Lewis Acid Assisted Reactions of *N*-(α-Aminoalkyl)benzotriazoles and Unactivated Alkenes for the Facile Synthesis of 4-, 2,4-, and 3,4-Substituted 1,2,3,4-Tetrahydroquinolines

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Received March 7, 1997

A range of substituted tetrahydroquinolines have been synthesized from benzotriazole derivatives and unactivated alkenes in the presence of a Lewis acid. These reactions utilize readily available starting materials and mild reaction conditions, and give high yields. The reaction mechanisms are discussed.

J. Heterocyclic Chem., **34**, 1259 (1997).

Introduction.

1,2,3,4-Tetrahydroquinolines play an important role in medicinal and industrial chemistry due to their significant biological and physiological activity, as recently reviewed [1]. Many synthetic methods have been reported for the synthesis of 1,2,3,4-tetrahydroquinolines [1], including direct reductions of quinolines [2] and 1,2-dihydroquinolines [3], modification of other 1,2,3,4-tetrahydroquinolines [4], and ring closure of imines [1,5,6]. Among available methods, cycloaddition reactions of *N*-arylalkyleneiminium cations with olefins [7] are highly attractive, but existing application of these methods all display some limitations: (i) starting materials difficult to obtain and/or manipulate [5e,7c,g,j]; (ii) only activated alkenes useful [5b,7d,i,j,l-n]; (iii) 2-substituted and *N*-unsubstituted 1,2,3,4-tetrahydroquinolines difficult to prepare [7c,f-h].

The mechanism of the reactions of *N*-arylalkyleneiminium cations with olefins remains uncertain. Early work of Swan [7a] proposed a polar 1,4-cycloaddition for electron-rich alkenes; however, Shono *et al.* [7c] rationalized their results as a two-step process. In support of the latter mechanism, Mellor and co-workers [7d,e] isolated the reaction intermediates, which were then cyclized to give the tetrahydroquinolines; the observed high stereospecificities of the olefins (usually interpreted as evidence of a concerted cyclization reaction) were interpreted as analogous to high stereoselectivities observed in related multi-step cyclizations [8]. Additionally, Murahashi *et al.* [7f] found that *trans*-1,3-dimethyl-4-(trimethylsilylmethyl)-1,2,3,4-tetrahydroquinoline was obtained stereoselectively (*trans/cis* = 94/6) by the titanium tetrachloride-induced reaction of *N*-(*t*-butyldioxymethyl)-*N*-methylaniline with crotyltrimethylsilane (*E/Z* = 4/1). More recently, Beifuss and co-workers [7g,h] again observed high stereospecificity for these reactions: the stereochemistries of the dienophiles (*E* or *Z*) were preserved almost completely, even though AM1 and PM3 calculations showed that the *trans*-tetrahydroquinoline was more stable than the *cis*-isomer. Together with the fact that no side products could be isolated, these workers [7g,h] interpreted their results in terms of a one-step concerted polar cycloaddition.

We now report our new results on the synthesis of substituted 1,2,3,4-tetrahydroquinolines from readily available and crystalline *N*-(α–aminoalkyl)benzotriazoles [9] and present more evidence for the reaction mechanism.

Results and Discussion.

α-Aminomethylbenzotriazole **1** reacted with 1-octene in the presence of boron trifluoride etherate (2 equivalents) to give tetrahydroquinoline **3a** in 85% isolated yield (Scheme 1). Among other Lewis acids used for the same reaction, tin(IV) chloride (0.5-2 equivalents) and titanium(IV) chloride (2 equivalents) gave **3a** in 98% and 79% yields, respectively; zinc bromide (2 equivalents) resulted only in *N*-methylaniline and *N,N*-dimethylaniline and no reaction occured using ytterbium triflate (10 mol%). It has been reported [10] that α-aminomethylenebenzotriazole is in equilibrium with

Table 1

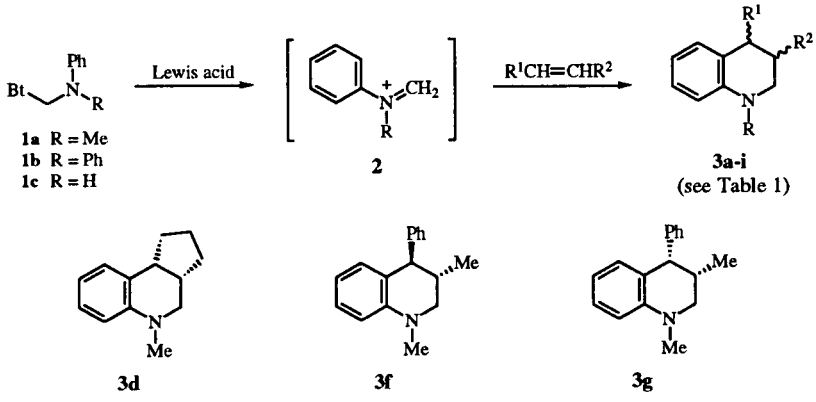
Reactions of Aminobenzotriazoles **1** with Alkenes in the Presence of Lewis Acid

Product [a]	R	R^1	R^2	Lewis acid	yield (%) [b]
3a	Me	*n*-C_6H_{13}	H	BF_3Et_2O	85
3a	Me	*n*-C_6H_{13}	H	$SnCl_4$	98
3b	Me	*n*-C_4H_9	H	BF_3Et_2O	84
3c	Me	*n*-C_8H_{17}	H	BF_3Et_2O	87
3d	Me	Ph	H	BF_3Et_2O	95
3e [c]	Me	-$(CH_2)_3$-		BF_3Et_2O	94
3f [c]	Ph	-$(CH_2)_3$-		$SnCl_4$	97
3g [d]	Me	Ph	CH_3	$SnCl_4$	98
3h [e]	Me	Ph	CH_3	$SnCl_4$	86
3i	H	-$(CH_2)_3$-		$SnCl_4$	39

[a] All compounds were characterized by ^1H, ^{13}C nmr and mass spectrometry, satisfactory microanalyses were obtained for novel compounds. [b] GC yields; except for **3d**, which is isolated yield. [c] Only *cis*-isomer is obtained from *cis*-alkene. [d] Only *trans*-isomer is obtained from *trans*-alkene. [e] A *cis/trans* = 95/5 mixture of β-methylstyrene was used and the product had a *cis/trans* = 95/5 ratio as well.

Scheme 1

1, alkenes (1.5-2.0 equivalents), Lewis acid, CH_2Cl_2, 0° 2 hours

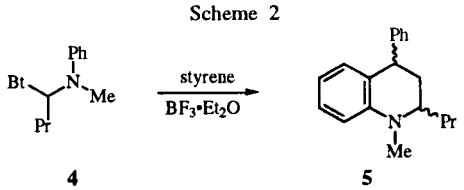


the iminium cation **2** in solutions. Our results show that while zinc bromide may shift the equilibrium to the iminium cation, boron trifluoride etherate, stannic chloride, and titanium tetrachloride also assist the iminium cation **2** in reaction with 1-octene to afford 1,2,3,4-tetrahydroquinoline **3a**.

Various unactivated 1-alkenes and 1,2-disubstituted alkenes reacted with α-aminomethylenebenzotriazole **1a,b** in the presence of boron trifluoride etherate or stannic chloride to afford 4-substituted or 3,4-disubstituted 1,2,3,4-tetrahydroquinoline **3b-h** in excellent yields (Table 1). All of the reactions of 1,2-disubstituted alkenes, *trans*-β-methylstyrene, *cis*-β-methylstyrene and cyclopentene, were stereospecific and produced the corresponding 3,4-disubstituted 1,2,3,4-tetrahydroquinoline **3e-h** with retention of the stereochemistries of the dienophiles (Scheme 1). These observations support a concerted cationic [4+2] cycloaddition in this reaction system.

The presently reported protocol has two major advantages. The first one is that unactivated 1-alkenes and 1,2-disubstituted alkenes can be used, as exemplified above. Secondly, this method can be employed for the preparation of *N*-unsubstituted and 2-substituted tetrahydroquinolines. The reaction of α-(phenylamino)methylenebenzotriazole (**1c**) and cyclopentene, under the same conditions, resulted in *N*-unsubstituted 1,2,3,4-tetrahydroquinoline **3i** in 39% yield. The reaction between α-alkylsubstituted benzotriazole compound **4** and styrene was performed under the same conditions to synthesize 2,4-substituted tetrahydroquinoline **5** as a two diastereomer mixture (1.4/1) in 80% yield (Scheme 2).

Scheme 2



4 **5**

In summary, an improved method for the synthesis of 1,2,3,4-tetrahydroquinolines has been studied. This method features wide applicability for the synthesis of 1,4-, 1,2,4-, 1,3,4- and 4-substituted tetrahydroquinolines and high yields and utilizes readily available, crystalline α-aminoalkylbenzotriazoles as starting materials.

EXPERIMENTAL

All melting points were measured on a hot-stage microscope and are uncorrected. The ^1H and ^{13}C nmr data were collected on a VXR-300 spectrometer (300 MHz and 75 MHz respectively), with tetramethylsilane as internal reference in deuteriochloroform. All mass spectra were determined on a HP5890 Series II Capillary GC operating in split mode with helium carrier gas and fitted with a mass selective detector. The column used was an HP5 capillary column 30 m x 0.25 mm, with 0.25 μ film thickness of 5% phenylmethylsilicone gum. The temperature program used initial temperature 50° for 1 minute, then ramped at 20° min^{-1} to 250°. The gc yield was determined by integration areas of all the ions from gc/ms. Column chromatography was carried out using 230-400 mesh silica.

The preparation and characterization of the α-aminoalkylbenzotriazoles **1a-c** have been published [11]. *N*-[(*N*-Methyl-*N*-phenylamino)butyl]benzotriazole (**4**), was synthesized from benzotriazole, *N*-methylaniline and butyraldehyde in 61% yield, as needles (4:1 ethyl acetate:hexanes), mp 77-79°; ^1H nmr (two isomers, Bt^1:Bt^2 = 2:1, peaks for minor isomer in square brackets): δ 8.03-8.00 (m, 1H), 7.32-7.22 (m, 3H) [7.86 (dd, 2H, J = 6.5, 3.1 Hz), 7.34 (dd, 2H, J = 6.6, 3.0 Hz)], 7.09-7.04 (m, 2H), 6.94-6.80 (m, 3H), 6.41 (t, 1H, J = 7.4 Hz) [6.55 (t, 1H, J = 7.4 Hz)], 2.77 (s, 3H) [3.18 (s, 3H)], 2.63 (q, 2H, J = 7.6 Hz) [2.50-2.41 (m, 2H)], 1.58-1.44 (m, 2H) [1.40-1.18 (m, 2H)], 1.05 (t, 3H, J = 7.4 Hz) [0.99 (t, 3H, J = 7.3 Hz)]; ^{13}C nmr: δ 149.4, 145.8, 143.9, 133.2, 129.4, 129.2, 127.1, 126.1, 123.8, 120.0, 119.7, 119.4, 118.3, 115.9, 115.0, 110.2, 80.5, 75.4, 35.4, 33.9, 32.2, 31.1, 19.3, 19.0, 13.7, 13.6.

Anal. Calcd. for $C_{17}H_{20}N_4$: C, 72.81; H, 7.19; N, 19.99. Found: C, 72.88; H, 7.10; N, 20.17.

General Procedure for the Preparation of Tetrahydroquinolines **3** or **5** *via* Benzotriazole Derivatives (**1**).

To a solution of benzotriazole **1** or **4** (2 mmoles), and alkene (2 equivalents) in dry methylene chloride (10 ml) at 0°, Lewis acid (2 equivalents) in dry methylene chloride (10 ml) was added under an inert atmosphere. After being stirred for two hours, water was added (8 ml). The mixture was seperated and the aqueous layer was extracted with methylene chloride (2 x 10 ml). The combined organics were washed with brine, dried over sodium sulfate and evaporated to give a residue, which was then purified by column chromatography to give the pure product; known compounds **3a-e**, **3g,h**, **5** were characterized by comparison of their nmr spectral data with literature values.

1-Methyl-4-hexyl-1,2,3,4-tetrahydroquinoline (**3a**) [7c].

This compound was obtained as an oil; ^{1}H nmr: δ 7.10-6.98 (m, 2H), 6.64-6.57 (m, 2H), 3.26 (dt, 1H, J = 11.2, 4.0 Hz), 3.09-3.16 (m, 1H), 2.88 (s, 3H), 2.73-2.68 (m, 1H), 2.04-1.92 (m, 1H), 1.84-1.77 (m, 1H), 1.67-1.25 (m, 10H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C nmr: δ 145.9, 128.4, 127.2, 127.0, 115.8, 110.8, 47.6, 38.9, 36.6, 36.2, 31.9, 29.5, 27.0, 26.4, 22.7, 14.1.

1-Methyl-4-butyl-1,2,3,4-tetrahydroquinoline (**3b**) [12].

This compound was obtained as an oil; ^{1}H nmr: δ 7.14-7.03 (m, 2H), 6.67-6.61 (m, 2H), 3.30 (dt, 1H, J = 10.8, 3.6 Hz), 3.12-3.19 (m, 1H), 2.92 (s, 3H), 2.76-2.70 (m, 1H), 2.05-1.95 (m, 1H), 1.88-1.81 (m, 1H), 1.72-1.29 (m, 6H), 0.94 (t, 3H, J = 6.9 Hz); ^{13}C nmr: δ 145.9, 128.4, 127.1, 127.0, 115.8, 110.7, 47.6, 38.9, 36.3, 36.2, 29.2, 26.4, 22.9, 14.1; ms: m/z 203 (M^+, 26%), 146 (100).

1-Methyl-4-octyl-1,2,3,4-tetrahydroquinoline (**3c**) [7k].

This compound was obtained as an oil; ^{1}H nmr: δ 7.10-6.99 (m, 2H), 6.64-6.58 (m, 2H), 3.26 (dt, 1H, J = 11.4, 4.2 Hz), 3.09-3.16 (m, 1H), 2.88 (s, 3H), 2.73- 2.67 (m, 1H), 2.02-1.92 (m, 1H), 1.85-1.77 (m, 1H), 1.64-1.28 (m, 14H), 0.89 (t, 3H, J = 6.0 Hz); ^{13}C nmr: δ 145.9, 128.4, 127.1, 127.0, 115.8, 110.7, 47.6, 38.9, 36.6, 36.2, 31.9, 29.8, 29.6, 29.4, 27.1, 26.4, 22.7, 14.1; ms: m/z 259 (M^+, 26%), 146 (100).

1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (**3d**) [7c].

This compound was obtained as an oil; ^{1}H nmr: δ 7.08-7.32 (m, 6H), 6.75 (d, 1H, J = 7.4 Hz), 6.68 (d, 1H, J = 8.1 Hz), 6.57 (t, 1H, J = 7.1 Hz), 4.14 (t, 1H, J = 6.2 Hz), 3.16-3.22 (m, 2H), 2.94 (s, 3H), 2.22-2.27 (m, 1H), 2.07-2.13 (m, 1H); ^{13}C nmr: δ 146.8, 146.6, 129.9, 128.6, 128.3, 127.5, 126.1, 124.8, 116.2, 111.0, 48.5, 43.4, 39.2, 31.1; ms: m/z 223 (M^+, 100%), 208 (29), 144 (75).

1-Methyl-3,4-*cis*-propano-1,2,3,4-tetrahydroquinoline (**3e**) [7g].

This compound was obtained as an oil; ^{1}H nmr: δ 7.11-7.04 (m, 2H), 6.71-6.63 (m, 2H), 3.03-2.91 (m, 2H), 2.83 (s, 3H), 2.68 (t, 1H, J = 10.5 Hz), 2.46-2.35 (m, 1H), 2.22-2.11 (m, 1H), 2.01-1.90 (m, 1H), 1.71-1.34 (m, 4H); ^{13}C nmr: δ 146.8, 129.4, 127.8, 126.4, 117.1, 111.4, 54.2, 41.1, 39.5, 36.2, 35.8, 29.8, 23.6; ms: m/z 187 (M^+, 73%), 144 (100).

1-Phenyl-3,4-*cis*-propano-1,2,3,4-tetrahydroquinoline (**3f**).

This compound was obtained as an oil; ^{1}H nmr: δ 7.27-7.32 (m, 2H), 7.16-7.18 (m, 3H), 7.02 (t, 1H, J = 7.1 Hz), 6.92 (t, 1H, J = 7.5 Hz), 6.84 (d, 1H, J = 8.0 Hz), 7.76 (t, 1H, J = 7.2 Hz), 3.50 (dd, 1H, J = 11.8, 4.5 Hz), 3.20-3.07 (m, 2H), 2.48-2.44 (m, 1H), 2.24-2.23 (m, 1H), 1.98-1.93 (m, 1H), 1.71-1.41 (m, 4H); ^{13}C nmr: δ 148.0, 144.1, 129.9, 129.7, 129.2, 125.8, 123.5, 122.8, 119.1, 116.1, 52.4, 41.1, 36.6, 35.7, 29.7, 23.9.

Anal. Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.92; H, 8.02; N, 5.83.

trans-1,3-Dimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (**3g**) [7g].

This compound was obtained as white needles (ether), mp 85-86°; ^{1}H nmr: δ 7.21-7.32 (m, 3H), 7.06-7.12 (m, 3H), 6.60-6.67 (m, 2H), 6.52 (t, 1H, J = 7.2 Hz), 3.64 (d, 1H, J = 9.0 Hz), 3.20 (dd, 1H, J = 11.2, 3.8 Hz), 3.01-2.97 (m, 1H), 2.95 (s, 3H), 2.25-2.20 (m, 1H), 0.91 (d, 3H, J = 6.6 Hz); 13C nmr: δ 146.5, 145.7, 130.2, 129.1, 128.2, 127.2, 126.1, 125.3, 116.4, 110.7, 56.6, 51.8, 39.3, 34.9, 18.1; ms: m/z 237 (M^+, 100%), 222 (16), 144 (61).

cis-1,3-Dimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (**3h**) [7g].

This compound was obtained as white needles (ether), mp 77-78°; ^{1}H nmr: δ 7.09-7.25 (m, 4H), 7.00 (d, 2H, J = 6.9 Hz), 6.88 (d, 1H, J = 7.2 Hz), 6.69 (d, 1H, J = 8.2 Hz), 6.55 (t, 1H, J = 7.4 Hz), 3.99 (d, 1H, J = 5.0 Hz), 3.01 (d, 2H, J = 3.4 Hz), 2.99 (s, 3H), 2.40-2.35 (m, 1H), 0.78 (d, 3H, J = 6.9 Hz); ^{13}C nmr: δ 145.9, 142.8, 130.1, 130.0, 127.6, 125.9, 125.0, 115.9, 110.5, 53.4, 49.0, 38.7, 31.2, 16.4.

3,4-*cis*-propano-1,2,3,4-tetrahydroquinoline (**3i**).

This compound was obtained as white needles (hexanes), mp 43-45°; ^{1}H nmr: δ 7.08 (d, 1H, J = 7.5 Hz), 6.96 (t, 1H, J = 7.5 Hz), 6.67 (t, 1H, J = 7.3 Hz), 6.54 (d, 1H, J = 8.0 Hz), 3.82 (br s, 1H), 3.10 (dd, 1H, J = 11.0, 5.0 Hz), 2.98 (dd, 1H, J = 7.8, 6.3 Hz), 2.79 (t, 1H, J = 10.4 Hz), 2.38-2.30 (m, 1H), 2.20-2.12 (m, 1H), 2.01-1.91 (m, 1H), 1.73-1.41 (m, 4H); ^{13}C nmr: δ 144.8, 129.9, 126.4, 126.2, 117.7, 114.6, 44.5, 40.7, 36.4, 35.3, 29.4, 23.6.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.46; H, 8.96; N, 8.04.

1-Methyl-2-propyl-4-phenyl-1,2,3,4-tetrahydroquinoline (**5**) [5e].

This compound was obtained as a diastereomeric mixture (1.4:1) and colorless oil; ^{1}H nmr: δ 7.07-7.34 (m, 6H), 6.49-6.65 (m, 3H), 3.94-4.06 (m, 1H), 3.24-3.40 (m, 1H), 2.96 and 2.97 (s, 3H), 1.98-2.32 (m, 2H), 1.26-1.68 (m, 4H), 0.86 and 0.95 (t, 3H, J = 7.1 Hz); ^{13}C nmr: δ 147.3, 146.0, 144.6, 129.2, 128.7, 128.4, 127.7, 127.3, 126.4, 126.3, 125.2, 115.9, 115.3, 112.1, 110.6, 58.6, 58.5, 43.1, 40.1, 38.2, 37.3, 36.7, 36.2, 34.6, 33.8, 29.7, 19.2, 18.2, 14.3; ms: m/z 265 (M^+, 19%), 222 (100).

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