The Nucleophilic Substitution Reaction of *p*-Chloronitrobenzene with *N*-Substituted Cyclic Amines under High Pressure[1)]

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(Received April 5, 1995)

An aromatic nucleophilic substitution (S_NAr) reaction of *p*-chloronitrobenzene with *N*-substituted pyrrolidines under high pressure gave *p*-pyrrolidinonitrobenzene and ring-opening products through quaternary ammonium salt. The selectivity of dealkylation and ring-opening depends on the electronic and steric factors of *N*-substituents. The reactions with *N*-methylaziridine and *N*-methylazetidine gave ring-opening products without affording any demethylation product.

Nucleophilic substitution of aromatic halides with amines is not so easy as the substitution reaction of aliphatic halides.[2)] It is limited to the reaction of halides having strong electron-withdrawing substituents with amines of strong nucleophilicity. In our previous work, we have reported that these S_NAr reactions of aromatic halides with primary and secondary amines are effectively accelerated under high pressure to give the corresponding secondary and tertiary arylamines.[3)] Because the reactivity of tertiary amines due to steric hindrance is low in comparison with that of primary and secondary amines, the title reaction has not been easy to start under ordinary pressure. To the best of our knowledge, the only S_NAr reaction with tertiary amines reported is the reaction of heteroaromatic halide such as 2-chlorobenzothiazole with tertiary amines under high pressure.[4)] For example, the reaction with *N*-methylpyrrolidine has been reported to give the demethylation product in high yield without affording any ring-opening product.[4)] Therefore, in this paper we would like to describe the S_NAr reactions of *p*-chloronitrobenzene with various *N*-substituted pyrrolidines under high pressure of 0.75 GPa in order to clarify the steric and electronic effects of *N*-substituted cyclic amines on selectivity of dealkylation and ring-opening processes. The effect of ring strain on the selectivity was also studied in the reaction of *p*-chloronitrobenzene with *N*-methylaziridine and *N*-methylazetidine.

Results and Discussion

The Substituent Effect on the Reaction of *p*-Chloronitrobenzene (1B) with *N*-Substituted Pyrrolidines. The reaction of *p*-chloronitrobenzene (**1B**) with 4.0 molar amounts of *N*-methylpyrrolidine (**2a**) in tetrahydrofuran (THF) under high pressure (0.75 GPa, 80 °C, 48 h) gave *p*-pyrrolidinonitrobenzene (**3a**: 36.7%) through demethylation and 1 : 2-product (**5a**: 62.4%) through pyrrolidine-ring-opening (Table 1, Run 1) (Scheme 1). These products shown in Table 1 were characterized on the basis of the results of elemental analysis, spectral data as given in the experimental part.

The ratio of ring-opening products (**4a** and **5a**) to total yield of the products was 0.63 in the reaction of **1B** with **2a**. The reaction of *N*-ethylpyrrolidine (**2b**) gave ring-opening 1 : 1-product **4b** in low yield (4.5%), along with a similar deethylation product **3a** (3.8%) and ring-opening 1 : 2-product **5b** (62.2%) (Table 1, Run 2). The total yield of the reaction of **2b** is lower than the case of **2a**. An obvious increase of the ratio of ring-opening products to total yield was observed (0.95). The reactions of **1B** with *N*-propylpyrrolidine (**2c**), *N*-butylpyrrolidine (**2d**), and *N*-phenethylpyrrolidine (**2e**) also gave similar results, affording a dealkylation product **3a** and the corresponding ring-opening products **4** and **5** (Table 1, Runs 3—5).

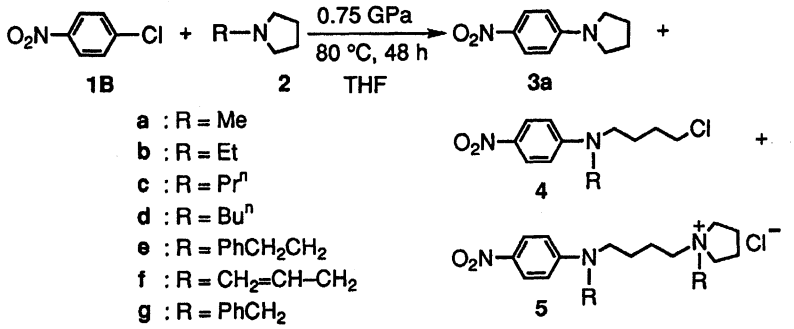
On the contrary, the reaction of *N*-allylpyrrolidine (**2f**) with **1B** increased the deallylation product **3a** (29.7%) with decrease of ring-opening products **4f** (1.0%) and **5f** (16.5%). The ^1H NMR spectrum of **4f** clearly showed the presence of allylic olefin protons at δ=5.10—5.25 and 5.77—5.88 ppm, together with the allylic sp^3 protons at 4.03 ppm. The ratio of ring-opening decreased to 0.37 (Table 1, Run 6). Because *N*-allyl- and *N*-propylpyrrolidines have similar bulkiness, the difference in the ratio may be attributed to the electronic effect of the *N*-substituents. In the transition state of deallylation, the positive charge on the nitrogen of quaternary ammonium salt can delocalize to an allyl group, as shown in Formula TS (Chart 1); this would accelerate the deallylation.

The reaction of *N*-benzylpyrrolidine (**2g**) with **1B**

Table 1. Yields[a] of the Reaction of **1B** with *N*-Substituted Pyrrolidines[b]

Run	Amine	Yield/%				(4+5)/Total	Recovered
	2	**3a**	**4**	**5**	Total		**1**/%
1	**2a**	36.7	0	62.4	99.1	0.63	0
2	**2b**	3.8	4.5	62.2	70.5	0.95	27.8
3	**2c**	1.9	2.7	56.8	61.4	0.97	36.5
4	**2d**	1.6	2.4	49.0	53.0	0.97	45.3
5	**2e**	1.4	1.7	39.1	42.2	0.97	56.8
6	**2f**	29.7	1.0	16.5	47.2	0.37	52.1
7	**2g**	8.1	0	0	17.6[c]	0	80.5

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **1B** and 4.0 mmol of amine, in THF (5 ml). c) Compounds **6** and **7** were obtained in 9.5 and 9.2% yields, respectively.



Scheme 1.

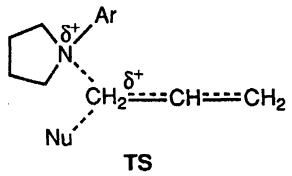
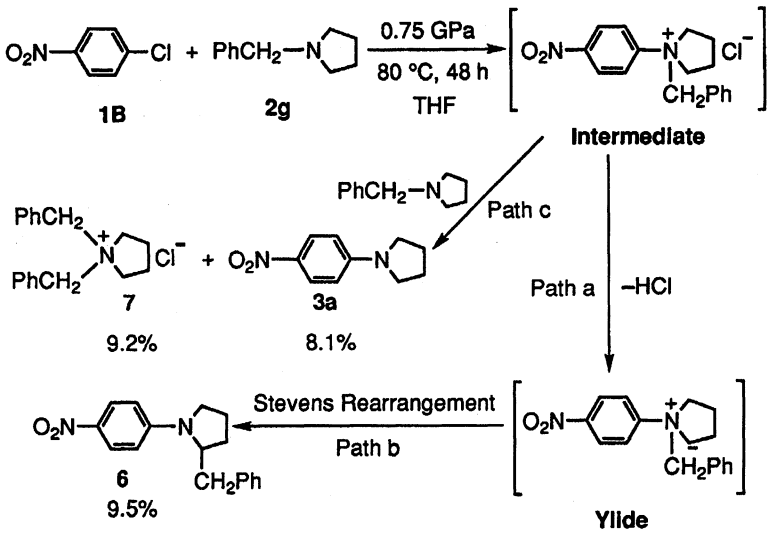


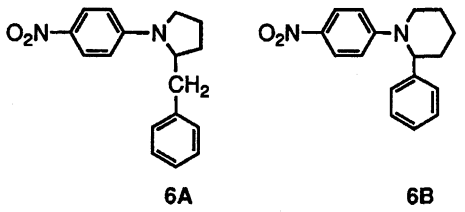
Chart 1.

gave the corresponding debenzylation product **3a** (8.1% yield) along with an unexpected 2-benzyl-*N*-(*p*-nitrophenyl)pyrrolidine (**6**)[5] (9.5% yield) and *N*,*N*-dibenzylpyrrolidinium chloride (**7**)[6] (9.2% yield), without the formation of ring-opening product (Scheme 2).

The elemental analysis showed that product **6** has a molecular formula of HCl elimination from the 1:1-adduct of **1B** and **2g**. The formula suggests two possible structures: **6A** and **6B** (Chart 2). To clarify the structure of **6**, ^{13}C–^1H COSY and ^1H–^1H COSY were measured (Figs. 1 and 2). The ^{13}C–^1H COSY spectrum indicates that the proton observed at 2.58 ppm as a multiplet in its ^1H NMR is connected to the methine carbon



Scheme 2.



6A 6B

Chart 2.

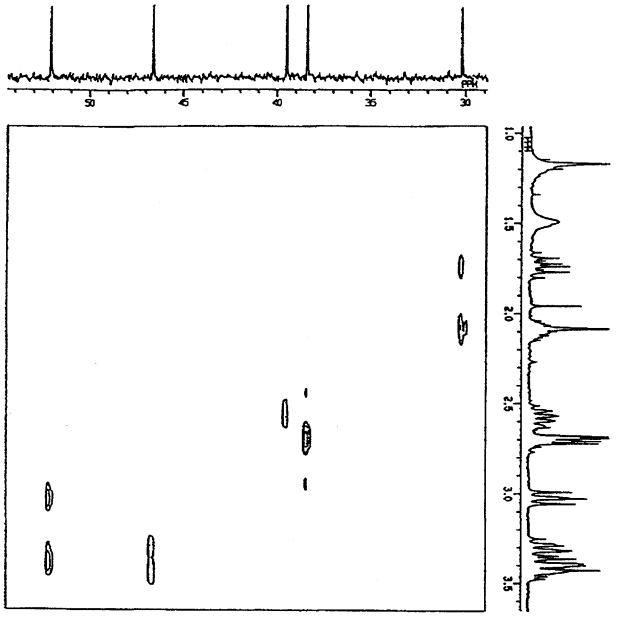


Fig. 1. C–H COSY spectrum of **6** measured in $CDCl_3$.

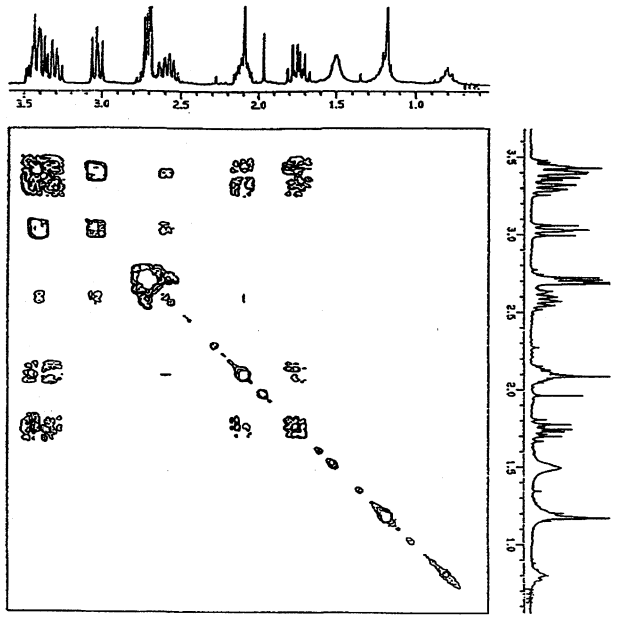


Fig. 2. H–H COSY spectrum of **6** measured in $CDCl_3$.

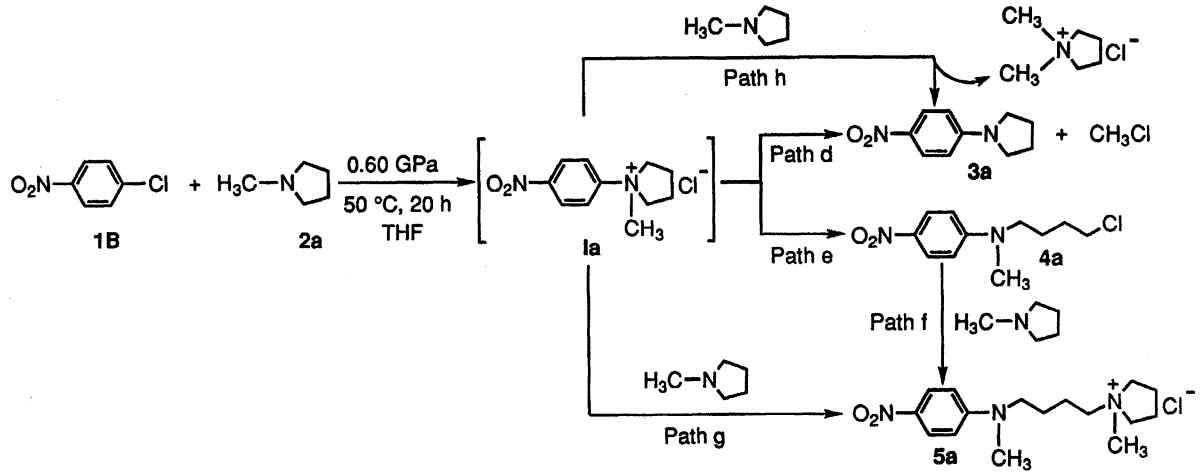
(at δ=40.47 ppm) (Fig. 1). Furthermore, several correlations between neighboring protons were also observed through ^1H–^1H COSY spectrum measurements (Fig. 2); these spectra showed clearly that the real structure of **6** is **6A**.

The preference of the debenzylation to ring-opening is also explained by an electronic effect similar to the reaction of **2f**. The product **6** was presumably formed via a Stevens rearrangement of ylide intermediate, which would be formed by the deprotonation of *N*-benzyl-*N*-(*p*-nitrophenyl)-pyrrolidinium chloride at a methylene group of pyrrolidine ring adjacent to ammonium nitrogen (path a), followed by the migration of benzyl group (path b). High pressure is assumed to accelerate the rearrangement, because the Stevens rearrangement is usually limited to the reaction catalyzed by a strong base such as sodium amide under the ordinary pressure.[7)]

The product **7** seems to correlate with the debenzylation process of the quaternary ammonium ion intermediate to give **3a** (path c). Its formation is explained by two possible paths of the nucleophile attack of *N*-benzylpyrrolidine on the quaternary ammonium ion intermediate. The former one is direct formation of **7** and **3a**. The latter one produces **3a** and benzyl chloride, which reacts with *N*-benzylpyrrolidine to form product **7** in the following step. *N*-Phenyl- and *N*-(*p*-methoxyphenyl)pyrrolidine failed to react with **1** under the same reaction conditions.

The Reaction Mechanism and the Concentration Effect of Amine. To obtain information on the mechanism of this reaction, we also studied the effect of amine concentration on the product ratio of the reaction of **1B** with **2a**. The formation of **3a**, **4a**, and **5a** is explained by the initial formation of a quaternary ammonium chloride intermediate (**Ia**) through S_NAr reaction, which would give **3a** by the demethylation (path d), and **4a** by the ring-opening (path e), followed by the attack of **2a** to give **5a** (path f). There is a possibility of an alternative path to yield **5a** through the direct attack of **2a** on **Ia** (path g), as shown in Scheme 3.

In order to ascertain this mechanism, the effect of the concentration of *N*-methylpyrrolidine (**2a**) on the product ratio was investigated (Table 2). When amount of **2a** was increased from 1.0 to 10.0 mmol, we observed the decrease of the ratio of pyrrolidine-ring-opening products to demethylation product. The reaction of **1B** with an equimolar amount of **2a** gave a demethylation product (**3a**: 7.7%), and ring-opening products (**4a**: 11.3%, **5a**: 14.9%). When 10.0 molar amounts of **2a** was used, the yields of products **3a** (37.0%), **4a** (0.7%), and **5a** (48.0%) increased (Table 2, Run 4). The results shown in Table 2 indicate that the increase of the amount of **2a** caused an increase in the yield of **5a**, sacrificing the yield of **4a**. This is explained by the acceleration of the reaction of *N*-substituted butyl chloride (**4a**) with **2a** to give **5a** (path f). The decrease of the ratio, (**4a**+**5a**)/**3a**, from 3.4 to 1.3 was also observed. The effect of the concentration of **2a** on the decrease of ratio can be explained as follows: (a) path g does not play an important role in the formation of **5a**; (b) *N*-methylpyrrolidine accelerates the demethylation process of **Ia**



Scheme 3.

Table 2. Yields[a] of the Reaction Products of **1B** with **2a**[b]

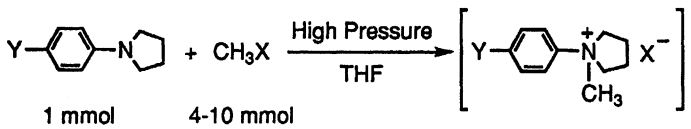
Run	Amine/mmol	Yield/%				Recovered	(4a+5a)/3a
		3a	4a	5a	Total	1B/%	
1	1.0	7.7	11.3	14.9	33.9	66.1	3.4
2	4.0	18.0	7.8	28.3	54.1	45.9	2.0
3	6.0	30.8	4.5	42.1	77.4	22.6	1.5
4	10.0	37.0	0.7	48.0	85.7	14.3	1.3

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **1B**, 0.60 GPa, 50 °C, 20 h, in THF (5 ml).

to give **3a** through path h.

However, the intermediate salt **Ia** is merely a proposed intermediate and has neither been isolated from these reactions nor been prepared independently by the various attempts to methylate **3a**. Therefore, in the next step, we intended to prepare a similar quaternary salt by the methods shown in Scheme 4. We carried out the reaction of *N*-phenylpyrrolidine with excess methyl iodide in THF solution at 50 °C under 0.50 GPa for 4 h and obtained a pale yellow crystalline solid **Ib**. The structure of **Ib** was determined on the basis of elemental analyses and spectroscopic measurements, as shown in the experimental part. Although **Ib** is stable for a few weeks at room temperature, it decomposed to give the demethylation product, *N*-phenylpyrrolidine, in very low yield (4.2%) under 0.75 GPa at 80 °C for 20 h in acetonitrile. We also succeeded in preparing yellow crystals of **Ic** in the reaction of *p*-pyrrolidinoacetophenone with excess methyl iodide under 0.60 GPa at 50 °C for 12 h; these also decomposed to give a demethylation product, *p*-pyrrolidinoacetophenone, in 8.2% under 0.75 GPa at 80 °C for 20 h in acetonitrile. On the other hand, white ammonium salt **Id** prepared by the reaction of *N*-phenylpyrrolidine with excess methyl chloride under high pressure (0.90 GPa at room temperature for 20 h in THF) was found to be extremely unstable at room temperature under atmospheric pressure; it gives the demethylation product immediately in nearly quantitative yield. Thus, according to the stability of these quaternary ammonium salt **Ib—d**, we may suppose that the failure to isolate the intermediate **Ia** can be ascribed to the instability of chloride salt of quaternary ammonium ion.

The Effect of Halide on the Selectivity of the Reaction. In our previous work on the reaction of *p*-halonitrobenzenes with pyrrolidine under high pressure



Ia: X = Cl, Y = NO_2
Ib: X = I, Y = H
Ic: X = I, Y = CH_3CO
Id: X = Cl, Y = H

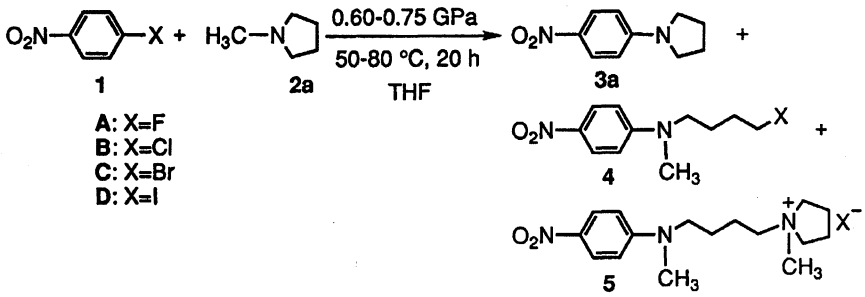
Scheme 4.

at 80 °C for 50 h, this order of reactivity (F>Cl>Br>I) was reported.[3] Bunnett and his co-workers pointed out the reactivity ratio of halides in the reaction of 1-halo-2,4-dinitrobenzenes with piperidine at 90.8 °C in methanol is F : Cl : Br : I = 3100 : 13.6 : 11.8 : 1.0.[5] These results are consistent with the polarizability or electronegativity of halogen. Therefore, the attack of nucleophile to aryl halide can be concluded to be the rate-determining step in the reaction of aryl halides with primary and secondary amines. However, the reaction of 1-halo-2,4-dinitrobenzenes with *N*-methylaniline in nitrobenzene or in 99.8% ethanol revealed that the order of reactivity was Br>Cl>F.[6] These results showed that two effects of halogen on the reactivity of S_NAr reaction of aryl halide with amine can be explained. Therefore, in order to investigate the effect of halogen on the reactivity of the S_NAr reaction of aryl halide with cyclic tertiary amine under high pressure, we carried out the reaction of *p*-halonitrobenzenes with *N*-methylpyrrolidine under the reaction conditions shown below (Scheme 5, Table 3).

The reaction of *p*-fluoronitrobenzene (**1A**) with **2a** under 0.60 GPa at 50 °C for 20 h gave demethylation product **3a** (6.8%), ring-opening product **4A** (0.8%) and **5A** (7.5%) together with recovered **1A** (83.2%) (Table 3, Run 1). A large coupling (47.18 Hz) of two methylene protons at 4.45 ppm with fluorine indicated that a fluorine atom correlates with the methylene group in **4A**. The reaction of *p*-bromonitrobenzene (**1C**) gave the demethylation product **3a** (37.9%) and the ring-opening 1 : 2-product **5C** (36.5%). The reaction of *p*-iodonitrobenzene (**1D**) gave demethylation product **3a** (11.3%) and the ring-opening 1 : 2-product **5D** (18.2%) along with recovered **1D** (69.3%). In these cases **1A** was found to be less reactive than **1B**, **1C** or **1D**. Similar results were obtained in these reactions under strong reaction conditions of 0.75 GPa at 80 °C for 20 h. These results indicated that the order of reactivity of halogen in the reaction of *p*-halonitrobenzenes with cyclic tertiary amines under high pressure is Br>Cl>I>F. This is consistent with the order of C–X bond-breaking reactivity, except for case of iodide.[6] Therefore, it can be assumed that the cleavage of halogen–Ar bond is the rate-determining step in the initial S_NAr reaction of aryl halides with cyclic tertiary amines under high pressure. The low reactivity of iodide is attributed to the bulkiness of iodine, which would hinder the formation of the intermediate.

According to the ratios of **(4+5)/3a** shown in Table 3, the selectivity of ring-opening reaction and demethylation of quaternary ammonium intermediate in the second step seems to depend on the halogen atom of aryl halide. Although the ratios of **(4+5)/3a** are not so largely affected by the reaction conditions (0.60 GPa, 50 °C; 0.75 GPa, 80 °C), the change of the values suggests the complicated mechanism (path d—h) of the second step of the reaction, as shown in Scheme 3.

The Ring Size Effect in the Reaction of 1B

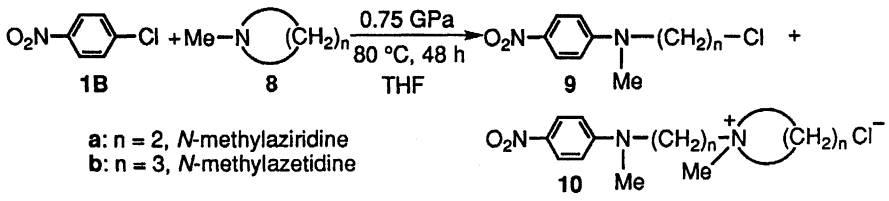


Scheme 5.

Table 3. Reaction of **1** with *N*-Methylpyrrolidine **2a**[a]

Run	X	Pressure	Temp	Yield/%[b]				Recovered	(4+5)/3a
		GPa	°C	3a	4	5	Total	1/%	
1	F	0.60	50	6.8	0.8	7.5	15.1	83.2	1.22
2	Cl	0.60	50	18.0	7.8	28.3	54.1	45.9	2.00
3	Br	0.60	50	37.9	0	36.5	74.4	24.7	0.96
4	I	0.60	50	11.3	0	18.2	29.5	69.3	1.61
5[c]	F	0.75	80	15.3	0	19.5	34.8	63.8	1.27
6	Cl	0.75	80	35.0	0	60.1	95.1	4.9	1.72
7[c]	Br	0.75	80	53.9	0	45.8	99.7	0	0.85
8[c]	I	0.75	80	26.7	0	36.3	63.0	36.1	1.36

a) Reaction conditions: 1.0 mmol of **1** and 4.0 mmol of **2a**, 20 h, in THF (5 ml). b) Isolated yield by medium-pressure column chromatography. c) The yields were determined by ^1H NMR.



Scheme 6.

Table 4. Yields[a] of the Reaction of **1B** with *N*-Methylaziridine and *N*-Methylazetidine[b]

Run	Amine	Yield/%			Recovered
		9	**10**	Total	**1B**/%
1	*N*-Methylaziridine	15.0	80.5	95.5	2.3
2	*N*-Methylazetidine	0.5	86.5	87.0	12.4

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **1B** and 4.0 mmol of amine, in THF (5 ml).

with *N*-Methylaziridine (8a) and *N*-Methylazetidine (8b). We also studied the reactions of **1B** with tertiary amines of three- and four-membered rings in order to investigate the effect of ring size on the ring-opening process of the quaternary ammonium salt intermediate (Table 4).

The reaction of **1B** with *N*-methylaziridine (**8a**) gave the ring-opening products **9a** (15.0%) and **10a** (80.5%), along with recovered **1B** (2.3%) without affording any demethylation product (Scheme 6). Although the reaction of *N*-methylazetidine (**8b**) also gave the ring-opening products in high total yield, as shown in Table 4, the yield of **9b** was very low. This can be attributed to the higher reactivity of **8b** towards **9b**. Table 4 also indicates that **8a** is more reactive than **8b** in the reaction with **1B** under high pressure.

In summary, the S_NAr reactions studied here proceed in a similar manner to those of the von Braun reaction of tertiary amines with cyanogen bromide. The chemical behaviors of the quaternary ammonium ion intermediates formed in the initial step of these two reactions are quite similar.[8] The bulkiness of the *N*-substituent seems to suppress the initial step to form the quaternary ammonium salt intermediate. The nucleophilic attack of chloride ion and tertiary amine on the alkyl group or a methylene carbon of pyrrolidine ring of the intermediate give the dealkylation or ring-opening products, respectively. The increase of bulkiness of *N*-substituent of the tertiary amine decreases dealkylation products by the nucleophilic attack on alkyl group. Highly strained aziridine and azetidine ring systems accelerate the ring-opening reactions, in comparison with the pyrrolidine system, due to the strong unstability of their quaternary ammonium salt intermediates.

Experimental

General. Melting points were measured with a Yanagimoto Melting Point Apparatus and are not corrected. IR spectra were recorded on a Perkin–Elmer model 983. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL EX-270 in a $CDCl_3$ or CD_3OD or DMSO-d_6 solution using TMS as an internal standard. Mass spectra were measured with a JEOL JMS-DX303 spectrometer.

Material. Commercial *p*-substituted aryl halides were purified by recrystallization. THF was purified by distillation after reflux over $LiAlH_4$, and stored with molecular sieves type 4A under nitrogen atmosphere. *N*-methylpyrrolidine and *N*-butylpyrrolidine were purified by distillation under nitrogen atmosphere after an appropriate drying procedure. The following compounds were prepared, referring to references. *N*-ethylpyrrolidine (**2b**),[9] *N*-propylpyrrolidine (**2c**),[9] *N*-phenethylpyrrolidine (**2e**),[10] *N*-allylpyrrolidine (**2f**),[11] *N*-benzylpyrrolidine (**2g**),[12] *N*-phenylpyrrolidine,[12] *N*-(*p*-methoxyphenyl)pyrrolidine,[13] *N*-ethylaziridine (**8a**),[14] *N*-ethylazetidine (**8b**).[14]

General Procedure for the S_NAr Reaction of 1 with Amines. A THF solution (5 cm^3) of **1** (1.0 mmol) with amine (4.0 mmol) was treated with high pressure in a Teflon® capsule using a Hikari Kouatsu High Pressure Apparatus under the cited reaction conditions. After the removal of solvent under reduced pressure, the residue was suspended in toluene, and ammonium salt was separated by filtration on a sintered glass-filter and the solid was rinsed several times with small amount of toluene. The combined toluene solution was concentrated under reduced pressure and the residue was separated by medium-pressure column chromatography on silica gel with ethyl acetate/hexane as an eluent. The solid was dissolved with methanol. After the evaporation of methanol, the residue was isolated by medium-pressure column chromatography on Lichroprep Si 60 with methanol/dichloromethane as an eluent. Products were characterized on the basis of ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis after separation by medium-pressure column chromatography and recrystallization.

All of ammonium salts crystallized from methanol–ethyl acetate did not melt under 250 °C, but underwent slow decomposition starting almost at 250 °C.

***p*-Pyrrolidinonitrobenzene (3a):** Yellow crystals (from benzene–heptane); mp 178.0—179.0 °C. It was characterized by comparing the spectroscopic data with the authentic sample prepared before.[2]

***N*-Methyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (4a):** Yellow crystals (from benzene–heptane); mp 88.5—89.2 °C; IR (KBr) 2951, 2921, 1593, 1523, 1477, 1294, 1105, 993, 947, 822, 753, and 697 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.82 (2H, m, CH_2), 1.83 (2H, m, CH_2), 3.09 (3H, s, Me), 3.48 (2H, t, J=6.93 Hz, NCH_2), 3.58 (2H, t, J=6.27 Hz, CH_2Cl), 6.61 (2H, d, J=9.56 Hz, arom-H), 8.12 (2H, d, J=9.56 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.33 (t, CH_2), 29.78 (t, CH_2), 38.71 (q, Me), 44.43 (t, NCH_2), 51.89 (t, $^2J_{C-H}$=3.66 Hz, CH_2Cl), 110.14 (d, arom-C), 126.26 (d,

arom-C), 136.90 (s, arom-C), 153.29 (s, arom-C). MS m/z (rel intensity) 242 (M^+; 13), 165 (100), 149 (3), 119 (31), 77 (C_6H_4+1; 2). Found: C, 54.55; H, 6.28; N, 11.38%. Calcd for $C_{11}H_{15}O_2N_2Cl$: C, 54.44; H, 6.23; N, 11.54%.

***N*-[4-(*N*-Methyl-*p*-nitrophenylamino)butyl]-*N*-methylpyrrolidinium Chloride (5a):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2949, 1599, 1574, 1522, 1473, 1395, 1334, 1200, 1117, 823, 753, 731, and 695 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6) δ=1.56 (2H, m, CH_2), 1.77 (2H, m, CH_2), 2.09 (4H, m, CH_2), 3.00 (3H, s, Me), 3.09 (3H, s, Me), 3.36 (2H, m, NCH_2), 3.48 (4H, m, N^+CH_2), 3.53 (2H, t, N^+CH_2), 6.81 (2H, d, J=9.57 Hz, arom-H), 8.05 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=20.45 (t, CH_2), 21.12 (t, CH_2), 23.37 (t, CH_2), 38.47 (q, Me), 47.53 (q, Me), 51.11 (t, NCH_2), 62.67 (t, N^+CH_2), 63.45 (t, N^+CH_2), 110.67 (d, arom-C), 125.94 (d, arom-C), 135.51 (s, arom-C), 153.46 (s, arom-C). Found: C, 58.39; H, 8.24; N, 12.67%. Calcd for $C_{16}H_{26}O_2N_3Cl$: C, 58.62; H, 7.99; N, 12.82%.

***N*-Ethyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (4b):** Yellow oil; IR (neat) 2927, 1595, 1513, 1482, 1308, 1200, 1112, 1075, 999, 824, 753, and 696 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.23 (3H, t, J=7.26 Hz, Me), 1.80—1.84 (4H, m, CH_2), 3.38—3.51 (4H, m, NCH_2), 3.59 (2H, t, J=5.94 Hz, CH_2Cl), 6.29 (2H, dd, J_1=9.57 Hz, J_2=2.31 Hz, arom-H), 8.11 (2H, dd, J_1=9.57 Hz, J_2=2.31 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=12.17 (q, Me), 24.75 (t, CH_2), 29.81 (t, CH_2), 44.40 (t, NCH_2), 45.49 (t, NCH_2), 49.92 (t, CH_2Cl), 110.01 (dd, $^2J_{CH}$=5.50 Hz, arom-C), 126.44 (dd, $^2J_{CH}$=4.88 Hz, arom-C), 136.63 (s, arom-C), 152.25 (s, arom-C). Found: m/z 256.0986. Calcd for $C_{12}H_{17}O_2N_2Cl$: M, 256.1318.

***N*-[4-(*N*-Ethyl-*p*-nitrophenylamino)butyl]-*N*-ethylpyrrolidinium Chloride (5b):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2978, 1779, 1674, 1595, 1516, 1481, 1407, 1311, 1277, 1201, 828, 796, 753, and 705 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6) δ=1.15 (3H, t, J=6.27 Hz, Me), 1.26 (3H, t, J=6.27 Hz, Me), 1.60—1.73 (4H, m, CH_2), 2.07 (4H, m, br, CH_2), 3.25—3.37 (4H, m, NCH_2), 3.43—3.52 (8H, m, N^+CH_2), 6.81 (2H, d, J=9.24 Hz, arom-H), 8.04 (2H, d, J=9.24 Hz, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=8.41 (q, Me), 11.93 (q, Me), 19.95 (t, CH_2), 21.43 (t, CH_2), 23.72 (t, CH_2), 49.27 (t, NCH_2), 52.18 (t, NCH_2), 54.20 (t, N^+CH_2), 57.86 (t, N^+CH_2), 61.61 (t, N^+CH_2), 110.47 (d, arom-C), 126.02 (d, arom-C), 135.21 (s, arom-C), 152.41 (s, arom-C). Found: C, 60.93; H, 8.45; N, 11.73%. Calcd for $C_{18}H_{30}O_2N_3Cl$: C, 60.75; H, 8.50; N, 11.81%.

***N*-Propyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (4c):** Yellow oil; IR (neat) 2938, 1590, 1516, 1485, 1301, 1204, 1108, 990, 832, 805, and 756 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.02 (3H, t, J=7.26 Hz, Me), 1.68 (2H, m, $C\underline{H}_2CH_3$), 1.81—1.84 (4H, m, $C\underline{H}_2C\underline{H}_2CH_2Cl$), 3.34 (2H, t, J=7.26 Hz, NCH_2), 3.42 (2H, t, J=5.26 Hz, NCH_2), 3.61 (2H, t, J=6.26 Hz, CH_2Cl), 6.57 (2H, d, J=9.57 Hz, arom-H), 8.10 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=11.30 (q, Me), 20.38 (t, CH_2), 24.56 (t, CH_2), 29.83 (t, CH_2), 44.44 (t, NCH_2), 50.57 (t, NCH_2), 53.01 (t, CH_2Cl), 110.12 (d, arom-C), 126.43 (d, arom-C), 136.65 (s, arom-C), 152.49 (s, arom-C). Found: m/z 270.1106. Calcd for $C_{13}H_{19}O_2N_2Cl$: M, 270.1135.

***N*-[4-(*N*-Propyl-*p*-nitrophenylamino)butyl]-*N*-propylpyrrolidinium Chloride (5c):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2965, 2881, 1674, 1595, 1516, 1478, 1473, 1313, 1204, 1131, 995, 822, 800, 753, and 722 cm^{-1}; ^1H NMR (270 MHz, CD_3OD) δ=0.92 (6H, m, Me), 1.58—1.70 (8H, m, CH_2), 2.08 (4H, m, CH_2), 3.19—3.52 (12H, m, NCH_2 and N^+CH_2), 6.80 (2H, d, J=9.57 Hz, arom-H), 8.03 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, CD_3OD) δ=10.76 (q, Me), 11.19 (q, Me), 16.44 (t, CH_2), 20.23 (t, CH_2), 20.28 (t, CH_2), 21.80 (t, CH_2), 23.79 (t, CH_2), 50.17 (t, NCH_2), 52.14 (t, NCH_2), 58.85 (t, N^+CH_2), 60.69 (t, N^+CH_2), 62.51 (t, N^+CH_2), 110.94 (d, arom-C), 126.41 (d, arom-C), 135.49 (s, arom-C), 153.06 (s, arom-C). Found: C, 62.44; H, 8.75; N, 11.09%. Calcd for $C_{20}H_{34}O_2N_3Cl$: C, 62.56; H, 8.93; N, 10.94%.

***N*-Butyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (4d):** Yellow oil; IR (neat) 2955, 2925, 2870, 1724, 1595, 1515, 1487, 1201, 1113, 824, and 753 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=0.98 (3H, t, J=7.26 Hz, Me), 1.37 (2H, m, CH_2), 1.61 (2H, m, CH_2), 1.79—1.81 (4H, m, CH_2), 3.34—3.44 (4H, m, NCH_2), 3.59 (2H, t, J=5.94 Hz, CH_2Cl), 6.57 (2H, d, J=9.57 Hz, arom-H), 8.10 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=13.87 (q, Me), 20.20 (t, CH_2), 24.55 (t, CH_2), 29.20 (t, CH_2), 29.81 (t, CH_2), 44.42 (t, NCH_2), 50.50 (t, NCH_2), 51.11 (t, CH_2Cl), 110.08 (d, arom-C), 126.42 (d, arom-C), 136.70 (s, arom-C), 152.43 (s, arom-C). Found: m/z 284.1284. Calcd for $C_{14}H_{21}N_2O_2Cl$: M, 284.1291.

***N*-[4-(*N*-Butyl-*p*-nitrophenylamino)butyl]-*N*-butylpyrrolidinium Chloride (5d):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2961, 2876, 1684, 1595, 1516, 1480, 1310, 1202, 1113, 826, 801, 754, and 719 cm^{-1}; ^1H NMR (270 MHz, CD_3OD) δ=0.96—1.03 (6H, m, Me), 1.36—1.45 (4H, m, CH_2), 1.59—1.81 (8H, m, CH_2), 2.20 (4H, m, br, CH_2), 3.26—3.56 (12H, m, NCH_2 and N^+CH_2), 6.73 (2H, dd, J_1=9.57 Hz, J_2=1.98 Hz, arom-H), 8.05 (2H, dd, J_1=9.57 Hz, J_2=1.98 Hz, arom-H); ^{13}C NMR (67.8 MHz, CD_3OD) δ=13.87 (q, Me), 14.25 (q, Me), 20.74 (t, CH_2), 21.09 (t, CH_2), 21.65 (t, CH_2), 22.91 (t, CH_2), 24.96 (t, CH_2), 26.16 (t, CH_2), 30.26 (t, CH_2), 51.26 (t, CH_2), 51.82 (t, CH_2), 60.64 (t, CH_2), 61.00 (t, CH_2), 64.02 (t, CH_2), 111.59 (d, arom-C), 127.24 (d, arom-C), 137.34 (s, arom-C), 154.25 (s, arom-C). Found: C, 64.41; H, 9.14; N, 10.30%. Calcd for $C_{22}H_{38}O_2N_3Cl$: C, 64.13; H, 9.30; N, 10.20%.

***N*-Phenethyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (4e):** Yellow oil; IR (neat) 2923, 2850, 1723, 1594, 1513, 1487, 1262, 1199, 1114, 825, 752, and 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.71—1.81 (4H, m, CH_2), 2.92 (2H, t, J=7.59 Hz, CH_2), 3.29 (2H, t, J=7.59 Hz, CH_2), 3.54 (2H, t, J=6.27 Hz, CH_2), 3.64 (2H, t, J=7.59 Hz, CH_2), 6.62 (2H, dd, J_1=9.56 Hz, J_2=2.03 Hz, arom-H), 7.18—7.36 (5H, m, Phenyl-H), 8.13 (2H, dd, J_1=9.56 Hz, J_2=2.03 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.46 (t, CH_2), 29.74 (t, CH_2), 33.39 (t, CH_2), 44.35 (t, CH_2), 50.80 (t, CH_2), 53.03 (t, CH_2), 110.24 (d, arom-C), 126.45 (d, arom-C), 126.79 (phenyl-C), 128.72 (phenyl-C), 128.81 (phenyl-C), 136.81 (s, arom-C), 138.35 (phenyl-C), 152.15 (s, arom-C). Found: m/z 332.1312. Calcd for $C_{18}H_{21}O_2N_2Cl$: M, 332.1291.

***N*-[4-(*N*-Phenyl-*p*-nitrophenylamino)butyl]-*N*-phenethylpyrrolidinium Chloride (5e):** Yellow crystal (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2933,

1594, 1516, 1477, 1302, 1199, 1112, 827, 753, and 701 cm^{-1}; ^1H NMR (270 MHz, CD_3OD) δ=1.60 (2H, m, CH_2), 1.78 (2H, m, CH_2), 2.22 (4H, m, CH_2), 2.94 (2H, t, J=6.27 Hz, CH_2), 3.07 (2H, t, CH_2), 3.34—3.43 (4H, m, CH_2), 3.53 (2H, t, br, N^+CH_2), 3.63 (4H, m, N^+CH_2), 3.73 (2H, t, J=7.59 Hz, N^+CH_2), 6.81 (2H, d, J=7.26 Hz, arom-H), 7.21—7.31 (10H, m, Phenyl-H), 8.10 (2H, d, J=7.26 Hz, arom-H); ^{13}C NMR (67.8 MHz, CD_3OD) δ=22.57 (t, CH_2), 23.73 (t, CH_2), 25.69 (t, CH_2), 31.38 (t, CH_2), 35.03 (t, CH_2), 52.33 (t, CH_2), 54.62 (t, CH_2), 62.66 (t, N^+CH_2), 62.68 (t, N^+CH_2), 65.09 (t, N^+CH_2), 112.60 (d, arom-C), 128.06 (d, arom-C), 128.39 (d, phenyl-C), 129.22 (d, phenyl-C), 130.49 (d, phenyl-C), 130.56 (d, phenyl-C), 130.80 (d, phenyl-C), 130.84 (d, phenyl-C), 138.07 (s, arom-C), 138.55 (s, phenyl-C), 141.00 (s, phenyl-C), 154.81 (s, arom-C). Found: C, 70.68; H, 7.77; N, 8.05%. Calcd for $C_{30}H_{38}O_2N_3Cl$: C, 70.92; H, 7.54; N, 8.27%.

***N*- Allyl- *N*- (4- chlorobutyl)- *p*- nitroaniline (4f):** Yellow oil; IR (neat) 2960, 2930, 2713, 1639, 1589, 1530, 1452, 1336, 1296, 1205, 1163, 1107, 995, 937, and 820 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.83—1.87 (4H, m, CH_2), 3.44 (2H, t, J=7.58 Hz, NCH_2), 3.59 (2H, t, J=5.94 Hz, CH_2Cl), 4.03 (2H, m, $NC\underline{H}_2$–CH=CH_2), 5.10—5.25 (2H, m, CH=C$\underline{H}_2$), 5.77—5.88 (1H, m, C$\underline{H}$=CH_2), 6.60 (2H, d, J=9.57 Hz, arom-H), 8.11 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.61 (t, CH_2), 29.77 (t, CH_2), 44.40 (t, NCH_2), 50.44 (t, CH_2Cl), 53.24 (t, N$\underline{C}H_2$–CH=CH_2), 110.43 (d, arom-C), 117.04 (t, olefin-C), 126.28 (d, arom-C), 131.75 (d, olefin-C), 137.10 (s, arom-C), 152.72 (s, arom-C). Found: m/z 268.0944. Calcd for $C_{13}H_{17}O_2N_2Cl$: M, 268.0978.

***N*-[4-(*N*-Allyl-*p*-nitrophenylamino)butyl]-*N*-allylpyrrolidinium Chloride (5f):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2956, 1773, 1735, 1676, 1595, 1514, 1481, 1314, 1252, 1201, 1113, 993, 952, 798, and 706 cm^{-1}; ^1H NMR (270 MHz, CD_3OD) δ=1.65—1.93 (4H, m, CH_2), 2.21 (4H, m, br, CH_2), 3.30—3.63 (8H, m, NCH_2 and N^+CH_2), 4.12 (2H, m, $NC\underline{H}_2$–CH=CH_2), 5.09—5.18 (2H, m, NCH_2–CH=C$\underline{H}_2$), 5.67—5.74 (4H, m, $N^+C\underline{H}_2$–CH=C$\underline{H}_2$), 5.81—5.95 (1H, m, NCH_2–C$\underline{H}$=CH_2), 5.96—6.14 (1H, m, N^+CH_2–C$\underline{H}$=CH_2), 6.76 (2H, dd, J_1=9.57 Hz, J_2=3.63 Hz, arom-H), 8.06 (2H, dd, J_1=9.57 Hz, J_2=3.63 Hz, arom-H).

2-Benzyl-1-(*p*-nitrophenyl)pyrrolidine (6): Yellow crystals (from benzene–heptane); mp 110.4—111.2 °C; IR (KBr) 2959, 2919, 2850, 1603, 1520, 1487, 1400, 1317, 1261, 1113, 1095, 1023, 803, 753, and 702 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.68—2.16 (2H, m, 4-CH_2), 2.58 (1H, m, 2-CH), 2.70—2.76 (2H, m, Benzyl-CH_2), 3.01—3.49 (4H, m, 3-CH_2 and 5-CH_2), 6.36 (2H, dd, J_1=9.24 Hz, J_2=1.98 Hz, arom-H), 7.11—7.29 (5H, m, phenyl-H), 8.03 (2H, dd, J_1=9.24 Hz, J_2=1.98 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=31.18 (t, 4-CH_2), 39.35 (t, benzyl-CH_2), 40.47 (d, 2-CH), 47.59 (t, 5-CH_2), 53.07 (t, 3-CH_2), 110.28 (d, arom-C), 126.29 (d, arom-C), 126.42 (d, phenyl-C), 128.61 (d, phenyl-C), 128.63 (d, phenyl-C), 136.68 (s, arom-C), 139.87 (s, phenyl-C), 151.77 (s, arom-C). Found: C, 72.28; H, 6.72; N, 10.12%. Calcd for $C_{17}H_{18}O_2N_2$: C, 72.32; H, 6.43; N, 9.92%.

***N*,*N*′-Dibenzylpyrrolidinium Chloride (7):** Yellow crystals (from ethanol); mp>250 °C; IR (KBr) 1676, 1452, 1206, 1135, 839, 801, 757, 722, and 705 cm^{-1}; ^1H NMR (270 MHz, CD_3OD) δ=2.08 (4H, m, CH_2), 3.54 (4H, m, N^+CH_2), 4.60 (4H, s, benzyl-CH_2), 7.47—7.60 (10H, m, phenyl-H); ^{13}C NMR (67.8 MHz, CD_3OD) δ=23.04 (t, CH_2), 55.65 (t, N^+CH_2), 60.46 (t, benzyl-CH_2), 130.10 (s, phenyl-C), 131.33 (d, phenyl-C), 132.71 (d, phenyl-C), 135.08 (d, phenyl-C). Found: C, 74.92; H, 7.94; N, 4.66%. Calcd for $C_{18}H_{22}NCl$: C, 75.11; H, 7.70; N, 4.87%.

***N*- Methyl- *N*- phenylpyrrolidinium Iodide (1b):** Pale yellow crystals (from dichloromethane–toluene); mp 152.8—154.3 °C; IR (KBr) 1594, 1493, 1476, 1450, 1339, 1319, 1306, 1248, 1201, 1156, 1083, 1035, 1006, 931, 876, 832, 778, and 693 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=2.33—2.52 (4H, m, CH_2), 3.71 (3H, s, Me), 4.07—4.76 (4H, m, N^+CH_2), 7.50—7.63 (3H, m, 3-, and 4-phenyl-H), 7.94 (2H, d, J=8.25 Hz, 2-phenyl-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=21.03 (t, CH_2), 55.78 (q, Me), 66.67 (t, N^+CH_2), 121.06 (d, phenyl-C), 130.49 (d, phenyl-C), 130.64 (d, phenyl-C), 145.93 (s, phenyl-C). Found: C, 45.55; H, 5.52; N, 4.85%. Calcd for $C_{11}H_{16}NI$: C, 45.69; H, 5.58; N, 4.84%.

***N*- Methyl- *N*- (*p*- acetylphenyl)pyrrolidinium Iodide (1c):** Yellow crystals (from dichloromethane–toluene); mp 143.3—144.1 °C; IR (KBr) 3099, 1684, 1601, 1466, 1449, 1437, 1415, 1366, 1316, 1301, 1273, 1257, 1200, 1129, 1114, 1012, 963, 931, 865, 852, 841, and 669 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=2.19—2.26 (4H, m, CH_2), 2.66 (3H, s, COMe), 3.43 (3H, s, N^+Me), 3.98—4.38 (4H, m, N^+CH_2), 8.05 (2H, d, J=8.91 Hz, arom-H), 8.17 (2H, d, J=8.91 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=20.33 (t, CH_2), 27.04 (q, CO$\underline{Me}$), 53.95 (q, N^+Me), 65.27 (t, N^+CH_2), 122.01 (d, arom-C), 129.82 (d, arom-C), 137.66 (s, arom-C), 149.92 (s, arom-C), 196.99 (s, CO). Found: C, 46.90; H, 5.39; N, 4.24%. Calcd for $C_{13}H_{18}ONI$: C, 47.15; H, 5.48; N, 4.23%.

***N*-Methyl-*N*-(4-fluorobutyl)-*p*-nitroaniline (4A):** Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ=1.68—1.81 (4H, m, CH_2), 3.09 (3H, s, Me), 3.50 (2H, t, J=7.59 Hz, NCH_2), 4.45 (2H, dt, $J_{H,F}$=47.18 Hz, $J_{H,H}$=5.61 Hz, CH_2F), 6.61 (2H, dd, J_1=9.56 Hz, J_2=2.30 Hz, arom-H), 8.12 (2H, dd, J_1=9.56 Hz, J_2=2.30 Hz, 3-H arom-H).

***N*- [4- (*N*- Methyl- *p*- nitrophenylamino)butyl]- *N*- methylpyrrolidinium Fluoride (5A):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; 2956, 1597, 1518, 1479, 1431, 1390, 1315, 1203, 825, 800, 754, 723, and 707 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6) δ=1.53 (2H, m, CH_2), 1.56 (2H, m, CH_2), 2.08 (4H, m, CH_2), 2.98 (3H, s, Me), 3.08 (3H, s, Me), 3.31—3.55 (8H, m, $ArNCH_2$ and N^+CH_2), 6.81 (2H, d, J=9.57 Hz, arom-H), 8.05 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=20.44 (t, CH_2), 21.12 (t, CH_2), 23.33 (t, CH_2), 38.46 (q, Me), 47.55 (q, Me), 51.10 (t, NCH_2), 62.69 (t, N^+CH_2), 63.46 (t, N^+CH_2), 110.66 (d, arom-C), 125.92 (d, arom-C), 135.52 (s, arom-C), 153.44 (s, arom-C). Found: C, 61.78; H, 8.49; N, 13.24%. Calcd for $C_{16}H_{26}O_2N_3F$: C, 61.71; H, 8.42; N, 13.49%.

***N*- [4- (*N*- Methyl- *p*- nitrophenylamino)butyl]- *N*- methylpyrrolidinium Bromide (5C):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2948, 1598, 1522, 1475, 1393, 1332, 1199, 1116, 822, 753, 729, and 706 cm^{-1}; ^1H NMR (270 MHz, DMSO-d_6) δ=1.58 (2H, m, CH_2), 1.80 (2H, m, CH_2), 2.11 (4H, m, CH_2), 3.03 (3H, s, Me), 3.10 (3H, s, Me), 3.38—3.57 (8H, m, $ArNCH_2$ and N^+CH_2), 6.83 (2H, d, J=9.57 Hz, arom-H), 8.05 (2H,

d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=20.48 (t, CH_2), 21.14 (t, CH_2), 23.31 (t, CH_2), 38.45 (q, Me), 47.63 (q, Me), 51.13 (t, NCH_2), 62.70 (t, N^+CH_2), 63.50 (t, N^+CH_2), 110.95 (d, arom-C), 125.95 (d, arom-C), 135.48 (s, arom-C), 153.49 (s, arom-C). Found: C, 51.74; H, 7.23; N, 11.04%. Calcd for $C_{16}H_{26}O_2N_3Br$: C, 51.62; H, 7.04; N, 11.29%.

***N*-[4-(*N*-Methyl-*p*-nitrophenylamino)butyl]-*N*-methylpyrrolidinium Iodide (5D):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2953, 1596, 1518, 1473, 1395, 1309, 1201, 1112, 999, 932, 823, 754, 732, and 706 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-d_6) δ=1.56 (2H, m, CH_2), 1.76 (2H, m, CH_2), 2.09 (4H, m, CH_2), 2.98 (3H, s, Me), 3.08 (3H, s, Me), 3.31—3.55 (8H, m, $ArNCH_2$ and N^+CH_2), 6.81 (2H, d, J=9.24 Hz, arom-H), 8.05 (2H, d, J=9.24 Hz, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=20.47 (t, CH_2), 21.14 (t, CH_2), 23.34 (t, CH_2), 38.48 (q, Me), 47.64 (q, Me), 51.13 (t, NCH_2), 62.73 (t, N^+CH_2), 63.51 (t, N^+CH_2), 110.69 (d, arom-C), 125.96 (d, arom-C), 135.54 (s, arom-C), 153.48 (s, arom-C). Found: C, 45.59; H, 6.35; N, 10.21%. Calcd for $C_{16}H_{26}O_2N_3I$: C, 45.83; H, 6.25; N, 10.02%.

***N*-Methyl-*N*-(2-chloroethyl)-*p*-nitroaniline (9a):** Yellow crystals (from benzene–heptane); mp 92.2—93.0 °C; IR (KBr) 2961, 2917, 1596, 1585, 1516, 1490, 1429, 1387, 1330, 1286, 1255, 1223, 1203, 1186, 1114, 1035, 1024, 995, 951, 836, 754, 730, and 696 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=3.16 (3H, s, Me), 3.69 (2H, t, J=6.60 Hz, NCH_2), 3.81 (2H, t, J=6.60 Hz, CH_2Cl), 6.65 (2H, d, J=9.57 Hz, arom-H), 8.13 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=39.44 (q, Me), 40.14 (t, NCH_2), 53.95 (t, CH_2Cl), 110.40 (dd, $^2J_{C-H}$=6.11 Hz, arom-C), 126.18 (dd, $^2J_{C-H}$=4.88 Hz, arom-C), 137.67 (s, arom-C), 152.80 (s, arom-C). Found: C, 50.56; H, 5.15; N, 12.85%. Calcd for $C_9H_{11}O_2N_2Cl$: C, 50.36; H, 5.17; N, 13.05%.

***N*-[2-(*N*-Methyl-*p*-nitrophenylamino)ethyl]-*N*-methylaziridinium Chloride (10a):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 3010, 1683, 1597, 1516, 1483, 1429, 1387, 1326, 1264, 1205, 1115, 832, 802, 753, and 722 cm^{-1}; ^{1}H NMR (270 MHz, CD_3OD) δ=3.07 (3H, s, Me), 3.18 (3H, s, Me), 3.52 (2H, t, br, NCH_2) 3.86—4.10 (6H, m, N^+CH_2), 6.85 (2H, d, J=9.57 Hz, arom-H), 8.09 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, CD_3OD) δ=39.81 (q, Me), 43.95 (q, Me), 46.47 (t, CH_2), 48.81 (t, CH_2), 59.41 (t, CH_2), 113.04 (dd, $^2J_{C-H}$=5.49 Hz, arom-C), 127.94 (dd, $^2J_{C-H}$=4.89 Hz, arom-C), 139.87 (s, arom-C), 155.26 (s, arom-C). Found: C, 52.87; H, 6.84; N, 15.62%. Calcd for $C_{12}H_{18}O_2N_3Cl$: C, 53.04; H, 6.68; N, 15.46%.

***N*-Methyl-*N*-(2-chloropropyl)-*p*-nitroaniline (9b):** Yellow crystals (from benzene–heptane); mp 62.7—63.5 °C; IR (KBr) 2921, 1594, 1576, 1476, 1436, 1388, 1310, 1292, 1235, 1213, 1199, 1114, 1071, 993, 984, 956, 820, 784, 752, and 668 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.10 (2H, m, CH_2), 3.12 (3H, s, Me), 3.59—3.67 (4H, m, NCH_2 and CH_2Cl), 6.64 (2H, d, J=9.57 Hz, arom-H), 8.10 (2H, d, J=9.57 Hz, arom-H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=29.58 (t, CH_2), 38.93 (q, Me), 42.16 (t, NCH_2), 49.50 (t, CH_2Cl), 110.20 (d, arom-C), 126.17 (d, arom-C), 137.00 (s, arom-C), 153.20 (s, arom-C). Found: C, 52.46; H, 5.52; N, 12.25%. Calcd for $C_{10}H_{13}O_2N_2Cl$: C, 52.52; H, 5.73; N, 12.25%.

***N*-[3-(*N*-Methyl-*p*-nitrophenylamino)propyl]-*N*-methylazetidinium Chloride (10b):** Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2852, 2801, 1596, 1518, 1482, 1388, 1309, 1202, 1111, 1061, 996, 953, 828, 754, and 696 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-d_6) δ=1.76—1.88 (4H, m, CH_2), 3.06 (3H, s, Me), 3.11 (3H, s, Me), 3.50—3.60 (9H, m, NCH_2 and N^+CH_2), 6.79 (2H, d, br, arom-H), 8.02 (2H, d, br, arom-H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ=17.93 (t, CH_2), 29.82 (t, CH_2), 38.93 (q, Me), 43.28 (q, Me), 44.14 (t, NCH_2), 48.21 (t, N^+CH_2), 56.29 (t, N^+CH_2), 110.28 (d, arom-C), 126.01 (d, arom-C), 134.84 (s, arom-C), 152.30 (s, arom-C). Found: C, 56.25; H, 7.31; N, 14.09%. Calcd for $C_{14}H_{22}O_2N_3Cl$: C, 56.09; H, 7.40; N, 14.02%.

The authors are grateful to Mr. Hiroshi Moriguchi, Faculty of Engineering, Osaka University, for the measurements of mass spectra.

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