



Thioethers O 0580

DOI: 10.1002/chin.201123069

23-069

## Sequential One-Pot Reactions of Thioformates with Lithium Silylacetylides, Arylmagnesium Halides, and Electrophiles Leading to Formation of Propargyl Sul-

**fides.** — One-pot reactions of thioformates with lithium silylacetylides, arylmagnesium halides, and electrophiles are described. The pathway for this process begins with addition of lithium (trimethylsilyl)acetylide to the thioformate C=S carbon, followed by the addition of the arylmagnesium halide to the sulfur atom of the C=S group in the in-situ generated propynethial. The intermediacy of the propynethial in this process is confirmed by trapping with cyclopentadiene [→(VII)]. — (MURAI\*, T.; OHASHI, T.; SHIBAHARA, F.; Chem. Lett. 40 (2011) 1, 70-71,

http://dx.doi.org/10.1246/cl.2011.70; Dep. Chem., Fac. Eng., Gifu Univ., Yanagido, Gifu 501-11, Japan; Eng.) — M. Bohle

$$\begin{array}{c} \text{S} \quad \text{Me} \\ \text{H} \quad \text{O} \quad \text{Bu} \end{array} \begin{array}{c} \text{1. 1.5 equiv. Me}_3 \text{Si-C} \equiv \text{C-Li (II), A)} \\ \text{2. 3.3 equiv. Ph-MgBr (III)} \\ \text{THF, -18°C} \end{array} \begin{array}{c} \text{Ne}_3 \text{Si C} \quad \text{CC} \end{array} \begin{array}{c} \text{Ph} \quad \text{a R}^1 : -\text{Me}_1 \times : -\text{I} \quad 66\% \\ \text{b R}^1 : -\text{SiMe}_3 ; \times : -\text{CI} \quad 60\% \\ \text{c R}^1 : \quad \text{SiMe}_3 ; \times : -\text{CI} \quad 60\% \\ \text{c R}^1 : \quad \text{CH}_2 ; \times : -\text{Br} \quad 62\% \\ \text{CH}_2 : \text{CH}$$

A): Et<sub>2</sub>0, -78 -> -18°C

$$I = \frac{1.1.5 \text{ equiv. (II), A}}{2.20 \text{ equiv. } (VI), -18 -> +25°C}$$

$$Me_3Si = \frac{1.1.5 \text{ equiv. (II), A}}{\text{Me}_3Si} = \frac{1.1.5 \text{ equiv. (II), A}}{\text{Me}_3S$$

VII 65% (61:39 m.d.)