# InI $_{3}$-Catalyzed Synthesis of Thioethers Using Thiosilanes 

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$\mathrm{R}-\mathrm{OAc} \xrightarrow[\mathrm{PhMe} \text {, r.t. }]{$| $\mathrm{TMSSPh}(2.0 \text { equiv) }$ |
| :---: |
| $\operatorname{lnI}_{3}(10 \mathrm{~mol} \%)$ |$} \quad \mathrm{R}-\mathrm{SPh}$

}
up to $90 \%$ yield
$\mathrm{R}=$ (un)saturated aliphatics, aryl carbonyls, adamantyl, $\mathrm{OMe}-, \mathrm{Cl}$ - and $\mathrm{CO}_{2} \mathrm{Et}-$ substituted benzyl, heterobenzyl, propargyl, ferrocene groups

## Selected examples:


$82 \%$ yield

89\% yield

$75 \%$ yield

$41 \%$ yield

57\% yield

28\% yield

$44 \%$ yield

58\% yield

Significance: Herein, the authors disclose an indium triiodide catalyzed substitution of the acetoxy group in various alkyl acetates using thiosilanes. This method successfully converts various primary, secondary and tertiary alkyls, as well as propargylic, allylic and benzylic systems into the appropriate thioethers with a high functional group tolerance.

Comment: The corresponding thioethers are obtained in good to excellent yields. In the case of primary alkyl acetates and $\alpha$-acetoxy carbonyl derivatives, substitution is supposed to proceed via an $S_{N} 2$ reaction, whereas benzylic, allylic, porpargylic and secondary or tertiary alkyl acetates are substituted by an $\mathrm{S}_{\mathrm{N}} 1$-type mechanism.

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[^0]:    synfacts Contributors: Paul Knochel, Nadja M. Barl
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