ADDITION OF PROPARGYLTRIMETHYLSILANE TO *N*-METHYLENEAMINE EQUIVALENTS: GENERATION AND ELECTROPHILIC CYCLIZATION OF VINYLIC CARBOCATIONS[1]

Hyun-Joon Ha,* Young-Seong Lee, and Young-Gil Ahn

Department of Chemistry, Hankuk University of Foreign Studies
Yongin, Kyunggi-Do, 449-791 Korea

Abstract - Lewis acid induced *N*-methyleneamine equivalents from *N*-(methoxymethyl)anilines or 1,3,5-triphenylhexahydro-1,3,5-triazines reacted with propargyltrimethylsilanes to give *N*-buta-2,3-dienylanilines, 4-methylene-1,2,3,4-tetrahydroquinolines and its oxidized product of 4-methylquinolines. These products came from branching reactions of the elimination and electrophilic aromatic substitution from the same vinylic carbocation intermediate.

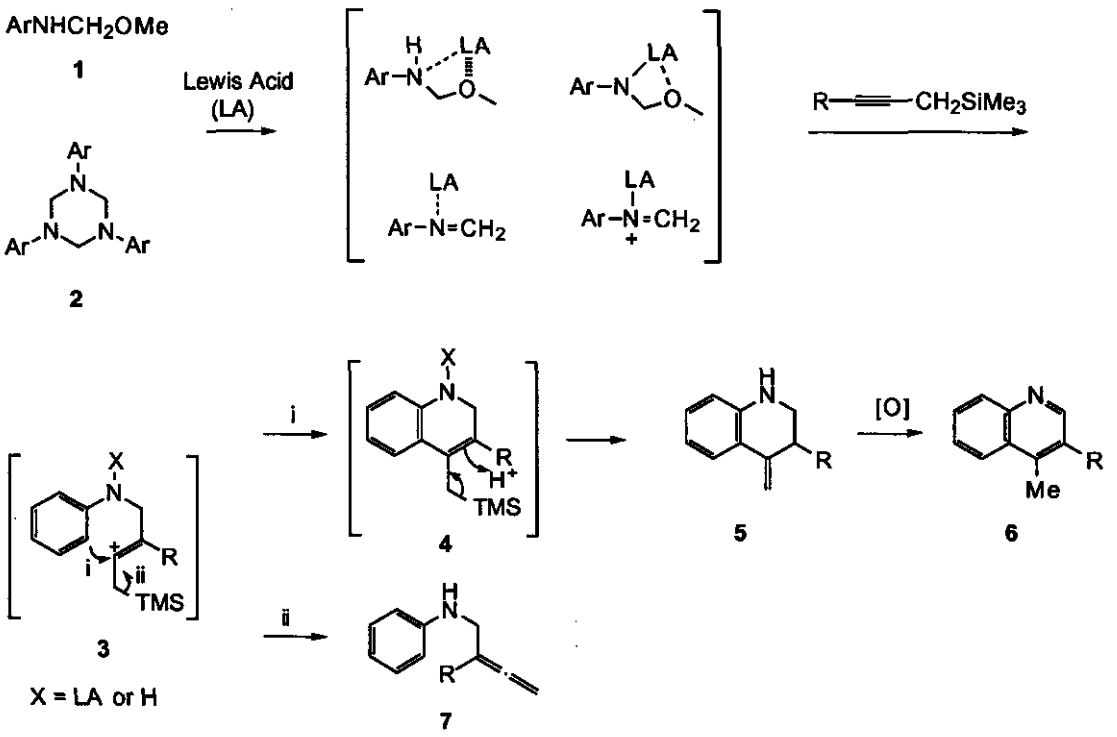
Limitted number of methods to generate vinyl cations has been reported consisting of electrophilic addition to triple bond of alkynes or the cumulene bond of allenes.[2] The mechanistic detail of the electrophilic addition of alkyne is in dispute.[3] Furthermore its synthetic application is very rare. In this paper we wish to show generation and utilization of vinyl cation as an intermediate for the synthesis of poly-substituted quinolines.[4]

A series of our previous reports shows that *N*-methyleneamine equivalents[5] could be generated *in situ* from *N*-methoxymethylamines or hexahydro-1,3,5-triazines in the presence of a Lewis acid and served as electrophiles for the synthesis of aminomethylated products.[6,7] One of those reactions is addition to allyl nucleophiles leading to the selective synthesis of 1,2,3,4-tetrahydroquinolines and homoallylic amines through branching reactions from the same cationic intermediates.[7c] Based on this observation

generation and utilization of vinyl cation is possible from the addition of *N*-methylenamine equivalents to propargyl nucleophiles.

N-(Methoxymethyl)anilines (**1**) and 1,3,5-triphenylhexahydro-1,3,5-triazines (**2**) with diverse substituents on benzene ring reacted with propargyltrimethylsilanes[8,9] in the presence of $TiCl_4$ to give a mixture of 4-methylene-1,2,3,4-tetrahydroquinolines (**5**), its oxidized product of 4-methylquinolines (**6**), and *N*-buta-2,3-dienylanilines (**7**).

Scheme



This reaction proceeded well with the most of compounds bearing the substituents of 2-Me, 2,5-Cl_2 and 4-NO_2 on the benzene ring. Among Lewis acids of $TiCl_4$, $SnCl_4$, $AlCl_3$, and TMSOTf, $TiCl_4$ was the best for most of the substrates. The reactions with $BF_3{\cdot}OEt_2$ yielded **6** as a dominant product while all the others with $TiCl_4$ and $SnCl_4$ gave a mixture of **5**, **6** and **7**. The reactions were successful not only with simple propargyltrimethylsilane (R = H) but with 2-butynyltrimethylsilanes (R = Me) to yield moderate amount of 3,4-dimethylquinolines (Table).

For the mechanistic detail *N*-(methoxymethyl)aniline and 1,3,5-triphenylhexahydro-1,3,5-triazine yield the *N*-methyleneamine equivalents in the presence of a Lewis acid assumed to be coordinated complexes as shown in the Scheme. The addition of propargylTMS forms the vinylic carbocation intermediate (**3**) which is stabilized by a β-silicon atom. The subsequent branching from the vinyl cation occurs in two different pathways of electrophilic aromatic cyclization (pathway i) and the removal of TMS (pathway ii). The similar branching from the vinylic carbocation intermediate was reported consisting of propargyltrimethylsilane and *N*-alkoxycarbonyliminium ions from carbamate in the presence of Lewis acid to yield both of the cyclized oxazinones and allenes.[9b]

Table. Reactions of *N*-methoxymethylaniline (**1**) or 1,3,5-triphenylhexahydro-1,3,5-triazine (**2**) with propargyltrimethylsilane in the presence of Lewis acid.

Substrate	Ar	R	Lewis Acid	5	6	7
1a	Ph	H	$TiCl_4$	26	41	12
1a	Ph	H	$SnCl_4$	18	34	8
1a	Ph	H	$BF_3{\cdot}OEt_2$		58	
1a	Ph	Me	$BF_3{\cdot}OEt_2$		47	
1b	2-Me-C_6H_4	H	$BF_3{\cdot}OEt_2$		43	
1c	2,5-Cl_2-C_6H_3	H	$TiCl_4$	23	29	22
1c	2,5-Cl_2-C_6H_3	H	$BF_3{\cdot}OEt_2$		48	
1d	4-NO_2-C_6H_4	H	$TiCl_4$	6	30	23
1d	4-NO_2-C_6H_4	H	$BF_3{\cdot}OEt_2$		46	
2a	Ph	H	$TiCl_4$	19	31	29
2a	Ph	H	$BF_3{\cdot}OEt_2$		41	
2a	Ph	Me	$BF_3{\cdot}OEt_2$		48	
2b	2-Me-C_6H_4	H	$BF_3{\cdot}OEt_2$		41	
2c	2,5-Cl_2-C_6H_3	H	$TiCl_4$	13	21	27
2c	2,5-Cl_2-C_6H_3	H	$BF_3{\cdot}OEt_2$		62	
2c	4-F-C_6H_4	H	$BF_3{\cdot}OEt_2$		56	

Pathway i yielded the cyclized product (**4**) which was converted to 4-methylene-1,2,3,4-tetrahydroquinolines (**5**) in the way of well-known allylTMS protodesilylation in the presence of Lewis acid.[10] Then some of them were oxidized under the reaction conditions to yield mixtures of **5** and **6**.[11]

Most of the compounds (**5**) were converted slowly to **6** by standing at room temperature under the air in a few days. With $BF_3 \cdot OEt_2$ was yielded **6** as a dominant product. Relatively lower nucleophilicity of $BF_3 \cdot OEt_2$ toward the silyl group compared to $TiCl_4$ might prolong the lifetime of vinyl cation to be cyclized and oxidized to yield **6**.[12] 4-Methylene-1,2,3,4-tetrahydroquinilone (**5**) was aromatized oxidatively to **6** with DDQ in 1,4-dioxane. This procedure was applicable for the general synthesis of poly-substituteded quinolines.

This reaction sequence of addition of *N*-methyleneamine equivalent to alkyne followed by interamolecular cyclization of vinylic carbocation intermediate is supported by the observation of *N*-buta-2,3-dienylaniline as a minor product discarding the possibility of $[4\pi+2\pi]$ cycloaddition mechanism with subsequent tautomerization pathway.[13,14] However, the observation that the reaction with $BF_3 \cdot OEt_2$ yielded **6** as a dominant product does not allow to remove the possibility of the different reaction pathway compared to those with either $TiCl_4$ or $SnCl_4$. Still there is a chance to have $[4\pi+2\pi]$ cycloaddition and the following oxidative desilylation mechanism.[10b] Pathway ii with the removal of TMS from vinylic carbocation intermediate yielded *N*-buta-2,3-dienylaniline. When the life time of the initially generated vinyl cation is not long enough to be cyclized the pathway i is suppressed. With propargyltriphenyltin[15] instead of propargyltrimethylsilane as a nucleophile in the presence of $TiCl_4$ was obtained *N*-buta-2,3-dienylaniline in 36% isolated yield without detectable amount of the cyclized product. This supports the initial formation of vinyl cation intermediate between *N*-methyleneamine equivalents and propargyl compounds, and the subsequent removal of triphenyltin group. The weakness of carbon-tin bond compared to carbon-silicon bond shorten the lifetime of the vinylic carbocation and suppressed the cyclization process.[16,7e]

In conclusion we could obtained vinylic carbocation intermediate and its branching to the cyclization in the way of electrophilic aromatic substitution to yield quinolines and to the elimination to give *N*-buta-2,3-dienylaniline.

EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Gemini 200 (200 MHz for ^{1}H and 50.3 MHz for ^{13}C). Chemical shifts were given in ppm using TMS as internal standard. MS spectral data were obtained using a Hewlett Packard Model 5985B spectrometer or a Kratos Concept 1-S double focusing mass spectrometer. Elemental analysis was taken on a Perkin-Elmer 240 DS elemental analyzer. The silica gel used for column chromatography was Merck 200-230 mesh. Thin layer chromatography was carried out

with Merck 60F-254 plates with 0.25 mm thickness. *N*-Methoxymethylanilines were prepared by the reported method.[7a] propargyltrimethylsilane purchased from Fluka was distilled prior to use. All the other chemicals were reagent grade and used without further purification. 1,3,5-Trisubstituted hexahydro-1,3,5-triazines were obtained by the conventional method with amine and formaldehyde. Some of the *N*-methoxymethylanilines and 1,3,5-triphenylhexahydro-1,3,5-triazines were inter-convertible.[7c] 2-Butynyltrimethylsilanes was prepared from methylation of lithiated propargyltrimethylsilane with MeI in THF followed by distillation.

General Procedure: To a stirred solution of *N*-methoxymethylanilines (**1**) (3.0 mmol) or 1,3,5-triphenylhexahydro-1,3,5-triazine (**2**) (1.0 mmol) in CH_2Cl_2 (10 mL) under nitrogen atmosphere was slowly added the Lewis acid (3.1 mmol) at -78°C. After being stirred for 10 min propargyltrimethylsilanes (9.1 mmol) was added to it. The resulting solution was stirred at -78°C until all starting materials were consumed on TLC. The reaction mixture was poured into ice-water. The resulting solution was neutralized with cold sat. $NaHCO_3$ solution. The reaction product was extracted with CH_2Cl_2. Organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction product was purified by flash chromatography. To obtain only quinoline (**6**) the crude reaction product containing both of **5** and **6** was dissloved in 1,4-dioxanes (5 mL) and acetic acid (500 mg) and reacted with DDQ (114 mg, 0.5 mmol). After refluxing an hour the reaction was stopped by adding sat. $NaHCO_3$ solution, and the organic material was extracted with EtOAc, which was treated as above and purified by flash chromatography.

4-Methylene-1,2,3,4-tetrahydroquinoline (5a): oil; δ_H (200 MHz; $CDCl_3$) 2.56 (2 H, t, J = 6.0 Hz), 3.26 (2 H, t, J = 6.0 Hz), 3.88 (1 H, br s), 4. 71 (1 H, d, J = 1.0 Hz), 5.32 (1 H, d, J = 1.0 Hz), 6.44 (1 H, dd, J = 8.1 and 1.2 Hz), 6.62 (1 H, td, J = 7.2, and 1.2 Hz), 6.93 (1 H, td, J = 7.2 and 1.2 Hz) and 7.41 (1 H, dd, J = 8.1 and 1.2 Hz). Anal. Calcd for $C_{10}H_{11}N$: C, 82.7; H, 7.64; N, 9.65. Found: C, 82.5; H, 7.66; N, 9.54.

4-Methylene-5,8-dichloro-1,2,3,4-tetrahydroquinoline (5c): oil; δ_H (200 MHz; $CDCl_3$) 2.41 (2 H, t, J = 6.0 Hz), 3.42 (2 H, t, J = 6.0 Hz), 4.62 (1 H, br s), 5.22 (1 H, td, J = 2.6 and 1.0 Hz), 5.77 (1 H, d, J = 1.0), 6.52 (1 H, d, J = 8.6 Hz) and 6.91 (1 H, d, J = 8.6 Hz); δ_C (50.3 MHz, $CDCl_3$) 31.9, 43.0, 116.2, 116.5, 118.1, 119.1, 128.0, 130.3, 137.1 and 141.7. Anal. Calcd for $C_{10}H_9NCl_2$: C, 56.1; H, 4.24; N, 6.54. Found: C, 56.4; H, 4.38; N, 6.81.

4-Methylene-6-nitro-1,2,3,4-tetrahydroquinoline (5d): oil; δ_H (200 MHz; $CDCl_3$) 2.57 (2 H, t, J = 6.1 Hz), 3.40 (2 H, t, J = 6.1 Hz), 4.37 (1 H, br s), 4. 90 (1 H, s), 5.48 (1 H, s), 6.38 (1 H, d, J = 8.6 Hz), 7.86 (1 H, dd, J = 8.6, and 2.6) and 8.28 (1 H, d, J = 2.6). Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.2; H, 5.30; N, 14.7. Found: C, 63.3; H, 5.18; N, 14.5.

4-Methylquinoline (6a): oil; δ_H (200 MHz; $CDCl_3$) 2.58 (3 H, d, J = 1.0 Hz), 7.10 (1 H, d, J = 4.4 Hz), 7.47 (1 H, t, J = 8.2 Hz), 7.61 (1 H, t, J = 8.2 Hz), 7.87 (1 H, dd, J = 8.2 and 1.0 Hz), 8.02 (1 H, dd, J = 8.4 and 0.8 Hz) and 8.67 (1 H, d, J = 4.4 Hz); δ_C (50.3 MHz, $CDCl_3$) 18.4, 121.8, 123.8, 126.2, 128.2, 129.1, 130.0, 144.3, 147.9 and 150.2 [HREIMS. Found: 143.0741. $C_{10}H_9N(M^+)$ requires: 143.0735].

4,8-Dimethylquinoline (6b): oil; δ_H (200 MHz; $CDCl_3$) 2.63 (3 H, s), 2.76 (3 H, d, J = 1.0), 7.17 (1 H, d, J = 4.6 Hz), 7.39 (1 H, t, J = 7.8 Hz), 7.47 (1 H, d, J = 8.0 Hz), 7.78 (1 H, d, J = 8.0 Hz) and 8.74 (1 H, d, J = 4.6 Hz); δ_C (50.3 MHz, $CDCl_3$) 18.5, 18.9, 121.8, 121.9, 126.2, 128.1, 129.8, 130.6, 137.2, 145.3 and 148.7; m/z 157 (M^+, 100%), 142 (45), 120 (17), 115 (20). Anal. Calcd for $C_{11}H_{11}N$: C, 84.0; H, 7.05; N, 8.91. Found: C, 84.2; H, 6.84; N, 8.82.

5,8-Dichloro-4-methylquinoline (6c): oil; δ_H (200 MHz; $CDCl_3$) 2.66 (3 H, d, J = 1.0), 7.23 (1 H, d, J = 4.2 Hz), 7.48 (1 H, d, J = 9.2 Hz), 7.89 (1 H, d, J = 9.0 Hz), and 8.70 (1 H, d, J = 4.2 Hz); δ_C (50.3 MHz, $CDCl_3$) 18.7, 122.1, 125.4, 126.8, 127.9, 128.1, 135.8, 146.1, 147.3 and 150.3. Anal. Calcd for $C_{10}H_7NCl_2$: C, 56.6; H, 3.33; N, 6.60. Found: C, 56.4; H, 3.29; N, 6.41.

6-Nitro-4-methylquinoline (6d): oil; δ_H (200 MHz; $CDCl_3$) 2.75 (3 H, d, J = 1.0), 7.33 (1 H, d, J = 4.2 Hz), 8.15 (1 H, d, J = 9.4 Hz), 8.41 (1 H, dd, J = 9.2 and 2.6 Hz), 8.87 (1 H, d, J = 4.4 Hz) and 8.91 (1 H, d, J = 2.6 Hz); δ_C (50.3 MHz, $CDCl_3$) 18.6, 121.0, 122.6, 123.5, 127.4, 131.9, 145.2, 146.8, 150.3 and 153.6; m/z 188 (M^+, 100%), 142 (41), 129 (25) and 115 (76). Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.8; H, 4.28; N, 14.9. Found: C, 63.6; H, 4.15; N, 15.1.

6-Fluoro-4-methylquiniline (6e): oil; δ_H (200 MHz; $CDCl_3$) 2.60 (3 H, d, J = 1.2), 7.19 (1 H, d, J = 4.4 Hz), 7.35 - 7.54 (2 H, m), 8.06 (1 H, dd, J = 9.0 and 5.4 Hz) and 8.67 (1 H, d, J = 4.4 Hz); δ_C (50.3 MHz, $CDCl_3$) 18.6, 107.2, 107.6, 119.2, 119.7, 122.4, 132.2, 132.4, 144.2, 144.4, 144.7, 149.1, 149.2, 158.1 and 163.0. Anal. Calcd for $C_{10}H_8NF$: C, 74.5; H, 5.00; N, 8.69. Found: C, 74.8; H, 4.82; N, 8.43.

3,4-Dimethylquinoline (6f): oil; δ_H (200 MHz; $CDCl_3$) 2.36 (3 H, s), 2.50 (3 H, s), 7.43(1 H, t, J = 8.4 Hz), 7.51 (1 H, t, J = 8.4 Hz), 7.90 (1 H, d, J = 8.8 Hz), 7.96 (1 H, d, J = 8.8 Hz) and 8.56 (1 H, s); δ_C (50.3 MHz, $CDCl_3$) 13.9, 17.2, 123.7, 126.2, 127.9, 128.4, 129.9, 141.0, 146.8 and 152.5. Anal. Calcd for $C_{11}H_{11}N$: C, 84.0; H, 7.05; N, 8.91. Found: C, 84.3; H, 7.15; N, 8.78.

***N*-Buta-2,3-dienylaniline (7a):** oil; δ_H (200 MHz; $CDCl_3$) 3.71 - 3.78 (2 H, m), 4.71 - 4.79 (2 H, m), 5.23 (1 H, quin, J = 6.2 Hz), and 6.51 - 6.94 (5 H, m); δ_C (50.3 MHz, $CDCl_3$) 55.4, 76.7, 88.6, 110.2, 116.8, 121.3, 147.1 and 208.7. Anal. Calcd for $C_{10}H_{11}N$: C, 82.7; H, 7.64; N, 9.65. Found: C, 82.6; H, 7.82; N, 9.58.

***N*-Buta-2,3-dienyl-2,5-dichloroaniline (7c):** oil; δ_H (200 MHz; $CDCl_3$) 3.72 - 3.76 (2 H, m), 4.80 - 4.84 (2 H, m), 5.22 (1 H, quin, J = 6.0 Hz), 6.52 - 6.59 (2 H, m) and 7.07 (1 H, d, J = 8.2 Hz). Anal. Calcd for $C_{10}H_9NCl_2$: C, 56.1; H, 4.24; N, 6.54. Found: C, 56.4; H, 4.41; N, 6.62.

***N*-Buta-2,3-dienyl-4-nitroaniline (7d):** oil; δ_H (200 MHz; $CDCl_3$) 3.94 - 4.00 (2 H, m), 4.71 - 4.78 (2 H, m), 5.11 (1 H, quin, J = 6.2 Hz), 6.61 (2 H, dd, J = 6.4 and 2.2 Hz) and 8.04 (2 H, dd, J = 6.4 and 2.2 Hz); δ_C (50.3 MHz, $CDCl_3$) 49.6, 77.4, 85.9, 111.1, 126.1, 137.7, 152.8 and 209.1; m/z 190 (M^+, 2%), 151 (100) and 105 (22). Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.2; H, 5.30; N, 14.7. Found: C, 63.4; H, 5.52; N, 14.8.

ACKNOWLEDGEMENT

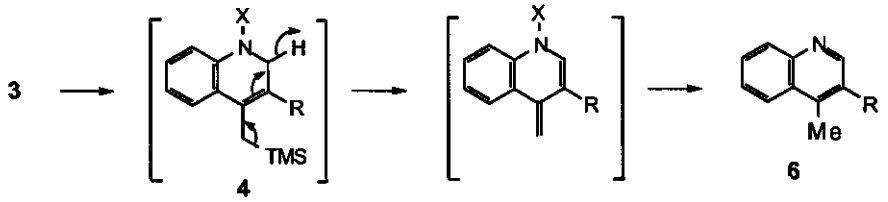
This work was supported by the Korea Science and Engineering Foundation (No.94-0501-08-3 and CBM) and Ministry of Education (BSRI-96-3437). We are also grateful to Prof. Chan-Mo Yu for providing propargyltriphenyltin.

REFERENCES AND NOTES

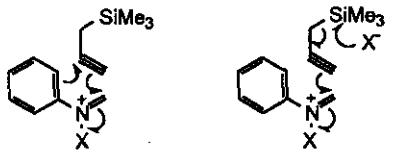
1. This paper is part 8 in the series of "Lewis acid induced synthetic equivalents of imines and iminium ions". For part 7 see, H.-J. Ha, Y.-G. Ahn, J. Do., H. Yun, H.-Y. Koh, J. C. Lee, and K.-B. Lee, *Bull. Kor. Chem. Soc.*, 1997, **18**, 347.
2. (a) P. E. Peterson and R. J. Bopp, *J. Am. Chem. Soc.*, 1967, **89**, 1283. (b) J. P. Bianchini and A. Guillemonat, *Bull. Soc. Chim. Fr.*, 1968, 2120. (c) C. U. Pittman, Jr., *J. Chem. Soc., Chem. Commun.*, 1969, 122. (d) M. L. Poutsma and P. A. Ibarbia, *J. Am. Chem. Soc.*, 1971, **93**, 440. (e) W. F. Verhelst and W, Drenth, *J. Am. Chem. Soc.*, 1974, **96**, 6692 (f) F. Marcuzzi and G. Melloni, *J. Am. Chem. Soc.*, 1976, **98**, 3295. (g) D. J. Pasto, M. F. Miles, and S.-K. Chou, *J. Org. Chem.*, 1977, **42**, 3098. (h) M. Edens, D. Boerner, C. R. Chase, D. Nass, and M. D. Schiavelli, *J. Org. Chem.*, 1977, **42**, 3403.
3. (a) H. M.Weiss, *J. Chem. Educ.*, 1993, **70**, 873. (b) T. T. Tidwell, *J. Chem. Educ.*, 1996, **73**, 1081. (c) H. M.Weiss, *J. Chem. Educ.*, 1996, **73**, 1082.
4. (a) Y. Ogata, A. Kawasaki, and S. Suyama, *J. Chem. Soc. (B)*, 1969, 805. (b) R. M. Magid, O. S. Fruchey, W. L. Johnson, and T. G. Allen, *J. Org. Chem.*, 1979, **44**, 359. (c) A. Sugumori, T. Yamada, H. Ishida, M. Nose, K. Terashima, and N. Oohata, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3905. (d) R. C. Larock and S. Babu, *Tetrahedron Lett.*, 1987, **28**, 5291. (e) H. McNab and M. E.-A. Murray, *J. Chem. Soc., Perkin. Trans. I*, 1988, 333. (f) R. C. Larock and M.-Y. Kuo, *Tetrahedron Lett.*, 1991, **32**, 569. (g) P. J. Campos, C.-Q. Tan, M. A. Rodriguez, and E. J. Anon, *J. Org. Chem.*, 1996, **61**, 7195. (h) S. Kobayashi and S. Nagayama, *J. Am. Chem. Soc.*, **1996**, *118*, 8977. (i) J. I. Ubeda, M. Villacampa, and C. Avendano, *Synlett*, 1997, 285. (j) K. Uchiyama, Y. Hayashi, and K. Narasaka, *Synlett* 1997, 445.
5. The structure of *N*-methyleneamine equivalents were not fully characterized yet. But we can speculated the structures as shown in the bracket of the scheme.[7c]
6. For a comprehensive review see, (a) M. Tramontini and L. Angiolini, *Tetrahedron*, 1990, **46**, 1791; (b) E. F. Kleinman, in Comprehensive Organic Synthesis, ed. by B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 2, pp. 893-973. (c) M. Tramontini and L. Angiolini, Mannich Bases Chemistry and Uses; CRC Press: Boca Raton, FL, 1994.
7. (a) H.-J. Ha, G.-S. Nam, and K. P. Park, *Tetrahedron Lett.*, 1990, **31**, 1567. (b) H.-J. Ha, G.-S. Nam, and K. P. Park, *Bull. Kor. Chem. Soc.*, 1990, **11**, 485. (c) H.-J. Ha, G.-S. Nam, and K. P. Park, *Synth. Commun.*, 1991, **21**, 155. (d) H.-J. Ha and Y.-G. Ahn, *Synth. Commun.*, 1995, **25**, 969. (e) H.-J. Ha, Y.-G. Ahn, and J.-K. Chon, *J. Chem. Soc., Perkin Trans. I*, 1995, 2631. (f) H.-J. Ha, K.-H. Kang, A.-G. Ahn, and S.-J. Oh, *Heterocycles*, 1997, **45**, 277. (g) H.-J. Ha, K.-

H. Kang, J.-M. Suh, and Y.-G. Ahn, *Tetrahedron Lett.*, 1996, **37**, 7069. (h) H.-J. Ha and Y.-G. Ahn, *Synth. Commun.*, 1997, **27**, 1543.

8. For a comprehensive review see, W. P. Weber, Silicon Reagents for Organic Synthesis; Springer-Verlag: New York, 1983, pp. 129 - 158.
9. Addition of propargyltrimethylsilanes to the α-position of amines, see, (a) H. Hiemstra, H. P. Fortgens, and W. N. Speckamp, *Tetrahedron Lett.*, 1984, **25**, 3115. (b) P. M. Esch, H. Hiemstra, and W. N. Speckamp, *Tetrahedron Lett.*, 1988, **29**, 367.
10. (a) I. Fleming and I. Paterson, *Synthesis*, 1979, 446. (b) At this moment can be proposed an alternative pathway that is independent to the formation of **5**, i.e. direct elimination of TMS from **4** to **6**.



11. Similar proteodesilylation of **4** (X= Acetyl) was reported without isolation of allyl silanes in the presence of $TiCl_4$.[9b]
12. M. Santelli and J.-M. Pons, Lewis Acids and Selectivity in Organic Chemistry; CRC Press: Boca Raton, FL, 1996.
13. There is still another possibility that the formation of **4** and **7** starting from **2** proceeds by a concerted cationic cyclization and concerted elimination reaction as followings.



14. The [4π+2π] cycloaddition with subsequent tautomerization pathway was proposed for the synthesis of 1,2,3,4-tetrahydroquinolines from 2-azabutadiene based on the exceptionally high stereoselectivities. (a) U. Beifuss and S. Ledderhose, *J. Chem. Soc. Chem. Commun.*, 1995, 2137. (b) U. Beifuss, O. Kunz, S. Ledderhose, M. Taraschewski, and C. Tonko, *Synlett* 1996, 34. (c) A. S. Caille, L. Trimble, C. Berthelette, and C. K. Lau, *Synlett* 1996, 669.
15. Reactions of propargyl and allenic organometallics with imines and iminium ions were reported. (a) G. Courtois, M. Harama, and Ph. Miginiac, *J. Organomet. Chem.*, 1980, **198**, 1. (b) G. Courtois, M. Harama, and Ph. Miginiac, *J. Organomet. Chem.*, 1981, **218**, 1. (c) G. Courtois, M. Harama, and Ph. Miginiac, *J. Organomet. Chem.*, 1981, **218**, 275. (d) G. Courtois, D. Mesnard, B. Dugue, and Ph. Miginiac, *Bull. Soc. Chim. Fr.*, 1987, 93 (e) Y. Ryu and G. Kim, *J. Org. Chem.*, 1995, **60**, 103.
16. Bond dissociation energies of C-Si and C-Sn are 414 and 297±17 KJ/mol at 289K respectively in the molecules of s-C_4H_9-$Si(CH_3)_3$ and CH_3-$Sn(CH_3)_3$. D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, 1982, **33**, 493.

Received, 25th July, 1997