

Essentially the same mechanism has been proposed for the bromination of norbornylene.⁷

Quantum mechanically, preference for inversion in the above electrophilic displacement is reasonable. The carbon atom undergoing displacement would be somewhat electron-deficient (resembling a carbonium ion), and p character is preferred to s in an incompletely filled orbital. The essential difference between concerted electrophilic and nucleophilic displacement is the filling of orbitals, the system X—C—Y having only one electron pair in the bonding orbital during electrophilic displacement but having a second pair in a non-bonding orbital, to which the contribution of the central carbon atom is nearly zero, in nucleophilic displacement. Electron repulsion in the non-bonding orbital makes inversion practically mandatory in nucleophilic displacement, while its absence leaves the stereochemistry more flexible in electrophilic displacements. In electrophilic displacements where the carbon atom acquires considerable carbanion character, the central orbital would acquire more s character (sp^3) and retention would be favored. Any cyclic three-center bonding resulting from orbital overlap of X and Y would also tend to favor retention.

Because of the inherently tentative interpretation of any unprecedented results, we are searching for analogous reactions to support or revise our initial conclusions.

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(7) J. D. Roberts, E. R. Trumbull, R. W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

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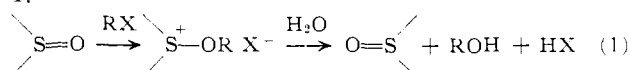
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THE INVERSION OF SULFOXIDE CONFIGURATION

Sir:

The configurational stability of sulfoxides was confirmed in 1926 with the resolution of three sulfoxides by Harrison, Kenyon and Phillips.¹ Soon thereafter examples of geometrical isomerism attributable to the sulfoxide grouping were provided.² This communication now reports the first examples of the inversion of the configuration of the sulfoxide group.³

The recent report⁴ that alkyloxysulfonium salts hydrolyze in isotopically enriched water to yield the parent sulfoxide containing oxygen-18 suggested that such a reaction might proceed with inversion of configuration 1.



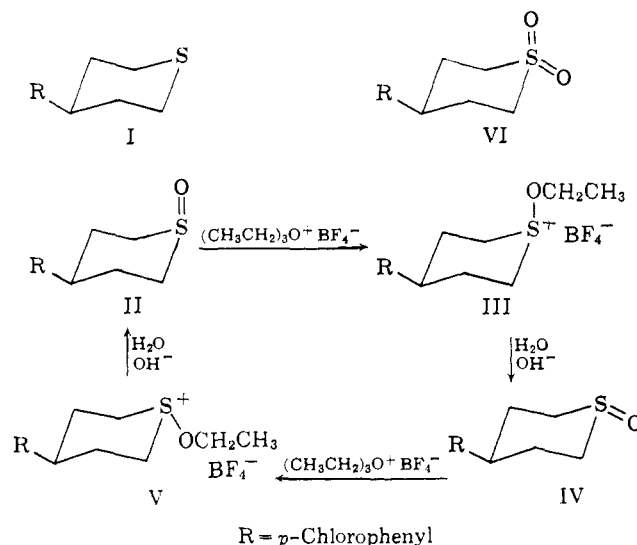
In the present study *cis*-4-(*p*-chlorophenyl)-thian-1-oxide (II) was transformed to the corresponding *trans*

(1) P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 2079 (1926).

(2) E. V. Bell and G. M. Bennett, *ibid.*, 1798 (1927).

(3) Walden inversion has been shown to occur during trans-esterification of sulfonic esters which have related molecular dissymmetry at the sulfur atom: H. Phillips, *ibid.*, **127**, 2552 (1925).

(4) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).



isomer (IV) *via* hydrolysis of an intermediate O-alkyl sulfoxide adduct. To complete the cycle, the *trans* sulfoxide in like manner was converted to the *cis* as shown in the annexed scheme and described in detail below.

Cyclization of 3-(*p*-chlorophenyl)-1,5-dibromopentane⁵ was effected with sodium sulfide in absolute ethanol to provide 4-(*p*-chlorophenyl)-thiane (I), m.p. 70–71°. (*Anal.* Calcd. for $C_{11}H_{13}ClS$: C, 62.11; H, 6.16. Found: C, 62.10; H, 6.22.)

Oxidation of the sulfide I with aqueous sodium metaperiodate⁶ and recrystallization of the crude sulfoxide⁷ from ethyl acetate provided pure *cis*-4-(*p*-chlorophenyl)-thian-1-oxide, m.p. 172.5–173°, $\nu_{\text{max}}^{\text{CCl}_4}$ 1058 cm^{-1} , ($S = 0$). (*Anal.* Calcd. for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; S, 14.04. Found: C, 57.78; H, 5.76; S, 13.81.) The dipole moment of II in benzene solution was found to be 3.98 ± 0.02 D,⁸ in fair agreement with 4.30 D. calculated⁴ from models and model compounds⁹ for the chair conformation of the *cis* sulfoxide.

Alkylation of II with triethyloxonium fluoroborate¹⁰ in methylene chloride afforded in 76% yield the desired kinetically-controlled alkylation product,¹¹ *cis*-4-(*p*-chlorophenyl)-1-ethoxythioniacyclohexane fluoroborate (III), m.p. 107–108°. (*Anal.* Calcd. for $C_{13}H_{18}BClF_4OS$: C, 45.32; H, 5.26; neut. equiv., 344.5. Found: C, 45.13, 45.55; H, 5.30, 5.22; neut. equiv., 347.)

When III was dissolved in dilute aqueous sodium hydroxide, one equivalent of base was consumed and shiny platelets of a new sulfoxide, m.p. 119–121°, precipitated in 93% yield. Recrystallization from ethyl acetate–hexane provided pure *trans*-4-(*p*-chlorophenyl)-thian-1-oxide (IV), m.p. 120–120.5°, $\nu_{\text{max}}^{\text{CCl}_4}$ 1054 cm^{-1} , ($S = 0$), dipole moment in benzene 2.60 D.⁸ (calcd. for chair conformation of *trans* sulfoxide, 2.24 D.). (*Anal.*

(5) N. L. Allinger and S. Greenberg, *ibid.*, **81**, 5733 (1959).

(6) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(7) It is noteworthy that oxidation of I with periodate provided a mixture consisting of 70% *cis* sulfoxide (II) and 30% *trans* sulfoxide (IV) as ascertained by infrared analysis. On the other hand, oxidation of I with hydrogen peroxide in acetone or with perbenzoic acid in chloroform yielded approximately 30% II and 70% IV. The implications of these and similar data bearing on the mechanism of oxidation of sulfides will be discussed in the full paper. At the same time detailed infrared studies of these compounds will be presented.

(8) The dielectric and density measurements were made by Mr. C. L. Neumann of these Laboratories.

(9) Thian-1-oxide, 4.19 D. [A. I. Vogel and C. W. N. Cumper, *J. Chem. Soc.*, 3521 (1959)] and *p*-chlorotoluene, 1.95 D. [N. L. Allinger, S. P. Jindal and M. A. DaRooge, *J. Org. Chem.*, **27**, 4290 (1962)].

(10) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willang, *J. prakt. Chem.*, **154**, 83 (1939).

(11) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

Calcd. for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73. Found: C, 57.55; H, 5.76.) Material identical (m.p., m.m.p. and infrared spectrum) with IV was obtained by chromatography of the residue from the mother liquors from the recrystallization of II. In agreement with the structural assignments, II was eluted from alumina prior to IV.

Reaction of IV with triethyloxonium fluoroborate gave in 83% yield *trans*-4-(*p*-chlorophenyl)-1-ethoxythionia-cyclohexane fluoroborate (V), m.p. 166–167°. (*Anal.* Calcd. for $C_{13}H_{15}BClF_4OS$: C, 45.32; H, 5.26; neut. equiv., 344.5. Found: C, 45.33; H, 5.06; neut. equiv., 343.) Hydrolysis of V with dilute alkali provided in 92% crude yield the *cis* sulfoxide II identical (m.p., m.m.p. and infrared spectrum) after a single recrystallization with that obtained above by the oxidation of the sulfide with periodate.

Infrared spectra indicated that the crude sulfoxides IV and II isolated from solvolysis of III and V, respectively, contained less than 5% of contaminating isomeric sulfoxide. In these examples a hydrolytic pathway involving inversion at the sulfur atom significantly predominates over alternates, *e.g.*, carbon-oxygen cleavage.

Oxidation of the sulfide I with potassium permanganate in glacial acetic acid gave 4-(*p*-chlorophenyl)thian-1,1-dioxide (VI), m.p. 208–209°, $\nu_{\max}^{CH_2Cl_2}$ 1300, 1120 cm^{-1} , (SO_2). (*Anal.* Calcd. for $C_{11}H_{13}ClO_2S$: C, 54.07; H, 5.35. Found: C, 53.90; H, 5.58.) The same sulfone was obtained by oxidation of II and IV with permanganate.

Work now in progress in this Laboratory will provide additional examples of sulfoxide inversion, including the interconversion of optical isomers.

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ISOTOPE EFFECTS IN RECOIL TRITIUM REACTIONS WITH HYDROCARBONS¹

Sir:

The two highest yield reactions of recoil tritium atoms in scavenged alkane systems are almost invariably those involving abstraction of a hydrogen atom or substitution for it by the tritium atom. Several recent publications have concerned themselves with the mechanistic significance of the relative yields of these two reactions, both from individual molecules alone^{2–5} and from two parent alkane molecules in competition with one another in the same system.⁶ One suggested interpretation of these measured yields^{4,5} is consistent with most of the data, but appears to be in direct conflict with previously reported isotope effects observed in hydrogen abstraction from methane by recoil tritium.⁷

In the context of the simple model for the reactions of a very energetic atom slowing down into an energy range for which chemical bond formation is possible,^{2,8–10} several effects could possibly exist that might

(1) This research was supported by A.E.C. Contract No. AT-(11-1)-407, and by a National Science Foundation Pre-doctoral Fellowship (J.W.R.).

(2) D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961).

(3) R. Wolfgang, *et al.*, "Chemical Effects of Nuclear Transformations," Vol. 2, I.A.E.A., Vienna, 1961, p. 83.

(4) R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 4586 (1962).

(5) H. C. Jurgeleit and R. Wolfgang, *ibid.*, in press.

(6) J. W. Root and F. S. Rowland, *ibid.*, **84**, 3027 (1962).

(7) J. K. Lee, B. Musgrave and F. S. Rowland, *J. Phys. Chem.*, **64**, 1950, (1960).

(8) P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661, 2665 (1960).

(9) R. J. Cross and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961).

(10) A. Sokolowska, L. Haskin, and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 2469 (1962).

lead to differences in results measured for isotopically-substituted molecules. If the average energy loss per non-reacting collision is affected by isotopic substitution, different numbers of "hot" collisions would be expected in traversing a given energy range, and thereby could lead to different fractions reacting in that energy range for isotopic molecules. Isotope effects arising from differences in average energy loss are designated here as moderator isotope effects, and have been invoked in explanation of experiments involving CH_4 vs. CD_4 , and CH_3F vs. CD_3F .^{5,9}

If either the energy range over which the substitution reaction occurs or the probability of the reaction per collision varies with isotopic substitution, then isotopic differences could appear. The over-all effect of these two possible differences will be defined here as probability integral isotope effects. In any particular real system, any or all of these sources of isotopic variation could be present.

In general, moderator and probability integral isotope effects can be distinguished through experiments involving measurements of reactions occurring simultaneously in the same system.^{6,10} In such direct competitions possible variations from moderator differences are essentially eliminated since all the molecules are exposed to the same spectrum of tritium energies.

The abstraction reaction has been reinvestigated with higher precision measurements on CH_2D_2 as shown in Table I. The substitution of T for H has been tested for isotope effects through competitions between protonated and deuterated methanes and *n*-butanes, as summarized in Table II. The samples were analyzed by radio-gas chromatography; the nuclear reaction $He^3(n,p)H^3$ served as the tritium source.

TABLE I

RELATIVE YIELD OF TRITIATED MOLECULES FROM TYPICAL RECOIL TRITIUM EXPERIMENTS WITH CH_2D_2

Sample number	Scavenger ^a (cm.)	HT + DT		Yields (relative units) ^a		
		HT/DT	DT/RT	HT	DT	Methane- <i>t</i>
438	None	2.34	1.11	94	39	119
440	0.02 I ₂	1.51	0.86	41	27	79
392	1.02 O ₂	1.34	0.79	34	26	75
443	3.27 O ₂	1.34	0.79	36	27	79
445	4.90 O ₂	1.32	0.79	35	27	78

^a Total pressure 100 cm., including 1.0–1.6 cm. of He³; irradiated for 60 min. in a neutron flux of 5×10^{10} neutrons/cm.²/sec. A yield of 75 represents 25% of the total tritium activity stopped in the gas phase.

TABLE II

DISTRIBUTION OF RADIOACTIVITY BETWEEN PARENT COMPOUNDS FOR COMPETITIVE RECOIL TRITIUM REACTIONS IN THE GAS PHASE

Experiment number	<i>n</i> -Butane	Methane	Pressure ratio		Specific activity ratio	
			butane/methane	Obsd.	Cor. ^a	
418	C ₄ H ₁₀	CD ₄	0.109	2.91	2.98	
419	C ₄ H ₁₀	CD ₄	.109	2.89	2.96	
422	C ₄ H ₁₀	CH ₄	.113	2.19	2.23 ^b	
423	C ₄ H ₁₀	CH ₄	.113	2.26	2.30	
412	C ₄ D ₁₀	CH ₄	.112	1.81	1.88	

^a Corrected for production of methane-*t* by reaction of T with *n*-butane. ^b The original measurements of substitution into fully-protonated methane and butane⁶ gave values for the specific activity ratio ranging from 2.29 to 2.60. This scatter has now been eliminated, and the lower limit is approximately correct.

We conclude from Table I that the isotope effect in hydrogen abstraction is essentially constant at 1.32 for HT/DT¹¹ between 1 and 5% O₂. Similarly, an isotopic preference for the recoil tritium substitution of T for H vs. T for D can be estimated from Table II: for CH₄ and CD₄ vs. *n*-C₄H₁₀, 2.97/2.27 = 1.31, and for C₄H₁₀

(11) Corrected for CH₃D impurity in the CH₂D₂.