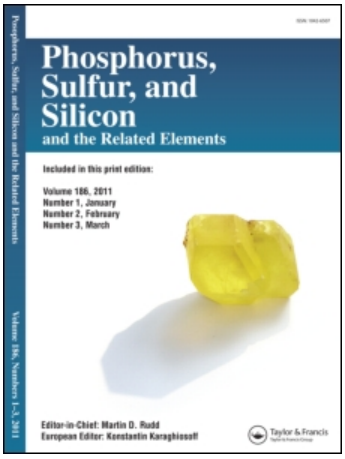


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# REACTION OF AMINOSULFENATES AND DIALKYL SULFOXYLATES WITH METHYL TRIFLUOROMETHANESULFONATE AND SODIUM IODIDE: NMR SPECTROSCOPIC STUDIES

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Treatment of aminosulfenates and dialkyl sulfoxylates with methyl trifluoromethanesulfonate–sodium iodide reagent proved to be a convenient method for synthesis of sulfinamides and sulfinates, respectively. It was demonstrated by means of low temperature $^1$H-NMR spectroscopy that methylation of morpholine- and piperidinesulfenates by TfOMe occurs at the sulfur atom leading to the corresponding alkoxyaminomethylsulfonium salts.



Recently, it has been found that dialkyl sulfoxylates (**1**) react with alkyl halides at elevated temperatures to give alkanesulfinic acid esters (**2**).[1,2]

$$\underset{\mathbf{1}}{RO{-}S{-}OR} + R'X \rightarrow \underset{\mathbf{2}}{R'{-}\overset{\overset{O}{\|}}{S}{-}OR} + RX \qquad (1)$$

The analogous reaction with aminosulfenates, **3**, is more complex and gives different products depending on the structure of the starting ester.[3] Thus, alkyl morpholinesulfenates (**3a, c**) and alkyl piperidinesulfenates (**3b, d**) upon heating with alkyl halides produce the corresponding alkanesulfinamides, **4a–d**, while methyl *N,N*-dimethylaminosulfenate (**3e**) under the same reaction conditions gives ammonium halides, elemental sulfur and sulfur containing polymers.

$$\underset{\mathbf{3}}{R_2N{-}S{-}OR'} + R''X \rightarrow \underset{\mathbf{4}}{R_2N{-}\overset{\overset{O}{\|}}{S}{-}R''} + R'X \qquad (2)$$

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**a** $R_2 = O\langle^{CH_2-CH_2-}_{CH_2-CH_2-}$ $R' = Me$

**b** $R_2 = CH_2\langle^{CH_2-CH_2-}_{CH_2-CH_2-}$ $R' = Me$

$R'' X = MeI$

**c** $R_2 = O\langle^{CH_2-CH_2-}_{CH_2-CH_2-}$ $R' = Pr^n$

**d** $R_2 = CH_2\langle^{CH_2-CH_2-}_{CH_2-CH_2-}$ $R' = Pr^n$

$$Me_2N-\underset{\underset{O}{\|}}{S}-OMe + R''X \rightarrow Me_2\overset{+}{N}R''_2X^- + S_8 + S - \text{cont-polymers} \qquad (3)$$

**3e**

$R''X$ = MeI, EtI, AllBr, $PhCH_2Br$

The formation of sulfinates **2** (reaction (1)) and sulfinamides **4** (reaction (2)) was assumed to be a two-steps process involving dialkoxysulfonium salts, **5**, and aminoalkoxysulfonium salts, **6**, respectively, as intermediates.

$$RO-\overset{+}{\underset{\underset{R'}{|}}{S}}-OR\ X^- \qquad R_2N-\overset{+}{\underset{\underset{R''}{|}}{S}}-OR'\ X^- \qquad R_2\overset{+}{N}-\underset{\underset{R''}{|}}{S}-OR'\ X^-$$

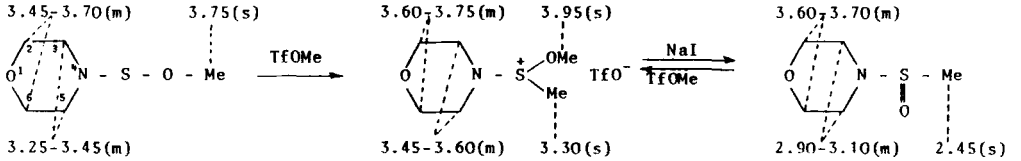
**5** **6** **7**

The different reaction course with **3e** was explained by assuming that the first reaction step is not the alkylation at sulfur but at nitrogen. This should lead to the formation of the unstable ammonium salt **7** which decomposes to the products shown in equation (3).

The aim of the present work was to support experimentally by means of $^1$H-NMR spectroscopy our mechanistic proposals. However, since the alkylation of sulfoxylates **1** and sulfenamides **3** by alkyl halides takes place at elevated temperatures and since the formation of salts **5** and **6** is most probably the rate-determining step, it seemed to us to be impossible to detect and characterize them under such conditions. Therefore, we decided to change the experimental procedure for synthetic and spectroscopic studies and to use, instead of alkyl halides, the more reactive alkylating agent—methyl trifluoromethanesulfonate (TfOMe).[4] It was expected to methylate **1** and **3** at low temperatures and to afford more stable salts **5** and **6** due to very weak nuclophilic properties of trifluoromethanesulfonate anion.

In the first set of experiments methyl morpholinesulfenate (**3a**) and methyl piperidinesulfenate (**3b**) were treated with equimolar amounts of TfOMe at $-20°C$ in $CH_3NO_2$ solution and after a short time with sodium iodide to check whether this procedure will lead to the same products as shown in equation (2). In fact, we have found that in both cases the corresponding sulfinamides **4a** and **4b** were produced in comparable yields to those previously reported.[3] When no sodium iodide was added and the reaction mixture was allowed to reach room temperature, the methylation products underwent a total decomposition within 30 min.

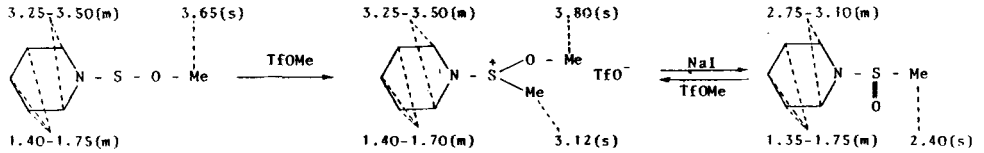
The $^1$H-NMR spectra, recorded immediately after mixing **3a** with TfOMe at $-20°C$, in $CD_3NO_2$ solution revealed the formation of the intermediate salt **6a** as evidenced by the following resonance signals: (1) a multiplet at 3.60–3.75 ppm ascribed to methylene protons at $C_2$ and $C_6$ of the morpholine ring, (2) a multiplet at 3.45–3.60 ppm ascribed to methylene protons at $C_3$ and $C_5$ of the morpholine ring, (3) a singlet at 3.95 ppm ascribed to the methoxy protons, (4) a new singlet (in comparison with the spectrum of **3a**) at 3.30 ppm ascribed to the S-methyl protons. The latter assignment rests on several facts. First of all, the chemical shift of the new methyl group is comparable to those of the S-methyl groups in other structurally related sulfonium salts ($\delta$ = 3.37 ppm in $MeS(OMe)_2^+$;[5] $\delta$ = 3.36 ppm in $MeS(NMe_2)_2^+$).[6] Moreover, the chemical shift of the morpholine ring methylene protons at $C_3$ and $C_5$ in the salt **6a** is very close to that of the substrate **3a**. This should not be the case if alternative *N*-methylation of **3a** occurred. Finally, the reaction of morpholine methanesulfinamide **4a** with TfOMe was found to give the same intermediate salt **6a** as shown by $^1$H-NMR spectra. This provides a clear-cut evidence that methylation of **3a** occurs at the sulfur atom and not at nitrogen.




3a 6a 4a

SCHEME 1

Similar results have been obtained with aminosulfenate **3b**. The spectral assignments to the intermediary sulfonium salt **6b** as well as the proton chemical shifts for **3b** and **4b** are given below (Scheme 2).




3b 6b 4b

SCHEME 2

Unfortunately, our attempts to confirm the formation of the intermediate salt (of the type **7**) in the reaction between methyl dimethylaminosulfenate (**3e**) and TfOMe were unsuccessful due to its immediate decomposition even at low temperatures. Most probably for the same reasons we were not able to observe in the $^1$H-NMR spectra the intermediate(s) formed in the reaction between *N*,*N*-dimethyl methane-

sulfinamide (**8**) and TfOMe. The only information, that has been obtained from these experiments, is that each of the two reactions discussed above leads to entirely different decomposition products. This suggests that in each case a different intermediate must be formed. The different behaviour of aminosulfenates **3a, b** and **3e** towards TfOMe may be taken, however, as an indirect evidence for *N*-methylation of the latter as it was originally suggested.

In view of the fact that the conversion of aminosulfenates **3** into sulfinamides **4** using TfOMe—NaI as reagent can be accomplished under mild conditions we extended our studies to dialkylsulfoxylates **1**. As expected, treatment of **1a–c** with TfOMe—NaI affords the corresponding sulfinates **2a–c**, however, in yields a little bit lower than those obtained by using alkyl halides.

$$(RO_2)S \xrightarrow[-RI]{TfOMe/NaI} Me-\overset{\overset{O}{\|}}{S}-OR$$

**1** **2**

| | | | |
|---|---|---|---|
| **a** | $R = Pr^n$ | **a** | 47% yield |
| **b** | $R = Pr^i$ | **b** | 52% yield |
| **c** | $R = Bu^n$ | **c** | 44% yield |

The present procedure for the synthesis of sulfinates **2** may be advantageous in such cases where the alkoxy substituent is sensitive to heat.



## EXPERIMENTAL SECTION

$^1$H-NMR spectra were obtained with a VARIAN 100 MHz spectrometer. Chemical shifts are given in ppm downfield from hexamethyldisiloxane as a standard.

The starting alkyl aminosulfenates (**3**) and dialkyl sulfoxylates (**1**) were obtained according to the procedures described previously.[1-3]

*General procedure for the reaction of aminosulfenate* **3a** *and* **3b** *with TfOMe and NaI.* To a solution of aminosulfenate (**3**) (2.5 mmole) in 1 ml of $CD_3NO_2$ methyl trifluoromethanesulfonate (TfOMe) (0.41 g ≡ 0.28 ml, 2.5 mmole) was added dropwise at −20°C. After 5 min the $^1$H-NMR spectrum was recorded at room temperature. The solution was than cooled back to −20°C and added to a solution of sodium iodide (0.375 g, 2.5 mmole) in 5 ml of acetone. The resulting mixture was shaken occasionally and allowed to reach room temperature. After about 2 hours it was diluted with chloroform and washed with a diluted solution of $Na_2S_2O_3$. The organic layer was dried over $Na_2SO_4$ and evaporated to give the corresponding sulfinamide (**4**), which was identified by comparison of its $^1$H-NMR spectrum with that of the authentic sample.

The sulfinamides **4a** and **4b** were methylated with TfOMe under the same conditions.

*Attempted alkylation of methyl N,N-dimethylaminosulfenate* (**3e**). Methylation of **3e** was performed by an equimolar amount of TfOMe in $CD_3NO_2$ and $CD_3CN$ at −40°C. The $^1$H-NMR spectra were recorded at −40°C immediately after mixing **3e** with TfOMe and revealed complete decomposition of the reagents. Similar result was obtained when *N,N*-dimethyl methanesulfinamide (**8**) was reacted with TfOMe under the same conditions.

*General procedure for the reaction of dialkyl sulfoxylates* (**1**) *with TfOMe and NaI.* To a solution of sulfoxylate (**1**) (10 mmole) in 2 ml of $CH_3NO_2$ an equimolar amount of TfOMe was added at −15°C. After 5 min a solution of sodium iodide (10 mmole) in 15 ml of acetone was added and the mixture was allowed to reach room temperature (ca 2 h): Chloroform (5 ml) was added and the solution was washed with a diluted solution of $Na_2S_2O_3$ and then with water. The organic layer was dried over $MgSO_4$. After

evaporation the products were purified by short column chromatography (silica gel, ethyl ether : *n*-hexane 2 : 1 as an eluent) and identified by comparison with authentic samples by means of IR and $^1$H-NMR spectra.[7]

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