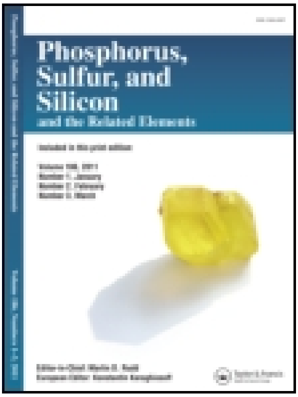

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Electrophilic Trifluoromethylation of Vinyl Sulfides

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Electrophilic Trifluoromethylation of Vinyl Sulfides

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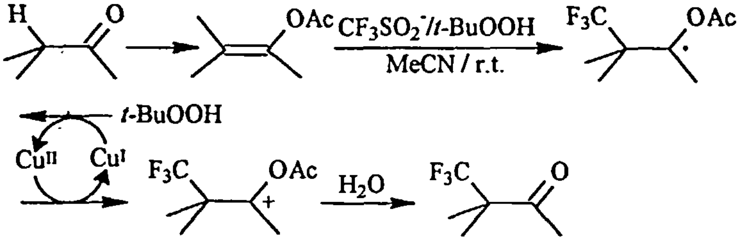
Thioketals of α-(trifluoromethyl)ketones were prepared from CF_3SO_2Na, *t*-BuOOH, methanol, catalytic Cu(II) and vinyl sulfides.

Keywords: vinyl sulfides; trifluoromethylation; sodium triflinate

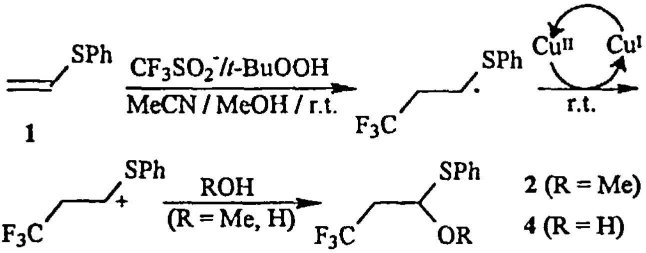
INTRODUCTION

Single-electron oxidation of sodium triflinate (CF_3SO_2Na) by *t*-butyl hydroperoxide delivers the electrophilic trifluoromethyl radical which can be trapped by disulfides[1], aromatics[2] or enol esters[3]. In the two latter cases, provided that Cu(II) is added as catalyst, the reaction results in the formal substitution of a proton by an equivalent of a $^+CF_3$ cation. From ketones, the following mechanism has been proposed[3].



RESULTS AND DISCUSSION

The same reaction has been applied to phenyl vinyl sulfide **1**. However, the resulting trifluoromethylated cation, strongly stabilized by the sulfur atom, cannot evolve through deprotonation to provide a trifluoromethylated vinyl sulfide. In order to prevent polymerization, it must be trapped by a nucleophile : methanol, used as co-sovent with acetonitrile, is an adequate one. Thus, α-(trifluoromethyl)thioketal **2**, which constitutes a protected form of α-(trifluoromethyl)acetaldehyde **3**, was formed (crude yield: 54 %, isolated yield: 41 %). Water, brought by *t*-BuOOH, was also a minor trapping agent which delivered α-(trifluoromethyl)hemithioketal **4** (crude yield: 20 %). During chromatography, **4** was deprotected to volatile **3**. Nevertheless, to obtain the best results, **1** must not be in contact with unsolvated Cu(II) since, in this case, it was oxidized to acetylene and diphenyl disulfide to a large extend. When Cu(II) was solvated by methanol prior addition of **1**, this oxidation occured to a very small extend, as shown from the amount of $PhSCF_3$ resulting from PhSSPh and $\cdot CF_3$ (yield: 7 %) : **2** and **4** were obtained in fair yields.



Because of the stabilization of anions in α-position to a sulfur atom, it can be imagined that **2** could be deprotonated then alkylated, constituting, in this respect, a valuable equivalent of the $CF_3CH_2C(O)^-$ anion.

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