Weigert and Roberts[16] on some halogenated cyclopropanes in which they characterized for the first time the nature of hybridization in a three-member ring system. Although the paucity of $J_{^{13}C-^{13}C}$ data still prevents any final conclusions, all available evidence suggests that the major factor of $J_{^{13}C-^{13}C}$ is a hybridizational one and that measurable polarization effects are less significant than they are in the related $J_{^{13}C-H}$ couplings.

The values given in Table I were obtained on a Varian AFS-60 spectrometer utilizing proton decoupling and time-averaging techniques. The spectrometer was operated in the external lock mode, allowing proton decoupling power to be introduced to the sample through the internal lock circuitry. Operation in this configuration capitalizes on the advantages of the proton-decoupling technique[17] (i.e., signal enhancement through multiplet collapse and a favorable nuclear Overhauser enhancement). This mode of operation, however, does suffer from certain magnetic field inhomogeneities which limit the accuracy of our measurements to a value approaching 1 cps. In the external lock mode, long-term magnetic field drifts between the reference and analytical samples along the x-axis limit our accuracy in defining the position of the carbon-13 satellite peaks. The signal width is also broadened by decay in the homogeneity of the field along the y axis as the Autoshim circuitry provided in the AFS-60 operates only in the internal lock mode. Even with these difficulties, $^{13}C-^{13}C$ splittings can be readily observed on the C-1024 TAD after several hundred sweeps. As an indication of the sensitivity of the method it is noted that only 0.04 and 0.03%, respectively, of the neopentane and t-butyl molecules have two adjacent ^{13}C isotopes due to the relatively low abundance (1.1%) of this carbon isotope.

(16) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 5962 (1967). The authors wish to thank these workers for providing a prepublication manuscript of this very interesting work.
(17) E. G. Paul and D. M. Grant, *ibid.*, **86**, 2977 (1964).

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Ferrocene-Photosensitized cis–trans Isomerization of Piperylene

Sir:

A recent study by Dannenberg and Richards indicates that the photostationary state observed in ferrocene-sensitized piperylene isomerization and the product distribution for the ferrocene-sensitized dimerization of isoprene are the same as those reported for high-energy sensitizers.[1,2] They also report that ferrocene accelerates the photoisomerization of *trans*-piperylene

(1) J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).
(2) J. J. Dannenberg, Ph.D. Thesis, California Institute of Technology, 1967.

by a factor of five. Most of these photoisomerization studies were conducted in benzene as solvent.[3] We have observed that ferrocene behaves as a low-energy photosensitizer in the *cis–trans* isomerization of piperylene in *trans*-1,2-dimethylcyclohexane solvent and that the rate of photoisomerization is low. The mechanism of photosensitization is consistent with that demonstrated in other photoisomerization studies involving triplet–triplet energy transfer from sensitizer to olefin.[4–7] Our preliminary studies in benzene as solvent yielded the same photostationary-state composition that was reported by Dannenberg and Richards.[1,2] This suggests that there is a marked solvent effect in the ferrocene-sensitized isomerization of piperylene.

All experiments were conducted using degassed solutions sealed in quartz cells. Two irradiation systems were employed. The first consisted of a Hanovia 450-w medium-pressure mercury lamp in a cylindrical reactor. The second was a PEK 200-w short-arc mercury lamp mounted on an optical bench with quartz lens and a mirror to provide a collimated beam. Most of the experiments were conducted in Phillips research grade *trans*-1,2-dimethylcyclohexane which was purified with activated silica gel to remove absorbing impurities. Benzene obtained commercially from James A. Hinton (99.99%) was used without further purification. Matheson Coleman and Bell ferrocene was sublimed before use, and Baker *cis*- and *trans*-piperylenes were purified by preparative vapor phase chromatography. All samples were degassed by the freeze–pump–thaw technique.

Our energy-transfer results with *trans*-1,2-dimethylcyclohexane agree with the intramolecular energy partitioning scheme which has been suggested for ferrocene.[8,9] No *cis–trans* conversion was observed upon excitation at 4400 Å using a 4000 Å cut-off filter (Corning C.S. 3-73). Photosensitization occurred, however, after excitation at 3240 Å and/or 2650 Å (Figure 1).[10] The rate of conversion in our ferrocene sample was slower than that in the "blank" (i.e., similar piperylene solutions without ferrocene) for excitation in the 2650-Å region. In a typical experiment a solution containing 0.20 M ferrocene and 0.05 M *trans*-piperylene in *trans*-1,2-dimethylcyclohexane was irradiated along with the corresponding "blank" using a 0.05 M *trans*-piperylene solution as the filter. Table I summarizes conversion rates and light absorption characteristics of the two solutions in the 2500–2800-Å region. No light of wavelengths less than 2500 Å was transmitted by the filter solution.

The data in Table I show that the conversion rate in the ferrocene sample that can be attributed to direct

(3) J. H. Richards, private communication.
(4) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
(5) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(6) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).
(7) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).
(8) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).
(9) A careful reexamination of the anomalous emission from ferrocene has shown that most of the reported phosphorescence stems from solvent impurities. There still remains some evidence, however, of a weak emission around 5200 Å (R. S. Becker, private communication).
(10) A 3130-Å filter train was used for the 3240-Å excitation which consisted of a Corning C.S. 7-54 glass filter, a 1-mm-thick Corning C.S. 0-53 filter, and 2.0 cm cell of 0.0005 M K$_2$CrO$_4$.

excitation of piperylene is only 0.02%/hr ($^{0.5}/_{50}$ of 1.7%/hr). Consequently, ferrocene does act as a photosensitizer. The quantum yield for photosensitized *cis–trans* isomerization of a 0.15 M ferrocene–0.20 M *cis*-piperylene solution using the 3130-Å filter train is 0.0026 ± 0.0004. The benzophenone-sensitized isomerization of *cis*-piperylene was used as an actinometer to measure the absolute light intensity in this study.[11]

Table I. Excitation in 2500–2800-Å Region

Sample	R_i, %/hr[a]	$A(P)$, %[b]	$R_i(P)$, %/hr[c]
Blank	1.7	~50	1.7
Ferrocene–piperylene	0.4	<0.5	0.02

[a] R_i is the initial conversion rate. [b] $A(P)$ is the per cent light absorbed by piperylene. [c] $R_i(P)$ is the initial conversion rate due to piperylene excitation.

It has been reported that photosensitizers whose triplet-state energies are greater than the energy of the piperylene triplet (high-energy sensitizers) sensitize both *cis*- and *trans*-piperylenes at a diffusion-controlled rate and yield the same photostationary-state composition, *i.e.*, 55% *trans*- and 45% *cis*-piperylenes.[4–6] The photostationary-state composition for ferrocene photosensitization in *trans*-1,2-dimethylcyclohexane cannot be reliably determined directly because of the low rate of conversion, but our studies suggest that the composition is greater than 55% *trans*-piperylene. An alternate approach was also taken which involves the ratio of initial conversion rates in two sensitized samples, one initially containing *cis*-piperylene and the other *trans*-. A kinetics analysis of the energy-transfer mechanism for high-energy sensitizers indicates that the ratio of the initial rate of *trans* to *cis* conversion and the initial rate of *cis* to *trans* conversion equals the *cis–trans* ratio at the photostationary state, *i.e.*, 45:55. This technique was tested using benzophenone, a high-energy sensitizer. The measured ratio of initial rates agreed with the ratio determined by irradiating to the photostationary state (0.78 ± 0.03) and with the ratio reported in the literature (0.81[4,5]). To determine if ferrocene behaves as a high-energy sensitizer, we irradiated simultaneously a 0.15 M ferrocene–0.20 M *cis*-piperylene solution and a 0.15 M ferrocene–0.20 M *trans*-piperylene solution using a 2800-Å cut-off filter (Corning C.S. 0-53). The ratio of initial conversion rates yielded 0.41 ± 0.05. Other experiments gave the same ratio for excitation at 3240 and 2650 Å and for solutions containing 0.15 M ferrocene and 0.05 M piperylene. We therefore propose that ferrocene is acting as a low-energy sensitizer in *trans*-1,2-dimethylcyclohexane. The energy-transfer process is pictured in Figure 1 using Scott and Becker's assignments for ferrocene's electronic states.[12,13] The ferrocene excited triplet responsible for energy transfer is probably the lowest ($^3E_{1g}{}^-$); however, the $^3E_{1g}{}^+$ level may also be involved if the reported emission of ferrocene from this
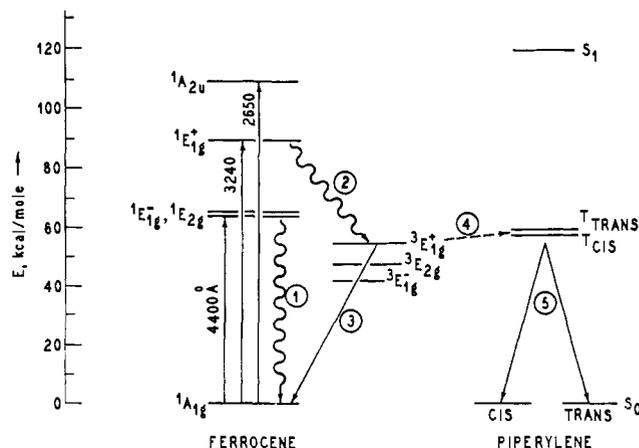

Figure 1. Mechanistic scheme for energy transfer from excited ferrocene to piperylene: (1) relaxation of ferrocene singlet state, (2) ferrocene intersystem crossing, (3) possible ferrocene phosphorescence, (4) triplet–triplet energy transfer, (5) relaxation of piperylene triplet state to *cis*- and *trans*-piperylenes.

state is real.[8,9,14] Our preliminary studies of ferrocene sensitization in benzene solvent using the 3130-Å filter train yielded an initial rates ratio of 0.82 ± 0.10. This is in agreement with the photostationary-state composition found by Dannenberg and Richards[1–3] and suggests that there is a marked solvent effect in this system.

The proposed mechanism of Dannenberg and Richards for ferrocene photosensitization involves a ground-state ferrocene–piperylene complex that dissociates to ferrocene in its lowest triplet ($^3E_{1g}{}^-$) and to a triplet piperylene after 3240- and/or 2650-Å excitation. The mechanism requires that the $^3E_{1g}{}^- \leftarrow {}^1A_{1g}$ energy of ferrocene be about 32 kcal/mole.[2] This is inconsistent with theoretical and experimental studies which show that this lowest singlet–triplet transition has an absorption maximum at 40.5 kcal/mole.[12–14] Ultraviolet and nuclear magnetic resonance spectra were presented by the investigators as evidence for the existence of the ferrocene–piperylene complex. We were unable to detect a complex by nmr using a Varian Model A-60 spectrometer, but we observed small shifts in the ferrocene ultraviolet absorption spectrum for wavelengths less than 3100 Å. We are led to conclude that if an appreciable amount of complex is formed, the energy-transfer mechanism may be one where the complex in its singlet state (isoenergetic with ferrocene's $^1E_{1g}{}^+$ state) intersystem-crosses to its triplet state (ferrocene's $^3E_{1g}{}^+$ state) and then dissociates to ferrocene in its ground state and to a triplet piperylene which isomerizes. The latter mechanism was one of several possibilities considered by Dannenberg.[2]

(14) A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967).

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(11) The quantum yield of intersystem crossing was found to be 1.0 for benzophenone using potassium ferrioxalate actinometry.
(12) D. R. Scott, Ph.D. Thesis, University of Houston, 1965.
(13) D. R. Scott and R. S. Becker, *J. Organometal. Chem.* (Amsterdam), **4**, 409 (1965).