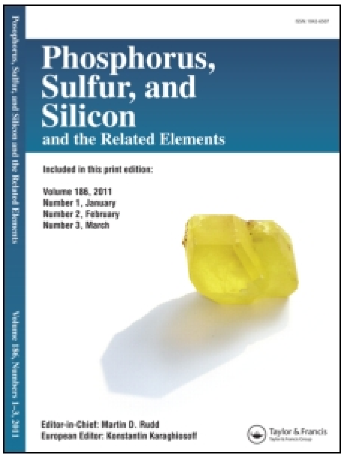

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NUCLEOPHILIC SUBSTITUTION AT SULFINYL AND SULFONYL CENTRES: STEREOCHEMICAL AND KINETIC STUDIES

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To cite this Article Mikołajczyk, Marian(1986) 'NUCLEOPHILIC SUBSTITUTION AT SULFINYL AND SULFONYL CENTRES: STEREOCHEMICAL AND KINETIC STUDIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 27: 1, 31 — 42

To link to this Article: DOI: 10.1080/03086648608072756

URL: http://dx.doi.org/10.1080/03086648608072756

Phosphorus and Sulfur, 1986, Vol. 27, pp. 31–42
0308-664X/86/2702-0031/$20.00/0

NUCLEOPHILIC SUBSTITUTION AT SULFINYL AND SULFONYL CENTRES: STEREOCHEMICAL AND KINETIC STUDIES*

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The mechanism and stereochemistry of nucleophilic substitution reactions at sulfur (S_N—S) are discussed in the light of experimental results obtained in the author's laboratory. The first part of this short review article is devoted to the acid-catalyzed alcoholysis of chiral sulfinates and sulfinamides. In the second part, the results of kinetic studies of the isotopic chloride-chloride exchange reaction in sulfonyl chlorides are presented.

The mechanism and steric course of nucleophilic substitution reaction at the heteroatomic center, X, (X = P, S, Si, Ge, etc.) have been the main points of interest of many research groups all over the world in the last three decades.[1-3] However, in spite of the fact that much experimental material on this subject has been accumulated, it is still difficult to predict correctly the stereochemistry of a particular S_N—X reaction because there are many specific internal and external factors which can essentially influence its mechanism and stereochemistry.

One of the most important questions about the mechanism of substitution at sulfur as well as at other heteroatoms is whether such reaction occurs synchronously according to an S_N2—S mechanism or stepwise by an addition-elimination mechanism, A–E, involving a tetra- or pentacoordinate sulfurane intermediate that is formed by addition of the nucleophile (N) to the substrate.[4] Both possible mechanistic pathways together with the corresponding energy profiles are shown in Figure 1.

The second closely related problem concerns the relationship between the structure of sulfurane intermediates (and other valency-shell expanded compounds) and the stereochemical course of nucleophilic substitution. It is generally accepted that diaxial or diequatorial disposal of entering (N) and leaving (L) group in a transient sulfurane intermediate should lead to inversion of configuration at sulfur whereas the steric course of axial-equatorial substitution is predicted to be retention (see Figure 2).

However, this rather clear relationship may be disturbed by permutational isomerization of sulfurane species. The latter process consists in the internal ligand reorganization changing the relative positions of ligands in a trigonal-bipyramidal structure and is commonly called pseudorotation.[5] A single pseudorotation process according to the Berry mechanism is visualized below (Figure 3). Since the energy required for pseudorotation is usually very low, this process may have an important influence on the stereochemistry of nucleophilic substitution. Therefore, the mecha-

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*This lecture is dedicated to the memory of the late Professor Dr. Tadeusz Urbański who died on May 29, 1985.

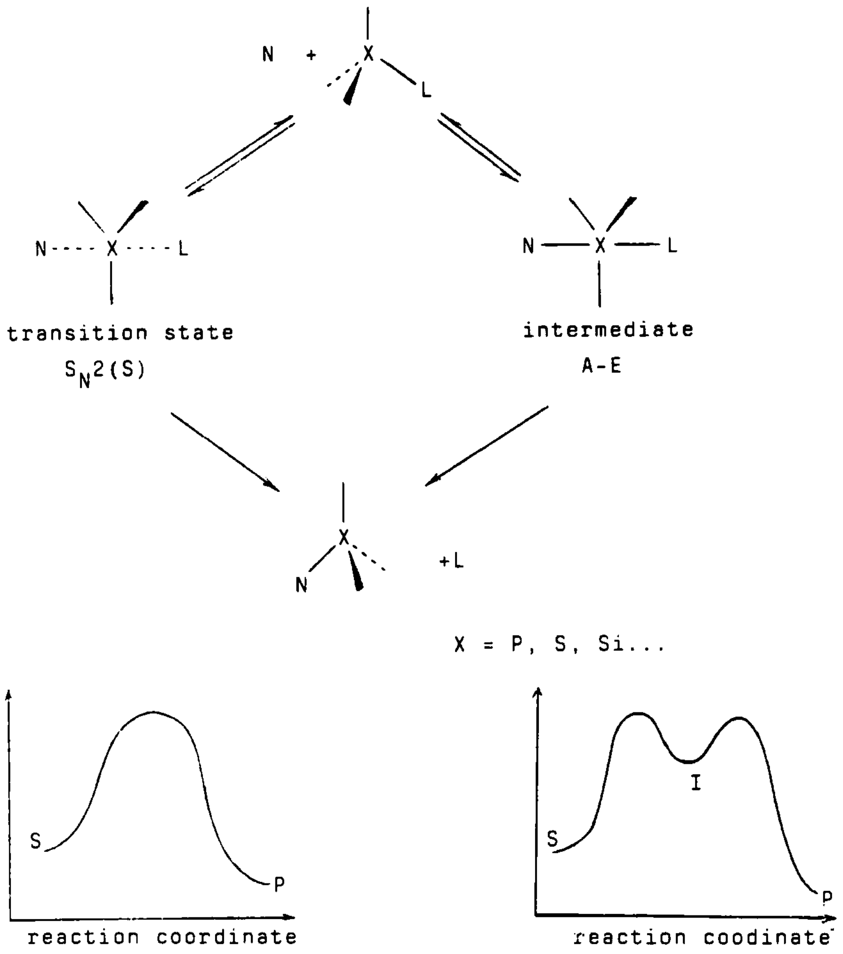


FIGURE 1 S_{N^2} and A–E mechanisms for nucleophilic substitution at the heteroatomic center.

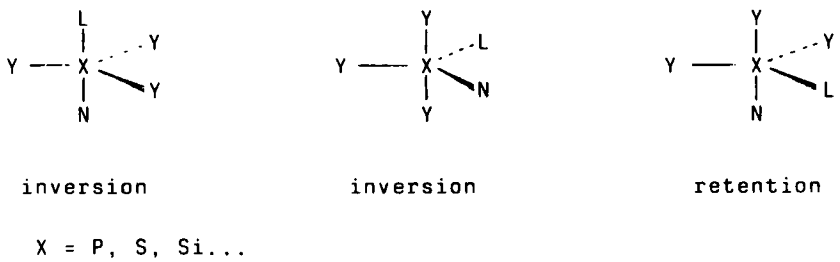


FIGURE 2 Relationship between the positions of attacking nucleophile and leaving group in the trigonal bipyramid and the steric course of nucleophilic substitution at the heteroatomic center.

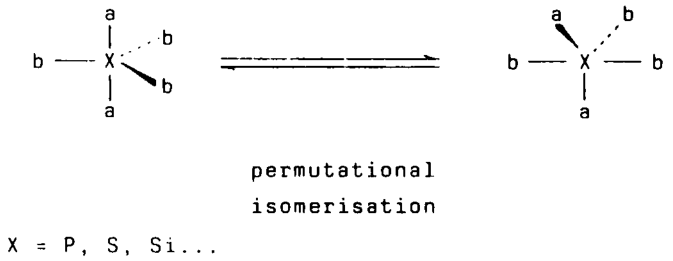
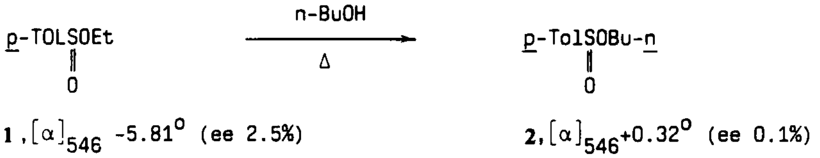


FIGURE 3 A single pseudorotation process of the trigonal bipyramidal compound.

nism and stereochemical outcome of a substitution reaction are difficult to predict and may strongly depend on the reaction partners and the specific reaction conditions applied.

For the past few years, work in the author's laboratory has centered on the preparation and reactions of chiral sulfinyl compounds, especially those with the sulfur atom as a sole center of chirality.[1,6] The essential purpose of these studies was to gain further experimental insight into the complex nature of the S_N—S reactions. The recent results obtained in this laboratory are reported in the present account.

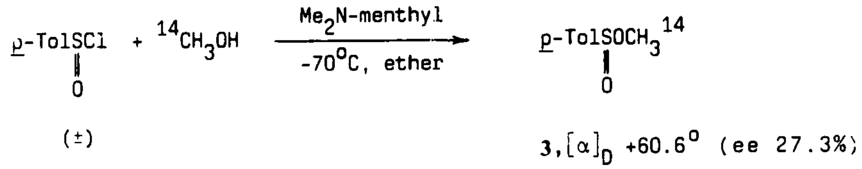
In the majority of reported cases, nucleophilic substitution reactions at chiral sulfur lead to inversion of configuration. Historically, the thermal transesterification of (−)-ethyl *p*-toluenesulfinate (**1**) with *n*-butanol affording (+)-*n*-butyl *p*-toluenesulfinate (**2**) (eq. 1) described by Phillips[7] in 1925 is the first nucleophilic substitution reaction at chiral sulfur involving a Walden type inversion.



$$\underline{p}\text{-TOL}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{OEt} \xrightarrow[\Delta]{n\text{-BuOH}} \underline{p}\text{-Tol}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{OBu-}\underline{n} \qquad (1)$$

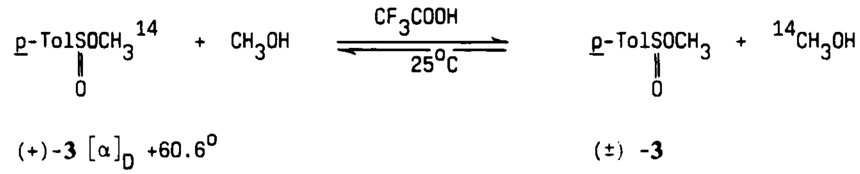
1, $[\alpha]_{546}$ -5.81° (ee 2.5%) **2**, $[\alpha]_{546}$ $+0.32^{\circ}$ (ee 0.1%)

However, according to our calculations of the ee values for the starting ester (−)-**1** and resulting (+)-**2** the stereospecificity of the reaction shown above is extremely low. Moreover, in our hands the same reaction using (−)-**1**, $[\alpha]_D$ − 25.7°, performed under the conditions described by Phillips gave completely racemic sulfinate **2**. Therefore, in order to establish unequivocally the steric course of the transesterification reaction of sulfinates we have synthesized chiral methyl *p*-toluenesulfinate, (**3**), containing ^{14}C in the methoxy group (eq. 2) and measured the rate of racemization of **3** and isotopic methoxy-methoxy exchange in methanol in the presence of trifluoroacetic acid (eq. 3).[8]



$$\underline{p}\text{-Tol}\underset{\underset{\text{O}}{\|}}{\text{S}}\text{Cl} + {}^{14}\text{CH}_3\text{OH} \xrightarrow[-70^{\circ}\text{C, ether}]{\text{Me}_2\text{N-menthyl}} \underline{p}\text{-Tol}\underset{\underset{\text{O}}{|}}{\text{S}}\text{OCH}_3{}^{14} \qquad (2)$$

(±) **3**, $[\alpha]_D$ $+60.6^{\circ}$ (ee 27.3%)



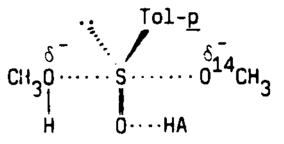
$$\underline{p}\text{-Tol}\underset{\overset{\|}{O}}{S}OCH_3^{14} + CH_3OH \underset{25^{o}C}{\overset{CF_3COOH}{\rightleftharpoons}} \underline{p}\text{-Tol}\underset{\overset{\|}{O}}{S}OCH_3 + {}^{14}CH_3OH \qquad (3)$$

(+)-**3** $[\alpha]_D$ +60.6° (±) -**3**

$$k_{rac} = (6.25 \pm 0.01)\, 10^{-5}\, s^{-1}$$
$$k_{ex} = (2.94 \pm 0.04)\, 10^{-5}\, s^{-1}$$

The fact that sulfinate **3** loses its optical rotation practically twice as fast as it loses the radioactive methoxy group provides clear-cut evidence for a full inversion of configuration in the elementary process of the methoxy-methoxy exchange at the chiral sulfinyl center.

Although it was gratifying to support the original statement of Phillips concerning the steric course of the transesterification reaction of sulfinates, one should emphasize that observation of inversion in the reaction investigated as well as in many other nucleophilic substitutions at chiral sulfur does not allow us to distinguish between the S_N2—S and A–E mechanisms. The methoxy–methoxy exchange in **3** may occur via a transition state **4** or through a transient sulfurane intermediate **5**. The only conclusion, which may be drawn, is that sulfurane **5**, if formed, should undergo decomposition faster than pseudorotation. The possibility of the operation of an addition-elimination mechanism and the formation of **5** as a very unstable reaction intermediate is quite probable in view of the recent finding by Perkins and Martin[9] who have succeeded in the preparation of 10-S-4-sulfuranoxide **6**—a bicyclic analogue of **5**.



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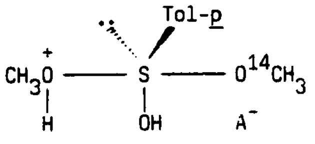

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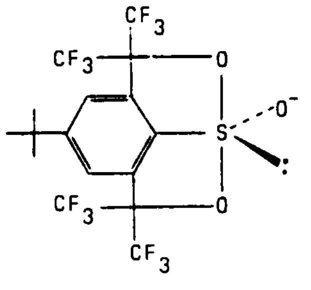
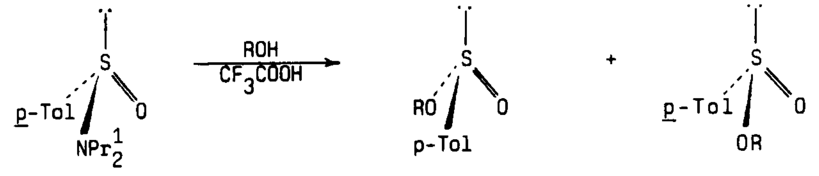


6

For the reasons given above, much more interesting are such cases of nucleophilic substitution reaction at sulfur that occur with retention of configuration. Analysis of all the examples[10] reported so far in the literature indicates that retention at sulfur was due to the formation of a four-membered ring sulfurane intermediate with an apical-equatorial arrangement of entering and leaving groups. In this context, it was interesting to find that the steric course of the reaction of chiral *N*, *N*-diisopropyl *p*-toluenesulfinamide (7) with alcohols catalyzed by trifluoracetic acid (eq. 4) varies from inversion to predominant retention of configuration depending on various factors such as: the structure of the alcohol used, the nature of solvent and the presence of inorganic salts added to the reaction medium.[11]



(4)

(+)-(S)-7 (−)-(S)-8 (+)-(R)-8

The inversion to retention ratios observed in the reaction of (+)-(S)-7 with various alcohols are summarized in Table I. In contrast to the acid-catalyzed alcoholysis of *N*, *N*-diethyl *p*-toluenesulfinamide (9) reported earlier,[11] the reaction of (+)-(S)-7 with primary alcohols was not fully stereospecific and occurred with predominant inversion. Moreover, in the case of isopropyl alcohol and its hexadeutero and hexafluoro analogues, cyclohexanol and cyclopentanol *predominant retention was unexpectedly observed.* These results indicate that steric factors in the attacking alcohol and departing dialkylamino group exert an important influence on the steric course of acid-catalyzed alcoholysis of sulfinamides.

It was also found that the presence of silver perchlorate induces a considerable change in the inversion to retention ratio. Generally, the added silver salt favors the formation of the inversion product (see eq. 5). The most interesting result is that

TABLE I

Acid-catalyzed alcoholysis of (+)-(S)-*N*, *N*-diisopropyl *p*-toluenesulfinamide (7)

Alcohol	Sulfinate (**8**)	% Inversion	% Retention
MeOH	**8a**	69	31
EtOH	**8b**	54	46
n-PrOH	**8c**	58	42
i-PrOH	**8d**	41	59
i-PrOH-d_6	**8e**	45	55
i-PrOH—F_6	**8f**	48	52
c-HexOH	**8g**	26	74
c-PentOH	**8h**	48	52
Pentanol-3	**8i**	52.5	47.5
i-BuOH	**8j**	51.5	48.5

predominant inversion was observed with isopropyl alcohol and cyclohexanol which reacted with predominant retention in the absence of this salt.

$$(+)\text{-}(S)\text{-}\mathbf{7}\ \xrightarrow[\text{CF}_3\text{COOH+AgClO}_4]{\text{ROH}}\ (-)\text{-}(S)\text{-}\mathbf{8}\ +\ (+)\text{-}(R)\text{-}\mathbf{8} \tag{5}$$

	Inv/Ret Ratio
R = Me	100/0
Et	91/9
n-Pr	100/0
i-Pr	82/8
c-Hex	65.5/34.5

The effect of silver perchlorate on the steric course of acid-catalyzed alcoholysis of chiral **7** prompted us[12] to investigate more closely the stereochemistry of trifluoroacetic acid-catalyzed reaction of (+)-(S)-**7** with isopropyl alcohol in the presence of other inorganic salts (eq. 6). The results of this set of experiments are summarized below.

$$(+)\text{-}(S)\text{-}\mathbf{7}\ +\ \underline{\text{i}}\text{-PrOH}\ \xrightarrow{\text{CF}_3\text{COOH + KA}}\ (-)\text{-}(S)\text{-}\mathbf{8d}\ +\ (+)\text{-}(R)\text{-}\mathbf{8d} \tag{6}$$

KA	Prevailing stereochemistry	KA	Prevailing stereochemistry
$CoCl_2$	55% Ret.	$Co(NO_3)_3$	73% Inv.
NiC_2O_4	71% Ret.	$Ni(NO_3)_2$	66% Inv.
Ag_2CO_3	65% Ret.	$AgClO_4$	82% Inv.
$Ag_2Cr_2O_7$	67% Ret.	$AgNO_3$	53% Inv.
Ag_2SO_4	63% Ret.	$Ce(NO_3)_3$	71% Inv.
$HgBr_2$	69% Ret.	$CrCl_3$	50.5% Inv.
$Cd(OAc)_2$	68% Ret.		

An inspection of these results clearly shows, firstly, that the added inorganic salts may dramatically change the overall stereochemistry of the investigated reaction and, secondly, that both the cation and anion play an important role in this regard.

Finally, the steric course of the reaction under discussion was found to be slightly solvent dependent. The results of *i*-PrOH reaction of (+)-(S)-**7** in various solvents are shown in eq. 7. Although the range of the solvents tested was rather narrow these preliminary results may suggest that the S—N-bond cleavage with retention of configuration will be favored in polar solvents.

$$(+)\text{-}(S)\text{-}\mathbf{7}\ +\ \underline{\text{i}}\text{-PrOH}\ \xrightarrow[\text{solvent}]{\text{CF}_3\text{COOH}}\ (-)\text{-}(S)\text{-}\mathbf{8d}\ +\ (+)\text{-}(R)\text{-}\mathbf{8d} \tag{7}$$

	Inv/Ret Ratio
Solv. = $CHCl_3$	55/45
C_6H_6	56/44
n-C_6H_{12}	58/42
CH_3CN	49/51

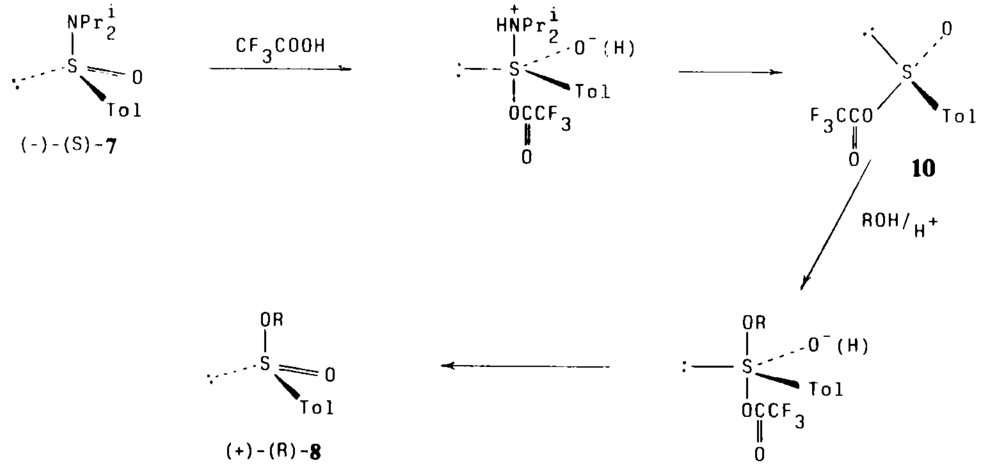


FIGURE 4 A possible two-step mechanism of alcoholysis of (−)-(S)-7 catalyzed by trifluoroacetic acid.

Before discussing the reaction mechanism one has to mention three additional experimental observations. The first is that reaction of sulfinamide (+)-**7** with alcohols catalyzed by other acids (CF_3SO_3H, $HSbF_6$, $HPF_6 \cdot Et_2O$, and $PhSO_3H$) occurred with full or predominant inversion of configuration resembling the results obtained with sulfinamide (+)-**9**. Secondly, sulfinamide (+)-**7** containing two bulky isopropyl groups at nitrogen, in contrast to (+)-**9**, we found to be optically stable under the reaction conditions. Thirdly, kinetic measurements[11] showed that acid-catalyzed alcoholysis of **7** is a typical bimolecular substitution at sulfur as evidenced by its activation parameters: $E_a = 79.7$ kJ/mol (16.3 kcal/mol), $\Delta S^{\ddagger} = -21.6$ e.u.

The special role of trifluoroacetic acid as a catalyst favoring the retention stereochemistry could suggest that the reaction investigated is not simple substitution at sulfur in **7** but it may proceed as a two-step reaction involving the formation of the mixed anhydride **10**. Since the formation of **10** as well as its subsequent alcoholysis should be accompanied by inversion of configuration, sulfinate **8** should be formed with retention of configuration as shown in Figure 4.

In order to support or rule out such a mechanistic possibility, the rate constant and steric course of acid-catalyzed *i*PrOH reaction of (+)-(S)-**7** were determined[12] at various concentrations of the added sodium trifluoroacetate (eq. 8). It was reasoned that the presence of trifluoroacetate anion should facilitate the formation of **10** thus increasing the percentage of retention.

$$(+)\text{-}(S)\text{-}\mathbf{7} + \underline{i}\text{-PrOH} \xrightarrow[CF_3COONa]{CF_3COOH} (-)\text{-}(S)\text{-}\mathbf{8d} + (+)\text{-}(R)\text{-}\mathbf{8d} \tag{8}$$

Concentration of CF_3COONa	Rate constant	Prevailing stereochemistry
0 mol	$k = (2.73 \pm 0.26)\,10^{-4}\ s^{-1}$	58% Retention
16 mol	$k = (3.29 \pm 0.06)\,10^{-4}\ s^{-1}$	58% Inversion
32 mol	$k = (3.56 \pm 0.18)\,10^{-4}\ s^{-1}$	59% Inversion

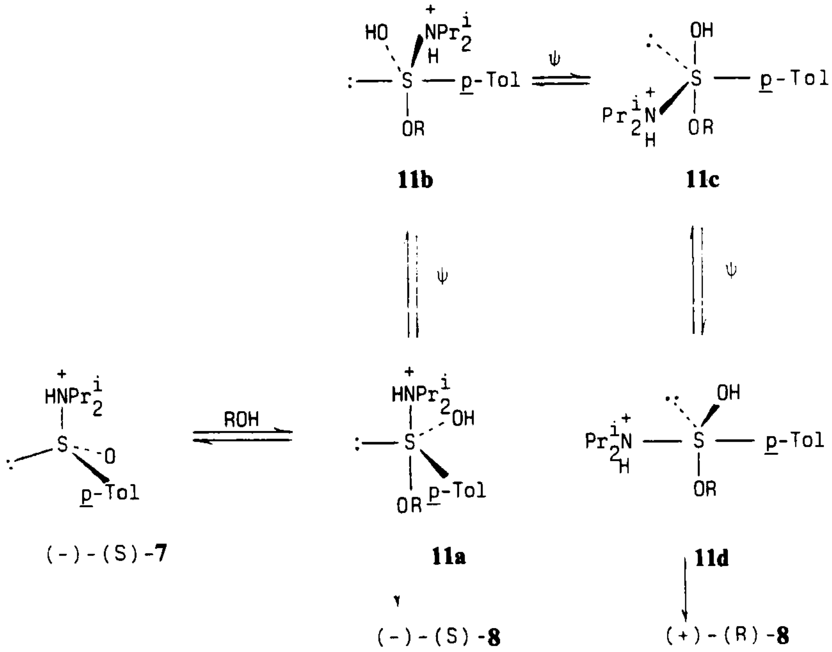
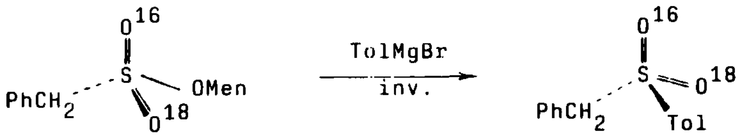


FIGURE 5 An A-E mechanism for acid-catalyzed alcoholysis of (−)-(S)-7.

As it is seen, the results obtained are not consistent with the proposal that **10** participates in the reaction mechanism. Therefore, the diverse stereochemistry of our reaction is most probably due to a competition between the inversion and retention processes. Such a situation may be best explained in terms of an addition-elimination mechanism involving a sulfurane intermediate that is able to undergo pseudorotation. Thus, the apical attack of an alcohol on the *N*-protonated sulfinamide (+)-(S)-**7** leads to the first sulfurane intermediate **11a**.[13] Its decomposition should afford (−)-(S)-**8** with inversion of configuration. After three consecutive pseudorotations of **11a** a new sulfurane **11d** may be formed which should decompose to (+)-(R)-**8** e.g. the product with retention of configuration (see Figure 5).

An alternative explanation, which may be put forward, consists in the parallel formation of the two sulfurane intermediates **11a** and **11c** which are responsible for inversion and retention, respectively. The relative stability and concentration of these sulfuranes will determine the ratio between (−)-(S)-**8** and (+)-(R)-**8**. In this context, it is interesting to point out that a high sensitivity of the steric course of the reaction to external factors such as the structure of an alcohol, the nature of acidic catalyst and solvent and the presence of inorganic salts strongly suggests that the energy difference between **11a** and **11c** may be very small.

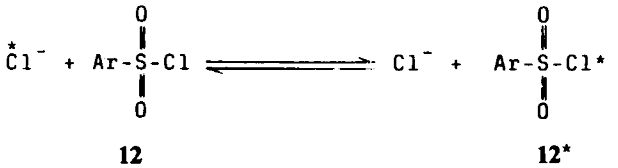
The question whether nucleophilic displacement reaction occurs synchronously or stepwise via a pentacoordinate sulfurane intermediate holds good in the case of sulfonyl compounds.[4] Generally, nucleophilic substitution at sulfonyl center has been shown to occur with inversion of configuration. Perhaps the most elegant evidence for inversion of configuration is that published by Sabol and Andersen[14] who have demonstrated that menthyl ester of phenylmethanesulfonic acid, chiral at sulfur by virtue of $^{16}O, ^{18}O$-isotopic substitution, gave on treatment with tolylmagnesium bromide chiral $[^{16}O, ^{18}O]$-benzyl tolyl sulfone with inverted configuration (eq. 9).



(9)

The inversion stereochemistry and the lack of ^{18}O-exchange during the hydrolysis of phenylbenzenesulfonate[15] were taken earlier as evidence supporting a synchronous mechanism for nucleophilic substitution at sulfonyl center. However, we know at present that the results of stereochemical as well as of ^{18}O-tracer studies are not satisfactory to exclude the formation of sulfurane intermediate in a two-step process.

One of the most important aspects of nucleophilic substitutions at sulfonyl center is kinetic sensitivity of such reactions to the nature of substituents bonded to the reactive center. The results of recent studies on the structure-reactivity relationship, mostly relative to hydrolysis, are not so unequivocal as in organic carbon chemistry. Both strong and weak substituents effects were observed. With the aim of obtaining new kinetic data on the mechanism of nucleophilic substitution at sulfonyl center we decided[16] to investigate the chlorine isotopic exchange reaction in benzenesulfonyl chlorides **12** (eq. 10).



$$\overset{*}{Cl}^- + Ar-\overset{O}{\underset{O}{S}}-Cl \rightleftharpoons Cl^- + Ar-\overset{O}{\underset{O}{S}}-Cl^* \qquad (10)$$

12 **12***

$Cl^* = NH_4Cl^{36}$

This reaction offers at least two advantages in comparison with solvolytic reactions of the same compounds. Firstly, it could be carried out in an aprotic medium such as acetonitrile, where no side and catalytic reactions occur, and, secondly, the relative role of bond making and bond breaking in the transition state (or intermediate) is eliminated due to the chemical identity of the product and substrate.

In the first set of experiments the kinetic effect of 11 *para*-substituents in a wide range of σ constants (-0.600 to $+0.430$) has been studied. The results obtained (Figure 6) showed that the fast isotopic exchange reaction between the *para*-substituted benzenesulfonyl chlorides **12** and ^{36}Cl-tetraethylammonium chloride in acetonitrile solution fits the correlational Hammett equation at 25°C ($r = 0.993$). The ρ-value obtained is equal to 2.09 ± 0.05.

It has been widely accepted that the positive ρ-values confirm the S_N2-mechanism and the high values of the reaction constant indicate that a reduction center is very sensitive to the substituent electronic effects[17]. Since the ρ-value for the isotopic

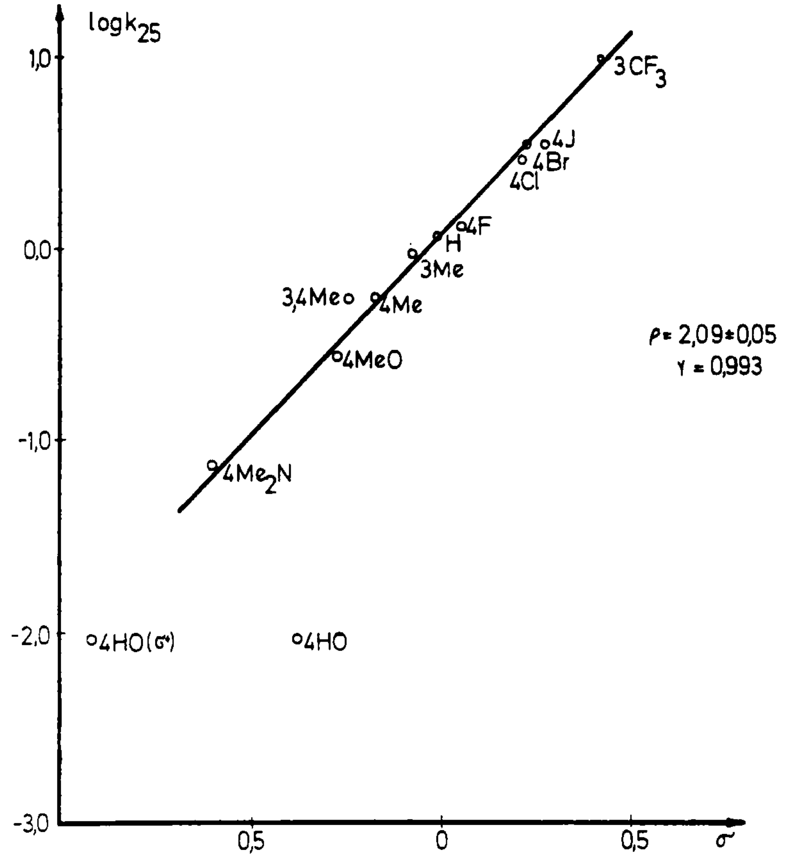
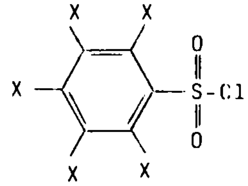


FIGURE 6 Dependence of the rate constant k_{25} upon the substituent constant in the isotopic chloride-chloride exchange in para-substituted sulfonyl chlorides **12**.

chloride-chloride exchange in sulfonyl chlorides **12** is highly positive, manifesting a great charge development on going from the reactants to a rate-determining step, one can conclude that it is indicative of a highly advanced bond making process, what may lead to the formation of a metastable intermediate, rather than a synchronous process of bond making and bond breaking in a transition state.

In the second set of experiments the effect of alkyl substituents in the benzene ring of **12** on the rate of isotopic chloride-chloride exchange was investigated. The experimentally determined reactivity order is shown below.

As it is seen, the most reactive are 2,4,6-trisubstituted benzenesulfonyl chlorides. More reactive than unsubstituted benzenesulfonyl chloride are also 2-ethyl-, 2-methyl- and 2,5-dimethyl-benzenesulfonyl chlorides. As the methyl group should retard the isotopic exchange due to the inductive effect, it is not surprising that 3-methyl-, 4-methyl-, 3,4-dimethyl- and 2,3,4,5,6-pentamethylsulfonyl chlorides are less reactive than the unsubstituted one. Generally, the results obtained point to a noticeably accelerating effect of an ortho-alkyl group. This is in a sharp contrast to the nucleophilic substitution reactions at a carbonyl center[18] where ortho-substituents in the benzene ring show a strong retarding effect.



$2,4,6\text{-Me} > 2,4,6\text{-Pr}^{i} \sim 2,4,6\text{-Et} > 2\text{-Et} > 2,5\text{-Me} > 2\text{-Me} > \text{H} > 2\text{-Pr}^{i} > 2,4\text{-Me} \sim 3\text{-Me}$

$2,3,4,5,6\text{-Me} > 4\text{-Me} \sim 3,4\text{-Me}$

FIGURE 7 Reactivity order of the alkyl substituted benzene-sulfonyl chlorides 12 in the isotopic chloride-chloride exchange reaction.

With regard to the nature of this special accelerating effect of ortho-alkyl substituents, it is interesting to compare the rates of isotopic chlorine exchange reaction of 2-substituted alkylbenzenesulfonyl chlorides. The reactivity order is as follows:

$$2\text{-Et} > 2\text{-Me} > 2\text{-Pr}^{i}$$

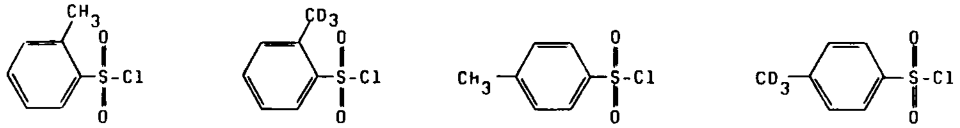
As the inductive effect decreasing the rate may be assumed to be comparable for all three substituents, it is obvious that the nature of the accelerating kinetic ortho-substituent effect in the reaction of benzenesulfonyl chlorides must be steric in origin. In our opinion this is connected with the strain relief on going from the tetrahedral sulfonyl chloride structure in the initial state to the trigonal bipyramid in the intermediate.[16]

In accord with this view are the results with 2-CD_3- and 4-CD_3-substituted benzenesulfonyl chlorides. The comparison of the kinetic data (Table II) shows that the ortho-CD_3 compound is more reactive than the para-CD_3 analogue.

More interestingly, the accelerating effect of the ortho-CH_3 group is stronger than that of the ortho-CD_3 group ($k_{o\text{-}CH_3}/k_{o\text{-}CD_3} = 1.15$). The last difference in the rate constants may be best explained on the basis of the fact that the effective size of the CD_3 group is smaller than that of the CH_3 group.[19]

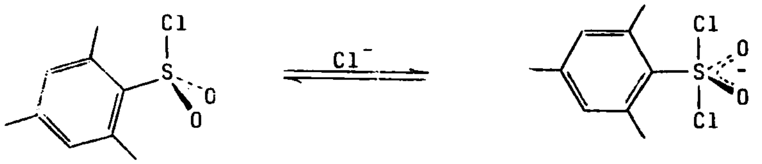
TABLE II

Comparison of rate constants and Arrhenius and Eyring activation parameters of *ortho*- and *para*-toluenosulfonyl chlorides with their deuterated analogues



Substituent	k_{CH_3}/k_{CD_3}	ΔE [kJ · mol^{-1}]	Δ(log A) [l · mol^{-1} · s^{-1}]	Δ(ΔH*) [kJ · mol^{-1}]	Δ(ΔS*) [J · mol^{-1} · s^{-1}]	Δ(ΔG*) [kJ · mol^{-1}]
2-CH_3 2-CD_3	1.15 ± 0.04	−1.7	−0.28	−1.7	5.5	−0.1
4-CH_3 4-CD_3	0.92 ± 0.04	−1.2	−0.25	−1.2	4.7	0.3

All the results obtained so far on the isotopic chloride-chloride exchange in sulfonyl chlorides **12** strongly suggest that the reaction occurs according to the addition-elimination mechanism[20] via the intermediate sulfurane **13** having a trigonal-bipyramidal structure with the attacking and leaving chlorine atoms in apical positions (eq. 11).



(11)

12 **13**

ACKNOWLEDGMENT

This work was supported by the Polish Academy of Sciences within the project MR-I-12. I am very indebted to my coworkers: Dr. J. Drabowicz, Dr. B. Bujnicki and Mss. M. Gajl for their valuable contributions to realization of this research program. Special thanks are to Dr. W. Reimschüssel from the Institute of Applied Radiochemistry of the Technical University of Lodz for his fruitful cooperation in the study on the isotopic chloride-chloride exchange in sulfonyl chlorides. I am also very grateful to Prof. Dr. R. Neidlein, Director of the Pharmaceutical-Chemical Institute of the University of Heidelberg for all the working facilities and help during my short stay as a visiting professor at the University of Heidelberg.

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