

ADDITION OF PROPARGYLTRIMETHYLSILANE TO *N*-METHYLENEAMINE EQUIVALENTS: GENERATION AND ELECTROPHILIC CYCLIZATION OF VINYLIC CARBOCATIONS¹

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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.

Limited 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 equivalents⁵ 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

For the mechanistic detail *N*-(methoxymethyl)aniline and 1,3,5-triphenylhexahydro-1,3,5-triazine yield the *N*-methylenamine 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 ·OEt ₂		58	
1a	Ph	Me	BF ₃ ·OEt ₂		47	
1b	2-Me-C ₆ H ₄	H	BF ₃ ·OEt ₂		43	
1c	2,5-Cl ₂ -C ₆ H ₃	H	TiCl ₄	23	29	22
1c	2,5-Cl ₂ -C ₆ H ₃	H	BF ₃ ·OEt ₂		48	
1d	4-NO ₂ -C ₆ H ₄	H	TiCl ₄	6	30	23
1d	4-NO ₂ -C ₆ H ₄	H	BF ₃ ·OEt ₂		46	
2a	Ph	H	TiCl ₄	19	31	29
2a	Ph	H	BF ₃ ·OEt ₂		41	
2a	Ph	Me	BF ₃ ·OEt ₂		48	
2b	2-Me-C ₆ H ₄	H	BF ₃ ·OEt ₂		41	
2c	2,5-Cl ₂ -C ₆ H ₃	H	TiCl ₄	13	21	27
2c	2,5-Cl ₂ -C ₆ H ₃	H	BF ₃ ·OEt ₂		62	
2c	4-F-C ₆ H ₄	H	BF ₃ ·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 $\text{BF}_3 \cdot \text{OEt}_2$ was yielded **6** as a dominant product. Relatively lower nucleophilicity of $\text{BF}_3 \cdot \text{OEt}_2$ 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-substituted quinolines.

This reaction sequence of addition of *N*-methylethylamine equivalent to alkyne followed by intermolecular 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 $\text{BF}_3 \cdot \text{OEt}_2$ 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 propargyltriphenyltin¹⁵ 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*-methylethylamine 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

¹H-NMR and ¹³C-NMR spectra were recorded on a Gemini 200 (200 MHz for ¹H and 50.3 MHz for ¹³C). 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 CH₂Cl₂ (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. NaHCO₃ solution. The reaction product was extracted with CH₂Cl₂. Organic layer was washed successively with water and brine, dried over anhydrous Na₂SO₄, 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 dissolved 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. NaHCO₃ 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; CDCl₃) 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 C₁₀H₁₁N: 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; CDCl₃) 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, CDCl₃) 31.9, 43.0, 116.2, 116.5, 118.1, 119.1, 128.0, 130.3, 137.1 and 141.7. Anal. Calcd for C₁₀H₉Cl₂N: 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; CDCl₃) 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 C₁₀H₁₀N₂O₂: 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; CDCl₃) 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, CDCl₃) 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. C₁₀H₉N(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 $\text{C}_{11}\text{H}_{11}\text{N}$: 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 $\text{C}_{10}\text{H}_7\text{NCl}_2$: 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 $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$: C, 63.8; H, 4.28; N, 14.9. Found: C, 63.6; H, 4.15; N, 15.1.

6-Fluoro-4-methylquinoline (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 $\text{C}_{10}\text{H}_8\text{NF}$: 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 $\text{C}_{11}\text{H}_{11}\text{N}$: 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 $\text{C}_{10}\text{H}_{11}\text{N}$: 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 $\text{C}_{10}\text{H}_9\text{NCl}_2$: 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 $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2$: C, 63.2; H, 5.30; N, 14.7. Found: C, 63.4; H, 5.52; N, 14.8.

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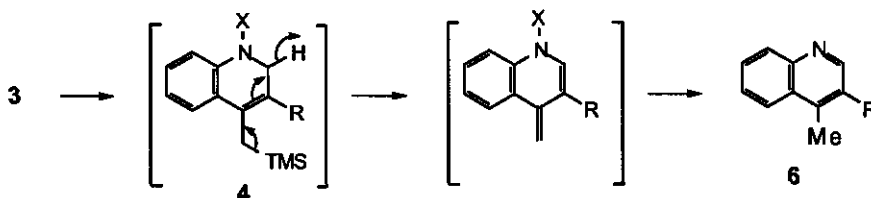
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REFERENCES AND NOTES

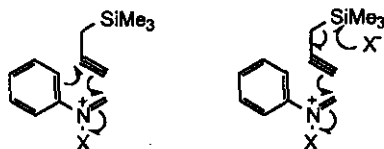
1. This paper is part 8 in the series of "Lewis acid induced synthetic equivalents of imines and iminium ions". For part 7 see, H.-J. Ha, Y.-G. Ahn, J. Do., H. Yun, H.-Y. Koh, J. C. Lee, and K.-B. Lee, *Bull. Kor. Chem. Soc.*, 1997, **18**, 347.
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