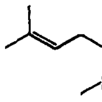
original sulfide isomerization. Treatment of salt **10** with *n*-butyllithium at $-30°$[7] gave the expected rearrangement product **11**[12] (bp 94° (12 mm); $n^{24.5}\text{D}$ 1.4918; nmr (carbon tetrachloride), δ 1.61–1.77 (12 H, four CH_3), 1.91 (3 H, SCH_3), 2.16 (2 H, multiplet, $-CH_2-$), 330 (1 H, multiplet, >CHS–, $J_1 = 10, J_2 = 8, J_3 = 6.5$ cps), 5.08 (2 H, multiplet, olefinic)), reduced by sodium in liquid ammonia[13] to the squalene-like hydrocarbon **12** (bp 169° (740 mm); $n^{24}\text{D}$ 1.4490; nmr (carbon tetrachloride), δ 1.58 (6 H, two CH_3), 1.67 (6 H, two CH_3), 1.98 (4 H, multiplet, $-CH_2-$), 5.08 (2 H, multiplet, olefinic)), along with some 19% of the double bond isomer **13** (nmr (carbon tetrachloride), δ 0.94 (6 H, two CH_3, $J = 6.5$ cps), 1.58 (3 H, one CH_3), 1.68 (3 H, one CH_3), 2.63 (2 H, multiplet, $-CH_2-$), 4.90–5.30 (3 H, multiplet, vinylic)). The homogeneous hydrocarbon **12**, purified by gas–liquid partition chromatography,[14] was identical in all spectroscopic and gas–liquid partition chromatographic properties with those of an authentic sample.[15]



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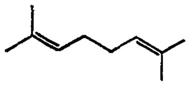

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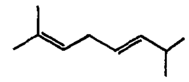

13

These results confirm the chemical validity of the postulated mechanism[16] and lead in general to a simple procedure for coupling allyl units in the tail-to-tail manner,[17] since the unsymmetrical sulfides are readily available from the corresponding disulfides.[9]

Acknowledgments. We are indebted to Eli Lilly and Company, Indianapolis, Ind., for their generous financial support. One of us (R. E. H.) wishes to thank the Sun Oil Company for a fellowship.

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(12) Most runs gave material contaminated (15%) by the isomer resulting from rearrangement of the salt (8, R = CH_3). These two sulfides were separated by preparative gas–liquid partition chromatography.

(13) R. C. Krug and S. Tocker, *J. Org. Chem.*, **20**, 1 (1955). In our hands this is the preferred desulfurization procedure, since the more usual Raney nickel gave complex mixtures on reaction with allylic sulfides.

(14) All gas–liquid partition chromatographic separations were conducted on a 20 ft × 3/8 in. column of SE-30 on Chromosorb W (40–60).

(15) Repetition of the literature procedures for olefin **12** [*e.g.*, P. G. Stevens and S. C. Spalding, *J. Am. Chem. Soc.*, **71**, 1687 (1949)] involving dehydration of 2,7-dimethyloctane-2,7-diol gave mixtures of 1,6- and 2,6-dienes (nmr) which we were unable to separate. However, the Grignard coupling procedure [H. Staudinger, W. Kreis, and W. Schilt, *Helv. Chim. Acta*, 5, 743 (1922)] yielded a separable mixture of dienes.

(16) Nothing is yet known of the stereochemistry of the various centers created in such reactions.

(17) Coupling of allyl units in a tail-to-tail manner has also been described by K. B. Sharpless, R. P. Hanzlik, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **90**, 209 (1968).

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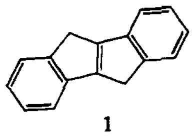
Tests of the Singlet Mechanism for *cis–trans* Photoisomerization of the Stilbenes

Sir:

The mechanism proposed for the direct photoisomerization of the perhydro- and perdeuteriostilbenes involves rotation about the central bond in the S^1 state and decay from a common twisted singlet state.[1] Intersystem crossing to the triplet states is considered inefficient,[2] and the only process competing with twisting about the central bond from *trans* S^1 states is fluorescence. The requirement, that inhibition of rotation about the central bond results in a corresponding increase in the fluorescence quantum yield, is a consequence of this mechanism. The following concerns tests of this requirement.

An electronic model of *trans*-stilbene which is restricted to a planar configuration is indeno[2,1-*a*]indene (**1**). **1** was prepared from ethyl phenylacetate using a modification of the available synthesis.[3–5] The ultraviolet absorption spectrum of **1** provides strong evidence that this molecule is a good electronic model for *trans*-stilbene. The fluorescence quantum yield, Φ_F, of **1** was determined using *p*-terphenyl and sodium salicylate as standards.[6] Using Berlman's value of 0.87 for the fluorescence quantum yield of *p*-terphenyl at room temperature in the presence of air,[8] the Φ_F of **1** at 295°K is found to be 0.94. Using Weber and Teale's value of 0.28 for Φ_F of sodium salicylate,[9] the Φ_F of **1** at 295°K is found to be 1.04.[10] In agreement with these observations, the fluorescence quantum yield of **1** is *temperature independent* in the range 301–77°K.[11] These findings, which contrast the observations with *trans*-stilbene,[12–14] are in agreement with the singlet mechanism for stilbene photoisomerization.



1

Also in accord with the singlet mechanism are the recent findings showing $S^1 \rightarrow T$ intersystem crossing to be inefficient for 1,2,3-triphenylcyclopropene (**2**)[15] and 1,2-diphenylcyclobutene (**3**).[16] In the latter case, Φ_F was shown to approach 1.0 at room temperature.[16]

The significance of the above observations lies in that a requirement of the singlet mechanism is fully realized.

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(1) J. Saltiel, *J. Am. Chem. Soc.*, **89**, 1037 (1967).

(2) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, 88, 2336 (1966).

(3) K. Brand and K. O. Müller, *Ber.*, **55**, 601 (1922).

(4) S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940).

(5) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

(6) The apparatus used for the fluorescence studies has been described.[7] Degassed solutions of **1** in methylcyclohexane–3-methylpentane (6:1) were employed. *p*-Terphenyl solutions were not degassed, and ethanol was used as solvent for sodium salicylate. *trans*-Stilbene and **1** used in this work were zone refined.

(7) (a) J. Eisinger, M. Gueron, and R. G. Shulman, "Advances in Biological and Medical Physics," Academic Press, New York, N. Y., 1967; (b) J. Eisinger, to be published.

(8) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 138.

(9) G. Weber and R. W. J. Teale, *Trans. Faraday Soc.*, **54**, 640, (1958).

(10) Our independent comparison of sodium salicylate and *p*-terphenyl fluorescence quantum yields gives 0.26 for the quantum yield of sodium salicylate if we assume Berlman's value for *p*-terphenyl.

(11) The estimated uncertainty in the relative fluorescence of **1** as a function of temperature is less than ±3%. No phosphorescence could be detected from **1** within this temperature range.

(12) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(13) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

(14) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 12 (1968).

(15) C. D. DeBoer and R. Breslow, *Tetrahedron Letters*, 1033 (1967).

(16) C. D. DeBoer and R. H. Schlessinger, *J. Am. Chem. Soc.*, **90**, 803 (1968).

These results are not presented as evidence against the triplet mechanism, since we cannot rule out the possibility that in *cis*- and *trans*-stilbenes $S^1 \rightarrow T$ intersystem crossing may require a molecular distortion (such as twisting about the central bond[17]) which is structurally prohibited in **1–3**.[19]

Recently, three lines of evidence were presented which are presumed to show that the direct photoisomerization of the stilbenes proceeds following intersystem crossing to triplet states.[20] We consider the first two lines of evidence not relevant to the mechanism of photoisomerization of unperturbed stilbene. External and internal heavy atom effects, or substituents which generally enhance intersystem crossing efficiency, could very well alter the mechanism of the photoisomerization so that triplet states may become involved.[21] The third line of evidence concerns the uncoupling of *trans*-stilbene fluorescence from its photoisomerization. It is stated that media of high viscosity, *e.g.*, glycerol, inhibit the isomerization without there being a corresponding increase in the quantum yield of fluorescence. It was concluded that high viscosity inhibits the *trans* → *cis* isomerization, while intersystem crossing continues to be the major pathway competing with fluorescence.[14,20]

If the reported glycerol data were accurate, the argument for the rejection of the singlet mechanism for stilbene isomerization would indeed be compelling. The following shows the reported data to be inaccurate.

(1) We find that the ratio of Φ_F for *trans*-stilbene to Φ_F for **1** at 77°K is 1.06. This value is within experimental error of unity, and we conclude that the quantum yield of fluorescence of *trans*-stilbene approaches a limiting value of unity rather than 0.75 as reported by the above workers.[20,22]

(2) Interpolation from the results of Malkin and Fischer yields 0.65 for Φ_F of *trans*-stilbene at $-80°$ in MCH–IH. This value and the ratio of quantum yields in ref 14 give 0.85 as the limiting Φ_F in glycerol at $-80°$.[23] Considering the experimental uncertainty in the measurements, this value cannot be regarded as significantly different from unity.

(3) As an independent check of the reported *cis* → *trans* and *trans* → *cis* quantum yields (Φ_c and Φ_t, respectively) photostationary states were determined at three temperatures.[24] Table I shows the poor agreement obtained between observed stationary-state compositions and compositions predicted by eq 1[25] using

$$\frac{[t]_s}{[c]_s} = \frac{\epsilon_c \Phi_c}{\epsilon_t \Phi_t} \qquad (1)$$

the reported quantum yields.[14,26]

Table I. Photostationary State Compositions in Glycerol

Temp, °C	% *cis* at photostationary state Obsd[a]	Predicted[b]
30	91.4	93.5
0	80.3	87.2
−21	62.6	75.0

[a] Estimated error ±1%. [b] From eq 1.

Although more work is required in order to establish conclusively that the processes of fluorescence and isomerization remain coupled in glycerol, points 1–3 suggest that the glycerol results are consistent with the singlet mechanism.

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[17] Proponents of the triplet mechanism have generally assumed a large barrier to rotation about the central bond in S^1;[12] *cf.*, however, ref 18.

[18] P. Borrell and H. H. Greenwood, *Proc. Roy. Soc.* (London), **A298**, 453 (1967).

[19] For the evidence against the involvement of triplet states in the direct photoisomerization, see ref 2.

[20] K. A. Muskat, D. Gegiou, and E. Fischer, *J. Am. Chem. Soc.*, **89**, 4814 (1967); see also ref 14.

[21] One of us has pointed this out previously for the case of the *p*-bromostilbenes.[2] For the first example of an external heavy atom effect on a photochemical reaction, see D. O. Cowan and R. L. Drisko, *ibid.*, **89**, 3068 (1967).

[22] In agreement with Malkin and Fischer, we find that the Φ_F ratio of *trans*-stilbene at 77°K to anthracene (in the presence of air) at room temperature is 4.43.[13]

[23] The ratios between corresponding values of the two sets of Fischer's fluorescence quantum yields in MCH–IH are 1.6, 1.86, 1.37, and 1.33 at 25, −80, −105, and −183°, respectively.[13,14,20]

[24] Stationary states were approached from both sides using 3130-Å light. Glycerol solutions were 3×10^{-5} *M* in each isomer and were degassed. Some of the stilbene was consumed in a side reaction which did not interfere with ultraviolet analysis of *cis:trans* ratios. Preliminary observations indicate that the side reaction involves dimerization of *trans*-stilbene! It is likely, therefore, that there are *trans*-stilbene aggregates in dilute glycerol solutions and that a limiting $\Phi_F < 1$ may be consistent with the singlet mechanism.

[25] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsel, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[26] The ratio of extinction coefficients at 3130 Å was found to be 0.147 ± 0.001 in the temperature range in question.

[27] National Institutes of Health Predoctoral Research Fellow, 1965–present.

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Monotropic[1] Crystalline Phases of *p*-Azoxyanisole from the Nematic Melt[2]

Sir:

A correlation between the molecular organization in the liquid-crystalline phase of a pure substance and the crystal structure of that substance was first suggested by Bernal and Crowfoot.[3] In particular, qualitative inferences about the molecular organization in nematic *p*-azoxyanisole have been made on the basis of two[3,4] structure determinations, the parallelism of the long molecular axes in the crystal supporting the belief that within each domain in the nematic phase the long molecular axes are still parallel (or nearly so). It was ex-

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[1] We intend this phrase to have the meaning given in A. Findlay, "The Phase Rule and Its Applications," 7th ed, Longmans, Green and Co., New York, N. Y., 1931, pp 35–36; namely that at atmospheric pressure and in contact with vapor there is *no* temperature at which the crystalline phase in question can be transformed *reversibly* into another crystalline phase. Almost equivalent is the simpler statement that there is no temperature range within which the crystalline phase in question is the thermodynamically stable phase. Several meanings have been attributed to "monotropic" in other work on liquid crystals.

[2] Based on a thesis submitted by R. C. R. to Duke University in partial fulfillment of the requirements for the Ph.D. degree.

[3] J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933).

[4] F. Würstlin, *Z. Krist.*, **88**, 185 (1934).