

Application of this generalization to the present results reveals that **3** corresponds to the (*S*) configuration of **1** if and only if CH₃ is taken as the large group and CD₃ as the medium-sized group. This finding is in harmony with the earlier conclusion that CH₃ exceeds CD₃ in effective bulk⁴ and underscores the remarkable sensitivity of this kinetic resolution to differences in group size, including the capability of discriminating between isotopic substituents.

As will be reported in detail elsewhere,⁸ the partial asymmetric alcoholysis of α -phenylbutyric anhydride in pyridine with optically active α -deuterated primary alcohols (RCHDOH) also affords optically active **2** in low optical yields. If the original generalization¹ is extended so that the H in stereoformula **3** is replaced by S (= small group), the signs of rotation of **2** correctly reflect the known absolute configurations of these alcohols, provided that the bulk of hydrogen is taken to be greater than that of deuterium, *i.e.*, R (= L) > H (= M) > D (= S).

exists no strict connection between group size and the priority sequence. Thus, although stereoformula **3** usually corresponds to the (*R*) configuration, it does not do so necessarily, as exemplified by **1** in the present work.

(8) A. Horeau and A. Nouaille, unpublished results.

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Light-Induced Pyramidal Inversion of Sulfoxides¹

Sir:

The stereomutation² of sulfoxides has been induced catalytically (by hydrogen chloride and dinitrogen tetroxide),³ *via* a sequence of reactions constituting a Walden cycle,⁴ and by heating at elevated temperatures.^{3c,5} We now wish to report the photochemical stereomutation of sulfoxides.⁶ To the best of our

(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) By *stereomutation* we mean the interconversion of stereoisomers, *i.e.*, of enantiomers (inversion, racemization) or of diastereomers (epimerization, *cis-trans* interconversion). The term "diastereomer" is here used in its most general sense: K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p. 51.

(3) (a) B. Iselin, *Helv. Chim. Acta*, **44**, 62 (1960); (b) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964); (c) C. R. Johnson and D. McCants, Jr., *ibid.*, **86**, 2935 (1964); **87**, 1109 (1965).

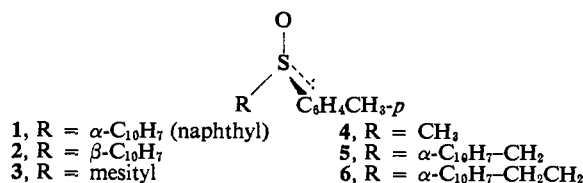
(4) C. R. Johnson, *ibid.*, **85**, 1020 (1963); C. R. Johnson and J. B. Sapp, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, Abstracts, p. 23Q.

(5) (a) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911); (b) H. Baw, G. M. Bennett, and P. Dearn, *J. Chem. Soc.*, 680 (1934); (c) G. Farina, F. Montanari, and A. Negrini, *Gazz. chim. ital.*, **89**, 1548 (1959); (d) H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964); (e) K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964).

(6) Prior work on the photochemistry of sulfoxides seems to have been restricted to the photosensitized oxidation of sulfoxides to sulfones (G. O. Schenck and C. H. Krauch, *Chem. Ber.*, **96**, 517 (1963)) and to

knowledge our observations constitute the first examples of an inversion of pyramidal molecules by photochemical means.⁷

Compounds **1-6** were employed in racemization



studies.⁸ Irradiation (Hanovia high-pressure quartz mercury vapor lamp (450 w.), immersed in a 300-ml. Pyrex irradiation flask with a capillary nitrogen inlet at the base) for 1 hr. of *ca.* 10⁻³ M ether solutions of (-)-(*S*)-**1**⁹ ($\epsilon_{300}^{\text{diox}}$ 7910), (+)-(*S*)-**2**¹¹ ($\epsilon_{300}^{\text{diox}}$ 2050), and (-)-(*S*)-**3**^{9,10} ($\epsilon_{300}^{\text{diox}}$ 1250) under oxygen-free nitrogen at room temperature, using a Pyrex filter sleeve (cut-off at wave lengths below 285 m μ), afforded completely racemized products,¹² with recoveries of 70% or greater.

Irradiation of **1** in the absence of a filter resulted in complete decomposition; naphthalene could be detected as one of the products.

Irradiation of a 0.1 M solution of (+)-(*R*)-**4**,^{10,13} $\lambda_{\text{max}}^{\text{diox}}$ 246 m μ (ϵ 5490), in ether (Pyrex filter) for 2 hr. resulted in 5-10% racemization and no decomposition; this result occasioned no surprise since $\epsilon_{300}^{\text{diox}}$ **5**. In the absence of a filter, irradiation of 6.5 \times 10⁻³ M **4** resulted in extensive decomposition. When the time of irradiation was limited to 10 min., a 40% yield of **4** could be recovered, 72% racemized.

In order to explore the possibility of photosensitization in the racemization, a 0.1 M solution of **4** was irradiated (Pyrex filter) for 2 hr. in the presence of 0.02 M naphthalene. A 99% recovery of sulfoxide was realized; the recovered material was 24% racemized. Sensitization has thus been demonstrated. Since *intra*-molecular sensitization was expected to be a more efficient process than the *inter*molecular counterpart,¹⁴

the formation of sulfoxides by photooxidation of thioethers (O. Hinsberg, *Ber.*, **45**, 2337 (1912); G. Hirohashi, *Nagasaki Igakkai Zasshi*, **31**, 706, 761 (1956); W. F. Forbes and W. E. Savage, *Photochem. Photobiol.*, **1**, 77 (1962); W. F. Forbes, D. E. Rivett, and W. E. Savage, *ibid.*, **1**, 97, 217 (1962); J. E. Eager, C. M. Roxburgh, and W. E. Savage, *ibid.*, **3**, 129 (1964)).

(7) As in the photoracemization of biphenyls (K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3521 (1963)), where the interconversion of enantiomers involves a torsional vibration, the mechanism of these transformations may not require bond breaking and bond re-formation but may merely involve a vibrational change, in this case an inversion of the sulfoxide pyramid. This question is presently under investigation.

(8) These compounds were prepared by the Grignard reaction of alkyl- or arylmagnesium halides with (-)-menthyl (-)-*p*-toluenesulfinate.^{9,10} All new compounds gave satisfactory elemental analyses.

(9) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964).

(10) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965).

(11) M.p. 134-135°, $[\alpha]_D^{25} +47^\circ$ (chloroform). The racemic form melts at 111-113°.

(12) Racemic products were isolated by chromatography and were identified by comparison of their solution infrared spectra and their thin layer chromatograms with those of the active precursors. Elemental analyses were satisfactory in all cases.

(13) The maximum rotation observed for this compound, $[\alpha]_D^{25} +156^\circ$ (ethanol), was somewhat higher than that previously reported,¹⁰ $[\alpha]_D^{25} +141^\circ$ (ethanol).

(14) It is well established that photoinduced stereomutation² may occur by intramolecular processes in which the absorbing chromophore is formally insulated from (although it may be spectroscopically coupled with) the center undergoing stereomutation; *cf.*, *e.g.*, W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, No. 12, 791 (1963); Mislow and Gordon⁷; H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965).

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.

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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

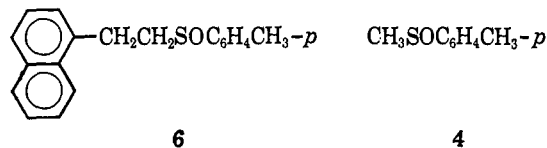
(1) The work was supported by the National Science Foundation under Grant No. GP-3375 at Princeton University and Grant No. GP-2488 at the California Institute of Technology.

(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.