

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 iso-lated imines	No. of $\alpha$ -di-imines	Half-wave potential, <sup>a</sup> V
Fe <sup>II</sup> (Me <sub>2</sub> [14]aneN <sub>4</sub> ) <sup>2+</sup>	0	0	+0.27
Fe <sup>II</sup> (Me <sub>4</sub> [14]aneN <sub>4</sub> ) <sup>2+</sup>	0	0	+0.38
Fe <sup>II</sup> ([14]4,11-dieneN <sub>4</sub> ) <sup>2+</sup>	2	0	+0.44
Fe <sup>II</sup> ([14]1,4,11-trieneN <sub>4</sub> ) <sup>2+</sup>	3	0	+0.51
Fe <sup>II</sup> ([14]1,4,8,11-tetraeneN <sub>4</sub> ) <sup>2+</sup>	4	0	+0.59
Fe <sup>II</sup> ([14]1,3,8-trieneN <sub>4</sub> ) <sup>2+</sup>	1	1	+0.72
Fe <sup>II</sup> ([14]1,3,7,11-tetraeneN <sub>4</sub> ) <sup>2+</sup>	2	1	+0.76
Fe <sup>II</sup> ([14]1,3,7,10-tetraeneN <sub>4</sub> ) <sup>2+</sup>	2	1	+0.82
Fe <sup>II</sup> ([14]1,3,8,10-tetraeneN <sub>4</sub> ) <sup>2+</sup>	0	2	+0.89

<sup>a</sup> These potentials are accurate to  $\pm 10$  mV and measured against an Ag/Ag<sup>+</sup> (0.1 M) reference electrode.

Only the complexes containing  $\alpha$ -diimine rings show well-defined, reversible reduction behavior. The outstanding example is Fe<sup>II</sup>([14]1,3,8,10-tetraeneN<sub>4</sub>)<sup>2+</sup> 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 Fe<sup>II</sup>([14]aneN<sub>4</sub>)<sup>2+</sup> 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.<sup>7,8</sup>

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

(7) R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Amer. Chem. Soc.*, **93**, 6332 (1971).

(8) T. H. Mosh, A. Ehrenberg, and A. J. Bearden, *Biochemistry*, **8**, 4159 (1969).

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### Stereochemistry of the Di- $\pi$ -methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LXIX<sup>1</sup>

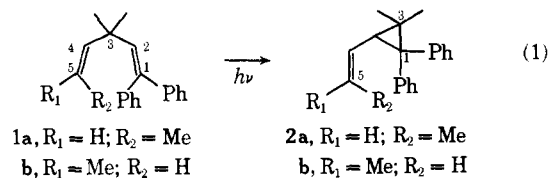
Sir:

We have previously noted that when  $\pi$  moieties are bound to a single carbon in a photochemical reactant, one observes a ubiquitous rearrangement affording a  $\pi$ -substituted cyclopropane; we termed this the di- $\pi$ -methane rearrangement<sup>2</sup> and have studied the multi-

(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).

plicity 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<sup>2</sup> suggested that inversion of configuration is preferred at C-3 but the stereochemistry at C-1 was left uncertain by these earlier studies.



The present investigation was initiated with the goal of establishing the stereochemistry of the di- $\pi$ -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<sup>3</sup> which reacted with benzylidetriphenylphosphorane to give the desired *cis*- and *trans*-phenyl dienes **3a** and **3b**. The *trans* isomer **3b** was obtained alone by use of benzylidenediethylphosphonate instead.<sup>4</sup>

The configurations of these compounds were based on (1) the presence in **3b** of the 10.35  $\mu$  infrared band characteristic<sup>5</sup> of *trans* 1,2-disubstituted alkenes coupled with the absence of this absorption in **3a**; (2) the vinyl AB quartet in **3a** with  $\tau$  3.67 and 4.34 chemical shifts and  $J = 12.8$  cps contrasted with a sharp singlet at  $\tau$  3.68 for two vinyl hydrogens in **3b** (this was compared with the known nmr spectrum<sup>6</sup> of the stereoisomeric analogs lacking the C-5 methyls where the *cis* isomer had an AB quartet with  $\tau$  3.46 and 4.33 chemical shifts and  $J = 13.2$  cps and the *trans* isomer displayed a sharp singlet at  $\tau$  3.80); and (3) the expectation<sup>7</sup> 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<sup>8</sup> *cis*- and *trans*-2,2-dimethyl-3-phenylcyclopro-

(3) M. Julia and M. Baillarge, *Bull. Soc. Chim. Fr.*, 734 (1966).

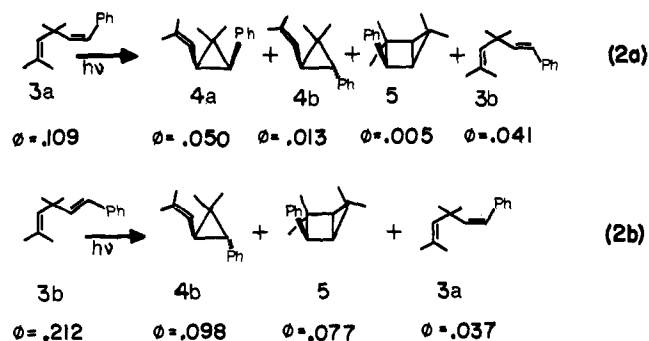
(4) Full synthetic detail will be given in our complete publication. Satisfactory analyses were obtained on all compounds.

(5) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 25.

(6) D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965).

(7) W. S. Wadsworth and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

(8) F. Sorm and J. Farkas, *Chem. Listy*, **52**, 688 (1958).



panecarboxylic acids, whose configurations rest on firm nmr evidence,<sup>9</sup> into the corresponding aldehydes and then reaction with isopropylidetriphenylphosphorane to give **4a** and **4b**, respectively. The structure of housane (**5**) is derived from nmr and comparison with the nmr data of Hammond.<sup>10</sup> 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- $\pi$ -methane rearrangement and only *cis*-*trans* interconversion. The efficiencies were  $\phi = 0.087$  for *cis*  $\rightarrow$  *trans* and  $\phi = 0.12$  for *trans*  $\rightarrow$  *cis*.

A most exciting result is that the di- $\pi$ -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  $\pi$  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  $\pi$ -system p orbital combined into two equivalent  $sp^3$  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  $\pi$  bond 1,2, is twisted *trans* to the isopropylidene group; and  $R_1$  and  $Me_2C=CH-$  become *trans* in the product. This motion is depicted in Figure 1. The new three-ring  $\sigma$  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- $\pi$ -methane rearrangement has been advanced by us previously,<sup>2b,c</sup> and this overlap is used in Figure 1.<sup>11</sup>

(9) D. J. Patel, M. E. H. Howeden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

(10) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5970 (1967).

(11) P. S. Mariano and J. K. Ko, *ibid.*, **94**, 1766 (1972). Mariano, in an elegant study, has arrived at similar conclusions by a different ap-

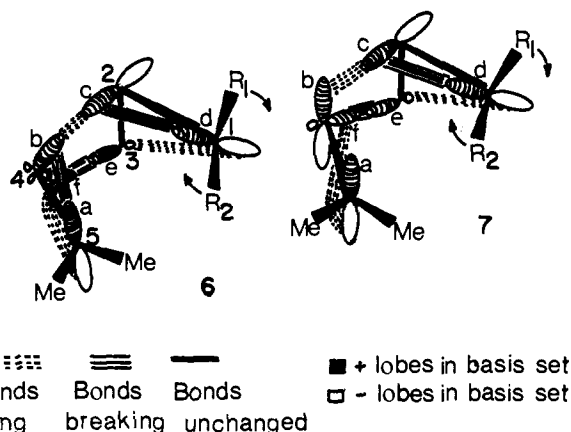


Figure 1. Reaction stereochemistry.

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,<sup>2b</sup> this stereochemistry is excited state allowed since the six electron array is of the Möbius variety.<sup>12</sup>

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.<sup>2b</sup>

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We acknowledge with pleasure Professor Mariano's private communication of his results.

(12) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

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## 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<sup>1</sup>

$$\Delta\nu_c = C_s K_j / kT \quad (1)$$

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

(1) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); H. J. Keller and K. E. Schwarzhau, *Angew. Chem., Int. Ed. Engl.*, **9**, 196 (1970).

(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.

(3) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(4) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. C. Staniforth, *ibid.*, 749 (1970).

(5) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).