

## Note

### Lewis acid catalyzed amino-Claisen rearrangement: A facile one pot synthesis of 2-allylarylamines from *N*-allylarylamines

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Boron trifluoride-diethyl ether complex efficiently catalyzes a variety of amino-Claisen rearrangements of *N*-allylarylamines **1a-g** to afford 2-allylarylamines **2a-g** in moderate to good yields. *N*-allylarylamines having electron deficient substituents undergo rearrangement at lower temperature than electron rich ones.

**Keywords:** Lewis acid catalysis, amino-Claisen rearrangement, *N*-allylarylamines, 2-allylarylamines

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2-Allylarylamines are useful synthons in palladium induced heteroannulation to give indoles<sup>1</sup>. In a quest to explore the feasibility of other amine substrates in this synthesis, a good method was required for the preparation of 2-allylarylamines. Though amino-Claisen rearrangement of *N*-allylarylamines provides a one pot synthetic entry to 2-allylarylamines but it is considerably less facile than the analogous conventional Claisen rearrangement of *O*-allylphenols probably because of the severe conditions required in the *aza* series that gives the products in low yields<sup>2</sup>. Though a variety of protic acids (H<sub>2</sub>SO<sub>4</sub>, TFA, HCl, *etc.*) as well as Lewis acids (ZnCl<sub>2</sub>, BF<sub>3</sub>, SnCl<sub>4</sub>, *etc.*) catalysts have been employed in conventional Claisen rearrangements<sup>3</sup> but there has been a great dearth of examples of acid catalysis in amino-Claisen rearrangements<sup>3,4</sup>.

It has been observed recently<sup>5</sup> that the protic acid salts of **1a-g** undergo rearrangement with greater facility than neat molecules in aqueous 2 *N* H<sub>2</sub>SO<sub>4</sub> and TFA but it produced side products too of uncertain structures. It has been suggested that side products result due to the hydration of the allyl chain with protic acids *viz* 2 *N* H<sub>2</sub>SO<sub>4</sub> and TFA in aqueous medium, at high temperature<sup>5</sup>. As this method

required a cumbersome purification process, therefore, it was not used further.

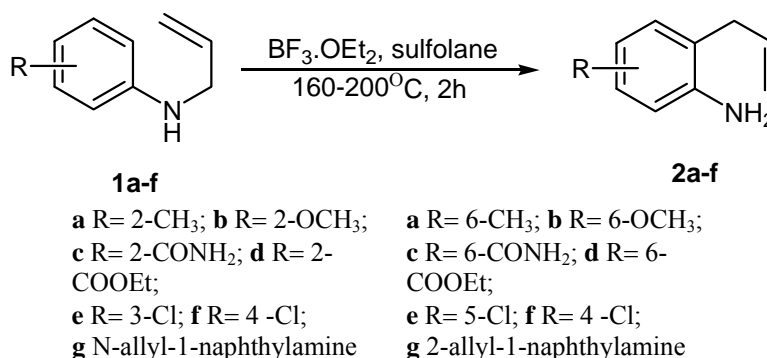
The application of ZnCl<sub>2</sub> as a Lewis acid catalyst in conventional Claisen rearrangement of *O*-allylphenols is well documented in the literature<sup>6</sup> but its use has been limited to only a few cases of amino-Claisen rearrangements<sup>7</sup>. To overcome the problems associated with the use of protic acids it was thought that it could be worthwhile to employ the Lewis acids for the conversion of **1** to **2**. Initial attempts to carry out amino-Claisen rearrangement of substrates bearing electron deficient groups using ZnCl<sub>2</sub> has not been very encouraging due to the very low yields of the products formed. A survey of the literature revealed that boron trifluoride-diethyl ether complex (BF<sub>3</sub>.OEt<sub>2</sub>) too has also been used as catalyst in the rearrangement of *O*-allylphenols<sup>8</sup>. However, despite its versatility, it received only little attention in amino-Claisen rearrangement in arylamine series<sup>9</sup>. This prompted the exploration of the generality of BF<sub>3</sub>.OEt<sub>2</sub> as employed to the amino-Claisen rearrangement of *N*-allylarylamines **1** to 2-allylarylamines **2**. The results which have emanated from this study have been described in this note.

### Results and Discussion

In a typical run, a mixture of *N*-allylarylamine **1a** and BF<sub>3</sub>.OEt<sub>2</sub> (0.5 equiv) in sulfolane was heated at 185-90°C under argon for 2 hr to furnish **2a** in 62% yield. Similarly other aromatic *N*-allylamines **1b-g** rearranged in BF<sub>3</sub>.OEt<sub>2</sub> to give the products **2b-g** in yields ranging from 56 to 65% (**Scheme I**). The use of this catalyst shortened the reaction time by 2 hr and reduced the formation of by-products.

Although this rearrangement tolerated the electron-rich as well as the electron deficient substituents present in *N*-allylarylamines but *N*-allylarylamines having electron deficient substituents underwent rearrangement at lower temperature than electron rich ones. This is consistent to the proposed mechanism of the amino-Claisen rearrangement<sup>10,11</sup>.

As BF<sub>3</sub>.OEt<sub>2</sub> catalyzed amino-Claisen rearrangement provides a mild and one pot entry to the 2-allylarylamines, therefore, this method may find a widespread application to the synthesis of complex 2-allylarylamines from *N*-allylarylamines.



Scheme I

Table I — Spectroscopic characterization data of 2-allylarylamines **2a-g**

Product	<sup>1</sup> H NMR (δ, ppm)	<sup>13</sup> C NMR (δ, ppm)	MS (m/z, relative intensity)
<b>2a</b>	6.96-6.72 (m, 2H, ArH), 6.58 (t, <i>J</i> =7.5Hz, 1H, ArH), 6.05-5.60 (m, 1H, —CH=), 5.20-4.90 (m, 2H, =CH <sub>2</sub> ), 3.32 (br. s, 2H, NH <sub>2</sub> ), 3.14 (d, <i>J</i> =6.5Hz, 2H, —CH <sub>2</sub> —), 2.06 (s, 3H, CH <sub>3</sub> )	147.23, 136.42, 130.38, 126.74, 124.67, 116.16, 118.85, 116.32, 36.76, 21.11	147 (100) [M] <sup>+</sup> , 146 (40), 132 (68), 120 (48), 117 (30)
<b>2b</b>	6.80-6.60 (m, 3H, ArH), 6.00-5.86 (m, 1H, —CH=), 5.12-5.04 (m, 2H, =CH <sub>2</sub> ), 3.81-3.78 (m, 5H, NH <sub>2</sub> , OCH <sub>3</sub> ), 3.32-3.28 (m, 2H, —CH <sub>2</sub> —)	145.86, 134.37, 124.06, 120.09, 117.64, 115.20, 132.71, 111.44, 55.54, 36.16	163 (100) [M] <sup>+</sup> , 162 (36), 148 (45), 136 (38), 120 (26), 93 (15)
<b>2c</b>	7.52-6.92 (m, 3H, ArH), 6.03-5.86 (m, 5H, —CH=, CONH <sub>2</sub> , NH <sub>2</sub> ), 5.19-5.10 (m, 2H, =CH <sub>2</sub> ), 3.30 (d, <i>J</i> =6.1Hz, 2H, —CH <sub>2</sub> —)	174.62, 147.78, 137.46, 134.68, 131.96, 119.92, 117.38, 118.22, 165.67, 36.83	176 (74) [M] <sup>+</sup> , 175 (32), 161 (32), 160 (15), 159 (100), 149 (38), 132 (41), 105 (18)
<b>2d</b>	7.83-7.79 (dd, <i>J</i> =1.7, 8.1Hz, 1H, ArH), 7.19-7.16 (dd, <i>J</i> =1.6, 8.2Hz, 1H, ArH), 6.63 (dd, <i>J</i> =7.3, 8.2Hz, 1H, ArH), 6.01-5.86 (m, 3H, NH <sub>2</sub> , —CH=), 5.16-5.07 (m, 2H, =CH <sub>2</sub> ), 4.40 (q, <i>J</i> =8.0Hz, 2H, CH <sub>2</sub> CH <sub>3</sub> ), 3.32 (dd, <i>J</i> =1.8, 6.3Hz, 2H, —CH <sub>2</sub> —), 1.30 (t, <i>J</i> =8.0Hz, 3H, CH <sub>3</sub> )	169.50, 150.15, 135.65, 127.32, 130.28, 122.26, 116.40, 118.40, 112.45, 60.23, 36.82, 12.25	205 (70) [M] <sup>+</sup> , 204 (26), 190 (30), 178 (32), 160 (25), 159 (100), 132 (28), 105 (15)
<b>2e</b>	7.01 (d, <i>J</i> =8.2Hz, 1H, ArH), 6.72 (dd, <i>J</i> =2.3, 8.2 Hz, 1H, ArH), 6.32 (d, <i>J</i> =2.5Hz, 1H, ArH), 6.02-5.89 (m, 1H, —CH=), 5.15-5.07 (m, 2H, =CH <sub>2</sub> ), 3.73 (s, 2H, NH <sub>2</sub> ), 3.37 (d, <i>J</i> =6.2Hz, 2H, —CH <sub>2</sub> —)	146.45, 137.16, 131.72, 131.50, 129.60, 122.36, 120.49, 117.10, 114.65, 36.65	169/167 (33/100) [M] <sup>+</sup> , 154/152 (12/36), 142/140 (68), 132 (22)
<b>2f</b>	7.02-6.97 (m, 2H, ArH), 6.62 (dd, <i>J</i> =9.1, 3.0Hz, 1H, ArH), 5.97-5.87 (m, 1H, —CH=), 3.81 (s, 2H, NH <sub>2</sub> ), 3.27 (d, <i>J</i> =6.2Hz, 2H, —CH <sub>2</sub> —)	143.78, 134.68, 130.20, 128.0, 125.76, 124.92, 117.35, 114.80, 36.67	169/167 (33/100) [M] <sup>+</sup> , 154/152 (15/45), 142/140 (81), 132 (20)
<b>2g</b>	7.74-7.06 (m, 6H, ArH), 6.03-5.89 (m, 1H, —CH=), 5.16-5.03 (m, 2H, =CH <sub>2</sub> ), 3.48 (m, 4H, —CH <sub>2</sub> —, NH <sub>2</sub> )	147.32, 137.12, 134.89, 129.98, 128.10, 127.29, 126.10, 123.18, 117.68, 116.68, 36.80	183 (100) [M] <sup>+</sup> , 182 (30), 168 (40), 156 (48), 155 (13)

All the products **2a-g** were characterized on the basis of elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR and MS data (Table I). The synthetic products **2a**, **2f** and **2g** were also characterized by direct comparison with their authentic samples prepared through known routes<sup>7b,12,13</sup>.

### Experimental Section

All the melting points are uncorrected. IR spectra were recorded on Pye Unicam Model SP3-300

infracord in neat and on KBr pellets; <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a FT NMR Bruker AM 300L spectrometer using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as solvent and TMS as an internal reference; and MS on a Jeol D-300(EI) spectrometer. All *N*-allylarylamines **1a-g** were prepared by the method reported previously<sup>5</sup>.

**General procedure for the preparation of 2-allylarylamines 2a-g from N-allylarylamines 1a-g.**

A mixture of *N*-allylarylamines **1a-g** (58.54 mmole), BF<sub>3</sub>.OEt<sub>2</sub> (3.6 mL, 29.27 mmole, 0.5 equiv.) and sulfolane (10 mL) were heated under argon at the temperatures 160-200°C for 2 hr. The mixture was cooled and poured into ice water (40 mL) and 10% HCl solution was added dropwise to make the solution acidic (pH 1). The solution was washed with CHCl<sub>3</sub> (2 × 40 mL), the aqueous layer was made alkaline with 10% NaOH solution and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined ether extracts were washed with H<sub>2</sub>O (40 mL), dried over MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel with hexane-ethylacetate (10:1) to afford 2-allylarylamines **2a-g**. All the products were obtained as oils [b.p. (°C/torr): **2a** (66-68/0.05); **2b** (88-89/0.01); **2d** (146-48/0.01); **2e** (109-10/1.8); **2f** (78-80/0.04); **2g** (92/0.01) (lit.<sup>13b</sup> 80/0.008)] excepting **2c**, which was obtained as a white solid, m.p. 148-49°C. Yields (%): **2a** (62); **2b** (65); **2c** (58); **2d** (60); **2e** (56); **2f** (61) and **2g** (63).

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