

SHORT
COMMUNICATIONS

Sulfenic Acid Esters as Promising Sulfonylating Agents

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Sulfenic acids and their derivatives possess a huge synthetic potential. However, except for sulfonyl halides [1, 2], they have not received due attention. Such derivatives as sulfenic acid esters and sulfenamides could be much more convenient electrophilic reagents for the preparation of β -sulfonyl ethers and amides. Alkyl sulfenates and sulfenamides are weak electrophiles [3], and their successful application in synthesis requires activation. We previously proposed a procedure for halosulfonylation of olefins with sulfenamides activated by Lewis acids [4] and phosphoryl halides [5]. The behavior of sulfenic acid esters in addition reactions at the double bond was not studied so far. With the goal of elucidating the possibility of using such reagents and optimizing the reaction conditions, we examined electrophilic addition of ethyl benzenesulfenate (**I**) to norbornene and cyclohexene in the presence of phosphoryl halides (POCl_3 and POBr_3). These reactions could provide information on stereochemistry of the addition, effective electrophilicity, and nature of electrophilic species.

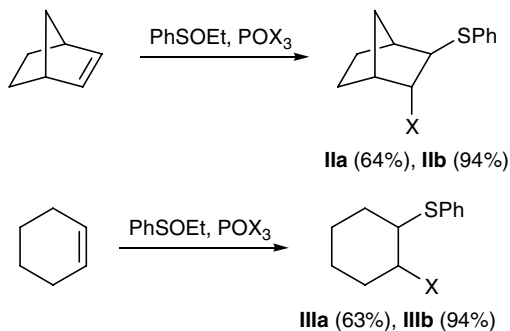
The reactions occurred under mild conditions, in chloroform at 20°C , and reduction of the temperature did not affect the yield to an appreciable extent. Ethyl benzenesulfenate (**I**) reacted with norbornene in the

presence of phosphoryl chloride or bromide to give the corresponding 2-halo-3-phenylsulfonylbicyclo[2.2.1]heptanes **IIa** and **IIb** as the only product (64 and 94%, respectively). The adducts have *trans* configuration, indicating electrophilic character of the process; and the absence of Wagner–Meerwein rearrangement products suggests low effective electrophilicity of the reagent. The reactions of ethyl benzenesulfenate (**I**) with cyclohexene in the presence of POCl_3 and POBr_3 also gave the corresponding 1-halo-2-phenylsulfonylcyclohexanes **IIIa** and **IIIb** as the only product (yield 63 and 94%, respectively).

General procedure for the addition of ethyl benzenesulfenate (I**) to olefins in the presence of phosphoryl halide.** Norbornene or cyclohexene, 2.1 mmol, was dissolved in anhydrous chloroform, 2 ml of a solution of 2.5 mmol of ethyl benzenesulfenate (**I**) in chloroform was added, the mixture was cooled to 0°C , and a solution of 2.5 mmol of POCl_3 or POBr_3 in chloroform was slowly added dropwise. The mixture was stirred until the reaction was complete and passed through a short filtering column, and the filtrate was evaporated under reduced pressure. The NMR spectra of the products coincided with those reported in [6].

Reactions with norbornene. *a.* The reaction of 0.2 g (2.1 mmol) of norbornene with 0.39 g (2.5 mmol) of ethyl benzenesulfenate in the presence of 0.39 g (2.5 mmol) of phosphoryl chloride gave (after chromatographic purification) 0.32 g (64%) of compound **IIa**. R_f 0.75. ^1H NMR spectrum, δ , ppm: 1.36–1.57 m (2H, *endo*-5-H, *endo*-6-H), 1.50 d (1H, *anti*-7-H, $J = 10.47$ Hz), 1.72 m (1H, *exo*-5-H), 1.86 d (1H, *syn*-7-H, $J = 10.47$ Hz), 2.05 m (1H, *exo*-6-H), 2.33 br.s (1H, 4-H), 2.52 br.s (1H, 1-H), 3.12 t (CHS, $J = 3.23$ Hz), 4.08 d (1H, CHCl , $J = 3.13$ Hz), 7.2–7.4 m (5H, H_{arom}).

b. The reaction of 0.2 g (2.1 mmol) of norbornene with 0.39 g (2.5 mmol) of ethyl benzenesulfenate in



the presence of 0.71 g (2.5 mmol) of phosphoryl bromide gave 0.56 g (94%) of compound **IIIb**. R_f 0.73. ^1H NMR spectrum, δ , ppm: 1.36–1.48 m (2H, *endo*-5-H, *anti*-7-H), 1.58 m (1H, *endo*-6-H), 1.72 m (1H, *exo*-5-H), 1.85 d (1H, *syn*-7-H, $J = 10.56$ Hz), 2.04 m (1H, *exo*-6-H), 2.30 br.s (1H, 4-H), 2.53 br.s (1H, 1-H), 3.22 t (1H, CHS, $J = 3.92$ Hz), 4.11 br.s (1H, CHBr), 7.2–7.4 m (5H, H_{arom}).

Reactions with cyclohexene. *a.* The reaction of 0.2 g (2.4 mmol) of cyclohexene with 0.45 g (2.9 mmol) of ethyl benzenesulfenamide in the presence of 0.45 g (2.9 mmol) of phosphoryl chloride gave 0.32 g (63%) of compound **IIIa**. R_f 0.75. ^1H NMR spectrum, δ , ppm: 1.44 m (2H, CH_2), 1.66 m (2H, CH_2), 1.80 m (2H, CH_2), 2.27 m (1H, CH_2), 2.39 m (1H, CH_2), 3.36 d (1H, CHS, $J = 4.30$ Hz), 4.06 d (1H, CHCl , $J = 3.13$ Hz), 7.2–7.4 m (5H, H_{arom}).

b. The reaction of 0.2 g (2.4 mmol) of cyclohexene with 0.45 g (2.9 mmol) of ethyl benzenesulfenamide in the presence of 0.83 g (2.9 mmol) of phosphoryl bromide gave 0.55 g (94%) of compound **IIIb**. R_f 0.73. ^1H NMR spectrum, δ , ppm: 1.50 m (2H, CH_2), 1.73 m (3H, CH_2), 1.92 m (1H, CH_2), 2.34 m (1H, CH_2), 2.47 m (1H, CH_2), 3.52 d (1H, CHS, $J = 4.31$ Hz), 4.30 s (1H, CHBr), 7.2–7.4 m (5H, H_{arom}).

The ^1H NMR spectra were recorded from solutions in CDCl_3 on a Bruker Avance spectrometer (400 MHz) at 28°C; the chemical shifts were measured relative to

HMDS as internal reference. The progress of reactions and the purity of products were monitored by TLC on silica gel plates (Silufol) using petroleum ether–ethyl acetate (3:1) as eluent.

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