

[R₂S-CH₂-OTf]⁺ OTf⁻ as a Reagent with an Optionally Mono- or Biselectrophilic Csp³ Center

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Sulfonium salts [R₂S-CH₂-OTf]⁺ OTf⁻ **1a,b** are synthetically versatile 1,1-biselectrophiles featuring the sulfonio- and triflato-substituents as leaving groups of differential nucleofugic power. Reactions with a number of neutral nucleophiles |Nu yield a series of novel sulfonio-methylated onium salts [R₂S-CH₂-Nu]²⁺ 2OTf⁻ **2–8** under very mild conditions. Structures of salts **2a**, **5a** and **6b** were confirmed by X-ray analysis. With certain N-heteroarenes exchange of both nucleofuges in **1a** was achieved, yielding the symmetrical 1,1-bisonium salts **9** and **10**. With pyridine(derivatives) selective substitution of the sulfoniofunction in 1,1-bisonium systems **2a** and **5a** was also realized. These reactions represent typical examples of nucleophilic substitutions at geminally bisonio substituted C_{sp}³ centers, which we recently have introduced as a novel variant of S_N2 reactivity.

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