cis* cation **18** gives only alcohol **19**[15] yet no trace of **19** was detected in the solvolysis product of the complexed primary ester (**14b**). The solvolytic intermediate is, therefore, the primary *trans* cation (**7**, $R_1 = CH_3$; $R_2 = H$) which does not rearrange to the *cis* cation (**18**) under solvolysis conditions. The *cis* cations **6** ($R_1 = R_2 = CH_3$) and **6** ($R_1 = C_6H_5$, $R_2 = CH_3$) can be eliminated as major intermediates in the solvolysis of the *ψ-endo* esters since they produce only *ψ-exo* alcohols on hydrolysis. However, a *cis* cation cannot be ruled out as a possible source of the 6% *ψ-exo* alcohol formed in solvolysis of **12b**. It is reasonable that solvolysis of the *ψ-exo* esters proceed in an analogous fashion *via trans* cations, although the hydrolysis experiments show that the observed *ψ-exo* alcohols could have originated from the *cis* cations. Finally, the stereospecificity of the solvolyses requires that interconversion of isomeric "*ψ-exo*" and "*ψ-endo*" cations **30** and **31** is slow relative to the rate of capture by solvent.

These solvolysis data provide no basis for deciding

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(29) 8% unassisted solvolysis with 80% inversion would give 6.4% *ψ-exo*-alcohol.

(30) Dienoic acids have lower pK_a values than their $Fe(CO)_3$ complexes: R. Pettit, G. F. Emerson, and J. E. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

(31) Experiments designed to test this point are now in progress.

(32) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

(33) See M. J. Nugent, Ph.D. Thesis, California Institute of Technology, 1965, p 44, for a discussion of this and other α-methyl effects.

(34) S. Winstein, J. Brown, K. C. Schreiber, and A. H. Schlesinger, *J. Amer. Chem. Soc.*, 74, 1140 (1952), and S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

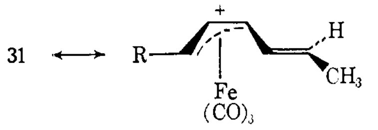
(35) $k(PhCH{=}CHCH_2Cl)/k(CH_3CH{=}CHCH_2Cl)$ in 50% aqueous ethanol at 44.6° is 8.5. C. A. Vernon, *J. Chem. Soc.*, 423 (1954). See also R. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

(36) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 619.

(37) Calculated using the method of Swain, *et al.*, and the data in Table III: C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Amer. Chem. Soc.*, **75**, 136 (1953).

(38) (a) This suggests that the tricarbonyl(*trans*-π-pentadienyl)iron cation intermediate is more stable than the trityl cation, despite the relative solvolysis rates; however, our value of k_{ODNB}/k_{H_2O} is inexact and conditions for trityl and our ion are different. Hill and Wiesner have recently reported data which can be interpreted to the effect that solvolysis rates underestimate the stability of ferrocenyl carbonyl cations *vs.* trityl cation; (b) E. A. Hill and R. Wiesner, *ibid.*, **91**, 509 (1969).

between the iron participation and hyperconjugation mechanisms. The former should lead to a cation in which all five carbons of the pentadienyl ligand are at least partially bonded to iron (**27**), while the latter should give cation **29** which is a tricarbonyl(π-allyl) cation[39] with a weakened bond between iron and the nearest carbon of an attached propenyl group. Ion **29** could alternatively be represented as a resonance hybrid of contributing structures **31** and **32**. The extreme π-allyl structure (**32**) is unlikely since it should be transformed rapidly into the more stable *cis* ion by rotation about the single bond joining the allyl and propenyl units.



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Protonation of Complexed Dienones

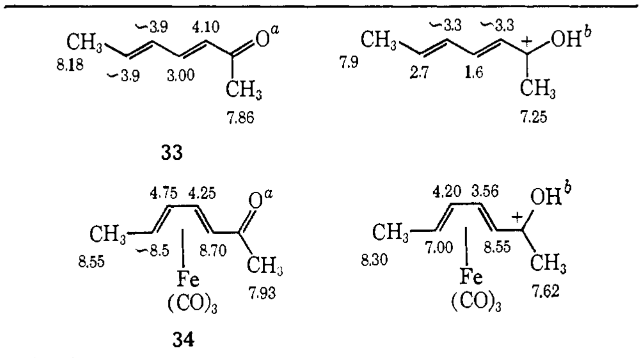
Results. Attempts to produce tricarbonyl(*trans*-π-pentadienyl)iron cations at low temperatures and to study them by nmr spectroscopy were unsuccessful. Treatment of the complexed dienols at low temperatures with strong acids such as SbF_5 and FSO_3H in liquid sulfur dioxide gave solutions which rapidly turned dark and became paramagnetic. At this point we turned to the study of protonated ketones as models of the desired cations.

The nmr spectrum of all-*trans*-3,5-heptadien-2-one (**33**) in the olefin region exhibits two quartets at low field and a discernible doublet, J = 16 Hz, at high field which partially merges with a multiplet on its low-field side. Assignment of the low- and high-field signals as H_4, virtually coupled to H_6,[40] and H_3 is consistent with chemical shifts observed for other enones and dienones[41,42] and the large values expected for vicinal coupling constants in an all-*trans*-diene.[43] The remaining multiplet is assigned to H_5 and H_6. Treatment of **33** with concentrated H_2SO_4 or SbF_5–SO_2 gives bright red solutions which exhibit virtually identical nmr spectra. The H_4 signal appears as a downfield quartet, J_{34} = 16 Hz, J_{45} = 12 Hz. Virtual coupling no longer occurs because δ_{56} is too large for H_5 and H_6 to behave as a strongly coupled set. H_3 and H_5 appear as three broad peaks near τ 4.0 and H_6 as a multiplet of at least six peaks centered at *ca.* τ 2.7. The OH signal was not detected presumably owing to exchange with solvent.

In the nmr spectrum of tricarbonyl(3,5-heptadien-2-one)iron (**34**) in $CDCl_3$ H_4 and H_5 appear as quartets at τ 4.25 and τ 4.75, respectively. The 7-methyl group and H_6 appear as a complex of overlapping signals near τ 8.5, and the highest field signal, a doublet J = 7 Hz, is assigned to H_3.[44] These assignments are based upon and required by subsequent work in these laboratories on methylated and deuterated derivatives of **34**.[45] The shifts are consistent with those observed for other tricarbonyl(diene)iron compounds.[46]

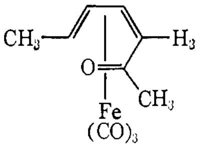
Treatment of the dienone complex (**34**) with concentrated H_2SO_4 gave a deep red solution which was reasonably stable at −10° and gave the nmr spectrum shown in Figure 2a. Identical spectra were obtained in D_2SO_4 and in SO_2 in the presence of small amounts of SbF_5. Material obtained by aqueous quenching of the D_2SO_4 solution showed no deuterium incorporation. The signals are assigned as shown in Table VI along with assignments for the other compounds. Again subsequent work requires assignment of H_3 as the high field doublet.[45] Scans up to τ 18.5 revealed no high field indicative of protonation on iron.[7,47]

Table VI. Chemical Shifts in τ Units for Protonated and Unprotonated Dienones



[a] In $CDCl_3$ relative to internal tetramethylsilane. [b] In H_2SO_4 relative to internal methylene chloride which is assumed to appear at τ 4.70.

If the sulfuric acid solution of **34** were allowed to warm above 0° or to stand for *ca.* 15–20 min, its nmr spectrum changed to a new spectrum (see Experimental Section). Quenching of this sample in aqueous sodium bicarbonate gave two compounds which could be separated by preparative tlc. These were the starting dienone complex (**34**) and a new compound (**35**) isolated in 17% yield. Oxidative cleavage of **35** with ferric chloride[10] gave as the major product *cis,trans*-3,5-heptadien-2-one (**36**) which was shown to be identical with an authentic sample[48] by glpc. Compound **35** is then tricarbonyl(*cis,trans*-3,5-heptadien-2-one)iron. Its nmr spectrum (shown in Figure 2b) (see Experimental Section for assignments) is uniquely consistent



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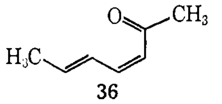

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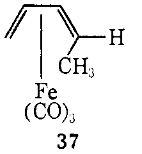

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[39] G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962); and G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (London), 836 (1964).

[40] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962). Conditions for observation of virtual coupling are fulfilled here; *e.g.*, $\delta_{56} \sim J_{56} \sim J_{45}$.

[41] (a) E. C. Freidrich, *J. Org. Chem.*, **33**, 413 (1968); (b) A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, **90**, 2347 (1968); (c) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).

[42] "High Resolution NMR Spectra Catalog," Vol. 1 and 2, Varian Associates, Palo Alto, Calif., 1963, spectra no. 60, 225, 328, 462, 544, and 617.

[43] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3451 (1965).

[44] Our initial assignments of H_3 and H_6 were reversed owing to an ambiguity in multiplicity of the signals and the expectation that the inductive effect of the ketone-carbonyl would deshield H_3 relative to H_6: N. A. Clinton, Ph.D. Thesis, University of Massachusetts, 1968.

[45] Unpublished work of R. A. Sahatjian. This work will be reported in detail in a later publication.

[46] G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

[47] M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

[48] Unpublished work of A. F. Kluge.

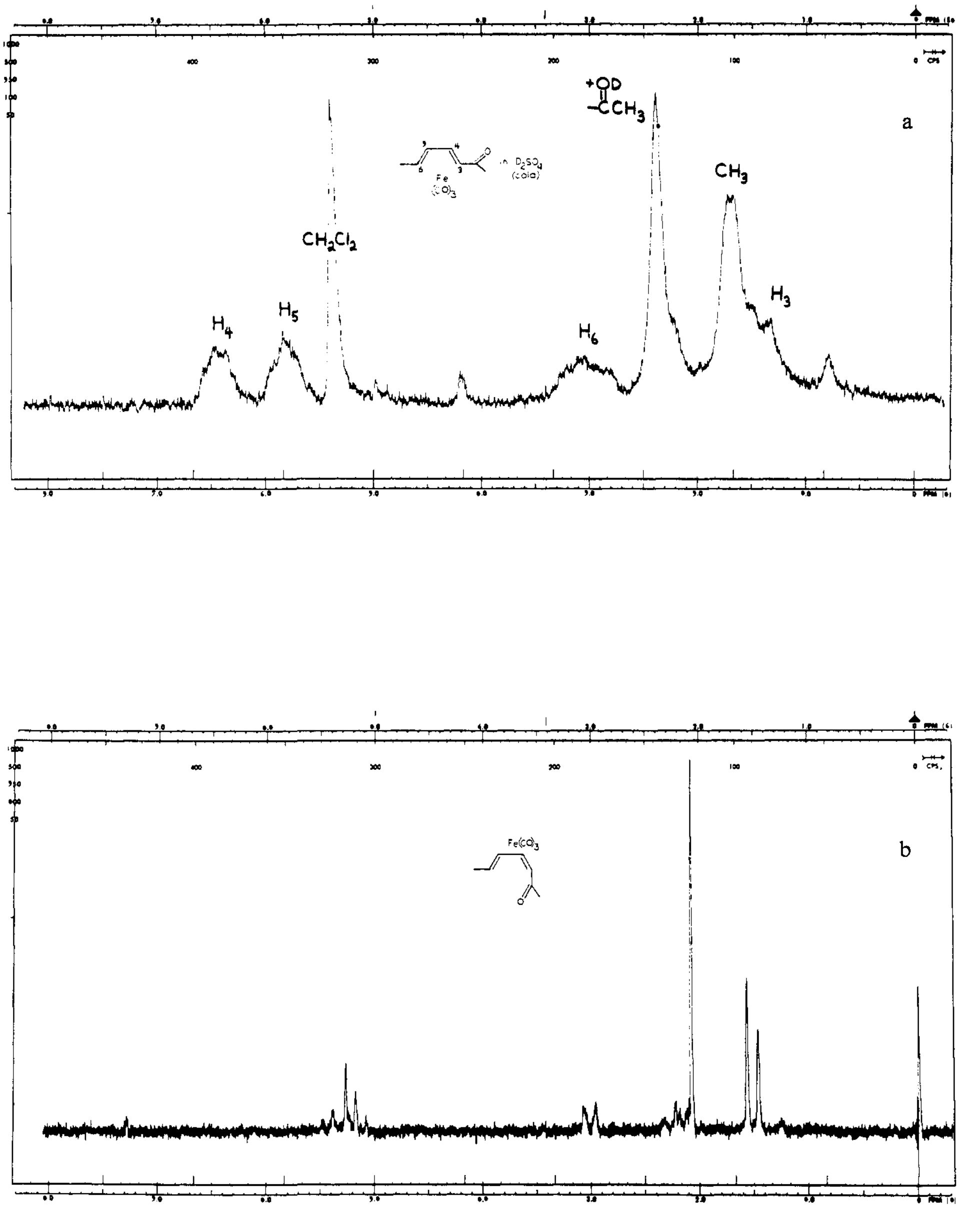


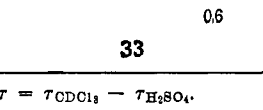
Figure 2. (a) Nmr spectrum of unrearranged tricarbonyl(*trans,trans*-3,5-heptadien-2-one)iron (**34**) in cold deuteriosulfuric acid (the signals at τ 5.8 and 9.2 are caused by impurities); (b) nmr spectrum of tricarbonyl(*cis,trans*-3,5-heptadien-2-one)iron (**35**) in deuteriochloroform. See Experimental Section for a complete assignment of the signals.

with this structure. Especially significant is the H_3 doublet, $J = 6.5$ Hz (*cis* coupling[49]), at τ 6.98 which is close to the shift of the analogous hydrogen in **37**.[46] Quenching of the H_2SO_4 solution of **34** with a suspension of sodium bicarbonate in methylene chloride gave pure **35**.

Protonation of cinnamylidene acetone gave an hydroxy pentadienyl cation similar to that obtained from **33**. Treatment of its $Fe(CO)_3$ complex with sulfuric acid, however, gave a complex nmr spectrum; and an aqueous quench produced no water-insoluble material.

Discussion. The downfield shifts caused by protonation of the dienones, $\Delta\tau$ values, are listed in Table VII. The nmr and uv spectra of protonated hexadienones have been interpreted in terms of O protonation.[41a,50] The identity of nmr spectra in H_2SO_4 and SbF_5 require O protonation for **33** since SbF_5 would not be expected to coordinate elsewhere. The case for O protonation of **34** with the inclusion of the D_2SO_4 data is even clearer, and the wide variation of $\Delta\tau$ values would seem to rule out protonation on terminal carbonyl in favor of protonation on the ketone carbonyl. Olah and

Table VII. $\Delta\tau$ Values for Dienones[a]



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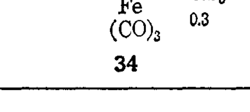

34

[a] $\Delta\tau = \tau_{CDCl_3} - \tau_{H_2SO_4}$.

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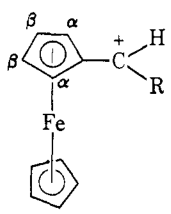
[49] J_{trans} for this bond is normally 8 Hz in dienone complexes; R. A. Sahatjian, unpublished work.

[50] V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).

Calin have pointed out that protonated saturated ketones are poor nmr models for secondary carbonium ions owing to the small importance of the hydroxycarbonium ion resonance contributor.[51] As expected, the protonated ketone improves as a model with increasing carbonium ion stability. Thus protonated enones and cyclohexadienones are good nmr models for allyl[51,52] and cyclohexadienyl[41a,50] carbonium ions themselves. The $\Delta\tau$ values we calculate for **33** show the alternation expected from MO or VB theory and correlate well with $\Delta\tau$ values computed by Sorensen for formation of pentadienyl cations from trienes in sulfuric acid.[53] Since cation **31** (R = CH_3 or C_6H_5) is apparently more stable than its uncomplexed analog, the protonated dienone **34** is potentially a good nmr model for it.

A striking feature of the $\Delta\tau$ values for **34** is the large shift for H_6, which is remote from the site of protonation, in relation to the shifts for the other hydrogens. A similar deshielding of β-hydrogens relative to α-hydrogens occurs in ferrocenylcarbinyl cations (**38**) and has been interpreted in terms of a shift of the iron atom away from C_β toward the carbinyl carbon.[54] Traylor and Ware, however, have argued that the nmr data on these ions are also consistent with a major contribution from hyperconjugation structure **39**;[11a] and Feinberg and Rosenblum have argued on the basis of new data that movement of iron does not occur.[55] The small $\Delta\tau$ value for H_3 which is closest to the protonated carbonyl group is equally unusual. The chemical shift of H_3 in protonated **34** (τ 8.55), even if one allows for possible diamagnetic anisotropic effects of the $Fe(CO)_3$ group, seems inconsistent with a major contribution of a π-allyl (hyperconjugation) type structure (see **32**) in which H_3 is olefinic. It is consistent with a shift of iron away from C_6 and toward the carbonyl carbon and C_2 on protonation.



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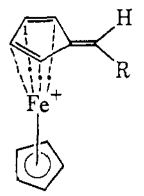

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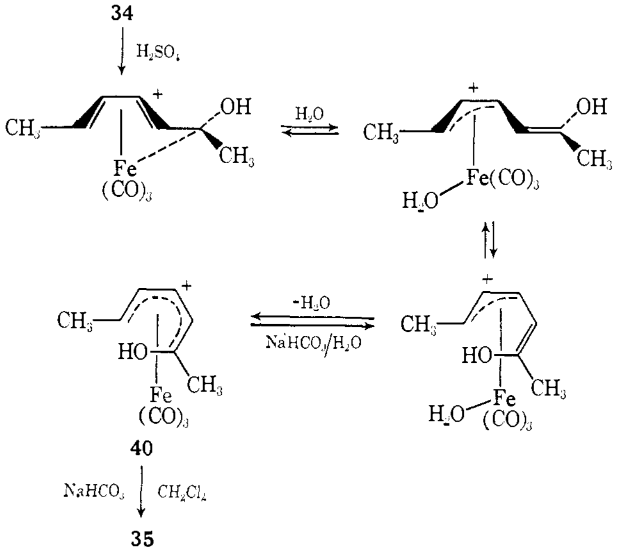
The question of how pertinent these data are to the structure of tricarbonyl(*trans*-π-pentadienyl)iron cations must still be answered. Neighboring group participation by iron in a carbonium ion already stabilized by an –OH group would be unusual.[56,57] On the other hand, the hyperconjugation mechanism should be able to operate in the protonated ketones yet the nmr data certainly do not seem to favor it. These questions will be taken up along with more data on protonated dienone complexes in a subsequent paper.[45]

The changes which occur subsequent to solution of **34** in H_2SO_4 and upon quenching can be accounted for as shown in Scheme I. The ion obtained in warm acid is reasonably formulated as the protonated *cis,trans*-dienone complex (**40**), analogous to the stable *cis* cations (**6**). The isomerization mechanism is one proposed by Mahler and Pettit[10] to account for transformations like **14a** → **18** → **19**. Aqueous quenching of **40** facilitates isomerization back to **34**, the product of thermodynamic control. Quenching in the absence of water or other nucleophilic catalysts, *e.g.*, in methylene chloride, gives the product of kinetic control, **35**. The ψ-*exo* stereochemistry of alcohols obtained by quenching tricarbonyl(*cis*-π-pentadienyl)iron cations like **6** (R_1 = R_2 = CH_3), **18**, and **20** is also in accord with this mechanism.

Scheme I



Difficulties encountered in the attempted protonation of complexed phenyl-substituted ketone are probably caused by sulfonation of the aromatic ring. Mahler and Pettit have shown that tricarbonyl(phenylbutadiene)iron undergoes Friedel-Crafts acylation in the *para* position of the phenyl ring under mild conditions,[58] and similar reactions have been subsequently carried out in our laboratories.[8]

Summary

Solvolysis of the complexed dienyl esters clearly proceeds with *exo* departure of the leaving group and a high degree of retention of configuration. In several of these reactions the intermediacy of tricarbonyl(*trans*-π-pentadienyl)iron cations has been demonstrated. Minimum rate factors for anchimeric assistance by the $Fe(CO)_3$ group have been estimated and range from 12 for **12b** to 8700 for **8b**, and the actual values may be considerably higher. Net stabilization of *trans*-pentadienyl cations by attachment of an $Fe(CO)_3$ group does occur in favorable cases. Nmr data from the protonated ketone **34** are difficult to interpret in terms of stabilization by carbon–iron hyperconjugation and can be rationalized in terms of five point attachment to the pentadienyl ligand. However, these data and their interpretation must be con-

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(51) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 938 (1968).

(52) D. M. Brouwer, *Tetrahedron Lett.*, 453 (1968).

(53) T. S. Sorensen, *J. Amer. Chem. Soc.*, **87**, 5057 (1965).

(54) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966).

(55) J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, **91**, 4324 (1969).

(56) We would like to thank Professor T. G. Traylor for making this point in the course of a stimulating discussion of this work.

(57) *Cf.* T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, **88**, 4934 (1966), and ref 11a.

(58) J. E. Mahler and R. Pettit, unpublished results quoted in R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 13 (1964).

sidered preliminary at this time. We are continuing solvolysis studies in order to test some of the interpretations presented here and are extending the studies of protonated dienones.

Experimental Section

General. Infrared spectra were recorded on a Beckman IR-10 instrument 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. Melting points were determined on a Mel Temp apparatus and are uncorrected. Elemental analyses were performed by the Schwartzkopf Microanalytical Latoratory, Woodside, N. Y.

ψ-*exo*-Tricarbonyl(3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron (8b). ψ-*exo*-Alcohol (**8a**) (1.0 g, 4.0 mmol) and 6.0 g (15 mmol) of bis(3,5-dinitrobenzoic) anhydride were stirred under nitrogen in 50 ml of anhydrous pyridine overnight at room temperature. The reaction mixture was taken up in 150 ml of benzene and washed with three 100-ml portions of saturated sodium carbonate, four 100-ml portions of 20% hydrochloric acid, and finally with 100 ml of water. Drying ($MgSO_4$) and evaporation of the light yellow solution gave an oil. The oil was dissolved in methylene chloride (*ca.* 2 ml), filtered, and Skellysolve F was added dropwise until crystallization began. After the first few crystals had formed, the solution was decanted; and more Skellysolve F was added to the supernate to give 0.9 g (51%) of **8b** as a light yellow solid: mp 103–103.5°; ir ($CHCl_3$) 3100 (Ar-H), 2040, 1980–1960 ($C\equiv O$), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.98 (t, 1, $J_{23} \sim J_{34} \sim$ 8.5 Hz), 8.4–8.65 (m, 7, 1-CH_3, 7-CH_3, and H_6), 4.83 (broad, 2, H_2 and H_5), 4.48 (m, 1, H_3), 0.50 (s, 3, Ar–*H*).

Anal. Calcd for $C_{17}H_{14}N_2O_9Fe$: C, 45.76; H, 3.16; N, 6.28; Fe, 12.52. Found: C, 45.64; H, 3.00; N, 6.30; Fe, 12.31.

ψ-*endo*-Tricarbonyl(3,5-heptadien-2-yl 3,5-dinitrobenzoate)iron (9b). ψ-*endo*-Alcohol **9a** (1.0 g, 4.0 mmol) and 6.0 g (15 mmol) of bis(3,5-dinitrobenzoic) anhydride were stirred under nitrogen in 100 ml of anhydrous pyridine overnight at room temperature. The reaction mixture was taken up into 300 ml of benzene and washed with three 100-ml portions of saturated sodium carbonate, four 50-ml portions of 20% hydrochloric acid, and finally with 100 ml of water. Drying ($MgSO_4$) and evaporation of the benzene solution left a yellow oil. Addition of 40 ml of Skellysolve F to a solution of this oil in 5 ml of methylene chloride gave 1.34 g of yellow solid. The solid was redissolved in the minimum amount of methylene chloride, and Skellysolve F was added until crystallization began. The first crystals were coated with a dark oil, so the clear solution was decanted. Addition of Skellysolve F to the supernate gave **9b** as 0.85 g (48%) of light yellow solid: mp 135–135.5°; ir ($CHCl_3$) 3100 (Ar-H), 2020, 1970 ($C\equiv O$), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.90 (t, 1, $J_{23} \sim J_{34} \sim$ 8 Hz, H_3), 8.3–8.7 (m, 7, 1-CH_3, 7-CH_3, H_6), 4.6–5.0 (m, broad, 3, H_2, H_4, H_5), 0.30 (s, 3, Ar–H).

Anal. Calcd for $C_{17}H_{14}N_2O_9Fe$: C, 45.76; H, 3.16; N, 6.28; Fe, 12.52. Found: C, 46.18; H, 3.29; N, 6.44; Fe, 12.55.

3,5-Heptadien-2-yl 3,5-Dinitrobenzoate (10b). 3,5-Heptadien-2-ol (**10a**) (2.0 g, 18 mmol) and 6.0 g (27.5 mmol) of 3,5-dinitrobenzoyl chloride were stirred in 50 ml of dry pyridine for 3 hr at room temperature. The reaction mixture was taken up in 500 ml of benzene and was washed with four 100-ml portions of saturated sodium carbonate, four 100-ml portions of 20% hydrochloric acid, and with 100 ml of water. Drying ($MgSO_4$) and evaporation of the benzene solution left a dark yellow oil. Dark material was removed by passing a solution of the oil in 50 ml of benzene through an 0.5-cm bed of alumina in a conical funnel. Evaporation of the filtrate gave **10b** as a light yellow oil (2.0 g, 37%). Attempts to distill this oil under vacuum led to decomposition, and alumina chromatography appeared to cause some isomerization. Physical properties: ir ($CHCl_3$) 3100 (Ar-H), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.40 and 8.25 (2d, 6, 1-CH_3, 7-CH_3), 3.7–4.6 (m, 5, H_{2-6}), 0.40 (s, 3, Ar–H).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.89; H, 4.61; N, 9.15. Found: C, 54.73; H, 4.66; N, 8.93.

ψ-*exo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-yl 3,5-dinitrobenzoate)iron (11b). ψ-*exo*-Alcohol **11a** (1.0 g, 3.2 mmol) and 6.0 g (15 mmol) of bis(3,5-dinitrobenzoic) anhydride were stirred under nitrogen in 100 ml of dry pyridine for 14 hr at room temperature. The reaction mixture was taken up in 500 ml of benzene and washed with four 100-ml portions of saturated sodium carbonate, four 100-ml portions of 20% hydrochloric acid, and with four 100-ml portions of 5% sodium hydroxide. Drying ($MgSO_4$) and evaporation of the benzene solution gave a brown solid which was triturated with 20 ml of Skellysolve F to give a yellow powder. The product was dissolved in 20 ml of methylene chloride, filtered, and reprecipitated by addition of 100 ml of Skellysolve F to give 1.15 g (71.5%) of **11b** as a yellow solid.

A small sample was dissolved in the minimum amount of methylene chloride. Skellysolve F was added slowly to this solution; and after the first crystals formed, the solution was decanted. Addition of Skellysolve F to the supernate gave an analytically pure material as a light yellow powder: mp >450°; ir ($CHCl_3$) 3100 (Ar-H), 2040, 1980 ($C\equiv O$), 1720 (ester $C=O$); nmr ($CDCl_3$) τ 8.65 (t, 1, $J_{23} \sim J_{34} \sim$ 8.5 Hz, H_3), 8.32 (d, 2, CH_3), 7.68 (d, 1, J_{56} = 8.5 Hz, H_6), 4.0–5.2 (m, 3, H_2, H_4, H_5), 2.69 (s, 5, –C_6H_5), 0.40 (s, 3, Ar–H).

Anal. Calcd for $C_{22}H_{16}N_2O_9Fe$: C, 51.98; H, 3.17; N, 5.51; Fe, 10.98. Found: C, 51.92; H, 3.16; N, 5.75; Fe, 10.61.

ψ-*endo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-yl 3,5-dinitrobenzoate)iron (12b). ψ-*endo*-Alcohol **12a** (1.0 g, 3.2 mmol) and 6.0 (15 mmol) of bis(3,5-dinitrobenzoic) anhydride were stirred under nitrogen in 100 ml of dry pyridine for 12 hr at room temperature. The reaction mixture was taken up in 500 ml of benzene and was washed with 100 ml of water, four 100-ml portions of saturated sodium bicarbonate, four 100-ml portions of 20% hydrochloric acid, and two 100-ml portions of 5% sodium hydroxide. Drying ($MgSO_4$) and evaporation of the benzene solution left a dark solid. This material was triturated with 20 ml of Skellysolve F, dissolved in 15 ml of methylene chloride, and precipitated by addition of 100 ml of Skellysolve F. The resulting dark solid was dissolved in a few milliliters of chloroform and filtered to give a light yellow solution. Addition of 100 ml of Skellysolve F gave 1.0 g (62%) of **12b** as a light yellow solid. Analytically pure **12b** was obtained by solution in the minimum amount of methylene chloride, filtration, and reprecipitation with Skellysolve F: mp >450° (darkens at 150°); ir ($CHCl_3$) 3100 (Ar–H), 2040, 1990–1960 ($C\equiv O$), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.53 (t, 1, $J_{23} \sim J_{34} \sim$ 9 Hz, H_3), 8.37 (d, J = 6 Hz, CH_3), 7.78 (d, 1, J_{56} = 9 Hz, H_6), 4.45–5.0 (m, 2, H_2, H_4), 4.16 (q, 1, J_{45} = 5, J_{56} = 9 Hz, H_5), 2.75 (s, 5, C_6H_5), 0.5 (s, 3, Ar–H).

Anal. Calcd for $C_{22}H_{16}N_2O_9Fe$: C, 51.98; H, 3.17; N, 5.51; Fe, 10.98. Found: C, 51.99; H, 3.30; N, 5.77; Fe, 10.63.

6-Phenyl-3,5-hexadien-2-yl 3,5-Dinitrobenzoate (13b). 6-Phenyl-3,5-hexadien-2-ol (**13a**) (5.0 g, 29 mmol) and 7.5 g (34 mmol) of 3,5-dinitrobenzoyl chloride in 50 ml of dry pyridine were heated on a steam bath for 2 hr. The cooled reaction mixture was taken up in 200 ml of benzene and washed with three 100-ml portions of saturated sodium bicarbonate, four 100-ml portions of 10% hydrochloric acid, and finally with 100 ml of water. Evaporation of the benzene solution gave an oil which smelled of pyridine. The oil was dissolved in 200 ml of ethyl ether and extracted with three 100-ml portions of 10% hydrochloric acid and then with 100 ml of water. Drying ($MgSO_4$) and evaporation of the ether solution left a brown oil. Trituration with a few milliters of ethyl ether gave a yellow solid which was collected by filtration and washed with 50 ml of Skellysolve F to give 3.65 g (29%) of **13b** as a light yellow solid, mp 109–110°.

An analytical sample was prepared by dissolving a portion of the solid in a minimum volume of methylene chloride and adding Skellysolve F until crystallization began. The first crystals, which were coated with a dark oil, were removed by filtration. Addition of more Skellysolve F to the filtrate gave a light yellow powder: mp 110°; ir ($CHCl_3$) 3100 (Ar-H), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.45 (d, 3, CH_3), 3.3–4.5 (m, 5, H_{2-6}), 2.75 (s, broad, 5, C_6H_5), 0.4 (s, 3, Ar-H).

Anal. Calcd for $C_{19}H_{16}N_2O_6$: C, 61.94; H, 4.38; N, 7.61. Found: C, 61.83; H, 4.29; N, 7.29.

Tricarbonyl(2,4-hexadien-1-yl 3,5-dinitrobenzoate)iron (14b). Tricarbonyl(2,4-hexadien-1-ol)iron (**14a**) was prepared by stirring 6.0 g (61 mmol) of 2,4-hexadien-1-ol and 35 g (97 mmol) of diiron enneacarbonyl in 50 ml of dry ethyl ether for 10 hr at room temperature. The reaction mixture was filtered and evaporated, and the resulting red oil was distilled under vacuum to give 3 ml of **14a** as a thick oil: bp 100° (1 mm) [lit.[15] bp 112° (1.3 mm)].

Tricarbonyl(2,4-hexadien-1-ol)iron (**14a**, 1.0 g, 4.2 mmol) and 6.0 g (15 mmol) of bis(3,5-dinitrobenzoic) anhydride were stirred in 50 ml of dry pyridine under nitrogen for 12 hr. The reaction mixture was taken up in 150 ml of benzene and was washed with four 100-ml portions of saturated sodium bicarbonate, with five

100-ml portions of 20% hydrochloric acid, and with water. Drying ($MgSO_4$) and evaporation of the light yellow benzene solution left an oil which was taken up in benzene and passed through a 4 × 1.5 cm plug of alumina. The light yellow filtrate was evaporated, and the residual oil was dissolved in 10 ml of methylene chloride to which 50 ml of Skellysolve F was subsequently added. Cooling this solution to −78° gave a yellow solid which was collected by filtration at −78° and redissolved in 5 ml of methylene chloride. This solution was filtered and then diluted with 50 ml of Skellysolve F. Cooling in ice gave 1.05 g (54%) of **14b** as a light yellow solid: mp 97.5°; ir ($CHCl_3$) 3100 (Ar-H), 2040, 1970 ($C\equiv O$), 1740 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.85 (q, 1, $J_{12} \sim J_{23} \sim 7$, Hz, H_2), 8.51 (s, 4, H_4, CH_3), 5.49 (d, 2, $J_{12} = 7$, Hz, $-CH_2-$), 4.45–5.0 (m, 2, H_3, H_4), 0.8 (s, 3, Ar-H).

Anal. Calcd for $C_{16}H_{12}N_2O_9Fe$: C, 44.46; H, 2.80; N, 6.48; Fe, 12.92. Found: C, 44.58; H, 2.94; N, 6.53; Fe, 12.94.

2,4-Hexadien-1-yl 3,5-Dinitrobenzoate (15b). 2,4-Hexadien-1-ol (2.0 g, 20 mmol) and 6.0 g (27.5 mmol) of 3,5-dinitrobenzoyl chloride in 50 ml of dry pyridine were heated on a steam bath for 1 hr. The reaction mixture was taken up in 200 ml of benzene and was washed with four 100-ml portions of saturated sodium carbonate, four 100-ml portions of 20% hydrochloric acid, and 100 ml of water. Drying ($MgSO_4$) and evaporation of the benzene solution gave a yellow solid. Two recrystallizations from Skellysolve C gave 1.22 g (20%) of **15b** as a light yellow solid: mp 84° (lit.[59] 85°); ir ($CHCl_3$) 3100 (Ar-H), 1730 cm^{-1} (ester $C=O$); nmr ($CDCl_3$) τ 8.18 (d, 3, J = 5.5 Hz, CH_3), 4.97 (2, d, J = 6 Hz, $-CH_2-$), 3.3–4.4 (m, 4, H_{2-5}), 0.4 (s, 3, Ar-H).

***ψ-exo*-Tricarbonyl(3,5-heptadien-2-yl acetate)iron (8-OAc).** *ψ-exo*-Alcohol **8a** (0.45 g, 1.8 mmol) and 1.62 g (15.9 mmol) of acetic anhydride were stirred in 7 ml of dry pyridine under nitrogen for 12 hr. Evaporation of the reaction mixture under vacuum left a yellow solid, mp 60–61°. Sublimation at 40° (0.1 mm) gave **8**-OAc as 0.44 g (85%) of a light yellow solid, mp 60.5–61°. A small portion of this material was dissolved in methylene chloride, filtered, and recovered by evaporation. Two recrystallizations of this material from the minimum amount of Skellysolve F at −78° gave analytically pure **8**-OAc: mp 61° (under nitrogen); ir (CCl_4) 2050, 1980–1950 ($C\equiv O$), 1735 (ester $C=O$), 1380, 1360 cm^{-1} ($C-O$); nmr ($CDCl_3$) τ 9.12 (t, 1, $J_{23} \sim J_{34} \sim 8.5$ Hz, H_3), 8.60 (apparent doublet, 7, 2-CH_3's, H_6), 8.00 (s, 3, CH_3CO-), 5.28, 5.98, 4.61 (three multiplets, H_2, H_4, H_5).

Anal. Calcd for $C_{12}H_{14}O_5Fe$: C, 49.01; H, 4.79; Fe, 18.99. Found: C, 48.60; H, 4.85; Fe, 18.78.

Bis(3,5-dinitrobenzoic) Anhydride. A mixture of 1 equiv of 3,5-dinitrobenzoic acid and 1.2 equiv of 3,5-dinitrobenzoyl chloride was heated for 5 hr at 220° in a large test tube fitted with a calcium chloride drying tube. The hot liquid was poured into an evaporating dish which was tilted during pouring so as to obtain a thin coating of the foil. After cooling, the solid product was flaked from the foil and ground into a fine powder. Trituration with ethyl ether removed residual acid chloride and left a white solid: mp 215–219° (lit.[60] mp 219–221°).

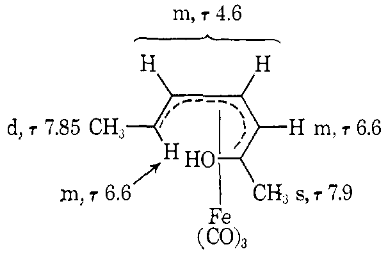
Methanolysis of 8-OAc and 8b. A 3×10^{-3} *M* solution of **8**-OAc was heated in methanol at 60°. Monitoring the reaction by tlc showed only one iron-containing product. Preparative runs were made by heating large amounts of **8**-OAc and **8b** in methanol and showed the same product by tlc. The methanol solutions were added to aqueous sodium bicarbonate, and extraction with ether and drying ($MgSO_4$) gave a light yellow solution. Evaporation of the ethereal solution gave a red oil which was chromatographically identical with the product obtained at higher dilution. The nmr spectrum of this material was uniquely consistent with the tricarbonyl(2-methoxy-3,5-heptadiene)iron structure (**17**): nmr ($CDCl_3$) 9.20 (t, 2, $J_{23} \sim J_{34} \sim 8$ Hz, H_3), 8.70 (d, 3, J_{12} = 6.5 Hz, 1-CH_3), 8.55–8.85 (m, 4, H_6, 7-CH_3), 6.98 (q, 1, J_{12} = 6.5, J_{23} = 8 Hz, H_2), 6.69 (s, 3, OCH_3), 4.75–5.1 (m, 2, H_4 and H_5).

A sample of *ψ-exo*-tricarbonyl(3,5-heptadien-2-ol)iron (**8a**) was heated in methanol containing 3×10^{-3} *M* acetic acid. The analysis showed that none of the methyl ether (**17**) was formed.

Preparation and Hydrolysis of Tricarbonyl(*π-cis*-1-phenyl-2,4-hexadien-1-yl)iron Fluoroborate (20). A small sample of *ψ-exo*-alcohol **11a** was added to a 48–50% fluoroboric acid solution, and the mixture was heated for 30 min to give a deep red solution. After heating, the sample was hydrolyzed by adding it to a large excess of water; and the resulting precipitate was recovered by ether extraction. Drying ($MgSO_4$) and evaporation of the ether left a solid. One recrystallization from Skellysolve B gave pure **11a**: mp 132–134°; ir ($CHCl_3$) identical with **11a**.

Protonation of Ketones 33 and 34. Ketone **33** was added to concentrated sulfuric acid with vigorous stirring at *ca.* 0°, and this solution was added to a precooled nmr tube. Methylene chloride was added to the tube as an internal standard, and the spectrum was recorded at 0–15°. In the case of the complexed ketone (**34**) addition of a cold methylene chloride solution of **34** to cold sulfuric acid resulted in extraction of the ketone into the acid and obviated difficulties encountered when solid **34** was added directly to sulfuric acid. The presence of methylene chloride seemed to speed the rate at which the sample became paramagnetic, so direct addition was used to study the isomerization of **34** to **35** in sulfuric acid. Small amounts of antimony pentafluoride were added to solutions of **33** and **34** in nmr tubes at −40° and spectra of the solutions were recorded at −40°.

Tricarbonyl(*cis,trans*-3,5-heptadien-2-one)iron (35). Tricarbonyl(*trans,trans*-3,5-heptadien-2-one)iron (**34**) was dissolved in concentrated sulfuric acid at 0°. After 15 min at 0° or a few minutes at room temperature the deep-red solution exhibits an nmr spectrum which was attributed to O-protonated **35** as shown below. This solution was poured into an aqueous suspension of sodium bicarbonate with vigorous stirring, and the organic products were recovered by extraction into ethyl ether. Drying ($MgSO_4$) and evaporation of the ether extracts left a red oil which was separated into two components by preparative tlc (silica gel–9:1 benzene–chloroform). The higher band was identified as the starting dienone complex (**34**) by tlc, ir, and nmr. Removal of the lower band gave the isomeric dienone complex (**35**) in 17% yield.



Quenching of the acid solution by pouring into excess sodium bicarbonate methylene chloride suspension with vigorous stirring followed by extraction of inorganic products into water gave a light yellow methylene chloride solution. Drying ($MgSO_4$) and evaporation left a red oil which exhibited ir and nmr spectra identical with those of **35** produced in the aqueous quench. Tlc analysis of this material showed no trace of **34**, thus it is pure **35**: ir (CCl_4) 2050, 1980 ($C\equiv O$), 1670 ($C=O$), 1350 cm^{-1} ($CH_3C=O$); nmr ($CDCl_3$) 8.48 (d, 3, J_{56} = 6 Hz, $-CH_3$), 7.91 (s, 3, $COCH_3$), 7.80 (m, 1, H_6), 6.98 (d, 1, J_{34} = 6.5 Hz, H_3), 4.72 (m, 2, H_4, H_5); see Figure 2b.

A small sample of **35** in ethyl ether was treated with small portions of ferric chloride until gas evolution ceased. The solution was filtered, and the filtrate was compared with an authentic sample of *cis,trans*-3,5-heptadien-2-one[47] by glpc using a 6 ft × 0.25 in. column packed with 25% DC-200 on 60–80 mesh Chromosorb W which was known to separate the *trans,trans* the *cis,trans* and the *trans,cis* isomers of this dienone.[47] The major cleavage product from **35** had an identical retention time and gave one peak when admixed with *cis,trans*-3,5-heptadien-2-one (**36**).

Kinetic Measurements. Acetone was purified by the method of Kochi and Hammond.[61] The purified acetone was distilled and then heated at reflux in a distilling apparatus while nitrogen was swept through the system. At this point 10% of the acetone was distilled with nitrogen flowing through the system, and the remainder was left in the still under a positive nitrogen pressure for storage. Samples were withdrawn at the time solvolysis solutions were being prepared by distillation as nitrogen was passed through the still and receiver. Distilled water was degassed, stored, and withdrawn in the same fashion.

Samples of the esters sufficient to give a *ca.* 3×10^{-3} *M* solution were weighed into a 250-ml round-bottomed flask equipped with a single 14/20 joint. The flask was flushed with nitrogen and 80 ml of acetone, and then 20 ml of water was pipeted in, and the flask was sealed with a red rubber serum cap. Glassware was calibrated

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(59) G. F. Woods, N. C. Bolgaine, and D. E. Duggan, *J. Amer. Chem. Soc.*, **65**, 1273 (1943).

(60) T. Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

(61) J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3443 (1953).

so that the solvent corresponded to 80% acetone–20% water (v/v) at 25°. A control experiment run at 50° for 18 hr using a serum cap which had been punctured nine times by a syringe needle showed negligible solvent loss. The sealed samples were immediately placed in a Sargent Thermonitor bath. Control experiments showed that in all cases the contents of the flask were in thermal equilibrium with the bath within 10 min. Samples were withdrawn by injecting 11 ml of nitrogen into the flask through the serum cap with a syringe and withdrawing 11 ml of solution. The sample was then forced into a flask cooled in ice. A 10-ml aliquot of the quenched solution was withdrawn with a pipet and delivered into a flask containing 2 drops of 0.1% of bromothymol blue indicator solution. The flask was flushed with a gentle stream of nitrogen and the aliquot was titrated with 10^{-2} *M* aqueous sodium hydroxide from a 5-ml buret. The end point used for uncomplexed esters was a green to blue color change. For the yellow organoiron esters a yellow to green color change was used. Titration of known amounts of 3,5-dinitrobenzoic acid in the presence of nonsolvolytically active organo iron compounds such as **8a** showed this procedure to be accurate.

Rate constants were determined by least-squares determination of the slope of the plot of $\ln A_\infty/(A_\infty - A_t)$ *vs.* time where A_∞ is the titer after at least 8 half-lives and A_t is the titer at time *t* by means of a Fortran computer program.

Solvolysis Products. General. The preliminary analysis of the products from the complexed ester was accomplished by sealing small samples of 3×10^{-3} *M* ester in an 80% aqueous acetone solution and heating to 60° for 4 hr. These samples, which were carefully degassed to prevent decomposition, were then opened and were added to sodium bicarbonate solution; and the organic material was extracted into ether. Tlc (silica gel–chloroform) showed that esters **8b**, **9b**, and **11b** gave only the alcohol from which they were synthesized. In the case of these three secondary alcohols thin layer chromatography (silica gel–chloroform) showed the presence of much less than 1% of the isomeric alcohol present. In each of these cases there was no more of the other diasteriomer present than that in the alcohol used for synthesis of the benzoate. In the case of the ψ-*endo*-phenyl-substituted ester (**12b**) the solvolysis product contained *ca.* 5% of the alcohol of inverted configuration (**11a**).

The analysis of the number of alcohols produced by solvolysis was achieved with these carefully degassed samples. The samples isolated for identification were involved in a workup and were subject to oxidative decomposition. This gave traces of uncomplexed alcohols which have the same R_f's as the ψ-*exo* isomers. It was therefore necessary to rely on the degassed samples to identify the number of alcohols produced and to rely on the isolation experiments simply to confirm the identity of the major product.

ψ-*exo*-Tricarbonyl(3,5-heptadiene-2-yl 3,5-dinitrobenzoate)iron (8b). A sample of **8b** was solvolyzed in 80% aqueous acetone for 10 half-lives and then poured into eight times its volume of saturated sodium bicarbonate solution. The organic material was extracted into ether using small volumes of solvent until the ether extracts were only lightly colored. The ether fractions were combined, and were dried ($MgSO_4$). The ether was removed under vacuum, and the sample was dissolved in chloroform and was passed through a short chromatography column (alumina eluted with chloroform) to remove products of decomposition. Evaporation of the yellow band gave a light yellow solid melting at 83.5–84.5°. This sample gave an ir spectrum that was identical with that of a known sample of the ψ-*exo*-tricarbonyl(3,5-heptadien-2-ol)iron **8a**.

ψ-*endo*-Tricarbonyl(3,5-heptadiene-2-yl 3,5-dinitrobenzoate)iron (9b). A sample of **9b** was solvolyzed in 80% aqueous acetone for 10 half-lives and added to eight times its volume of water. This mixture was extracted with small volumes of ether until the extracts were only slightly yellow. The extracts were combined and were dried ($MgSO_4$). The ether solution was filtered and was evaporated to give an oil. The oil was placed on a preparative plate coated with 1 mm of silica gel. Repeated elutions with chloroform gave two bands. The silica gel containing the band of higher R_f was removed from the plate, and the organic material was removed from the silica gel with acetone containing traces of methanol. This solvent was dried over anhydrous magnesium sulfate and evaporated to give a light yellow solid, mp 40–41°. The ir spectrum of this sample was identical with that of an authentic sample of the ψ-*endo*-tricarbonyl(3,5-heptadien-2-ol)iron (**9a**). The band containing the other product consists almost exclusively of uncomplexed alcohol produced during workup. Analytical thin layer chromatography shows this not to be present in the carefully degassed samples that are spotted with no workup.

ψ-*exo*-Tricarbonyl(6-phenyl-3,5-hexadiene-2-yl 3,5-dinitrobenzoate)iron (11b). A sample of **11b** was solvolyzed in 80% aqueous acetone. After a few hours the solution was added to eight times its volume of water. The resulting mixture was extracted with small volumes of ether until the extracts were only lightly colored. The ether extracts were combined and were dried ($MgSO_4$). Filtration and evaporation gave a yellow solid. To remove decomposition products, the sample was dissolved in chloroform and was passed through a short chromatographic column (10 × 1 cm, silica gel). The eluent was arbitrarily divided into three fractions. The first, which contained unsolvolyzed ester, melted at 126–132° while the other two melted at 129–134°. The melting point may be lowered by small amounts of uncomplexed material produced by decomposition during the workup or by unsolvolyzed ester. The ir spectrum of the second sample was identical with that of the authentic alcohol **11a** except for a small ester carbonyl peak. Analytical thin layer chromatography shows no impurity in the carefully degassed samples that were spotted with no workup.

Tricarbonyl(2,4-hexadiene-1-yl 3,5-dinitrobenzoate)iron (14b). A sample of **14b** was solvolyzed for 8 half-lives in 80% aqueous acetone and the solution was added to eight times its volume of saturated sodium bicarbonate. The organic material was removed by extraction into small volumes of ether until the ether extracts were only faintly yellow. The ether extracts were combined, were dried ($MgSO_4$), and were evaporated to give an oil. This was shown by nmr and ir spectroscopy to be identical with the known tricarbonyl(2,4-hexadien-1-ol)iron (**14a**).

A sample of tricarbonyl(3,5-hexadien-2-ol)iron (**19**) was prepared by dissolving tricarbonyl(2,4-hexadiene-1-yl 3,5-dinitrobenzoate)-iron (**14a**) in 48–50% fluoroboric acid and heating for a few minutes to give a red solution.[10] After 2 hr, the sample was hydrolyzed by pouring it into aqueous sodium bicarbonate. The organic products were extracted into ether and dried ($MgSO_4$). Evaporation of the ether solution gave a sample of **19** whose properties were in good agreement with those reported earlier.[10] Alcohol **19** can be separated from the product of solvolysis using tlc (silica gel, six elutions with 1:1 benzene–chloroform). The solvolysis product does not give a spot corresponding to **19** on tlc analysis.

ψ-*endo*-Tricarbonyl(6-phenyl-3,5-hexadien-2-yl 3,5-dinitrobenzoate)iron (12b). A sample of **12b** was heated in 80% aqueous acetone at 60° for 12 hr. The solvolysis solution was then added to a large volume of aqueous sodium bicarbonate which was in turn extracted with several portions of ethyl ether. Drying ($MgSO_4$) and evaporation of the ether solution left a yellow solid with a broad melting range. Preparative tlc (silica gel–chloroform) gave two bands. The upper band was identified as ψ-*endo* alcohol **12a** while the lower band appeared to be a mixture of ψ-*exo* and uncomplexed alcohols, **11a** and **13a**.

A carefully degassed 10^{-2} *M* solution of **12b** in 80% aqueous acetone was sealed under nitrogen and heated for 12 hr at 60°. The mixture was worked up as rapidly as possible by treatment with aqueous sodium bicarbonate and subsequent ether extraction. Equal weights of the solvolysis product and four standard ψ-*exo*–ψ-*endo* alcohol mixtures which contained 10, 7.5, 5, and 2.5% ψ-*exo* isomer were spotted side by side on each of several tlc plates, and the plates were eluted with chloroform. With iodine visualization the best match was between 5 and 7.5% ψ-*exo* alcohol. The iodine stained plates were heated briefly in an oven at 100° and were placed in an iodine chamber to cool. They were heated a second time to remove iodine, and the cooled plates were sprayed with a 10% aqueous ammonium thiocyanate solution to detect ferric ion. After drying in an oven the intensities of the red spots from the solvolysis products again indicated the presence of a little more than 5 but definitely not as much as 7.5% ψ-*exo* alcohol (**11a**). A similar tlc product analysis performed after *ca.* 3–4% solvolysis indicated an identical product composition.

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