The Nonstereospecific Addition of 2,4-Dinitrobenzenesulfenyl Chloride to *cis*- and *trans*-Anethole[1]

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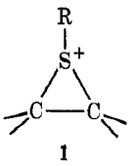
The addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*-anethole in 1,1,2,2-tetrachloroethane (TCE) at 30° gives 30% of the erythro (**2**) and 70% of the threo (**3**) Markovnikov adduct, while addition to *trans*-anethole forms **2** and **3** in 95 and 5% yields, respectively, under the same reaction conditions. The products in TCE at 30° slowly rearrange to an equilibrium mixture containing 51.8% **2** and 48.2% **3**. The nonstereospecific addition to *cis*-anethole must involve an open carbonium ion prior to the product-determining step. This result is in contrast to the usual trans addition of aryl and alkylsulfenyl chlorides to olefins. The addition to *trans*-anethole is highly stereoselective and it is not clear to what extent an open ion is involved in the reaction.

The reaction of aryl and alkylsulfenyl chlorides to olefins has been found to be a stereospecific trans addition by numerous workers.[2-4] Based upon this observation as well as other evidence, a mechanism involving an episulfonium ion (**1**) has been postulated for this reaction.[5]



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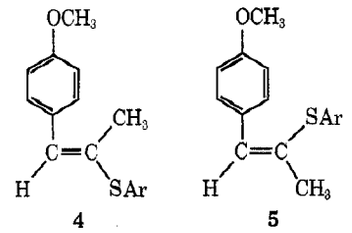
We wish to report the first case of a nonstereospecific addition of an arylsulfenyl chloride to an olefin and discuss its mechanistic implications.

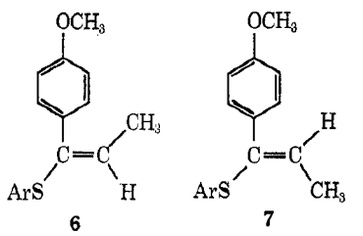
Results

The addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*-anethole at 30° in 1,1,2,2-tetrachloroethane (TCE) gives two products, **2** and **3**, in 30 and 70% yields, respectively, while addition to *trans*-anethole forms **2** and **3** in 95 and 5% yields, respectively, under the same reaction conditions. No difference in products was observed in the presence of added oxygen or in the presence or absence of light. It was found that the reaction products in TCE slowly rearrange to an equilibrium mixture which contains 51.8% **2** and 48.2% **3** at 30.92 ± 0.02°, in TCE. Compound **2** was obtained pure by fractional crystallization of the initial reaction mixture obtained from *trans*-anethole. Despite numerous attempts, **3** could not be obtained free of **2**. Compounds **2** and **3** are the erythro Markovnikov and the threo Markovikov adducts, respectively. Their structures were deduced from the following chemical and spectral information.

A mixture containing 64% **2** and 36% **3** was dehydrochlorinated by reaction with diazabicyclononene to produce a 50:50 mixture of cis and trans olefins in 85% yield. Four structures, **4**–**7**, are possible for these olefins. The structures assigned to the olefins are based on the coupling constants between the vinyl and methyl protons. For structures **4** and **5**, J should be approximately 2 Hz, while for structures **6** and **7**, J should be approximately 7 Hz. Since the observed



4 **5**

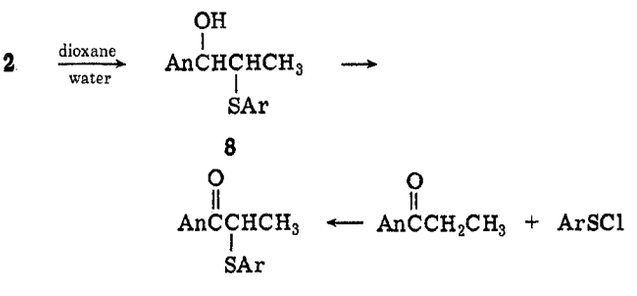


6 **7**

Ar = 2,4-dinitrophenyl

coupling constants are J = 2.0 and 1.0 Hz, **4** and **5** were assigned the structures of the olefins. These results indicate that the adducts **2** and **3** both have a structure with the chlorine in the 1 position and the ArS group in the 2 position.

Additional information regarding the structure of **2** is provided by the following experiment. A pure sample of **2** was solvolyzed in dioxane–water. The resulting alcohol **8** was oxidized to the ketone **9** using



8 **9**

Ar = *p*-methoxyphenyl

An = 2,4-dinitrophenyl

the Jones reagent. This ketone proved to be identical with the α-keto sulfide obtained from the reaction of 2,4-dinitrobenzenesulfenyl chloride and 4-methoxypropiophenone.

Final confirmation that **2** and **3** are configurational isomers is based on a comparison of the nmr spectra of **2** and **3** with the nmr spectra of the addition products of 4-chloro- and 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-phenylpropene. The data are

(1) Reactions of Sulfenyl Chlorides and their Derivatives. VII. Part VI: G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **50**, 2465 (1972).
(2) G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).
(3) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966).
(4) G. M. Beverly and D. R. Hogg, *Chem. Commun.*, 138 (1966).
(5) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).

TABLE I

NMR DATA OF 2 AND 3 AND THE ADDUCTS OF 4-CHLORO- AND 2,4-DINITROBENZENESULFENYL CHLORIDE TO *cis*- AND *trans*-1-PHENYLPROPENE

Compd	Ar	Configuration	δ_a	δ_b	δ_c
$PhCH^aCH^bCH_3^c$	**10a**, 4-Chloro	Threo	4.97 (d)	3.66 (m)	1.23 (d)
Cl SAr	**11a**, 4-Chloro	Erythro	4.82 (d)	3.49 (m)	1.38 (d)
	10b, 2,4-Dinitro	Threo	5.12 (d)	4.10 (m)	1.44 (d)
	11b, 2,4-Dinitro	Erythro	5.05 (d)	4.00 (m)	1.63 (d)
$PhCH^aCH^bCH_3^c$	**12a**, 4-Chloro	Threo	4.34 (d)	4.34 (m)	1.44 (d)
SAr Cl	**13a**, 4-Chloro	Erythro	4.22 (d)	4.22 (m)	1.54 (d)
	12b, 2,4-Dinitro	Threo	4.73 (d)	4.46 (m)	1.56 (d)
	13b, 2,4-Dinitro	Erythro	Unknown		
2			4.92 (d)	3.96 (m)	1.65 (d)
3			5.07 (d)	3.96 (m)	1.43 (d)

given in Table I. The nmr spectra of **2** and **3** are almost identical with those of **11b** and **10b**, respectively. The isomerization of **2** and **3** is particularly revealing, since it serves to establish their relative configurations. When **2** isomerizes to **3** the nmr signal of the methyl group (H_c) is shifted to higher field, while the doublet of the methine hydrogen (H_a) is shifted to lower field. If this were a Markovnikov to anti-Markovnikov isomerization, as found in the case of the adducts of 4-chlorobenzenesulfenyl chloride to 1-phenylpropene,[1] the signals for the methine proton (H_a) would be shifted to higher field, since protons next to chlorine are known to be deshielded relative to protons next to sulfur. Also the methyl protons (H_c) would be shifted to lower field. These relationships are evident from a comparison of the chemical shifts of H_c and H_a in the transformations **10a** → **12a**, **11a** → **13a**, and **10b** → **12b** in Table I.

These observed changes in chemical shifts upon isomerization of **2** to **3** as well as the chemical data are compatible with the assignment of their configuration as a pair of erythro–threo Markovnikov isomers. From an examination of the nmr spectra of a series of racemic erythro and threo isomers, it has been found that the methyl protons of the erythro isomer always appears at lower field than those of the threo isomer.[6] On this basis, **2** is the erythro Markovnikov while **3** is the threo Markovnikov adduct. The fact that the same two products result from the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and trans-anethole strongly supports this structural assignment.

The kinetics of the addition were carried out at 30.92 ± 0.02° in TCE as solvent. The change in concentration of 2,4-dinitrobenzenesulfenyl chloride with time was determined by a modification of the usual titration technique used to determine the concentration of sulfenyl chlorides.[7]

The data gave good straight lines for a second-order reaction, first order in both anethole and 2,4-dinitrobenzenesulfenyl chloride. Attempts to fit the data to a first- or third-order kinetic rate law produced curved plots. The second-order rate constants obtained by a least squares fit are listed in Table II.

The isomerization of **2** and **3** to an equilibrium mixture was followed by measuring the change in the area of their methyl signals in the nmr with time. The rate constants obtained by treating the data according to the method of Frost and Pearson[8] are listed in Table III.

TABLE II

SPECIFIC RATE CONSTANTS FOR THE ADDITION OF 2,4-DINITROBENZENESULFENYL CHLORIDE TO *cis*- AND *trans*-1-ANETHOLE

trans-Anethole

$[ArSCl]_0 \times 10^3$, mol/l.	$[Olefin]_0 \times 10^3$, mol/l.	$k \times 10^2$, M^{-1} sec^{-1}
8.06	10.91	2.04
7.26	11.63	2.13
7.63	10.68	1.89
9.86	6.05	1.94
7.00	13.50	1.89
5.72	8.45	1.93
		Av 1.97 ± 0.09

cis-Anethole

$[ArSCl]_0 \times 10^3$, mol/l.	$[Olefin]_0 \times 10^3$, mol/l.	$k \times 10^3$
5.79	8.29	3.82
5.07	9.46	3.87
5.54	7.19	3.90
		Av 3.86 ± 0.04

TABLE III

RATE OF ISOMERIZATION OF ERYTHRO- AND THREO MIXTURES

$$2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3$$

From excess **2**	$k_1 + k_{-1} = 7.3 \pm 0.5 \times 10^{-6}$ sec^{-1}
From excess **3**	$k_1 + k_{-1} = 6.9 \pm 0.2 \times 10^{-6}$ sec^{-1}
	$K = 1.07$
	$k_{-1} = 3.5 \times 10^{-6}$ sec^{-1}
	$k_1 = 3.8 \times 10^{-6}$ sec^{-1}

Discussion

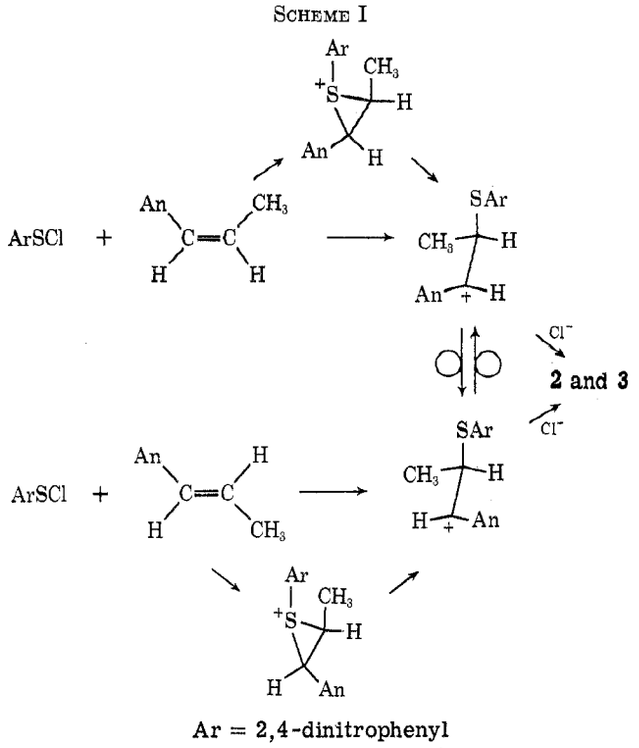
From the data presented it is clear that the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*-anethole is nonstereospecific. The addition to *trans*-anethole is highly stereoselective and may be stereospecific. We cannot rule out the possibility that the formation of the small amount of **3**, the threo isomer, is due to subsequent isomerization of the initially formed product

(6) G. H. Schmid, *Can. J. Chem.*, **46**, 3415 (1968).
(7) N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).
(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953, p 113.

2. These results are in contrast to the stereospecific trans addition observed for the reaction of 4-chloro- and 2,4-dinitrobenzenesulfenyl chloride to both *cis*- and *trans*-1-phenylpropene.[9] Despite this change in the stereochemistry of the products, the rate of the addition follows second-order kinetics, first order in olefin and first order in sulfenyl chloride, which is identical with that found for additions to simple olefins,[10] styrenes,[11] and acetylenes.[12]

These results indicate that adding a methoxy group to the 4 position of the phenyl group of *cis*-1-phenylpropene has caused a change in mechanism of the reaction. Clearly an open carbonium ion rather than a bridged ion is involved as an intermediate prior to the product determining step. However, it is not clear whether the open carbonium ion is the first-formed intermediate. Consequently there are two possible mechanisms consistent with the facts. The first involves a bridged transition state in the rate determining step leading to an episulfonium ion intermediate which then opens to an open carbonium ion intermediate. This open carbonium ion is now able to rotate to its isomeric carbonium ion, which upon reaction with chloride ion leads to nonstereospecific products. In this mechanism only the product determining transition states resemble the open carbonium ion intermediate. A second mechanism involves only one intermediate, an open carbonium ion. In this mechanism both the rate and product determining transition states resemble the open carbonium ion. These two mechanisms are illustrated in Scheme I.

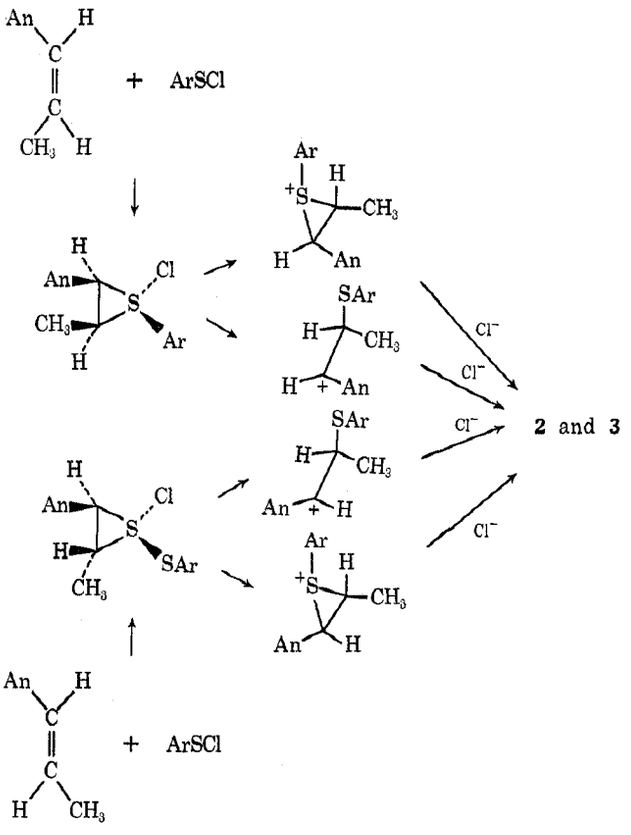
SCHEME I



Ar = 2,4-dinitrophenyl
An = 4-methoxyphenyl

A variant of the first mechanism involving the tetracoordinate covalently bonded sulfur intermediate proposed by Helmkamp[13] is also consistent with our data. In this mechanism the tetracoordinate sulfur intermediate can ionize to either an open carbonium ion or to an episulfonium ion as illustrated in Scheme II.

SCHEME II

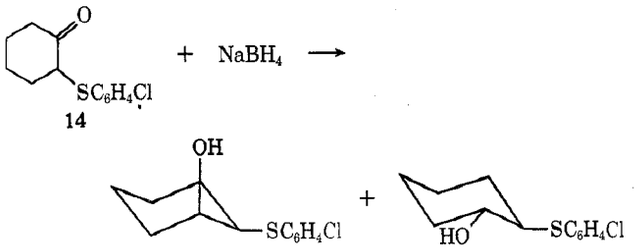


The rate data tends to support some type of bridged structure in the rate-determining step. The rate of addition to *trans*-anethole is faster than to the cis isomer even though the trans isomer is the more stable. Similar results were obtained in the addition of arylsulfenyl chlorides to *cis*- and *trans*-1-phenylpropene and were explained on the basis of increased steric strain in the rate-determining bridged transition state of the addition to the *cis* isomer. In the addition to *cis*-anethole this steric crowding in the bridged or the tetracovalent sulfur intermediate can be relieved by opening to the carbonium ion, whose stability seems to be comparable to that of the episulfonium ion. The highly stereoselective addition to the trans isomer is consistent with this idea, since less opening of the intermediate bridged ion would occur because there is less steric crowding in this intermediate.

The argument that addition to both isomers occurs by an open ion as the first intermediate and that the difference in product composition is due to a difference in the rate of rotation of the open carbonium ions cannot be entirely ruled out. Rotation of the open carbonium ion is not necessary to give nonstereospecific products. It has been found[14] that the $NaBH_4$ reduc-

(9) G. H. Schmid and V. M. Csizmadia, *Chem. Ind. (London)*, 1811 (1968).
(10) G. M. Beverly and D. R. Hogg, *J. Chem. Soc. B*, 175 (1971).
(11) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **75**, 6030 (1953).
(12) G. H. Schmid and M. Heinola, *ibid.*, **90**, 3466 (1968).
(13) D. C. Owsley, G. K. Helmkamp, and M. F. Retting, *ibid.*, **91**, 5239 (1969).
(14) G. H. Schmid and P. H. Fitzgerald, unpublished results.

tion of **14** gives 75% cis and 25% trans alcohol. If the reduction of the ketone is a good model for chloride attack on the open ion, then it is a bit surprising that addition to the trans isomer is so stereoselective.



We conclude on the basis of the data available that the experimental results for addition to *cis*-anethole are consistent with the formation of an open carbonium ion intermediate prior to the product determining step. For the addition to *trans*-anethole, it is not clear to what extent an open ion is involved in the reaction.

Experimental Section

All melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were recorded on Varian A-60 and HA-100 spectrophotometers using tetramethylsilane as internal reference. Microanalysis was carried out by A. B. Gygli Microanalysis Laboratories, Toronto, Ontario. *trans*-Anethole was obtained commercially from Eastman Organic Chemicals and purified by distillation, bp 76.5–77° (1.5 mm) [lit.[15] bp 81–81.5 (2.3 mm)]. *cis*-Anethole was obtained by photochemical isomerization and purified by preparative glc on a 25-ft. UCON column.

2,4-Dinitrobenzenesulfenyl chloride was prepared by the method of Kharasch and Lawson,[16] mp 96–97° (lit.[16] mp 97–98°).

***erythro*-1-*p*-Anisyl-1-chloro-2-(2′,4′-dinitrophenylthio)propane** (**2**) was isolated from the reaction mixture and purified by recrystallization from carbon tetrachloride, mp 134–135°.

Anal. Calcd for $C_{16}H_{15}O_5N_2ClS$: C, 50.20; H, 3.94; N, 7.31; Cl, 9.26; S, 8.37. Found: C, 50.58; H, 3.84; N, 7.36; Cl, 9.98; S, 8.39.

Dehydrochlorination of 2 and 3.—The erythro adduct **2** (2.0 g, 5.2 mmol) was heated under reflux in benzene until a mixture of 64% **2** and 36% **3** was obtained. This mixture was dehydrochlorinated by the method of Eiter and Oediger[17] using 1,5-diazabicyclo[4.3.0]nonene to give an 85% yield of a 50:50 mixture of two olefins: nmr ($CDCl_3$) 2.27 (d, 3 H), J = 1 Hz, 2.31 (d, 3 H, J = 2 Hz), 3.80 (s, 3 H), 3.91 (s, 3 H), 6.7–8.9 (14 H).

(15) Y. R. Naves and P. Ardizio, *Bull. Soc. Chim. Fr.*, 566 (1968).
(16) D. D. Lawson and N. Kharasch, *J. Org. Chem.*, **24**, 858 (1959).
(17) K. Eiter and H. Oediger, *Justus Liebigs Ann. Chem.*, **682**, 62 (1965).

Solvolysis of 2 and Oxidation of the Ketone. A solution of 2.00 g (5.22 mmol) of **2** in 100 ml of 60% dioxane–water was kept at 65° overnight. The reaction mixture was diluted with 100 ml of water, then extracted with three 75 ml portions of ether. The combined ether extracts were washed with water and dried over $MgSO_4$. Removal of the ether left a dark oil which was recrystallized from methylene chloride–pentane to 1.35 g of crude alcohol (71% yield), mp 105–110°, nmr 1.38 (d, 3 H), 4.83 (d, 1 H, J = 4 Hz), 6.65–8.8 (7 H).

A solution of 1.30 g of alcohol in 25 ml of acetone was titrated with the Jones reagent.[18] The solid Cr(III) salts were removed by filtration and 50 ml of water was added to the filtrate, which was then extracted with two 50-ml portions of ether. Removal of the ether left a yellow solid which was recrystallized from 95% ethanol to give 0.96 g of product, mp 150.5–151° (74% yield), identical with the α-keto sulfide isolated from the reaction of 2,4-dinitrobenzenesulfenyl chloride with 4-methoxypropiophenone, nmr ($CDCl_3$) 1.78 (d, 3 H), 3.92 (s, 3 H), 5.02 (g, 1 H), 7.0–8.4 (m, 7).

Anal. Calcd for $C_{16}H_{14}N_2SO_6$: C, 53.03; H, 3.89; N, 7.73; S, 8.85. Found: C, 53.20; H, 3.89; N, 7.79; S, 8.85.

1,1,2,2-Tetrachloroethane was purified by washing with concentrated H_2SO_4 until the acid wash remained colorless. The solvent was then washed with water until neutral, dried over K_2CO_3, and distilled from K_2CO_3 through a Vigreux column, bp 146° (lit.[18] bp 146°).

Kinetics of Addition of 2,4-Dinitrobenzenesulfenyl Chloride to *cis*- and *trans*-Anethole at 30.92 ± 0.02°.—Solutions of ArSCl and olefin in 1,1,2,2-tetrachloroethane (TCE) were equilibrated to bath temperatures, then mixed. Zero time was taken at half mixing. The change in concentration of ArSCl with time was followed by an aliquot technique. A 5 ml aliquot of the reacting mixture was added to 0.5 g NaI in a 125 ml separatory funnel. After the mixture was shaken vigorously for 3 min, 10 ml of water was added followed by 5 ml of 0.01 N $Na_2S_2O_3$ solution. The mixture was then shaken for 3 min. After the lower layer was drawn off (TCE), the excess thiosulfate was titrated with 0.005 N iodine solution. Second-order rate constants were obtained by a least squares fitting program.

Registry No.—**2**, 35031-15-3; **3**, 35031-16-4; **4**, 35031-17-5; **5**, 35031-18-6; **8**, 35031-19-7; **9**, 35031-20-0; **10a**, 22556-38-3; **10b**, 35031-22-2; **11a**, 22556-40-7; **11b**, 35031-24-4; **12a**, 22556-39-4; **12b**, 35031-26-6; **13a**, 22556-41-8; **13b**, 35031-28-8; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; *cis*-anethole, 25679-28-1; *trans*-anethole, 4180-23-8.

Acknowledgment.—Continued financial support from the National Research Council of Canada is gratefully acknowledged.

(18) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).