Rearrangement and Cyclization of *N*-Allyl Quaternary Anilinium Salts

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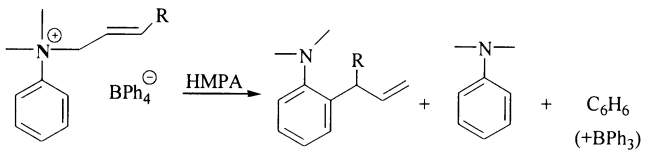
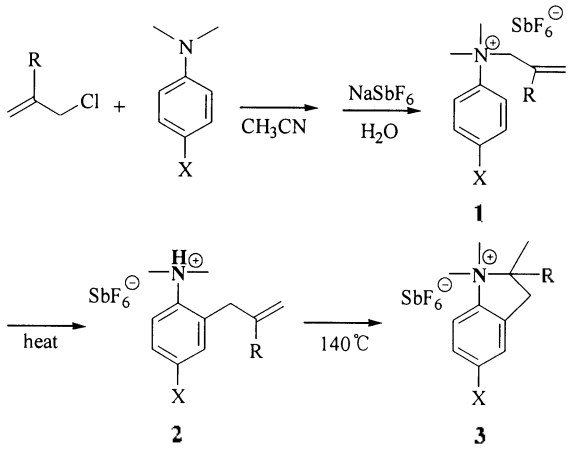
In general, allyl migration in *N*-allyl-arylamines, the aromatic amino-Claisen rearrangement, is not easily accomplished[1] and rearrangements of allyl group are observed only with the relief of ring strain,[2] with the use of Brönsted or Lewis acid catalyst[3,4] or with the use of zeolite.[5] Schmid *et al.* briefly describe the charge-induced aromatic amino-Claisen rearrangements of quaternary anilinium salts such as *N*-allyl-*N*,*N*-dimethylanilinium tetraphenylborates (BPh_4^-) as shown below.[4]



However, the yield is moderate (42%) and the reaction time is rather long (18 hours). Recently, we found that the benzyl group in *N*-benzyl-*N*,*N*-dimethylanilinium hexafluoroantimonates (SbF_6^-) migrates to the ortho or para position of aniline when heated in neat.[6] Since the rearrangement proceeded in high yield (77-92%) at relatively low temperature (120-140 °C), we were tempted to see if the allyl group instead of the benzyl group migrates in a similar fashion.

We prepared SbF_6^- salts of *N*-allyl-*N*,*N*-dimethylanilinium derivatives by reacting the corresponding allyl chloride with aniline derivatives in acetonitrile and exchanging Cl^- with SbF_6^- as reported in the literature[7] (Scheme 1). The prepared *N*-allyl-*N*,*N*-dimethylanilinium salts were purified by recrystallization(methanol); their ^1H NMR and ^{13}C NMR spectra were consistent with the assigned structures.

When the salts **1** were heated in neat at 120 °C for 1 hour, 2-allylanilinium salts **2**, the rearranged products, were obtained along with *N*,*N*-dimethylindolinium salts **3**. The ratio of the products **2** and **3** was dependent on the structure of the salts and the reaction temperature, and could be determined by the comparison of ^1H NMR integration intensity of the benzylic protons in crude mixtures. Table 1 lists the ratios of **2** and **3** when the salts **1** were heated at 120 °C. The cyclized salts **3** are believed to be produced by the addition of the proton at nitrogen atom in **2** to the olefin, followed by the intramolecular nucleophilic addition of nitrogen atom to the generated cations. Only indolinium salts **3** were obtained in good yields at 140 °C for 1 hour and the yields of indolinium salts produced at this conditions are shown in Table 1. The substituent in the aniline had little effect on the ratio of **2** and **3**, but methyl substitution on the allyl group retarded the cyclization reaction, which increased the ratio of **2d** and **2e** over **3d** and **3e**, respectively, at 120 °C and also lowered the yield of indolinium at 140 °C.



Scheme 1

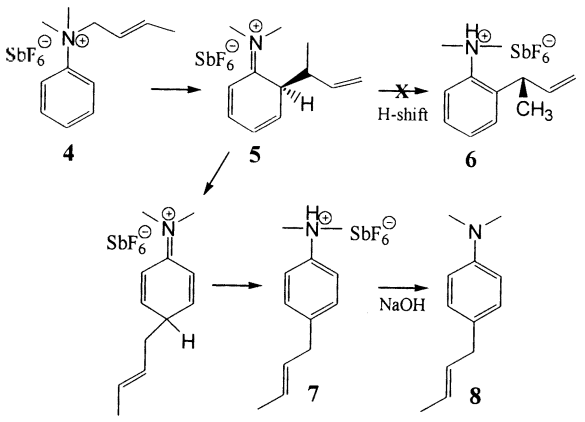
Such indoline derivatives were also observed when *N*-allyl-*N*-methylaniline derivatives were refluxed in the presence of $ZnCl_2$ in xylene or zeolite in hexane.[3,4] However, in this case, mixtures of products were always observed and yields of cyclized products, indoline derivatives, were not high. In the present study, more than 72% of indolinium salts was obtained as the only product in the shorter reaction time, which indicates that the rearrangement of allyl group is very efficient in this system.

When *N*-crotyl(substituted salt **4**), instead of *N*-allyl, was heated in neat at 140 °C, 4-crotylanilinium salt **7**, which resulted from a consecutive double [3,3] sigmatropic rearrangement, was obtained as the only product (92%) as shown in Scheme 2. No ortho rearranged product **6** was detected in the reaction mixture. High steric interaction during the course of H-shift between the methyl group in anilinium and methylallyl group at the ortho position probably prevents the conversion of **5** to **6**. A similar trend has been

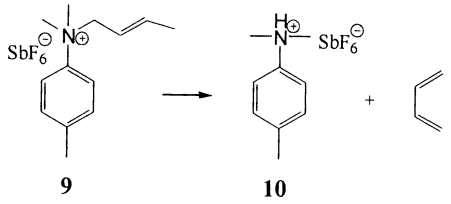
Table 1. Thermal rearrangement of *N*-allyl-*N*,*N*-dimethylanilinium salts (**1**)

	X	R	ratio of 2 : 3[a]	Yield of 3 (%)[b]
a	H	H	1 : 3.4	92
b	CH_3	H	1 : 3.2	90
c	OCH_3	H	1 : 4	95
d	H	CH_3	1.6 : 1	72
e	CH_3	CH_3	2 : 1	83

[a]Ratio of **2** and **3** at 120 °C for an hour. [b]Isolated yield of **3** at 140 °C for an hour.



Scheme 2



Scheme 3

observed in the Claisen rearrangement of crotyl phenyl ether.[8] The exclusive production of **7** from **4** indicates that this amino-Claisen rearrangement may undergo a concerted [3,3] sigmatropic pathway as in the usual Claisen rearrangement, although the involvement of allylic cation[7] can not be excluded. Anilinium hexafluoroantimonate **7** was easily converted to 4-crotyl-*N,N*-dimthylaniline **8** by 10% aqueous sodium hydroxide solution.

If para position of aniline was blocked, as in *N*-crotyl-*N,N*-dimethyl-*p*-toluidinium salt **9**, *N, N*-dimethyl-*p*-toluidinium salt **10** was produced in 75% yield (Scheme 3). In this case, butadiene was generated as a by-product, which could be readily removed. Since the generated salt **10** is a strong proton acid, it can serve as a good latent thermal proton acid generator.

We describe here a novel charge induced amino-Claisen rearrangement in *N*-allyl- and *N*-crotyl-*N,N*-dimethylanilinium SbF_6 salts, which resulted in high yield of rearranged products when heated in neat. Further studies to utilize the thermal acid generator in polymer synthesis and to use this amino-Claisen rearrangement in the synthesis of indoline derivatives are underway.

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10. The spectral properties of selected compounds are as follows. **3a**: mp 90-92 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 1.80 (d, 3H, J = 3.7 Hz), 3.31 (dd, 1H, J = 9.9, 6.4 Hz), 3.35 (s, 3H), 3.56 (m, 1H), 3.72 (s, 3H), 4.56 (m, 1H), 7.5-7.8 (m, 4H); ^{13}C NMR (125 MHz, acetone-d_6) 13.63, 35.16, 52.73, 77.43, 118.83, 127.96, 130.61, 132.36, 134.65, 149.19. **3b**: mp 101-103 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 1.77 (d, 3H, J = 4.0 Hz), 2.41 (s, 3H), 3.25 (dd, 1H, J = 9.9, 6.3 Hz), 3.31 (s, 3H), 3.51 (m, 1H), 3.68 (s, 3H), 4.52 (m, 1H), 7.3-7.7 (m, 3H); ^{13}C NMR (125 MHz, acetone-d_6) 13.64, 21.59, 35.06, 49.93, 52.77, 77.59, 118.38, 128.21, 131.13, 142.86, 146.92. **3c**: mp 75-76 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.79 (d, 3H, J = 6.7 Hz), 3.28 (dd, 1H, J = 10.1, 7.7 Hz), 3.33 (s, 3H), 3.51 (m, 1H), 3.70 (s, 3H), 3.87 (s, 3H), 4.55 (m, 1H), 7.0-7.7 (m, 3H); ^{13}C NMR (75 MHz, acetone-d_6) 13.23, 34.79, 49.66, 52.45, 56.34, 77.26, 111.82, 115.85, 119.32, 135.90, 141.49, 162.49. **3d**: mp 148-150 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.74 (s, 3H), 3,52 (s, 2H), 3.54 (s, 6H), 7.5-7.8 (m, 4H); ^{13}C NMR (75 MHz, acetone-d_6) 21.33, 41.06, 49.47, 83.55, 118.75, 127.78, 130.17, 131.82, 134.27, 147.68. **3e**: mp 152-153 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.72 (s, 3H), 2.42 (s, 3H), 3.45(s, 2H), 3.48 (s, 6H), 7.3-7.7 (m, 3H); ^{13}C NMR (75 MHz, acetone-d_6) 21.14, 22.36, 40.98, 49.50, 83.58, 118.32, 128.03, 130.62, 134.19, 142.27, 145.38. **7**: ^{1}H NMR (300 MHz, acetone-d_6) δ 1.67 (d, 3H, J = 6.0 Hz), 3.57 (s, 6H), 3.40 (br, 2H), 5.60 (m, 2H), 7.48 (d, 2H, J = 8.7 Hz), 7.75 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, acetone-d_6): 18.40, 39.25, 48.43, 121.99, 128.28, 130.46, 131.72, 141.00, 145.31. **8**: EI Ms *m/z* 175 $[M]^+$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (d, 3H, J = 5.8 Hz), 2.90 (s, 6H), 3.22 (d, 2H, J = 6.2 Hz), 5.51 (m, 2H), 6.70 (d, 2H, J = 8.7 Hz), 7.04 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 17.80, 38.01, 40.91, 113.09, 125.46, 129.02, 129.28, 130.92, 149.17. **10**: ^{1}H NMR (300 MHz, acetone-d_6) δ 2.42 (s, 3H), 3.57 (s, 6H), 7.48 (d, 2H, J = 8.1 Hz), 7.72 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, acetone-d_6) 20.88, 48.01, 119.57, 131.35, 139.18, 141.52.