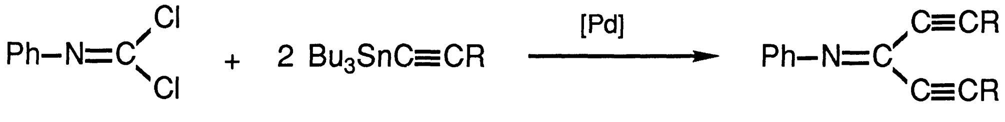
CHEMISTRY LETTERS, pp. 1261-1264, 1989.

Synthesis of Unsymmetrical Dialkynyl Imines. Stepwise Coupling of N-Phenyl Phenylthioimidoyl Chloride with Alkynyltin Compounds

Yoshihiko ITO,* Masahiko INOUYE, and Masahiro MURAKAMI
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto
University, Yoshida, Kyoto 606

A stepwise introduction of two different alkynyl groups onto the iminocarbon leading to the synthesis of unsymmetrical dialkynyl imines was achieved by palladium-catalyzed coupling reaction of N-phenyl phenylthioimidoyl chloride with alkynyltin compounds.

In the previous paper,[1] we reported a palladium-catalyzed coupling reaction of isocyanide dichloride **1** with alkynyltin compounds **2** to give symmetrical N-phenyl dialkynyl imines **3** in moderate yields, whose hydrolysis provided the corresponding dialkynyl ketones. However, all attempts to quit the coupling reaction at the stage of mono-substitution were unsuccessful.

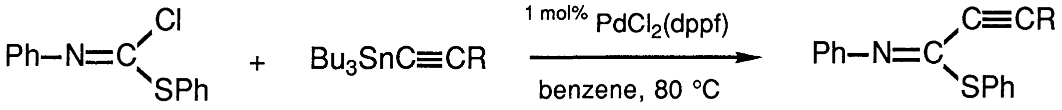


1 **2** **3** (1)

Herein, we wish to describe a synthetic method for the stepwise introduction of two different alkynyl groups onto the iminocarbon, leading to the formation of unsymmetrical dialkynyl imines **6**.

Reaction of N-phenyl phenylthioimidoyl chloride (**4**)[2] with alkynyltin compounds **2** was catalyzed by 1 mol% of dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) [$PdCl_2$(dppf)] to afford selectively mono-substituted products, N,S-diphenyl alkynecarbothioimidates **5** in moderate to good yields (Table 1).[3] Use of palladium catalysts such as tetrakis(triphenylphosphine)palladium(0), dichlorobis-(triphenylphosphine)palladium(II), and dichlorobis(tricyclohexylphosphine)palladium-

(II) in the coupling reaction gave a complex mixture of products including symmetrical N-phenyl dialkynyl imines **3** and N,S-diphenyl alkynecarbothioimidates **5**. The steric bulkiness of 1,1'-bis(diphenylphosphino)ferrocene ligand on palladium may retard further coupling of **5** with **2**.



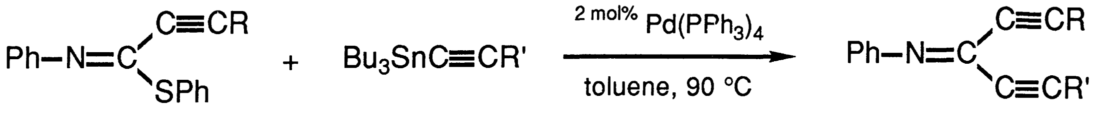
4 **2** **5**

(2)

Table 1. Selective Synthesis of N,S-Diphenyl Alkynecarbothioimidates

Entry	R-	Product	Yield/%
1	Me_3Si-	**5a**	93
2	$(MeO)Me_2C$-	**5b**	76
3	n-Bu-	**5c**	64
4	Ph-	**5d**	83
5	$CH_2=CH(CH_2)_3OCH_2$-	**5e**	83

The introduction of the second alkynyl groups on **5** was efficiently carried out by use of 2 mol% of tetrakis(triphenylphosphine)palladium(0) to give symmetrical and unsymmetrical dialkynylimines **6** in good yields (Table 2).



5 **2** **6**

(3)

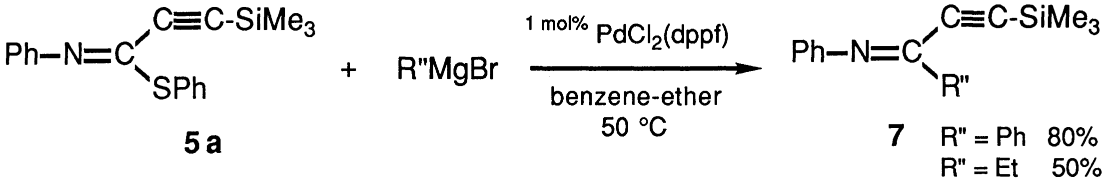
Table 2. Synthesis of Unsymmetrical Dialkynylimines

Entry	R-	R'-	Product	Yield/%
1	Me_3Si-	Me_3Si-	**6a**	75
2	Me_3Si-	$(MeO)Me_2C$-	**6b**	81
3	Me_3Si-	Ph-	**6c**	80
4	Me_3Si-	n-Bu-	**6d**	87
5	$(MeO)Me_2C$-	n-Bu-	**6e**	82

Typical experimental procedure for the preparation of unsymmetrical dialkynyl imines **6** from **4** was exemplified by the synthesis of **6d**: A solution of N-phenyl phenylthioimidoyl chloride (**4**, 12.0 mmol) and [(trimethylsilyl)ethynyl]tributyltin

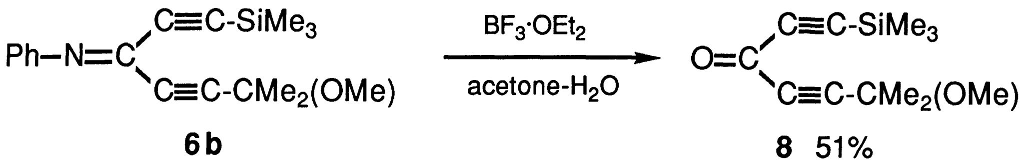
(13.5 mmol) and dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (0.12 mmol) in benzene (30 mL) was stirred at 80 °C for 5 h. After removal of benzene in vacuo, the reaction mixture was diluted with ether, treated with aqueous KF at room temperature for 10 min, and filtered to remove white precipitate of tributyltin(IV) fluoride. Extractive workup and filtration through a Florisil column followed by vacuum distillation afforded diphenyl [(trimethylsilyl)acetylene]carbothioimidate (**5a**)[4] in 93% yield. A solution of **5a** (0.50 mmol), 1-hexynyltributyltin (0.60 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.01 mmol) in toluene (1.5 mL) was heated at 90 °C for 5 h. Concentration followed by column chromatography on silica gel gave **6d**[5] in 87% yield.

The present coupling reaction is applicable to a general preparation of N-phenyl alkynyl imines **7**. For instance, the reaction of **5a** with Grignard reagent (R"MgBr) was catalyzed by 1 mol% of dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) to produce N-phenyl alkynylimines **7**.



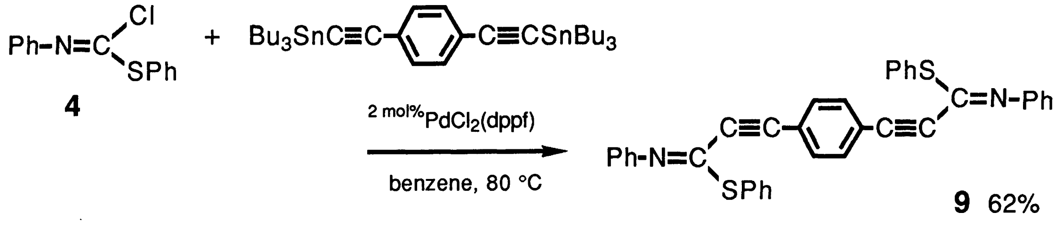
5a **7** R" = Ph 80% R" = Et 50% (4)

Unsymmetrical dialkynyl imines **6** thus prepared were hydrolyzed by $BF_3 \cdot OEt_2$ in acetone-H_2O to give the corresponding unsymmetrical dialkynyl ketones, as exemplified below.

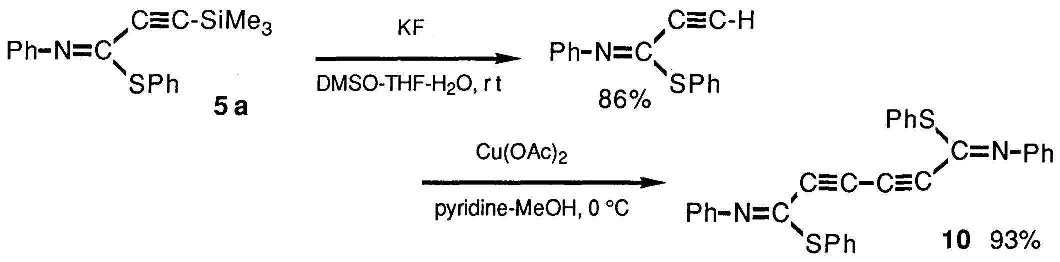


6b **8** 51% (5)

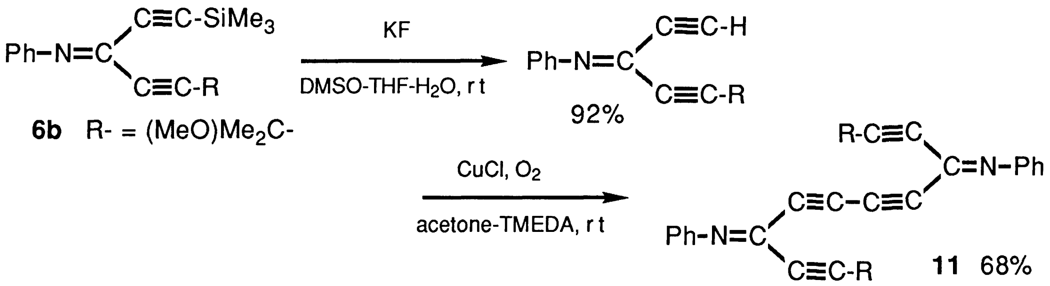
Utilization of the present synthesis of N-phenyl alkynyl imines was demonstrated by preparation of some other polyacetylenic imines (**9**, **10**,[6] and **11**[7]) as shown below.



4 **9** 62% (6)



(7)



(8)

Further synthetic transformations of diphenyl alkynecarbothioimidates **5** and unsymmetrical dialkynyl imines **6** are now in progress in our laboratory.

References

1) Y. Ito, M. Inouye, and M. Murakami, *Tetrahedron Lett.*, 29, 5379 (1988).

2) E. Kühle, *Angew.Chem., Int. Ed. Engl.*, 1, 647 (1962).

3) For palladium-catalyzed coupling reaction of imidoyl chlorides, see: T. Kobayashi, T. Sakakura, and M. Tanaka, *Tetrahedron Lett.*, 26, 3463 (1985); M. Kosugi, M. Koshiba, A. Atoh, H.Sano, and T. Migita, *Bull. Chem. Soc. Jpn.*, 59, 677 (1986).

4) **5a**: bp 147-150 °C/0.35 mmHg; mp 57-59 °C; IR (KBr) 1580(C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.04 (9 H, s), 6.98-7.67 (10 H, m); MS (20 eV) m/e 309 (M^+). Anal. Calcd for $C_{18}H_{19}NSSi$: C, 69.85; H, 6.19; N, 4.53. Found: C, 70.05; H, 6.13; N, 4.63.

5) **6d**: IR (neat) 2224(C≡C), 1556(C=N) cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of syn and anti isomers) δ 0.09 and 0.27 (9 H, s), 0.82 and 0.94 (3 H, t, J=8.0 Hz), 1.10-1.70 (4 H, m), 2.24 and 2.43 (2 H, t, J=6.0 Hz), 7.09-7.37 (5 H, m); MS (20 eV) m/e 281 (M^+). Anal. Calcd for $C_{18}H_{23}NSi$: C, 76.81; H, 8.24; N, 4.98. Found: C, 76.83; H, 8.37; N, 5.00.

6) I. D. Campbell and G. Eglinton, *Org. Synth.*, 45, 39 (1965).

7) D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, 37, 45 (1972).

(Received April 20, 1989)