

Figure 1. Photoelectron spectrum of 1,4-cyclohexadiene, obtained using the 304-Å helium line with interpretation according to a SPINDO/1 calculation. For the  $\pi$  orbitals the symmetry is indicated.<sup>10,11</sup>

carbon. For the carbon atom  $U_{ss} = -48.289$  eV and Slater exponent = 1.925. In the resonance integrals

$$H_{\mu\nu} = S_{\mu\nu}[I_{\mu}^A + I_{\nu}^B]f(R_{AB})$$

the factors  $f$  have different values for different types of interaction: for  $1s/1s$ ,  $j(R) = 0.13647$ ; for  $1s/2s$ ,  $f(R) = 0.17832$ ; for  $1s/2p\sigma$ ,  $f(R) = 0.35100$ ; for  $2s/2s$ ,  $f(R) = 0.20187 + 0.09500/R^2$ ; for  $2s/2p\sigma$ ,  $f(R) = 0.27625 + 0.13000/R^2$ ; for  $2p\sigma/2p\sigma$ ,  $f(R) = 0.47000 + 0.24000/R^2 + 100 \exp(-5R)$ ; for  $2p\pi/2p\pi$ ,  $f(R) = 0.40375 + 0.19000/R^2$ . The parameters were chosen to give reasonable agreement in the case of benzene (with interpretation according to Jonsson and Lindholm<sup>4</sup>), methane, ethane, ethylene, and acetylene.

To demonstrate the usefulness of the new procedure we will in this communication apply it to two molecules: 1,4-cyclohexadiene and *trans*-1,3-butadiene.

In the SPINDO calculation of cyclohexadiene the "planar" geometry discussed by Oberhammer and Bauer<sup>5</sup> was used (*cf.* ref 6, 7). The SPINDO orbital energies are compared in Figure 1 with the photoelectron spectrum, observed in our photoelectron spectrometer.<sup>8</sup> Its low-energy part agrees well with an earlier study.<sup>9</sup> It can be seen that the distribution of the orbital energies corresponds well to the maxima of the curve. This supports our method and indicates that also the form of the molecular orbitals is obtained approximately correctly from the SPINDO calculation.

The most interesting feature of the molecular orbitals of 1,4-cyclohexadiene is that the  $\sigma$  orbitals are nearly identical with the corresponding orbitals in benzene. Also the orbital energies are nearly the same as in benzene, although, of course, the degenerate benzene orbitals are split. The introduction of two extra hydrogens in cyclohexadiene does not influence the  $\sigma$ -orbital system much.

The  $\pi$  orbitals of 1,4-cyclohexadiene have no similarity with those of benzene. Owing to the two extra hydrogens the cyclohexadiene has four  $\pi$  orbitals. The two highest are in-phase ① and out-of-phase ② combinations of the ethylene  $\pi$  orbitals and the two lowest are similar combinations of the  $\text{CH}_2$  orbitals, ③ and ④. That the in-phase combination ① is highest depends upon the destabilizing influence of the two  $\text{CH}_2$  orbitals. This result is in good agreement with earlier

- (4) B. Ö. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969).  
 (5) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).  
 (6) G. Dalinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).  
 (7) J. Laane and R. C. Lord, *J. Mol. Spectrosc.*, **39**, 340 (1971).  
 (8) O. Edqvist, E. Lindholm, L. E. Selin, H. Sjögren, and L. Åsbrink, *Ark. Fys.*, **40**, 439 (1970); O. Edqvist, E. Lindholm, L. E. Selin, and L. Åsbrink, *Phys. Scr.*, **1**, 25 (1970).  
 (9) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

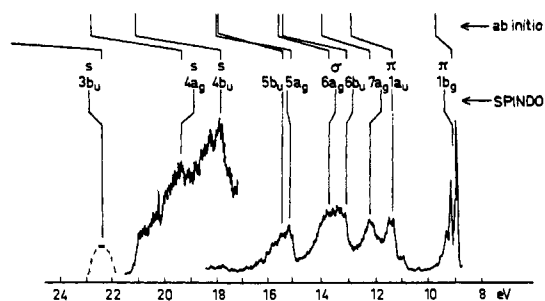


Figure 2. Photoelectron spectrum of butadiene<sup>16</sup> compared with orbital energies from SPINDO/1 and from an *ab initio* calculation.<sup>17</sup> The band at 22.4 eV was observed by Brundle and Robin.<sup>21</sup>

treatments of interaction through bonds<sup>10-12</sup> in this molecule.

In the SPINDO calculation of butadiene the geometry given by Haugen and Traetteberg<sup>13,14</sup> and Kuchitsu, *et al.*,<sup>15</sup> was used. The SPINDO orbital energies are compared in Figure 2 with the photoelectron spectrum observed by Turner.<sup>16</sup> It can be seen that the orbital energies correspond well to the different maxima of the photoelectron curve, especially when compared to the *ab initio* results<sup>17</sup> at the top of the figure.

Our calculation may contribute to recent discussions whether the second ionization potential in butadiene is  $\sigma$  or  $\pi$ . The *ab initio* calculations<sup>17,18</sup> indicate  $\pi$ , but semiempirical calculations<sup>19,20</sup> indicate  $\sigma$ . Brundle and Robin<sup>21</sup> tried to solve the problem by a study of fluoro-substituted butadienes and found evidence for  $\sigma$ . It follows, however, from Figure 2 that the SPINDO calculation indicates that the second ionization potential is  $\pi$ , in agreement with the *ab initio* calculations.

**Acknowledgments.** Discussions with Dr. H. Seip and Dr. M. Traetteberg are gratefully acknowledged.

- (10) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 706 (1970).  
 (11) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).  
 (12) E. Heilbronner, private communication.  
 (13) W. Haugen and M. Traetteberg in "Selected Topics in Structure Chemistry," Universitetsforlaget, Oslo, 1967.  
 (14) M. Traetteberg, private communication.  
 (15) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).  
 (16) D. W. Turner, C. Baker, A. D. Baker, and C. B. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.  
 (17) R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968).  
 (18) B. Dumbacher, *Theor. Chim. Acta*, **23**, 346 (1972).  
 (19) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).  
 (20) S. D. Worley, *Chem. Rev.*, **71**, 295 (1971).  
 (21) C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 5550 (1970).

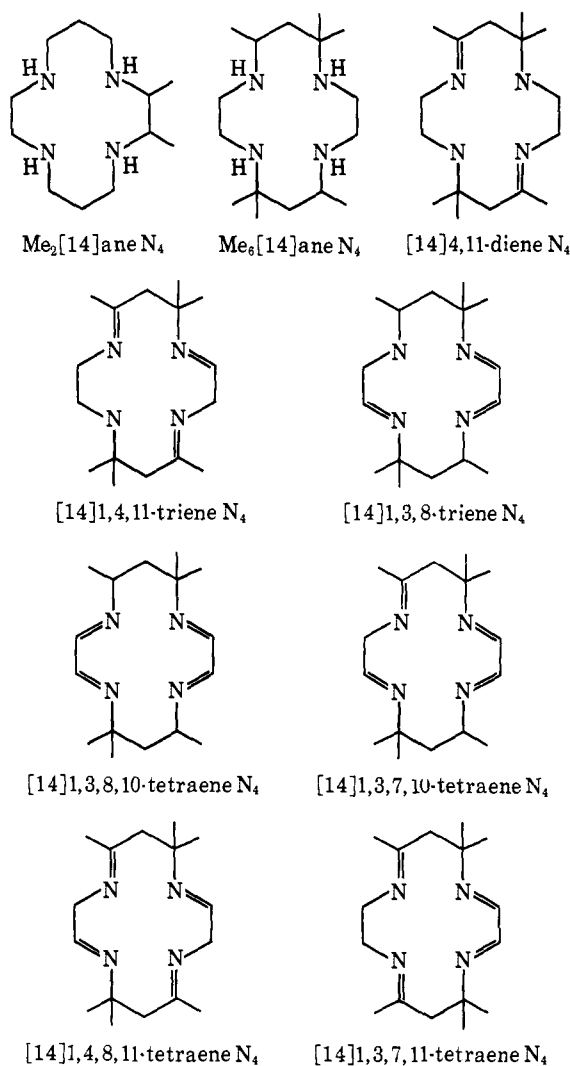
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### Synthesis and Electrochemical Behavior of a New Series of Macrocyclic Complexes of Iron Produced by Oxidative Dehydrogenation and Tautomerization

Sir:

The Fe(II) complexes of the ligands shown in Chart I constitute a distinctive series of compounds containing ligand systems with different degrees and types of

Chart I



unsaturation. All nine complexes are low-spin, six coordinate and contain two CH<sub>3</sub>C≡N molecules in the axial sites. Correct chemical analyses, ir ( $\nu_{C=N}$  of an isolated imine 1660 cm<sup>-1</sup> and  $\nu_{C=N}$  of  $\alpha$ -diimine 1520, 1620 cm<sup>-1</sup>, Nujol), conductance ( $\Lambda_M$  in CH<sub>3</sub>CN, 290–315 cm<sup>2</sup>/ohm mol), and nmr in CH<sub>3</sub>CN (isolated HC=N,  $\tau$  1.80 ppm;  $\alpha$ -diimine HC=N,  $\tau$  1.00 ppm) establish the integrity and structure of the macrocyclic derivatives.

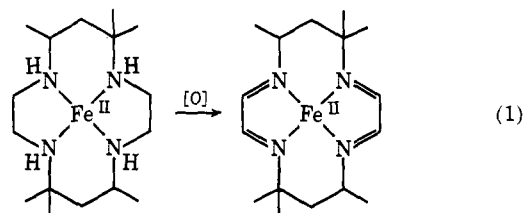
The iron(II) complexes of either of the well-known<sup>1</sup> starting ligands Me<sub>6</sub>[14]aneN<sub>4</sub> or Me<sub>6</sub>[14]4,11-dieneN<sub>4</sub> can be synthesized<sup>2,3</sup> from the ligands using iron(II) acetate or perchlorate in anhydrous acetonitrile. Me<sub>2</sub>[14]aneN<sub>4</sub> is prepared from the corresponding 1,3-diimine complexes after the manner of preparation of Me<sub>6</sub>[14]aneN<sub>4</sub>. They are air sensitive and, when dissolved in acetonitrile, react in a stepwise manner with molecular oxygen to yield structures containing dehydrogenated forms of the ligand. Fe<sup>II</sup>(Me<sub>6</sub>[14]aneN<sub>4</sub>)<sup>2+</sup>

(1) N. S. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968); L. F. Lindoy and D. H. Busch, "Preparative Inorganic Reactions," W. L. Jolly, Ed., Wiley, New York, N. Y., 1971, p 1 ff.

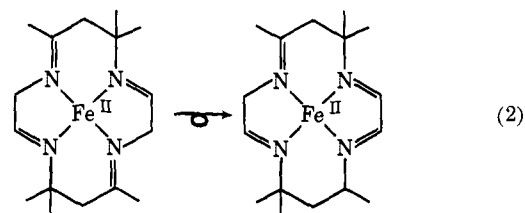
(2) V. L. Goedken, P. H. Merrell, J. C. Dabrowiak, and D. H. Busch, unpublished results; P. H. Merrell, V. L. Goedken, D. H. Busch, and J. A. Stone, *J. Amer. Chem. Soc.*, **92**, 7590 (1970).

(3) V. L. Goedken, P. H. Merrell, and D. H. Busch, *ibid.*, **94**, 3397 (1972); the nomenclature of these compounds as well as some of the preparations are reported in this source.

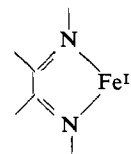
ultimately yields Fe<sup>II</sup>([14]1,3,8,10-tetraeneN<sub>4</sub>)<sup>2+</sup> which has  $\alpha$ -diimine functions in the five-membered rings.



Similar oxidations using Fe<sup>II</sup>([14]4,11-dieneN<sub>4</sub>)<sup>2+</sup> proceed in a manner analogous to the nickel(II) systems,<sup>2,4</sup> resulting in structures having isolated imine functions in the five-membered chelate rings ([14]1,4,11-trieneN<sub>4</sub> and [14]1,4,8,11-tetraeneN<sub>4</sub>). Similarly, Me<sub>6</sub>[14]-1,3,7,11-tetraeneN<sub>4</sub> is prepared from the complex of the *cis*-diimine Me<sub>6</sub>[14]4,14-dieneN<sub>4</sub>.<sup>3</sup> The product having four isolated imines, [14]1,4,8,11-tetraeneN<sub>4</sub>, undergoes a novel tautomerization process to produce a ligand containing an  $\alpha$ -diimine grouping. The process occurs slowly in CH<sub>3</sub>CN solution and appears to be promoted by the presence of the corresponding iron(III) complex.



The selectivity in positioning of the double bonds in the processes described above is a remarkable illustration of the special stability of the aromatic chelate ring.<sup>5</sup>



Reciprocally, the dependence of the stabilities of the various oxidation states of iron on the degree of unsaturation of the ligands and the unique stabilizing influence of the  $\alpha$ -diimine linkage on the divalent state of iron are sharply demonstrated by electrochemical<sup>6</sup> studies on ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, or PF<sub>6</sub><sup>-</sup> salts of the complexes Fe<sup>II</sup>(MAC)(CH<sub>3</sub>CN)<sub>2</sub><sup>2+</sup>. The iron(II) in all of the complexes is oxidized to the trivalent state in an electrochemically reversible manner (cyclic voltammetry, acetonitrile solutions; Et<sub>4</sub>NClO<sub>4</sub> supporting electrolyte vs. Ag/Ag<sup>+</sup> (0.1 M) reference electrode). Typically coulometric *n* values obtained were 0.96 and 1.03 for Fe<sup>II</sup>([14]4,11-dieneN<sub>4</sub>)<sup>2+</sup> and Fe<sup>II</sup>([14]1,4,11-trieneN<sub>4</sub>)<sup>2+</sup>, respectively. Chemically prepared iron(III) complexes reduce reversibly at the expected half-wave potentials. The value of  $E_{1/2}$  for the Fe<sup>II</sup>/Fe<sup>III</sup> couple becomes more positive by about 70 mV for each double bond introduced into the ligand (Table I). A more dramatic positive shift of  $E_{1/2}$  occurs, however, when an  $\alpha$ -di-

(4) N. F. Curtis, *Chem. Commun.*, 881 (1966).

(5) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).

(6) An electrochemical study on one of these compounds has recently appeared in the literature: cf. D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **11**, 980 (1972).

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>

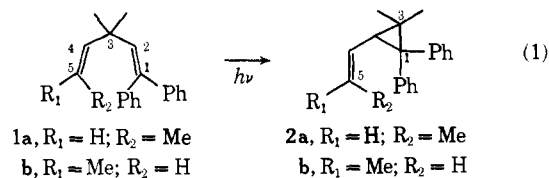
Sir:

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 benzylidene triphenylphosphorane 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).