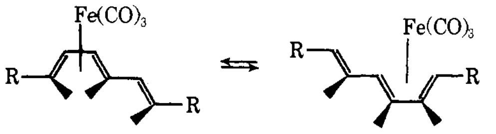
**Table I.** Rates of Interconversion and Racemization of Iron Complexes at 119.42 ± 0.03° [a]

| 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.

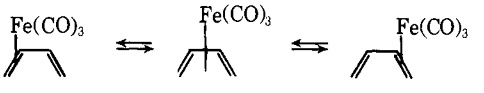
For the hexatriene complexes movement of the iron tricarbonyl back and forth is 2.6 times faster than racemization. This is consistent with the observation that movement of the Fe(CO)$_3$ group along the face of the triene should result in retention of configuration of an optically active complex (eq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



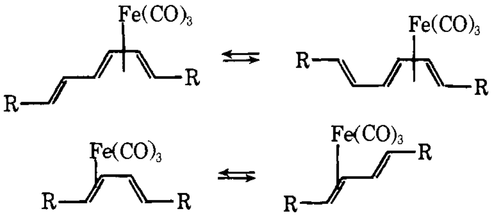
(3)

$$\begin{tikzcd} & \mathbf{1,1a} \arrow[dl, shift right, "18.6"'] \arrow[dr, shift left, "18.6"] & \\ \mathbf{2a} \arrow[ur, shift right, "1.0"'] \arrow[rr, shift left, "1.5"] & & \mathbf{2b} \arrow[ul, shift left, "1.0"] \arrow[ll, shift left, "1.5"] \end{tikzcd} \qquad (-)\text{-}\mathbf{2} \xrightarrow{2.6} (\pm)\text{-}\mathbf{2} \tag{4}$$

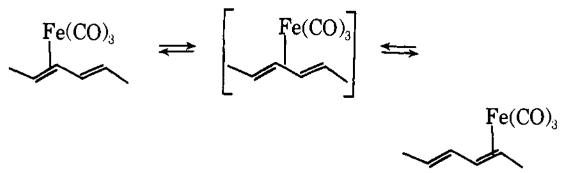
The relationship of racemization to shift isomerization of the above complexes follows from the conceptual dissection of these reactions into three processes. (1) Dissociation of a diene-*tetrahapto*iron tricarbonyl complex to an *s-cis*-diene-*dihapto*iron tricarbonyl species (eq 5). (2) Rotation about $\sigma$ 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)

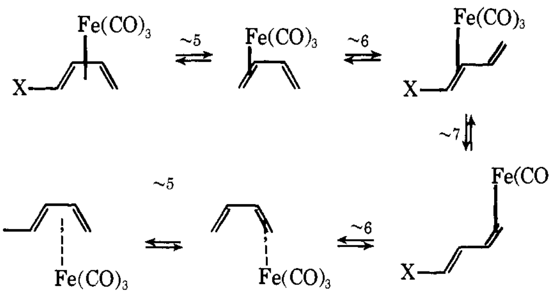


(6)

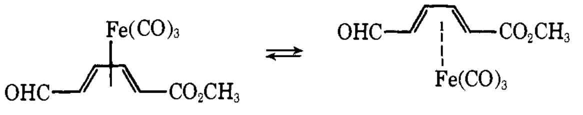


(7)

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 ($k_{\text{rac}}$ = 2.37 × 10$^{-4}$ min$^{-1}$ at 119.4°) by a first-order process (eq 9).



(8)



(9)

**Acknowledgment.** Partial support by the National Science Foundation is acknowledged.

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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.

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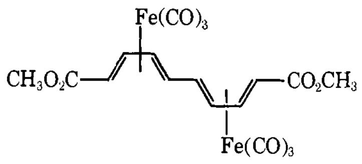
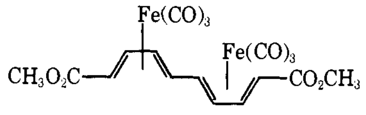
### Synthesis and Interconversion of Two Diastereoisomeric Polyene–Bis(iron tricarbonyl) Complexes

*Sir:*

We have synthesized the novel meso and optically active isomers of dimethyl 2,4,6,8-decatetraenedioate-(2,3,4,5-*tetrahapto*:6,7,8,9-*tetrahapto*bis(iron tricarbonyl) (**1** and **2**, respectively). The basic proposal was

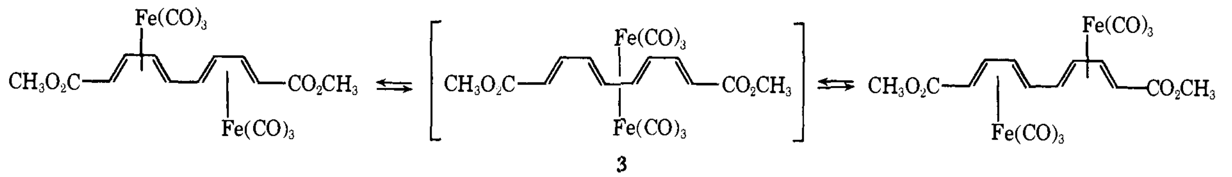


**1**



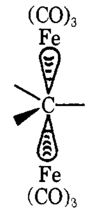
**2**

that racemization of the optically active complex (eq 1)

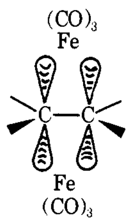


(1)

should proceed through the intermediate or transition state **3**. Knowing the rate of migration of iron tricarbonyls in mono(iron tricarbonyl) complexes,[1-3] one should be able to estimate the "cost" of two irons sharing a $\pi$ system in the manner



or



Treatment of (−)-dimethyl 2,4,6,8-decatetraenedioate-2,3,4,5-*tetrahapto*iron tricarbonyl[3] ($[\alpha]_{332} - [\alpha]_{375} = 18{,}830°$) ($c$ 0.042 $M$, methanol) with triiron dodecacarbonyl at 73–74° in benzene for 3.5 hr afforded in 18% yield the (−)-bis(iron tricarbonyl) complex **2**, mp 180° dec, $[\alpha]_{324} - [\alpha]_{368} = 16{,}710°$ ($c$ 0.035 $M$, methanol), and in 23% yield the less-soluble meso bis(iron tricarbonyl) complex **1**, mp 240° dec.[4]

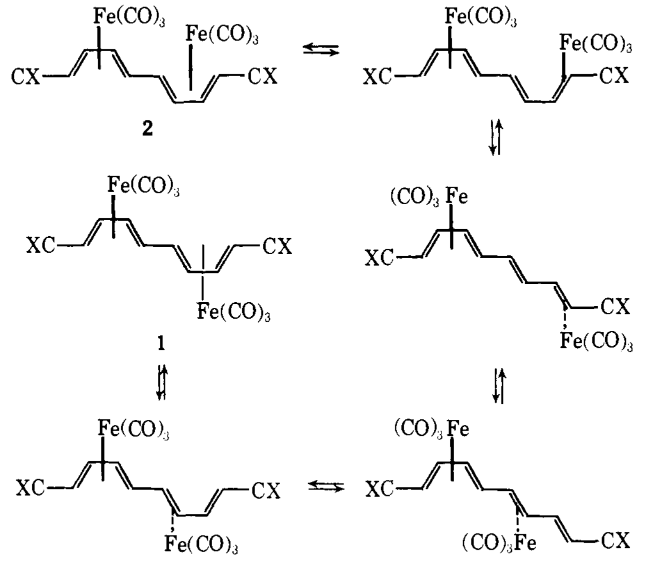
Complexes **1** and **2** were separable by recrystallization and thin-layer chromatography. The principal spectral distinction between the two isomers lies in the nmr shifts of $H_2(H_9)$ and $H_5(H_6)$, these being $\delta$ 1.17 and 1.47, respectively, for **2** and 1.13 and 1.33 for **1** ($CDCl_3$, 100 MHz). The configuration about the central $\sigma$ bond could not be determined from the nmr spectra of the complexes. The uv and mass spectra of the two complexes were very similar, the latter exhibiting parent ($m/e$ 502) ions.

Heating the optically active complex (−)-**2** in benzene led to loss of optical activity by a first-order concentration-independent process ($k_{\mathrm{rac}} = 11.8 \pm 0.6 \times 10^{-4}$ min$^{-1}$ at 110.4°). Heating (−)-**2** in benzene also led to its first-order isomerization to meso complex **1**, $k_{2\to1} = 13.0 \pm 4.5 \times 10^{-4}$ min$^{-1}$, $k_{1\to(-)\text{-}2} = 6.5 \pm 2.3 \times 10^{-4}$ min$^{-1}$ at 119.4°, $K_{\mathrm{eq}} = k_{2\to1}/k_{1\to(-)\text{-}2} = 2.0 \pm 0.4$.[5]

In view of the similarity of the rate constants for racemization of **2** and its conversion to **1** we conclude that formation of the meso complex is the major if not the only pathway available for racemization of **2**.

An "across the plane" process (Scheme I) similar to that proposed in the preceding paper[3] accounts for the **2** $\rightleftharpoons$ **1** equilibration and hence racemization of **2**. The rate of this process is similar to that found for racemization of other monoiron tricarbonyl complexes,[3] as is expected.

**Scheme I**



CX = CO$_2$CH$_3$

In summary then, although racemization of **2** may be observed, it proceeds *not* by a process involving iron tricarbonyls passing one another on opposite sides of the polyene chain but by a process localized in the 1,3-butadiene part of the complex.

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(1) H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, **87**, 3606 (1965).

(2) H. W. Whitlock, C. Reich, and W. D. Woessner, *ibid.*, **93**, 2483 (1971).

(3) H. W. Whitlock and R. L. Markezich, *ibid.*, **93**, 5290 (1971).

(4) Both **1** and **2** afforded satisfactory spectral and elemental analyses.

(5) The isomerization was followed by thin-layer separation of the mixture, which accounts for the rather large standard deviations. The possibility that these reactions are intermolecular has been ruled out by a number of ligand-exchange experiments using unlabeled complexes and deuterium-labeled monoiron tricarbonyl complexes.[3]

**Acknowledgment.** Partial support by the National Science Foundation is acknowledged.

(6) National Institutes of Health Predoctoral Fellow.

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*Received April 15, 1971*

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## The Photochemical Methanolysis of Arylcyclopropanes. Substituent Effects

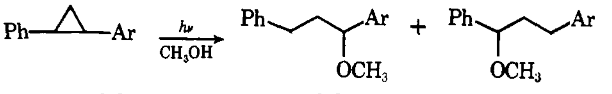
*Sir:*

In 1966 Griffin and coworkers[1] reported the photochemical addition of methanol to 1,2-diphenylcyclopropane and to other polyphenylcyclopropanes. As suggested by these investigators, the products can best be rationalized as arising from a polar addition to the excited three-ring compound. Thus the reaction is a very intriguing one, for the other photochemical reactions undergone by these cyclopropanes seem to be very adequately rationalized as proceeding *via* diradical intermediates.[1] Since the polar addition could occur *via* a variety of interesting pathways, we have studied the photochemical methanolysis of various aryl-substituted diphenylcyclopropanes in order to obtain more insight into the mechanism of this reaction.

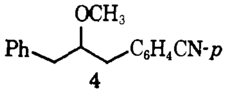
Irradiation[2] of a methanol solution of *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane (**1a**)[3] afforded, after initial rapid cis–trans isomerization, a 76% yield of a 60:40 (nmr) mixture of **2a** and **3a**.[4,5] Although **2a** and **3a** could not be separated on the several chromatographic systems tried, the mixture isolated had nmr and mass spectra consistent with the structures shown. Moreover, its behavior on thin-layer and gas chromatographic systems was identical with that of samples of **2a** and **3a** prepared *via* an independent route.[6] Likewise, the nmr spectrum of the mixture was seen to be a superposition of the spectra of the independently synthesized **2a** and **3a**.

Similarly, when a methanol solution of **1b** was irradiated a 47% yield of a 40:60 mixture of **2b** and **3b** was obtained.[4,5] In this case the ethers could be obtained essentially free of one another and identified.[8]

In marked contrast to the very slight effect of a methoxy group in orienting the addition, a para cyano moiety exerts complete control. When a methanol solution of **1c** was irradiated, two ethers, **3c** (33%)[8] and **4** (14%),[8] were isolated. However, **4** was shown to be a secondary photoproduct arising from the photoaddition of methanol to 3-(*p*-cyanophenyl)-1-phenylpropene, a photoproduct of **1c**.[9] Significantly, no **2c** was found.



**1a**, Ar = $p$-OCH$_3$-Ph **2a**, Ar = $p$-OCH$_3$-Ph **3a**, Ar = $p$-OCH$_3$-Ph
**1b**, Ar = $m$-OCH$_3$-Ph **2b**, Ar = $m$-OCH$_3$-Ph **3b**, Ar = $m$-OCH$_3$-Ph
**1c**, Ar = $p$-CN-Ph **2c**, Ar = $p$-CN-Ph **3c**, Ar = $p$-CN-Ph



**4**

Appropriate controls showed the observed transformations are truly photochemical and not thermal or acid-catalyzed dark reactions. Furthermore, similar to the diphenylcyclopropane case,[1] the transformation of **1a** proceeded equally well in the presence of 0.05 *M* sodium methoxide to give the same product distribution. Nmr analysis of reaction mixtures obtained upon irradiation in $CH_3OD$ showed that most if not all of the addition was to the cyclopropanes directly and not to olefins formed from the cyclopropanes.[10a,b] In addition, triplet sensitization of **1a–c** gave only cis–trans isomerization.[11]

These results provide a good indication of the nature of the species undergoing the addition. The very small effect of the para methoxy group in orienting the addition is quite surprising and is in contrast to what might be expected from a mechanism involving ionic intermediates, as in the photoaddition of alcohols to olefins,[12] or indeed any mechanism in which a very substantial charge is developed at the carbons undergoing the addition.[13,15] Likewise, the present reaction bears only a surface resemblance to the photochemical solvolysis of methoxy-substituted benzyl acetates,[16] where a meta methoxy group has a greater activating effect than a para methoxy.

On the other hand, the strong orienting effect of the para cyano group indicates that the ability of an aromatic ring to accept electron density from the cyclopropane ring is very important in orienting the addition. This is nicely in accord with recent uv studies of cyclopropyl-substituted aromatic compounds which show that cyclopropane rings behave as electron donors to aromatic rings and that excited state interaction be-

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(1) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966), and references therein.

(2) Irradiations were carried out under nitrogen with a Hanovia 450-W medium-pressure mercury arc fitted with a Vycor filter. Progress of the reactions was monitored by gas chromatography.

(3) Details of all synthetic and experimental procedures will be presented in a full paper.

(4) Other products, probably analogous to those found in the diphenylcyclopropane case,[1] were found.

(5) This ratio did not change on further irradiation.

(6) From the corresponding hydrochalcols[7] *via* a Williamson synthesis.[3]

(7) G. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, 73, 4509 (1951).

(8) Nmr and mass spectral data define the structures as shown.

(9) S. S. Hixson, manuscript in preparation.

(10) (a) Integration of the incompletely separated nmr signals of the C-2 and C-3 hydrogens of the products indicated at least 90% of the deuterium in **2a** and **3a**, 80% of that in **2b** and **3b**, and 95% of that in **3c** was located at C-3. The presence of a triplet for the C-1 hydrogens of **2b** and **3b** and a doublet of approximately equally intense triplets for the C-1 hydrogens of the **2a–3a** mixture likewise shows the lack of a substantial amount of deuterium at C-2. (b) Photochemical addition of methanol to 1,3-diarylpropenes does occur.[9]

(11) Triplet-sensitized cis–trans isomerization of 1,2-diphenylcyclopropane has been reported: G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966.

(12) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

(13) A para methoxy group exerts a large enhancement on the rate of cleavage of arylcyclopropanes by thallium triacetate and mercuric acetate.[14]

(14) R. J. Oullette, R. D. Robbins, and A. South, Jr., *J. Amer. Chem. Soc.*, 90, 1619 (1968); A. South, Jr., and R. J. Ouellette, *ibid.*, 90, 7064 (1968).

(15) (a) Thus a zwitterionic intermediate such as that discussed by Salem (Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971)) appears not to be involved. (b) Cram has invoked a zwitterionic intermediate to explain the photochemical methanolysis and racemization of [2.2]metaparacyclophanes. The analogy in photochemical reactivity between Cram's and the diarylcyclopropane systems in interesting. (c) M. H. Delton, R. E. Gilman, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2324 (1971).

(16) H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963).