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

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

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.

Acknowledgment. The research at Florida State University was supported by National Science Foundation Grants GP-5159 and GP-7941. A. A. L. thanks Dr. J. Eisinger for the use of the spectrofluorometer and Mrs. B. Feuer for technical assistance.

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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).

plicitly recognized by Bernal and Crowfoot[3] that the crystalline phase whose structure correlates with that of the nematic phase need not be the thermodynamically stable phase. Indeed, they noted the greater similarity of optical properties of nematic *p*-azoxyanisole to a monotropic "white" solid modification, reported earlier,[5,6] than to the stable yellow modification. On the basis of rather scanty optical evidence, however, Bernal and Crowfoot stated that the "white" and yellow forms differed "remarkably little except in habit," thus justifying a correlation between the nematic organization and the partially determined structure of the yellow form.

We wish to report the existence of *two* monotropic crystalline phases (hereafter denoted as solids I and II) of *p*-azoxyanisole in addition to the form stable at room temperature (denoted as solid III). Moreover, both solid I and solid II can be separately equilibrated with the nematic phase; this fact reopens the question of which modification has the structure which most properly correlates with the nematic organization. Furthermore, we find that supercooling the nematic melt usually results in the initial formation of solid I, so that kinetically it would appear that solid I (*not* solid III) has the structure most closely resembling that of the nematic phase.

Pure *p*-azoxyanisole, obtained by vacuum sublimation at 100° and 0.07 torr (preceded by three crystallizations from ethanol for lower quality commercial material), showed only the solid III → nematic transition at 117° when heated in a Perkin-Elmer DSC-1B differential scanning calorimeter. On cooling the nematic phase in this instrument, however, three distinguishable exothermic peaks always appeared: the nematic → solid I peak typically at 95 ± 5°; the solid II → solid III peak typically at 55 ± 10°; and the solid I → solid II peak typically as a spike on the low-temperature end of the nematic → solid I peak, or at the high-temperature end of the solid II → solid III peak, rarely as an isolated spike at about 90°. By reheating the sample immediately after N exothermic peaks had been observed, the transition solid N → nematic could be seen as an endothermic peak. The temperatures at which these peaks occurred are: solid I → nematic, 103°; solid II → nematic, 113°; solid III → nematic, 117°.

In order to verify the results of differential scanning calorimetry, we observed the behavior of *p*-azoxyanisole on a hot-stage polarizing microscope. As has often been noted, the nematic phase supercooled below 117° and solidified to a polycrystalline mass. The appearance of individual crystallites could not be distinguished in this mass, and so could not be compared to that of large crystals of solid III. Immediate reheating of this mass usually resulted in its melting to the nematic phase at 103° (a correction being made for a systematic discrepancy between the temperature reading of a "calibrated" DSC-1B and a "calibrated" thermometer for the hot stage). By carefully cooling the mixture of nematic phase and solid I, larger crystallites of solid I could be grown. These crystallites, light yellow in color, terminated in nearly colorless lamellae, obviously different in morphology from crystals of solid III grown from the nematic melt. If crystals of solid I were cooled until solid II formed, the crystal faces became somewhat irregular and the interference colors became patchy. Immediate reheating produced the nematic phase at 113°. If, instead of reheating solid II, one allowed it to cool further, the solid II → solid III transition could be observed as a cloudy wave front going through the material. The mosaic solid III resulting could be identified by the fact that on reheating, the nematic phase formed at 117°. Optically, however, it could not be distinguished from the solid II which was also a mosaic as a result of the previous solid I → solid II transition.

The surprising fact that at least one of these monotropic modifications of *p*-azoxyanisole has remained undetected is explainable by the difficulty in recognizing their individual crystal habits and by the infrequent use of differential scanning calorimetry with temperature decreasing. Thus the metastable phases of this compound could not be observed by Barrall, Porter, and Johnson[7] in their recent calorimetric investigation in which measurements were made during heating, if solid III were the only initial material. Temperature cycling resulting in nematic → solid transitions might give rise to solid II; if this occurred, the nearly infinite specific heat of the solid just above 112.5° observed on heating by Barrall, Porter, and Johnson would be understandable.[8] Solid I may be the "colorless" modification, crystallizing in thin rectangular lamellae, noted by Gattermann and Ritschke,[5] or the "quite colorless, at least, compared to the yellow..." modification of Vörlander[6] and of Bernal and Crowfoot.[3] Only the last-named workers were able to equilibrate the "white" form with the nematic phase, but the transition temperature of 84° was obtained by a crude method, based on very erroneous values of 94° and 150° for the solid III ↔ nematic and nematic ↔ isotropic transition temperatures, and cannot be positively identified with any of our reported transition temperatures. On the other hand, we have not been able to grow crystals of solids I or II suitable for measuring the optical properties attributed[3] to "white" *p*-azoxyanisole.

Using the symbolism of Demus and Sackmann,[9] the phase transformations of *p*-azoxyanisole should be written as shown in Scheme I where the two temperatures in brackets are mean values of observed transition temperatures, are rather variable, and have little thermodynamic significance. By contrast, the transition temperatures between each solid and the nematic phase are seen actually to follow the order required if solid II is monotropic with respect to solid III, and solid I is monotropic with respect to solid II.[8]

Scheme I

$$\begin{tikzcd}
\text{solid III} \arrow[r, leftrightarrow, "117^\circ"] & \text{nematic} \arrow[r, leftrightarrow, "135^\circ"] \arrow[d, leftrightarrow, "103^\circ"] \arrow[dl, leftrightarrow, "113^\circ"'] & \text{isotropic} \\
\text{solid II} \arrow[u, "{[59^\circ]}"] & \text{solid I} \arrow[l, "{[90^\circ]}"'] &
\end{tikzcd}$$

Further experimental details, heat capacities of all phases, values of ΔH of transitions, and photomicrographs will be submitted for publication.

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[5] L. Gattermann and A. Ritschke, *Ber. Bunsenges. Physik. Chem.*, **23**, 1738 (1890).

[6] D. Vorländer, *ibid.*, **40**, 1415 (1907).

[7] E. M. Barrall, II, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, **71**, 895 (1967).

[8] We are indebted to a referee for pointing the way to this realization.

[9] D. Demus and H. Sackmann, *Z. Physik. Chem.* (Leipzig), **222**, 127 (1963).

Acknowledgment. R. C. R. gratefully acknowledges a National Defense Education Act Traineeship while J. C. P. wishes to thank the Alfred P. Sloan Foundation for initial support in this general area of research. Both authors acknowledge continuing support by the National Science Foundation under Grant GP-7494.

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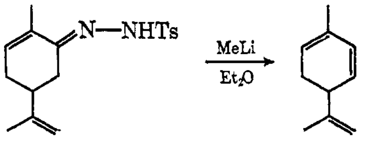
Preparation of Conjugated Dienes from Tosylhydrazones of α,β-Unsaturated Ketones and Alkyllithium Reagents[1,2]

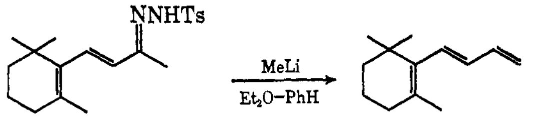
Sir:

The reaction of alkyllithium reagents with tosylhydrazones to yield the lesser substituted olefin without a carbon skeleton rearrangement has recently been reported.[3] This reaction finds great utility in the preparation of difficultly obtainable olefins such as 2-bornene[3a] and bicyclo[2.1.1]hexene.[3d]

An extension of this reaction using the tosylhydrazones of α,β-unsaturated ketones now permits the preparation of conjugated dienes in good to excellent yields. The reaction is of particular use in the synthesis of substituted 1,3-cyclohexadiene compounds which often are difficult to prepare in high purity and in quantity by other methods. Thus, in the presence of ≥ 2 equiv of methyllithium in ether or ether–benzene mixtures, carvone tosylhydrazone (I) gave in 80% yield, exclusively, 2-methyl-5-isopropenyl-1,3-cyclohexadiene (II),[4] showing that the elimination involved only the α hydrogen and that isomerization of other double bonds did not occur. A similar specificity is found in the preparation of the triene IV in a yield of 75–80% from β-ionone tosylhydrazone (III). Several other examples of the reaction are shown in Table I.



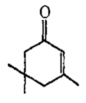
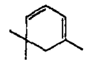
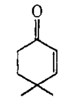
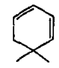
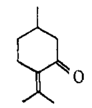
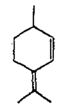
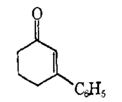
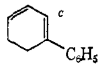
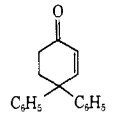
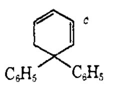
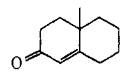
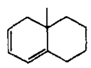
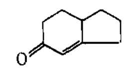
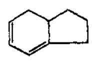
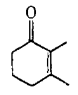
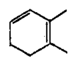
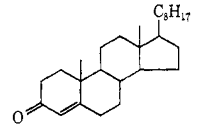
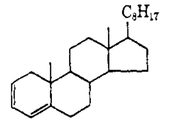
I II



III IV

In the course of the above investigation of dienes, the following features of the reaction were noted. In those cases where the tosylhydrazone, prepared in THF, did not precipitate from the reaction and permit ready isolation, excess benzene was added and the THF and benzene–water azeotrope were removed by distillation at atmospheric pressure. The resulting suspension of tosylhydrazone in benzene was allowed to react directly with methyllithium in ether. Methyllithium was found to be superior to n-butyllithium for the preparation of conjugated dienes, paralleling the behavior found for monoolefin production.[5] Dienes containing about 40% deuterium at the site of the original carbonyl group could be prepared by using deuterium oxide to decompose the reaction mixture. When the tosylhydrazone was added to n-butyllithium (inverse addition)[6] the deuterium content would be increased to approximately 60%. In some cases, sufficient toluene was found in the reaction mixture to make the isolation of the pure diene difficult. This toluene when formed in the presence of deuterium oxide contained deuterium only at the *para* position.

Table I. Reaction of α,β-Unsaturated Tosylhydrazones with Methyllithium

Tosylhydrazone of	Product	Yield, %
		100[a]
		85[b]
		100[a]
		40[b]
		55[b]
		85[b,d]
		60[b,d]
		87[b]
		80[b]

[a] Gas chromotographically pure. [b] Isolated yield. [c] Butyllithium used. [d] The reaetion and work-up were carried out below 10° to eliminate bond migration in the products.

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[1] This work was supported at Berkeley, in part, by Public Health Service Grant 00709, National Institute of Arthritis and Metabolic Diseases, U.S. Public Health Service, and at Boulder by National Science Foundation Grant GP 5753.

[2] This paper is part VIII in the tosylhydrazone series of the Boulder group. For paper VII, see R. H. Shapiro and K. Tomer, *Chem. Commun.*, 460 (1968).

[3] (a) R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967); (c) R. H. Shapiro, *Tetrahedron Letters*, 345 (1968); (d) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968).

[4] All structures were assigned on the basis of spectral evidence (nmr, uv, and mass spectrometry). Nmr decoupling experiments were performed in some cases to establish the peak assignments.

[5] R. H. Shapiro, J. H. Duncan, E. C. Hornaman, and J. W. Serum, unpublished observation.

[6] The incorporation efficiency appeared to depend upon the age of the alkyllithium; this effect is now being evaluated.