Letters to the Editor

Halo(trimethyl)silanes as activating coreagents in sulfenylation of olefins

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Sulfenylation reactions of alkenes have recently become of particular importance in both the theory and practice of organic synthesis.[1,2] Progress in this area is largely due to the effective electrophilicity concept[3,4] used to develop various ways of activating weak electrophiles.

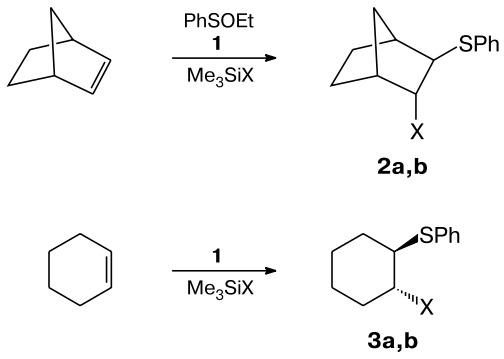
However, despite a great number of relevant investigations,[5] it is still far from discovering a versatile reagent that would allow rapid and easy access to β-halogenated aryl sulfides in high yields. The synthesis of β-brominated aryl sulfides is an especially pressing problem since the degradation rates of the reagents are often higher than the rate of addition.[6,7]

Sulfenic acid esters appear to be promising reagents. Earlier,[8] we have already demonstrated that sulfenic acid esters activated with phosphorus oxohalides can react with olefins. However, this method also has its inherent drawbacks, most substantial of which is separation of the target products from products of reagent degradation, *viz.*, phosphorus(v) acid esters.

Proceeding further in the study of addition of sulfenic acid esters to olefins and in a search for new, more suitable routes to β-halogenated aryl sulfides, we investigated reactions of ethyl benzenesulfenate activated with chloro- and bromo(trimethyl)silanes with such olefins as norbornene and cyclohexene. These compounds were chosen as model substrates because the reactions with them provide comprehensive information on the addition stereochemistry, the effective electrophilicity, and the nature of the electrophilic species.

We found that the reactions occur under mild conditions (CH_2Cl_2 as a solvent, 20 °C, 15—20 min). Ethyl benzenesulfenate (**1**) in the presence of bromo(trimethyl)silane or chloro(trimethyl)silane added to norbornene to give the corresponding β-halogenated phenyl sulfide **2** in high yields as the sole product (Scheme 1).

Scheme 1



X = Cl (**a**), Br (**b**)

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The *trans*-configuration of the product confirms the electrophilic character of the reaction, while the absence of the product of the Wagner—Meerwein rearrangement suggests the low effective electrophilicity of the reagent.

The reaction of ethyl benzenesulfenate (**1**) activated with halo(trimethyl)silanes with cyclohexene also gave rise to only one product, namely, β-halogenated phenyl sulfide **3** in >90% yields.

^{1}H NMR spectra were recorded on an Avance spectrometer (Bruker; 400 MHz) at 28 °C. Chemical shifts are given on the δ scale with reference to HMDS as the internal standard. The course of the reactions was monitored and the purity of the products was checked by TLC on fixed silica gel (Silufol) with light petroleum—ethyl acetate (3 : 1) as an eluent.

General procedure. A solution of ethyl benzenesulfenate[9] (**1**) (2.5 mmol, 2 mL) in chloroform was added in a flow of argon at ~20 °C to a vigorously stirred solution of an alkene (2.1 mmol) in anhydrous chloroform. Then a solution of bromo(trimethyl)silane or chloro(trimethyl)silane (2.5 mmol) in chloroform was slowly added dropwise. Stirring was continued until the reaction was completed (15—20 min). The reaction mixture was filtered through a column and the residue was concentrated *in vacuo*. The NMR spectra were identical with the literature data.[10]

3-*endo*-Chloro-2-*exo*-phenylthiobicyclo[2.2.1]heptane (2a) was obtained from norbornene (0.2 g, 2.1 mmol) and ethyl benzenesulfenate (0.39 g, 2.5 mmol) activated with chloro(trimethyl)silane (0.27 g, 2.5 mmol). The yield was 0.41 g (81%), R_f 0.75. ^{1}H NMR ($CDCl_3$), δ: 1.36—1.57 (m, 2 H, $H(5)_{endo}$, $H(6)_{endo}$); 1.50 (d, 1 H, $H(7)_{anti}$); 1.72 (m, 1 H, $H(5)_{exo}$); 1.86 (d, 1 H, $H(7)_{syn}$, J = 10.5 Hz); 2.05 (m, 1 H, $H(6)_{exo}$); 2.33 (br.s, 1 H, H(4)); 2.52 (br.s, 1 H, H(1)); 3.12 (t, 1 H, CH—S, J = 3.2 Hz); 4.08 (d, 1 H, CH—Cl, J = 3.1 Hz); 7.20—7.40 (m, 5 H, Ar).

2-*endo*-Bromo-3-*exo*-phenylthiobicyclo[2.2.1]heptane (2b) was obtained from norbornene (0.2 g, 2.1 mmol) and ethyl benzenesulfenate (0.39 g, 2.5 mmol) activated with bromo(trimethyl)silane (0.38 g, 2.5 mmol). The yield was 0.59 g (92%), R_f 0.73. ^{1}H NMR ($CDCl_3$), δ: 1.36—1.48 (m, 2 H, $H(5)_{endo}$, $H(7)_{anti}$); 1.58 (m, 1 H, $H(6)_{endo}$); 1.72 (m, 1 H, $H(5)_{exo}$); 1.85 (d, 1 H, $H(7)_{syn}$, J = 10.6 Hz); 2.04 (m, 1 H, $H(6)_{exo}$); 2.30 (br.s, 1 H, H(4)); 2.53 (br.s, 1 H, H(1)); 3.22 (t, 1 H, CH—S, J = 3.9 Hz); 4.11 (br.s, 1 H, CH—Cl); 7.20—7.40 (m, 5 H, Ar).

***trans*-1-Chloro-2-phenylthiocyclohexane (3a)** was obtained from cyclohexene (0.2 g, 2.4 mmol) and ethyl benzenesulfenate (0.45 g, 2.9 mmol) activated with chloro(trimethyl)silane (0.31 g, 2.9 mmol). The yield was 0.53 g (98%), R_f 0.75. ^{1}H NMR ($CDCl_3$), δ: 1.44, 1.66, 1.80 (all m, 2 H each, CH of cyclohexane); 2.27, 2.39 (both m, 1 H each, CH of cyclohexane); 3.36 (d, 1 H, CH—S, J = 4.3 Hz); 4.06 (d, 1 H, CH—Cl, J = 3.1 Hz); 7.20—7.40 (m, 5 H, Ar).

***trans*-1-Bromo-2-phenylthiocyclohexane (3b)** was obtained from cyclohexene (0.2 g, 2.4 mmol) and ethyl benzenesulfenate (0.45 g, 2.9 mmol) activated with bromo(trimethyl)silane (0.44 g, 2.9 mmol). The yield was 0.60 g (92%), R_f 0.73. ^{1}H NMR ($CDCl_3$), δ: 1.50 (m, 2 H, CH_2); 1.73 (m, 3 H, CH of cyclohexane); 1.92, 2.34, 2.47 (all m, 1 H each, CH of cyclohexane); 3.52 (d, 1 H, CH—S, J = 4.3 Hz); 4.30 (s, 1 H, CH—Cl); 7.20—7.40 (m, 5 H, Ar).

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