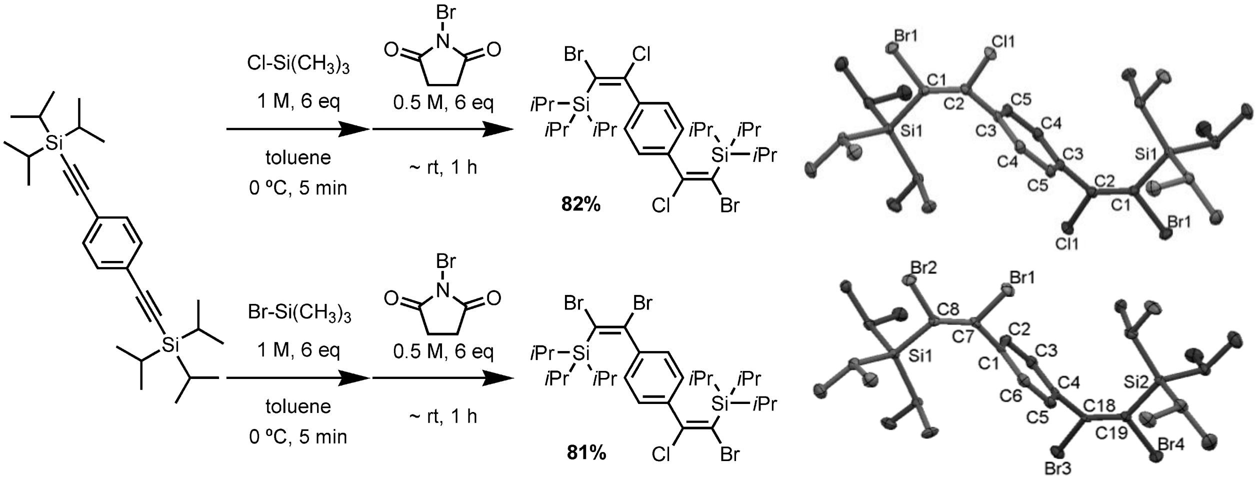
Regio- and stereoselective synthesis of scaffolds for differentially all-carbon tetrasubstituted olefins

Masataka Ide*, Tetsuo Iwasawa
Department of Materials Chemistry, Ryukoku University
Seta, Otsu, Shiga, 520-2194, Japan
iwasawa@rins.ryukoku.ac.jp

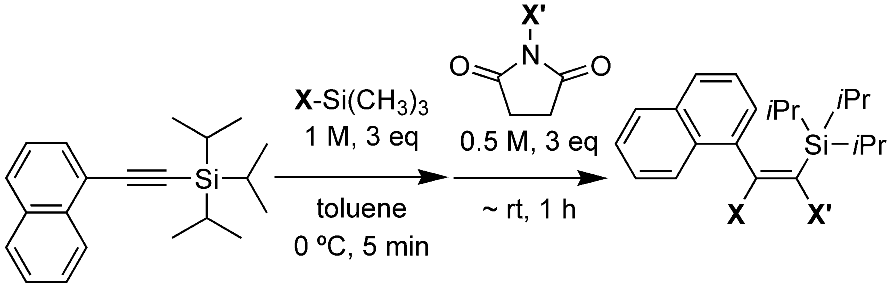
Regio- and stereoselective synthesis of differentially all-carbon tetrasubstituted olefins is significant issue in organic synthesis[1]; and the template strategy is one way to the olefins.[2,3] From the synthetic point of view, vicinal dihaloalkenyl silanes are good scaffolds because they have three tunable elements at vinyl positions. Despite the utility of vicinal dihaloalkenyl silanes, their synthetic availability still remains a challenge due to the inherent difficulty in regio- and stereoselective bis-halogenation of the corresponding silyl ethynylarenes. Employment of commercially available halogens is one way, but the halogens are occasionally unpleasant to work with. Particularly, bromine monochloride (BrCl) is typically gaseous (b.p. 5 ºC) and hygroscopic under an atmospheric air, which is apt to cause trouble to chemists in handling of reactions, purification, and safety. Herein we report the simple protocol enables an efficient regio- and stereoselective bis-halogenations of silyl ethynylarenes (**Scheme1**) .[4, 5] The *in situ* BrCl was readily prepared by reaction of chlorotrimethylsilane with *N*-bromosuccinimide, which then perfectly added to the triple bond in a *syn*-mode. The high-yielding transformations formed each olefin as a perfectly single isomer, which occurred at 0 ºC ~ room temperature in just 1 h. In addition, the reaction system has significance to generate BrCl *in situ* formally, because toxic BrCl is handling-difficult in bench experiments owing to its low boiling point of 5 ºC. Thus, the methods achieved the selective bis-halogenation of silyl ethynylarenes, and provide a potentially synthetic scaffold for synthesis of differentially all-carbon tetrasubstituted olefins.



Scheme 1. Regio- and stereoselective bis-halogenations of triisopropylsilyl ethynylarenes

Screenings of different patterns of halogen source (TMSX/NX'S; X, X' = I, Br, Cl) were tested (**Table 1**). For entry 8, the combination of TMSCl/NBS afforded the desired Br–Cl adduct **2**; on the other hand, for entry 4, the employment of TMSBr and NCS did not afford the desired **2** but strangely gave bisbrominated **1** in 97% yield.

Table 1. Effect of pairing of TMSX/NX'S on silyl ethynylarenes



1, X=X'=Br
2, X=Cl, X=Br
3, X=Cl, X=Cl

Entry	TMSX	NX'S	Product	Yield (%)	Recovered starting alkyne (%)
1	TMSI	NIS	-	0	~100
2	TMSI	NBS	**1**	78	15
3	TMSI	NCS	-[a]	26	73
4	TMSBr	NIS	**1**	97	0
5	TMSBr	NBS	**1**	85	0
6	TMSBr	NCS	**1**	71	0
7	TMSCl	NIS	-[a]	63	26
8	TMSCl	NBS	**2**	95	0
9	TMSCl	NCS	**3**	75	2
10	TMSI	-	-	0	-[b]
11	TMSBr	-	-	0	~100
12	TMSCl	-	-	0	~100
13	-	NIS	-	0	~100
14	-	NBS	-	0	~100
15	-	NCS	-	0	~100

[a] The reasonable Cl-I adduct was found in ^{1}H NMR spectra, but too labile to keep in pure form. [b] Multi spots on TLC were observed.

References

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