Lewis acid induced *N*-methyleneamine equivalents. Part 3.[1] Addition of allyl nucleophiles to $TiCl_4$-induced *N*-methyleneamine equivalents:[2] synthesis of 1,2,3,4-tetrahydroquinolines and homoallylic anilines

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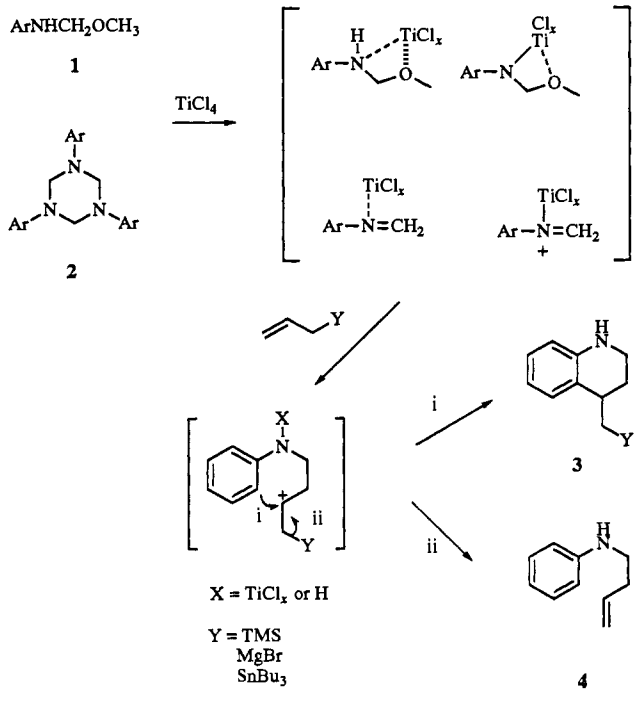
$TiCl_4$-induced *N*-methyleneamine equivalents from *N*-(methoxymethyl)anilines or 1,3,5-triphenylhexahydro-1,3,5-triazines have been treated with allyltrimethylsilane to give a mixture of 1,2,3,4-tetrahydroquinolines and homoallylic anilines arising from branching reactions from the same cationic intermediate. Changing the allylic nucleophile to allylmagnesium bromide and allyltributyltin leads to the reaction proceeding in only one direction and the selective synthesis of homoallylic anilines without the formation of quinolines.

The Mannich reaction[3] involving one of the simplest imines, methyleneamine (monomeric formaldehyde imine), is very limited from a synthetic viewpoint because it is difficult to generate the methyleneamine. It is only known in the gas phase through flash vacuum thermolysis.[4] Methods for the preparation of methyleneamine *in situ* have been devised by treating *N*-(methoxymethyl)amines[5] or *N*-(cyanomethyl)-amines[6] with alkyllithium for the synthesis of *N*-(α-substituted)-methylamines and β-lactams. Two other aminomethylation reactions with silyl enol ether have also been reported to be achieved from *N*-(alkoxymethyl)amines catalysed by iodotrimethylsilane[7] and from hexahydro-1,3,5-triazines catalysed by trifluoromethanesulfonic acid.[8]

Recently we reported that *N*-methyleneamine equivalents could be generated from *N*-(methoxymethyl)amines and (or) hexahydro-1,3,5-triazines in the presence of $TiCl_4$ as a Lewis acid. These have been used for aminomethylation reactions with nucleophiles such as trialkyl phosphites, trimethylsilyl cyanide and trimethylsilyl azide to give aminomethylphosphonates,[9] aminoacetonitriles[10] and aminomethyl azides,[2] respectively. In extending the synthetic utility of Lewis acid-induced *N*-methyleneamine equivalents from *N*-(methoxymethyl)aniline or 1,3,5-triphenylhexahydro-1,3,5-triazine we have succeeded in the addition of allyl nucleophiles to the α-position of amines. In this paper we describe the reaction of *N*-methyleneamine equivalents with allyl nucleophiles leading to the synthesis of 1,2,3,4-tetrahydroquinolines and homoallylic anilines *via* branching reactions from the same cationic intermediates. By a correct choice of nucleophile, facile synthesis of synthetically valuable homoallylic anilines was achieved by making the reaction proceed in one direction without the formation of tetrahydroquinolines (Table 1).

N-(Methoxymethyl)anilines **1** and triphenylhexahydro-1,3,5-triazines **2** with diverse substituents on the benzene ring react with allyltrimethylsilane (allylTMS) in the presence of $TiCl_4$ to give a mixture of 4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinolines **3** and homoallylic anilines **4**. The ratio of the two products depends on the substituents. Compounds **1a** and **2a** gave **3a** as a single product. However, compounds **1c** and **2c** with an electron donating methyl substituent gave more of the quinoline skeleton product while **1d** and **2e** with electron withdrawing substituents gave relatively less of the quinoline product. As an exception, **1b** produced almost equal amounts of **3b** and **4b** in high yield. A proposed mechanism for the production of methyleneamine equivalents is shown in Scheme 1. *N*-(Methoxymethyl)aniline and hexahydro-1,3,5-triazine are assumed to be coordinated to the $TiCl_4$ as shown in Scheme 1.[2,10] The addition of allylTMS forms the cationic intermediate (Y = TMS). Subsequent reaction from the carbonium ion† occurs via two different pathways: electrophilic aromatic cyclization (pathway i) and the removal of TMS (pathway ii). When the phenyl ring is electron-rich pathway i is relatively favoured. The overall yield and the ratio of **3** and **4** were not changed much by varying the amount of $TiCl_4$ or by using other Lewis acids such as $SnCl_4$, $AlCl_3$ or BF_3OEt_2. However, a facile synthesis of 1,2,3,4-tetrahydroquinolines *via* only pathway i has been reported to be achieved from the reaction with simple olefins (Y = CR^1R^2) as the nucleophile.[12]



Scheme 1

Although homoallylic anilines have wide utility,[13] methods

† In this case a classical carbonium ion is assumed to be generated while the non classical silicium cation was proposed for Lewis-acid promoted addition of allylsilane to various electrophiles.[11] The proposed classical carbonium ion is supported by the fact that no 2,3,4,5-tetrahydro-1-benzazepine was detected through the reaction.

Table 1 Reactions of *N*-(methoxymethyl)anilines **1** or 1,3,5-triphenylhexahydro-1,3,5-triazines **2** with allyltrimethylsilane (AllylTMS), allylmagnesium bromide (AllylMgBr) or allyltributyltin ($AllylSnBu_3$) in the presence of Lewis acid (LA)

Substrate	Ar	Lewis acid	Reagent	Ratio (Sub : LA : reagent)	Yield (%)[a,b] 3	4
1a	Ph	$TiCl_4$	AllylTMS	1 : 1.0 : 1.03	42	—
1b	2-MeO-C_6H_4	$TiCl_4$	AllylTMS	1 : 1.0 : 1.03	48	41
1c	2-Me-C_6H_4	$TiCl_4$	AllylTMS	1 : 1.0 : 1.03	46	16
1d	2,5-Cl_2-C_6H_3	$TiCl_4$	AllylTMS	1 : 1.0 : 1.03	36	38
2a	Ph	$TiCl_4$	AllylTMS	1 : 3.0 : 3.10	36	—
2c	2-Me-C_6H_4	$TiCl_4$	AllylTMS	1 : 3.0 : 3.10	39	28
2e	4-F-C_6H_4	$TiCl_4$	AllylTMS	1 : 3.0 : 3.10	25	27
1c	2-Me-C_6H_4	$TiCl_4$	AllylTMS	1 : 1.5 : 1.03	52	19
1c	2-Me-C_6H_4	$SnCl_4$	AllylTMS	1 : 1.5 : 1.03	41	17
1c	2-Me-C_6H_4	$AlCl_3$	AllylTMS	1 : 1.5 : 1.03	49	21
1c	2-Me-C_6H_4	BF_3OEt_2	AllylTMS	1 : 1.5 : 1.03	54	31
2c	2-Me-C_6H_4	BF_3OEt_2	AllylTMS	1 : 3.0 : 3.10	41	23
1a	Ph	$TiCl_4$	AllylMgBr	1 : 1.0 : 1.03	—	61
1b	2-MeO-C_6H_4	$TiCl_4$	AllylMgBr	1 : 1.0 : 1.03	—	43
1c	2-Me-C_6H_4	$TiCl_4$	AllylMgBr	1 : 1.0 : 1.03	—	59
1d	2,5-Cl_2-C_6H_3	$TiCl_4$	AllylMgBr	1 : 1.0 : 1.03	—	46
2a	Ph	$TiCl_4$	AllylMgBr	1 : 3.0 : 3.10	—	23
2b	2-MeO-C_6H_4	$TiCl_4$	AllylMgBr	1 : 3.0 : 3.10	—	45
2c	2-Me-C_6H_4	$TiCl_4$	AllylMgBr	1 : 3.0 : 3.10	—	22
2e	4-F-C_6H_4	$TiCl_4$	AllylMgBr	1 : 3.0 : 3.10	—	14
1a	Ph	$TiCl_4$	$AllylSnBu_3$	1 : 1.0 : 1.03	—	64
1b	2-MeO-C_6H_4	$TiCl_4$	$AllylSnBu_3$	1 : 1.0 : 1.03	—	45
1c	2-Me-C_6H_4	$TiCl_4$	$AllylSnBu_3$	1 : 1.0 : 1.03	—	79
1d	2,5-Cl_2-C_6H_3	$TiCl_4$	$AllylSnBu_3$	1 : 1.0 : 1.03	—	55
2a	Ph	$TiCl_4$	$AllylSnBu_3$	1 : 3.0 : 3.10	—	68
2b	2-MeO-C_6H_4	$TiCl_4$	$AllylSnBu_3$	1 : 3.0 : 3.10	—	59
2c	2-Me-C_6H_4	$TiCl_4$	$AllylSnBu_3$	1 : 3.0 : 3.10	—	37
2e	4-F-C_6H_4	$TiCl_4$	$AllylSnBu_3$	1 : 3.0 : 3.10	—	64

[a] Yield of isolated pure product, not optimized. [b] All new compounds were purified by either flash chromatography or short-path distillation.

for their synthesis[14] are relatively rare. Therefore, methods for the facile and selective synthesis of homoallylic anilines would be valuable. This can be achieved by suppressing the pathway i through reducing the lifetime of the cationic intermediate which is not to be reacted with the phenyl ring. This approach was successful when allylMgBr and $AllylSnBu_3$ were used as nucleophiles instead of allylTMS. The cationic intermediate generated from allylMgBr and $AllylSnBu_3$ does not survive electrophilic aromatic cyclization with the phenyl ring due to the weakness of the carbon–magnesium and carbon–tin bonds compared with the carbon–silicon bond.‡ Instead removal of Y (Y = MgBr, $SnBu_3$) according to the pathway ii becomes dominant. With all the substrates **1** and **2** with diverse substituents on the phenyl ring, only homoallylic anilines were obtained. The reactions with the more reactive allylMgBr gave relatively lower yields than with $AllylSnBu_3$ as the nucleophile.‡ The yield from the reaction with triphenylhexahydro-1,3,5-triazine as substrate was lower than from the corresponding *N*-(methoxymethyl)aniline with the recovery of starting amine.

We show herein generation and utilization of *N*-methyleneamine equivalents from *N*-(methoxymethyl)anilines or 1,3,5-triphenylhexahydro-1,3,5-triazines for the synthesis of 1,2,3,4-tetrahydroquinolines and homoallylic anilines. This is a particularly efficient way to produce homoallylic anilines when using allylMgBr and $AllylSnBu_3$ as nucleophiles while a classical Mannich reaction with iminium salts generated *in situ* gives bishomoallylic anilines.[18] Further efforts are in progress to prepare α-functionalized amines utilizing *N*-methyleneamine equivalents with several other nucleophiles in the presence of $TiCl_4$ as a Lewis acid.

‡ Bond dissociation energies of C–Si and C–Sn are 414 and 297 ± 17 KJ mol^{-1} at 289-K, respectively in Bu^s–$SiMe_3$ and Me–$SnMe_3$.[15] Allylstannane is known to be more reactive towards electrophilic allylation than allylsilanes.[16] Allylmagnesium is the most reactive. However, there is a chance that allylMgBr can react with $TiCl_4$ to produce an alkyltitanium(IV) compound prior to allylation of the substrate.[17]

Experimental

^1H NMR spectra were recorded on either a Bruker AC 200 (200 MHz) or a Varian Unity 500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on either a Bruker AC 200 (50.3 MHz) or a Varian Unity 500 (125.7 MHz) spectrometer. Chemical shifts are given in ppm using tetramethylsilane (TMS) as internal standard; *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer. Elemental analysis was taken on a Perkin-Elmer 240 DS elemental analyser. *N*-(Methoxymethyl)anilines were prepared by the reported method.[9a,10] 1,3,5-Triphenylhexahydro-1,3,5-triazines were obtained by the conventional method with amine and formaldehyde. Some of the *N*-(methoxymethyl)anilines and 1,3,5-triphenylhexahydro-1,3,5-triazines were interconvertible.[10]

General procedure for the synthesis of 4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline 3a

To a stirred solution of *N*-(methoxymethyl)aniline **1** (0.822 g, 6.0 mmol) or 1,3,5-triphenylhexahydro-1,3,5-triazine **2** (0.63 g, 2.0 mmol) in CH_2Cl_2 under nitrogen atmosphere was slowly added Lewis acid (6.0 mmol) at −78 °C. After being stirred for 10 min allyltrimethylsilane (0.708 g, 6.2 mmol) was added to it. The resulting solution was stirred at −78 °C for 30 min. When all the starting material had been consumed as judged by TLC the reaction mixture was poured into ice–water. The resulting solution was neutralized with cold sat. aqueous $NaHCO_3$. The reaction product was extracted with CH_2Cl_2. The organic layer

was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude reaction product was purified by flash chromatography to give the *title compound* **3a** (0.55 g, 42%), δ_H(500 MHz; $CDCl_3$) 0.07 [9 H, s, $(CH_3)_3Si$], 0.89 (1 H, dd, *J* 14.8 and 10.3, H_BCSi), 1.02 (1 H, dd, *J* 15.1 and J 3.9, H_ACSi), 1.67–1.73 (1 H, m, 3-H_A), 1.94–2.00 (1 H, m, 3-H_B), 2.88 (1 H, quintet, 4-H), 3.17 (1 H, td, *J* 10.2, 3.9, 2-H_A), 3.28 (1 H, td, *J* 10.1, 3.4, 2-H_A), 6.38 (1 H, d, *J* 8.3, 5-H), 6.54 (1 H, td, *J* 7.4 and 1.5, 7-H), 6.88 (1 H, td, *J* 8.3 and 1.4, 6-H) and 6.94 (1 H, d, *J* 7.4, 8-H); δ_C(125.7 MHz, $CDCl_3$) 0.5 (s, SiMe), 26.2 (CH_2Si), 29.7 (C-3), 32.5 (C-4), 39.0 (C-2), 114.7 (C-5), 117.4 (C-7), 127.1 (C-6), 128.8 (C-4a), 129.1 (C-8) and 144.3 (C-8a); ν_{max}(neat)/cm^{-1} 3410, 2950, 1604, 1499, 1314, 1252 and 838 (Found: C, 70.8; H, 9.3; N, 6.3. Calc. for $C_{13}H_{21}NSi$: C, 71.1; H, 9.65; N, 6.38%).

8-Methoxy-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline 3b. δ_H(200 MHz; $CDCl_3$) 0.09 (9 H, s), 0.88 (1 H, dd, *J* 14.7, 8.9), 1.13 (1 H, dd, *J* 14.7 and 4.1), 1.71–1.83 (1 H, m), 1.98–2.07 (1 H, m), 2.94–3.08 (1 H, m), 3.32–3.48 (2 H, m), 3.87 (3 H, s), 4.34 (1 H, br s) and 6.59–6.78 (3 H, m); δ_C(50.3 MHz; $CDCl_3$) 0.6, 25.9, 29.2, 31.8, 38.0, 55.4, 107.2, 115.6, 120.9, 121.0, 128.3 and 146.2 (Found: C, 67.5; H, 9.11; N, 5.54. Calc. for $C_{14}H_{23}NOSi$: C, 67.4; H, 9.29; N, 5.62%).

8-Methyl-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline 3c. δ_H(200 MHz; $CDCl_3$) 0.03 (9 H, s), 0.79 (1 H, dd, *J* 15.1, 11.0), 0.96 (1 H, dd, *J* 15.0 and 4.3), 1.58–1.66 (1 H, m), 1.84–1.91 (1 H, m), 2.00 (3 H, s), 2.85–2.92 (1 H, m), 3.17–3.36 (2 H, m), 3.46 (1 H, br s), 6.47 (1 H, t, 7.4), 6.76 (1 H, d, *J* 7.2) and 6.82 (1 H, d, *J* 7.5); δ_C(50.3 MHz; $CDCl_3$) 0.7, 17.8, 26.5, 29.5, 32.7, 39.1, 116.8, 121.4, 127.1, 128.2, 131.2 and 142.2 (Found: C, 71.8; H, 9.84; N, 6.21. Calc. for $C_{14}H_{23}NSi$: C, 72.0; H, 9.93; N, 6.00%).

5,8-Dichloro-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline 3d. δ_H(200 MHz; $CDCl_3$) 0.05 (9 H, s), 0.84 (1 H, dd, *J* 14.2, 9.1), 1.10 (1 H, dd, *J* 15.0 and 4.3), 1.61–1.78 (1 H, m), 1.95–2.05 (1 H, m), 2.88–2.96 (1 H, m), 3.21–3.39 (2 H, m), 3.52 (1 H, br s), 6.52 (1 H, d, *J* 7.8) and 7.05 (1 H, d, *J* 7.4) (Found: C, 53.9; H, 6.6; N, 4.85. Calc. for $C_{13}H_{19}Cl_2NSi$: C, 54.2; H, 6.64; N, 4.86%).

6-Fluoro-4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline 3e. δ_H(200 MHz; $CDCl_3$) 0.08 (9 H, s), 0.89 (1 H, dd, *J* 15.4, 11.2), 1.07 (1 H, dd, *J* 15.2 and 4.7), 1.67–1.78 (1 H, m), 1.94–2.06 (1 H, m), 2.84–3.01 (1 H, m), 3.18–3.40 (2 H, m), 3.49 (1 H, br s), 6.38–6.47 (1 H, m) and 6.62–6.81 (2 H, m) (Found: C, 65.7; H, 8.6; N, 5.8. Calc. for $C_{13}H_{20}FNSi$: C, 65.8; H, 8.49; N, 5.90%).

General procedure for the synthesis of *N*-But-3-enylaniline 4a

The reaction was carried out with allyltributyltin (2.05 g, 6.2 mmol) or allylmagnesium bromide (1.0 mol dm^{-3} in diethyl ether; 6.2 cm^3, 6.2 mmol) instead of allyltrimethylsilane in the same way for the 4-trimethylsilylmethyl-1,2,3,4-tetrahydroquinoline except for the following work-up procedure. After the reaction was complete with allyltributyltin a small amount of the alkyltin compounds remained in the product extract, as seen by a long tail on TLC. This was removed by stirring the concentrated organic layer in aqueous KF. The reaction product free from any alkyltin compounds was re-extracted with CH_2Cl_2. The 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 either flash chromatography or short-path distillation to give the *title compound* **4a** (0.57 g, 64%), δ_H(500 MHz; $CDCl_3$) 2.27 (2 H, q, *J* 7.0, CH_2C=), 3.07 (2 H, t, *J* 7.1, CH_2N), 3.48 (1 H, br s, NH), 5.03 (1 H, d, *J* 13.5, C=CH_{trans}), 5.07 (1 H, d, *J* 16, C=CH_{cis}), 5.66–5.73 (1 H, m, CCH=), 6.47–6.48 (1 H, m) 6.57–6.60 (2 H, m) and 7.01–7.08 (2 H, m); δ_C(125.7 MHz; $CDCl_3$) 33.5, 42.6, 112.7, 116.9, 117.1, 129.1, 135.6 and 148.0; ν_{max}(neat)/cm^{-1} 3408, 2921, 1602, 1504, 1320, 1262 and 748 (Found: C, 81.3; H, 8.8; N, 9.4. Calc. for $C_{10}H_{13}N$: C, 81.6; H, 8.90; N, 9.51%).

***N*-But-3-enyl-2-methoxyaniline 4b.** δ_H(500 MHz; $CDCl_3$) 2.32 (2 H, q, *J* 7.0), 3.10 (2 H, t, *J* 6.5), 3.72 (3 H, s), 4.08 (1 H, br s), 5.01 (1 H, d, *J* 11), 5.05 (1 H, d, *J* 17), 5.70–5.80 (1 H, m), 6.52 (1 H, d, *J* 8.0), 6.57 (1 H, t, *J* 7.5), 6.66 (1 H, d, *J* 7.0) and 6.78 (1 H, t, *J* 7.5); δ_C(125.7 MHz; $CDCl_3$) 33.6, 42.6, 55.3, 109.1, 109.2, 116.2, 116.6, 121.1, 135.7, 138.2 and 146.9 (Found: C, 74.8; H, 8.3; N, 7.8. Calc. for $C_{11}H_{15}NO$: C, 74.5; H, 8.53; N, 7.90%).

***N*-But-3-enyl-2-methylaniline 4c.** δ_H(500 MHz; $CDCl_3$) 2.01 (3 H, s), 2.32 (2 H, q, *J* 6.5), 3.17 (2 H, t, *J* 6.5), 3.38 (1 H, br s), 5.03 (1 H, d, *J* 13.5), 5.05 (1 H, d, *J* 16), 5.71–5.77 (1 H, m), 6.62 (1 H, dd, *J* 6.5, 1.0), 6.61 (1 H, d, *J* 8.5), 6.64 (1 H, t, *J* 7.0), 7.02 (1 H, d, *J* 7.1) and 7.10 (1 H, t, *J* 7.5); δ_C(125.7 MHz; $CDCl_3$) 17.3, 33.6, 42.5, 109.6, 116.7, 117.0, 121.8, 127.0, 129.9, 135.8 and 146.0 (Found: C, 81.8; H, 9.3; N, 8.5. Calc. for $C_{11}H_{15}N$: C, 81.9; H, 9.38; N, 8.69%).

***N*-But-3-enyl-2,5-dichloroaniline 4d.** δ_H(500 MHz; $CDCl_3$) 2.38 (2 H, q, *J* 6.5), 3.14 (2 H, t, *J* 6.7), 4.37 (1 H, br s, NH), 5.13 (1 H, d, *J* 9.8), 5.17 (1 H, d, *J* 15), 5.78–5.84 (1 H, m), 6.48 (1 H, d, *J* 6.5), 6.51 (1 H, d, *J* 6.2) and 7.03 (1 H, d, *J* 8.0); δ_C(125.7 MHz; $CDCl_3$) 33.2, 42.3, 116.0, 116.7, 117.6, 129.6, 131.3, 135.0, 135.8 and 144.6 (Found: C, 55.3; H, 5.3; N, 6.4. Calc. for $C_{10}H_{11}Cl_2N$: C, 55.6; H, 5.13; N, 6.48%).

***N*-But-3-enyl-4-fluoroaniline 4e.** δ_H(500 MHz; $CDCl_3$) 2.38 (2 H, q, *J* 7.0), 3.13 (2 H, t, *J* 6.8), 3.50 (1 H, br s), 5.12 (1 H, d, *J* 10.5), 5.15 (1 H, d, *J* 17.5), 5.78–5.86 (1 H, m), 6.53 (2 H, t, *J* 8.5) and 6.90 (2 H, t, *J* 9.0); δ_C(125.7 MHz; $CDCl_3$) 33.6, 43.4, 113.5, 113.6, 115.4, 115.6, 117.0, 135.5, 144.3, 154.9 and 156.6 (Found: C, 72.6; H, 7.45, N, 8.5. Calc. for $C_{10}H_{11}FN$: C, 72.7; H, 7.32, N, 8.48%).

Acknowledgements

We thank Dr Guncheol Kim of Hanhyo Institute of Technology for providing allyltributyltin. We are also grateful to Dr Youngwan Seo for the 500 MHz spectra. This research was supported in part from KOSEF and Ministry of Education through the Basic Science Research Institute Program.

References

1 For part 2 see, H.-J. Ha and Y.-G. Ahn, *Synth. Commun.*, 1995, **25**, 969.
2 Presented in part at the 10th International Conference on Organic Synthesis (ICOS-10), Bangalore, India, December 11–16, 1994.
3 For comprehensive reviews see (*a*) M. Tramontini and L. Angiolini, *Tetrahedron*, 1990, **46**, 1791; (*b*) E. F. Kleinman, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 2, pp. 893–973.
4 J.-C. Guillemin and J.-M. Denis, *Tetrahedron*, 1988, **44**, 4431 and references cited therein.
5 (*a*) J. Barluenga, A. M. Bayon and G. J. Asensio, *J. Chem. Soc., Chem. Commun.*, 1983, 1109; (*b*) J. Barluenga, A. M. Bayon and G. Asensio, *J. Chem. Soc., Chem. Commun.*, 1984, 427; (*c*) J. Barluenga, P. J. Campos and G. Canal, *Synthesis*, 1989, 33.
6 (*a*) L. E. Overman and R. M. Burk, *Tetrahedron Lett.*, 1984, **25**, 1635; (*b*) L. E. Overman and T. Osawa, *J. Am. Chem. Soc.*, 1985, **107**, 1698.
7 A, Hosomi, S. Iijima and H. Sakurai, *Tetrahedron Lett.*, 1982, **23**, 547.
8 K. Ikeda, K. Achiwa and M. Sekiya, *Tetrahedron Lett.*, 1983, **24**, 913.
9 (*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*) J. Barluenga, P. J. Campos, G. Canal and G. Asensio, *Synlett*, 1990, 261.
10 H.-J. Ha, G.-S. Nam and K. P. Park, *Synth. Commun.*, 1991, **21**, 155.
11 (*a*) S. R. Angle and J. P. Boyce, *Tetrahedron Lett.*, 1994, **35**, 6461; (*b*) A. Stahl, E. Steckhan and M. Nieger, *Tetrahedron Lett.*, 1994,

35, 7371; (*c*) G. P. Brengel, C. Rithner and A. I. Meyers, *J. Org. Chem.*, 1994, **59**, 5144.
12 (*a*) T. Shono, Y. Matsumura, K. Inoue, H. Ohmizu and S. Kashimura, *J. Am. Chem. Soc.*, 1982, **104**, 5753; (*b*) S.-I. Murahashi, T. Naota and T. Nakato, *Synlett*, 1992, 835.
13 (*a*) T. Ohsawa, M. Ihara and K. Fukumoto, *J. Org. Chem.*, 1983, **48**, 3644; (*b*) H. Togo, M. Fujii and M. Yokoyama, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 57.
14 (*a*) O. Wichterle and J. Rocek, *Collect. Czech. Chem. Commun.*, 1954, **19**, 282; (*b*) G. Pandey, K. Sudha Randi and U. T. Bhalerao, *Tetrahedron Lett.*, 1990, **31**, 1199.
15 D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, 1982, **33**, 493.
16 A. Hosomi, T. Imai, M. Endo and H. Sakurai, *J. Organomet. Chem.*, 1985, **285**, 95 and references cited therein.
17 M. T. Reetz, *Organotitanium Reagents in Organic Synthesis*, Springer-Verlag, New York, 1986, pp. 22–24.
18 P. A. Grieco and A. Bahsas, *J. Org. Chem.*, 1987, **52**, 1378.

Paper 5/02118I
Received 3rd *April* 1995
Accepted 28th *June* 1995