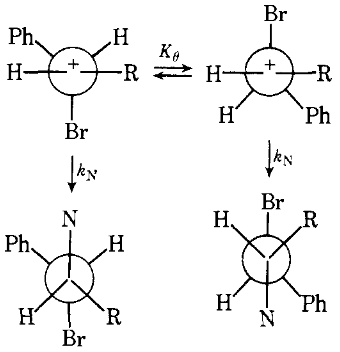
intermediate and closer to the $\pi$ complex in Freon 113 at $-35°$ than in methanol at $+25°$, but he reckons without the Freon 112 results. Since it is generally accepted that $\pi$ complex stability is rather insensitive to solvent,[11] this interpretation implies that the $\sigma$ complex would be more stable in Freon 113 than in methanol, a rather unlikely event! Thus, Olah's results are contradictory not only with ours but also with the Hammond postulate.[12] A possible source of error in his work in Freon 113 could be the choice of a competitive kinetic method; our data were obtained by direct measurement. It has been found[13,14] that the competitive methods frequently lead to a compression of the reactivity span which would, of course, give rise to the reported low value of $\rho$. It would seem, therefore, unwise to invoke for bromination in Freon 113 at $-35°$ any fundamentally new mechanism.

Since we find that *solvent changes cannot lead to significant variation in bromine bridging* as specific nucleophilic solvation is absent, the problem of solvent dependence of stereoselectivity must be resolved in other terms. In so far as our results have eliminated the conventional interpretation of this problem, a reexamination of the role of the solvent in determining stereochemistry is now necessary, knowing that the solvent intervenes only in the last step: nucleophilic trapping of the intermediate. Thus the influence of solvent probably lies in the competition between conformer equilibration $K_\theta$ and nucleophilic attack $k_N$ according to the scheme postulated by Collins[15] in order to account for the stereoselective reactions of carbonium ions.



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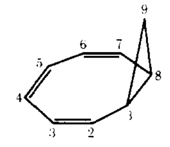
## On the Walk Rearrangement of Bicyclo[4.1.0]hepta-2,4-diene and of Bicyclo[2.1.0]pent-2-ene. A Semiempirical MO Study

*Sir:*

The 1,7-sigmatropic rearrangement of **1** and the 1,5-sigmatropic rearrangement of **2** proceed with inversion of configuration at the migrating carbon atom.[1] The 1,3-sigmatropic rearrangement of **3** is yet unknown.[2] Therefore **1** follows a path which is in accordance with orbital symmetry considerations[3] and **2** a path which is in accordance with the Berson–Salem hypothesis[4] (Table I).

Following simple arguments concerning ring strain,[5] the three-membered ring of **1** should be more stable than that of **3** and should be about as stable as in **2**. The same conclusions should also hold for an aromatic transition state,[6] favoring a stability order **4** > **5** > **6** for pericyclic bonding; in other words the less strained "forbidden concerted" transition state (with no pericyclic bonding) should compete in the reverse order **9** > **8** > **7**.



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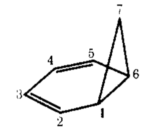

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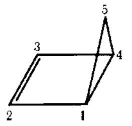

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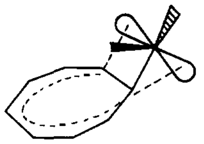
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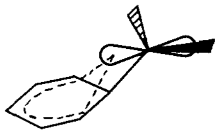
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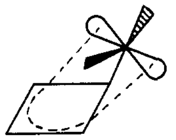
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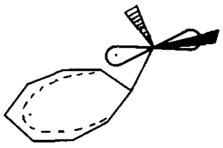
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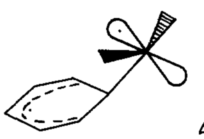
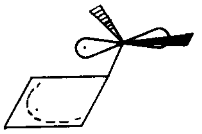

**8**


**9**

We wish to report optimized semiempirical MINDO/2 calculations[7] on the transition states **5**, **8** and **6**, **9** in the sigmatropic rearrangements of **2** and **3**, including configuration interaction[8] for proper bond dissociation. Due to computational expenses a study of the transition states in the thermal rearrangement of **1** was out of range. For the evaluation of the energy hypersurface as given in Figure 1, we proceeded in the following order: (a) assumption of the migrating carbon as a midpoint on the reaction coordinate, this implies a plane of symmetry through the migrating carbon atom and bisecting the polyene unit ($C_s$ symmetry); (b) determination of the conformation lowest in energy by optimizing bond lengths and bond angles, for the minimiza-

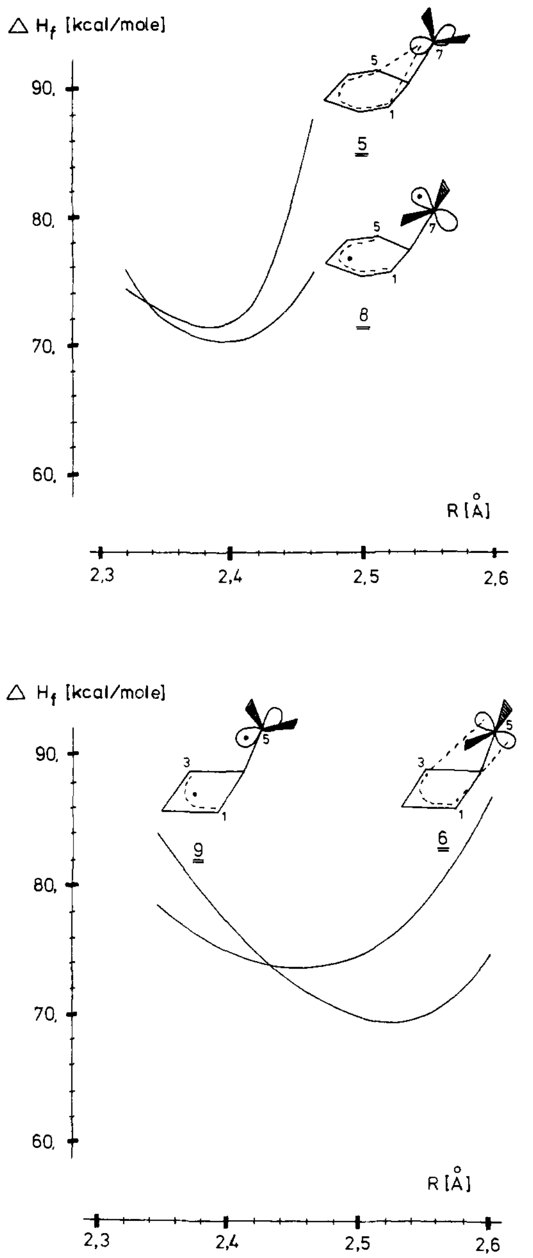


**Figure 1.** Heat of formation (at 25°) of the transition states **5**, **8** and **6**, **9** as a function of distance *R* (for **5** and **8**, $R_{C(1)C(7)} = R_{C(5)C(7)}$; for **6** and **9**, $R_{C(1)C(5)} = R_{C(3)C(5)}$).

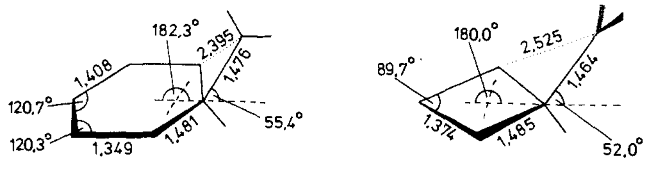


**Figure 2.** Optimized geometries lowest in energy.

Table I. Stereochemical Consequences According to the Considerations of Woodward and Hoffmann (WH)[3] and of Berson and Salem (BS)[4] for Sigmatropic Rearrangements of the Order (1,*n*), with *n* = 3, 5, 7

| Order of sigmatropic shift | WH | BS |
|---|---|---|
| (1,3) | si[a] | sr |
| (1,5) | sr | si |
| (1,7) | si | sr |

[a] s = suprafacial, i = inversion, r = retention.

tion of the total energy the Simplex algorithm was employed;[9] (c) evaluation of the hypersurface around the point lowest in energy by fixing bond lengths and bond angles and varying the distance, *R*. Having computed the total energy as a function of the distance, *R*, one finds two divergent tendencies: (a) a decreasing value for *R* increases the overlap between the p atomic orbital at the migrating carbon atom with the orbitals of the pentadienyl unit (in **5**) and the allyl unit (in **6**), accordingly the transition states allowed by Woodward and Hoffmann come to the fore; (b) on the contrary an increasing distance *R* reduces the ring strain in the transition state with pericyclic bonding.

A diagram of the optimized geometries lowest in energy is shown in Figure 2. The transition states suggest a geometry in which ring strain has been greatly released. Inversion over retention at the migrating carbon center is only slightly favored (1.4 kcal $mol^{-1}$) in **8**, but retention over inversion is strongly favored by 4.0 kcal $mol^{-1}$ in **9**. The migrating methylene unit in its diradical transition state **9** is more strongly bent away from the participating allyl unit than in the case of its counterpart **6** (by 9°), which shows inversion of configuration at the migrating carbon atom.

While the energy difference between an "WH-allowed" and "WH-forbidden" pathway for the reaction of **2** is very small, the "WH-forbidden" pathway for the reaction of **3** gains additional stability by the involvement of hyperconjugation.[10,11] This promotes planarity between the plane formed by the migrating methylene unit and the plane formed by the four-membered ring (see Figure 2). On this basis one can predict that in the 1,3-sigmatropic rearrangement of **3** the configuration at the migrating center will be retained. This establishes a reaction path directly in contrast to that required by the principle of "least motion".

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compressing the valence angle ($C_2C_3C_4$) lowers the antibonding orbital of the allyl unit thus favoring more suitable orbital interaction.

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## Electronic and Stereoelectronic Effects on the Intervalence Transfer Transition in Biferrocene Cations

*Sir:*

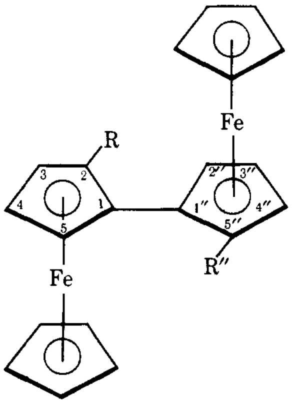
The mixed valence monocation of biferrocene (**1a**) has been thoroughly characterized by a variety of physical measurements.[1] A low energy transition, observed in the near-infrared, has been assigned to an intervalence transfer transition:

$$[\mathrm{Fe(II)—Fe(III)}] \xrightarrow{h\nu} [\mathrm{Fe(III)—Fe(II)}]^*$$

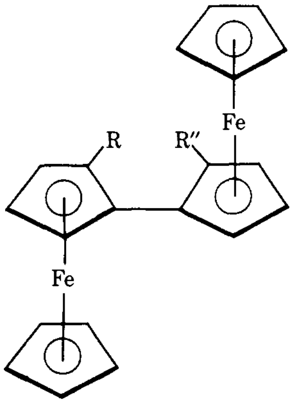
A simple model for intervalence transfer transitions has been proposed by Hush[2] and expounded by Day.[3] A corollary states that the energy of the Franck-Condon transition for a one-electron transfer in a symmetrical compound is determined by the amount of reorganizational energy involved. For an electron transfer in an unsymmetrical compound, the band is expected to be blue shifted because of a difference in energy between the initial and final states at the equilibrium configurations.

The intensity of the transition, however, depends on the amount of interaction (i.e., delocalization) between donor and acceptor sites.[4] Mayoh and Day[5] have recently shown that, in the absence of direct metal-metal overlap, the metal centers in mixed-valence compounds interact via ligand $\pi$ and $\pi^*$ orbitals.

In order to investigate the usefulness of this simple model in interpreting results in the biferrocene series, we examined the mixed-valence cations of three disubstituted biferrocenes (**1b**, **1c**, and **2**).[6,7]



**1a**, R = R'' = H
**b**, R = R'' = $CH_3$
**c**, R = $CH_3$; R'' = $CH_2OH$



**2**, R = R'' = $CH_3$

It has been shown that the presence of substituents adjacent to the fusion between the ferrocenyl groups affects the overall conformation of the molecule.[7,8] The 2,5''-disubstituted compounds (**1b** and **1c**) may adopt a trans conformation,[9] whereas the 2,2'' derivative (**2**), because of steric hindrance, probably adopts a skewed conformation. As a result, a reduced $\pi$ interaction in the "fulvalene" ligand is expected. It was shown that this effect satisfactorily explains the blue shift and reduced intensity in the $\pi \rightarrow \pi^*$ transition of the neutral 2,2''-disubstituted compounds.[7] The nonplanarity of the fused cyclopentadienyl rings should, in turn, reduce the extent of interaction between the mixed-valence metal centers in the cation but have little or no effect on the reorganizational energy.

Table I. Half-Wave Potentials for Substituted Biferrocenes[a,b]

| Compd | $E_{1/2}(1)$ | $E_{1/2}(2)$ | $\Delta E_{1/2}$[c] |
|---|---|---|---|
| 1a | 0.285 | 0.600 | 0.315 |
| 1b | 0.310 | 0.605 | 0.295 |
| 2 | 0.370 | 0.630 | 0.260 |
| 1c | 0.350 | 0.675 | 0.325 |

[a] Volts vs. SCE at 100 mV/sec (platinum disk electrode). [b] Acetonitrile containing $Et_4NClO_4$ (0.1 *M*). [c] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

Table II. Spectral Data for Biferrocene Cations

| Compd | Monocations[a] $\lambda_{max}$, nm ($\epsilon$)[c] Near-infrared | Monocations[a] $\lambda_{max}$, nm ($\epsilon$)[c] Visible | Dications[b] $\lambda_{max}$, nm ($\epsilon$)[c] Visible |
|---|---|---|---|
| 1a | 1800 (750) | 545 (2160)[d] | 480 (920), 660 (1000) |
| 1b | 1800 (560) | 560 (1850)[d] | 485 (860), 670 (1100) |
| 2 | 1800 (340) | 560 (1030)[d] | 480 (480), 660 (910) |
| 1c | 1680[e] (520) | 545 (2000)[d] | 485 (900), 665 (1100) |

[a] Acetonitrile containing $Et_4NClO_4$ (0.1 *M*). [b] Methylene chloride containing $n$-$Bu_4NBF_4$ (0.1 *M*). [c] Reproducible within 5%. [d] Shoulder at longer wavelength. [e] Because of solvent absorption, values in 1660–1740 nm region are interpolated.

To obtain absorption spectra of the mono- and dications of compounds **1b**, **1c**, and **2**, $10^{-3}$ *M* solutions were generated electrochemically. Oxidation by precisely 1F/mole yields the monocations, while exhaustive coulometric oxidation results in consumption of precisely 2F/mole and formation of the dications. The stability and identity of the cations were demonstrated by cyclic voltammetry and polarography.[10] Half-wave potentials for these compounds as measured by cyclic voltammetry are given in Table I. Each compound undergoes two reversible one-electron oxidations. A difference in peak potentials of 60 mV between the oxidation and reduction waves was used as the criterion for reversibility. Spectral data in the visible and near-infrared regions are given in Table II.

The spectral results obtained for the monocations in the near-infrared region do indeed reflect the predictions of the simple model. Within experimental limits, the maximum for the two dimethylbiferrocene cations is the same, whereas the intensity of the band is significantly reduced in the skewed 2,2''-dimethyl derivative.[11] In the case of the cation of the unsymmetrically substituted hydroxymethyl compound (**1c**), the intervalence transfer band is blue shifted some 120 nm (0.05 eV) as expected.

These results demonstrate the usefulness of the simple model in interpreting the results in the biferrocene series.[12] Mixed-valence biferrocenes fulfill the prerequisite of the Hush model[2,3] in that there is weak interaction between the donor and acceptor sites. Consequently, transitions due to the ferrocene and ferrocenium portions are expected to be seen. Table II lists the absorption maxima and intensities of the visible bands of the biferrocene mono- and dications. The 617-nm band observed for the ferrocenium ion has been assigned to a symmetry-allowed ligand to metal transition based on the effect of substituents.[13] A ferrocenyl group is electron donating[14] and as such should induce a red shift. The visible bands of the biferrocene monocations, however, are broad and unsymmetrical with maxima around 560 nm and shoulders at lower energy (~650 nm). We previously suggested that a second band in the visible