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. 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. Though a variety of protic acids (H₂SO₄, TFA, HCl, etc.) as well as Lewis acids (ZnCl₂, BF₃, SnCl₄, etc.) catalysts have been employed in conventional Claisen rearrangements but there has been a great dearth of examples of acid catalysis in amino-Claisen rearrangements.

It has been observed recently that the protic acid salts of 1a-g undergo rearrangement with greater facility than neat molecules in aqueous 2 N H₂SO₄ 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 H₂SO₄ and TFA in aqueous medium, at high temperature. As this method required a cumbersome purification process, therefore, it was not used further.

The application of ZnCl₂ as a Lewis acid catalyst in conventional Claisen rearrangement of O-allylphenols is well documented in the literature but its use has been limited to only a few cases of amino-Claisen rearrangements. 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 ZnCl₂ 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 (BF₃.OEt₂) too has also been used as catalyst in the rearrangement of O-allylphenols. However, despite its versatility, it received only little attention in amino-Claisen rearrangement in arylamine series. This prompted the exploration of the generality of BF₃.OEt₂ 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 BF₃.OEt₂ (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 BF₃.OEt₂ 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.

As BF₃.OEt₂ 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.
All the products 2a-g were characterized on the basis of elemental analysis, IR, 1H and 13C 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 routes7b,12,13.

**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; 1H and 13C NMR spectra were recorded on a FT NMR Bruker AM 300L spectrometer using CDCl3 and DMSO-d6 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 previously5.

**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\(_3\)OEt\(_2\) (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\(_3\) (2 × 40 mL), the aqueous layer was made alkaline with 10% NaOH solution and extracted with Et\(_2\)O (3 × 50 mL). The combined ether extracts were washed with H\(_2\)O (40 mL), dried over MgSO\(_4\) 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. 13b white solid, m.p. 14)] 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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References