ations may in general be used as a probe for bonding characteristics in sulfones seem justifiable.[11] These concepts will be developed in further papers exploring the magnitude and ramifications of symmetry factors in the reactions of sulfur-containing compounds.

Acknowledgment. This work was supported by the National Science Foundation.

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[11] The anomalous behavior of the thiirane dioxides stands as an apparent exception:[8a] N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

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Benzophenone-Sensitized Photoisomerization of the 2,4-Hexadienes in Solution

Sir:

In accounting for the nonstereospecific component of the photosensitized SO_2 extrusion from *cis*- and *trans*-dimethyldihydrothiophene dioxides we proposed the intermediacy of 2,4-hexadiene triplet states.[1] The following investigation of the sensitized photoisomerization of the 2,4-hexadienes was prompted by the recent report that 2,4-hexadiene triplet states may participate in an unusual quantum-chain process leading to very large *cis–trans* isomerization quantum yields.[2]

cis,cis-2,4-Hexadiene (*cc*), Analytical Sample from Chemical Samples, was used without purification. *cis,trans*-2,4-Hexadiene (*ct*), research grade from Aldrich, and *trans,trans*-2,4-hexadiene (*tt*), Columbia Organic Chemical Co., were bulb-to-bulb distilled. Benzophenone, Fisher reagent grade, was sublimed under reduced pressure. Purified chloranil-treated benzene,[1] containing methylcyclohexane as internal standard, was used as solvent. Quantum yield irradiations, 3130 Å, were carried out in parallel at 30° in a merry-go-round apparatus using a 450-W Hanovia mercury lamp.[3] For photostationary-state determinations samples were strapped on the Hanovia probe and irradiation at 30° was through a Pyrex filter. Analyses were by glpc on a 20 ft × $^1/_8$ in. column gradient-packed with segments of 40, 30, 20, and 10% β,β'-oxydipropionitrile on Chromosorb P. Initial compositions of the 2,4-hexadiene samples were: 99.25% *cc*, 0.60% *tc*, 0.15% *tt;* 98.11% *tc*, 1.89% *tt;* 0.62% *tc*, 99.28% *tt*. All samples were degassed to $<10^{-5}$ mm. Benzophenone-sensitized *trans* → *cis* photoisomerization of piperylene was used for actinometry.[4]

Isomerization quantum yields were measured at two diene concentrations using 0.050 *M* benzophenone. The results are given in Table I (estimated uncertainty ±10%). Photostationary states were approached from the *cc* and *tt* sides. The total diene concentration decreased by 35% during the irradiation period, probably because of competing dimerization.[5] The photostationary-state compositions are given in Table II. No other photoisomers were observed.[6]

Table I. Quantum Yields of 2,4-Hexadiene Isomerization[a]

[Diene], M^b	$\Phi_{tt\to ct}$	$\Phi_{cc\to ct}$	$\Phi_{ct\to tt}$	$\Phi_{cc\to tt}$	$\Phi_{ct\to cc}$	$\Phi_{tt\to cc}$	$\Sigma\Phi$
0.09	0.45	0.50	0.31	0.28	0.15	0.16	1.8_5
	0.48[c]	0.51		0.30		0.20	
0.8	0.52	0.48	0.36	0.29	0.16	0.19	2.0_0
	Av 0.48	0.50	0.33	0.29	0.16	0.18	1.9_4

[a] Corrected for back reaction;[4] no decrease in total diene concentration relative to standard, methylcyclohexane, was detected by glpc. Conversions ranged between 0.73 and 14.4%. [b] These are approximate values; absolute concentrations were determined by glpc using the internal standard as reference. [c] Second entries correspond to results from longer irradiation times and higher conversions.

Table II. Photostationary State for Benzophenone-Sensitized Isomerization of 2,4-Hexadienes

Starting diene, *M*	% *tt*	% *ct*	% *cc*
tt, 0.09	31.3 ± 0.3	50.2 ± 0.1	18.5 ± 0.2
cc, 0.09	31.3 ± 0.2	50.0 ± 0.4	18.7 ± 0.2

The isomerization quantum yields (Table I) disagree drastically with those reported in ref 2. In contrast with the previous measurements, the quantum yields are independent of initial diene concentration and irradiation time. A chain mechanism for isomerization does not operate in our system. The photostationary-state composition (Table II) differs somewhat from the composition reported in ref 2. The discrepancy may have resulted from residual chain isomerization in the earlier measurements causing a shift of the composition in the direction of thermal equilibrium. On this basis it seems likely that our results represent more closely the true photostationary state.

Possible mechanisms for the photoisomerization of the 2,4-hexadienes were discussed in detail in ref 2.[7] Our results show that absorption of one quantum of light by one of the diene isomers causes isomerization at both double bonds. Excitation transfer to any of the three dienes produces a common triplet state (s). The common triplet mechanism requires that the sum of all six quantum yields equal 2,[2] and that individual quantum yields should predict the composition at the photostationary state (eq 1–3; diffusion-controlled excitation to all three isomers is assumed).

$$\Phi_{tt\to ct} = \Phi_{cc\to ct} = [\%\ ct]_s \times 10^{-2} \tag{1}$$

$$\Phi_{ct\to tt} = \Phi_{cc\to tt} = [\%\ tt]_s \times 10^{-2} \tag{2}$$

$$\Phi_{ct\to cc} = \Phi_{tt\to cc} = [\%\ cc]_s \times 10^{-2} \tag{3}$$

Examination of Tables I and II shows that these requirements are fulfilled very well. The results are explained most economically by assuming the "1,4-biradical"[2] geometry, **1a**, for the common triplet state. Triplets of the "allylmethylene"[2] type **1b** have been predicted to be

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[1] J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, **89**, 2232 (1967).

[2] H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *ibid.*, **91**, 2852 (1969).

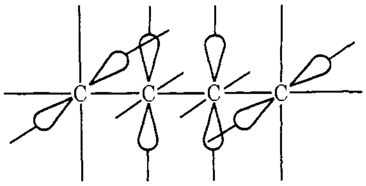
[3] J. Saltiel, *ibid.*, **90**, 6394 (1968); *cf.* F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

[4] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

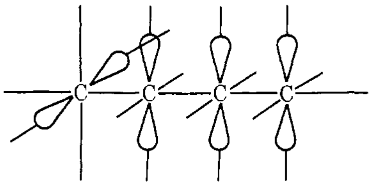
[5] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

[6] Direct excitation of the dienes yields several isomers; *cf.* R. Srinivasan, *ibid.*, **90**, 4498 (1968).

[7] The mechanistic implications of this study were first discussed by Dr. R. S. H. Liu; *cf.* R. S. H. Liu, Ph.D. Thesis, California Institute of Technology, 1964, pp 124–126.



1a



1b

lower in energy than those of type **1a**.[8] Triplets **1b** can account for the results only if the nonplanar distortion is rapidly transferred from one end of the molecule to the other.[2,9]

Acknowledgment. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by National Science Foundation Grant GP-7941.

[8] R. Hoffmann, *Tetrahedron,* **22,** 521 (1966). The calculations were for 1,3-butadiene and no distinction between triplets and singlets was made.

[9] NOTE ADDED IN PROOF. We have discussed our results with Professor G. S. Hammond and Dr. B. M. Monroe. Since, it appears, the main difference in operation is our use of freshly distilled 2,4-hexadienes and since we have some indication that undistilled diene isomerizes somewhat faster than distilled diene, we agree that it is probable that distillation eliminated some photoactive impurity.

[10] (a) Petroleum Research Fund Fellow. (b) Petroleum Research Fund Scholar.

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Differentiation of Relative Configurations in the *erythro* and *threo* Forms of 1,2-Diferrocenyl-1,2-diphenylethane and 1,2-Diferrocenyl-1,2-diphenyl-1,2-ethanediol

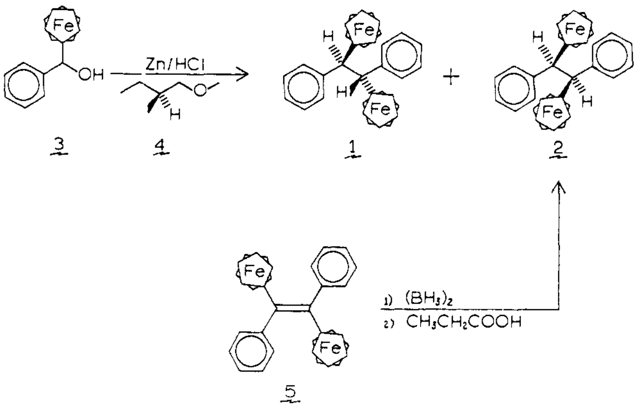
Sir:

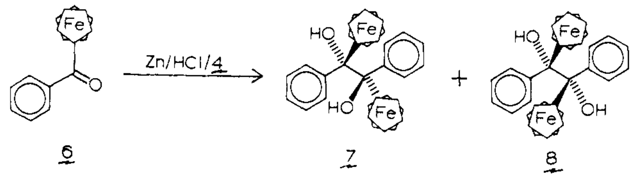
A little explored area of stereoselectivity lies in the use of optically active solvents in reaction processes. In principle, one might expect to observe enantiomeric enrichment (asymmetric selection[1]) in the chiral products of such processes if the diastereomeric transition states, resulting from interaction of a chiral solvent with the transition states leading to enantiomeric products, give rise to a $\Delta\Delta G^{\ddagger}$ large enough to provide a significant rate difference in the formation of each enantiomer.[2]

We report now two examples of this type of asymmetric selection which are noteworthy not only because they serve as illustrations of the principle stated above but also because they provide rigorous bases for assignments of relative stereochemistry to previously unassigned stereomers.

The diastereomeric forms (*erythro* and *threo*) of 1,2-diferrocenyl-1,2-diphenylethane[3] occur among the products of Clemmensen reduction of benzoylferrocene.[4] While these stereomers have been separated[5] (mp[3] 218–220° and 276–278°), no configurational assignments have been made. In the present work it has been shown that the lower and higher melting isomers are the *erythro* (**1**) and *threo* (**2**) forms, respectively.

Treatment of (±)-ferrocenylphenylcarbinol (**3**) in (+)-(*S*)-1-methoxy-2-methylbutane (**4**) ($[\alpha]^{21}\mathrm{D}$ 0.032°; lit.[6] $[\alpha]^{18}\mathrm{D}$ 0.34°) with zinc and hydrochloric acid gave the lower melting diastereomer (mp 218–222°) in 45% yield and the higher melting form (mp 276–278°) in 31% yield. Of the two purified products, only the higher melting isomer was optically active ($[\alpha]^{22}_{546}$ 26.1 ± 1.7° (*c* 0.176, benzene)), showing it, therefore, to be the *threo* form **2**.





In another experiment where a higher molar ratio of the optically active solvent **4** to **3** was used (51 as compared to 32 in the initial experiment), the *threo* isomer **2** was produced in lower material yield but in higher optical yield ($[\alpha]^{22}_{546}$ 57.3 ± 5.5° (*c* 0.183, benzene)), indicating perhaps the presence of an interesting dependence of optical yield on the concentration of the chiral solvent.

These results have also allowed assignment of stereochemistry to 1,2-diferrocenyl-1,2-diphenylethene, another product of the Clemmensen reduction of benzoylferrocene[4] which is produced in that reaction in only one of its two diastereomeric forms. Hydroboration of the olefin, followed by treatment with propionic acid,

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[1] S. I. Goldberg and M. S. Sahli, *J. Org. Chem.,* **32,** 2059 (1967).

[2] Optically active solvents, or solvent additives, that have been used successfully are: (+)-bornyldimethylamine (M. Betti and E. Lucchi, *Boll. Sci. Fac. Chim. Ind. Bologna,* 2 (1940)); (+)-2,3-dimethoxybutane (H. L. Cohen and G. F. Wright, *J. Org. Chem.,* **18,** 432 (1953); A. G. Brook, H. L. Cohen, and G. F. Wright, *ibid.,* **18,** 447 (1953); K. R. Bharucha, H. L. Cohen, and G. F. Wright, *ibid.,* **19,** 1097 (1954); N. Allentoff and G. F. Wright, *Can. J. Chem.,* **35,** 900 (1957); N. Allentoff and G. F. Wright, *J. Org. Chem.,* **22,** 1 (1957)); (+)-mannitol hexamethyl ether and (−)-arabitol pentamethyl ether (N. Allentoff and G. F. Wright, *ibid.,* **22,** 1 (1957)). For an account of others see J. Mathieu and J. Weill-Raynal, *Bull. Soc. Chim. Fr.,* 1211 (1968). For an account of some early unsuccessful experiments in this area see P. D. Ritchie, "Asymmetric Synthesis and Asymmetric Induction," Oxford University Press, 1933, p 78 ff.

[3] A. Berger, W. E. McEwen, and J. Kleinberg, *J. Amer. Chem. Soc.,* **83,** 2274 (1961).

[4] S. I. Goldberg and M. L. McGregor, *J. Org. Chem.,* **33,** 2568 (1968).

[5] S. I. Goldberg and W. D. Bailey, unpublished.

[6] H. G. Rule, E. B. Smith, and J. Harrower, *J. Chem. Soc.,* 376 (1933).