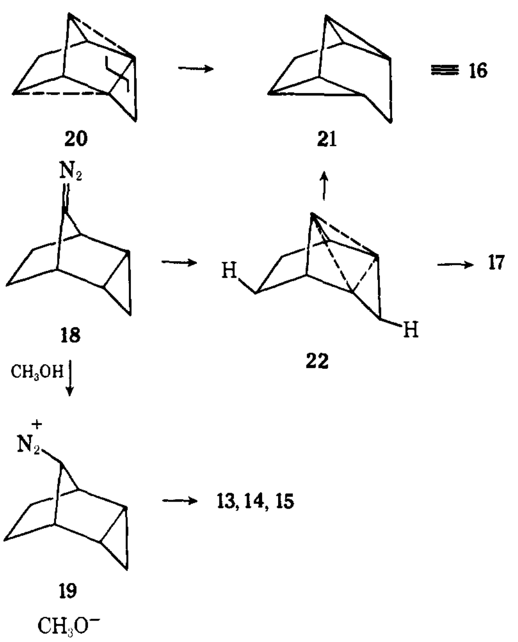

Thus, decomposition of diazo compound **18** generates a bivalent intermediate, which rearranges *via* bond formation between C-2 and C-8, fission at C-2–C-4, and bonding between C-4 and C-6, with concomitant hydrogen migration (**20**) to generate **21** (equivalent to **16**). Therefore, it seems clear that the carbene intermediate rearranges with transannular trishomocyclopropenyl participation. It would also seem likely that delocalization is present in the intermediate.[9] Whether or not this interaction is chemically significant is a matter to be determined by further experimentation. Representing the intermediate as **22**, the formation of tetracyclic **16** by a C-6 → C-8 hydrogen shift is a symmetry-allowed process $({}_{\sigma}2_{a} + {}_{\omega}2_{a} + {}_{\omega}0_{a})$.[10] In harmony with this, in run 1 (Table I) it is found that tetracyclic **16** contains 23% d_1; therefore a simple C-6 → C-8 shift represents the major reaction pathway, although perhaps not the sole pathway.[11]

It appears, therefore, that *exo*-8-carbenatricyclooctane rearranges by 1,2-alkyl migration and *endo*-8-carbenatricyclooctane rearranges *via* a trishomocyclopropenyl interaction with loss of a proton either from C-6 to form **16** or from C-3 to form tricyclooctene **17**.

[9] R. Gleiter and R. Hoffmann, *ibid.*, 90, 5457 (1968).

[10] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 169–173.

[11] An intermolecular process for conversion of **22** to **16**, involving loss of a proton from **22**, generation of a carbanion related to **16**, and subsequent protonation, would be expected to exhibit a deuterium isotope effect near unity for deuterium incorporation; K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

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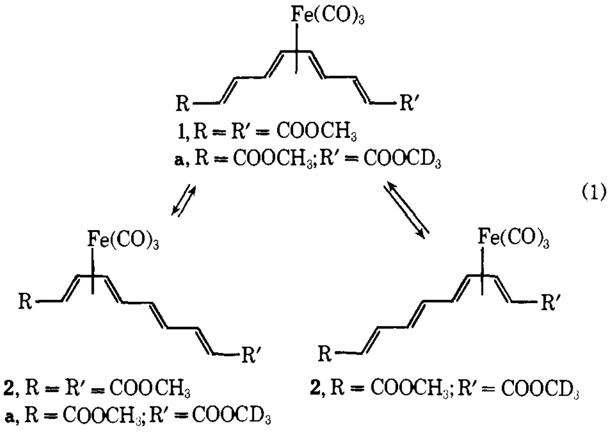
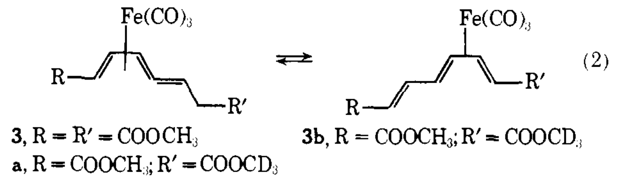
Shift Isomerization and Racemization of Some Polyene–*Tetrahapto*iron Tricarbonyl Complexes

Sir:

We have studied the relationship between racemization and shift isomer interconversion in two series of polyene–*tetrahapto*iron tricarbonyl complexes: optically active and deuterated complexes of 1,8-dicarbomethoxy-1,3,5,7-octatetraene (eq 1) and optically active

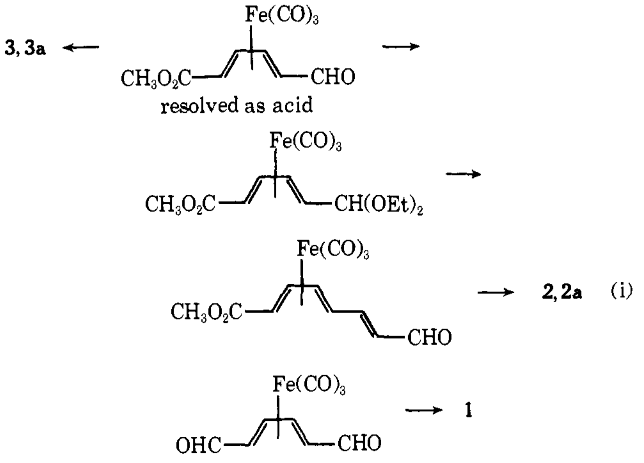


and deuterated complexes of 1,6-dicarbomethoxy-1,3,5-hexatriene (eq 2).[1] For the octatetraene complexes



rates of the following processes were determined: interconversion of middle (**1**) and end (**2**) shift isomers; interconversion of the two end isomers (**2a** and **2b**); racemization of the optically active end isomer (−)-**2**. For the hexatriene complexes rates of the following processes were measured: interconversion of the two deuterated complexes **3a** and **3b**; racemization of optically active (−)-**3**. All of the above reactions followed

[1] These complexes were prepared from the appropriate aldehyde and carbomethoxymethylenetriphenylphosphorane by general procedures described earlier (eq i).[2,3] All had the expected analytical and spectral propertes: **1**, mp 107.5–109°; nmr (C_6D_6) 3.46 (OCH_3); **2**, mp 123–125°; nmr δ 3.37 (OCH_3), 3.48 (OCH_3); **3**, mp 97–98°; nmr δ 3.40 (OCH_3), 3.47 (OCH_3). In **2a** the resonance at δ 3.48 was absent, while in **3a** the resonance at δ 3.47 was absent.



[2] H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, **87**, 2606 (1965).

[3] H. Whitlock, C. R. Reich, and W. D. Woessner, *ibid.*, **93**, 2483 (1971).

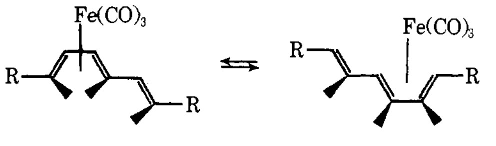
Table I. Rates of Interconversion and Racemization of Iron Complexes at 119.42 ± 0.03° [a]

Complex	$k \times 10^4$, min^{-1}	$k' \times 10^4$, min^{-1}	$K = k/k'$
$\mathbf{3a} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathbf{3b}^b$	6.91 ± 0.35	7.44 ± 0.37	0.93 ± 0.02[f]
$(-)\text{-}\mathbf{3}^c \xrightarrow{k} (\pm)\text{-}\mathbf{3}$	2.70 ± 0.11		
$\mathbf{1} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathbf{2}^d$	95.23 ± 3.81	5.10 ± 0.20	18.6 ± 0.4
$\mathbf{2a} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathbf{2b}^e$	10.15 ± 0.81	9.90 ± 0.79	1.03 ± 0.04
$(-)\text{-}\mathbf{2}^c \xrightarrow{k} (\pm)\text{-}\mathbf{2}$	13.16 ± 0.32		

[a] All rates were measured in degassed benzene by using the relative intensities of the methoxy resonances of the various shift isomers. [b] From **3a**. [c] By optical activity. [d] From **1**. [e] From **2a**. [f] Standard deviation.

first-order concentration-independent kinetics.[4] The rate and equilibrium constants determined for these two sets of processes are tabulated in Table I.

For the hexatriene complexes movement of the iron tricarbonyl back and forth is 2.6 times faster than racemization. This is consistent with the observation that movement of the $Fe(CO)_3$ group along the face of the triene should result in retention of configuration of an optically active complex (eq 3). The behavior



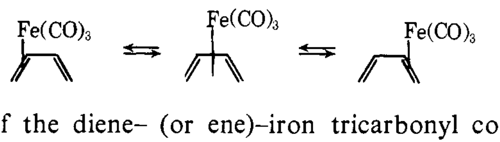
(3)

of the octatetraene complexes is summarized in eq 4; here also[3] interconversion of the two end isomers **2a** and **2b** is faster than can be accounted for by a linear (**2a** ⇄ **1a** ⇄ **2b**) mechanism.

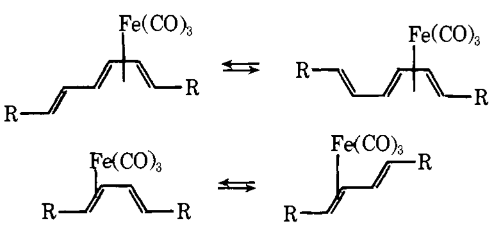
$$\begin{tikzcd}
& \mathbf{1,1a} \arrow[dl, shift right, "18.6"'] \arrow[dr, shift left, "18.6"] & \\
\mathbf{2a} \arrow[ur, shift right, "1.0"'] \arrow[rr, shift left, "1.5"] & & \mathbf{2b} \arrow[ul, shift left, "1.0"'] \arrow[ll, shift left, "1.5"]
\end{tikzcd}$$

$$(-)\text{-}\mathbf{2} \xrightarrow{2.6} (\pm)\text{-}\mathbf{2} \qquad (4)$$

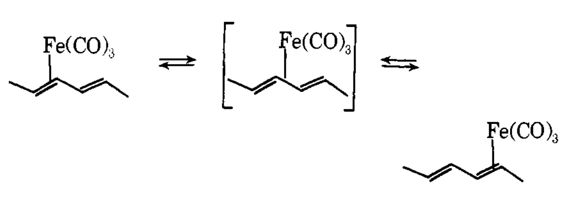
The relationship of racemization to shift isomerization of the above complexes follows from the conceptual dissection of these reactions into three processes. (1) Dissociation of a diene-*tetrahapto*iron tricarbonyl complex to an *s-cis*-diene-*dihapto*iron tricarbonyl species (eq 5). (2) Rotation about σ bonds that are not part of the diene- (or ene)-iron tricarbonyl complex (eq 6). (3) Direct interconversion of two *s-trans*-diene-1,2-*dihapto* complexes with the possible intermediacy of the 3,4-*dihapto* complex (eq 7).



(5)

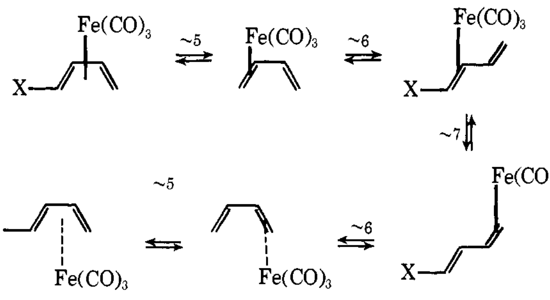


(6)

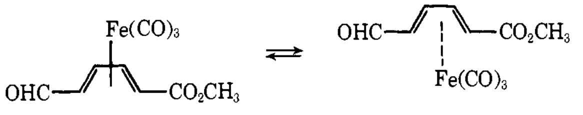


(7)

Equations 5 and 6 account for shift isomerization (but *not* racemization) of the hexatriene complexes. Equation 7 affords, in combination with eq 5 and 6, a mechanism for racemization of diene-*tetrahapto*iron tricarbonyls (eq 8) that includes the cases of **2** and **3**. In agreement with this proposed mechanism is the observation that (+)-methyl 5-formyl-2,4-pentadienoate-iron tricarbonyl racemizes ($k_{rac} = 2.37 \times 10^{-4}$ min^{-1} at 119.4°) by a first-order process (eq 9).



(8)



(9)

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Synthesis and Interconversion of Two Diastereoisomeric Polyene–Bis(iron tricarbonyl) Complexes

Sir:

We have synthesized the novel meso and optically active isomers of dimethyl 2,4,6,8-decatetraenedio-

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[4] A much slower second-order ligand-exchange process could be observed on heating the complexes with equimolar amounts of free deuterium-labeled ligand.

[5] National Institutes of Health Predoctoral Fellow.