LIQUID SULFUR DIOXIDE PROMOTES TRANSFORMATIONS INVOLVING CARBENIUM ION INTERMEDIATES

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Due to its high polarity and Lewis acid properties liquid sulfur dioxide can be used as strongly ionizing solvent. It promotes various organic reactions that involve ionic intermediates.1,2

We have found that liquid sulfur dioxide facilitates reactions known for carbenium ion intermediates:

a) indium triflate-catalyzed Ritter reaction of tertiary and non-activated secondary alcohols (transformation A);

b) catalyst-free glycosylation of alcohols and thiols with glycosyl fluorides (transformation B). Also indium and hafnium triflate catalyzed alkyne hydration (transformation C) proceeded well in liquid sulfur dioxide. Reactions run in $\text{SO}_2$ provide products in better isolated yields compared to protocols based on common solvents.

A) $R^1\text{OH} + R^2\text{CN} \xrightarrow{\text{In(OTf)}_3, \text{SO}_2\text{(liq.)} 100^\circ C} R^2\text{CN}R^1$

B) $\text{OPiv}^\text{OPiv} + R-XH \xrightarrow{\text{X: O or S, SO}_2\text{(liq.) 100^\circ C}} R-XR$

C) $\text{R} + \text{H}_2\text{O} \xrightarrow{\text{In(OTf)}_3 \text{ or Hf(OTf)}_4, \text{SO}_2\text{(liq.) 60^\circ C}} R$

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References