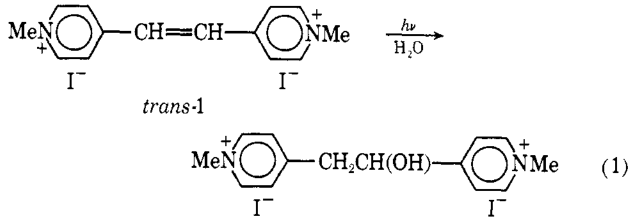
amples. Irradiation of an aqueous solution of the dimethiodide of *trans*-1,2-bis(4-pyridyl)ethylene (**1**)[6] with the 3130-Å line of a medium-pressure lamp[7] leads to efficient ($\varphi = 0.41$) and quantitative production of the dimethiodide of 1,2-bis(4-pyridyl)ethanol (**2**) (eq 1).

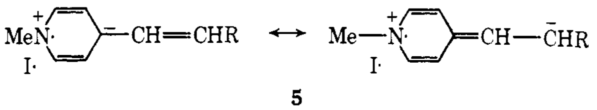


(1)

2

The reaction is conveniently followed *via* spectral changes in the uv. No isomerization to the *cis* isomer is detected.[9] Product **2** melts at 240° dec and has in the nmr (D_2O) δ 8.33 (m, 8, aromatic), 5.42 (t, 1, ArC*H*(OH)-CH_2–), 4.40 (s, 3, N-methyl), 4.37 (s, 3, N-methyl), and 3.50 (d, 2, ArCH(OH)CH_2Ar).[10] Irradiation of the dimethiodide of *trans*-1,2-bis(3-pyridyl)ethylene (**3**) under the same conditions leads to the corresponding ethanol **4** but with lower efficiency ($\varphi = 0.04$). Ethers are formed by reaction of **1** and **3** with alcohols. The reactions apparently originate from excited singlets of **1** and **3** since sensitizers such as benzophenone and Michler's ketone fail to promote the reaction. Triplet-energy transfer apparently does occur in these systems since **1** quenches the photopinacolization of benzophenone in methanol.[11]

To postulate electrophilic attack[2] on electron-deficient olefins such as **1** and **3** is unattractive. One mechanistic possibility for the photohydration is electron or charge transfer from iodide ion to the olefin in the excited state. A species such as **5** might be expected[12] to



5

add alcohol or water *via* proton abstraction and subsequent nucleophilic attack. Many pyridine methiodides show charge-transfer transitions in the region 3500–5000 Å.[12] We do not detect such transitions in acetonitrile or aqueous solutions of **1** and **3**; however they may be buried under the stilbene-like $\pi \rightarrow \pi^*$ transitions.[13] Evidence against a charge-transfer mechanism comes from our finding that the dihydrochloride of *trans*-1,2-bis(4-pyridyl)ethylene, for which charge-transfer processes should be unlikely, photohydrates efficiently under conditions used for **1** and **3**.

The probable mechanism for the photohydration consists of nucleophilic attack on the excited olefin and subsequent proton abstraction. This mechanism seems especially reasonable since we find that the intense fluorescence of **1** and **3** in acetonitrile is quenched by several nucleophiles, including water, ethanol, and pyridine. Data for quenching of the fluorescence of **1** and **3** by water are given in Table I. The values in Table I indicate that water quenching is about an order of magnitude slower than diffusion controlled.[14] Although water-quenching constants for **1** and **3** are comparable, quantum efficiencies for photohydration of the two differ considerably. This difference is probably related to stabilities of the intermediate (ground-state) olefin–nucleophile adducts; the adduct from **1** should be considerably stabilized relative to that from **3**. Dissociation of the nucleophile–olefin adduct probably lowers the quantum efficiency from unity in both cases.[9] These reactions are somewhat similar to the photohydration reactions reported for the pyrimidines;[16] it is possible that a similar mechanism is operative for the cyclic DNA bases.

Table I. Quenching of Fluorescence of **1** and **3** by Water

Compd	Slope[a]	$\varphi^0{}_f{}^b$	$\tau_s{}^c$	k_q, l. mol^{-1} sec^{-1}
1	0.25	0.06	1.1×10^{-10}	2.3×10^9
3	4.4	0.95	1.6×10^{-9}	2.7×10^9

[a] Slope from a linear Stern-Volmer plot of φ^0/φ *vs.* (H_2O). [b] Fluorescence quantum efficiency determined with *trans*-stilbene as a standard (see ref 5). [c] Calculated singlet lifetime in seconds.

Acknowledgment. We are grateful for support of this work, in part by the U. S. Army Research Office, Durham (Grant DA-ARO-D-31-124-G1097), and in part by the U. S. Public Health Service (Grant GM 15,238-02). We thank Mr. B. M. Zarnegar and B. M. Hickman for technical assistance.

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[6] Satisfactory analyses were obtained for all new compounds.

[7] Irradiations carried out in a "merry-go-round" apparatus[8] using glass and solution filters; concentration of 1, 4×10^{-4} *M*.

[8] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

[9] The *cis* isomer of **1** undergoes concurrent photohydration and isomerization to *trans*.

[10] The nmr spectrum of **2** showed splitting beyond those listed which are perhaps caused by the nitrogen. The spectrum of the free base, *vide infra*, is better resolved.

[11] We thank one of the referees for suggesting this experiment.

[12] E. M. Kosower, *Progr. Phys. Org. Chem.*, 3, 81 (1965), and references therein.

[13] The fact that 1 and 3 fluoresce rather efficiently (*vide infra*) may indicate that iodide ion is not close enough to the olefin in dilute aqueous or acetonitrile solutions to perturb electronic transitions.

[14] $k_{\rm diff}$ for acetonitrile is calculated[15] to be 1.9×10^{10} l. mol^{-1} sec^{-1}.

[15] F. Wilkinson, *Advan. Photochem.*, 3, 241 (1964).

[16] J. G. Burr, *ibid.*, 6, 193 (1968).

[17] National Aeronautics and Space Administration Predoctoral Fellow, 1966–present.

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Received July 8, 1969

The Stereoelectronic Course of the Triene–Sulfur Dioxide Reaction

Sir:

Examples of antarafacial[1] (conrotatory) cycloaddition are rare.[2] We[3a] and others[3b] have previously shown

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[1] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968). The terms antarafacial and suprafacial, introduced originally to describe sigmatropic hydrogen migration, are extended here in obvious fashion to cycloadditions in preference to the previously used[3] descriptors, conrotatory and disrotatory, respectively. The new terms apply more literally to cases in which no actual rotation takes place. For a comprehensive review of orbital symmetry control, see G. B. Gill, *Quart. Rev.* (London), 22, 338 (1968).

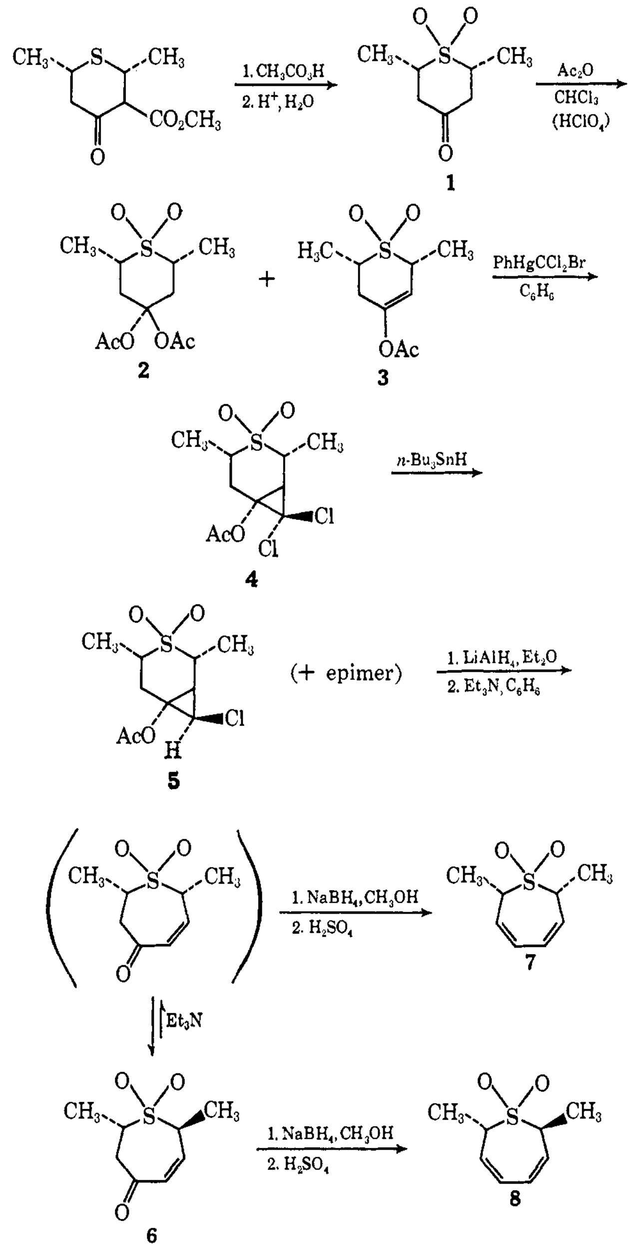
[2] R. B. Woodward, in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 217, cites but one example, which need not be concerted.

[3] (a) W. L. Mock, *J. Amer. Chem. Soc.*, 88, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, 88, 2858 (1966).

that, in the case of sulfolenes, cycloelimination yielding dienes and sulfur dioxide is a concerted, suprafacial (disrotatory) process. We here report that the decomposition of 2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide is also a stereospecific (and hence concerted) process, which occurs in an antarafacial mode in accordance with expectations from symmetry considerations.[4]

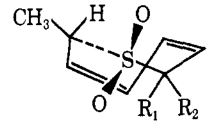
Attempts to observe 1,6 addition[5] of sulfur dioxide to suitable diterminally substituted trienes failed; in all cases, either 1,4 addition or no sulfone was obtained. Hence, the retro reaction was examined after indirect synthesis of the stereoisomers of 2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide. The requisite sulfones were secured as shown in Scheme I.[6]

Scheme I. Synthesis of 2,7-Dimethyl-2,7-dihydrothiepin 1,1-Dioxides[6]



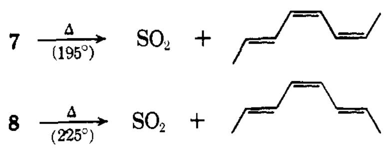
The substance **2** is the stereochemical reference point for the sequence; its nmr spectrum shows nonequivalent acetoxy groups, uniquely requiring that the (equivalent) methyls adjacent to the sulfonyl group be *cis* to one another. The ring expansion process **3** → **6** is that of Stork and De Selms.[7] Stereochemical control was lost in **5** → **6** due (presumably) to epimerization *via* the sulfonyl-stabilized, vinylogous enolate of **6**. Only the favored *trans*-dimethyl keto sulfone **6** was isolable. However, the reduction–dehydration procedure, when applied to a mixture of **6** and its *cis* epimer, yielded serviceable amounts of **7** (mp 53°) as well as **8** (mp 83°). The latter (**8**) could be obtained cleanly from recrystallized **6**. Confirmation of assigned stereochemistry was obtained by comparison of the reduction products of **6**, **7**, and **8** with the products of ring expansion of **1** by an independent route without possibility of epimerization next to the sulfonyl group.[8]

Fragmentation of **7** and **8** into sulfur dioxide and octatrienes was carried out in the injection port of a gas chromatograph at 195–260°. Subsequent glpc analysis[9] revealed that **7** gave almost exclusively *trans,cis,-cis*-2,4,6-octatriene whereas **8** gave *trans,cis,trans*-2,4,6-octatriene. Stereospecificity in each case exceeded 97%. The assignment of triene stereochemistry is based upon information furnished by Professor E. N. Marvell who has unambiguously prepared and characterized each isomer.[10]



7, $R_1 = CH_3; R_2 = H$

8, $R_1 = H; R_2 = CH_3$



The stereochemical results require that the decomposition be a *trans*, concerted[3a] elimination, *i.e.*, an antarafacial process. By inference the addition reaction,[5] the microscopic reverse, is likewise preferentially antarafacial. Examination of models indicates no ring strain or other steric prohibition against *cis* elimination (relative to *trans*—in particular for **7**). Furthermore, π overlap (in the absence of symmetry constraints[1]) appears comparable or better for suprafacial elimination. Consequently, the conclusions that stereoelectronic factors are here dominant and that symmetry consider-

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[4] The molecular orbitals of W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950), and of S. P. Ionov and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 7, 252 (1966), are implied for sulfur dioxide and the sulfones.

[5] W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).

[6] The numbered intermediates are all new, crystalline substances giving satisfactory C and H analyses (with the exception of 7, for which a limited quantity of material was available). Spectral data support each of the structures assigned.

[7] G. Stork, M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, 105 (1966); R. C. De Selms and T.-W. Lin, *Tetrahedron*, **23**, 1479 (1967).

[8] Ring expansion of 1 by a new variant of the Lewis acid catalyzed diazoacetic ester method of W. T. Tai and E. W. Warnhoff, *Can. J. Chem.*, **42**, 1333 (1964), followed by acidic decarbethoxylation gave a solid, seven-membered cyclic keto sulfone, mp 104° (2,4-DNP mp 213–214°), which is enantiomeric with the catalytic hydrogenation (1 equiv of H_2, Pd–C) product (liquid, 2,4-DNP mp 236–237°) of 6. Borohydride reduction of the tosylhydrazone of the former (solid) keto sulfone yielded *cis*-2,7-dimethylthiapane 1,1-dioxide, which is enantiomeric with the catalytic hydrogenation (2 equiv of H_2, Pd–C) product of 8. The *cis*- and *trans*-dimethylthiapane dioxides (separable by glpc) were isomerized to the same equilibrium mixture in dimethyl sulfoxide containing potassium *t*-butylate.

[9] Tris(2-cyanoethoxy)propane column at 85°.

[10] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

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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Received June 20, 1969

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]	$\Phi_{tt\rightarrow ct}$	$\Phi_{cc\rightarrow ct}$	$\Phi_{ct\rightarrow tt}$	$\Phi_{cc\rightarrow tt}$	$\Phi_{ct\rightarrow cc}$	$\Phi_{tt\rightarrow cc}$	$\Sigma\Phi$
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).

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

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

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

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.