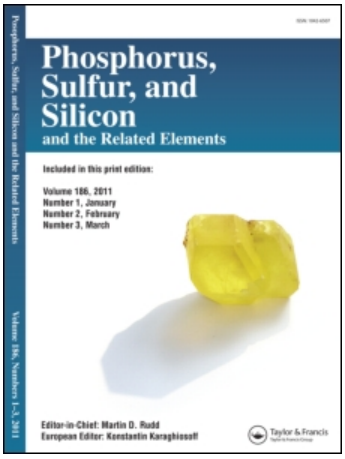

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Thio- and Oxo-Acids of Tricoordinated Sulfur: Synthetic and Stereochemical Aspects

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THIO- AND OXO-ACIDS OF TRICOORDINATED SULFUR: SYNTHETIC AND STEREOCHEMICAL ASPECTS

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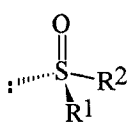
This account describes the first synthesis, characterization and reactivity of the relatively stable thiosulfinic acid salts. New approaches for the preparation of optically active sulfinic acid salts and sulfones, which are chiral due to ^{16}O, ^{18}O isotopic substitution, as well as measurement of their chirooptical properties are also presented.

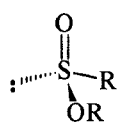
Key words: thiosulfinic acid salts, chiral $^{16}O,^{18}O$-sulfinic acids salts, sulfinyl chlorides, optically active sulfoxides, optically active $^{16}O,^{18}O$-sulfones, optical activity, circular dichroism.

INTRODUCTION

Since the classical works of Walden[1] on stereochemistry of the nucleophilic substitution at the carbon atom in α-halogeno-substituted carboxylic acids, it has become evident that a full understanding of the mechanism of this process is not possible without the detailed knowledge of its stereochemistry. To establish the stereochemical course of a reaction it is necessary to carry out a series of experiments using the properly constructed optically active model compounds. Therefore, their preparation still constitutes the synthetic challenge of a prime importance. This is especially true in the chemistry of organic sulfur compounds because all stable organosulfur compounds with the ligand number from 2 to 6 can, in principle, be prepared in optically active form.[2,3] Among them, tricoordinated, tetravalent organosulfur derivatives represent the richest family. During the last three decades most of the studies related with the chemistry of these compounds have been concentrated on the synthesis and interconversion of optically active sulfoxides **I**, sulfinates **II**, thiosulfinates **III** and sulfinamides **IV**.[2,4]



I



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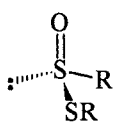

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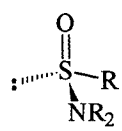
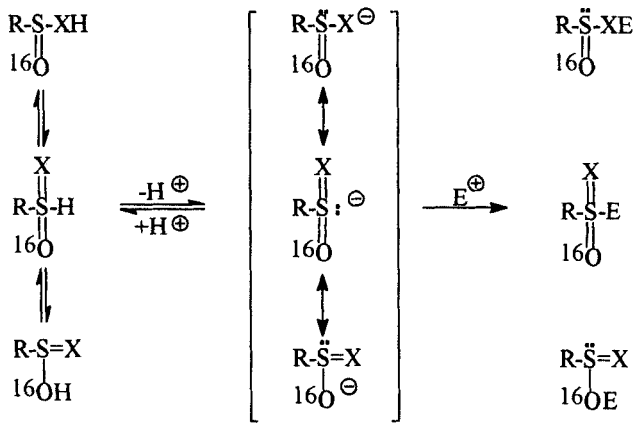


IV

All these compounds can formally be derived from the well-known sulfinic acids **V** and thiosulfinic acids **VIa** which have recently been isolated as the appropriate salts.[5] Considering the stereochemical features of both tricoordinated, tetravalent oxoacids of sulfur, **Va** and **VIa** it should be noted that the former are effectively achiral because their anions are symmetrical and therefore achiral. Replacement of one of the two oxygen atoms in sulfinic acids **V** by sulfur leads to the thiosulfinic acids **VIa** - a new class of chiral organosulfur compounds.

The sulfinic acids themselves become chiral when two different isotopes of oxygen are simultaneously bonded to the sulfur atom as in the sulfinic acids **VIIa** containng ^{16}O and ^{18}O oxygen atoms.

It is obvious that both the chiral thiosulfinate anions **VIb** and sulfinate anions **VIIb** can be described by three mesomeric forms. Therefore, their protonation could lead to three tautomeric forms of the acids **VIa** and **VIIa** and the reaction with an electrophile E^+ could result in the formation of three isomeric products **VIc** and **VIIc** (Scheme 1).



V, VIa or **VII a** **V, VIb, VIIb** **VIc, VIIc**

V,: X=^{16}O; **VI**; X=S; **VII**; X=^{18}O

Scheme 1

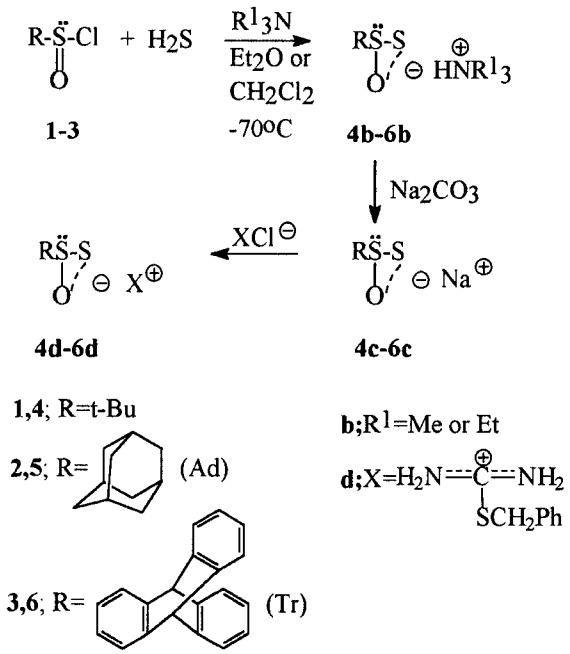
In this paper three main topics will be discussed: (a) the first synthesis and characterization of the relatively stable salts of thiosulfinic acids **VIa**, (b) reactivity of thiosulfinic acid anions **VIb**, (c) new approaches to the synthesis of chiral $^{16}O,^{18}O$-sulfinic acid salts **VIIc** and some of their derivatives. Measurements of their chirooptical properties will also be briefly discussed.

SYNTHESIS AND CHARACTERIZATION OF THE THIOSULFINIC ACIDS SALTS

Among a few possible approaches for the preparation of thiosulfinic acids, the

reaction of sulfinyl chlorides with hydrogen sulfide in the presence of tertiary amines can be considered as a simplest one. Its synthetic advantage results mainly from easy availability of a variety of sulfinyl chlorides. They can be prepared either by the oxidative chlorination of thiols or disulfides, according to the recently reported[6] improvment of the Schank modification[7] of the standard Douglas's procedure,[8] or by the reaction of the parent sulfinic acids with thionyl chloride.[9,10] Taking into account the well-known fact that the chemical stability of many unstable organosulfur species increases considerably when the sterically demanding substituents constitute the basic element of a considered structure, we decided to use in our studies t-butanesulfinyl chloride **1**, adamantanesulfinyl chloride **2** and triptycenesulfinyl chloride **3** showing such a property.

Reactions of the sulfinyl chlorides **1-3** with hydrogen sulfide in the presence of a tertiary amine (trimethyl- or triethylamine) at -70°C in ether or dichloromethane gave in high yields (75-87%) the corresponding trialkylammonium salts of the thiosulfinic acids **4b**, **5b, 6b**. These salts have been found to be relatively unstable. Therefore, in order to increase their stability and for the ease of characterization they were converted first into sodium **4c-6c** and then into S-benzylthiuronium **4d-6d** salts. The sodium salts **4c-6c** were formed almost quantitatively upon treatment of an aqueous solution of the crude ammonium salts **4b-6b** with sodium carbonate. In turn, from aqueous solutions of the sodium salts **4c-6c** the corresponding S-benzylthiuronium salts **4-6d** were precipitated in ca. 70% yields after addition of equimolar amounts of S-benzylthiuronium hydrochloride (Scheme 2).



Scheme 2

Taking advantage of the fact that the sulfenic acid **7a** is stable,[11] we were able

to convert it, upon treatment with elemental sulfur in the presence of triethylamine or sodium methoxide, to the corresponding salts **6b** or **6c** (equation 1). This reaction resembles the well-known addition of elemental sulfur to dialkyl phosphites to form monothiophosphates.[12]

$$\mathbf{6c} \xleftarrow[78\%]{MeONa/1/8S_8} \underset{\mathbf{7a}}{TrSOH} \xrightarrow[88\%]{Et_3N,\ 1/8S_8} \mathbf{6b} \quad (R^1{=}Et) \quad (eq.1)$$

We were not able to isolate analytically pure salts of the thioacids **4a-6a** because of their slow decomposition. However, their ^1H and ^{13}C spectral properties compared with those for the salts of other known oxoacids of tri- and tetracoordinated sulfur (the trimethylammonium salts of t-butanesulfinic acid **8a**, t-butanesulfonic acid **8b**, t-butanethiosulfonic acid **8c** and the sodium salts of triptycenesulfinic acid **9a**, triptycenesulfonic acid **9b** and triptycenethiosulfinic acid **9c**) unequivocally showed that in the reaction of the sulfinyl chlorides **1-3** with hydrogen sulfide the corresponding thiosulfinic acids **4a-6a** are formed as single reaction products. (Table 1 and 2).

Table 1. Selected ^1H and ^{13}C-NMR data for the trimethylammonium salts of t-butane-oxoacids of sulfur.

Salt		^1H-NMR [ppm][b]		^{13}C-NMR [ppm][b]		
No	Structure[a]	$(CH_3)_3C$	$(CH_3)_3NH$	$(\underline{CH_3})_3C$	$(CH_3)_3\underline{C}$	$(CH_3)_3NH$
4a	$RS(O)S^-$	1.30	2.96	22.70	52.70	43.20
8a	RSO_2^-	1.15	2.97	19.49	52.36	43.14
8b	RSO_3^-	1.29	2.64	23.39	56.60	43.50
8c	RSO_2S^-	1.41	3.08	25.30	57.65	45.00

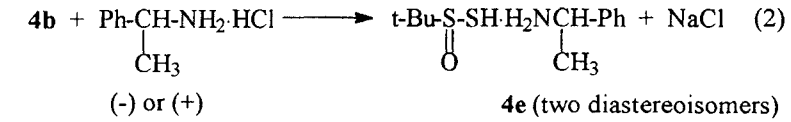
[a] only a single mesomeric structure is given
[b] measured with TMS as an internal standard.

Table 2. Selected ^1H and ^{13}C-NMR data for the sodium salts of triptycene-oxoacids of sulfur.

Salt		^1H-NMR [ppm][b]	^{13}C-NMR [ppm][b]	
No	Structure[a]	H_{10}	C_9	C_{10}
6c	$TrS(O)S^-$	5.61	75.56	54.64
9a	$TrSO_2^-$	5.62	83.23	55.64
9b	$TrSO_3^-$	5.66	75.80	55.65
9c	$TrSO_2S^-$	5.62	72.37	55.26

[a,b] see footnotes in Table 1.

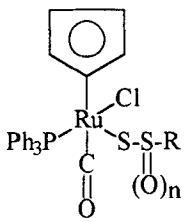
A simple proof of a chiral structure of the thiosulfinic acids **4a-6a** was provided by the ^{1}H-NMR spectrum of the salt of t-butanethiosulfinic acid with (-)- or (+)-α-methylbenzylamine (salt **4e**, equation 2).



(2)

In the ^{1}H-NMR spectrum of this salt, recorded in a chloroform-*d* solution, two singlets at 0.985 and 1.020 ppm, were observed. These absorptions of equal intensity can unequivocally be ascribed to the protons of the t-butyl group. Their occurrence shows that the salt investigated is a mixture of two diastereoisomeric salts thus demonstrating chirality of the thiosulfinic acid anion.

In this context, it is of interest to note that the chirality of a few thiosulfinic acid anions has also been supported[13] by the ^{1}H-NMR spectra of their ruthenium complexes having the general structure **10** in which the second chirality center is located on the suitable substituted ruthenium atom. Due to the diastereoisomeric nature of these complexes, the absorption due to the presence of the substituents bonded directly to the sulfinyl sulfur atom are doubled.



10 n=1,2
R=n-Pr; i-Pr; p-Tol

A final proof of the structure was provided by an X-ray structural analysis (Figure 1) of the S-benzylthiuronium salt of adamantanethiosulfinic acid **5d**. It showed a slightly distorted tetrahedral arrangement of the substituents (carbon, oxygen, sulfur and lone electron pair) around the central sulfur atom in the anion of the thioacid **5a**. The S1-O and S1-S2 distances of 1.536 and 2.025 A suggest delocalization of the negative charge in the anion.

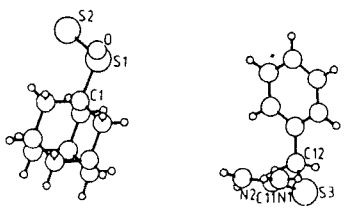
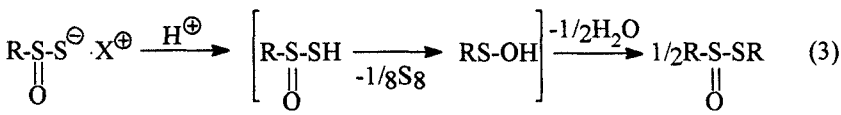


Figure 1: Molecular structure of **5d**.

REACTIVITY OF THIOSULFINIC ACIDS AND THEIR ANIONS

Stability of the salts of thiosulfinic acids **4a-6a** strongly depends on the nature of a cation and sterically demanding substituent bonded to the sulfinyl sulfur atom. Thus, the trialkylammonium salts **4b** and **5b** are stable at low temperatures in organic solvents for a few days. However, the salt **6b** undergoes a slow oxidation into the corresponding thiosulfonic acid salt **9d**. The sodium salts of t-butane- and adamantanethiosulfinic acids (**4c** and **5c**, respectively) are stable in aqueous solutions and the corresponding S-benzylthiuronium salts **4d** and **5d** could be isolated as the almost analytically pure samples. On the other hand, all attempts to isolate the thiosulfinic acids **4a-6a** showed that they undergo very rapid decomposition even at temperatures below 0°C. The salts of t-butanethiosulfinic acid **4a** and adamantanethiosulfinic acid **5a** afford upon acidification elemental sulfur and the thiosulfinates **11a** and **11b**, obviously via the sulfenic acids **7b** and **7c** as intermediates. Triptycenethiosulfinic acid **6a** gives, after elimination of sulfur, the stable triptycenesulfenic acid **7a** (equation 3).

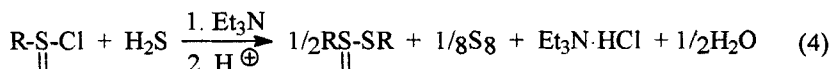


(3)

4b-d-6b-d **4a-6a** **7a-c** **11a,b**

a, R=Tr **a**, R=t-Bu
b, R=t-Bu **b**, R=Ad
c, R=Ad

The fact that the thiosulfinic acids **4a** and **5a** undergo a clean decomposition to the symmetrical thiosulfinates **11a** and **11b** constitutes a key element of a new synthesis of this type of sulfinic acid derivatives. This procedure, schematically represented by equation 4, allows the direct preparation of the thioloesters **11a-e** starting from the sulfinyl chlorides **1-2** and **12a-c**, which do not contain hydrogen on the α-carbon atom of a substituent bonded to the sulfinyl sulfur atom.

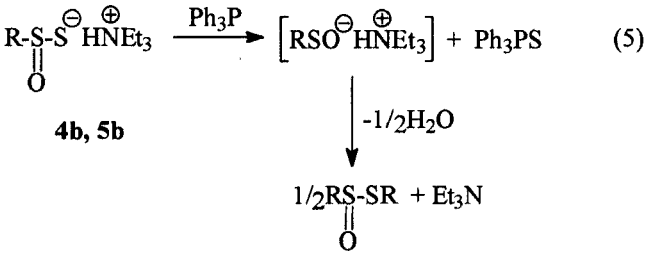


(4)

1-2 and **12a-c** **11a-e**

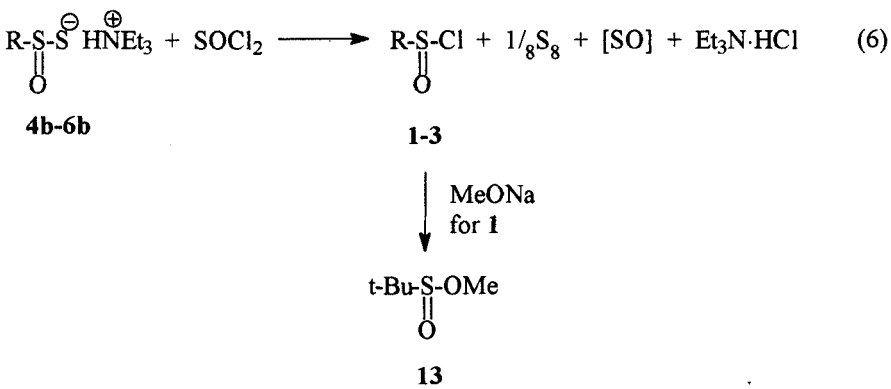
R	RS(O)Cl No	RS(O)SR No	Yield [%]
t-Bu	**1**	**11a**	100
Ad	**2**	**11b**	100
Ph	**12a**	**11c**	85.1
p-Tol	**12b**	**11d**	79.5
p-Cl-C_6H_4	**12c**	**11e**	81.3

Of interest is that the thiosulfinates **11a** and **11b** could also be isolated in almost quantitative yields when the triethylammonium salts of **4b** and **5b** were treated with triphenylphosphine as a desulfuration agent. In the case of the salt **6b** this conversion, taking place for a few hours even at -78°C, afforded the free thioacid **7a** (equation 5).



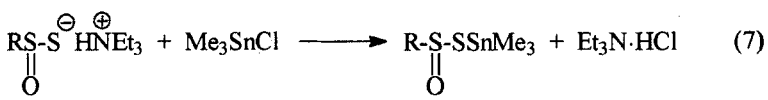
4b, 5b **11a-b** (5)

In the reaction of the ammonium salts **4b-6b** with thionyl chloride the corresponding sulfinyl chlorides **1-3** were exclusively formed. Their formation has been ascertained by the ^{1}H and ^{13}C-NMR spectral analysis of the crude reaction products as well as by the conversion of the isolated sulfinyl chloride **1** into the corresponding methyl t-butanesulfinate **13** (equation 6).



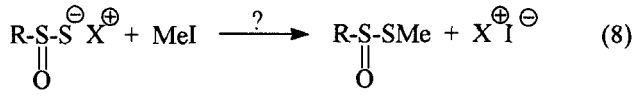
4b-6b **1-3** **13** (6)

Trimethyltin chloride **14** was found to react with the ammonium salts **4b** and **5b** to form the stannyl derivatives **15a** and **15b** in moderate yields (~50%) (equation 7). Their thiolo-structure was supported by the presence of a strong IR absorption band at 1050cm^{-1} characteristic for the S=O grouping.



4b,5b **14** **15a,b**
a R=t-Bu
b R=Ad (7)

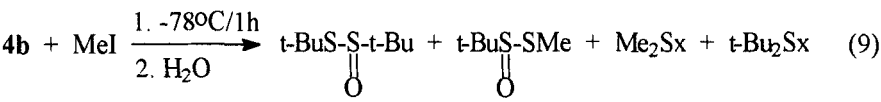
According to the HSAB concept[14] the softest nucleophilic center of the thiosulfinic acid anion should be located on the sulfenyl sulfur atom. Therefore, it can be expected that its alkylation using a soft methylation agent such as methyl iodide will result in the clean formation of the corresponding S-methyl thiosulfinates **16** (equation 8).



(8)

4b-d-6b-d **16**

However, a detailed analysis of the reaction between the triethylammonium salt **4b** and methyl iodide revealed its more complex character. The ^{1}H and ^{13}C-NMR spectra recorded for the crude reaction products showed that the reaction course and final results are strongly influenced by the reaction time and conditions. Thus, when the reaction of **4b** with equimolar amount of methyl iodide was carried out at -78°C for 1 hour and rapidly worked-up by an aqueous washing to remove the formed triethylammonium hydroiodide, the symmetrical thiosulfinate **11a** and the expected thiosulfinate **16a** were formed in a 2:1 ratio. They were accompanied by small amounts of methyl- and t-butyl polysulfides **17** and **18** (equation 9).



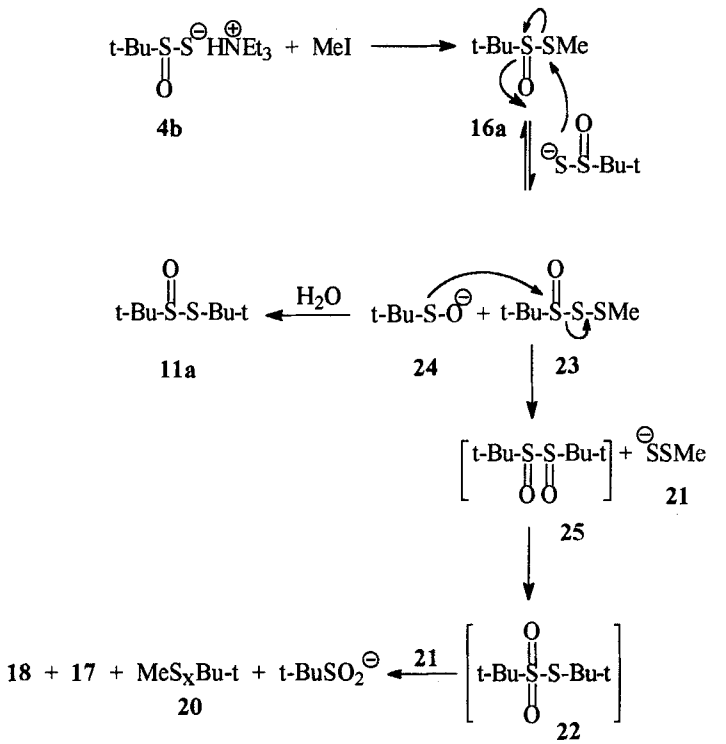
(9)

11a **16a** **17** **18**

2 1

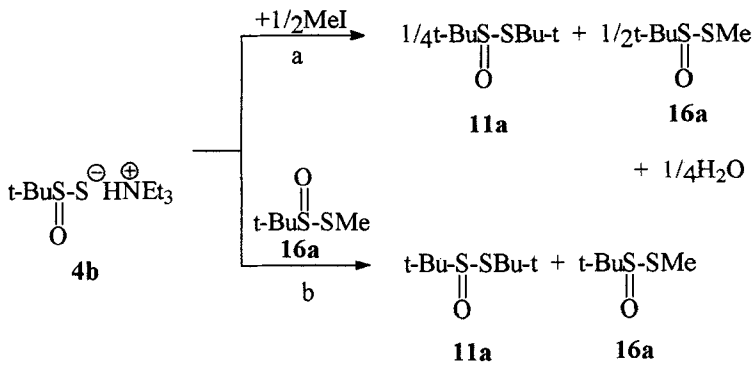
On the other hand, when the reaction mixture was allowed to stand for 24 hrs and then subjected to an aqueous work-up, the expected thioloester **16a** and symmetrical thiosulfinate **11a** were formed in a 3:1 ratio and the content of the polysulfides **17** and **18** was much higher. Moreover, the triethyl ammonium salts of t-butanesulfinic acid **8b** was also found among the minor by-products. Such a relationship clearly indicates that the seemingly simple methylation reaction is complex and involves many subsequent reactions. The proposed basic processes leading to the main reaction products are summarized in Scheme 3.

There is no doubt that the first reaction is the methylation of the sulfenyl sulfur atom in **4b** to give the expected thiosulfinate **16a**. In the next step, this thioloester reacts with the anion of **4b** to form the unsymmetrical anhydride **23** and the anion of t-butanesulfenic acid **24**. Their subsequent reaction results in the formation of the transient bis-sulfoxide **25** which collapses to the thiosulfonate **22**. Simultaneously in the reaction of the anion **24** with water the thiosulfinate **11a** is produced.



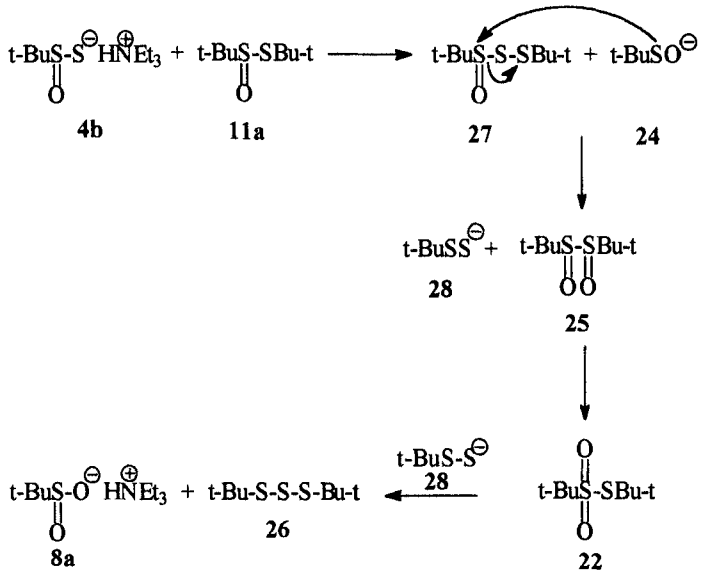
Scheme 3

This mechanistic proposal was strongly supported by additional experiment which confirmed that the thiosulfinates **16a** and **11a** are simultaneously formed either in the reaction between the salt **4b** and a half equivalent of methyl iodide (equation 10a), or by mixing this salt with the independently prepared S-methyl t-butanethiosulfinate **16a** (equation 10b).



(10)

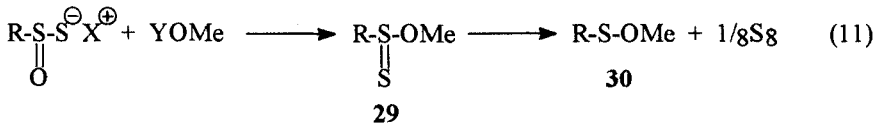
It is of interest to point out that in the reaction between the ammonium salt **4b** and the more sterically hindered S-t-butyl t-butanethiosulfinate **11a** a mixture of the trisulfide **26** and the ammonium salt of t-butanesulfinic acid **8a** was formed. The formation of these two products can be rationalized by a sequence of reactions shown below (Scheme 4).



Scheme 4

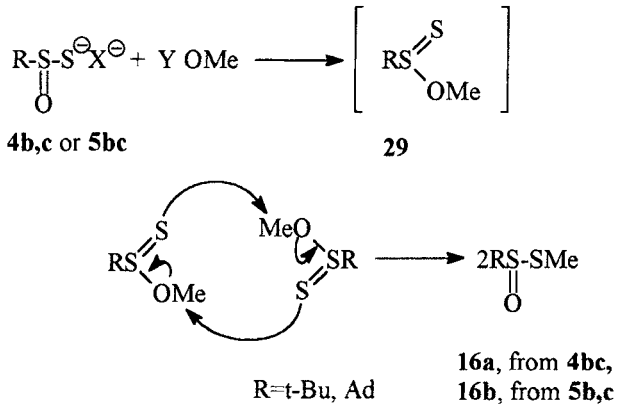
In accord with the HSAB concept,[14] the oxygen atom of a thiosulfinate anion should constitute its hardest nucleophilic center. Therefore, it was expected, especially if one takes into account the results of the alkylation of sulfinic acids anions, that hard alkylation agents such as dimethyl sulfate, O-methyl trifluoromethanesulfonate, trimethyloxonium tetrafluoroborate should react at the oxygen atom of this anion to give O-methylated products **29** (equation 11).

Furthermore, due to the presence of a weak sulfur-sulfur double bond these thionoesters should undergo an easy decomposition to the corresponding sulfenic esters **30** as the final reaction products.



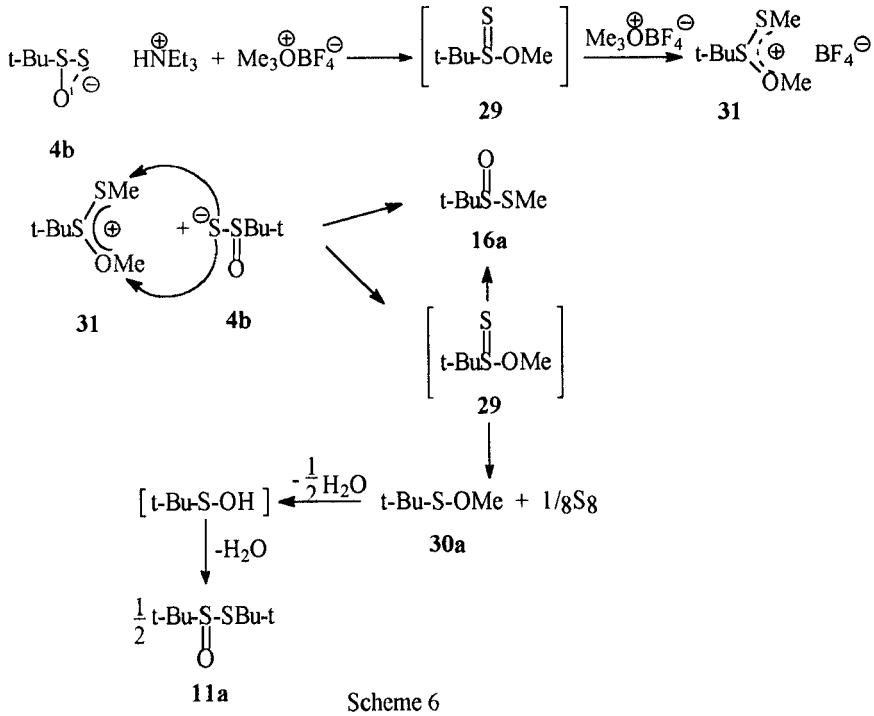
(11)

It was found, however, that methylation of the salts **4b,c** and **5b,c** with dimethyl sulfate as well as with O-methyl trifluoromethanesulfonate affords the corresponding S-methyl thiosulfinates **16a,b** as single reaction products (Scheme 5).



Scheme 5

A simple explanation of such unexpected results is to assume that the above shown methylation reaction takes place on the sulfenyl sulfur as a soft nucleophilic center of the thiosulfinate anion and is very fast in comparison with that by methyl iodide. Therefore, the considered reaction is very clean and free of by-products. The exclusive formation of the thioloesters **16a,b** can alternateively be rationalized, in keeping with the HSAB concept, by assuming that methylation of the salts **4b,c** and **5b,c** affords the expected thionoesters **29** which instantaneously undergo intermolecular isomerization to the final reaction products (Scheme 5).



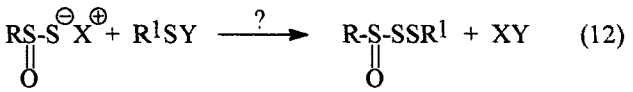
Scheme 6

Methylation of the salt **4b** by trimethyloxonium tetrafluoroborate occurs in a complex way and depending on the work-up procedure, mixtures of the thiosulfinates **11a** and **16a** or the polysulfides **17** and **18** were isolated as the main reaction products.

The thioloesters **11a** and **16a** were isolated in a 2:1 ratio when the reaction mixture was worked-up just after complete consumption of the tetrafluoroborate. Their formation can be explained by a sequence of reactions shown in Scheme 6.

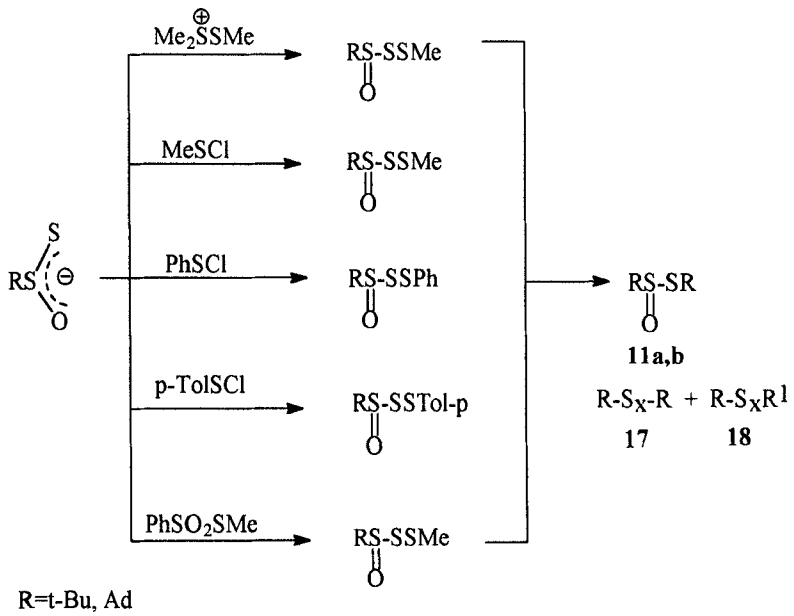
The first reaction in this sequence involves O-methylation of **4b** to give the thionoester **29**. The subsequent methylation of the thiono-sulfur in **29** leads to the sulfonium salt **31**. This salt can be demethylated by the anion **4b** to form both the thioloester **16a** and the thionoester **29**. The latter may undergo isomerization to **16a** or conversion to **11a** as shown above (in Scheme 6).

Due to the soft character of the sulfenyl sulfur atom of a thiosulfinic acid anion its reaction with sulfenyl derivatives should lead to the formation of the sulfinyl-sulfenyl thioanhydrides shown in equation 12.

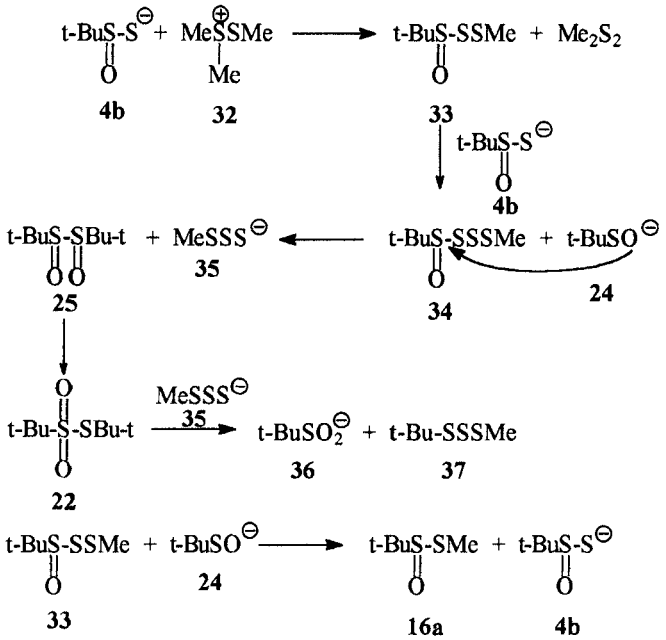


(12)

It was found, however, that all the sulfenylation reactions collected in Scheme 7 afforded mixtures of the corresponding symmetrical thiosulfinates **11a** and **11b** and the symmetrical and unsymmetrical polysulfides **17** and **18**. A sequence of reactions collected in Scheme 8 seems to be the most logical way on which the observed products of sulfenylation of the anion **4b** by S-methyl thiomethylsulfonium chloride **32** can be formed.

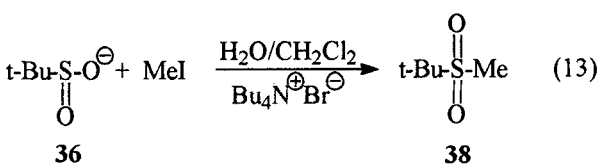


Scheme 7



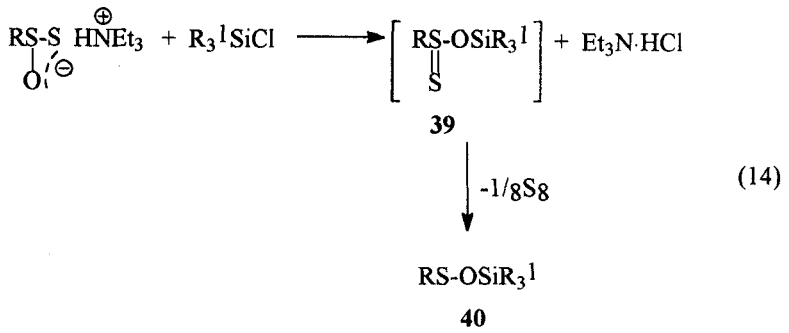
Scheme 8

The first reaction in this sequence affords the thioanhydride **33** and dimethyl disulfide. The thioanhydride **33** reacts with an excess of the anion **4b** to form the thioanhydride **34** and the t-butanesulfenic acid anion **24**. Their mutual reaction leads to the formation of the α-disulfoxide **25** and the methyltrisulfide anion **35**. The α-disulfoxide **25** rearranges instantaneously to the thiosulfonate **22** which reacts further with the anion **35** to form the anion **36** and the polysulfide **37**. The formation of the sulfinic acid anion **36** was proved by its conversion into methyl t-butyl sulfone **38** upon the two-phase methylation with methyl iodide (equation 13).



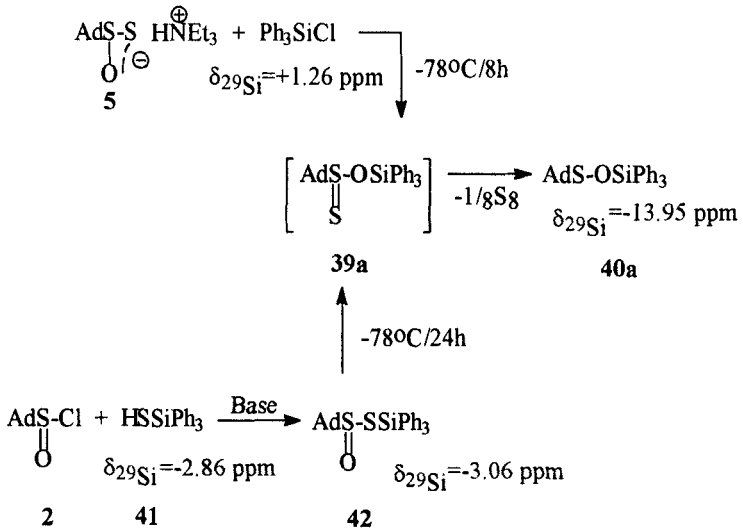
(13)

Taking into account the above discussed results of the alkylation and sulfenylation reactions of the thiosulfinic acid anion, one could expect that its silylation will lead to the formation of the corresponding O-silylated products **39**. Due to the presence of the unstable double sulfur-sulfur bond the letter should eliminate sulfur and give the corresponding O-silylated sulfenic acids **40** (equation 14).



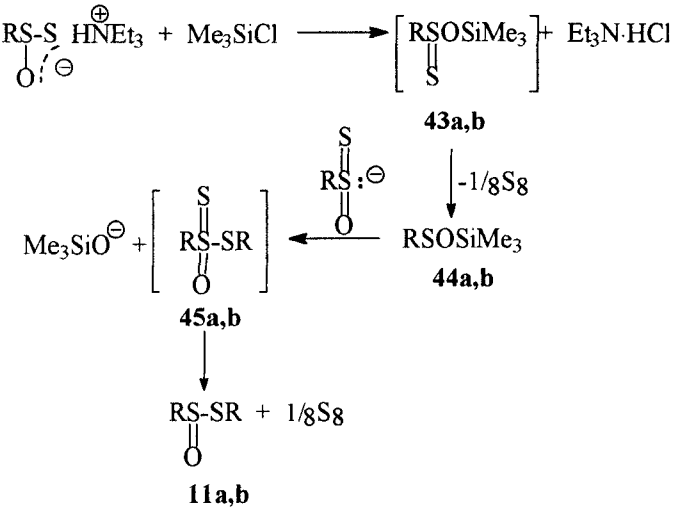
(14)

The use of chlorotriphenylsilane for silylation of the salt **5b** and following the reaction course by the ^{29}Si-NMR technique allowed an easy identification of the products formed. Independently, condensation of adamantanesulfinyl chloride **2** with triphenylsilanethiol was carried out. The results of both reactions are schematically presented in Scheme 10. An inspection of the above data clearly indicates that the silylation of the anion **5b** takes place on the oxygen atom to give the O-silylated product **39a** which rearranges immediately to the stable O-silylated sulfenyl ester **40a**.



Scheme 9

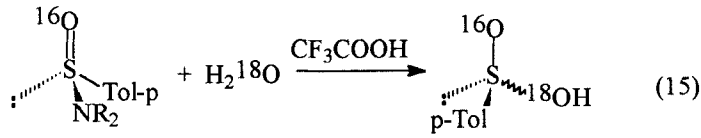
When chlorotrimethylsilane was used as a silylation agent, the considered reaction afforded only the symmetrical thiosulfinates **11a,b** and elemental sulfur. No traces of the expected silylated products were detected by the ^{29}Si-NMR technique. Most probably, the reaction occurs as shown in Scheme 10.



Scheme 10

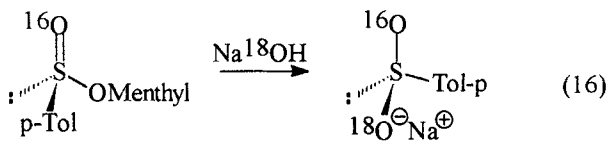
NEW SYNTHESES OF CHIRAL $^{16}O,^{18}O$ SULFINIC ACID SALTS

In our first experiments we attempted to synthesize chiral p-toluenesulfinic acid **47a** containing ^{16}O and ^{18}O oxygen atoms by the trifluoroacetic acid-catalyzed hydrolysis of the optically active p-toluenesulfinamides **46** using $H_2{}^{18}O$ as a source of the oxygen ^{18}O (equation 15).[15] We observed, however, that under the acidic reaction conditions the newly formed chiral sulfinic acid **47a** exchanged very rapidly the oxygen atoms what led to its instantaneous racemization.



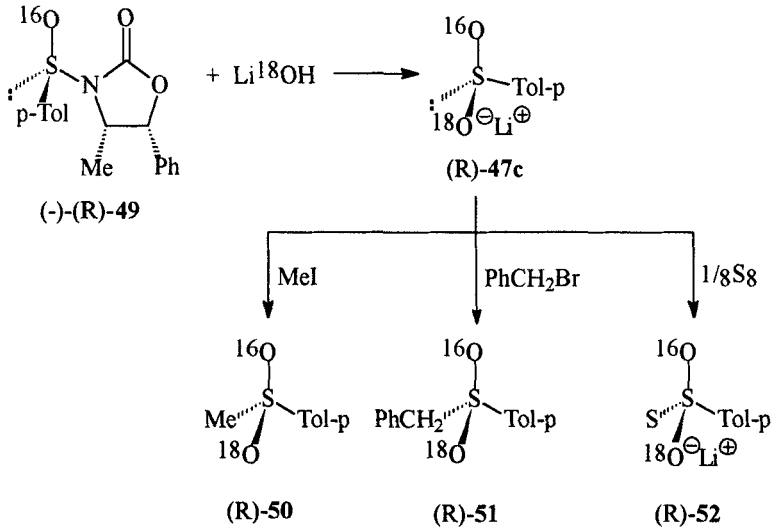
(+)-(S)-**46** (±)-**47a** (15)

Some time later, we were kindly informed by Professor K.K.Andersen[16] on his successful preparation of the sodium salt of this acid **47b** by the base-catalyzed hydrolysis of (-)-(S)-O-menthyl p-toluenesulfinate **48** with ^{18}O-labeled sodium hydroxide (equation 16).



(-)-(S)-**48** (R)-**47b** (16)

Our successful approach for the preparation of the lithium salt **47c** of this chiral sulfinic acid was based on the reaction between the diastereoisomerically pure sulfinamide **49**,[17] and lithium hydroxide $Li^{18}OH$. Because we were not able to determine the ^{18}O-content in the salt **47c**, it was converted into the chiral sulfones **50** and **51** by the two-phase alkylation with methyl iodide and benzyl bromide, respectively. The lithium salt of thiosulfonic acid **52** was also isolated upon addition of elemental sulfur to the salt **47c** (Scheme 11).

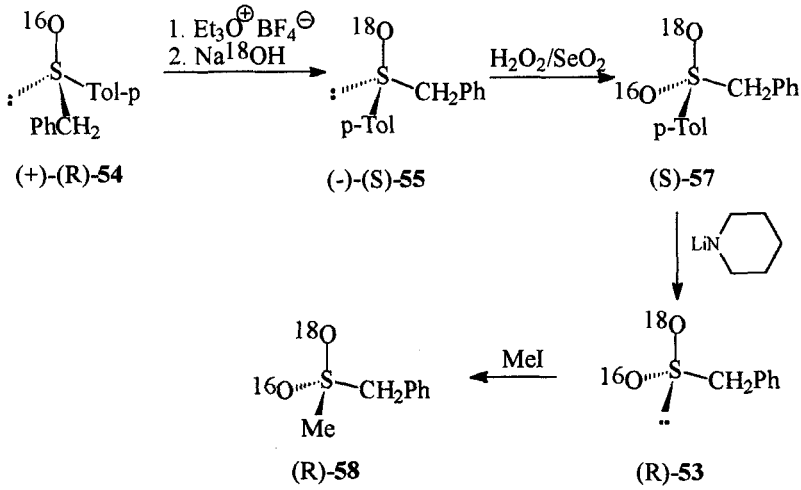


Scheme 11

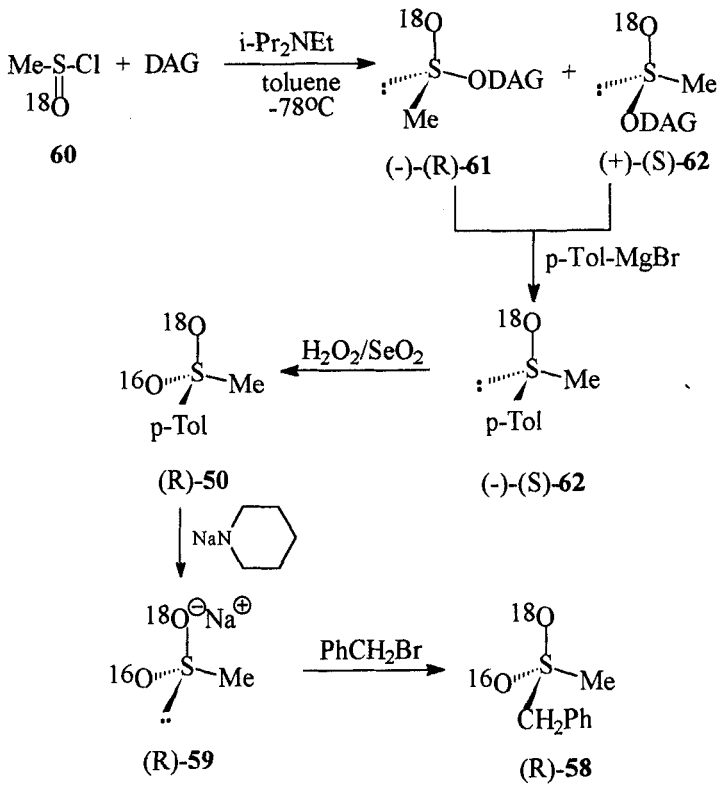
The second method, outlined in Scheme 12, allowed the synthesis of the chiral sodium salt of ^{16}O, ^{18}O-phenylmethanesulfinic acid **53**. The synthesis started from optically pure benzyl p-tolyl sulfoxide **54**,[18] which was converted into the corresponding ^{18}O-analogue **55** via alkylation with triethyloxonium[19] tetrafluoroborate followed by hydrolysis of the initially formed sulfonium salt **56** with sodium hydroxide $Na\ ^{18}OH$. The sulfoxide **55** was then oxidized to the chiral ^{16}O, ^{18}O-sulfone **57** with hydrogen peroxide/selenium dioxide system.[20] The latter upon heating with an excess of sodium amide[21] afforded the desired salt **53** which was converted into chiral ^{16}O, ^{18}O-methyl benzyl sulfone **58** by the two phase alkylation with methyl iodide (Scheme 12).

The third approach, which allowed the preparation of chiral methanesulfinic acid salt **59**, takes advantage of the use of ^{18}O-labelled methanesulfinyl chloride **60** as a substrate. This chloride has recently become easily available by the oxidative chlorination of dimethyl disulfide with sulfuryl chloride in the presence of hexamethyldisiloxane containing ^{18}O.[22] The condensation of **60** with diacetoneglucose (DAG),[23] afforded the corresponding sulfinate **61** which, without purification, was converted to optically active methyl p-tolyl sulfoxide **62** containing the oxygen ^{18}O. Oxidation of this sulfoxide with H_2O_2/SeO_2[20] system gave chiral methyl p-tolyl sulfone **50**. Heating the latter with an excess of sodium piperidine[21] afforded the expected

sodium salt **59**. For characterization purposes this salt was converted into the chiral $^{16}O,^{18}O$-methyl benzyl sulfone **58** by alkylation with benzyl bromide (Scheme 13).



Scheme 12



Scheme 13

CIRCULAR DICHROISM OF CHIRAL $^{16}O,^{18}O$-SULFINIC ACID SALTS AND SULFONES

Due to the fact that chirality of $^{16}O,^{18}O$-sulfinic acid salts and sulfones described above results from the presence of two isotopes of oxygen bonded to the same tetracoordinated sulfur atom, their optical rotations at 589-320 nm are extremely low and cannot be measured exactly. On the other hand, these compounds show interesting optical rotatory power in the region of 200-250 nm. It is obvious that the observed Cotton effects are related to the relevant electronic absorptions. The lithium salt of ^{16}O, ^{18}O-p-toluenesulfinic acid **47** exhibits in the UV region well defined maxima at 260 nm, 220 nm and 200 nm (Figure 2). All absorptions are most probably related to aromatic transitions. The band at ca 260 nm results from the B_{2u}-benzene like transition. The absorption at ca 220 nm is related to the B_{1u} transition in the aromatic ring. Among them only the absorption at 220 nm shows optical activity. The Cotton effect related to this absorption has negative sign. Similar Cotton effects, having higher amplitudes (Figure 3), can also be observed for the sulfones **50** and **51** prepared by alkylation of the salt **47c** with methyl iodide or benzyl bromide, respectively.

At present it is too early to predict if there is a clear relationship between the sign of these Cotton effects and the absolute configuration of the asymmetric center located on the isotopically substituted tetracoordinated sulfur atom. The studies on this problem are in progress in our laboratory.

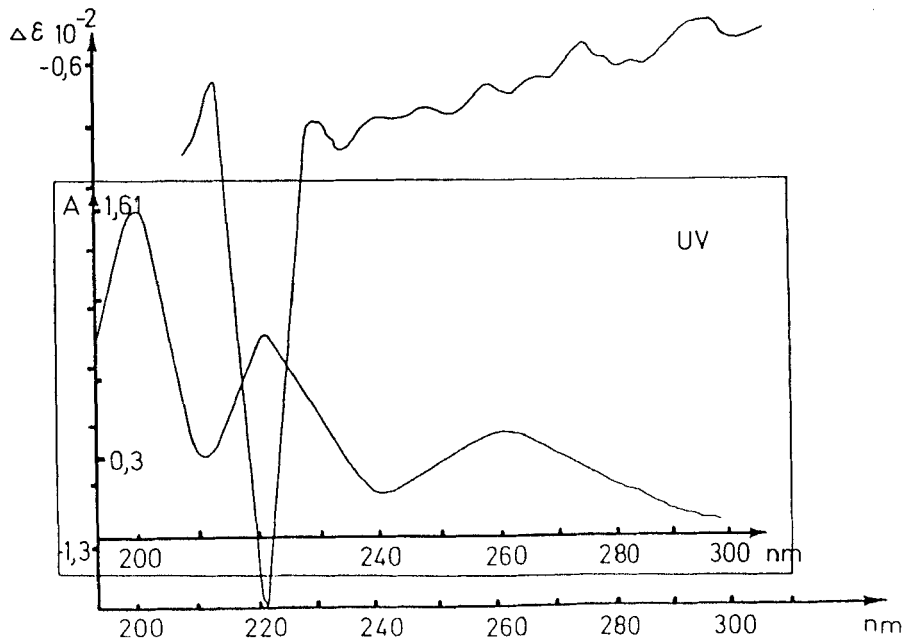


Figure 2: CD curve and ultraviolet spectrum of **47c**

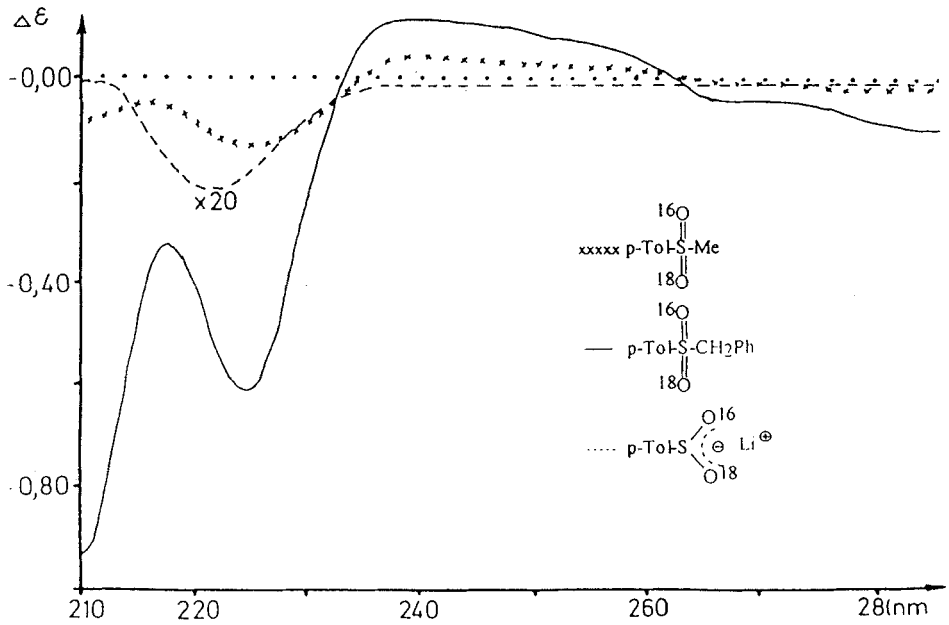


Figure 3: CD curves of **47c**, **50** and **51**.

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