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Stereochemical Course of the Reaction of Iron Carbonyl with Diastereomeric Vinyloxiranes

Sir:

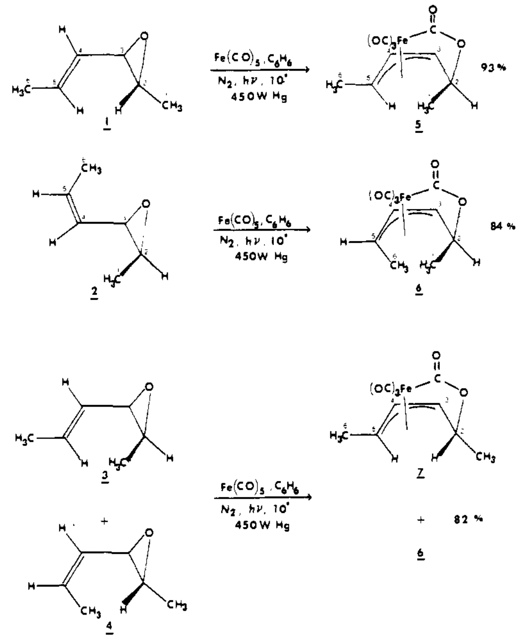
The reaction of the vinylcyclopropyl system with iron carbonyl has been investigated extensively.[1] Recently the analogous reaction with vinyloxiranes has been reported.[2] This latter system appeared amenable to a detailed stereochemical analysis, and we report results of the reaction using diastereomeric vinyloxiranes.

Starting with the three pure dienes (*E*,*E*)-2,4; (*Z*,*Z*)-2,4; and (*Z*,*E*)-2,4-hexadienes, monoepoxidation yielded the vinyloxiranes **1**, **2**, **3** + **4**, respectively.[3] Both thermally and photochemically these compounds reacted with iron carbonyl to yield ferrelactone complexes. The thermal reaction yielded mixtures of diastereomers[5] but the photochemical reaction[6] proceeded *completely stereospecifically* (Scheme I).

The starting point for unraveling the stereochemical structures of complexes **5**, **6**, and **7** was an X-ray crystallographic determination on **7**. With this established, NMR studies enabled elucidation of the structures of **5** and **6**.

Ferrelactone **7** crystallized in the centrosymmetric orthorhombic space group *Pbca*. The cell dimensions were *a* = 12.0732 (16) Å, *c* = 12.2010 (15) Å, and ρ_{calcd} = 1.575 g/cm^3 for *Z* = 8. X-Ray diffraction data ($2\theta_{max}$ = 50°, Mo Kα radiation) were collected with a Picker FACS-1 diffractiometer and the structure was solved via Patterson, Fourier, and least-squares refinement methods. The final discrepancy indices were R_F = 3.21%, R_{wF} = 3.06% for 2377 independent reflections. The molecular structure, with selected bond distances, is shown in Figure 1.

Scheme I



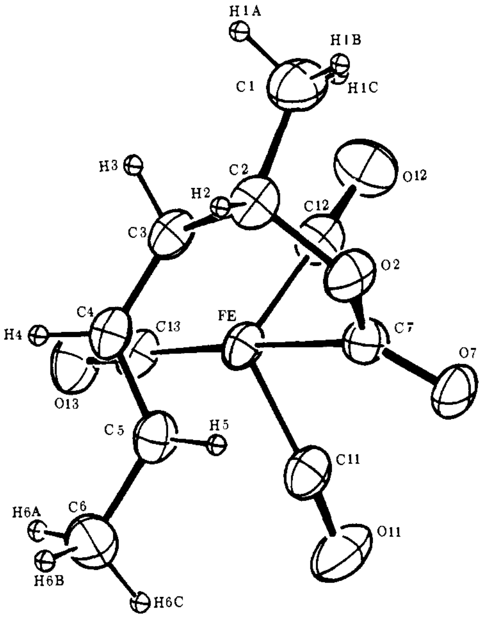


Figure 1. Molecular geometry of ferrelactone **7**. Important intraligand bond distances (in Å) are: C(1)-C(2) = 1.503 (5), C(2)-C(3) = 1.510 (4), C(3)-C(4) = 1.406 (3), C(4)-C(5) = 1.389 (4), C(5)-C(6) = 1.498 (4); C(2)-O(2) = 1.438 (3), O(2)-C(7) = 1.364 (3), C(7)-O(7) = 1.211 (3). Iron-carbon bond distances are: Fe···C(3) = 2.090 (2), Fe···C(4) = 2.077 (3), Fe···C(5) = 2.209 (3), and Fe-C(7) = 1.985 (2).

Using the ^{1}H NMR spectrum of **7** as a reference the relative stereochemistries of **5** and **6** were determined by analysis of coupling constants and induced chemical shifts (Table I). First, comparing **5** and **7** the only difference in coupling constant is the vicinal coupling $^3J_{2,3}$ of 4.0 Hz in **5**

Table I NMR Data for Ferrelactones[a]

Compound	Position	Chemical shifts (ppm)	Coupling constants (Hz)
5	1	1.34	$J_{1,2}$ = 6.5
	2	4.39	$J_{2,3}$ = 4.0
	3	4.58	$J_{3,4}$ = undetermined
	4	4.63	$J_{4,5}$ = 12.0
	5	4.14	$J_{5,6}$ = 6.0
	6	1.88	
6	1	1.43	$J_{1,2}$ = 6.5
	2	4.60	$J_{2,3}$ = 5.2
	3	5.13	$J_{3,4}$ = 8.7
	4	4.31	$J_{4,5}$ = 9.7
	5	4.81	$J_{5,6}$ = 7.4
	6	1.80	
7	1	1.32	$J_{1,2}$ = 6.5
	2	4.25	$J_{2,3}$ = 1.2
	3	4.38	$J_{3,4}$ = 7.5
	4	4.77	$J_{4,5}$ = 12.0
	5	4.03	$J_{5,6}$ = 6.0
	6	1.84	

[a] NMR spectra were obtained using a Varian HA-100 or HR 220 with TMS as internal standard at δ 0.00 ppm and $CDCl_3$ as solvent.

compared to 1.2 Hz for trans $^3J_{2,3}$ in **7** suggesting a cis arrangement for these protons in **5**. Similarly $^3J_{2,3}$ of 5.2 Hz in **6** indicates a cis relationship. Considering the C_4 and C_5 protons, values of 12.0 Hz in **7** and **5** fix these as trans while a value of 9.75 Hz indicates a cis orientation in **6**. Further evidence for the relative stereochemistry at C_4 and C_5 in **5**, **6**, and **7** was obtained by observing induced chemical shifts using Eu(fod)$_3$. The induced downfield shifts for the C_5 proton in **5**, **6**, and **7** were 10.0, 9.9, and 3.8 ppm per mole of Eu(fod)$_3$ per mole of ferrelactone, respectively. The downfield shifts for the C_5-methyl group in **7**, **5**, and **6** were 2.1, 2.1, and 5.8 ppm per mole of Eu(fod)$_3$ per mole of ferrelactone, respectively. Assuming a model in which the shift reagent is coordinated with the lactone ring, the relative large shift of the C_5 methyl group and relatively small shift of the C_5 proton in **6** indicates a cis stereochemistry. Since **7** is known to be trans (X-ray), similarity in its shift behavior with **5** indicates a trans stereochemistry for the latter.

With the structures of ferrelactones **5**, **6**, and **7** established, the stereochemical results may be summarized as follows: **1** → **5** proceeds with *retention* of configuration about the C_4–C_5 double bond, but a *change* in the relative configuration between C_2 relative to C_3. This change amounts to rotation about the C_2–C_3 bond. Reaction **2** → **6** proceeds with overall *retention* of the stereochemical relationships between reactant and product.

In the sequence of reaction steps leading to the ferrelactone the generation of the allylic system is of key importance. A priori this could occur in two distinct ways, namely, initial complexation of the double bond with photochemically generated $Fe(CO)_4$ followed by cleavage of the oxido ring and lactone formation, or, alternatively, initial complexation of the oxido oxygen with the electrophilic $Fe(CO)_4$ and ring cleavage followed by lactone formation. Since neither route uniquely accounts for the observed stereochemical course, the mechanistic aspects of this reaction remain a continuing research objective.

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(3) Epoxidation[4] of *trans,trans*-2,4-hexadiene (CH_3CO_3H, CH_2Cl_2, 0°) yielded **1** in 89% yield: bp 21–22 (0.05 mm); NMR δ H_1 1.29, H_2 2.86, H_3 3.00, H_4 5.91, and H_8 1.70; J (Hz) $J_{1,2}$ 5.2, $J_{2,3}$ 2.2, $J_{3,4}$ 8.1, $J_{3,5}$ 0.4, $J_{4,5}$ 15.6, $J_{4,6}$ 1.6, and $J_{5,6}$ 6.6. *cis,cis*-2,4-Hexadiene yielded **2**: bp 20–21 (0.08 mm); NMR δ H_1 1.25, H_2 3.19, H_3 3.62, H_4 5.22, H_5 5.85, and H_8 1.78; J (Hz) $J_{1,2}$ 5.5, $J_{2,3}$ 4.4, $J_{3,4}$ 8.1, $J_{3,5}$ 1.0, $J_{4,5}$ 11.1, $J_{4,6}$ 1.7, and $J_{5,6}$ 7.1. *cis,trans*-2,4-Hexadiene yielded **3** and **4**, and they were not separable by fractional distillation.

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(6) Irradiations *were carried* out in an *all* quartz system. Compound **5** had mp 130–131°. Anal. Calcd for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 45.22; H, 3.90. Acyl carbonyl 1672 cm^{-1}; C≡O, 1990, 2004, and 2034 cm^{-1}. Compound **6** had mp 103–104. Anal. Calcd for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 44.99; H, 3.86. Acyl carbonyl, 1674; C≡O, 1999, 2008, and 2040 cm^{-1}. Compound 7 had mp 108–109°. Anal. for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 45.00; H, 3.89. Acyl carbonyl, 1670 cm^{-1}; C≡O, 1995, 2005, and 2035 cm^{-1}. The starting 2,3-oxidohex-4-enes were stable under the photolytic conditions in the absence of $Fe(CO)_5$.

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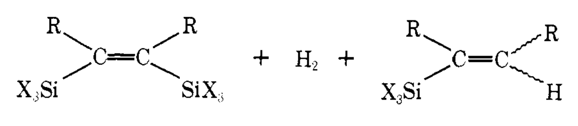
A Novel Dehydrogenative Cis Double Silylation of Internal Acetylenes with Hydrosilanes. Catalysis by Diethyl(bipyridyl)nickel(II)

Sir:

There have been two types of addition reactions of silicon hydrides to carbon–carbon multiple bonds in the presence of transition metal catalysts. One is the well-known hydrosilylation[1] and the other the recently discovered, nickel or palladium catalyzed, double silylation of dienes and acetylenes with disilicon hydrides involving the cleavage of the Si-Si bond while leaving intact the Si-H bond.[2] We report here the third type of addition reaction, viz., dehydrogenative, stereoselective cis double silylation of internal acetylenes with monosilicon hydrides catalyzed by diethyl(bipyridyl)nickel(II), as represented by eq 1.



(1)