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REACTIONS OF SULFENIC AND SULFOXYLIC ACID DERIVATIVES WITH OLEFINS IN THE PRESENCE OF SULFUR TRIOXIDE AND ITS COMPLEXES

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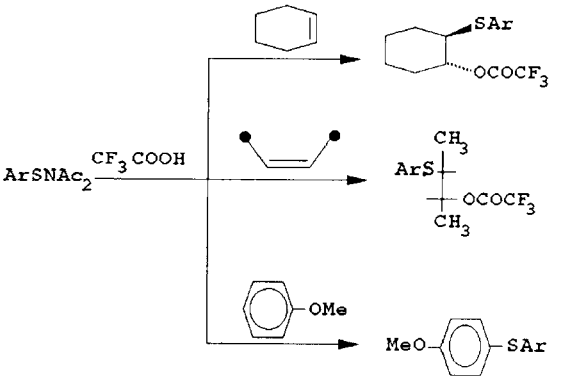
The present review deals with the application of sulfenic [RS–OH] and sulfoxylic [HO–S–OH] acid derivatives in electrophilic addition reactions. We consider a new method for generation of reactive electrophilic sulfenylating species from sulfenic/sulfoxylic acid derivatives and sulfur trioxide (or its complexes). This *autoreview* covers our results in the systematic study of SO_3-mediated addition to olefins and of sulfenylation of olefins with these novel electrophiles. The reactions of disulfides, sulfenyl chlorides, sulfenamides, alkyl sulfenates, aminosulfenyl halides and thiobisamines with a wide range of unsaturated compounds are discussed. A special chapter concerns the acid-catalyzed nucleophilic substitution of the products obtained.

Key words: alkenes, sulfenic acid derivatives, sulfenylation, sulfoxylic acid derivatives, sulfur trioxide.

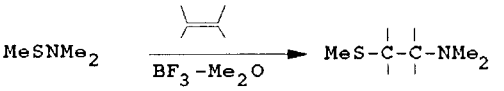
CONTENTS

1. INTRODUCTION

In recent years there has been a substantial increase in interest in derivatives of sulfenic acids. New work in this area has been connected with the application of sulfenamides in organic synthesis. In spite of the fact that amides of sulfenic acids have been known for many years[1] their use in organic synthesis has been restricted to a fairly narrow range of reactions. In particular reactions of sulfenamides with olefins were unknown until 1981 when Abramovich and Pilski reported a new method of electrophilic sulfenylation with *N,N*-diacetyl-4-nitrobenzenesulfenamide in the presence of trifluoroacetic acid.[2]



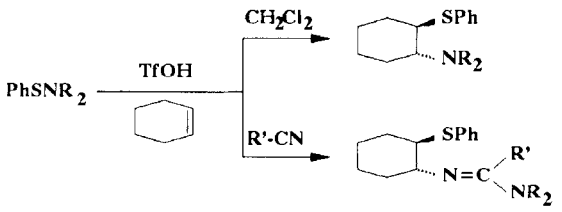
Two alternative methods were contributed by Caserio and Kim in 1982.[3] The first consists in the application of BF_3–Me_2O:



The second is activation with a trimethyloxonium salt:

The first method, namely BF_3-promoted electrophilic addition, has been developed by Benati, Spagnolo, and Montevecchi[4] who provided a detailed account of the generation of electrophilic sulfenylating species from sulfenanilides and their reactions with alkenes and alkynes in different solvents.

In 1984 Brownbridge reported successful activation of the addition of sulfenamides by triflic acid (or its trimethylsilyl ester in the presence of catalytic amounts of free acid) in dichloromethane or nucleophilic acetonitrile.[5]



Concerning the synthetic value of thiobisamines or alkyl esters of sulfenic and sulfoxylic acids, these compounds have not been sufficiently investigated to show fully their application potential in general organic synthesis. On the other hand, it should be noted that we have been developing a new strategy for the activation of weak electrophiles through their reaction with sulfur trioxide. This method consists of converting a reagent X–Y into a stronger electrophilic reagent **A** through the introduction of sulfur trioxide at the X–Y single bond:

$$X\text{–}Y + SO_3 \rightarrow \underset{\mathbf{A}}{X^{\delta+}\text{–}^{\delta-}OSO_2Y}$$

The prospects and the synthetic significance of this technique were demonstrated for the activation of such compounds as alkyl nitrites,[6] alkyl nitrates,[7] acyl fluorides[8] *N*-chloroamines,[9] alkyl hypochlorites[10] and even molecular chlorine[11] with sulfur trioxide.

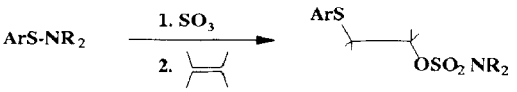
The investigation of the properties of reagents of the $X\text{–}OSO_2Y$ type indicates that they are effective sources of electrophilic particles X^+, both in aromatic substitution and in addition reactions to unsaturated systems. In most cases the reactions take place with high rates and under mild conditions.

We had been able to extend this strategy for the transformation of weak electrophilic reagents into "effective strong electrophiles" (see reference[12] for the origin of this term) to derivatives of sulfenic and sulfoxylic acids, namely, to sulfenyl amides, sulfenyl chlorides, disulfides, alkyl sulfenates, aminosulfenyl halides, and thiobisamines.

To summarize, in this Report emphasis is given to the applications of this novel strategy for the sulfonate activation of electrophilic reactivity in regard to sulfenylating agents.

2. REACTIONS OF SULFENAMIDES

As a rule, sulfenamides do not react with olefins,[13] but the addition can be carried out under strong protic or Lewis acid catalysis (*vide supra*). We have shown that sulfenamides react with SO_3 and then with some olefins to give sulfides containing a sulfamate group.[14,15]



Sulfenamides react with an equimolar amount of sulfur trioxide in dry methylene chloride at $-80\,°C$. In contrast to the results of SO_3 insertion into the Cl–X bond of *N*-chloro-

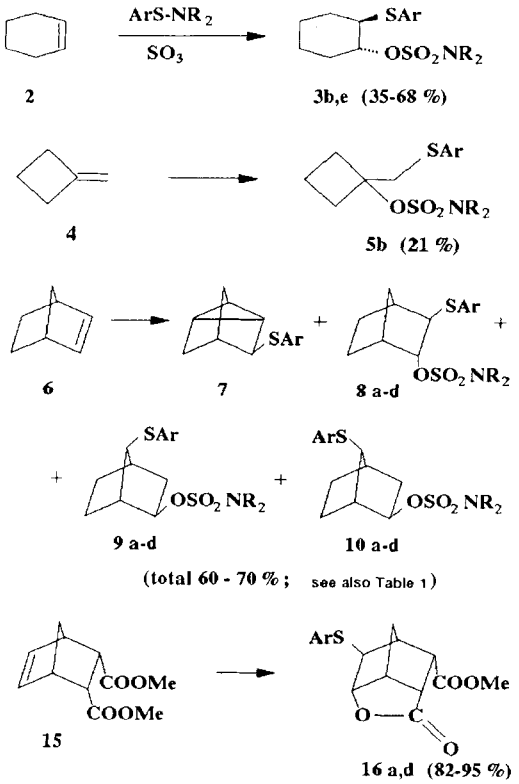
amines and of molecular chlorine (for these reactions the insertion was stringently proved by ^{35}Cl NQR spectra[16]) we failed to isolate and hence to characterize the extremely unstable products of SO_3 insertion into the S–X bond. Therefore the structure of the electrophilic sulfenylating reagent (in the sense of a choice between structure **B** and **C**) was not established. (It is worth noting that the Lewis-type adduct **B** is, in principle, also an electrophilic sulfenylating reagent).

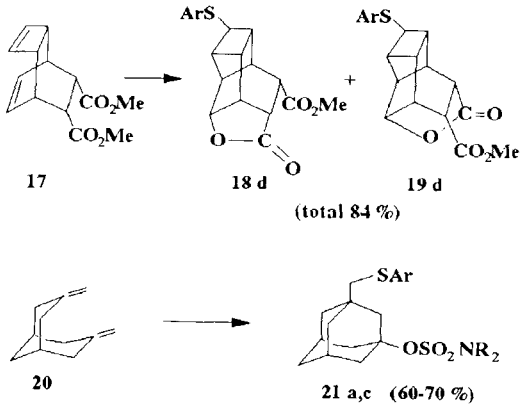
$$ArS\text{-}NR_2 + SO_3 \rightleftharpoons \underset{\underset{\underline{B}}{SO_3^-}}{[ArS\text{-}\overset{+}{N}R_2}} \rightleftharpoons \underset{\underline{C}}{ArS\text{-}OSO_2NR_2]}$$

Our belief that insertion of SO_3 takes place is based on (i) an analysis of the structure and the composition of the addition products and (ii) NQR data for the essentially analogous reactions of R_2NCl and Cl_2.

Reactions of **C** with olefins were carried out at about $-85\,°C$. Then the reaction mixture was allowed to warm to room temperature. The subsequent work-up included removal of the solvent and purification by column chromatography.

ArS-NR$_2$ 1 Ar=Ph; R,R= Me$_2$ (a), Et$_2$ (b), (CH$_2$CH$_2$)$_2$O (c);
Ar=p-NO$_2$Ph; R,R= Me$_2$ (d), Et$_2$ (e), (CH$_2$CH$_2$)$_2$O (f);





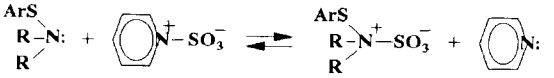
These selected examples indicate that our novel electrophilic reagents can be regarded as reactive electrophiles: their "effective electrophilicity" is sufficient to give rise to skeletal rearrangements typical of carbocationic intermediates. The *trans* stereospecificity of the addition to cyclohexene is typical for a sulfenylation reaction.

2.1. *Use of Complexed SO_3*

As a result of our search for optimum conditions we found that direct activation of weak electrophiles by sulfur trioxide itself has a series of disadvantages, such as the need to work with freshly distilled sulfur trioxide at very low temperatures; the presence of acidic impurities in the reaction mixture reduces considerably the stability and the yield of the expected products, i.e. arylthio substituted sulfamates. These shortcomings can be avoided if complexed sulfur trioxide, e.g. Py–SO_3 is used. The use of the pyridine–sulfur trioxide complex for the sulfonate activation of weak electrophiles in reactions with olefins increases the yield of the desired sulfamates, but the greater usefulness of activation by complexed SO_3 may primarily be attributed to a considerable simplification of the experimental procedure. Both factors enhance the preparative value of the method.[17]

General procedure. Equimolar amounts of Py–SO_3, ArS–NR_2, and olefin are stirred for 1–3 h in dry CH_2Cl_2 at room temperature; the solvent is removed *in vacuo*; the residue is chromatographed.

It is clear that use of complexed SO_3 is restricted by the SO_3-philicity (more correctly -affinity) of the compounds to be activated.



Sulfenyl amides turned out to be satisfactorily reactive. Suffice it to note that the reaction

Table 1.

Product	SO_3	Py–SO_3	Et_3N–SO_3
nortricyclene **7a**	21%	29%	32%
2,3-adduct **8a**	16%	34%	30%
rearranged products **9, 10a**	32%	9%	—

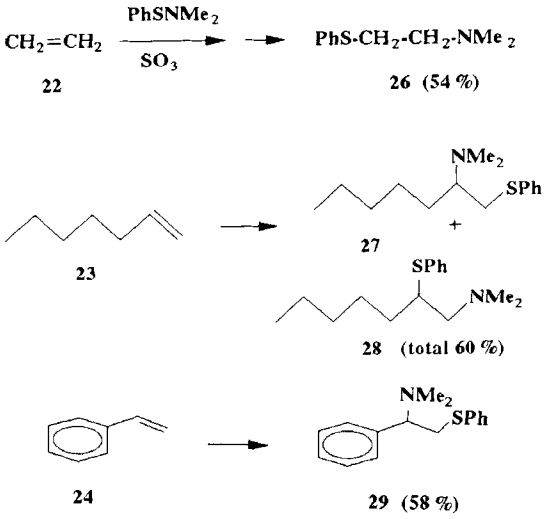
of *N,N*-dimethylbenzenesulfenamide **1a** with norbornene in the presence of Py–SO_3 took only half an hour for completion.

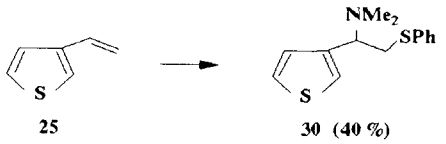
The activation by Py–SO_3 has certain peculiarities. We compared the results of activation with SO_3 and Py–SO_3 in the reaction of sulfenamide **1a** with norbornene. Both reactions afforded the same products, but the activation with Py–SO_3 increased the yield of the 2,3-adduct and decreased the yield of rearranged sulfamates (see Table 1). Thus, for the present case, the sulfenylating species possesses a lower "effective electrophilicity".

Reactions with Et_3N–SO_3 are subject to the same tendency, and the rearranged products **9a** and **10a** are not isolated at all.

2.2. *Aminosulfenylation of Olefins*

Sulfur trioxide mediated reactions of sulfenamides were found to be sensitive both to the type of olefin and to the substituents at the nitrogen atom of the sulfenamide. Up to this point we have considered reactions of sulfenyl sulfamates with polycyclic olefins, which furnish arylthio substituted sulfamates. In contrast, reactions with terminal olefins give quite different results. For instance, the amino sulfides **26–30** were isolated as principal products of the reactions of *N,N*-dimethylbenzenesulfenyl amide **1a** with terminal olefins in the presence of SO_3 or Py–SO_3 in moderate to good yields. The amino sulfides **26–30** were isolated by hydrolysis of the betaines formed — *vide infra*).



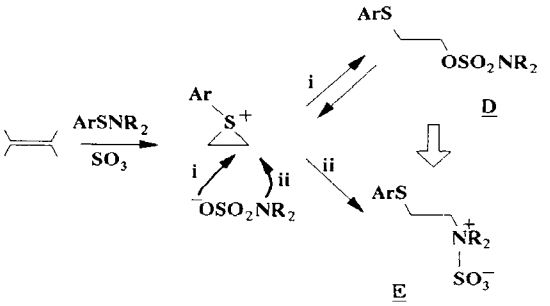


25 30 (40 %)

As mentioned above, the nature of the reactants is of great influence on the outcome of the aminosulfenylation. The following brief discussion serves to clear up some aspects of this problem.

Obviously, a sulfamate anion has two nucleophilic centers, the oxygen and the nitrogen atom, and hence can attack an episulfonium ion to give, in principle, both *O*- and *N*-sulfamates (or betaines), i.e. **D** and **E** (see Scheme).

It is known from the literature that *O*-alkyl sulfamates can be converted into betaines (under drastic conditions such as heating and use of special solvents).[18] Therefore one may assume that an *O*-sulfamate of type **D** is formed only by direct *O*-nucleophilic opening of the episulfonium ring with the ambident sulfamate anion, but a betaine of type **E** can either be formed by direct *N*-nucleophilic opening of the episulfonium ring, or by a stepwise process including the formation of an *O*-sulfamate **D** and then fast sulfamate-betaine rearrangement.

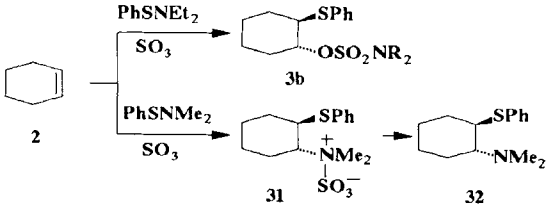


Unfortunately, we were unable to isolate a transient product in the reactions with terminal olefins, but it seems likely that the presumed *O*-sulfamate **D** is formed as an intermediate (TLC monitoring provides indirect evidence of its intermediate formation for the present instance). If so, the following general "rationalization" of aminosulfenylations can be provided for consideration: *first*, the sulfenyl sulfamate attacks the olefinic double bond to give an episulfonium ion; *second*, an *O*-sulfamate of type **D** is formed as a product of kinetic control; and *third*, the *O*-sulfamate **D** undergoes fast sulfamate-betaine rearrangement to give the *N*-sulfamate **E**.

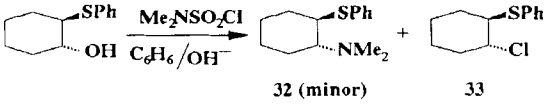
Therefore, the following problem can be posed: which factors influence the reaction to give *O*-sulfamates **D** as principal products, and which factors lead to the formation of betaines **E**?

Two factors are known from the literature: higher temperature and use of special solvents. The third factor is steric hindrance of substituents at the nitrogen atoms of the sulfamate group. Such rearrangements have been found to be the most effective for *N*-methyl derivatives, but *N*-propyl and more bulky sulfamates fail to rearrange.

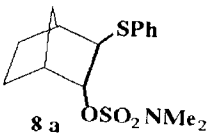
Indeed, we have shown that reaction of *N,N*-diethylbenzenesulfenamide **1b** with cyclohexane in the presence of SO_3 leads to the *O*-sulfamate **3b**. In contrast, the corresponding reaction of the *N,N*-dimethyl substituted sulfenamide **1a** leads to the betaine **31**:



An independent "classic" synthesis of the *N,N*-dimethylsulfamate starting from 2-phenylthiocyclohexanol and sulfamoyl chloride furnished the amine **32** (and the corresponding chloride), but not the *O*-sulfamate:



On the other hand, the ease of the formation of sulfide betaines of type **E** at room temperature and even at $-85\,°C$ indicates that the introduction of the arylthio group into the β-position of the sulfamate sharply increases the rate of rearrangement. This phenomenon undoubtedly arises from nucleophilic participation of a sulfur lone electron pair. The effectiveness of this participation depends on the dihedral angle of the $ArS–C–C–OSO_2NR_2$ fragment and reaches its maximum as the dihedral angle approaches 180°. On the other hand there is no participation if the dihedral angle is 90° (i.e. the C–S bond is perpendicular to the C–O bond). For illustration: the configuration of the S–C–C–O fragment of the rather stable *trans*-2,3-sulfido sulfamate **8a** is found by X-ray analysis[19] to be approximately perpendicular (dihedral angle 111°), but not anti-periplanar.



8a

On this basis the thio-sulfamations of olefins by sulfenamides in the presence of SO_3 can be divided into three different types:

(i) nucleophilic participation of a sulfur lone electron pair is partially restricted or impossible in the addition products; this is the case in reactions with some rigid olefins and, especially, reactions followed by skeletal rearrangements (in this case the arylthio and the sulfamate group are not vicinal); thus, sulfamato sulfides are obtained as principal products;

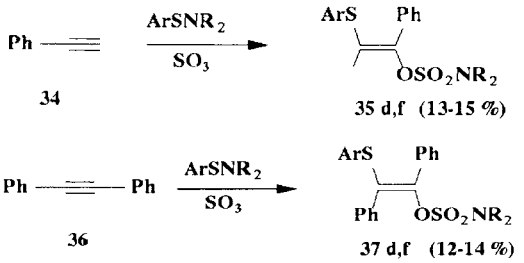
(ii) reaction of *N*-methyl or *N*-ethyl substituted sulfenamides with olefins results in conformationally flexible products. In this case the formation of an anti-periplanar conformation in the fragment $ArS–C–C–OSO_2NR_2$ becomes possible;

and hence favorable conditions for the sulfamate–betaine rearrangement are easily achieved. Such olefins furnish amino sulfides in good yields;

(iii) an intermediate type of reaction — reactions with insufficiently flexible but not totally rigid olefins (e.g. cyclohexane). The direction of this conversion depends dramatically on the kind of alkyls at the nitrogen atom: the sulfamate–betaine rearrangement takes place easily with *N,N*-dimethylsulfamates, but much more drastic conditions are required to rearrange *N,N*-diethylsulfamates.

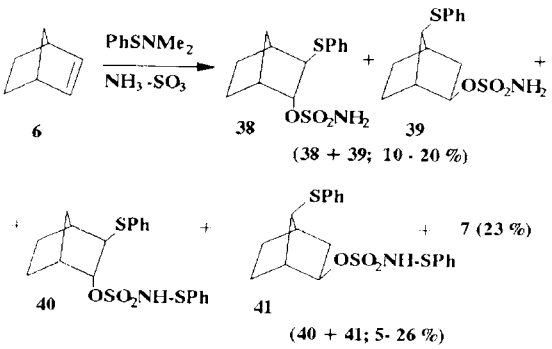
2.3. *Sulfamato-Sulfenylation of Alkynes*

We have also examined the SO_3-mediated addition of sulfenamides with acetylenes. In contrast to the analogous reactions of olefins, reactions with acetylenes are not found to be of preparative value. (The reaction in the presence of complexed SO_3 requires refluxing for several days, and the isolated yields of the expected vinyl sulfamates **35** and **37** leave much to be desired).[20]



2.4. *Reactions in the Presence of Sulfamic Acids*

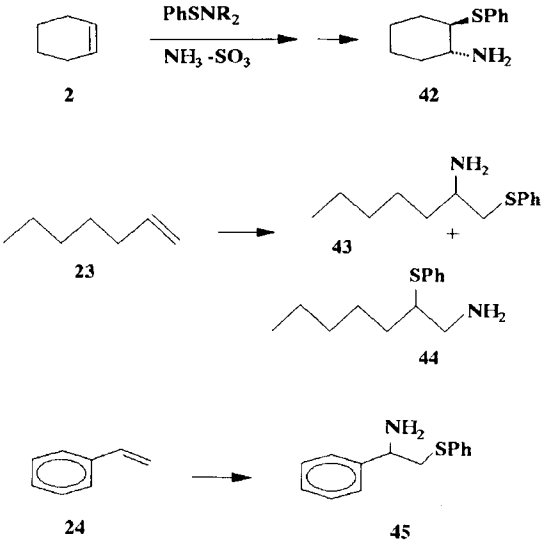
Sulfamic acid (NH_3–SO_3) can be regarded as a complex of SO_3 with ammonia. We have examined the reaction of sulfenamides with bicyclic olefins in the presence of sulfamic acid and found that NH_3–SO_3 reacts as a protic acid to give *N*-unsubstituted sulfamates.[21]



The NH_2-sulfamates **38** and **39** were formed together with the products of secondary *N*-sulfenylation, i.e. **40** and **41**. The yield of the *N*-phenylthio derivatives **40** and **41** was found to be favored by excess sulfenylating reagent in the reaction mixture.

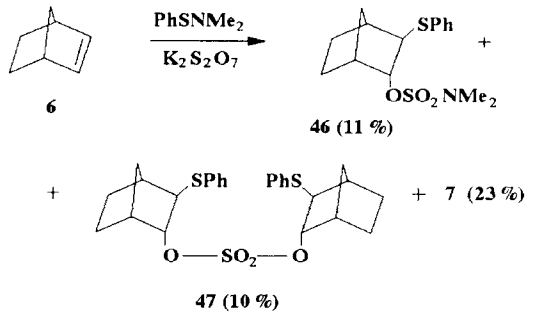
These reactions constitute an unusual example of *the incorporation of a sulfamic acid anion as an external nucleophile in Ad_E-processes.* When *N*-alkyl substituted sulfamic acids were used as reactants, the corresponding *N*-alkylsulfamates of arylthio substituted cycloalkanols were isolated as the principal products.

Use of a conformationally biased cyclohexane and of terminal olefins allows us to obtain the primary amines **42–45** (30–50% after the necessary work-up to hydrolyze the betaines).[22]



2.5. Reactions in the Presence of Potassium Pyrosulfate

Considering potassium pyrosulfate ($K_2S_2O_7$) as a complex of SO_3 with K_2SO_4, we explored the reactions of sulfenamides with olefins in the presence of this commercially available salt. We found that SO_3-mediated addition can be promoted by $K_2S_2O_7$, but the presence of released sulfate anion complicates the reaction picture. As a result of competitive bonding of sulfamate *vs.* sulfate anion in the second step of the Ad_E-reaction a mixture of phenylthio substituted cycloalkyl sulfamates and sulfates was obtained.[23] For instance:

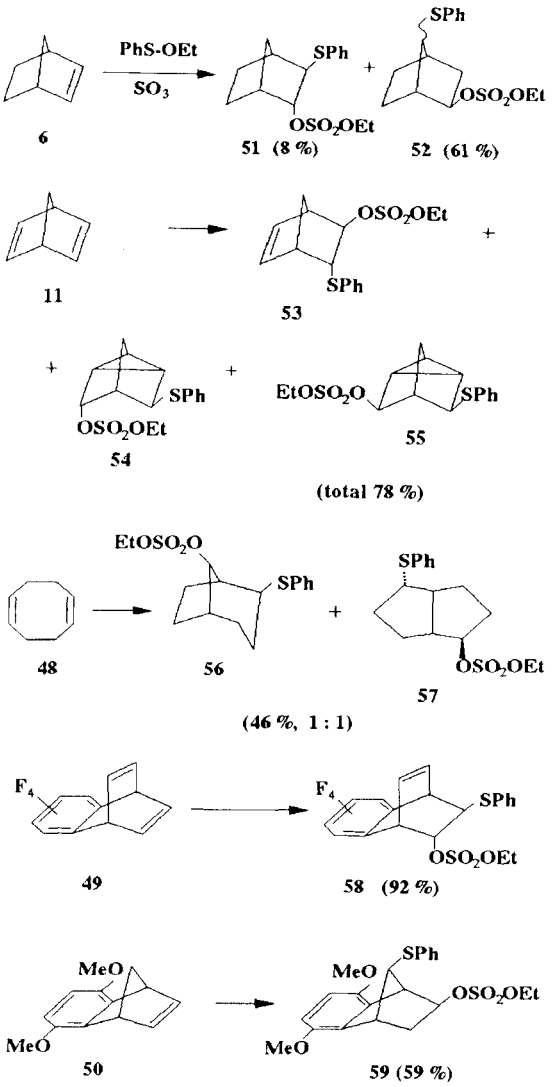


Corresponding reactions with other rigid olefins proceed analogously. The General Procedure resembles that of the reaction with Py–SO_3.

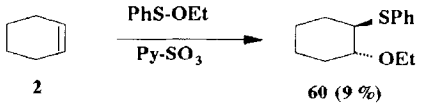
3. REACTIONS OF ALKYL SULFENATES

Alkyl sulfenates as well as sulfenamides do not react with olefins, but their addition can be promoted by boron trifluoride.[24]

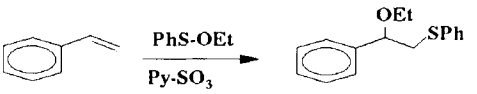
Ethyl benzenesulfenate reacts with SO_3 (or Py–SO_3) and then with cycloalkenes to give the sulfates **51–59**.[25]



As expected, the reaction with styrene or cyclohexene furnished the ethyl ethers **60** and **61**. In these cases (since an anti-periplanar conformation of the phenylthio and $EtOSO_2O$ groups is feasible), the nucleophilic participation of the adjacent thio group gives rise to the formation of these ethers.



2 **60 (9 %)**



24 **61 (55 %)**

4. REACTIONS OF SULFENYL CHLORIDES AND OF DISULFIDES

Although sulfenyl chlorides have been under comprehensive investigation for a long time (for a review see[26]) there is considerable current interest in the chemistry of these derivatives of sulfenic acids. Unfortunately, the use of the addition of sulfenyl chlorides to olefins is limited by the fact that most of these reactions usually give rise to 1,2-adducts, and the incorporation of external nucleophiles as well as skeletal rearrangements have been rarely observed. One of the principal problems is how to increase the electrophilic reactivity of sulfenylating species in addition reactions.

In principle activation of the electrophilic reagent X–Y can be achieved by polarization of the X–Y bond. In connection with Ad_E-reactions of sulfenyl chlorides a number of methods have been proposed to solve this problem. For instance, the use of a more polar solvent or a solvent with higher "ionizing power"[27] leads to increased "effective electrophilicity" of the sulfenyl chloride. In particular, formic acid has been shown to be the best choice as solvent and reactant.[28] A more developed polarization up to complete ionization of X–Y can be gained by *in situ* displacement of Y by a much more nucleofugal anion such as ClO_4^-[29] or by application of ionic reagents of the type $RS^+MY_n^-$ generated from sulfenyl halides[30]:

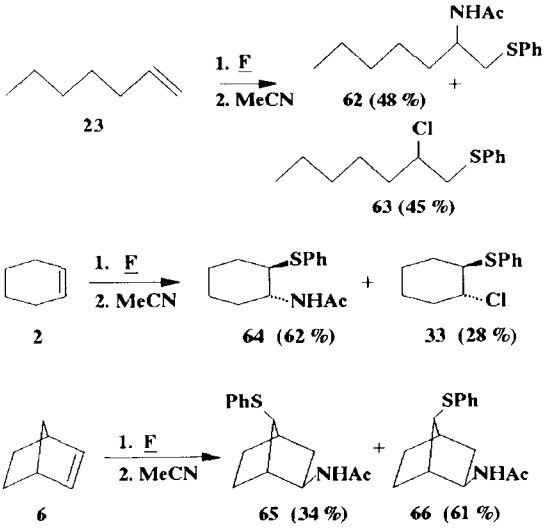
$$RS\text{–}Z + AgMY_n \Rightarrow RS^+MY_n^-$$

We expected that the reaction of SO_3 with PhS–Cl would yield benzenesulfenyl chlorosulfonate **F** as the product of the insertion of sulfur trioxide into the S–Cl bond of the sulfenyl chloride:

$$PhS\text{–}Cl + SO_3 \rightarrow \underset{\mathbf{F}}{PhS\text{–}OSO_2Cl}$$

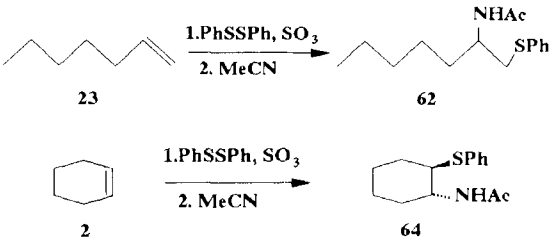
If so, the electrophilic reactivity of the novel reagent **F** should be sharply increased compared to PhS–Cl.

Indeed, the following series of addition reactions of the sulfenyl chlorosulfate **F** has confirmed this hypothesis.[8]



As can be seen the thioamides **62**, **64**, and **65–66** were obtained, together with considerable amounts of the corresponding chloro sulfides **63** and **33** (except in the reaction with norbornene). This demonstrates that the conversion of PhS–Cl to PhS–OSO_2Cl is reversible.

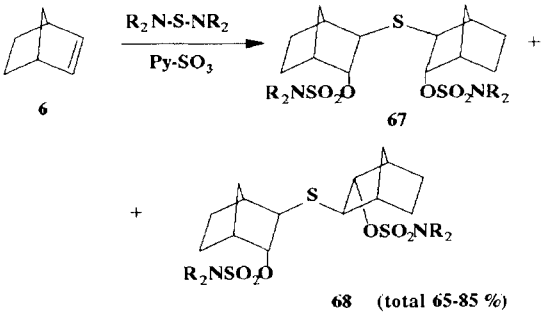
We were also able to apply this approach successfully to reactions of diaryl disulfides[31] which usually react with olefins via a radical pathway. (For heterolytic reactions of disulfides in the presence of BF_3 studied by Trost and co-workers see ref.[32]). These results coincide with the results of the corresponding reactions with ArS–Cl.



In the reactions of both sulfenyl chlorides and disulfides we failed to isolate the products of the incorporation of a chlorosulfonate or phenylthiosulfonate anion in the second step of the Ad_E-process. Taking into account a nucleophilic participation of the adjacent phenylthio group in the 1,2-products, one may expect that such covalent chlorosulfonates or sulfonates containing Bunte salt moieties are extremely unstable.

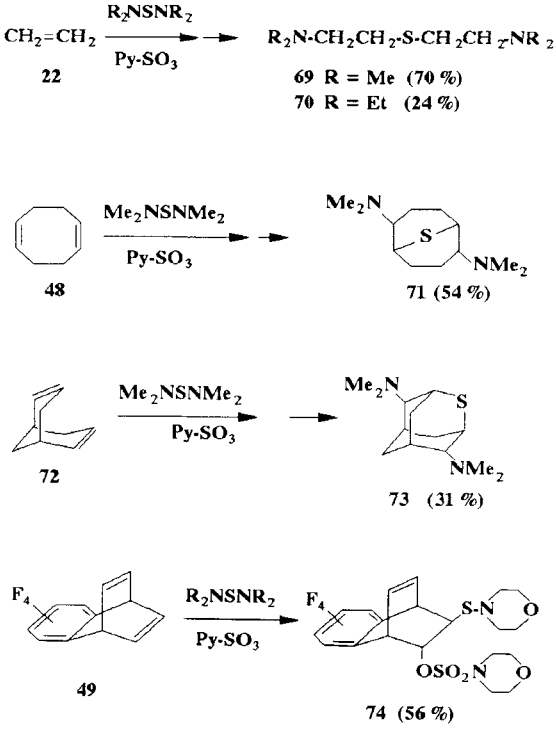
5. REACTIONS OF THIOBISAMINES

Thiobisamines (or diamino sulfides) possess two S–N bonds and hence a broader synthetic potential. SO_3-Mediated reaction of thiobisamines with rigid cyclic olefins leads to the formation of sulfides containing two sulfamate groups.[33]

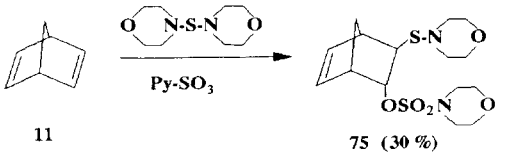


It is important to note that the addition of bifunctional electrophiles to cyclic olefins leads in principle to a mixture of diastereomers. For instance, the addition of SCl_2 to cyclohexene proceeds *trans*-stereospecifically to give a mixture of two diastereomers.[34] Essentially the same problem arises for the SO_3-mediated addition of thiobisamines to norbornene. In the present case the stereochemical problem of configuration assignment was solved directly by an X-ray structural study of the diastereomer **67**.[35]

In contrast the reaction with terminal olefins furnishes diamino sulfides. The formation of the diamines **71** and **73** indicates that an anti-periplanar conformation of the S–C–C–Z fragment can be attained in some rigid products, such as those possessing a thiabicyclo[3.3.1]nonane or thiaadamantane structure.[15]



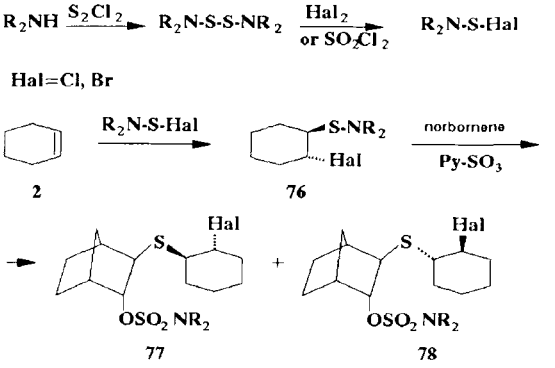
A closely related problem is the following: *Does the insertion of two molecules of SO_3 occur simultaneously or stepwise?* The SO_3-mediated addition of thiobismorpholine to tetrafluorobenzobarrelene (TFBB) demonstrates that the insertion takes place step by step.[36] This reaction proceeds to give the sulfamate **74** (the product of a single insertion) and no disulfamate is formed, not even in the presence of excess Py–SO_3 and TFBB. Use of excess thiobisamine allowed us to obtain the product of single insertion for the simple diene norbornadiene.



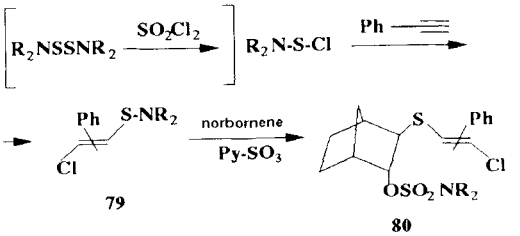
11 75 (30 %)

6. REACTIONS OF AMINOSULFENYL HALIDES

It is known from the literature that aminosulfenyl halides react with olefins to give β-chloroalkanesulfenyl amides.[37] We have found that such *aliphatic* sulfenamides react with olefins in the presence of Py–SO_3 as do *arene*sulfenyl amides. On this basis we developed a novel method for the synthesis of unsymmetrical sulfides containing β-halo-β'-sulfamate groups.[38]



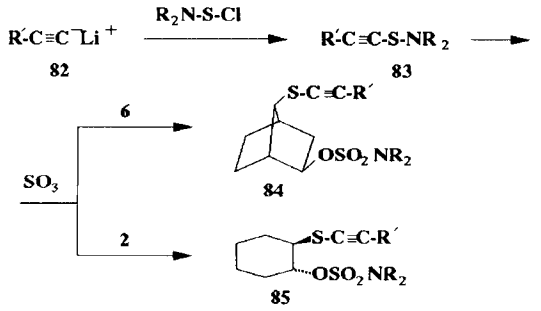
If an acetylene is used in the first step of the reaction, the second step, namely the SO_3-mediated addition, can be regarded as an electrophilic *vinyl*sulfenylation:[39]



79 80

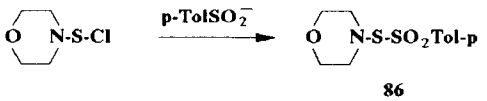
It is worth noting that this three-step "one pot" synthesis allows us to obtain rather complex vinyl sulfides from readily available starting materials. The yields of **77**, **78** and **80** after purification were 20–25% (based on diamino disulfides). This corresponds to an average yield of 60–65% estimated for each step of these three-step syntheses.

Analogously, electrophilic *alkynyl*sulfenylation of olefins was carried out starting with the lithium acetylenides **82**.[40]

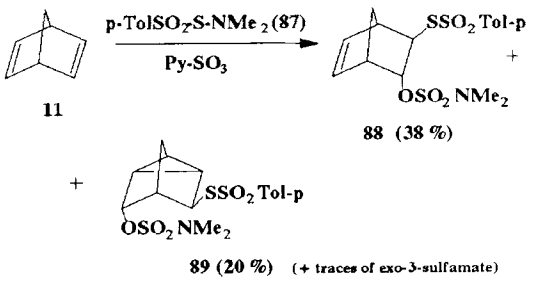


The nucleophilic participation of a lone electron pair on sulfur is reduced in alkynyl sulfides such as **85**; thus, the *O*-sulfamates turn out to be quite stable, even when a conformationally flexible olefin like cyclohexene is used as substrate (cf. Section 2.2.).

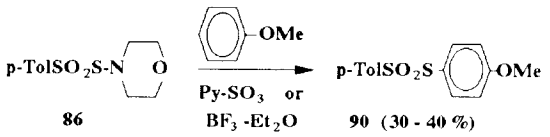
N-Morpholinosulfenyl chloride was found by Markley and Dunbar[41] to react with *p*-toluenesulfinate to give *S*-tosylsulfenyl morpholide (*S*-morpholino-*p*-toluenethiol-sulfonate) **86**.



Its use as a sulfenylating species permits us to synthesize thiolsulfonates by electrophilic introduction of an RSO_2S group into the substrate molecule. For instance, *N*,*N*-dimethyl-*S*-tosylsulfenamide **87** reacts with norbornadiene in the presence of $Py–SO_3$ to give the thiolsulfonates **88–89** containing a dialkylsulfamate group.[42]



The reaction of *S*-tosyl-sulfenmorpholide **86** with anisole in the presence of $Py–SO_3$ or $BF_3–Et_2O$ yields the thiolsulfonate **90** as a product of aromatic substitution.



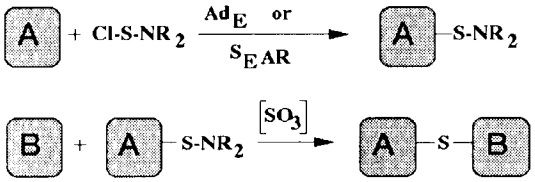
As a rule, syntheses of unsymmetrical thiolsulfonates are based on nucleophilic substitution by thiosulfonate anion:

$$R\text{–}X + {}^{-}SSO_2R' \rightarrow RSSO_2R' + X^{-}$$

Consequently, the electrophilic addition of *S*-sulfonyl sulfenamides promoted by SO_3 or Lewis acids can be considered as an example of the synthetic application of polarity reversal (*umpolung*) of a thiosulfonate. At present, our efforts are focused on syntheses and the application of the sulfonate activation concept to other representatives of *S*-sulfonyl sulfenamides, namely, *S*-sulfamoylsulfenamides **91**, *S*-alkoxysulfonyl sulfenamides **92**, and the *aza*-analog Bunte salts **93**.

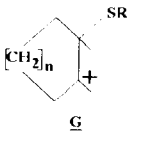
$$R_2NSO_2\text{–}SNR_2' \textbf{ (91)},\ ROSO_2\text{–}SNR_2' \textbf{ (92)},\ Q^{+}\ {}^{-}OSO_2\text{–}S\text{–}NR_2 \textbf{ (93)}$$

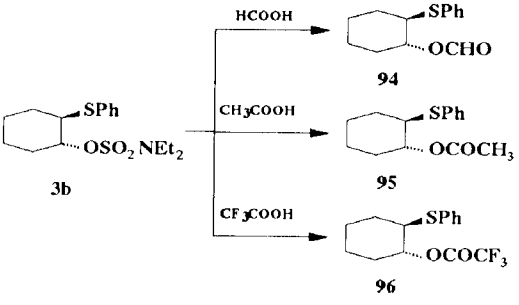
Regarding the use of aminosulfenyl halides in general this synthetic approach can be adapted to the stepwise "sewing" together via a sulfur bridge of any two molecules containing a π- or σ-nucleophilic center.



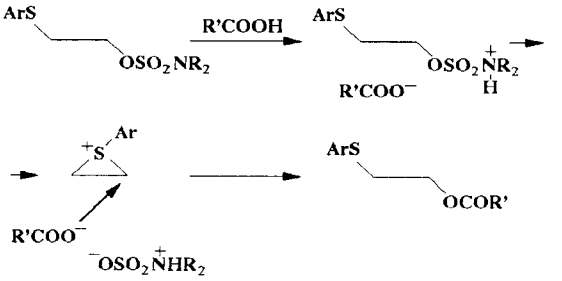
7. ACID CATALYZED NUCLEOPHILIC SUBSTITUTION OF A SULFAMATE GROUP

It is known that the nucleofugal properties of the protonated sulfamate group increase sharply in comparison with the neutral group. In addition to this effect, the nucleophilic participation of the adjacent arylthio group allows us to consider β-arylthio-containing cycloalkyl sulfamates as the synthetic equivalent of a β-sulfidocycloalkyl cation **G** in acid-catalyzed nucleophilic substitutions of the sulfamate group. As expected, reaction of **3b** with formic, acetic, or trifluoroacetic acid proceeds smoothly to give the *trans*-acylates **94–96** in excellent yields.[43]

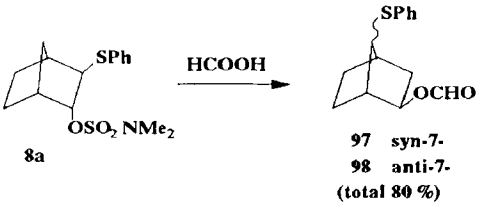




All reactions are accompanied by conservation of the *trans* stereochemistry. This enables us to conclude that the reactions proceed via an episulfonium ion intermediate:



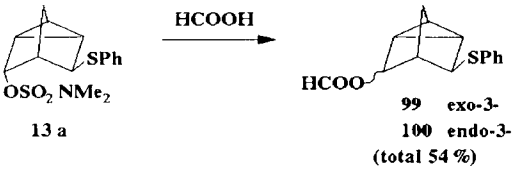
Formolysis of the disubstituted norbornane **8a** gives rise to the rearranged products **97** and **98**:



8a

97 syn-7-
98 anti-7-
(total 80 %)

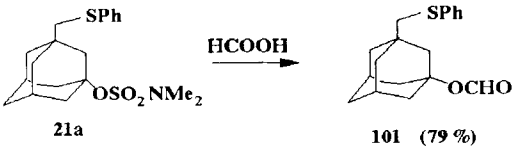
The corresponding reaction of the 3,5-disubstituted nortricyclene **13a** is accompanied by epimerization at C-3.



13 a

99 exo-3-
100 endo-3-
(total 54 %)

The formyloxy substituted adamantane **101** was readily obtained by solvolysis of the sulfamate **21a** with formic acid.



21a

101 (79 %)

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