imine linkage is introduced into the macrocyclic complex (Table I).

Table I. Reversible Oxidation Potentials for the Fe(II)–Fe(III) Couples of the Macrocyclic Iron Complexes in Acetonitrile Solution

Complex	No. of isolated imines	No. of α-diimines	Half-wave potential,[a] V
$\mathrm{Fe^{II}(Me_2[14]aneN_4)^{2+}}$	0	0	+0.27
$\mathrm{Fe^{II}(Me_6[14]aneN_4)^{2+}}$	0	0	+0.38
$\mathrm{Fe^{II}([14]4,11\text{-}dieneN_4)^{2+}}$	2	0	+0.44
$\mathrm{Fe^{II}([14]1,4,11\text{-}trieneN_4)^{2+}}$	3	0	+0.51
$\mathrm{Fe^{II}([14]1,4,8,11\text{-}tetraeneN_4)^{2+}}$	4	0	+0.59
$\mathrm{Fe^{II}([14]1,3,8\text{-}trieneN_4)^{2+}}$	1	1	+0.76
$\mathrm{Fe^{II}([14]1,3,7,11\text{-}tetraeneN_4)^{2+}}$	2	1	+0.72
$\mathrm{Fe^{II}([14]1,3,7,10\text{-}tetraeneN_4)^{2+}}$	2	1	+0.82
$\mathrm{Fe^{II}([14]1,3,8,10\text{-}tetraeneN_4)^{2+}}$	0	2	+0.89

[a] These potentials are accurate to ±10 mV and measured against an $\mathrm{Ag|Ag^+}$ (0.1 *M*) reference electrode.

Only the complexes containing α-diimine rings show well-defined, reversible reduction behavior. The outstanding example is $\mathrm{Fe^{II}([14]1,3,8,10\text{-}tetraeneN_4)^{2+}}$ which exhibits three very well defined one-electron reduction steps (at −0.80, −1.41, and −1.83 V, respectively), producing complexes formally containing Fe(I), Fe(0), and Fe(−1). The iron complexes having isolated imines, as well as the $\mathrm{Fe^{II}([14]aneN_4)^{2+}}$ complexes, all reduce irreversibly in acetonitrile solution, typically at cathodic potentials in the range of $-2.1 \rightarrow -2.2$ V. Despite a determined search, no definitive evidence has yet been found for an oxidation state of iron higher than three in these complexes, in contrast to expectations and evidence relating to iron–porphyrin systems.[7,8]

Acknowledgment. This work was supported by the National Institutes of Health and the National Science Foundation.

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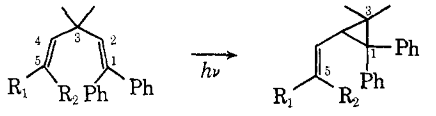
Received March 6, 1972

Stereochemistry of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LXIX[1]

Sir:

We have previously noted that when π moieties are bound to a single carbon in a photochemical reactant, one observes a ubiquitous rearrangement affording a π-substituted cyclopropane; we termed this the di-π-methane rearrangement[2] and have studied the multiplicity and stereochemistry of the reaction. There are three centers of stereochemistry involved, and previously we showed that the configuration at carbon 5 of the cis and trans isomers of 1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**1a** and **1b**) is retained. Preliminary evidence[2] suggested that inversion of configuration is preferred at C-3 but the stereochemistry at C-1 was left uncertain by these earlier studies.



(1)

1a, $R_1 = H$; $R_2 = Me$
b, $R_1 = Me$; $R_2 = H$

2a, $R_1 = H$; $R_2 = Me$
b, $R_1 = Me$; $R_2 = H$

The present investigation was initiated with the goal of establishing the stereochemistry of the di-π-methane rearrangement at carbon 1. For this purpose the photochemistry of the *cis*- and *trans*-1-phenyl-3,3,5-trimethyl-1,4-hexadienes (**3a** and **3b**) was investigated.

The synthesis utilized 2,2,4-trimethyl-3-pentenal[3] which reacted with benzylidenetriphenylphosphorane to give the desired *cis*- and *trans*-phenyl dienes **3a** and **3b**. The trans isomer **3b** was obtained alone by use of benzylidenediethylphosphonate instead.[4]

The configurations of these compounds were based on (1) the presence in **3b** of the 10.35 μ infrared band characteristic[5] of trans 1,2-disubstituted alkenes coupled with the absence of this absorption in **3a**; (2) the vinyl AB quartet in **3a** with τ 3.67 and 4.34 chemical shifts and $J = 12.8$ cps contrasted with a sharp singlet at τ 3.68 for two vinyl hydrogens in **3b** (this was compared with the known nmr spectrum[6] of the stereoisomeric analogs lacking the C-5 methyls where the cis isomer had an AB quartet with τ 3.46 and 4.33 chemical shifts and $J = 13.2$ cps and the trans isomer displayed a sharp singlet at τ 3.80); and (3) the expectation[7] that the phosphonium ylid reaction should give a predominance of cis product while the phosphonate ylid should lead preferentially to trans.

Direct photolysis of *trans*-phenyl diene **3b** gave primarily *trans*-3,3-dimethyl-2-(2′,2′-dimethylvinyl)-1-phenylcyclopropane (**4b**). Additionally, there were obtained lesser amounts of *syn*-2,2,5,5-tetramethyl-3-phenylbicyclo[2.1.0]pentane (**5**) and traces of the *cis*-vinyl cyclopropane **4a**.

Similar irradiation of the *cis*-phenyl diene **3a** gave predominantly *cis*-3,3-dimethyl-2-(2′,2′-dimethylvinyl)-1-phenylcyclopropane (**4a**) as the kinetic product; long irradiation led to heavy formation of *trans*-vinylcyclopropane **4b**, due to cis–trans isomerization coupled with the sevenfold greater extinction coefficient of the trans stereoisomer **3b**.

The quantum yields are given in eq 2; these derive from runs taken as low as 3–5% conversion.

The structures for the *cis*- and *trans*-vinylcyclopropanes **4a** and **4b** were established by conversion of the known[8] *cis*- and *trans*-2,2-dimethyl-3-phenylcyclopro-

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(1) For Paper LXVIII, see H. E. Zimmerman and R. D. Little, *J. Chem. Soc., Chem. Commun.*, 698 (1972).

(2) (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); (c) H. E. Zimmerman and G. A. Samuelson, *ibid.*, **91**, 5307 (1969).

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(4) Full synthetic detail will be given in our complete publication. Satisfactory analyses were obtained on all compounds.

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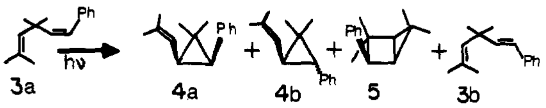
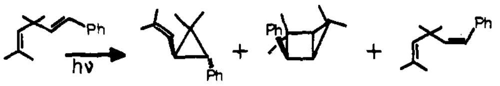


3a 4a 4b 5 3b

φ = .109 φ = .050 φ = .013 φ = .005 φ = .041

(2a)



3b 4b 5 3a

φ = .212 φ = .098 φ = .077 φ = .037

(2b)

panecarboxylic acids, whose configurations rest on firm nmr evidence,[9] into the corresponding aldehydes and then reaction with isopropylidenetriphenylphosphorane to give **4a** and **4b**, respectively. The structure of housane (**5**) is derived from nmr and comparison with the nmr data of Hammond.[10] The stereochemistry there rested on the H-3 and H-4 nmr coupling constants for syn and anti isomers of 2 and 0 cps, respectively.

In contrast to the direct irradiations, benzophenone sensitized photolyses of the *cis-* and *trans*-phenyl dienes **3a** and **3b** gave no di-π-methane rearrangement and only cis–trans interconversion. The efficiencies were $\phi = 0.087$ for cis → trans and $\phi = 0.12$ for trans → cis.

A most exciting result is that the di-π-methane rearrangement of the phenyl dienes **3a** and **3b** is stereospecific, and the situation at C-1 parallels that at C-5 in that cis reactant leads preferentially to cis product and trans reactant gives trans product.

The lack of specificity in housane (**5**) formation may derive from loss of stereochemistry in a 1,4 biradical formed by 2,4 bonding and then intersystem crossing to triplet, but the evidence that **5** is the kinetic product is less certain due to experimental limitations. The greater housane formation from the *trans*-diene **3b** is reasonable since the syn,syn conformation is more likely for this isomer than for **3a**.

The stereochemistry of the reaction is most readily understood in terms of the drawings in Figure 1. For convenience the syn,syn geometry is drawn, in which the two π bonds and the methane carbon 3 are in the U-shaped conformation. The stereochemical reasoning, however, is independent of which conformation is utilized. In inspecting Figure 1, one should recognize that the two representations **6** and **7** are equivalent. The former differs in showing the isobutenylidene sp^2 hybrid and one π-system p orbital combined into two equivalent sp^5 hybrids at C-4.

It is seen in the reaction that group R_1, which is initially trans with respect to the methane carbon C-3 on π bond 1,2, is twisted trans to the isopropylidene group; and R_1 and $\mathrm{Me_2C{=}CH}$– become trans in the product. This motion is depicted in Figure 1. The new three-ring σ bond must then arise from overlap of the anti lobe at carbon 1. As mentioned, tentative evidence for a preference for inversion of configuration at the methane carbon in the di-π-methane rearrangement has been advanced by us previously,[2b,c] and this overlap is used in Figure 1.[11]

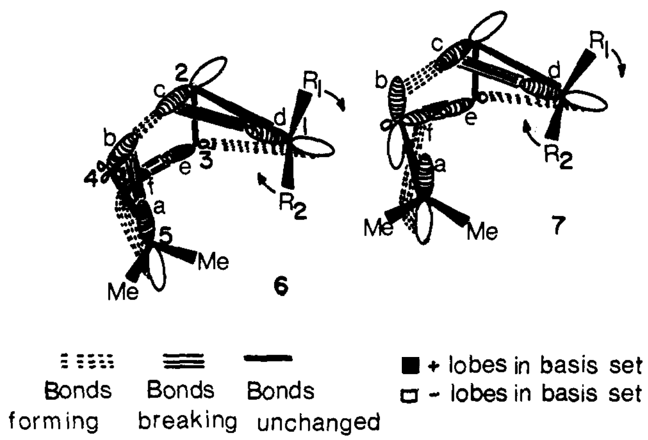


Figure 1. Reaction stereochemistry.

Least motion might be considered as a potential factor in controlling the reaction stereochemistry. However, presently it is seen that an approximately equal twist is required to arrive at either stereochemistry at C-1.

As noted earlier,[2b] this stereochemistry is excited state allowed since the six electron array is of the Möbius variety.[12]

Finally, still another case is available in which the singlet excited state rearranges *via* a concerted process with a cyclic orbital array while the triplet leads to a biradical and subsequent energy dissipation by double bond twisting.[2b]

Acknowledgment. Support of this research by AROD and NSF is gratefully acknowledged.

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Received April 6, 1972

The Use of Shift Reagents in Nuclear Magnetic Resonance Studies of Chemical Exchange

Sir:

A paramagnetic complex shifts the magnetic resonance frequency of nuclei in polar solvents by[1]

$$\Delta\nu_c = C_sK_i/kT \qquad (1)$$

where C_s is the concentration of complex and K_i is a contact shift constant characteristic of each set of nuclei and the applied field. Complexes, such as Eu(thd)$_3$ and Pr(thd)$_3$,[2] produce[3-5] "chemical shifts" be-

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(2) Eu(thd)$_3$ represents tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-europium(III), also designated as Eu(DPM)$_3$. Eu(fod)$_3$ represents tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III). Pr(thd)$_3$ and Pr(fod)$_3$ represent the praseodymium(III) complexes.

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