ヨードトリメチルシランを用いた一段階*α*-ハロスチレン誘導体の合成

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Summary a) Sato, A. H.; Mihara, S.; Iwasawa, T. *Tetrahedron Lett.* **2012**, *53*, 3585-3589. b) 特願 2012-170680

1) $Si(CH_3)_3$ + Br —Sonogashira→ $Si(CH_3)_3$ —1) $(CH_3)_3SiI$ 2) H_2O→ I — **88%**

2) —O— $Si(CH_3)_3$ **1.02 g** —1) $(CH_3)_3SiI$ 2) H_2O→ H_3CO — I — **68%**

Background

H —$(CH_3)_3SiCl$/ NaI/ H_2O, CH_3CN, rt, 1 h→ I — **conv. 77% (81% purity)**

Kamiya, N.; Chikami, Y.; Ishii, Y. *Synlett*, **1990**, 675-676.
Kawaguchi, S.; Ogawa, A. *Org. Lett.*, **2010**, *12*, 1893-1895.

H —cat. $Ni(dppp)Cl_2$, dibal-H THF, rt, 2h; NIS, rt, 1 h→ I — **> 98%**

Gao, F.; Hoveyda, A. H. *J. Am. Chem. Soc.*, **2010**, *132*, 10961-10963.

Approach

1M $(CH_3)_3SiI$ in CH_2Cl_2, CH_2Cl_2, -78 °C 15 min; H_2O, ~ 0 °C, 50 min, 0 °C, 10 min → I — **88%**

$Si(CH_3)_3$ → I — **88%**

Effect of the trialkylsilyl groups

SiR_3 —1M $(CH_3)_3SiI$ in CH_2Cl_2 (1.5 eq), CH_2Cl_2, -78 °C, 15 min; H_2O (20 eq), ~ 0 °C, 50 min, 0 °C, 10 min→ I

R	yield (%)	Recovered alkyne (%)
CH_3	88	0
CH_2CH_3	80	13
$CH(CH_3)_2$	54	45

Mixture of D_2O (10 eq) and H_2O (10 eq)

1) 1M $(CH_3)_3SiI$ in CH_2Cl_2; 2) D_2O/H_2O (each 10 eq) → I, H, H + (*E*) + (*Z*)

50% 23% 8%

$Si(CH_3)_3$ → I, D, D + (*E*) + (*Z*) + I, H, H

48% 12% 12% 12%

Plausible pathway

$(CH_3)_3SiI + D_2O \longrightarrow DI + (CH_3)_3SiOH$

Ar — $Si(CH_3)_3$ + DI → [Ar, D, $Si(CH_3)_3$ ⊕ ⇌ Ar, $Si(CH_3)_3$, D ⊕]

$I^\ominus$ → Ar, D, I, $Si(CH_3)_3$ + Ar, $Si(CH_3)_3$, I, D —DI→

Ar, D, I, D + Ar, D, I, H + Ar, H, I, D + $(CH_3)_3SiI$

Evaluation of the reactivity of several alkynes

R — 1M $(CH_3)_3SiI$ in CH_2Cl_2, CH_2Cl_2, -78 °C, 15 min; H_2O, ~ 0 °C, 50 min, 0 °C, 10 min → I

$^nC_5H_{11}$ **72%** | OCH_3 **71%** | H_3CO **60%** | H_3CO **72%**

45% | Br **68%** [a] | Cl **76%** [a] | CH_2CH_3 **69%** [a]

[a] Satd. aq. NH_4Cl was added instead of H_2O.

R — $Si(CH_3)_3$ — 1M $(CH_3)_3SiI$ in CH_2Cl_2, CH_2Cl_2, -78 °C, 15 min; H_2O, ~ rt, 60 min → I

70%

92% | H_3CO **68% (1.02 g Scale)**

45%