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Thermal rearrangement of *N*-benzylanilinium hexafluoroantimonates

Jeongkyu Park,[a] Jung-Hyu Shin [a,*] and Changjin Lee [b]

[a]*Department of Chemistry, Seoul National University, Seoul 151-742, South Korea*

[b]*Advanced Materials Division, Korea Research Institute of Chemical Technology, Yusung, Taejeon 305-600, South Korea*

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Abstract

We prepared *p*-substituted *N*-benzylanilinium hexafluoroantimonates, known cationic initiators, and examined their thermal reaction. The thermal reaction produced 2- or 4-benzylanilinium salts as the major products, which resulted from the rearrangement of the benzyl group. The reaction proceeded at lower temperature with higher yield when the substituent in the benzyl group was electron donating.

Keywords: rearrangement; *N*-benzylanilinium hexafluoroantimonates; benzyl migration.

Cationic compounds are attracting interest due to their ability to initiate polymerization by thermal and photochemical stimulation.[1–4] Recently, Nakano and Endo reported that *N*-benzylanilinium hexafluoroantimonate (SbF_6^-) can be successfully employed as a latent thermal initiator for the polymerization of glycidyl phenyl ether.[3a] The benzyl cation was postulated as an initiating species generated from the thermal activation of the *N*-benzylanilinium SbF_6^-.

In the course of studying the effect of substituents on the stability and reactivity of carbocations,[5] we became interested in the fate of the thermally generated benzyl cation from *N*-benzylanilinium SbF_6^-. We found that 2- and 4-benzylanilinium salts were produced when the salt was heated neat. These products were the rearrangement adducts of benzyl group from the nitrogen atom to the 2- or 4-position of the aniline ring. Although benzyl quaternary ammonium salts are known to undergo the Sommelet–Hauser or Stevens rearrangement, the reactions usually require a strong base or fluoride anion to produce ammonium ylides, which are the key intermediates for the rearrangement.[6,7] Since we are not aware of any reports concerning the rearrangement of the benzyl group in *N*-benzylanilinium salts in non-basic conditions, we decided to explore the thermal rearrangement further.

We prepared *N*-(*p*-substituted)benzyl-*N*,*N*-dimethylanilinium SbF_6^- (**1**) by reacting the corresponding benzyl chloride with aniline derivatives in acetonitrile and exchanging the chloride anion with SbF_6^-

* Corresponding author.

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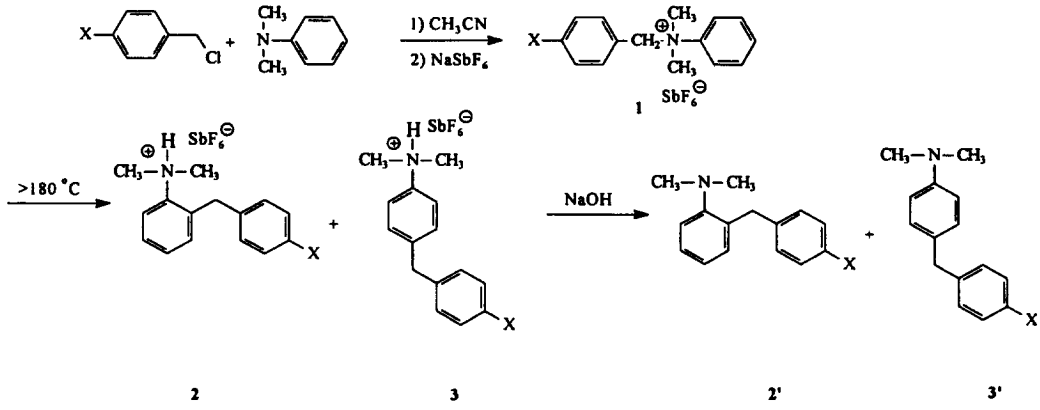
as reported in the literature[3c] (Scheme 1). The prepared *N*-benzylanilinium salts were purified by recrystallization; their ^{1}H NMR spectra were consistent with the assigned structures.



Scheme 1.

Thermal reaction was carried out by heating 1 g of the salt at 180°C or higher temperature for 2 h with stirring under nitrogen atmosphere. The crude reaction mixtures were dissolved in chloroform and precipitated out from the solution on cooling. To neutralize the anilinium hydrohexafluoroantimonate **2** and **3**, 1 g of the crude salt in 15 ml of dichloromethane solution was shaken with 25 ml of 10% aqueous sodium hydroxide solution, and the organic layer was separated. The aqueous layer was extracted with 20 ml of dichloromethane and the combined organic extract was washed with water. After drying over $MgSO_4$ and evaporating the volatiles, the residue was filtered through a short silica column. The ratio of the isomers **2'** and **3'** was determined by the comparison of integration intensity of the benzylic protons in neutalized anilines. Silica gel column chromatography provided partial separation of pure **2'** and **3'**, which were analyzed by NMR and MS.[8]

To determine the substituent effect on the reactivity of each *N*-benzylanilinium salt, approximately 30 mg of an *N*-benzylanilinium salt was placed in an NMR tube and the tube was heated at 180°C for 30 min. After cooling down, acetone-d_6 was added to the NMR tube and the ^{1}H NMR spectrum was recorded. Conversion of the starting materials to the products was estimated by the integration of the benzylic protons, which in rearranged products appeared at about a 1 to 0.4 ppm higher field than those in the starting materials. Table 1 lists the yields, isomer ratios and conversion of the *N*-benzylanilinium SbF_6^-. The yields of the rearrangement products were higher and the required reaction temperature was lower with the electron donating substituent.

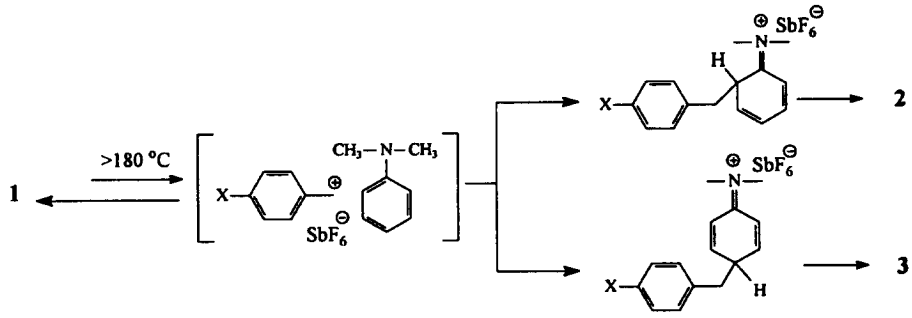
From the above results, we propose the generation of benzylic cation as the first step to produce the

Table 1
Thermal rearrangement of quaternary ammonium salts (**1**)

	X	Yield (%)[a]	Reaction temperature (°C) / time	ratio of 2': 3'	Conversion (%)[b]
a	H	77(62)	190 (2h)	4.2 : 1.0	12
b	OCH_3	95(75)	130 (0.5h)	1.0 : 3.4	100 (100)
c	Cl	72(55)	190 (2h)	4.0 : 1.0	12
d	CH_3	92 (69)	180 (0.5h)	5.0 : 1.0	100 (79)

a) Yields of anilinium salts **2** and **3**. Numbers in parentheses are combined yield of **2'** and **3'** after neutralization. b) Relative conversion at 180℃(0.5h). Numbers in parentheses are conversion at 170℃(0.5h).

rearrangement products as depicted in Scheme 2. Thus, the salt **1** was in fast equilibrium to a tight ion pair of benzyl cation and SbF_6^- at the elevated temperature, and the short lived benzyl cation was added to the electron rich *N,N*-dimethylaniline to undergo the usual electrophilic alkylation. The tight ion pair of benzyl cation and SbF_6^- was postulated because the reaction produced a higher ratio of *ortho* isomers than the usual electrophilic aromatic substitution reaction. Only the methoxy substituent gave more *para* added product, which indicates that methoxy group stabilized benzyl cation probably had a life span long enough to migrate to the *para* position of aniline ring. Trapping the benzyl cation by heating **1** in the presence of triphenylmethane, which is known as the usual hydride donor,[9] proved unsuccessful. This also suggested that there existed a fast equilibrium of **1** to the corresponding benzyl cation ion pair and that the benzyl cation existed as a tight ion pair.



Scheme 2.

In summary, we showed that thermal activation of *N*-benzylanilinium SbF_6^- produced 2- or 4-benzylanilinium SbF_6^-, which resulted from the migration of the benzyl group. The results of the present study provide a better understanding of the mechanism of acid generation from the cationic salts and their polymerization reaction. Since the generated benzylanilinium SbF_6^- was a strong protonic acid, and the temperature for the thermal activation can be controlled by judicious selection of substituents, *N*-benzylanilinium SbF_6^- may find uses in organic synthesis and polymerization as a latent protonic acid generator.[10]

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8. The spectral properties of the isolated products were as follows. **2a′**: EIMS *m/z*: 211[M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–7.33 (m, 9H), 4.17 (s, 2H), 2.73 (s, 6H). **3a′**: EIMS *m/z*: 211 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.25 (m, 5H), 7.05 (d, 2H), 6.68 (d, 2H), 3.88 (s, 2H), 2.89 (s, 6H). **2b′**: EIMs *m/z*: 242 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00–7.24 (m, 6H), 6.81 (d, 2H), 4.03 (s, 2H), 3.77 (s, 3H), 2.67 (s, 6H). **3b′**: EIMS *m/z*: 242 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, 2H), 7.04 (d, 2H), 6.80 (d, 2H), 6.68 (d, 2H), 3.82 (s, 2H), 3.77 (s, 3H), 2.89 (s, 6H). **2c′**: EIMS *m/z*: 245 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89–7.23 (m, 8H), 4.04 (s, 2H), 2.65 (s, 6H). **3c′**: EIMS *m/z*: 245 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, 2H), 7.10 (d, 2H), 7.01 (d, 2H), 6.67 (d, 2H), 3.84 (s, 2H), 2.90 (s, 6H). **2d′**: EIMS *m/z*: 225 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91–7.19 (m, 8H), 4.02 (s, 2H), 2.64 (s, 6H), 2.26 (s, 3H). **3d′**: EIMS *m/z*: 225 [M]$^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–7.07 (m, 6H), 6.68 (d, 2H), 3.84 (s, 2H), 2.89 (s, 6H), 2.16 (s, 3H).
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