Reactions of *N*-Aryl-1*H*-benzotriazolyl-1-methanamines with Allyl Trimethylsilanes. A Facile Route to Trialkylsilane Tetrahydroquinolines

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N-Aryl-1*H*-benzotriazolyl-1-methanamines **1**, easily accessible from the condensation of anilines with formaldehyde and benzotriazole, undergo Lewis acid assisted reactions with allyltrimethylsilanes to give 4-(trimethylsilyl)methyl-1,2,3,4-tetrahydroquinolines **2** in good to high yields.

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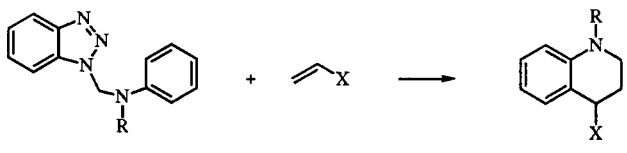
Introduction.

1,2,3,4-Tetrahydroquinolines are of great interest due to their biological activities; other industrial applications of tetrahydroquinolines include components of imaging compositions [1], recording materials [2], photoreceptors [3], adhesives [4], and polymerization catalysts [5].

Numerous synthetic methods have been reported for the synthesis of 1,2,3,4-tetrahydroquinolines [6] including: (i) reduction of the heterocyclic ring in quinolines [7] and 1,2-dihydroquinolines [8], (ii) condensation of anilines with two molecules of aldehydes [9], (iii) cross-coupling of *ortho*-substituted anilines by acid or metal catalysis [10], and (iv) ring closure of aniline imines [11]. The nature, number, and relative location of the substituents on the nitrogen atom, heterocyclic ring, and aromatic ring of tetrahydroquinolines are the key parameters in determining the optimum synthetic method. Cycloaddition reactions of *N*-aryl alkyleneiminium cations with olefins, a subcategory of route iv, are attractive because of their versatility [12]. Benzotriazole-mediated methodology can provide 2-, 3-, and 4-monosubstituted and 3,4-disubstituted tetrahydroquinolines by the treatment of *N*-(α-aminoalkyl)benzotriazoles with 1,3-dienes [13], α,β-unsaturated ethers [14], *N*-vinylamides [15], enolizable aldehydes [9b] or unactivated alkenes [16] (Scheme 1).

Scheme 1



1

R = H, Me, Ph X = OEt, NR'COR", Carbazol-9-yl, Ph, Propene-2-yl

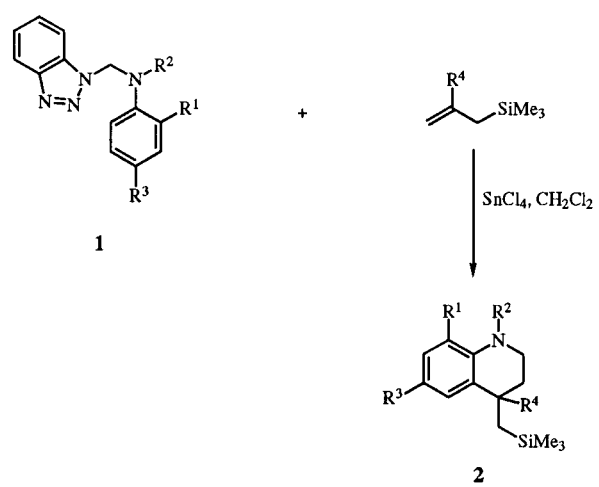
Recent attention has been focused on the synthesis and application of allylsilanes as synthetic reagents [17]. The Hosomi-Sakurai Lewis acid catalyzed addition of trimethylallylsilane to electrophiles has been well investigated [18]. However, the only reported preparations of tetrahydroquinolines [19] from allylsilanes and *N*-arylalkylene iminium cations start from triphenylhexahydro-1,3,5-triazine or from *N*-(alkoxymethyl)anilines, which need to be prepared by electrochemical or ruthenium catalyzed oxidation of *N*-methylanilines, and gave homoallylic anilines as significant by-products.

We now extend the Lewis acid induced reactions of *N*-aryl-1*H*-benzotriazole-1-methanamines **1** to include allylsilanes.

Results and Discussions.

N-Phenyl-1*H*-benzotriazolyl-1-methanamine (**1a**) and allyl trimethylsilane in the presence of stannic chloride gave 4-(trimethylsilyl)methyl-1,2,3,4-tetrahydroquinoline (**2a**) in 85% isolated yield (Table 1, entry 1). Derivatives of **1a** substituted on the phenyl ring (**1b**, **1c**) and *N*-atom (**1d**) similarly gave tetrahydroquinolines **2b**, **2d** and **2e**. When (2-methylallyl) trimethylsilane was used as the substrate, a quaternary carbon was formed at the 4-position of tetrahydroquinoline to give 4,4-disubstituted tetrahydroquinolines (Table 1, entry 3, 6, 8, 10) which are difficult to make by other routes (*e.g.* route i, reduction of quinolines or 1,2-dihydroquinolines).

Scheme 2



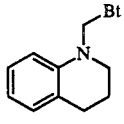
1 **2**

Table 1

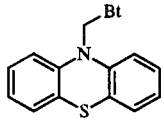
Reactions of *N*-Aryl-1*H*-benzotriazole-1-methanamine **1** with Allylsilanes in the Presence of Lewis Acid

Entry	Aminal **1**		Substrate	Product **2**	Yield (%) [a]
1	**1a**	$R^1 = R^2 = H$, $R^3 = H$	$R^4 = H$	**2a**	85
2	**1b**	$R^1 = Me$, $R^2 = H$, $R^3 = H$	$R^4 = H$	**2b**	76
3	**1b**	$R^1 = Me$, $R^2 = H$, $R^3 = H$	$R^4 = Me$	**2c**	67
4	**1c**	$R^1 = Cl$, $R^2 = H$, $R^3 = H$	$R^4 = H$	**2d**	62
5	**1d**	$R^1 = H$, $R^2 = Ph$, $R^3 = H$	$R^4 = H$	**2e**	85
6	**1d**	$R^1 = H$, $R^2 = Ph$, $R^3 = H$	$R^4 = Me$	**2f**	87
7	**1e**	[b]	$R^4 = H$	**2g**	69
8	**1e**	[b]	$R^4 = Me$	**2h**	86
9	**1f**	[b]	$R^4 = H$	**2i**	81
10	**1g**	[b]	$R^4 = Me$	**2j**	71
11	**1h**	$R^1 = R^2 = H$, $R^3 = OMe$	$R^4 = H$	**2k**	75

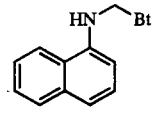
[a] Isolated yields; [b] The structures of **1e**, **1f** and **1g** are:



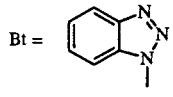
1e



1f

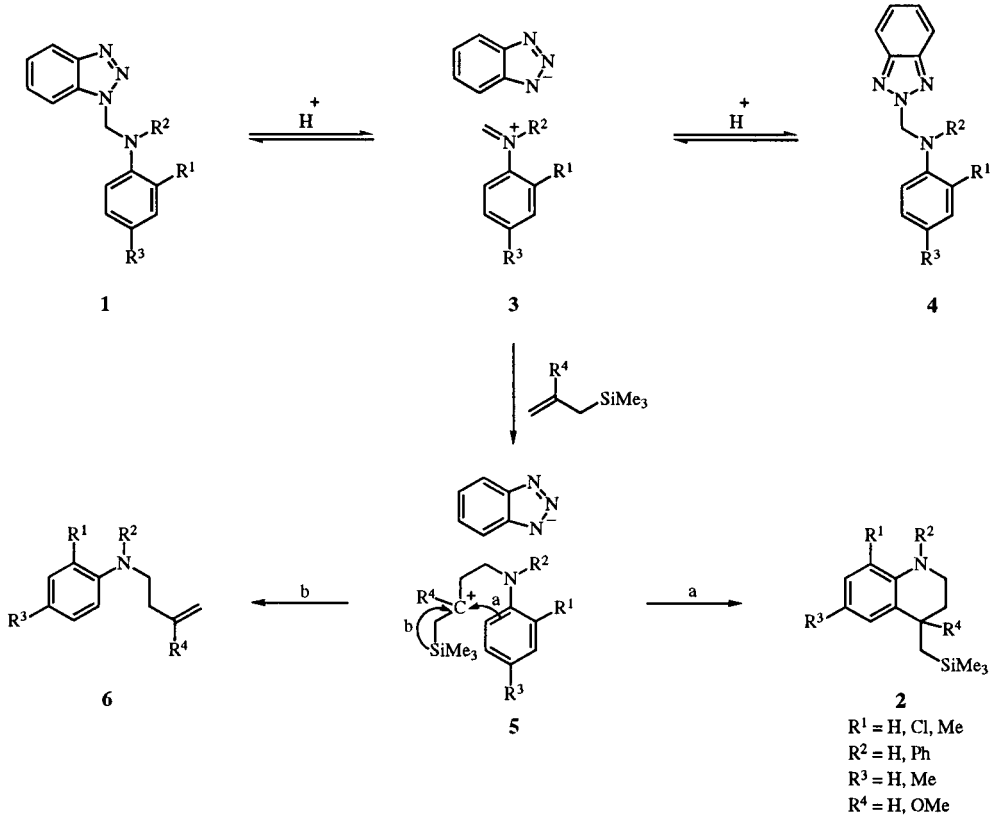


1g



N-Aryl-1*H*-benzotriazolyl-1-methanamines **1** undergo reversible equilibration with the benzotriazol-2-yl derivatives **4**. The isomerization, proceeding *via* the ion pair **3** (Scheme 3), is slow at room temperature, but rapid upon heating or acidification; a small amount of acid can cause a dramatic rate increase [20]. Subsequent addition of allyltrimethylsilanes to **3** forms the cationic intermediate **5** from which there are two competitive pathways: a)

Scheme 3



1 **3** **4**

6 **5** **2**

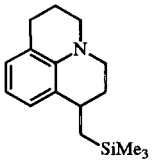
R^1 = H, Cl, Me
R^2 = H, Ph
R^3 = H, Me
R^4 = H, OMe

intramolecular electrophilic aromatic attack to give tetrahydroquinoline silanes **2**, and b) loss of the trimethylsilyl group to produce homoallylic anilines **6**. Tetrahydroquinoline silanes **5** comprise >90% of the crude products, which shows that route a) dominates.

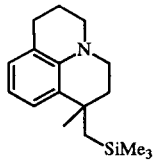
The benzotriazole group both stabilizes starting material **1** and renders it reactive enough to readily produce iminium cations **3**. Changing the benzotriazole group (Bt) of **1a** and **1c** to the methoxy (OMe) group reduces the yields (**2a**: 42%; **2c**: 46%), and **2c** is accompanied with 16% of the homoallyl aniline by-product [19a].

This method was extended by having a naphthyl ring instead of a phenyl ring (**2j**, entry 10), and commencing with aniline derivatives in which the nitrogen atom is built into a heterocyclic system. This latter extension allowed the addition of a another ring to the system as exemplified by the conversion of a tetrahydroquinoline derivative into julolidines **2g**, **2h** and a phenothiazine derivative into **2i** (Scheme 4).

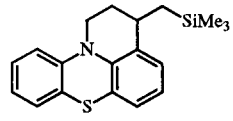
Scheme 4



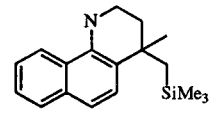
2g



2h



2i



2j

In conclusion, tetrahydroquinoline trialkylsilanes have been prepared from readily available, crystalline *N*-aryl-1*H*-benzotriazolyl-1-methanamines in good to high yields.

EXPERIMENTAL

The nmr spectra were recorded on a Varian Gemini-300 in deuteriochloroform with tetramethylsilane as the internal reference for ^{1}H (300 MHz) or solvent as the internal reference for ^{13}C (75 MHz). Elemental analyses (CHN) were carried out with a Carlo Erba 1106 instrument. The preparation and characterization of the *N*-aryl-1*H*-benzotriazolyl-1-methanamines **1a-1g** were in accordance with the literature [13,16,21].

General Procedure for the Preparation of Tetrahydroquinolines **2** *via* Benzotriazole Derivatives **1**.

Allyltrimethylsilane (2 equivalents) was added to a solution of *N*-aryl-1*H*-benzotriazolyl-1-methanamine **1** (2 mmoles) in dry methylene chloride (20 ml) at -78° under an inert atmosphere. Then stannic chloride (0.2 ml) was added to the stirred mixture. The resulting mixture was kept at -78° for 2 hours and then allowed to warm up to room temperature overnight. A sodium hydroxide solution (2*N*, 20 ml) was added. The layers were separated, and the aqueous layer was extracted with methylene chloride (3 x 30 ml). The combined organic materials were washed with brine, dried over sodium sulfate and concentrated under reduced pressure to give a residue, which was then purified by column chromatography to give the pure product. All the products are oily and stable enough to keep at room temperature for months without any change. Known compounds **2a**, **2b** were characterized by comparison of their nmr spectral data with literature values [19a].

4-Trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline (**2a**).

This compound had ^{1}H nmr: δ 0.10 (s, 9H), 0.85-0.95 (m, 1H),1.03-1.09 (m, 1H), 1.70-1.78 (m, 1H), 1.96-2.04 (m, 1H), 2.94-2.98 (m, 1H), 3.24-3.31 (m, 1H), 3.35-3.43 (m, 1H), 3.85 (br s, 1H), 6.46-6.51 (m, 1H), 6.61-6.68 (m, 1H), 6.94-7.06 (m, 2H); ^{13}C nmr: δ 0.6, 25.6, 29.1, 31.8, 38.4, 114.0, 116.8, 126.5, 128.3, 128.5, 143.8; ms: m/z 220 (M^+, 10%), 132 (100).

8-Methyl-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline (**2b**).

This compound had ^{1}H nmr: δ 0.08 (s, 9H), 0.76-0.86 (m, 1H), 0.92-0.98 (m, 1H), 1.62-1.67 (m, 1H),1.86-1.95 (m, 1H), 1.99 (s, 3H), 2.87-2.91 (m, 1H), 3.23-3.34 (m, 2H), 3.55 (br s, 1H), 6.52 (t, J = 7.4 Hz, 1H), 6.80-6.84 (m, 2H); ^{13}C nmr: δ 0.6, 17.2, 26.0, 28.9, 32.0, 38.5, 116.2, 120.9, 126.5, 127.6, 127.8, 141.7.

8-Methyl-4-trimethylsilylmethyl-4'-methyl-1,2,3,4-tetrahydroquinoline (**2c**).

This compound had ^{1}H nmr: δ 0.00 (s, 9H), 1.17, 1.25 (AB, J = 14.8 Hz, 2H), 1.40 (s, 3H), 1.75-1.81 (m, 1H), 1.91-1.98 (m, 1H), 2.11 (s, 3H), 3.38-3.42 (m, 2H), 3.72 (br s, 1H), 6.62 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.1 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H); ^{13}C nmr: δ 0.8, 17.5, 32.8, 33.3, 34.7, 36.8, 38.7, 116.2, 120.8, 124.5, 127.5, 131.3, 141.3.

Anal. Calcd. for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18; N, 5.66. Found: C, 73.19; H, 10.66; N, 6.02.

8-Chloro-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline (**2d**).

This compound had ^{1}H nmr: δ 0.19 (s, 9H), 0.82-0.93 (m, 2H), 1.62-1.68 (m, 1H), 1.83-1.87 (m, 1H), 2.87-2.91 (m, 1H), 3.27-3.36 (m, 2H), 4.37 (br s, 1H), 6.47 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H); ^{13}C nmr: δ -0.6, 25.4, 28.2, 32.2, 37.9, 116.1, 118.0, 126.5, 126.8, 129.4, 139.7.

Anal. Calcd. for $C_{13}H_{20}NSiCl$: C, 61.51; H, 7.94; N, 5.52. Found: C, 61.32; H, 8.37; N, 5.63.

1-Phenyl-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline (**2e**).

This compound had ^{1}H nmr: δ -0.03 (s, 9H), 0.80-0.90 (m, 1H), 0.95-1.08 (m, 1H), 1.72-1.78 (m, 1H), 2.00-2.04 (m, 1H), 2.89-2.95 (m, 1H), 3.51-3.57 (m, 2H), 6.63-6.68 (m, 1H), 6.74-6.77 (m, 1H), 6.83-6.88 (m, 1H), 6.90-6.98 (m, 1H), 7.02-7.04 (m, 1H), 7.11-7.18 (m, 2H), 7.21-7.26 (m, 2H); ^{13}C nmr: δ -0.6, 24.0, 30.4, 32.9, 46.8, 116.7, 118.7, 122.9, 123.3, 126.2, 128.1, 129.3, 132.4, 143.1, 148.2; ms: m/z 295 (M^+, 70%), 208 (100).

Anal. Calcd. for $C_{19}H_{25}NSi$: C, 77.23; H, 8.53; N, 4.74. Found: C, 76.81; H, 9.02; N, 4.83.

1-Phenyl-4-trimethylsilylmethyl-4'-methyl-1,2,3,4-tetrahydroquinoline (**2f**).

This compound had ^{1}H nmr: δ 0.00 (s, 9H), 1.23 (s, 2H), 1.46 (s, 3H), 1.80-1.88 (m, 1H), 2.03-2.09 (m, 1H), 3.58-3.66 (m, 1H), 3.70-3.79 (m, 1H), 6.77-6.87 (m, 2H), 6.93-6.98 (m, 1H), 7.06-7.11 (m, 1H), 7.23-7.39 (m, 5H); ^{13}C nmr: δ 0.7, 31.6, 32.0, 35.0, 37.9, 46.8, 116.5, 118.5, 122.9, 123.5, 126.0, 126.4, 129.2, 134.9, 142.7, 148.3.

Anal. Calcd. for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79; N, 4.53. Found: C, 77.35; H, 9.25; N, 4.85.

3-Trimethylsilylmethyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]-quinoline (**2g**).

This compound had ^{1}H nmr: δ 0.16 (s, 9H), 0.97 (dd, J = 10.5, 15.0 Hz, 1H), 1.10 (dd, J = 3.9, 12.0 Hz, 1H), 1.78-1.84 (m, 1H), 2.03-2.13 (m, 3H), 2.83-2.87 (m, 2H), 2.98-3.05 (m, 1H), 3.10-3.17 (m, 1H), 3.22-3.31 (m, 3H), 6.62 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.1 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H); ^{13}C nmr: δ -0.6, 22.1, 26.0, 27.8, 28.9, 32.5, 46.4, 50.1, 115.5, 121.4, 126.1, 126.7, 128.6, 141.8; ms: m/z 259 (M^+, 40%), 172 (100).

Anal. Calcd. for $C_{16}H_{25}NSi$: C, 74.08; H, 9.72; N, 5.40. Found: C, 74.46; H, 9.99; N, 5.68.

1-Methyl-1-trimethylsilylmethyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido-[3,2,1-*ij*]quinoline (**2h**).

This compound had ^{1}H nmr: δ 0.00 (s, 9H), 1.15, 1.20 (AB, J = 14.8 Hz, 2H), 1.38 (s, 3H), 1.74-1.82 (m, 1H), 1.93-2.02 (m, 3H), 2.78-2.80 (m, 2H), 3.14-3.22 (m, 4H), 6.57 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 6.9 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H); ^{13}C nmr: δ 0.7, 22.2, 28.0, 32.8, 33.2, 35.0, 36.8, 46.7, 50.4, 115.6, 121.4, 124.3, 126.7, 132.1, 141.5.

Anal. Calcd. for $C_{17}H_{27}NSi$: C, 74.66; H, 9.95; N, 5.12. Found: C, 74.83; H, 10.68; N, 5.43.

3-Trimethylsilylmethyl-2,3-dihydro-1*H*-pyrido[3,2,1-*kj*]phenothiazine (**2i**).

This compound had ^{1}H nmr: δ 0.07 (s, 9H), 0.75 (dd, J = 9.9, 15.0 Hz, 1H), 0.90 (dd, J = 4.5, 15.0 Hz, 1H), 1.80-1.86 (m, 1H), 2.05-2.08 (m, 1H), 2.81-2.85 (m, 1H), 3.47-3.52 (m, 1H), 3.59-3.63 (m, 1H), 6.66-6.71 (m, 1H), 6.75-6.81 (m, 4H), 6.96-7.05 (m, 2H); ^{13}C nmr: δ -0.6, 24.2, 28.2, 32.6, 42.4, 112.7, 120.0, 121.7, 121.8, 122.2, 125.0, 126.8, 127.0, 127.2, 131.4, 140.2, 144.5.

Anal. Calcd. for $C_{19}H_{23}NSiS$: C, 70.10; H, 7.12; N, 4.30. Found: C, 69.71; H, 7.50; N, 4.44.

4-Methyl-4-trimethylsilylmethyl-1,2,3,4-tetrahydrobenzo[*h*]quinoline (**2j**).

This compound had ^{1}H nmr: δ 0.01 (s, 9H), 1.25, 1.31 (AB, J = 14.9 Hz, 2H), 1.46 (s, 3H), 1.83-1.87 (m, 1H), 2.03-2.07 (m, 1H), 3.41-3.47 (m, 2H), 4.42 (br s, 1H), 7.22-7.25 (m, 1H), 7.41-7.44 (m, 3H), 7.69-7.77 (m, 2H); ^{13}C nmr: δ 0.8, 33.1, 33.4, 34.8, 37.0, 38.9, 116.8, 119.8, 123.1, 124.6, 124.8, 125.5, 125.8, 128.3, 132.6, 137.6; hrms Calcd. for $C_{18}H_{25}NSi$ 283.1756. Found: 283.1756.

6-Methoxy-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline (**2k**).

This compound had ^{1}H nmr: δ 0.03 (s, 9H), 0.80 (dd, J = 10.5, 14.4 Hz, 1H), 0.98 (dd, J = 3.6, 15.0 Hz, 1H), 1.58-1.66 (m, 1H), 1.86-1.94 (m, 1H), 2.80-2.86 (m, 1H), 3.08-3.15 (m, 1H), 3.20-3.27 (m, 1H), 3.65 (s, 3H), 6.33 (d, J = 8.5 Hz, 1H), 6.96-7.05 (m, 2H); ^{13}C nmr: δ 0.63, 25.8, 29.5, 32.1, 38.9, 55.8, 112.4, 114.4, 115.2, 129.9, 138.0, 151.7.

Anal. Calcd. for $C_{14}H_{23}NOSi$: C, 67.42; H, 9.29. Found: C, 67.19; H, 9.58.

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