Thermal Racemization of Diaryl, Alkyl Aryl, and Dialkyl Sulfoxides by Pyramidal Inversion[1,2]

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Abstract: Rate constants and activation parameters have been determined for the thermal racemization of diverse diaryl, alkyl aryl, and dialkyl sulfoxides. The results are discussed in terms of a pyramidal inversion mechanism. Rate constants and activation parameters fall into a narrow range of values; $\Delta H^{\ddagger} = 35$–42 kcal/mol and $\Delta S^{\ddagger} = -8$ to $+4$ eu. Steric effects are in evidence, bulky groups attached to sulfur giving rise to rate accelerations; these effects appear to originate largely in the $T\Delta S^{\ddagger}$ term. Small electronic effects are discernible, and in the case of substituents with electron-releasing properties the observed rate deceleration appears to correlate with $\sigma_R{}^0$.

Stereoisomeric sulfoxides may be interconverted chemically,[4-7] photochemically,[8] or by heating.[4,6,9] Although the configurational lability of the sulfoxide pyramid at elevated temperatures has long been recognized,[4,9] no systematic study has been reported dealing with the relationship between structure and rate of thermal stereomutation, and with the mechanisms of such interconversions. The present account is the first of three companion papers[10] on the thermal racemization of diaryl, alkyl aryl, and dialkyl sulfoxides, and discusses those systems whose mechanism of racemization appears to involve the interconversion of enantiomers by pyramidal inversion without cleavage of the carbon–sulfur bond.

The compounds investigated in this study were chosen with a view to providing a broad spectrum of structural variables, within the limits set forth below.

Alkyl sulfoxides containing β-hydrogens generally undergo pyrolysis by *cis* elimination to olefins[11] at the temperatures required to effect racemization. Our choice of alkyl groups was consequently restricted to those which contain no β-hydrogens (*e.g.*, methyl, neopentyl, benzyl) and those which contain β-hydrogens but in which pyrolytic elimination is precluded, either because of constraints on the transition-state geometry imposed by the particular system[12] or because β-elimination would lead to highly strained olefins, as is the case for small bicyclic molecules in which the bridgehead carbon is bonded to the sulfoxide sulfur. Accordingly, the present paper includes a report on the racemization of sulfoxides containing methyl, neopentyl, and adamantyl[13] groups attached to the sulfur atom; a discussion of benzyl and allyl sulfoxides will be reserved for the following papers[10] since the racemization of these compounds does not involve pyramidal inversion.

A further limitation on our selection of compounds was dictated by the synthetic approach. In all but one of the preparations we employed the Grignard synthesis of sulfoxides from sulfinate esters,[14] whose general convenience[15] and capability of furnishing compounds of high optical purity[16] made it the method of choice.[17] Nevertheless, this method is restricted to the prep-

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[2] For preliminary accounts of this work, see D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); K. Mislow, *Record Chem. Progr.*, **28**, 217 (1967).

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[4] K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

[5] B. Iselin, *Helv. Chim. Acta*, **44**, 61 (1961); S. Oae, T. Kitao, and Y. Kitaoka, *Chem. Ind.* (London), 291 (1961); K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); J. Day and D. J. Cram, *ibid.*, **87**, 4398 (1965); S. Oae, N. Kunieda, and W. Tagaki, *Chem. Ind.* (London), 1790 (1965); S. Oae and M. Kise, *Tetrahedron Lett.*, 1409 (1967); H. Ruis, D. B. McCormick, and L. D. Wright, *J. Org. Chem.*, 32, 2010 (1967); P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 552 (1967); E. Jonsson, *Tetrahedron Lett.*, 3675 (1967); *Acta Chem. Scand.*, **21**, 1277 (1967).

[6] C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, **86**, 2935 (1964); **87**, 1109 (1965).

[7] J. Jacobus and K. Mislow, *ibid.*, **89**, 5228 (1967).

[8] K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *ibid.*, **87**, 4958 (1965).

[9] H. Baw, G. M. Bennett, and P. Dearns, *J. Chem. Soc.*, 680 (1934); G. Farina, F. Montanari, and A. Negrini, *Gazz. Chim. Ital.*, **89**, 1548 (1959); H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964); K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 2957 (1964); J. Chickos and K. Mislow, *ibid.*, **89**, 4815 (1967). The thermal epimerization of a *sulfite* has been noted by P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963).

[10] See accompanying papers: (a) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4861 (1968); (b) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *ibid.*, **90**, 4869 (1968).

[11] C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, **82**, 1810 (1960); L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 3570 (1962); C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964); T. J. Wallace, *J. Amer. Chem. Soc.*, **86**, 2018 (1964); D. N. Jones and M. A. Saeed, *Proc. Chem. Soc.*, **81**, (1964); S. I. Goldberg and M. S. Sahli, *Tetrahedron Lett.*, 4441 (1965); I. D. Entwhistle and R. A. W. Johnstone, *Chem. Commun.*, 29 (1965); D. G. Barnard-Smith and J. F. Ford, *ibid.*, 120 (1965); D. W. Emerson, A. P. Craig, and I. N. Potts, Jr., *J. Org. Chem.*, **32**, 102 (1967); D. N. Jones and M. J. Green, *J. Chem. Soc., C*, 532 (1967); J. L. Kice and J. D. Campbell, *J. Org. Chem.*, **32**, 1631 (1967); J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967); S. I. Goldberg and M. S. Sahli, *J. Org. Chem.*, **32**, 2059 (1967).

[12] Such is the case in the thiane oxides studied by Henbest and Khan[9] and by Johnson and McCants.[6] The latter authors have drawn attention to the "inaccessibility of the β-hydrogens to the sulfoxide oxygen" in the cyclic transition state of pyrolysis.

[13] The pathway to adamantene by pyrolytic elimination of adamantyl sulfoxides is blocked by the high strain inherent in adamantene (J. Bredt, *Ann.*, **437**, 1 (1924); F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950); L. K. Montgomery and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 4750 (1960)), and consequently in the transition state leading to its formation.

[14] K. K. Andersen, *Tetrahedron Lett.*, 93 (1962).

[15] A single diastereomerically pure ester, *i.e.*, menthyl *p*-toluenesulfinate, served as precursor to the preparation of all the *p*-tolyl sulfoxides listed in Table I.

[16] For example: (a) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, **86**, 5637 (1964); (b) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965); (c) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *ibid.*, **90**, 4835 (1968).

[17] High optical purity ensures that the precision of the polarimetric readings is maximized.

Table I. First-Order Rate Constants of Thermal Racemization[a] of Aryl *p*-Tolyl Sulfoxides

R in $RSOC_6H_4CH_3$-*p*	Compd	*T*, °C	$k \times 10^5$,[b] sec^{-1}	Period of observation[c]	k/k_{Ph}[d]
9-Anthryl[e]	**1**	190	(41.2 ± 0.3)	4	(*Ca.* 68)[f]
		190	(42.4 ± 0.3)	4	
2,4,6-$(CH_3)_3C_6H_2$	**2**	180	15.3 ± 0.1	3	59[g]
		190	37.2 ± 0.3	3	
		190	35.8 ± 0.1	3	
		200	84.2 ± 0.8	4	
2-$CH_3C_6H_4$	**3**	200	3.15 ± 0.02	3	2.2
		210	7.02 ± 0.07	2	
		220	15.9 ± 0.1	3	
1-$C_{10}H_7$	**4**	210	7.02 ± 0.04	2	2.2
4-$CF_3C_6H_4$	**5**	210	6.16 ± 0.02	2	1.9
3-$CF_3C_6H_4$	**6**	210	3.37 ± 0.03	2	1.1
C_6H_5	**7**	200	1.44 ± 0.02	2	1.0
		210	3.16 ± 0.03	2	
		210	3.19 ± 0.02	2	
		220	7.17 ± 0.05	3	
4-ClC_6H_4	**8**	210	2.47 ± 0.01	2	0.81
		210	2.70 ± 0.03	2	
4-$CH_3OC_6H_4$	**9**	210	1.82 ± 0.04	1	0.57
2-$CH_3OC_6H_4$	**10**	210	1.59 ± 0.01	3	0.50
2-ClC_6H_4	**11**	210	0.922 ± 0.003	2	0.29

[a] In *p*-xylene. [b] First-order rate constants are tabulated with probable errors. [c] In units of $t_{1/2}$ (half-life). [d] Rate constant for $RSOC_6H_4CH_3$-*p* (*k*) relative to that for **7** (k_{Ph}) at 210°. [e] Values of *k* for **1** include, and are uncorrected for, loss of optical activity by decomposition. See text for explanation. [f] *k* relative to k_{Ph} at 190°. The k_{Ph}^{190} value was obtained by extrapolation ($k_{Ph}^{190} = 6.16 \times 10^{-6}$ sec^{-1}). [g] The k^{210} value was obtained by extrapolation ($k^{210} = 1.86 \times 10^{-3}$ sec^{-1}).

aration of sulfoxides which do not undergo further reactions with the Grignard reagent,[18] and the synthesis has not been adapted to the preparation of cyclic sulfoxides in which the sulfur atom constitutes an integral part of the ring system.[19] A further and unexpected difficulty arose in the preparation of adamantyl sulfoxides. Various attempts to prepare adamantylmagnesium bromide from 1-bromoadamantane and magnesium resulted in 1,1′-bisadamantyl as a major product,[20] and although we were able to prepare adamantyl *p*-tolyl sulfoxide by the Grignard synthesis in very low (5%) yield,[21] we ultimately had to resort to asymmetric oxidation[22] of adamantyl methyl sulfide in order to prepare the corresponding optically active sulfoxide. As expected,[22] the asymmetric oxidation afforded material of low rotation.

Results

The rates of thermal racemization of various diaryl, alkyl aryl, and dialkyl sulfoxides in *p*-xylene were determined at temperatures in the neighborhood of 200°. The results of this study are collected in Tables I and II. Polarimetric measurements were carried out over a period of one to four half-lives and the products were examined by glpc. It was found that with the exception of compounds **1**, **12**, **14**, and **16**, the loss of optical activity of the sulfoxides could be safely ascribed to racemization (*i.e.*, interconversion of enantiomers) since less than 3% decomposition could have been detected by this method of analysis. In the case of compounds **12**, **14**, and **16**, glpc analysis revealed that extensive decomposition had taken place over the full period of observation (Table II) and that in each case at least two decomposition products had been formed. We were able to identify one of the products of pyrolysis of **12** as neopentyl *p*-tolyl sulfide and one of the products of pyrolysis of **14** as 1-adamantanethiol. It is conceivable that these compounds formed by a pathway involving as a first step cleavage into a thiol and an aldehyde ($RSOCH_2R' \rightarrow RSH + R'CHO$),[23] followed by reduction of unreacted sulfoxide by thiol.[24]

All of the rates of racemization were cleanly first order over the period of observation. In the case of compounds **12**, **14**, and **16**, the loss of optical activity with time was corrected for decomposition (see Experimental Section). As demonstrated in four cases (**1**, **2**, **7**, and **8**) measurements in repeat runs were reasonably reproducible. For five of the key sulfoxides, measurements were carried out at several temperatures and activation parameters calculated; the results are collected in Table III.

Discussion

To judge from the order of the reaction rates, the racemizations of the sulfoxides studied in this work are unimolecular processes; intermolecular pathways can thus be excluded. Furthermore, a homolytic dissociation–recombination mechanism can be dismissed on the following grounds. For the racemization of benzyl *p*-tolyl sulfoxide, strong evidence has been adduced for a homolytic dissociation–recombination mechanism, and a pyramidal inversion mechanism has been rigorously excluded.[10a] Equating the acti-

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(18) For this reason, sulfoxides containing nitro or carbonyl groups were excluded from our study.

(19) For this reason we made no attempt to study the rates of racemization of suitable[12] cyclic systems, *e.g.*, of 3,3-dimethylthiane 1-oxide.

(20) P. T. Lansbury and J. D. Sidler [*Chem. Commun.*, 373 (1965)] similarly reported that substantial amounts of the coupling product 1,1′-bisadamantyl resulted in attempts to prepare 1-adamantyllithium by exchange of 1-iodoadamantane with *t*-butyllithium.

(21) In contrast, adamantane-1-carboxylic acid has been prepared in 40% yield by the carbonation of adamantylmagnesium bromide (J. E. Norlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966)).

(22) A. Mayr, F. Montanari, and M. Tramontini, *Gazz. Chim. Ital.*, **90**, 739 (1960); K. Mislow, M. M. Green, and M. Raban, *J. Amer. Chem. Soc.*, **87**, 2761 (1965).

(23) Similar to the pyrolytic cleavage of di-*n*-butyl sulfoxide (Barnard-Smith and Ford[11]).

(24) C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963); T. J. Wallace and J. J. Mahon, *J. Amer. Chem. Soc.*, **86**, 4099 (1964).

Table II. First-Order Rate Constants of Thermal Racemization[a] of Alkyl Aryl and Dialkyl Sulfoxides, RSOR′

R	R′	Compd	T, °C	$k \times 10^5$,[b] sec^{-1}	Period of observn[c]	k/k_{Ph}[d]	k/k_{Me}[e,f]
4-$CH_3C_6H_4$	$(CH_3)_3CCH_2$	**12**[g]	210	4.26 ± 0.04	2 (0.82)	1.3	19
CH_3	2,4,6-$(CH_3)_3C_6H_2$	**13**	210	3.88 ± 0.01	2	1.2	18
CH_3	1-Adamantyl	**14**[g]	210	1.16 ± 0.03	2 (0.77)	0.36	5.2
4-$CH_3C_6H_4$	1-Adamantyl	**15**	210	0.69 ± 0.01	1	0.22	3.1
			220	1.74 ± 0.02	1		
			230	4.06 ± 0.03	1		
4-$CH_3C_6H_4$	CH_3	**16**[g]	220	0.49 ± 0.01	1 (0.91)	0.070[f]	1.0
			230	1.10 ± 0.02	1 (0.87)		
			240	2.21 ± 0.06	2 (0.59)		
			250	4.72 ± 0.07	1 (0.58)		

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] In units of $t_{1/2}$ (half-life). Numbers in parentheses state the fraction of sulfoxide left after decomposition over the full period of observation. [d] Rate constant for RSOR′ (k) relative to that for **7** (k_{Ph}) at 210°. [e] Rate constant for RSOR′ (k) relative to that for **16** (k_{Me}) at 210°. [f] The value for $k_{Me}{}^{210}$ (0.219×10^{-5} sec^{-1}) was obtained by extrapolation. [g] Corrected for decomposition.

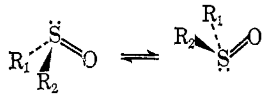
Table III. Activation Parameters[a] for Racemization of Sulfoxides, $RSOC_6H_4CH_3$-*p*

R	Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	Log A, sec^{-1}
2,4,6-$(CH_3)_3C_6H_2$	**2**	35.4	1.3	36.3	13.7
2-$CH_3C_6H_4$	**3**	36.6	−2.8	37.5	12.8
C_6H_5	**7**	36.2	−5.1	37.2	12.3
1-Adamantyl	**15**	42.0	3.8	43.0	14.3
CH_3	**16**	37.4	−8.0	38.4	11.7

[a] In *p*-xylene.

vation energy for racemization of benzyl *p*-tolyl sulfoxide, 44 kcal/mol,[10a] with the upper limit of the bond dissociation energy, $D(C_6H_5CH_2\text{–}SOC_6H_4CH_3)$, and given that the bond dissociation energies of various benzylic carbon–sulfur bonds are 12–25 kcal/mol lower than those of the corresponding alkyl or aryl carbon–sulfur bonds,[25] it follows that the bond dissociation energies of alkyl and aryl sulfoxides **1–16** have values somewhere in the neighborhood of 56–69 kcal/mol. Since none of the activation energies of racemization observed for the present group of compounds (Table III) even approaches the lower limit of the above estimate, it seems safe to conclude that the homolytic racemization mechanism[10a] is not operative in these cases.

In the absence of evidence to the contrary, the most economic hypothesis consistent with our results is that sulfoxides exemplified by compounds **1–16** undergo racemization by a molecular vibration, *i.e.*, by pyramidal inversion without carbon–sulfur bond scission.



In this process the enantiomers are interconverted *via* a transition state which is symmetrically disposed along the reaction coordinate and which contains the sulfur atom and the three attached atoms (C, C, O) arranged in a planar array. The three bond angles subtended by the sulfur atom in the transition state add up to 2π but, because of the lack of axial symmetry, they will all be different. Taking into account the possibility of conformational changes due to torsion around the carbon–sulfur bonds, it should be noted that many or most of the accessible transition states do not necessarily have planes of symmetry, but may be envisaged as assuming, in principle, a multitude of chiral or achiral conformations with aryl rings twisted out of the O–S–C plane to various extents. The symmetry of the disposition of the transition state along the reaction coordinate therefore refers to the average of the various conformations possible for ground and transition states. It must also be emphasized that while the pyramidal inversion mechanism is generally believed to involve a single energy barrier separating the enantiomeric ground states,[26] the possibility cannot be rigorously excluded that, at least for the sulfoxides, an intermediate intervenes in the inversion process. However, in the absence of evidence pointing in this direction, this eventuality will be ignored in the present discussion.

Granted a pyramidal inversion mechanism for the racemization of sulfoxides **1–16**, we next turn to a discussion of the structural parameters which are responsible for the observed variation in rates (Tables I and II).

On the basis of a simple model for pyramidal inversion employed by Costain and Sutherland,[27] Weston,[28] and Miller, *et al.*,[26] the energy barrier for inversion (V_i) may be estimated by use of a quadratic potential (Hookes's law) function. Miller, *et al.*,[26] showed that reasonable estimates of V_i may often be obtained by neglecting tunneling, entropy factors, solvation, and resonance effects, and that the magnitude of V_i depends principally on the amount of angle bending necessary to go from ground to transition state and on the angle bending force constants. Although, in the absence of reliable input data, quantitative estimates of a similar nature are not warranted for sulfoxides **1–16**, we are basing the subsequent qualitative interpretation on the same "naive" model for inversion,[26–28] in the expectation that at least some of the features of the observed dependence of rate on structure may thus be accounted for.

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(25) Primary carbon–sulfur bond dissociation energies in thiols (D(R–SH)), methyl sulfides ($D(R\text{–}SCH_3)$), and methyl sulfones ($D(R\text{–}SO_2CH_3)$) have the following values (in kilocalories per mole): 73 ± 5, 72 ± 5, and 62 ± 3 when R = methyl, 78 ± 5, 77 ± 5, and 73 ± 3 when R = phenyl, and 53 ± 2, 51.5 ± 2, and 49.5 ± 2.5 when R = benzyl (H. Mackle, *Tetrahedron Lett.*, **19**, 1159 (1963)). No corresponding values for the carbon–sulfur bond dissociation energy of sulfoxides ($D(R\text{–}SOCH_3)$) have been reported.

(26) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

(27) C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

(28) R. E. Weston, Jr., *J. Amer. Chem. Soc.*, **76**, 2645 (1954).

It is reasonable to assume that in the ground state of acyclic sulfoxides, the three bond angles vary only slightly with the nature of the groups attached to the sulfur atom. This assumption is based on the observation that in phosphines, pyramidal molecules which bear some analogy to the sulfoxides, the C–P–C bond angles remain sensibly invariant, regardless of the nature of the groups attached to the phosphorus atom.[29,30] Making the further reasonable assumption that bond bending force constants vary but little in the group of sulfoxides investigated, one would expect that the rate of racemization of sulfoxides by the pyramidal inversion mechanism should not be unduly influenced by variations in the structure of the groups attached to sulfur. Inspection of the results collected in Tables I and II indeed reveals that k is remarkably insensitive to changes in the nature of the ligand groups on sulfur. Thus, with the exception of **1**, **2**, and **16**, the rate constants of racemization of diaryl, alkyl aryl, and dialkyl sulfoxides vary by at most a factor of 10 (k/k_{Ph} ranges from 0.22 to 2.2), and even for the exceptions mentioned above the rate constants deviate from the central range by only one order of magnitude. The activation parameters for racemization (Table III) bear out this conclusion: the values for E_a, which are measures of V_i, cover a rather narrow range, from 36.3 kcal/mol for **2** to 43.0 kcal/mol for **15**. The same conclusion may be expressed yet another way: for all of the compounds investigated, changes of rotation with time may be conveniently followed in the narrow temperature range 190–220°, giving values of k with low probable errors.

A variety of effects, operating individually or in combination, may be held accountable for the dependence of k on structure which is observed within the narrow range discussed above. None of the factors are major, and at this point our discussion must take a highly speculative turn. Nevertheless, though conjectural in kind, our comments may serve to lay the basis for future experiments and are therefore recorded below.

An effect of steric origin is manifested in the rate of racemization of mesityl *p*-tolyl sulfoxide (**2**), which exceeds that of phenyl *p*-tolyl sulfoxide (**7**) by a factor of 59 at 210°. Even a single *o*-methyl group, as in *o*-tolyl *p*-tolyl sulfoxide (**3**), still exerts a slight accelerating effect ($k/k_{\mathrm{Ph}} = 2.2$), equalling that of 1-naphthyl *p*-tolyl sulfoxide (**4**) where, with respect to nonbonded interactions, the 8-carbon atom of the 1-naphthyl group takes the place of the methyl carbon of the *o*-tolyl group. Similarly, neopentyl *p*-tolyl and 1-adamantyl *p*-tolyl sulfoxides (**12** and **15**) racemize 19 and 3 times as rapidly as methyl *p*-tolyl sulfoxide (**16**), and methyl mesityl and methyl 1-adamantyl sulfoxides (**13** and **14**) racemize 18 and 5 times as rapidly as **16**. 9-Anthryl *p*-tolyl sulfoxide (**1**) was prepared with a view to testing this effect further: it was expected, by analogy with the similarity exhibited by k of **4** with k of **3**, that k of **1** might resemble k of **2**, the 1,8-carbons of the 9-anthryl group taking the place of the 2,6-methyl carbons of the mesityl group. However, although the rates of loss of optical activity of **1** and **2** at 190° are remarkably similar ($k = 4 \times 10^{-4}$ sec^{-1}), **1** suffers extensive decomposition at that temperature (in contrast to **2**) and any comparison between the two compounds is thus vitiated.

While a *prima facie* case can be made for the action of a steric effect in the cases described above, it is difficult to formulate a simple hypothesis which would provide a mechanism for the operation of this effect. In our preliminary communication,[2] it was suggested that nonbonded repulsive interactions between the groups attached to sulfur in the ground state of the sulfoxide were responsible for the rate acceleration exhibited by sulfoxides **2**–**4**, and that the driving force for this acceleration was the relief of nonbonded strain in the planar or near-planar transition state. This interpretation of steric acceleration was based on an analogy with the B-strain hypothesis which had been invoked to account for the acceleration of solvolysis rates of tertiary halides.[31] We take this opportunity to revise our earlier, preliminary conclusions on two grounds. First, one would expect that a significant change in bond angles would accompany the nonbonded repulsive interaction in the ground state which was held responsible[2] for the rate acceleration in **2**. However, it was recently demonstrated[30] that the C–P–C bond angle in a closely related system, the triarylphosphines, remains essentially constant at 102°, whether the aryl group be phenyl, *o*-tolyl, or mesityl. There is no reason to postulate substantially different behavior for the sulfoxides which, by analogy with the phosphines,[30] should be able to relieve nonbonded strain by torsion around the carbon–sulfur bond. Second, refined calculations of the activation parameters (Table III) indicate that the largest differences in the rates of pyramidal inversion reside not in activation enthalpy differences, which would have been consistent with our original B-strain hypothesis,[2] but rather in activation entropy differences. Thus, $\Delta H^{\ddagger}$ of **2** is only 0.8 kcal/mol less than $\Delta H^{\ddagger}$ of **7**, but $\Delta S^{\ddagger}$ of **2** is more positive by 6.4 eu than $\Delta S^{\ddagger}$ of **7**, so that the activation energy barrier in **2** is lowered by 3 kcal/mol at 210° just through the contribution of the entropy term ($T\Delta S^{\ddagger}$). Similarly, $\Delta H^{\ddagger}$ of **3** differs negligibly from $\Delta H^{\ddagger}$ of **7**, but $\Delta S^{\ddagger}$ of **3** is more positive by 2.3 eu than $\Delta S^{\ddagger}$ of **7**, so that the rate acceleration of **3** relative to **7** is due almost entirely to the agency of the entropy effect ($T\Delta\Delta S^{\ddagger} = 1$ kcal/mol at 210°). A comparison of **15** and **16** is even more striking: because $\Delta S^{\ddagger}$ of **15** is more positive by 11.8 eu than $\Delta S^{\ddagger}$ of **16** ($T\Delta\Delta S^{\ddagger} =$ 5.8 kcal/mol at 220°), **15** racemizes 3.5 times as fast as **16** at 220° even though $\Delta H^{\ddagger}$ of **15** is 4.6 kcal/mol greater than $\Delta H^{\ddagger}$ of **16**.

The importance of the entropy factor suggests the possible need for modification of arguments based on B strain advanced in connection with the pyramidal inversion of aziridines[32] and sulfonium salts.[33] The entropy effect may result from changes in rotational degrees of freedom: as suggested by the trend of $\Delta S^{\ddagger}$ values for **2**, **3**, and **7** (Table III), the sulfoxides probably suffer some loss of rotational freedom in the pyramidal ground state,[34] a conformational restriction which is

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(29) A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(30) E. J. Halpern and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5224 (1967).

(31) H. C. Brown, *Science*, **103**, 385 (1946).

(32) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5203 (1958); F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967).

(33) D. Darwish and G. Tourigny, *ibid.*, **88**, 4303 (1966).

relieved with the spread of bond angles in the transition state.

Table IV. Rates of Racemization and Substituent Parameters in Sulfoxides, $RC_6H_4SOC_6H_4CH_3$-*p*

R	Compd	k/k_{Ph}[a]	σ_I[b]	σ_R^0	σ^0[d]	σ[e]
4-CH_3O	**9**	0.58	+0.26	−0.43[c]	−0.16	−0.27
4-Cl	**8**	0.81	+0.47	−0.18[c]	+0.29	+0.23
H	**7**	1.0	0.00	0.00	0.00	0.00
3-CF_3	**6**	1.1	+0.42	+0.02[f]	+0.44	+0.43
4-CF_3	**5**	1.9	+0.42	+0.10[g,h]	+0.52	+0.54

[a] See Table I, footnote *d*. [b] Reference 34; *cf.* also R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85,** 709 (1963). The σ_I values for *meta* and *para* substituents are assumed to be "essentially equal."[35a] [c] Calculated from shielding parameters from *meta*- and *para*-substituted fluorobenzenes (CCl_4 solution).[36] [d] Defined[36] as $\sigma^0 = \sigma_R^0 + \sigma_I$. [e] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23,** 420 (1958). [f] Reference 35 lists $\sigma_R^0 = +0.02$ for *m*-CF_3. [g] For a recent discussion of the interaction of fluoroalkyl groups into the benzene π-electron system, see W. A. Sheppard, *J. Amer. Chem. Soc.*, **87,** 2410 (1965). [h] See also the data of Taft, *et al.*[36] (calculated according to the equation $\delta_p^F - \delta_m^F = 2.97\sigma_R^0$). This value agrees with the σ_R^0 value for CF_3 ($\pm\sigma_R^0 = 0.115$) calculated from ir band intensities by R. T. C. Brownlee, A. R. Katritzky, and R. T. Topsom, *J. Amer. Chem. Soc.*, **88,** 1413 (1966). However, for +R substituents σ_R^- might be the more appropriate measure.[36]

Electronic effects seem to play a minor role. Leaving aside the *ortho*-substituted sulfoxides, four derivatives of **7**, *i.e.*, **5**, **6**, **8**, and **9**, are relevant for discussion in this connection. The range of rate constants in this group of compounds is small, no k value differing from k_{Ph} by more than a factor of 2. There is no correlation with substituent parameters,[35] as illustrated in Table IV for Hammett σ^0 values; for example, both *p*-chlorophenyl *p*-tolyl sulfoxide (**8**) and *p*-methoxyphenyl *p*-tolyl sulfoxide (**9**) racemize more slowly than **7**, even though the σ and σ^0 values of the two *para* substituents are opposite in sign. However, it appears that inductive effects, whether transmitted through field interaction or internal bond polarization, are negligible, as judged by the very slight rate enhancement in **6** due to the strongly electron-withdrawing +I group, *m*-CF_3, and that when the σ_I term in the expression[36] for σ^0 ($\sigma^0 = \sigma_R^0 + \sigma_I$) is neglected, there is an unmistakable trend correlating the resulting σ^0 (= σ_R^0) values with log k for compounds with −R groups, *i.e.*, *p*-Cl (**8**) and *p*-CH_3O (**9**), relative to **7**. In other words, the rates of racemization of aryl sulfoxides bearing −R groups in the *para* position show a dependence on the resonance interaction of the group with the benzene ring, *i.e.*, on the resonance polar effect[37] as measured by σ_R^0: the greater the electron transmission into the benzene ring (*i.e.*, the more negative σ_R^0), the slower the racemization. Remembering that σ^0 constants exclude polar effects arising from direct resonance interaction between the substituents and the reaction center (*i.e.*, the sulfur atom), this result can be rationalized by the argument that the buildup of π electron density in the *para* position adjacent to the sulfur atom by electron releasing −R groups raises the barrier to pyramidal inversion by electron repulsion with the unshared electron pair on sulfur, an effect which should be greater in the transition state than in the ground state. This interpretation is analogous to the postulation that electrostatic repulsion between unshared electron pairs is responsible for increases in activation energy to pyramidal inversion of amines[38] and aziridines[39] which contain atoms with unshared electron pairs attached to the nitrogen atom, and for the resistance to *syn-anti* isomerization of similarly substituted imines by the lateral-shift mechanism.[40] While one cannot ignore the additional possibility that pπ–dπ conjugation involving the vacant 3d orbital on sulfur may also play a role in determining the relative barrier heights of sulfoxides **7**–**9**,[41] this factor is difficult to evaluate.

A similar interpretation may be invoked to account for the relatively high barrier to pyramidal inversion of sulfoxides relative to that of other second row systems ($:MX_3$) whose rates of racemization by this mechanism have been studied. Sulfoxides (present work) racemize at temperatures around 200° in *p*-xylene with E_a = 36–43 kcal/mol and log A 12–14 (sec^{-1}), whereas methylphenyl-*n*-propylphosphine racemizes[42] at 130° in hydrocarbon solvents with E_a = 30–31 kcal/mol and log A 12 (sec^{-1}), and 1-adamantylethylmethylsulfonium perchlorate racemizes[43] at 30–50° in acetic acid with $\Delta H^{\ddagger} = 26$ kcal/mol and $\Delta S^{\ddagger} = +8$ eu. While the low barrier to inversion of the charged sulfonium salts as compared to their uncharged, isoelectronic counterparts, the phosphines, may be due to solvation effects,[43] the high barrier to pyramidal inversion of sulfoxides, as compared to phosphines, may be tentatively attributed to repulsive electrostatic interactions between the lone pair on sulfur and the oxygen lone pairs which are only partly delocalized into the sulfur 3d orbitals.[44]

The rapid rate of racemization of **5** relative to **7** is not satisfactorily correlated with σ_R^0 (Table IV) and suggests the operation of a different electronic effect: conceivably the *p*-CF_3 group becomes directly conjugated with the sulfinyl group through overlap with the electron pair on sulfur *via* the pπ orbitals of the benzene ring,[45] thus effecting a lowering of the activation energy barrier; similar conjugative effects have been proposed[32] to account for the lowering of the barrier to nitrogen inversion in aziridines.

The above interpretation of the data presented in Table IV may be summarized as

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(34) The same effect has been proposed[16b] to account for differences in the ORD of **2**, **3**, and **7**.

(35) (a) P. R. Wells, *Chem. Rev.*, **63,** 171 (1963); (b) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2,** 323 (1964).

(36) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, **81,** 5352 (1959); R. W. Taft, Jr., *J. Phys. Chem.*, **64,** 1805 (1960); R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85,** 3146 (1963).

(37) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 578 ff.

(38) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, **87,** 4089 (1965).

(39) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89,** 357 (1967); S. J. Brois, *ibid.*, **90,** 506, 508 (1968); A. Mannschreck, R. Radeglia, E. Gründemann, and R. Ohme, *Chem. Ber.*, **100,** 1778 (1967).

(40) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88,** 2775 (1966).

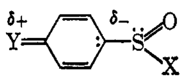
(41) Such conjugation is evidenced in the nmr spectra of vinyl sulfonium salts (M. C. Caserio, R. E. Pratt, and R. J. Holland, *ibid.*, **88,** 5747 (1966)).

(42) L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964).

(43) R. Scartazzini and K. Mislow, *ibid.*, 2719 (1967).

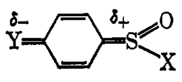
(44) A. B. Burg, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p 35 ff.

(45) See Table IV, footnote *g*.



$Y = -R, \sigma_R^0 < O$

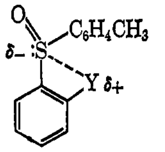
electron repulsion
higher barrier



$Y = +R, \sigma_R^0 > O$

direct conjugation
lower barrier

The *o*-methoxy- and *o*-chloro-substituted phenyl *p*-tolyl sulfoxides (**10** and **11**) exhibit a larger rate retardation, relative to **7**, than do their *para*-substituted counterparts (**9** and **8**, respectively); the effect is particularly pronounced for the chloro substituent ($k(o)/k(p)$ = 0.35). The electronic effects discussed above should plainly still be operative, and in that respect the k values are at least in the right direction. However, the steric effect should operate in the opposite direction (*i.e.*, toward rate enhancement) by a factor of 2.2 since the methyl and chloro groups in **3** and **11** are roughly isomorphous, and it is therefore clear that a new factor is exerting a retarding influence on the rate. The new effect may have its origin in repulsive nonbonding interactions between unshared electron pairs on the *ortho* substituents and sulfur; alternatively, extraannular neighboring group overlap (a sort of chelation) between the lone pairs of electrons on chlorine or oxygen and the available 3d orbital on sulfur may conceivably be implicated.



This kind of interaction was suggested by an X-ray diffraction study of methyl *o*-nitrobenzenesulfenate,[46] in which it had been shown that the nitro group is coplanar with the benzene ring and that the distance between one of the oxygen atoms on the nitro group and the sulfur atom is "extraordinarily short." Furthermore, a similar effect was recently proposed[47] to account for the abnormally slow rate of chlorination of *o*-nitrobenzenesulfenyl chlorides. However, an nmr study of relevant compounds[48] failed to reveal any evidence for the operation of this effect in the *ground state*, and it is particularly doubtful, in view of the need to form a strained four-membered ring, that neighboring group effects are significantly operative in the transition state for racemization of **10** and **11**.[49]

We reiterate our position that the detailed interpretation of small effects, especially on the basis of a limited set of data, renders our conclusions tentative, vulnerable, and subject to revision. Nevertheless, although the weight placed on our present exposition thus remains less than could be wished for, our speculations are based on what appear to be suggestive trends and merit further investigation, particularly so since no other studies have thus far appeared dealing systematically with substituent effects on the rates of pyramidal inversion. We are engaged in pursuing further the problem of developing substituent constants for rates of pyramidal inversion and of investigating the utility of such constants for correlative and predictive purposes.

Experimental Section[50]

Procedure for Kinetic Runs. The kinetics were carried out by the sealed tube method, using stock solutions of the sulfoxides (*c* 1–2%) in *p*-xylene sealed in micro Carius tubes. The *p*-xylene (Matheson Coleman and Bell) was distilled through a 2-ft bubble cap column prior to use. Approximately 2-ml aliquots of the sulfoxide solutions were placed in the tubes which were then evacuated before being immersed into a Dry Ice–acetone bath. When the xylene solutions had frozen, the tubes were alternately filled with dry nitrogen and reevacuated five times. The tubes were then sealed under vacuum. The tubes, five to ten in number, were placed in a high-temperature Colora Ultra Thermostat circulating bath preset and maintained throughout the duration of the runs at the set temperature within ±0.2°. After a 15–20-min initial equilibration period, the "zero-time" tube was withdrawn and immediately quenched by immersion in cold water. The remainder of the tubes were withdrawn at intervals ranging from 15 min to several hours, as desired. Rotations (α) of solutions from each of the tubes were read from six to ten times and the average value of α was used in the rate calculations; the average deviations of α were ±0.01°. At the completion of the runs, the solutions were checked for decomposition by glpc. A 2-ft 10% silicone gum rubber on 60–80 Chromosorb W column was used for the diaryl sulfoxides and a 2-ft 10% Carbowax 20M on 60–80 Chromosorb W column was used for the dialkyl and alkyl aryl sulfoxides. If decomposition had occurred during the run, aliquots of the contents of each tube were injected into the gas chromatograph three times in succession and the average amount of sulfoxide remaining was determined either by planimetry or by cutting out and weighing the areas under the sulfoxide peaks. The correction for decomposition was applied by dividing the observed rotation at time t by the fraction of sulfoxide remaining at that time, compared to the amount of sulfoxide at zero time. The corrected rotations were used in the calculations of rate constants of compounds **12**, **14**, and **16**. The first-order rate constants for racemization were calculated from the slope ($-k/2.303$) obtained from the best straight line (linear least squares) plot of log α *vs.* t. The Arrhenius activation energy, E_a, was calculated from the slope (E_a/R) of the best straight line (linear least squares) plot of ln k *vs.* T^{-1}. The preexponential factor (A) was obtained from the Arrhenius equation, $k = Ae^{-E_a/RT}$. The transition-state activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were calculated from the Arrhenius activation parameters using the relationships[51]

$$\Delta H^{\ddagger} = E_a - RT$$

$$\Delta S^{\ddagger} = 4.574 \log (A/T) - 49.203$$

All of the calculations were carried out on an IBM 7094 computer using a conventional FORTRAN IV program.

Preparation of the Sulfoxides. The diaryl sulfoxides in Table I were all prepared by the Grignard synthesis[14] from diastereomerically pure *l*-menthyl *p*-toluenesulfinate and were therefore of high optical purity.[16,17] The preparation and physical properties of sulfoxides **2**,[16] **3**,[16] **4**,[16a] **7**,[16] and **9**[16a] have been described before. The alkyl sulfoxides in Table II were also prepared by the Grignard synthesis with the exception of compound **14** which was prepared by asymmetric oxidation of the corresponding sulfide. Compound **14** is therefore largely racemic. The preparation and physical properties of sulfoxides **13**[7] and **16**[16b] have been described before. The physical properties of previously unreported sulfoxides are reported in Table V.

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(46) W. C. Hamilton and S. J. LaPlaca, *J. Amer. Chem. Soc.*, **86**, 2289 (1964).

(47) E. N. Givens and H. Kwart, *ibid.*, **90**, 378, 386 (1968).

(48) J. Jacobus, unpublished work. Among the compounds investigated were *o*-, *m*-, and *p*-methoxyphenyl methyl and *p*-tolyl sulfoxides, *o*- and *p*-nitrophenyl methyl sulfides and sulfoxides, ethyl *o*- and *p*-nitrobenzenesulfenates, and *o*- and *p*-methylthio- and methylsulfinylacetophenones.

(49) It remains to be seen whether the racemization of *o*-nitrophenyl sulfoxides exhibits anomalies which would have to be ascribed to a neighboring group effect.

(50) Elemental analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Polarimetric measurements were determined visually on a Schmidt and Haensch polarimeter, using a 2-dm tube. Nmr spectra were measured on a Varian A-60A spectrometer and refer to *ca.* 10% solutions in deuteriochloroform unless otherwise specified, with tetramethylsilane serving as internal standard.

(51) S. Glasstone, J. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

Table V. Characteristics of Optically Active Sulfoxides, RSOR′

Compd	R	R′	Absolute confign[a]	Bp (mm) or mp, °C	[α]D, deg[b]	Calcd, %				Found, %			
						C	H	S	Halogen	C	H	S	Halogen
1	9-Anthryl	4-$CH_3C_6H_4$	*S*	172–173	−309[c]	79.71	5.10	10.13	...	79.55	4.97	10.58	...
5	4-$CF_3C_6H_4$	4-$CH_3C_6H_4$	*S*	40–42	+57	59.14	3.90	11.28	20.04	58.87	3.92	11.38	20.00
6	3-$CF_3C_6H_4$	4-$CH_3C_6H_4$	*S*	95 (0.3)[d]	+58	59.14	3.90	11.28	20.04	59.58	4.14	11.34	20.06
8[e]	4-ClC_6H_4	4-$CH_3C_6H_4$	*S*	76–78	+25[c]	62.28	4.39	12.79	14.15	62.27	4.62	12.49	14.00
10	2-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	*S*	83–84	−221	68.26	5.73	13.02	...	67.98	5.66	...	...
11	2-ClC_6H_4	4-$CH_3C_6H_4$	*S*	90.5–91	−120	62.28	4.39	12.79	14.15	61.95	4.27	12.40	13.94
12	$(CH_3)_3CCH_2$	4-$CH_3C_6H_4$	*R*	100 (0.1)[d]	+220[c]	68.52	8.62	15.25	...	68.38	8.63	15.23	...
14[f]	1-Adamantyl	CH_3		71–77	−2.9	66.61	9.15	16.17	...	66.49	8.99	16.11	...
15	1-Adamantyl	4-$CH_3C_6H_4$	*R*	103–104	+107[c]	74.40	8.08	11.69	...	74.11	8.11	11.82	...

[a] All the sulfoxides in Table V except for **14** were prepared by the Grignard synthesis from (−)-menthyl (−)-*p*-toluenesulfinate which has the *S* configuration at sulfur.[16c] Since the Grignard reaction proceeds with inversion of configuration at sulfur,[16c] the absolute configuration of the sulfoxides is thus established. [b] Solvent ethanol unless otherwise specified. [c] Solvent acetone. [d] Boiling points (kugelrohr) are approximate. [e] M. Axelrod, Ph.D. Thesis, Princeton University, 1966. [f] Prepared by asymmetric oxidation.

The general procedure used for preparing optically active sulfoxides by the Grignard synthesis was as follows. A one- to twofold mole equivalent of the Grignard reagent in ether prepared in the usual manner was filtered through a plug of glass wool and added dropwise to a stirred solution of the *l*-menthyl *p*-toluenesulfinate[16] (mp 104–105°, $[\alpha]^{26}D$ −202° (acetone)) in ether. There was an immediate reaction with the formation of a gummy precipitate. When the addition of the Grignard solution was complete, enough THF was added to the ether solution to dissolve the gummy residue. After stirring for 15 min the reaction mixture was hydrolyzed by the addition of a saturated solution of ammonium chloride. The ether layer was washed with water and the solvent removed under reduced pressure. The residue was steam distilled from a 10–20% KOH solution until no more menthol came over. The residual sulfoxide was extracted into methylene chloride which was then washed with water, dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using benzene and benzene–ethyl acetate as the eluents. The sulfoxides do not usually elute until the solvent contains some ethyl acetate. The solid sulfoxides were recrystallized from petroleum ether or petroleum ether–acetone mixtures.

Since a great deal of difficulty was encountered in preparing 1-adamantyl *p*-tolyl sulfoxide and since 1-adamantyl methyl sulfoxide was prepared by asymmetric oxidation of 1-adamantyl methyl sulfide, a full account of the preparation of these two sulfoxides is provided below.

1-Adamantyl *p*-Tolyl Sulfoxide (15). A solution of 1-bromoadamantane (15 g, 0.070 mol) and 2 g of ethylene bromide (as entrainer) in 300 ml of anhydrous ether was added dropwise to a stirred suspension of 4.86 g (0.20 mol) of magnesium powder (Baker and Adamson) in a few milliliters of ether, blanketed under nitrogen. After addition was completed (*ca.* 1 hr) the reactants were stirred for an additional period of 30 min. A solution of *l*-menthyl *p*-toluenesulfinate (4.89 g, 0.020 mol, $[\alpha]^{26}D$ −202° (acetone)) in 100 ml of ether was added rapidly to the steel gray Grignard solution; a green color appeared on contact of the reactants. Upon completion of the addition, the reaction mixture was stirred for an additional 15 min. The ether solution was filtered through a plug of glass wool into a separatory funnel containing a saturated solution of ammonium chloride. The organic layer was washed with saturated aqueous ammonium chloride, dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure and the white semisolid residue was chromatographed on 50 g of silica gel, eluting first with benzene and then with benzene–ethyl acetate to remove the sulfoxide. The product was recrystallized several times from petroleum ether (bp 60–70°) until a constant mp of 103–104° was reached. The yield of sulfoxide was 0.865 g, a 4.5% yield based on the ester. The compound had $[\alpha]^{26}D$ +107° (*c* 1.24, acetone).

The nmr spectrum showed a complex multiplet at τ 8.15–8.50 (12 H) assigned to the methylene protons of the adamantyl group, another multiplet at τ 7.75–8.1 (3 H) assigned to the methine protons of the adamantyl group, a singlet at τ 7.58 (3 H) assigned to the *p*-tolyl methyl group,[16b] and a quartet at τ 2.42–2.85 (4 H) assigned to the aromatic protons.

Anal. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08; S, 11.69. Found: C, 74.11; H, 8.11; S, 11.82.

1-Adamantyl Methyl Sulfide. 1-Adamantanethiol[52] (16.4 g, 0.098 mol) was added to a solution prepared by dissolving 2.53 g (0.11 g-atom) of sodium in 200 ml of absolute ethanol and the solution was heated to reflux under nitrogen. A solution of 14.2 g (0.10 mol) of methyl iodide in 100 ml of ethanol was added dropwise over a period of 1 hr to the solution of sodium 1-adamantanethiolate. After the reaction mixture had been heated under reflux for 1 hr, 2.80 g (0.020 mol) of methyl iodide in 10 ml of ethanol was added. Refluxing was continued for an additional 15 hr. The volume of the ethanol solution was reduced to 75 ml under reduced pressure and the solution was diluted with 200 ml of water. The sulfide was extracted with petroleum ether (bp 60–70°) and the extracts were washed with 20% KOH solution. Removal of the solvent left 16.8 g of crude sulfide which was stored overnight over 5 g of KOH pellets. Water (50 ml) was added and the sulfide was extracted into ether. The ether layer was washed with water, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was further dried over Molecular Sieves (Fisher 4A) and distilled (kugelrohr), bp ~70° (0.05 mm). The sulfide still contained *ca.* 1% of the thiol as judged by glpc. The nmr spectrum exhibited a sharp singlet at τ 8.00 (3 H) assigned to the methyl group, which was superimposed on a complex multiplet at τ 7.8–8.4 (15 H) assigned to the adamantyl protons.

Anal. Calcd for $C_{11}H_{18}S$: C, 72.46; H, 9.95; S, 17.59. Found: C, 72.22; H, 9.80; S, 17.45.

1-Adamantyl Methyl Sulfoxide (14). A solution of *d*-percamphoric acid was prepared according to the procedure of Milas and McAlevy,[53] except that twice the reported scale was used and cold chloroform was substituted for "fresh cold ether." The solution, calibrated iodometrically, had 0.1345 g-atom of active oxygen per liter. An aliquot of 224 ml (0.030 g-atom of active oxygen) was added over a period of 2 hr to a stirred solution of 1-adamantyl methyl sulfide (5.46 g, 0.030 mol) in 100 ml of chloroform. The reaction mixture was maintained at −30 ± 5° throughout the addition. The chloroform solution was washed with two 100-ml portions of a saturated solution of sodium bicarbonate and then with water. The organic layer was dried over sodium sulfate and filtered. The solvent was removed under reduced pressure, leaving an almost colorless residual oil which was chromatographed on 70 g of silica gel. After elution with benzene, followed by 200 ml of benzene–ethyl acetate (1:1), the sulfoxide was eluted with 500 ml of ethyl acetate. Removal of the solvent left a liquid residue which solidified on standing. This material was then distilled (kugelrohr), bp ~120° (0.2 mm). The distillate (2.6 g, 44%) crystallized on standing, mp 71–77°, $[\alpha]^{22}D$ −2.9° (*c* 1.9, ethanol).

The nmr spectrum exhibited a singlet at τ 7.64 (3 H) assigned to the methyl group[54] and a complex multiplet at τ 7.5–8.5 (15 H) assigned to the adamantyl protons. The ir spectrum (Nujol) showed the expected S–O stretching frequencies near 1050 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}OS$: C, 66.61; H, 9.15; S, 16.17. Found: C, 66.49; H, 8.99; S, 16.11.

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[52] J. R. Geigy, AG., Belgian Patent 629,370 (Oct 21, 1963).

[53] N. A. Milas and A. McAlevy, *J. Amer. Chem. Soc.*, **55**, 349 (1933).

[54] This value differs markedly from the chemical shift (τ 7.31–7.33, chloroform) of the S–CH_3 protons in aryl methyl sulfoxides (Ar = C_6H_5, *p*-$CH_3C_6H_4$, *o*-, *m*- and *p*-$CH_3OC_6H_4$).[16b,48] The chemical shift of the S–CH_3 protons in ethyl methyl and isopropyl methyl sulfoxides is τ 7.45 and 7.51 (chloroform), respectively. Evidently the adamantyl group exerts a significant shielding effect on the S–CH_3 protons.