Novel sulfo-sulfenylating reagents based on S—SO_2-containing compounds

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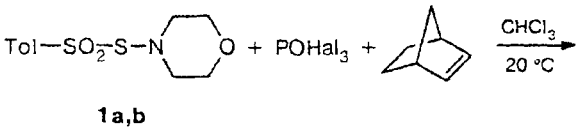
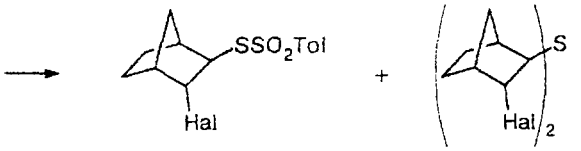
Previously, we suggested a preparative method that allows a thiosulfonate group (Ar—SO_2—S) to be introduced into molecules of unsaturated compounds upon reacting arylsulfonylsulfenyl chlorides with alkenes.[1] This reaction follows the mechanism of electrophilic addition to give *trans*-2-(chloroalkyl) arylthiosulfonates. The use of *S*-sulfonylsulfenamides[2] and *S*-sulfonylthiosulfenamides[3] as sulfo-sulfenylating reagents also leads to β-substituted alkyl thiosulfonates. However, in the case of *S*-sulfonyl- and *S*-sulfonylthiosulfenamides, activation with Lewis acids (SO_3 or BF_3) is required for electrophilic addition to occur. In addition, the reaction usually results in a large number of products, which significantly decreases the yield of the target thiosulfonates. Thus, it is topical to search for new reagents for electrophilic sulfo-sulfenylation.

Recently, we have shown the possibility of activation of sulfur-containing weak electrophiles such as sulfenamides and thio- and dithiobisamines with phosphorus or sulfur oxohalides ($POBr_3$, $POCl_3$, $SOCl_2$, and SO_2Cl_2).[4—8] However, no attempts to activate in this way sulfenylating reagents containing an S^{II}-bound $ArSO_2$ fragment have been made so far.

It was found that *N*-(tosylthio)morpholine (**1**) in the presence of phosphorus oxobromide or oxochloride is added to norbornene to give a mixture of products, namely, thiosulfonate **2** and sulfide **3**:



1a,b

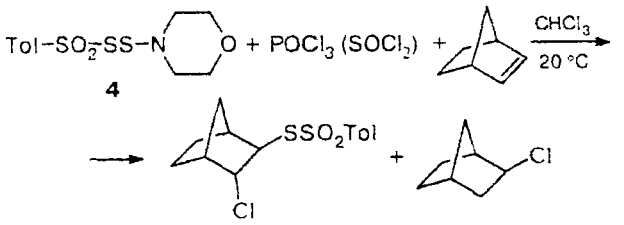


2a (39%) **3a** (27%)
2b (53%) **3b** (21%)

Hal = Cl (**a**); Br (**b**)

The electrophilic character of the reaction is confirmed by the *trans*-configuration of its products. The formation of bis(halonorbornyl) sulfide **3**, along with the expected thiosulfonate **2**, is probably due to the fact that not only the S—N bond but also the S—SO_2 bond in the starting compound can be activated under the reaction conditions.

N-(Tosyldithio)morpholine (**4**) containing a disulfide bridge also reacts with norbornene in the presence of $SOCl_2$ or $POCl_3$ to give a mixture of β-chlorothiosulfonate **2a** and monochloronorbornane **5**:



	$POCl_3$	$SOCl_2$
Yield **2a**	28%	50%
Yield **5**	53%	31%

Hence, it was shown that *S*-tosyl- and *S*-(tosylthio)sulfenamides activated with phosphorus or sulfur oxohalides can be involved in electrophilic addition to the C=C bond of alkenes. Provided the sulfo-sulfenylation conditions are optimized, these reactions can serve as a convenient method for the synthesis of β-chloroalkyl arylthiosulfonates.

Reactions of *S*-tosyl- and *S*-(tosylthio)sulfenamides with norbornene in the presence of phosphorus and sulfur oxohalides (general procedure). $POHal_3$ or $SOCl_2$ (1 mmol) was added to a solution of *S*-tosyl- or *S*-(tosylthio)sulfenamide (1 mmol) and norbornene (1.1 mmol) in anhydrous $CHCl_3$. The reaction mixture was stirred until the sulfenamide disappeared (24—48 h, monitoring by TLC), passed through a filter column with Al_2O_3 (h = 5 cm), and concentrated *in vacuo*. The residue was separated by chromatography on silica gel with a 1 : 4 AcOEt—light petroleum mixture as an eluent.

***endo*-2-Bromo-*exo*-3-(tosylthio)bicyclo[2.2.1]heptane (2b).** R_f 0.85. ^{1}H NMR ($CDCl_3$), δ: 7.82 (d, 2 H, H arom., J = 8.9 Hz); 7.34 (d, 2 H, H arom., J = 8.9 Hz); 3.92 (dd, 1 H, HCBr, J_1 = 3.9 Hz, J_2 = 2.4 Hz); 3.92 (dd, 1 H, HCS, J_1 = 3.9 Hz, J_2 = 1.9 Hz); 3.11 (br.s, 1 H, HC(1)); 2.97 (br.s, 1 H, HC(4)); 2.36 (s, 3 H, CH_3); 2.10—1.00 (m, 6 H, CH_2 norbornane). Found (%): C, 46.75; H, 4.41; S, 17.96. $C_{14}H_{17}BrO_2S_2$. Calculated (%): C, 46.54; H, 4.74; S 17.75.

The spectral and chromatographic parameters of compounds **2a**,[1] **3a**,[8] **3b**,[7] **5**[9] correspond to those obtained earlier.

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