Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

GENERATION OF *trans*-π-PENTADIENYLIRON TRICARBONYL CATIONS FROM PROTONATION OF (*trans,trans*-2,4-HEXADIENAL)IRON TRICARBONYL

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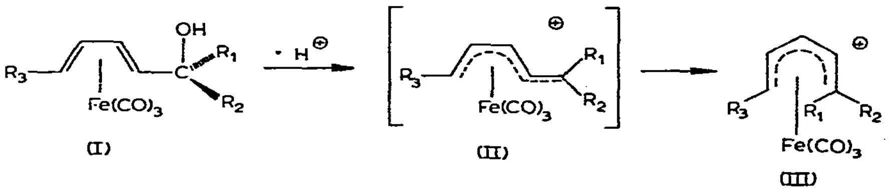
(Received March 21st, 1972)

SUMMARY

Protonation of (*trans,trans*-2,4-hexadienal)iron tricarbonyl, (V), has been shown to yield two *trans*-pentadienyliron cations, an *s-cis* form, (VIa) and an *s-trans* form (VIb), in an approximately equal ratio. This ratio represents a kinetically controlled product distribution and indicates that the original unprotonated aldehyde complex was present in equally populated *s-cis* and *s-trans* forms. Both *trans* ions, (VIa) and (VIb) isomerize to the *cis* ion (VIIb), $\Delta F^{\neq} = 18.5$ kcal/mol. From an analysis of the kinetics and NMR line widths it is clear that the barrier to rotation about the C_1–C_2 bond in (VI) is at least 15 kcal/mol and probably considerably exceeds this number. At temperatures below −100° the OH protons of (VIa) and (VIb) can be observed owing to slow exchange at this temperature. Chemical shifts of these protons indicate extensive charge delocalization.

INTRODUCTION

Reports of preparation and characterization of *cis*-pentadienyliron tricarbonyl cations have been extensive[1]. The possibility that *trans*-pentadienyliron tricarbonyl cations, (II), might also be stable was first suggested and explored by Mahler and Pettit[1a]. Although Pettit did not directly observe the *trans* ions, he postulated that they were likely involved as intermediates in the formation of the *cis* ions, (III), from the (*trans*-pentadienol)iron complexes, (I).



The initial formation of a *trans* ion from systems such as (I) received strong support from the observations of Clinton and Lillya[2] that the solvolysis of several

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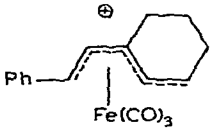
dinitrobenzoate esters of structure (I) proceeded with complete or nearly complete retention of configuration. These experiments indicated *trans* ions were formed and had sufficiently long lifetimes under solvolytic conditions to undergo nucleophilic attack before isomerization to *cis* ions.

Recently both Sorensen[3] and Lillya[4] have reported direct observations of *trans* ions. Sorensen has observed that the *trans* ion (II), $R_1=R_2=R_3=CH_3$, is in equilibrium with the corresponding *cis* ion, while Lillya has observed the *trans* ion (IV) in which the ring structure constrains the ion in a *trans* form.



(IV)

Lillya and coworkers[2,5] have recently reported the protonation of a series of (*trans,trans*-dieneone)iron tricarbonyl complexes. Lillya has shown that these species are good models for the *trans*-pentadienyliron cations and from analysis of the proton chemical shifts in these species argues for a conjugative stabilization of the ion rather than stabilization by neighboring group participation of iron.

In this paper we wish to report a detailed NMR study of the protonation of (*trans,trans*-2,4-hexadienal)iron tricarbonyl, (V), which lends considerable insight into the structure of the *trans* pentadienyliron cations formed and the energetics involved in their interconversion and their rearrangement to *cis* ions. Data reported here also yield information regarding the equilibrium between the *s-cis* and *s-trans* forms of the unprotonated aldehyde complex, (V).

RESULTS AND DISCUSSION

The proton chemical shifts and coupling constants for (*trans,trans*-2,4-hexadienal)iron tricarbonyl, (V), in $CDCl_3$ are summarized in Table 1. When (V) in CD_2Cl_2 is protonated at $-120°$ in HSO_3F/SO_2ClF (1/3 v/v) the NMR spectrum of the resultant solution recorded at $-50°$ indicates the formation of two *trans* ions (VIa) and (VIb) in the ratio of ca. 1/1. Ion (VIa) has the *s-cis* configuration about C_1–C_2 while ion (VIb) has the *s-trans* configuration. The NMR data for these ions is summarized in Table 1. The assignment of the two isomers observed is based primarily on the difference in the H_1–H_2 coupling constant with the larger coupling (10.5 Hz) being assigned to the *trans* arrangement of H_1–H_2[6]. Once this assignment is made all other resonances and coupling constants could be unambiguosly assigned on the basis of spin–spin decoupling experiments.

When the solution of ions (VIa) and (VIb) is warmed to $-28°$ they undergo quantitative rearrangement to the *cis* ion (VIIb) with a first-order rate constant*, $k=$ca. 2×10^{-4} sec^{-1} corresponding to $\Delta F^{\neq}$ of ca. 18.5 kcal/mol. Assignment of structure (VIIb) is based on the H_1–H_2 coupling constant (10 Hz) whose magnitude indicates a *trans* coupling and the assumed steric preference of an *anti*-OH *versus* a

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* Assuming the Pettit mechanism of isomerization[1a], this may represent a pseudo first-order rate constant.

TABLE 1

NMR SPECTRAL DATA FOR (V), (VIa), (VIb), AND (VIIb)[a]

Compound	*Chemical shifts*[a,b]						*Coupling constants*[c]
	H_1	H_2	H_3	H_4	H_5	5-CH_3	
(V)	0.76	8.96	4.50	4.97	8.57	8.72	$J_{1,2}$ 4.4, $J_{2,3}$ 8.2, $J_{2,4}$ 1.0, $J_{3,4}$ 5.0, $J_{3,5}$ 1.0, $J_{4,5}$ 8.1
(VIa)	1.26	8.65	3.46	4.10	6.78	8.23	$J_{1,2}$ 4, $J_{2,3}$ 8.5, $J_{3,4}$ 5, $J_{4,5}$ 9, $J(CH_3–H_5)$ 5
(VIb)	1.90	8.05	3.89	4.24	6.43	8.23	$J_{1,2}$ 10.5, $J_{2,3}$ 8, $J_{3,4}$ 5, $J_{4,5}$ 9, $J(CH_3–H_5)$ 5
(VIIb)	3.97	4.81	3.51	4.40	7.47	8.25	$J_{1,2}$ 10, $J_{2,3}$ 7, $J_{3,4}$ 7, $J_{4,5}$ 11, $J(CH_3–H_5)$ 6

[a] Spectra were obtained on a Varian HA-100 MHz spectrometer. For (V) spectra were recorded in degassed $CDCl_3$ at 30° using internal TMS as a lock signal and standard. For (VIa) and (VIb) spectra were recorded at $-50°$ while for (VIIb) at $-30°$ in HSO_3F/SO_2ClF (1/3 v/v) using HSO_3F as the lock signal and internal CH_2Cl_2 (τ 4.70) as the standard. At -50 to $-30°$ no OH signal is observed (see text). [b] Chemical shifts recorded in τ. [c] Coupling constants in Hz. Coupling constants and shift assignments completely verified by spin–spin decoupling experiments.

syn-OH[3]. The following additional important observations were made: (1) Throughout the isomerization to (VIIb), (VIa) and (VIb) remain in a 1/1 ratio. (2) (VIIb) is the only detectable rearrangement product; no intermediates are visible. (3) Spectra of ions (VIa) and (VIb) could be recorded at temperatures as high as 0° ($t_{\frac{1}{2}}$ at 0° ca. 2 min) at which temperature the H_1 and H_2 resonances remain sharp and unbroadened (< 1 Hz).

These observations together with additional information (see below) allow several observations to be made about the free energies of activation and equilibrium constants for the processes shown in Scheme 1*. Applying the slow exchange equation[7] for NMR line-broadening indicates that if H_1 and H_2 signals are sharp and unbroadened (< 1 Hz) at 0° the rate constants for interconversion (k_{2a} and k_{2b}) must be less than ca. 3 $\sec^{-1}$ indicating a barrier for interconversion ($\Delta F^{\neq}$) of greater than ca. 15 kcal/mol. The fact that (VIa) and (VIb) rearrange cleanly to (VIIb) [no (VIIa) detected] with $\Delta F^{\neq} = 18.5$ kcal/mol and (VIa) and (VIb) remain in equal proportions indicates one of the following situations:

(1) The production of (VIIb) occurs exclusively from (VIb) thus necessitating that the barrier for interconversion of (VIa) and (VIb) lies between 15 and 18 kcal/mol. If the barrier for interconversion were greater than 18 kcal/mol, k_{2a} would be on the order of k_{3b} and (VIa) would thus increase relative to (VIb) during the isomerization;

or (2) Both (VIa) and (VIb) isomerize to (VIIa) and (VIIb), respectively, at approximately equal rates ($k_{3a} \approx k_{3b}$) but (VIIa) once formed isomerizes rapidly to (VIIb) (*i.e.* $k_{4a} \geqslant 5k_{3a}$). This would imply that $K_4 \geqslant$ ca. 50 and that $\Delta F^{\neq}$ for conversion of (VIIa) to (VIIb) is less than or equal to ca. 18 kcal/mol.

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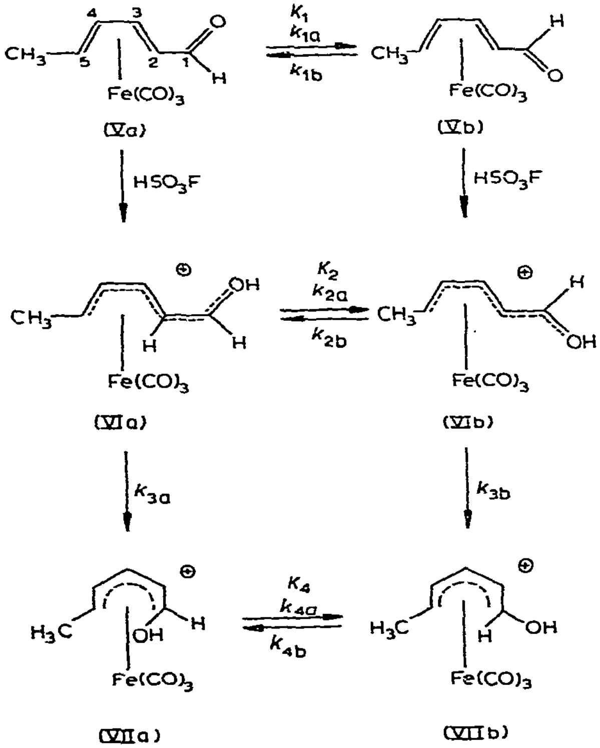
* In analogy with Sorensen's[3] and Lillya's[4] reports of stereospecific conversion of *trans* to *cis* ions, (VIa) upon isomerization should lead to (VIIa), while (VIb) should lead to (VIIb).

Although the present data do not allow a clear choice to be made the authors presently favor the latter explanation. In terms of the Pettit mechanism for geometric isomerization[1a] it is not unreasonable that $k_{3a}=k_{3b}$. Based on Sorensen's observation of facile conversion of (III), $R_1=R_3=CH_3$, $R_2=H$, to (III), $R_1=R_2=CH_3$, $R_1=H$, at 0° (no rate constant quoted) it would not seem unreasonable for the rate of rotation for the hydroxyl-substituted (VIIa) to be somewhat greater.

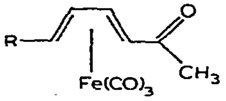
SCHEME 1



The barrier to C_1–C_2 rotation in protonated benzaldehyde is approximately 15.5 kcal/mol[8]. It is therefore perhaps not so surprising that the C_1–C_2 rotational barrier in (VI) is at least this large since the (diene)iron tricarbonyl group appears to be considerably better than the phenyl group at stabilizing positive charge, based on Lillya's solvolysis data[2a,b]. In fact, a barrier considerably larger than 15 kcal/mol might be expected.

With a C_1–C_2 rotational barrier of greater than 15 kcal/mol the half-lives of species (VIa) and (VIb) become of the order of many hours at temperatures below −80°; therefore, the results of low temperature protonation and observations should yield a kinetically controlled ratio of (VIa) to (VIb) corresponding to the (Va) to (Vb) equilibrium ratio. This would allow estimation of K_1 and, if the kinetic ratio were not equal to the thermodynamic ratio of (VIa) to (VIb), possible measurement of the rotational barrier by observing the equilibration of the two isomers. Careful protonation of (V) at −125° and immediate observation of the solution at −100° shows (VIa) and (VIb) in the same ca. 1/1 ratio as previously observed*. This experiment then indicates that K_1 is approximately 1. Indeed, if the barrier to interconversion of (VIa) and (VIb) is greater than ca. 20 kcal/mol the 1/1 ratio may represent a kinetic rather than a thermodynamic distribution even at −28° where interconversion would not be competitive with rearrangement to (VIIb).

The fact that both *s-cis* and *s-trans* conformers are equally populated in (V) is in contrast to the observation of Lillya[2c] for ketones (VIII) in which the *s-cis* form is the only detected conformer.



(VIII a) R = CH_3

(VIII b) R = C_6H_5

Further support of the contention that $K_1 = 1$ is that solutions of (V) in CS_2 exhibit two equal intensity carbonyl stretching frequencies at 1687 and 1699 cm^{-1} corresponding to (Va) and (Vb)**. This is consistent with the observation that (VIIIa) and (VIIIb), which exist predominately as *s-cis* conformers, exhibit only single bands, while α,β unsaturated enones[10] and 2,4-dienones[2c], in which the *s-cis* and *s-trans* conformers are each significantly populated, exhibit different stretching frequencies for the two forms.

EXPERIMENTAL

General

Low temperature NMR spectra were recorded either on the Jeolco C-60HL spectrometer for temperatures below −90° or on the Varian HA-100 spectrometer. All decoupling experiments were performed on the Varian instrument. For sharpest spectra it was necessary to tune the spectrometers at low temperatures after thorough thermal equilibration with a sample of $HSO_3F/SO_2ClF/CH_2Cl_2$. Infrared spectra were recorded in CS_2 solution on a Perkin–Elmer 421 spectrometer. Fluorosulfonic acid was obtained commercially from Allied Chemical, redistilled and sealed in ampoules under nitrogen before use. Sulfuryl chloride floride was obtained from Allied Chemical and used as received.

Protonation of complexes

Samples were prepared at low temperatures directly in NMR tubes and sealed under vacuum. The basic apparatus used consisted of an NMR tube sealed to a 24/40 male joint. Between the joint and the NMR tube was a high vacuum stopcock.

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* At −114° two additional broad signals appear at τ −1.25 and τ −1.90 integrating for ca. one proton. At temperature above −114° the signals broaden further and eventually merge (ca. −80°) with the acid signal. Based on their chemical shifts and temperature dependence these are clearly the OH proton signals for (VIa) and (VIb) which are observable due to slow exchange at these temperatures. It is clear that very substantial positive charge delocalization is occurring by comparing the OH shifts with OH shifts of other protonated ketones and aldehydes[9]. These resonances are at even higher fields than those for protonated benzophenone and dicyclopropylketone[9a].

** Thus far, attempts to obtain the barrier of interconversion between (Va) and (Vb) using low temperature NMR have been unsuccessful.

The apparatus was flushed with nitrogen passed through the high vacuum stopcock and the NMR tube was then cooled to −78°. HSO_3F (0.15 ml) and SO_2ClF (0.30 ml) were placed in the NMR tube and mixed with a long glass rod. This mixture was degassed on a vacuum line and removed under nitrogen to the low temperature bath and cooled to ca. −120°. A second "buffer" layer of SO_2ClF (0.15 ml) was carefully condensed onto the top of the acid mixture. A degassed solution of iron complex (50 mg) in CD_2Cl_2 (0.20 ml) which had been previously prepared in a Schlenk tube was carefully transferred under nitrogen with a capillary dropper onto the "buffer" layer. After the CD_2Cl_2 layer had cooled to −120° (ca. 15 sec) the layers were mixed rapidly until a homogeneous dark red solution was obtained. The apparatus was then transferred to a vacuum line, the tube cooled with liquid nitrogen and then sealed under high vacuum. The sealed tubes were then stored under liquid nitrogen until NMR spectra were recorded. Using this technique very sharp spectra could be obtained with no evidence of line broadening due to paramagnetic impurities.

(trans,trans-2,4-Hexadienal)iron tricarbonyl (V)

This compound was prepared as reported by Pettit[1a]. Before use the complex was bulb to bulb distilled under high vacuum into a Schlenk tube and thereafter handled under purified nitrogen.

ACKNOWLEDGEMENTS

Partial support of this work by the National Science Foundation (Grant numbers GU-2059 and GP-29580) is gratefully acknowledged.

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