

the photoracemizations of **5** and **6** were studied. Irradiation of $0.5 \times 10^{-3} M$ (-)-(*R*)-**5** ($\epsilon_{300}^{\text{diox}}$ 8800) in ether (Pyrex filter) for 2 min. resulted in 75% decomposition. The recovered material was 57% racemized. The extraordinary photolability of **5** possibly results from facilitated carbon-sulfur bond fission through formation of a resonance-stabilized α -naphthylcarbiny radical. In contrast, irradiation of $2 \times 10^{-3} M$ (+)-(*R*)-**6**¹⁵ ($\epsilon_{300}^{\text{diox}}$ 4600) in ether (Pyrex filter) for 1 hr. gave an 84% recovery of completely racemized¹² **6**. This result provides striking evidence for the intramolecular sensitization process.

Irradiation of (+)-(*S*)-methyl *n*-butyl sulfoxide¹⁰ ($[\alpha]^{25\text{D}} +41.7^\circ$ (isooctane), $\lambda_{\text{sh}}^{\text{diox}}$ 222 m μ , ϵ 1110) for 10 min. (Vycor filter, cut-off below 220 m μ) resulted in extensive decomposition. Undecomposed sulfoxide, recovered in 62% yield, had $[\alpha]^{25\text{D}} +41.6^\circ$ (isooctane). Addition of naphthalene did not result in detectable racemization. It would thus appear that the arene-sulfinyl chromophore¹⁰ is required for the photoracemization.

In an extension of the above results to *cis-trans* interconversions, irradiation of *cis*-thianthrene 5,10-dioxide ($\epsilon_{300}^{\text{diox}}$ 13) in dioxane (Pyrex filter) for 2 hr. gave complete recovery of starting material, whereas similar treatment of the *trans* isomer ($\epsilon_{300}^{\text{diox}}$ 1050) resulted in complete conversion to the *cis* isomer. The characteristically higher extinction of *trans*- relative to *cis*-thianthrene 5,10-dioxide in the wave length region above 260 m μ ^{5e} permits generalization of this result to include other thianthrene 5,10-dioxides. It is noteworthy that the thermal^{5e} and photochemical stereomutations of thianthrene 5,10-dioxides proceed in the same direction, *i.e.*, toward the *cis* isomer.

(15) M.p. 72–73°, $[\alpha]^{25\text{D}} +132^\circ$ (ethanol). The racemate melts at 88–89°.

(16) National Aeronautics and Space Administration Fellow, 1964 to present.

Kurt Mislow, Michael Axelrod,¹⁶ Dennis R. Rayner
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Hans Gotthardt, Lelia M. Coyne, George S. Hammond
Contribution No. 3295
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109
Received August 30, 1965

Energy Transfer in the Racemization of Aryl Sulfoxides^{1,2}

Sir:

In the accompanying communication⁴ we have described photochemical stereomutation reactions of a number of aryl sulfoxides. In at least two of the examples reported it is reasonably clear that transfer of energy from a naphthalene unit to a *p*-toluenesulfinyl unit must be an important feature of the photoreactions. In the irradiation of **6**⁵ the primary absorption process

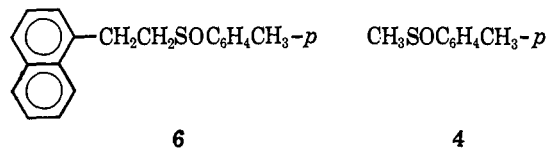
(1) The work was supported by the National Science Foundation under Grant No. GP-3375 at Princeton University and Grant No. GP-2488 at the California Institute of Technology.

(2) Mechanisms of Photochemical Reactions in Solution. XXXVI. Part XXXV is ref. 3.

(3) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4009 (1965).

(4) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4958 (1965).

must produce excitation principally located in the naphthalene nucleus, and in the racemization of **4**, sensitized by naphthalene, virtually all of the incident light was



absorbed by naphthalene.

In many cases preliminary understanding of the mechanisms of photoreactions are more easily derived from study of sensitized reactions than from study of those involving direct excitation.⁶ Consequently we have carried out a preliminary, quantitative study of the two reactions involving intra- and intermolecular-sensitized isomerization. In all the experiments a filter system designed to isolate the group of lines around 3130 Å. was used. The principal tool used in the study was quenching of the reactions by addition of piperylene (1,3-pentadiene). Pertinent observations are: (1) the initial quantum yield for isomerization of **6** is 1.1–1.2 (*i.e.*, the quantum yield for conversion of optically pure material to its enantiomer is 0.55–0.60), (2) racemization of **6** is strongly quenched by piperylene but occurs ($\Phi \cong 0.17$) even when piperylene is employed as the solvent, (3) racemization of **4** sensitized by naphthalene can be completely quenched by 1.0 *M* piperylene, and (4) the rate of the unsensitized isomerization of **4** is reduced only to ~54% of the unquenched value in neat piperylene. Representative data are shown in Tables I and II.

Table I. Photoracemization of Compound **6** in Benzene Solution at 25–27°

Series ^a	Concn. of piperylene, <i>M</i>	Racemization, %
A	0	47
A	0.01	47
A	0.10	44
B	0	46
B	0.1	42
B	1.0	18.5
B	3.0	16
B	6.0	10
B	10.0	8

^a Samples in a given series were irradiated in parallel.

The very high quantum yield with **6** is, by itself, an indication that singlet excitation must be transferred from the naphthalene nucleus to the *p*-toluenesulfinyl group⁷ since naphthalene derivatives ordinarily undergo intersystem crossing to triplets with efficiencies of 50% or less.⁸ The same conclusion is suggested by the requirement of high concentrations of **4** to effect sensitized isomerization. However, quenching by piperylene shows that some triplets must be involved in racemization since the diene has no low-lying excited sing-

(5) The numbering system used in ref. 4 is maintained in this report.

(6) G. S. Hammond, *et al.*, *J. Japan. Chem.*, in press.

(7) Reaction in a vibrationally excited ground state formed by internal conversion is another possibility but seems unlikely because of the high quantum efficiency.

(8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, in press.

let states.^{9,10} On the other hand, the failure of piperylene to completely quench racemization of **6** or **4** (when the latter is excited directly) may imply that excited singlets can undergo rapid inversion.

Table II. Direct and Sensitized Excitation of Compound **4** in Benzene Solution at 25–27°C^a

Series ^{b,c}	Concentration, <i>M</i>		Racemization, %
	Naphthalene	Piperylene	
C	0	0	8.7
C	0	1.0	5.7
C	0	10.0	4.7
C	0.1	0	35
C	0.1	1.0	0
C	0.1	10.0	0
D	0.1	0	37
D	0.1	0.01	31
D	0.1	0.10	10

^a For purposes of semiquantitative comparison, the irradiation times were 24 times as long as in experiments reported in Table I.

^b Samples in a given series were irradiated under identical conditions.

^c Concentration of **4** was 0.01 *M* in all experiments.

When compound **6** was irradiated in an MCIP glass¹¹ at 77°K., a strong emission, very similar to the phosphorescence of naphthalene, was recorded.

Consideration of all the facts and their individual implications leads to two alternative conclusions. First, one might assume that transfer of both singlet and triplet excitation from naphthalene units to arene-sulfinyl groups occurs and that both excited singlets and triplets isomerize.¹² This view would probably require that triplet excitation ultimately returns to the naphthalene unit of **6** in order to account for the phosphorescence of that compound, although it must be pointed out that isomerization and emission were observed under very different physical conditions. Alternatively, we might decline to treat the chromophores in **6** as isolated and maintain that weak coupling between two unsaturated systems effects continuous sharing of the excitation between them. This would allow increase in the intersystem crossing efficiency of **6** in comparison with other naphthalene derivatives and account for naphthalene-like emission from a triplet state of **6** which is also capable of undergoing isomerization. In a recent study of internal energy transfer,¹³ one example was found in which the action of two unconjugated chromophores was cooperative. The sensitized isomerization of **4** may involve triplets exclusively, with the rate constant for energy transfer from naphthalene to **4** being $\leq 10^{-2}$ times that for transfer from naphthalene to piperylene. It seems almost certain that direct excitation of **4** leads to isomerization by both singlet and triplet mechanisms. We prefer the second explanation since the efficient transfer of singlet excitation would require the existence of low-lying excited singlet states of tolyl sulfoxides. Careful examination of light ab-

(9) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(10) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **87**, 3778 (1965).

(11) Five parts of methylcyclohexane—one part of isopentane.

(12) Evidence indicating that excited singlets and triplets of simple ketones have similar reactivity has recently been reported.³

(13) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 2322 (1965).

sorption by concentrated solutions of **4** gives no indication of weak transitions in the 3500–5000-Å. region.

(14) National Aeronautics and Space Administration Fellow, 1964 to present.

George S. Hammond, Hans Gotthardt, Lelia M. Coyne

Contribution No. 3273

Gates and Crellin Laboratories of Chemistry

California Institute of Technology

Pasadena, California 91109

Michael Axelrod,¹⁴ Dennis R. Rayner, Kurt Mislow

Department of Chemistry, Princeton University

Princeton, New Jersey 08540

Received August 30, 1965

Triplet Methylene Formation on Photolysis of Ketene and Diazomethane¹

Sir:

We present results which reconcile a recently discovered anomaly between gas phase and liquid phase behavior of diazomethane–methylene radical systems and which contrast the behavior of ketene and diazomethane systems.

It has been shown^{2a} that triplet methylene (³CH₂) arises on photolysis of ketene at ~ 3200 Å.^{2b}; the proportion *increases* with pressure from some small or zero value at low total pressures and reaches a quasi-constant plateau of $\sim 29\%$ at pressures under, and near, 1 atm.^{2a} A similar pressure dependence, although possibly lesser percentage of ³CH₂, was also found^{3,4} on photolysis of diazomethane at 4300 Å. Whitten and Rabinovitch⁴ recently pointed out a new dilemma relative to this triplet behavior; namely, it appears that only (or mainly) ¹CH₂ arises in liquid phase systems upon photolysis of diazomethane. Thus the insertion into various C–H hydrocarbon bonds is known^{5,6} to be more statistical than the usual gas phase behavior, while it has now been shown that statistical insertion is a concomitant of singlet rather than of triplet methylene which abstracts H atoms.^{3,4} Also, in unpublished work, F. H. Dorer has noted that the characteristic triplet products⁷ of reaction of ³CH₂ with *cis*-butene-2 dropped markedly when a diazomethane–butene system (4300 Å.) was liquefied at 0°.

The liquid behavior is not necessarily at odds with the gas phase results. One explanation might attribute the liquid phase decline in ³CH₂ proportion to effects on the mechanism arising from ternary, rather than binary, interactions. However, a second possible explanation⁴ is that collisional processes play a crucial role in inhibiting the formation of ³CH₂ in the liquid and that the proportion of ³CH₂ could pass through a maximum in the gas phase. Thus, consider in Scheme I a modified (and abbreviated) version of the mechanism described by Porter and Connelly⁸ for ketene photolysis;

(1) This work was supported by the Office of Naval Research.

(2) (a) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964). (b) ³CH₂ has now been shown to be produced at other wave lengths as well with ketene; see S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

(3) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964 (1965).

(4) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, in press.

(5) W. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(6) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

(7) F. J. Duncan and R. J. Cvetanović, *ibid.*, **84**, 3593 (1962).