

# Addition of Allyltributylstannane to Schiff Bases in the Presence of SnCl<sub>4</sub>

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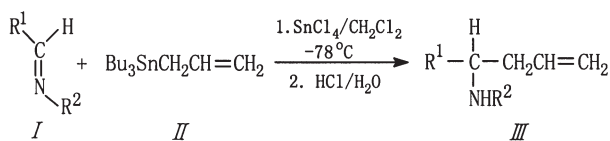
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Some homoallylamines have been prepared *via* addition of allyltributylstannane to Schiff bases in the presence of SnCl<sub>4</sub> and the reaction mechanism has been suggested according to separated intermediate.

Homoallylamines are valuable intermediates in organic synthesis, in particular in the synthesis of some natural nitrogen-containing products, such as ( $\pm$ )statine [1], ( $\pm$ )coniine [2]. These amines are prepared by nucleophilic addition on C=N double bond in Schiff base. In general allylic organometallic reagents, such as allylmagnesium [3], allyllead [4], allylzinc [5], allylstannane [6], allylcopper [7], *etc.* are used as nucleophiles of this reaction. The addition of allylstannane to imines is carried out only at suitable temperature, pressure and in the presence of the Lewis acid. In the present work, we report on the addition of allyltributylstannane to the C=N double bond in Schiff bases and it goes on smoothly in the presence of catalysts and at atmospheric pressure.

Using SnCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> as shown in Scheme 1 homoallylamines were formed in satisfactory yields. The homoallylamines IIIa—IIIc obtained from this reaction are shown in Table 1.



Scheme 1

The reaction is a nucleophilic addition at carbon atom in imines. When the R<sup>1</sup> is an alkyl or donor of an aromatic group, the addition is carried out difficultly. While the R<sup>1</sup> is electron-withdrawing group, the reaction is able to proceed smoothly, since nucleophiles bind easily to the carbon atom on the C=N bond.

It is found that the amine I can form a complex with SnCl<sub>4</sub>, such as IV (Scheme 2). When Ia

and SnCl<sub>4</sub> reacted in CH<sub>2</sub>Cl<sub>2</sub>, the complex IVa was separated. It is clear that SnCl<sub>4</sub> is able to activate the C=N bond through forming a complex with substrate. So we suggest a plausible mechanism *via* the intermediate complex IV for this addition reaction.

## EXPERIMENTAL

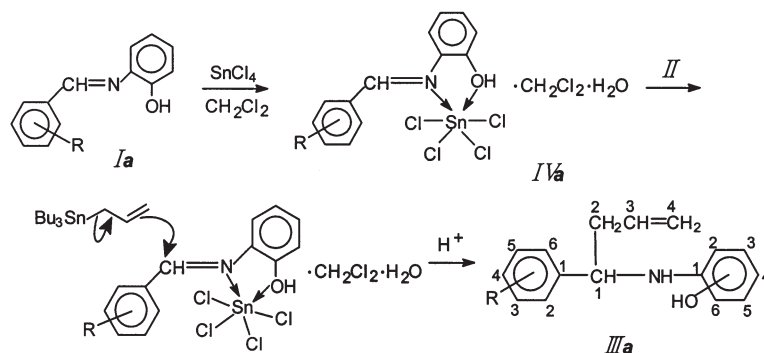
The IR spectra were recorded on a Nicolet 170SX spectrometer using KBr discs or liquid films. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AM-400 apparatus using CDCl<sub>3</sub> or CCl<sub>4</sub> as solvent and Me<sub>4</sub>Si as internal standard. Mass spectra were taken on an HP 5988A spectrometer. Melting points were determined with a Kofler apparatus. The elemental analyses were carried out on a Carlo Erba 1106 instrument.

## General Procedure for Addition

Imine (1 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) were introduced in 100 cm<sup>3</sup> four-neck flask under argon atmosphere. The solution was cooled to -78 °C and SnCl<sub>4</sub> (0.23 cm<sup>3</sup>, 1 mmol) and then allyltributylstannane (0.5 cm<sup>3</sup>, 1.5 mmol) were added dropwise under stirring. After reacting for 1 h, the mixture was warmed slowly to room temperature under stirring until the reaction was complete (TLC). 10 % hydrochloric acid (5 cm<sup>3</sup>) was introduced and the mixture was hydrolyzed. The organic phase was separated out and purified by chromatography on silica gel column using a mixture petroleum ether—acetone ( $\varphi_r = (5-10):1$ ) as eluant. After removing solvent under reduced pressure, the product was obtained.

*N*-(2-Hydroxyphenyl)-1-(3-nitrophenyl)but-3-enamine (IIIa). M.p. = 83–84 °C. IR spectrum,

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Scheme 2

Table 1. Addition Products and their Yields

Product	R <sup>1</sup>	R <sup>2</sup>	Aspect	Yield/%
IIIa	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	2-HOC <sub>6</sub> H <sub>4</sub>	Yellowish crystal	80
IIIb	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	2-HOC <sub>6</sub> H <sub>4</sub>	Yellow crystal	74
IIIc	3-BrC <sub>6</sub> H <sub>4</sub>	2-HOC <sub>6</sub> H <sub>4</sub>	Colourless solid	65
III d	C <sub>6</sub> H <sub>5</sub>	2-MeOC <sub>6</sub> H <sub>4</sub>	Colourless oil liquid	76
III e	2-HOC <sub>6</sub> H <sub>4</sub>	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	82
III f	2-HOC <sub>6</sub> H <sub>4</sub>	2-ClC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	72
III g	2-HOC <sub>6</sub> H <sub>4</sub>	2-BrC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	71
III h	2-HOC <sub>6</sub> H <sub>4</sub>		Yellowish oil liquid	67
III i	2-HOC <sub>6</sub> H <sub>4</sub>	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Yellowish oil liquid	63
III j	C <sub>6</sub> H <sub>5</sub>	2-ClC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	73
III k	C <sub>6</sub> H <sub>5</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	56
III l	C <sub>6</sub> H <sub>5</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	Yellowish oil liquid	77

$\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3393 (NH), 3072 (OH), 1516, 1353 (NO<sub>2</sub>), 1430, 930 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.56–2.68 (m, 2H, H-2), 4.50 (t,  $J = 6.4$  Hz, 1H, H-1), 4.92 (bs, 1H, NH), 5.19 (d,  $J = 10.0$  Hz, 1H, H-4), 5.21 (d,  $J = 17.0$  Hz, 1H, H-4), 5.72–5.82 (m, 1H, H-3), 6.29 (d,  $J = 7.6$  Hz, 1H, H-6), 6.59 (d,  $J = 7.6$  Hz, 1H, H-5), 6.68 (t,  $J = 7.6$  Hz, 1H, H-4), 6.72 (d,  $J = 7.6$  Hz, 1H, H-3), 7.50 (dd,  $J = 8.0$  Hz, 7.6 Hz, 1H, H-5), 7.72 (d,  $J = 7.6$  Hz, 1H, H-6), 8.11 (d,  $J = 8.0$  Hz, 1H, H-4), 8.26 (bs, 1H, H-2). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>),  $\delta$ : 57.1 (C-1), 42.8 (C-2), 133.3 (C-3), 117.9 (C-4), 135.3 (C-1), 121.4 (2C, C-2,4), 146.1 (C-3), 119.1 (C-4), 129.5 (C-5), 132.7 (C-6), 143.3 (C-1), 148.5 (C-2), 114.3 (C-4), 122.2 (C-5), 112.8 (C-6). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 284 (5, M<sup>+</sup>), 243 (100), 197 (23), 41 (5).

*N*-(2-Hydroxyphenyl)-1-(4-nitrophenyl)but-3-enamine (IIIb). M.p. = 97–98°C. IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3445 (NH), 3406 (OH), 1512, 1337 (NO<sub>2</sub>), 1442, 926 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.54–2.69 (m, 2H, H-2), 4.49 (t,  $J = 6.4$  Hz, 1H, H-1), 5.00 (bs, 1H, NH), 5.18 (d,  $J = 10.5$  Hz, 1H, H-4), 5.22 (d,  $J = 15.8$  Hz, 1H, H-4), 5.70–5.81 (m, 1H, H-3), 6.24 (d,  $J = 7.4$  Hz, 1H, H-6), 6.60 (t,  $J = 7.4$  Hz, 1H, H-5), 6.67 (t,  $J = 7.4$  Hz, 1H, H-4), 6.73 (d,  $J = 7.4$  Hz, 1H, H-3), 7.55 (dd,  $J = 8.6$  Hz, 2.6 Hz, 2H, H-2,6), 8.18 (dd,  $J = 8.6$  Hz, 2.6 Hz, 2H,

H-3,5). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 284 (5, M<sup>+</sup>), 243 (100, M – allyl), 197 (36, M – allyl – NO<sub>2</sub>), 41 (8).

*N*-(2-Hydroxyphenyl)-1-(3-bromophenyl)but-3-enamine (IIIc). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3420 (NH), 3336 (OH), 1444, 920 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.60 (m, 2H, H-2), 4.34 (t,  $J = 6.2$  Hz, 1H, H-1), 4.98 (bs, 1H, NH), 5.14 (d,  $J = 11.4$  Hz, 1H, H-4), 5.18 (d,  $J = 18.2$  Hz, 1H, H-4), 5.66–5.78 (m, 1H, H-3), 6.37 (d,  $J = 7.6$  Hz, 1H, H-6), 6.61 (t,  $J = 7.4$  Hz, 1H, H-5), 6.66 (d,  $J = 7.4$  Hz, 1H, H-4), 6.73 (d,  $J = 7.4$  Hz, 1H, H-3), 7.17 (t,  $J = 7.6$  Hz, 1H, H-5), 7.30 (d,  $J = 7.6$  Hz, 1H, H-6), 7.36 (d,  $J = 7.6$  Hz, 1H, H-4), 7.52 (s, 1H, H-2). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 317 (3, M<sup>+</sup>), 319 (3, M + 2), 278 (100), 276 (98, M – allyl), 197 (5, M – allyl – Br), 41 (8).

*N*-(2-Methoxyphenyl)-1-phenylbut-3-enamine (III d). IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 3423 (NH), 1455, 918 (=CH), 1224, 1030 (COC). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.62–2.74 (m, 2H, H-2), 3.95 (s, 3H, OCH<sub>3</sub>), 4.48 (t,  $J = 6.7$  Hz, 1H, H-1), 4.92 (bs, 1H, NH), 5.23 (d,  $J = 10.1$  Hz, 1H, H-4), 5.28 (dd,  $J = 17.1$  Hz, 1.7 Hz, 1H, H-4), 5.63–5.93 (m, 1H, H-3), 6.41 (dd,  $J = 7.6$  Hz, 1.6 Hz, 2H, H-4,5), 6.65 (dd,  $J = 7.6$  Hz, 1.6 Hz, 2H, H-3,6), 7.31 (td,  $J = 7.6$  Hz, 1.6 Hz, 2H, H-3,5), 7.40 (td,  $J = 7.6$  Hz, 1.6 Hz, 1H, H-4), 7.47 (dd,  $J = 7.6$  Hz, 1.6 Hz, 2H, H-2,6). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 253 (7, M<sup>+</sup>), 212 (100, M – allyl).

*N*-(3-Nitrophenyl)-1-(2-hydroxyphenyl)but-3-enamine (IIIe). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3400 (NH), 3347 (OH), 1527, 1348 (NO<sub>2</sub>), 1455, 916 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.63—2.72 (m, 2H, H-2), 4.02 (bs, 1H, NH), 4.51 (dd,  $J = 8.8$  Hz, 5.2 Hz, 1H, H-3), 5.27 (d,  $J = 10.4$  Hz, 1H, H-4), 5.31 (d,  $J = 17.2$  Hz, 1H, H-4), 5.81—5.87 (m, 1H, H-3), 6.81 (d,  $J = 8.0$  Hz, 1H, H-3), 6.93—7.28 (m, 6H, other protons of Ar), 7.63 (d,  $J = 8.4$  Hz, 1H, H-3), 7.91 (bs, 1H, ArOH). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 284 (M<sup>+</sup>), 243 (100, M - allyl), 197 (28, M - allyl - NO<sub>2</sub>), 41 (5).

*N*-(2-Chlorophenyl)-1-(2-hydroxyphenyl)but-3-enamine (III f). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3410 (NH), 3324 (OH), 1457, 923 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.59—2.66 (m, 2H, H-2), 4.28 (d,  $J = 10.0$  Hz, 1H, H-4), 5.23 (d,  $J = 16.8$  Hz, 1H, H-4), 5.69—5.79 (m, 1H, H-3), 6.59 (d,  $J = 8.0$  Hz, 1H, H-3), 6.65 (d,  $J = 8.0$  Hz, 1H, H-5), 6.78 (d,  $J = 8.0$  Hz, 1H, H-6), 7.17 (dd,  $J = 8.0$  Hz, 1.4 Hz, 1H, H-3), 6.87—7.08 (m, 4H, other protons of Ar), 8.62 (bs, 1H, ArOH). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 273 (M<sup>+</sup>), 232 (100, M - allyl), 234 (35), 196 (8).

*N*-(2-Bromophenyl)-1-(2-hydroxyphenyl)but-3-enamine (III g). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3380 (NH), 3317 (OH), 1454, 914 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.65—2.73 (m, 2H, H-2), 4.18 (t,  $J = 8.0$  Hz, 1H, H-1), 5.27 (d,  $J = 10.0$  Hz, 1H, H-4), 5.32 (d,  $J = 17.2$  Hz, 1H, H-4), 5.67—5.75 (m, 1H, H-3), 6.59 (d,  $J = 8.4$  Hz, 1H, H-3), 6.66 (d,  $J = 8.4$  Hz, 1H, H-6), 6.70 (d,  $J = 8.0$  Hz, 1H, H-6), 6.78 (d,  $J = 8.0$  Hz, 1H, H-3), 6.85—7.20 (m, 4H, other protons of Ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 317 (6, M<sup>+</sup>), 319 (6, M + 2), 276 (100, M - allyl), 278 (95), 41 (12).

*N*-(1-Benzothiazolyl)-1-(2-hydroxyphenyl)but-3-enamine (III h). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3390 (NH), 3240 (OH), 1452, 920 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.78—2.90 (m, 2H, H-2), 4.94 (t,  $J = 7.2$  Hz, 1H, H-1), 5.12 (d,  $J = 10.4$  Hz, 1H, H-4), 5.21 (d,  $J = 16.8$  Hz, 1H, H-4), 5.81 (m, 1H, H-3), 6.87 (t,  $J = 7.6$  Hz, 1H, H-5), 6.98 (d,  $J = 7.6$  Hz, 1H, H-3), 7.11—7.16 (m, 2H, H-6,7), 7.22—7.33 (m, 2H, H-4,5), 7.51—7.55 (m, 2H, H-4,6). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 296 (16, M<sup>+</sup>), 255 (100, M - allyl), 41 (4).

*N*-(2,5-Dichlorophenyl)-1-(2-hydroxyphenyl)but-3-enamine (III i). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3386 (NH), 3318 (OH), 1453, 917 (=CH), 1074 (C—Cl). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.62—2.75 (m, 2H, H-2), 4.58 (t,  $J = 8.0$  Hz, 1H, H-1), 4.97 (d,  $J = 10.4$  Hz, 1H, H-4), 5.05 (d,  $J = 16.8$  Hz, 1H, H-4), 5.69—5.78 (m, 1H, H-3), 6.75—7.17 (m, other protons of Ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 307 (4, M<sup>+</sup>), 266 (100, M - allyl), 268 (65), 270 (10), 231 (8, M - allyl - Cl), 196 (12, M - allyl - 2Cl), 41 (6).

*N*-(2-Chlorophenyl)-1-phenylbut-3-enamine (III j). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3412 (NH), 1457, 920

(=CH), 1071 (C—Cl). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.52—2.67 (m, 2H, H-2), 4.42 (dd,  $J = 7.6$  Hz, 1H, H-1), 4.89 (bs, 1H, NH), 5.18 (d,  $J = 10.2$  Hz, 1H, H-4), 5.23 (d,  $J = 17.6$  Hz, 1H, H-4), 5.74—5.80 (m, 1H, H-3), 6.33 (d,  $J = 8.0$  Hz, 1H, H-6), 6.55 (t,  $J = 7.4$  Hz, 1H, H-5), 6.92 (t,  $J = 7.4$  Hz, 1H, H-4), 7.25—7.51 (m, other protons of Ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 257 (3, M<sup>+</sup>), 259 (1, M + 2), 216 (100, M - allyl), 218 (34), 41 (4).

*N*-(4-Chlorophenyl)-1-phenylbut-3-enamine (III k). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3414 (NH), 1453, 919 (=CH), 1090 (C—Cl). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.50—2.60 (m, 2H, H-2), 4.25 (dd,  $J = 7.0$  Hz, 6.0 Hz, 1H, H-1), 5.05 (d,  $J = 10.0$  Hz, 1H, H-4), 5.09 (d,  $J = 16.6$  Hz, 1H, H-4), 5.58—5.60 (m, 1H, H-3), 6.41 (d,  $J = 8.0$  Hz, 2H, H-2,6), 6.94 (d,  $J = 8.0$  Hz, 2H, H-3,5), 7.18 (m, 1H, H-4), 7.23 (bs, 4H, H-2,3,5,6). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 257 (3, M<sup>+</sup>), 216 (100, M - allyl), 218 (31), 181 (4, M - allyl - Cl), 41 (10).

*N*-(4-Bromophenyl)-1-phenylbut-3-enamine (III l). IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3410 (NH), 1455, 920 (=CH). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.45—2.65 (m, 2H, H-2), 4.28 (bs, 1H, NH), 4.35 (dd,  $J = 8.0$  Hz, 5.2 Hz, 1H, H-1), 5.17 (d,  $J = 9.2$  Hz, 1H, H-4), 5.20 (d,  $J = 16.8$  Hz, 1H, H-4), 5.72—5.79 (m, 1H, H-3), 6.37 (dd,  $J = 8.4$  Hz, 2.0 Hz, 2H, H-2,6), 7.15 (dd,  $J = 8.4$  Hz, 2.0 Hz, 2H, H-3,5), 7.26 (m, 1H, H-4), 7.33 (bs, 4H, other protons of Ar). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 301 (6, M<sup>+</sup>), 303 (6), 260 (99, M - allyl), 262 (100).

IVa: Yellow solid, IR spectrum,  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3088 (OH), 1694 (C=N), 242, 391 (Sn—N), 514 (Sn—O), 312 (Sn—Cl). For C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>4</sub>Sn  $w_i$ (found)/% ( $w_i$ (calc.)/%): 27.33 (27.74) (C), 2.47 (2.33) (H), 4.60 (4.63) (N).

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