Reaction of Mono-, Di-, and Trichloronitrobenzenes with *N*-Methyl Substituted Cyclic Tertiary Amines under High Pressure[1)]

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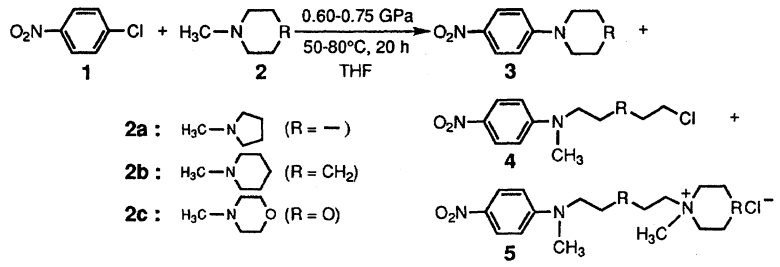
The reactions of mono-, di-, and trichloronitrobenzenes with 1-methylpyrrolidine under high pressure gave products of demethylation and ring-opening through a quaternary pyrrolidinium chloride intermediate formed by the S_NAr reaction. On the other hand, the reactions with 1-methylpiperidine and 4-methylmorpholine gave only demethylation products. The selectivities of the reactions of 1-methylpyrrolidine with these chloronitrobenzenes were found to be effected by the neighboring substituent to the pyrrolidinium group.

A nucleophilic substitution reaction of aromatic halides with amines is usually reluctant compared with the corresponding reaction of aliphatic halides,[2)] and has been reported to be effectively accelerated by high pressure.[3,4)] Because of the lower nucleophilicity of the tertiary amine than that of the primary and secondary amines, the title reaction has been recognized as being difficult to proceed under ordinary pressure. To the best of our knowledge, only a few papers have reported on the S_NAr reaction of aromatic halide with tertiary amines.[5)] Matsumoto et al. have reported on the reaction of heteroaromatic halides with acyclic tertiary amines under high pressure, while focusing on the selectivity of the dealkylation of quaternary ammonium halide intermediates.[5)] Here, we wish to report on the S_NAr reactions of aromatic chlorides with cyclic tertiary amines, such as 1-methylpyrrolidine, 1-methylpiperidine, and 4-methylmorpholine, in order to confirm the structural effect on the selectivity between the ring-opening and demethylation of the quaternary ammonium chloride formed as an intermediate of the initial S_NAr reaction.

The reaction of *p*-chloronitrobenzene (**1**) with 4.0 molar amounts of 1-methylpyrrolidine under high pressure (0.6 GPa, 50 °C, 20 h, in tetrahydrofuran (THF)) gave 4-(1-pyrrolidinyl)nitrobenzene (**3a**), *N*-methyl-*N*-(4-chlorobutyl)-*p*-nitroaniline (**4a**), and 1-methyl-1-[4-(*N*-methyl-4-nitroanilino)butyl]pyrrolidinium chloride (**5a**) in 18.0, 7.8, and 28.3% yields, respectively, together with the recovered **1** (46%) (Table 1, Run 1). On the other hand, the reaction of **1** with 1-methylpiperidine (**2b**) and 4-methylmorpholine (**2c**) gave the corresponding *p*-piperidino- (**3b**) and *p*-morpholinonitrobenzenes (**3c**) as the sole products in low yields (Scheme 1). Under the forced reaction conditions (0.75 GPa, 80 °C) 1-methylpyrrolidine gave products **3a** and **5a** in high total yields without affording **4a** (Table 1, Run 4). The reactions with **2b** and **2c** are also accelerated under these reaction conditions to give higher yields of the products (Runs 5 and 6). The fact that the ring-opening products were formed only in the reaction of 1-methylpyrrolidine seems to be attributed to the ring strain of the pyrrolidine ring system,[6)] compared to those of piperidine and morpholine. A mechanistic study concerning the ring-opening reaction will be published in this journal.[6)]

When *o*-chloronitrobenzene (**6**) was treated with 4.0 molar amounts of 1-methylpyrrolidine (**2a**) under high pressure (0.75 GPa, 80 °C, 20 h, in THF), demethylation product **7a** and the quaternary ammonium chloride **8a** were obtained in 8.2 and 24.5% yields, respectively (Scheme 2). The ratio of the ring-opening product to the demethylation product (**8a**/**7a**) was 3.0, which is larger than the corresponding value observed in the reaction of *p*-chloronitrobenzene with **2a** (**5a**/**3a**= 1.7; Table 1, Run 4). This indicates that the nitro group on the ortho position to the pyrrolidinium group of the quaternary ammonium intermediate affects the selectivity of the reaction so as to increase the ring-opening product. The total yields of the reactions (95.1% from **1** and 32.7% from **6**) indicate that the reactivity of **6** with **2a** was lower than in the case of **1** under the same reaction conditions. This may be attributed to the steric hindrance of the neighboring nitro group to the chlorine atom where the initial attack of **2a** occurs.

The reaction of 2,4-dichloronitrobenzene (**9**) with **2a** under high pressure (0.60 GPa at 50 °C for 20 h) gave the corresponding demethylation and ring-opening products initiated by the S_NAr reactions at the para and ortho positions to the nitro group. However, the yield of the products derived from ortho-substitution is very

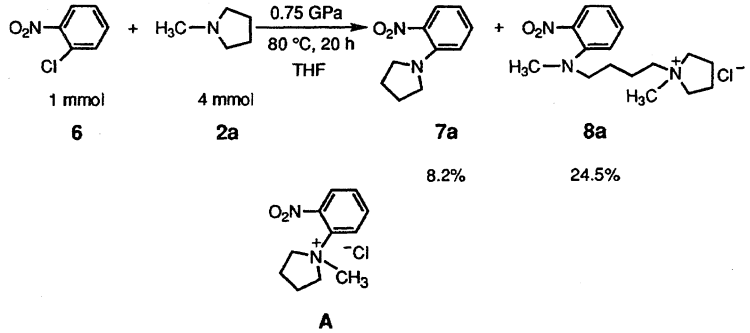


Scheme 1.

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

Run	Amine	Pressure	Temp	Yield/%				Recovered
		GPa	°C	**3**	**4**	**5**	Total	**1**/%
1	1-Methylpyrrolidine	0.60	50	18.0	7.8	28.3	54.1	45.9
2	1-Methylpiperidine	0.60	50	6.4	0	0	6.4	91.0
3	4-Methylmorpholine	0.60	50	0.3	0	0	0.3	96.5
4	1-Methylpyrrolidine	0.75	80	35.0	0	60.1	95.1	4.9
5	1-Methylpiperidine	0.75	80	52.9	0	0	52.9	44.0
6[c]	4-Methylmorpholine	0.75	80	14.8	0	0	14.8	81.9

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **1** and 4.0 mmol of amines, 20 h, in THF (5 ml). c) Reaction time is 40h.



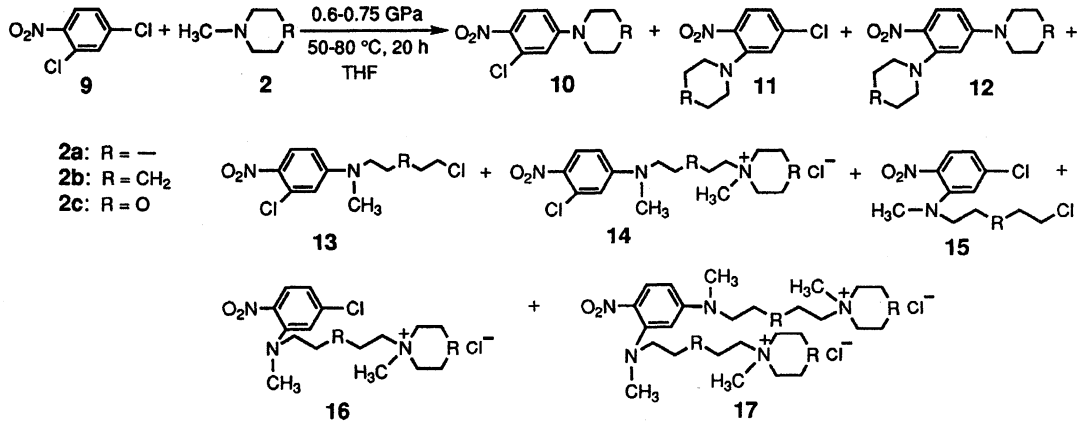
Scheme 2.

low (**11a**: 1.4%, **15a**: 0.8%, **16a**: 1.6%) compared to that of para-substitution (**10a**: 27.5%, **13a**: 26.5%, and **14a**: 29.5%) (Table 2, Run 1) (Scheme 3). The reaction of **9** with **2b** gave only the demethylation product **10b** in 48.6% yield through a para-substitution (Run 2). The reaction of **2a** under forced reaction conditions (0.75 GPa at 80 °C for 20 h) increased the yield of **10a** to 32.8%, and increased the yield of pyrrolidinium salt **14a** to 60.2% by accelerating the reaction of **13a** with **2a**, together with a small amount of para-ortho-disubstitution products (**12** and **17**) (Run 4). The forced-reaction conditions also accelerate the reactions of **2b** and **2c** to give demethylation products **10b** and **10c** in high and moderate yields (91.9 and 34.7%), without yielding a ring-opening product (Runs 5 and 6). These results have suggested that the chlorine atom at the para position to the nitro group has a higher reactivity than does the ortho-chlorine atom in the reaction of **9**

Table 2. Yields[a] of the Reaction Products of **9** with Amines[b]

Run	Amine	Pressure	Temp	Yield/%									Recovered
	2	GPa	°C	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	Total	**9**/%
1	**2a**	0.60	50	27.5	1.4	0	26.5	29.5	0.8	1.6	0	87.3	11.1
2	**2b**	0.60	50	48.6	0	0	0	0	0	0	0	48.6	47.7
3	**2c**	0.60	50	0	0	0	0	0	0	0	0	0	100
4	**2a**	0.75	80	32.8	1.3	0.3	0	60.2	0	1.1	3.2	98.9	0
5	**2b**	0.75	80	91.9	0	0	0	0	0	0	0	91.9	7.1
6	**2c**	0.75	80	34.7	0	0	0	0	0	0	0	34.7	60.5

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **9** and 4.0 mmol of amines, 20 h, in THF (5 ml).

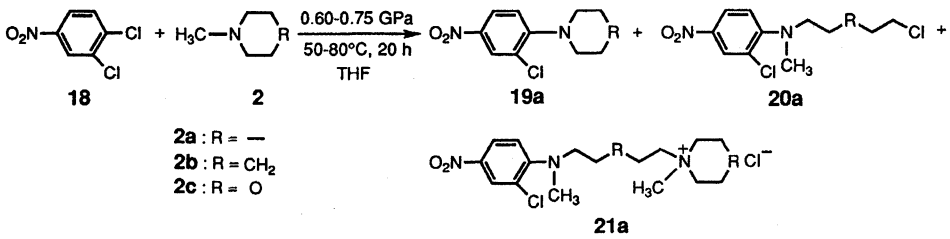


Scheme 3.

toward *N*-methyl substituted cyclic amines.

According to our previous work, the reaction of **9** with pyrrolidine gave ortho and para-substitution products in 93.0 and 2.4% yields, respectively.[4b] The ratio of the ortho-substitution product to the para-substitution product was 39 : 1. On the contrary, in the reaction of **9** with **2a**, the ortho and para-substitution products were obtained in 6.2 and 93.3% total yields, respectively, under the same reaction conditions. The ratio of the ortho-substitution products to the para-substitution products is 1 : 15. These results are attributed to the bulkiness of the methyl group of **2a**, which hinders the formation of a quaternary ammonium salt intermediate by an attack at the ortho-chlorine atom of **9** in the initial step of the reaction.

The reaction of 3,4-dichloronitrobenzene (**18**) with *N*-methyl substituted cyclic tertiary amines occurred only at the para-chlorine atom (Scheme 4). The reaction of **2a** gave the demethylation product (**19a**: 12.8%) and ring-opening products (**20a**: 3.4%, **21a**: 54.7%) under 0.60 GPa at 50 °C for 20 h (Table 3, Run 1). The forced reaction conditions (0.75 GPa at 80 °C for 20 h) increased the yield of **19a** to 14.8%, and accelerated the second reaction of **20a** with **2a**, giving **21a** in higher yield (84.1%). Although **18** reacted with **2b** to give the demethylation product **19b**, the yield was very low (12.3%) (Run 5). 4-Methylmorpholine (**2c**) did not react with **18** under the same reaction conditions (Run 6). These results indicate that the reactivity of **18** is lower than that of **9**, which is attributable to the steric hindrance of the neighboring *m*-chlorine atom. Furthermore, the ratio of the ring-opening products to the demethylation product, (**20a**+**21a**)/**19a**, was observed to be 4.5—5.6, which is larger than the value of the reaction of **9** with **2a** at the para position ((**13a**+**14a**)/**10a**=2.0—1.8). The increased selectivity of ring-opening seems to be attributed to the ortho-effect of the chlorine atom at the ortho position of the



Scheme 4.

Table 3. Yields[a] of the Reaction Products of **18** with Amines[b]

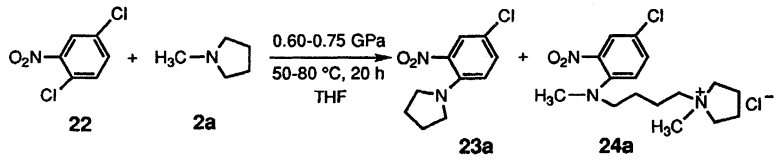
Run	Amine	Pressure	Temp	Yield/%				Recovered
		GPa	°C	**19**	**20**	**21**	Total	**18**/%
1	1-Methylpyrrolidine	0.60	50	12.8	3.4	54.7	70.9	26.4
2	1-Methylpiperidine	0.60	50	0	0	0	0	100
3	4-Methylmorpholine	0.60	50	0	0	0	0	100
4	1-Methylpyrrolidine	0.75	80	14.8	0	84.1	98.9	0
5	1-Methylpiperidine	0.75	80	12.3	0	0	12.3	87.7
6	4-Methylmorpholine	0.75	80	0	0	0	0	100

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **18** and 4.0 mmol of amines, 20 h, in THF (5 ml).

reaction center (C_4).

The reaction of 2,5-dichloronitrobenzene (**22**) with **2a** also gave the demethylation product (**23a**) and the ring-opening 1:2-product (**24a**), as shown in Table 4 (Scheme 5), through an ortho-chlorine substitution in the same manner as the reaction of **22a** with secondary amines.[4b] The ratio **24a**/**23a** (=2.3) was close to the value observed in the reaction of **6** (**8a**/**7a**=3.0).

The reaction of 2,4,5-trichloronitrobenzene (**25**) with **2a** at 0.60 GPa, 50 °C gave mainly the demethylation product **26a** (17.7%) and the ring-opening 1:2-product **30a** (73.6%) through para-chlorine atom substitution, along with a small amount of the ortho-substitution product (**27a**) and the ortho-para-disubstitution products (**28a** and **31a**) (Table 5, Run 1) (Scheme 6). Under forced reaction conditions an ortho-para-disubstitution product (**31a**) was obtained in 30.5% yield with sacrificing the yield of **30a** (48.6%) through a second attack of **2a** on the ortho-chlorine atom of **30a** (Run 4). Although the reaction of **25** with **2b** at 0.75 GPa gave the demethylation product **26b** in 40.8% (Run 5), no reaction was observed with **2c** under the same reaction

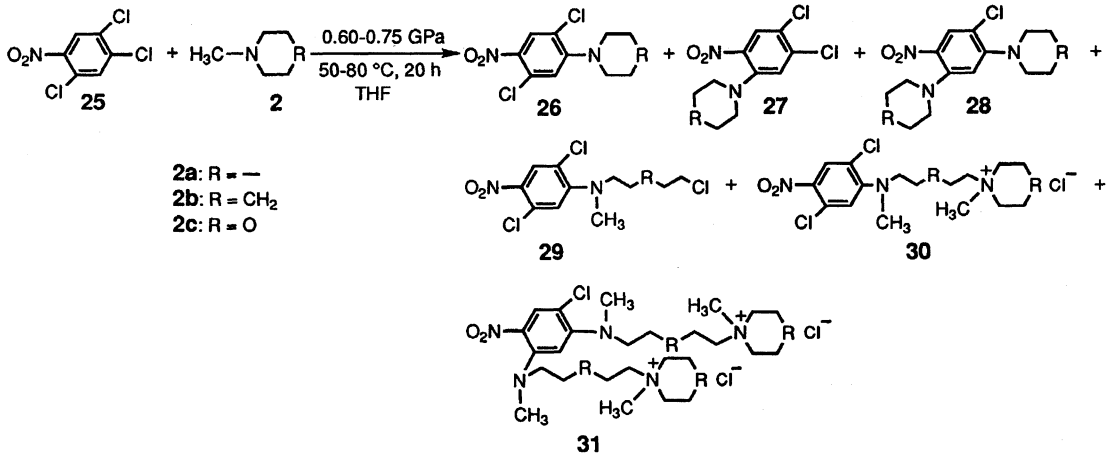


Scheme 5.

Table 4. Yields[a] of the Reaction Products of **22** with **2a**[b]

Run	Amine	Pressure	Temp	Yield/%			Recovered
		GPa	°C	**23a**	**24a**	Total	**22**/%
1	1-Methylpyrrolidine	0.60	50	3.8	8.8	12.6	86.3
2	1-Methylpyrrolidine	0.75	80	21.7	50.4	72.1	27.3

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **22** and 4.0 mmol of **2a**, 20 h, in THF (5 ml).



Scheme 6.

Table 5. Yields[a] of the Reaction Products of **25** with Amines[b]

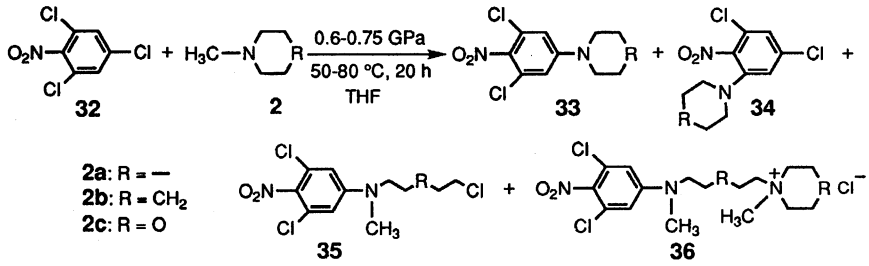
Run	Amine	Pressure	Temp	Yield/%							Recovered
	2	GPa	°C	**26**	**27**	**28**	**29**	**30**	**31**	Total	**25**/%
1	**2a**	0.60	50	17.7	5.5	0.7	1.3	73.6	0	98.8	0
2	**2b**	0.60	50	0	0	0	0	0	0	0	100
3	**2c**	0.60	50	0	0	0	0	0	0	0	100
4	**2a**	0.75	80	13.1	5.7	1.5	0	48.6	30.5	99.4	0
5	**2b**	0.75	80	40.8	0	0	0	0	0	40.8	56.9
6	**2c**	0.75	80	0	0	0	0	0	0	0	100

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **25** and 4.0 mmol of amines, 20 h, in THF (5 ml).

conditions (Run 6).

A similar high selectivity of para-chlorine atom substitution was observed in the reaction of 2,4,6-trichloronitrobenzene (**32**) with *N*-methyl cyclic amines (**2a**, **2b**, and **2c**) (Table 6) (Scheme 7). The reaction with **2a** indicates that the ratio of the ring-opening product to the demethylation product (**36a**/**33a**=1.3) (Table 6, Run 4) is close to that of the reaction of **1** ((**4a**+**5a**)/**3a**= 1.7), described above. Predominant para-chlorine atom substitution was observed in the reaction of 2,3,4-trichloronitrobenzene (**37**) with **2a** in the ratio of the ring-opening and demethylation (**40a**/**38a**=4.7) (Table 7, Run 4) (Scheme 8).

In this study the behavior of quaternary ammonium chloride intermediates obtained by the S_NAr reaction of various mono-, di-, and trichloronitrobenzenes with cyclic tertiary amines, such as 1-methylpyrrolidine, 1-methylpiperidine, and 4-methylmorpholine, was concluded to be effected by the ring system of the cyclic amines and neighboring group.

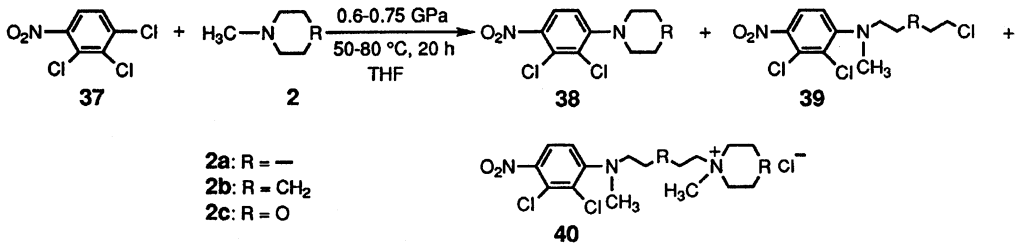


Scheme 7.

Table 6. Yields[a] of the Reaction Products of **32** with Amines[b]

Run	Amine	Pressure	Temp	Yield/%					Recovered
	2	GPa	°C	**33**	**34**	**35**	**36**	Total	**32**/%
1	**2a**	0.60	50	40.4	0.2	2.8	55.8	99.2	0
2	**2b**	0.60	50	0	0	0	0	0	100
3	**2c**	0.60	50	0	0	0	0	0	100
4	**2a**	0.75	80	44.0	0.4	0	55.1	99.5	0
5	**2b**	0.75	80	83.1	0	0	0	83.1	15.7
6	**2c**	0.75	80	0	0	0	0	0	100

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **32** and 4.0 mmol of amines, 20 h, in THF (5 ml).



Scheme 8.

Table 7. Yields[a] of the Reaction Products of **37** with Amines[b]

Run	Amine	Pressure	Temp	Yield/%				Recovered
	2	GPa	°C	**38**	**39**	**40**	Total	**37**/%
1	**2a**	0.60	50	15.0	3.7	60.1	78.8	20.8
2	**2b**	0.60	50	0	0	0	0	100
3	**2c**	0.60	50	0	0	0	0	100
4	**2a**	0.75	80	17.5	0	81.5	99.0	0
5	**2b**	0.75	80	8.5	0	0	8.5	88.1
6	**2c**	0.75	80	0	0	0	0	100

a) Isolated yield by medium-pressure column chromatography. b) Reaction conditions: 1.0 mmol of **37** and 4.0 mmol of amines, 20 h, in THF (5 ml).

Experimental

General. The melting points were measured with a Yanagimoto Melting Point Apparatus, and are not corrected. The 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 DMSO-d_6 solution using TMS as an internal standard. Mass spectra were measured with a JEOL JMS-DX303 spectrometer.

Material. Commercially available chloronitrobenzenes were purified by recrystallization. THF was purified by distillation after reflux over $LiAlH_4$, and stored with molecular-sieve type 4A under a nitrogen atmosphere. The amines were purified by distillation under a nitrogen atmosphere after an appropriate drying procedure.

General Procedure for the S_NAr Reaction of Chloronitrobenzenes with Amines. A THF solution (5 ml) of **1** (1.0 mmol) and amine (4.0 mol) was treated at high pressure in a Teflon® capsule using a Hikari Kouatsu High Pressure Apparatus under the cited reaction conditions. After removing the solvent under reduced pressure, the residue was suspended in toluene, and quaternary ammonium salt was separated by filtration on a sintered-glass filter, the solid was then rinsed several times with a 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. After evaporating the solvent under reduced pressure the solid was dissolved in methanol. The obtained residue by the evaporation of methanol was isolated by medium pressure column chromatography on Lichroprep Si 60 with methanol/dichloromethane as an eluent. The 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 the quaternary ammonium salts crystallized from methanol–ethyl acetate started to undergo slow decomposition at around 250 °C without melting.

4-(1-Pyrrolidinyl)nitrobenzene (3): Yellow crystals (from benzene–heptane); mp 178.0—179.0 °C. It was characterized by comparing the spectroscopic data with the authentic sample.[4b)]

***N*-(4-Chlorobutyl)-*N*-methyl-*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 ($CDCl_3$, 270 MHz) 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 ($CDCl_3$, 67.80 MHz) 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 (13, M^+), 165 (100), 149 (3), 119 (31), 77 (2, C_6H_4+1). 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%.

1-Methyl-1-[4-(*N*-methyl-4-nitroanilino)butyl]-pyrrolidinium 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}; ^{1}H NMR (DMSO-d_6, 270 MHz) 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 (DMSO-d_6, 67.8 MHz) 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%.

4-Piperidinonitrobenzene (3b): Yellow crystals (from benzene–heptane); mp 107.4—108.2 °C; IR (KBr) 2978, 2854, 1576, 1526, 1465, 1398, 1289, 1102, 990, 946, 820, 747, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=1.67 (2H, m, CH_2), 1.69 (4H, m, CH_2), 3.44 (4H, t, J=5.28 Hz, NCH_2), 6.79 (2H, d, J=9.56 Hz, arom-H), 8.10 (2H, d, J=9.56 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.22 (t, CH_2), 25.26 (t, CH_2), 48.37 (t, NCH_2), 112.30 (d, arom-C), 126.13 (d, arom-C), 137.43 (s, arom-C), 154.88 (s, arom-C); MS (EI) m/z (rel intensity) 205 (100, M^+-1), 165 (14), 159 (20), 150 (13), 92 (2), 77 (7, C_6H_4+1). Found: C, 64.19; H, 6.28; N, 13.50%. Calcd for $C_{11}H_{14}O_2N_2$: C, 64.06; H, 6.84; N, 13.58%.

4-Morpholinonitrobenzene (3c): Yellow crystals (from benzene–heptane); mp 158.0—159.0 °C; IR (KBr) 2900, 2867, 1601, 1582, 1508, 1482, 1386, 1321, 1243, 1120, 1108, 926, 826, 754, and 654 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=3.38 (4H, t, J=4.95 Hz, NCH_2), 3.87 (4H, t, J=4.95 Hz, CH_2O), 6.84 (2H, d, J=9.56 Hz, arom-H), 8.14 (2H, d, J=9.56 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=47.07 (t, NCH_2), 66.32 (t, CH_2O), 112.57 (d, arom-C), 125.85 (d, arom-C), 138.89 (s, arom-C), 154.95 (s, arom-C); MS (El) m/z (rel intensity) 208 (100, M^+), 192 (3), 177 (3), 161 (5), 150 (68), 120 (9), 104 (8), 78 (23, C_6H_4+2). Found: C, 57.67; H, 5.81; N, 13.40%. Calcd for $C_{10}H_{12}O_3N_2$: C, 57.68; H, 5.81; N, 13.45%.

2-(1-Pyrrolidinyl)nitrobenzene (7a): Yellow oil; IR (neat) 2923, 2872, 1557, 1508, 1442, 1377, 1360, 1336, 1271, 1180, 1166, 1077, 1043, 960, 846, 767, 736, 707, and 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=1.99 (4H, m, CH_2), 3.22 (4H, m, NCH_2), 6.71 (1H, ddd, J=8.58, 8.25, 1.32 Hz, arom-H), 6.91 (1H, dd, J=8.91, 1.32 Hz, arom-H), 7.36 (1H, ddd, J=8.58, 8.91, 1.65 Hz, arom-H), 7.74 (1H, dd, J=8.25, 1.65 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.71 (t, CH_2), 50.32 (t, $^2J_{C-H}$=2.45 Hz, NCH_2), 115.44 (d, arom-C), 115.84 (d, arom-C), 126.71 (d, arom-C), 132.91 (d, arom-C), 137.09 (s, arom-C), 142.72 (s, arom-C). Found: m/z 192.0898. Calcd for $C_{10}H_{12}O_2N_2$: M, 192.0896.

1-Methyl-1-[4-(*N*-methyl-2-nitroanilino)butyl]-pyrrolidinium Chloride (8a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (neat) 2945, 1606, 1549, 1508, 1464, 1343, 1267, 1200, 1003, 930, 882, 812, and 707 cm^{-1}; ^{1}H NMR (DMSO-d_6, 270 MHz) δ=1.54 (2H, m, CH_2), 1.70 (2H, m, CH_2), 2.07 (4H, m, CH_2), 2.74 (3H, s, Me), 2.96 (3H, s, Me), 3.20 (2H, m, NCH_2), 3.28—3.51 (6H, m, N^+CH_2), 6.96 (1H, ddd, J=8.58, 8.25, 1.32 Hz, arom-H), 7.30 (1H, dd, J=8.91, 1.65 Hz, arom-H), 7.52 (1H, ddd, J=8.58, 8.91, 1.65 Hz, arom-H), 7.75 (1H, dd, J=8.25, 1.65 Hz, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.29 (t, CH_2), 21.10 (t, CH_2), 23.63 (t, CH_2), 40.50 (q, Me), 47.52 (q, Me), 53.02 (t, NCH_2), 62.65 (t, N^+CH_2), 63.42 (t, N^+CH_2), 119.31 (d, arom-C), 120.38 (d, arom-C), 125.74 (d,

arom-C), 133.30 (d, arom-C), 140.75 (s, arom-C), 145.00 (s, arom-C);

2-Chloro-4(1-pyrrolidinyl)nitrobenzene (10a): Yellow crystals (from benzene–heptane); mp 122.90—123.60 °C; IR (KBr) 2978, 2859, 1596, 1507, 1485, 1432, 1386, 1352, 1317, 1292, 1262, 1153, 1134, 1047, 1028, 981, 871, 828, 807, 793, 746, 678, and 657 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz), δ=2.07 (4H, m, CH_2), 3.35 (4H, m, NCH_2), 6.35 (1H, d, J=9.24 Hz, arom-H), 6.46 (1H, s, arom-H), 8.00 (1H, d, J=9.24 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz), δ=25.26 (t, CH_2), 47.84 (t, NCH_2), 109.24 (d, arom-C), 113.06 (d, arom-C), 128.82 (d, arom-C), 130.48 (s, arom-C), 134.28 (s, arom-C), 150.75 (s, arom-C); MS (EI) m/z 226 (100, M^+), 210 (5), 196 (26), 179 (25), 170 (13), 154 (6), 144 (15), 117 (7), 102 (5), 89 (6), 75 (8, C_6H_3). Found: C, 53.08; H, 4.91; N, 12.26%. Calcd for $C_{10}H_{11}O_2N_2Cl$: C, 52.99; H, 4.89; N, 12.36%.

4-Chloro-2(1-pyrrolidinyl)nitrobenzene (11a): Yellow crystals (from benzene–heptane); mp 86.3—87.1 °C; IR (KBr) 2974, 2859, 1596, 1550, 1509, 1457, 1386, 1317, 1291, 1262, 1184, 1028, 827, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.20 (4H, m, CH_2), 3.21 (4H, m, NCH_2), 6.67 (1H, d, J=8.91 Hz, arom-H), 6.89 (1H, s, arom-H), 7.68 (1H, d, J=8.91 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.70 (t, CH_2), 50.53 (t, NCH_2), 115.45 (d, arom-C), 115.61 (d, arom-C), 127.97 (d, arom-C), 135.52 (s, arom-C), 139.05 (s, arom-C), 143.28 (s, arom-C). Found: C, 52.97; H, 4.85; N, 12.38%. Calcd for $C_{10}H_{11}O_2N_2Cl$: C, 52.99; H, 4.89; N, 12.36%.

2,4-Di(1-pyrrolidinyl)nitrobenzene (12a): Yellow crystals (from benzene–heptane); mp 139.5—140.0 °C; IR (KBr) 2961, 2850, 1607, 1550, 1508, 1355, 1313, 1264, 1225, 1181, 1100, 876, 795, 692, and 669 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.96 (4H, m, CH_2), 2.03 (4H, m, CH_2), 3.25 (4H, m, NCH_2), 3.36 (4H, m, NCH_2), 5.74 (1H, s, arom-H), 6.00 (1H, d, J=9.57 Hz, arom-H), 7.90 (1H, d, J=9.57 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.42 (t, CH_2), 25.74 (t, CH_2), 47.71 (t, NCH_2), 50.93 (t, NCH_2), 94.83 (d, arom-C), 102.21 (d, arom-C), 127.63 (s, arom-C), 129.96 (d, arom-C), 146.36 (s, arom-C), 151.28 (s, arom-C); MS (EI) m/z (rel intensity) 261 (37, M^++1), 244 (100), 227 (25), 213 (16), 200 (10), 188 (16), 161 (8), 145 (7), 117 (5), 106 (7), 86 (4), 77 (3, C_6H_3+2). Found: C, 64.16; H, 7.32; N, 16.04%. Calcd for $C_{14}H_{19}O_2N_3$: C, 64.35; H, 7.33; N, 16.08%.

***N*- (4- Chlorobutyl)- *N*- methyl- 3- chloro- 4- nitroaniline (13a):** Yellow crystals (from benzene–heptane); mp 78.5—79.3 °C; IR (KBr) 2961, 2920, 1596, 1559, 1520, 1483, 1312, 1291, 1254, 1220, 1187, 1135, 1101, 1031, 848, 813, 742, and 716 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.80 (2H, m, CH_2), 1.81 (2H, m, CH_2), 3.07 (3H, s, Me), 3.45 (2H, t, J=7.26 Hz, NCH_2), 3.59 (2H, t, J=5.94 Hz, CH_2Cl), 6.54 (1H, d, J=9.57 Hz, arom-H), 6.66 (1H, s, arom-H), 8.06 (1H, d, J=9.57 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.22 (t, CH_2), 29.63 (t, CH_2), 38.57 (q, Me), 44.37 (t, NCH_2), 51.74 (t, CH_2Cl), 109.30 (d, arom-C), 113.01 (d, arom-C), 128.80 (d, arom-H), 130.65 (s, arom-C), 135.01 (s, arom-C), 152.33 (s, arom-C); MS (EI) m/z (rel intensity) 226 (100, M^+), 210 (5), 196 (27), 179 (26), 170 (14), 154 (6), 144 (15), 117 (7), 102 (5), 89 (6), 75 (8, C_6H_3). Found: C, 47.70; H, 5.07; N, 10.09%. Calcd for $C_{11}H_{14}O_2N_2Cl_2$: C, 47.67; H, 5.09; N, 10.11%.

1-Methyl-1-[4-(*N*-methyl-3-chloro-4-nitroanilino)-butyl]pyrrolidinium Chloride (14a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (neat) 2953, 1689, 1596, 1560, 1513, 1489, 1310, 1270, 1202, 1140, 1033, 832, 810, 746, 719, 706, and 685 cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.57 (2H, m, CH_2), 1.80 (2H, m, CH_2), 2.11 (4H, m, CH_2), 3.05 (3H, s, Me), 3.09 (3H, s, Me), 3.18 (2H, m, NCH_2), 3.48 (4H, m, N^+CH_2), 3.54 (2H, m, N^+CH_2), 6.83 (1H, d, J=10.23 Hz, arom-H), 6.84 (1H, s, arom-H), 8.03 (1H, d, J=10.23 Hz, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.40 (t, CH_2), 21.10 (t, CH_2), 23.28 (t, CH_2), 47.50 (q, Me), 48.50 (q, Me), 51.03 (t, NCH_2), 62.54 (t, N^+CH_2), 63.38 (t, N^+CH_2), 109.96 (d, arom-C), 112.63 (d, arom-C), 128.78 (d, arom-C), 129.35 (s, arom-C), 133.55 (s, arom-C), 152.57 (s, arom-C). Found: C, 52.81; H, 7.12; N, 11.84%. Calcd for $C_{16}H_{25}O_2N_3Cl_2$: C, 53.04; H, 6.96; N, 11.60%.

***N*- (4- Chlorobutyl)- *N*- methyl- 5- chloro- 2- nitroaniline (15a):** Yellow oil; IR (neat) 2919, 2848, 1598, 1553, 1499, 1339, 1285, 1107, 857, 805, and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.77—1.82 (4H, m, CH_2), 2.82 (3H, s, Me), 3.20 (2H, t, J=6.93 Hz, NCH_2), 3.56 (2H, t, J=6.27 Hz, CH_2Cl), 6.81 (1H, d, J=8.91 Hz, arom-H), 7.03 (1H, s, arom-H), 7.70 (1H, d, J=8.91 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.52 (t, CH_2), 29.53 (t, CH_2), 40.19 (q, Me), 44.57 (t, NCH_2), 53.52 (t, CH_2Cl), 118.62 (d, arom-C), 119.29 (d, arom-C), 127.89 (d, arom-C), 136.43 (s, arom-C), 139.33 (s, arom-C), 146.61 (s, arom-C). Found: m/z 276.0426. Calcd for $C_{11}H_{14}O_2N_2Cl_2$: M, 276.0432.

1-Methyl-1-[4-(*N*-methyl-5-chloro-2-nitroanilino)-butyl]pyrrolidinium Chloride (16a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.56 (2H, m, CH_2), 1.87 (2H, m, CH_2), 2.07 (4H, m, CH_2), 2.76 (3H, s, Me), 2.96 (3H, s, Me), 3.27 (2H, m, NCH_2), 3.40—3.51 (6H, m, N^+CH_2), 6.95 (1H, d, J=8.91 Hz, arom-H), 7.32 (1H, s, arom-H), 7.81 (1H, d, J=8.91 Hz, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=21.09 (t, CH_2), 22.74 (t, CH_2), 23.58 (t, CH_2), 40.30 (q, Me), 47.49 (q, Me), 48.57 (t, NCH_2), 52.66 (t, N^+CH_2), 54.83 (t, N^+CH_2), 118.19 (d, arom-C), 119.17 (d, arom-C), 127.96 (d, arom-C), 128.52 (s, arom-C), 138.10 (s, arom-C), 145.98 (s, arom-C).

(17a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.55—1.74 (8H, m, CH_2), 2.09 (8H, m, CH_2), 2.78 (3H, s, Me), 2.96 (3H, s, Me), 3.00 (3H, s, Me), 3.05 (3H, s, Me), 3.16 (4H, m, NCH_2), 3.31—3.57 (12H, m, N^+CH_2), 6.12 (1H, s, arom-H), 6.38 (1H, d, J=9.57 Hz, arom-H), 7.87 (1H, d, J=9.57 Hz, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.35 (t, CH_2), 20.46 (t, CH_2), 21.09 (t, CH_2), 21.02 (t, CH_2), 23.54 (t, CH_2), 23.56 (t, CH_2), 38.67 (q, Me), 40.25 (q, Me), 47.50 (q, Me), 47.53 (q, Me), 50.96 (t, NCH_2), 53.50 (t, NCH_2), 62.60 (t, N^+CH_2), 62.64 (t, N^+CH_2), 63.38 (t, N^+CH_2), 63.40 (t, N^+CH_2), 99.78 (d, arom-C), 104.05 (d, arom-C), 128.52 (d, arom-C), 129.46 (s, arom-C), 149.35 (s, arom-C), 153.01 (s, arom-C).

2-Chloro-4-piperidinonitrobenzene (10b): Yellow prisms (from benzene–heptane); mp 66.4—67.2 °C; IR (KBr) 2941, 2859, 1594, 1563, 1499, 1448, 1319, 1253, 1126, 1069, 941, 851, 825, 740, 676, and 640 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.68 (6H, m, CH_2), 3.40 (4H, t, J=5.28 Hz, NCH_2), 6.68 (1H, d, J=9.57 Hz, arom-H),

6.79 (1H, s, arom-H), 7.99 (1H, d, J=9.57 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=23.98 (t, CH_2), 25.10 (t, CH_2), 48.10 (t, NCH_2), 110.85 (d, arom-C), 114.92 (d, arom-C), 128.63 (d, arom-C), 130.49 (s, arom-C), 135.29 (s, arom-C), 153.63 (s, arom-C); MS (EI) m/z (rel intensity) 240 (100, M^+), 224 (4), 210 (17), 199 (17), 193 (22), 184 (12), 165 (3), 154 (10), 138 (5), 126 (5), 110 (3), 102 (7), 89 (2), 75 (7, C_6H_3). Found: C, 54.91; H, 5.39; N, 11.63%. Calcd for $C_{11}H_{13}O_2N_2Cl$: C, 54.89; H, 5.44; N, 11.64%.

2-Chloro-4-morpholinonitrobenzene (10c): Yellow crystals (from benzene–heptane); mp 127.4—128.4 °C; IR (KBr) 2975, 2903, 1595, 1564, 1500, 1491, 1457, 1443, 1381, 1330, 1309, 1283, 1266, 1242, 1217, 1184, 1141, 1124, 1071, 1063, 1025, 950, 869, 834, 809, 783, and 679 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=3.35 (4H, t, J=4.95 Hz, NCH_2), 3.86 (4H, t, J=4.95 Hz, CH_2O), 6.73 (1H, d, J=9.57 Hz, arom-H), 6.84 (1H, s, arom-H), 8.00 (1H, d, J=9.57 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=46.78 (t, NCH_2), 66.13 (t, $^2J_{C-H}$=3.05 Hz, CH_2O), 111.12 (d, arom-C), 115.31 (d, arom-C), 128.36 (d, arom-C), 130.22 (s, arom-C), 137.02 (s, arom-C), 153.77 (s, arom-C); MS (EI) m/z (rel intensity) 242 (100, M^+), 226 (3), 212 (7), 195 (4), 184 (92), 165 (2), 154 (17), 149 (5), 138 (6), 125 (2), 102 (11), 75 (8, C_6H_3). Found: C, 49.31; H, 4.58; N, 11.52%. Calcd for $C_{10}H_{11}O_3N_2Cl$: C, 49.50; H, 4.57; N, 11.54%.

3- Chloro- 4- (1- pyrrolidinyl)nitrobenzene (19a): Yellow crystals (from benzene–heptane); mp 96.1—96.8 °C; IR (KBr) 2997, 2885, 2843, 1588, 1500, 1490, 1457, 1369, 1356, 1304, 1276, 1265, 1127, 956, 892, 865, 796, 770, 745, and 652 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=2.00 (4H, m, CH_2), 3.65 (4H, m, NCH_2), 6.66 (1H, d, J=9.57 Hz, arom-H), 7.98 (1H, d, J=9.57 Hz, arom-H), 8.17 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.74 (t, CH_2), 51.41 (t, NCH_2), 114.10 (d, arom-C), 118.05 (s, arom-C), 123.74 (d, arom-C), 128.25 (d, arom-C), 137.67 (s, arom-C), 150.64 (s, arom-C); MS (EI) m/z (rel intensity) 225 (100, M^+), 210 (2), 198 (6), 191 (25), 179 (28), 170 (24), 154 (2), 145 (7), 117 (5), 102 (4), 89 (5), 75 (7, C_6H_3). Found: C, 52.86; H, 4.68; N, 12.59%. Calcd for $C_{10}H_{11}O_2N_2Cl$: C, 52.99; H, 4.89; N, 12.36%.

***N*- (4- Chlorobutyl)- *N*- methyl- 2- chloro- 4- nitroaniline (20a):** Yellow oil; IR (neat) 2958, 2932, 1599, 1552, 1515, 1479, 1215, 1130, 1034, 815, 746, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=1.81 (2H, m, CH_2), 1.83 (2H, m, CH_2), 2.95 (3H, s, Me), 3.29 (2H, t, J=7.25 Hz, NCH_2), 3.57 (2H, t, J=5.94 Hz, CH_2Cl), 7.00 (1H, d, J=9.24 Hz, arom-H), 8.07 (1H, d, J=9.24 Hz, arom-H), 8.24 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.80 (t, CH_2), 29.72 (t, CH_2), 40.14 (q, Me), 44.63 (t, $^2J_{C-H}$=4.28 Hz, NCH_2), 54.01 (t, CH_2Cl), 118.88 (d, arom-C), 123.24 (d, arom-C), 125.65 (s, arom-C), 127.13 (d, arom-C), 140.99 (s, arom-C), 155.09 (s, arom-C); MS (EI) m/z (rel intensity) 276 (12, M^+), 225 (2), 199 (100), 185 (7), 153 (29), 139 (3), 118 (3), 77 (2, C_6H_3+2). Found: 276.0435. Calcd for $C_{11}H_{14}O_2N_2Cl_2$: M, 276.0432.

1-Methyl-1-[4-(*N*-methyl-2-chloro-4-nitroanilino)-butyl]pyrrolidinium Chloride (21a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (neat) 2981, 2861, 1598, 1502, 1480, 1459, 1351, 1320, 1258, 1149, 1132, 1048, 979, 806, 794, 682, and 653 cm^{-1}; ^{1}H NMR (DMSO-d_6, 270 MHz), δ=1.65 (2H, m, CH_2), 1.69 (2H, m, CH_2), 2.10 (4H, m, CH_2), 2.95 (3H, s, Me), 3.01 (3H, s, Me), 3.33 (2H, m, NCH_2), 3.40 (4H, m, N^+CH_2), 3.50 (2H, t, J=7.59 Hz, N^+CH_2), 7.28 (1H, d, J=9.24 Hz, arom-H), 8.11 (1H, d, J=9.24 Hz, arom-H), 8.19 (1H, s, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.51 (t, CH_2), 21.14 (t, CH_2), 23.95 (t, CH_2), 40.03 (q, Me), 47.53 (q, Me), 53.52 (t, NCH_2), 62.67 (t, N^+CH_2), 63.46 (t, N^+CH_2), 119.72 (d, arom-C), 123.62 (d, arom-C), 123.87 (d, arom-C), 126.50 (d, arom-C), 140.01 (s, arom-C), 154.79 (s, arom-C). Found: C, 53.24; H, 7.06; N, 11.83%. Calcd for $C_{16}H_{25}O_2N_3Cl_2$: C, 53.04; H, 6.96; N, 11.60%.

3-Chloro-4-piperidinonitrobenzene (19b): Yellow crystals (from benzene–heptane); ^{1}H NMR ($CDCl_3$, 270 MHz) δ=1.64 (2H, m, CH_2), 1.77 (4H, m, CH_2), 3.15 (4H, t, J=5.61 Hz, NCH_2), 7.01 (1H, d, J=9.24 Hz, arom-H), 8.08 (1H, d, J=9.24 Hz, arom-H), 8.23 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=23.96 (t, CH_2), 25.83 (t, CH_2), 52.10 (t, $^2J_{C-H}$=3.67 Hz, NCH_2), 119.18 (d, arom-C), 123.36 (d, arom-C), 126.63 (d, arom-C), 127.32 (s, arom-C), 141.46 (s, arom-C), 155.96 (s, arom-C).

5- Chloro- 2- (1- pyrrolidinyl)nitrobenzene (23a): Orange crystals (from benzene–heptane); mp 76.5—76.8 °C; IR (KBr) 2970, 2871, 1608, 1547, 1509, 1410, 1365, 1332, 1260, 1163, 1106, 1076, 959, 880, 798, 744, 754, and 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=1.99 (4H, m, CH_2), 3.20 (4H, m, NCH_2), 6.85 (1H, d, J=9.24 Hz, arom-H), 7.31 (1H, d, J=9.24 Hz, arom-H), 7.74 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=26.70 (t, CH_2), 50.51 (t, NCH_2), 117.07 (d, arom-C), 119.93 (s, arom-C), 125.99 (d, arom-C), 132.96 (d, arom-C), 136.65 (s, arom-C), 141.39 (s, arom-C); MS (EI) m/z (rel intensity) 226 (45, M^+), 209 (88), 192 (6), 179 (100), 165 (6), 153 (20), 138 (40), 125 (5), 117 (22), 105 (6), 99 (4), 89 (6), 75 (12, C_6H_3). Found: C, 53.05; H, 4.91; N, 12.36%. Calcd for $C_{10}H_{11}O_2N_2Cl$: C, 52.99; H, 4.89; N, 12.36%.

1-Methyl-1-[4-(*N*-methyl-4-chloro-2-nitroanilino)-butyl]pyrrolidinium Chloride (24a): Orange prisms (from methanol–ethyl acetate); mp>250 °C; IR (neat) 2949, 1605, 1550, 1509, 1459, 1344, 1267, 1199, 1171, 1154, 1120, 1002, 881, 820, 776, and 719 cm^{-1}; ^{1}H NMR (DMSO-d_6, 270 MHz) δ=1.54 (2H, m, CH_2), 1.69 (2H, m, CH_2), 2.07 (4H, m, CH_2), 2.74 (3H, s, Me), 2.97 (3H, s, Me), 3.22 (2H, t, NCH_2), 3.30—3.51 (6H, m, N^+CH_2), 7.35 (1H, d, J=8.91 Hz, arom-H), 7.56 (1H, d, J=8.91 Hz, arom-H), 7.87 (1H, s, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.24 (t, CH_2), 21.07 (t, CH_2), 23.59 (t, CH_2), 38.75 (q, Me), 47.47 (q, Me), 52.91 (t, $^2J_{C-H}$=3.06 Hz, NCH_2), 62.55 (t, N^+CH_2), 63.36 (t, N^+CH_2), 122.01 (s, arom-C), 122.06 (d, arom-C), 125.07 (d, arom-C), 132.99 (d, arom-C), 140.14 (s, arom-C), 143.82 (s, arom-C). Found: C, 52.91; H, 7.11; N, 11.48%. Calcd for $C_{16}H_{25}O_2N_3Cl_2$: C, 53.04; H, 6.96; N, 11.60%.

2,5-Dichloro-4-(1-pyrrolidinyl)nitrobenzene (26a): Yellow crystals (from benzene–heptane); mp 131.1—132.0 °C; IR (KBr) 2982, 2851, 1582, 1540, 1498, 1457, 1425, 1327, 1303, 1264, 1151, 1116, 1073, 1000, 894, 867, 823, 796, 747, 685, and 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ=2.00 (4H, m, CH_2), 3.64 (4H, m, NCH_2), 6.68 (1H, s, arom-H), 8.12 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.73 (t, CH_2), 51.39 (t, NCH_2), 116.51 (d, $^2J_{C-H}$=9.77 Hz, arom-C), 116.71 (d, arom-C), 128.33 (d, $^2J_{C-H}$=8.99 Hz, arom-C), 130.56 (d, arom-C), 135.46 (s, arom-C), 149.47 (d, $^2J_{C-H}$=8.55 Hz, arom-C); MS (EI) m/z (rel intensity) 259 (100, M^+-1), 244 (3), 225 (32), 213 (30), 204 (22), 178

(12), 151 (7), 136 (5), 123 (6), 109 (7), 97 (3), 89 (2), 74 (4, C_6H_2). Found: C, 46.00; H, 3.89; N, 10.76%. Calcd for $C_{10}H_{10}O_2N_2Cl_2$: C, 46.00; H, 3.86; N, 10.73%.

4,5-Dichloro-2-(1-pyrrolidinyl)nitrobenzene (27a): Yellow crystals (from benzene–heptane); mp 114.4—115.1 °C; IR (KBr) 2944, 2864, 1606, 1538, 1500, 1481, 1460, 1420, 1367, 1342, 1322, 1266, 1135, 997, 893, 755, and 677 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=2.00 (4H, m, CH_2), 3.19 (4H, m, NCH_2), 7.01 (1H, s, arom-H), 7.85 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.70 (t, CH_2), 50.68 (t, NCH_2), 116.99 (d, arom-C), 118.32 (s, arom-C), 127.62 (d, arom-C), 135.29 (s, arom-C), 137.34 (s, arom-C), 141.58 (s, arom-C); MS (EI) m/z (rel intensity) 260 (40, M^+), 243 (97), 226 (7), 213 (100), 199 (7), 187 (23), 172 (35), 151 (17), 139 (6), 109 (10), 97 (3), 87 (3), 74 (4, C_6H_2). Found: C, 46.16; H, 3.86; N, 10.66%. Calcd for $C_{10}H_{10}O_2N_2Cl_2$: C, 46.00; H, 3.86; N, 10.73%.

5-Chloro-2,4-di(1-pyrrolidinyl)nitrobenzene (28a): Yellow crystals (from benzene–heptane); mp 160.5—161.0 °C; IR (KBr) 2966, 2883, 1589, 1539, 1498, 1475, 1457, 1319, 1261, 1133, 1105, 888, 798, 752, 718, and 683 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.94—1.99 (8H, m, CH_2), 3.22 (4H, m, NCH_2), 3.56 (4H, m, NCH_2), 5.97 (1H, s, arom-H), 7.94 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.66 (t, CH_2), 25.71 (t, CH_2), 50.91 (t, NCH_2), 51.12 (t, NCH_2), 99.55 (d, arom-C), 108.57 (s, arom-C), 128.16 (s, arom-C), 130.67 (d, arom-C), 144.05 (s, arom-C), 149.95 (s, arom-C); MS (EI) m/z (rel intensity) 295 (47, M^+), 278 (100), 261 (22), 247 (21), 235 (6), 222 (17), 214 (11), 195 (9), 165 (2), 139 (6), 123 (8), 117 (4), 103 (7), 89 (3). Found: C, 56.78; H, 6.10; N, 14.13%. Calcd for $C_{14}H_{18}O_2N_3Cl$: C, 56.85; H, 6.13; N, 14.21%.

***N*-(4-Chlorobutyl)-*N*-methyl-2,5-dichloro-4-nitroaniline (29a):** Yellow oil; IR (neat) 2923, 2851, 1578, 1558, 1506, 1462, 1325, 1257, 1173, 1076, 989, 893, 812, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.81—1.84 (4H, m, CH_2), 2.94 (3H, s, Me), 3.28 (2H, t, J=7.26 Hz, NCH_2), 3.58 (2H, t, J=5.94 Hz, CH_2Cl), 7.00 (1H, s, arom-H), 8.09 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.76 (t, CH_2), 29.62 (t, CH_2), 39.99 (q, Me), 44.53 (t, $^2J_{C-H}$=3.06 Hz, NCH_2), 53.82 (t, $^2J_{C-H}$=3.66 Hz, CH_2Cl), 121.58 (d, arom-C), 123.58 (s, arom-C), 127.57 (s, arom-C), 129.23 (d, arom-C), 139.19 (s, arom-C), 153.73 (s, arom-C). Found: m/z 310.0034. Calcd for $C_{11}H_{13}O_2N_3Cl_3$: M, 310.0042.

1-Methyl-4-(*N*-methyl-2,5-dichloro-4-nitroanilino)-butylpyrrolidinium Chloride (30a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2953, 1602, 1553, 1499, 1462, 1350, 1322, 1264, 1152, 1123, 1008, 879, 820, 779, 766, and 723 cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.71 (4H, m, CH_2), 2.11 (4H, m, CH_2), 2.96 (3H, s, Me), 3.05 (3H, s, Me), 3.34 (2H, t, NCH_2), 3.47 (2H, t, N^+CH_2), 3.54 (4H, t, N^+CH_2), 7.30 (1H, s, arom-H), 8.18 (1H, s, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.44 (t, CH_2), 21.09 (t, CH_2), 23.95 (t, CH_2), 47.46 (q, Me), 48.47 (q, Me), 53.33 (t, NCH_2), 62.54 (t, N^+CH_2), 63.37 (t, N^+CH_2), 121.52 (d, arom-C), 122.40 (s, arom-C), 126.27 (s, arom-C), 128.82 (d, arom-C), 138.53 (s, arom-C), 153.43 (s, arom-C). Found: C, 48.22; H, 6.16; N, 10.73%. Calcd for $C_{16}H_{24}O_2N_3Cl_3$: C, 48.44; H, 6.10; N, 10.59%.

(31a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2967, 1598, 1565, 1549, 1487, 1461, 1356, 1317, 1268, 1243, 1154, 1121, 1005, 887, 817, 809, 778, 761, and 715 cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.64—1.69 (8H, m, CH_2), 2.09 (8H, m, CH_2), 2.79 (3H, s, Me), 2.89 (3H, s, Me), 3.01 (3H, s, Me), 3.03 (3H, s, Me), 3.26 (4H, m, NCH_2), 3.45—3.50 (12H, m, N^+CH_2), 6.67 (1H, s, arom-H), 7.90 (1H, s, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.41 (t, CH_2), 20.62 (t, CH_2), 21.20 (t, CH_2), 21.28 (t, CH_2), 23.71 (t, CH_2), 23.95 (t, CH_2), 39.81 (q, Me), 40.37 (q, Me), 47.62 (q, Me), 48.63 (q, Me), 53.02 (t, NCH_2), 53.59 (t, NCH_2), 62.74 (t, N^+CH_2), 62.82 (t, N^+CH_2), 63.53 (t, N^+CH_2), 63.81 (t, N^+CH_2), 109.85 (d, arom-C), 114.60 (s, arom-C), 129.06 (d, arom-C), 132.18 (s, arom-C), 146.49 (s, arom-C), 153.91 (s, arom-C). Found: C, 55.31; H, 8.02; N, 12.13%. Calcd for $C_{26}H_{46}O_2N_5Cl_3$: C, 55.07; H, 8.18; N, 12.35%.

2,5-Dichloro-4-piperidinonitrobenzene (26b): Yellow crystals (from benzene–heptane); mp 59.1—59.7 °C; IR (KBr) 2935, 2848, 1577, 1559, 1509, 1481, 1463, 1449, 1412, 1338, 1317, 1281, 1268, 1238, 1209, 1153, 1144, 1132, 1110, 1081, 1046, 1028, 1018, 965, 954, 917, 892, 854, 839, 800, 791, 750, 695, and 664 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.64 (2H, m, CH_2), 1.76 (4H, m, CH_2), 3.14 (4H, t, J=5.60 Hz, NCH_2), 7.02 (1H, s, arom-H), 8.06 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=23.78 (t, CH_2), 25.68 (t, CH_2), 51.90 (t, $^2J_{C-H}$=3.66 Hz, NCH_2), 122.13 (d, arom-C), 125.42 (s, arom-C), 127.47 (s, arom-C), 128.61 (d, arom-C), 139.80 (s, arom-C), 154.55 (s, arom-C); MS (EI) m/z (rel intensity) 273 (100, M^+), 257 (17), 227 (26), 218 (10), 193 (6), 172 (5), 136 (4), 109 (5). Found: C, 47.94; H, 4.38; N, 10.10%. Calcd for $C_{11}H_{12}O_2N_2Cl_2$: C, 48.02; H, 4.40; N, 10.18%.

2,6-Dichloro-4-(1-pyrrolidinyl)nitrobenzene (33a): Yellow crystals (from benzene–heptane); mp 136.2—137.1 °C; IR (KBr) 2972, 2864, 1584, 1541, 1516, 1498, 1456, 1374, 1345, 1254, 1234, 1182, 1158, 876, 850, and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=2.05 (4H, m, CH_2), 3.29 (4H, m, NCH_2), 6.39 (2H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 Hz) δ=25.30 (t, CH_2), 47.76 (t, NCH_2), 110.34 (d, arom-C), 127.78 (s, arom-C), 136.82 (s, arom-C), 148.28 (s, arom-C); MS (EI) m/z (rel intensity) 260 (100, M^+), 244 (6), 230 (59), 214 (34), 204 (8), 188 (8), 178 (21), 166 (6), 151 (10), 136 (5), 109 (12), 97 (4), 89 (2), 74 (5, C_6H_2). Found: C, 46.15; H, 3.93; N, 10.70%. Calcd for $C_{10}H_{10}O_2N_2Cl_2$: C, 46.00; H, 3.86; N, 10.73%.

2,4-Dichloro-6-(1-pyrrolidinyl)nitrobenzene (34a): Yellow crystals (from benzene–heptane); mp 76.1—77.0 °C; IR (KBr) 2923, 2852, 1593, 1526, 1457, 1369, 1349, 1280, 1258, 1135, 1077, 1014, and 859 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.97 (4H, m, CH_2), 3.27 (4H, m, NCH_2), 6.68 (1H, s, arom-H), 6.74 (1H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.35 (CH_2), 48.75 (NCH_2), 113.96 (arom-C), 116.42 (arom-C), 127.91 (arom-C), 132.54 (arom-C), 136.31 (arom-C), 141.84 (arom-C); MS (EI) m/z (rel intensity) 260 (46, M^+), 243 (93), 227 (13), 213 (100), 199 (12), 187 (28), 179 (17), 172 (37), 151 (23), 145 (16), 139 (11), 124 (6), 109 (13), 97 (5), 89 (6), 74 (7, C_6H_2). Found: m/z 260.0148. Calcd for $C_{10}H_{10}O_2N_2Cl_2$: M, 260.0119.

***N*-(4-Chlorobutyl)-*N*-methyl-3,5-dichloro-4-nitroaniline (35a):** Yellow prisms (from benzene–heptane); mp 100.3—101.2 °C; IR (KBr) 2924, 1588, 1546, 1506, 1346, 1256, 1219, 1105, 1048, and 725 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.75—1.84 (4H, m, CH_2), 3.00 (3H, s, Me), 3.38 (2H, t, J=7.26 Hz, NCH_2), 3.58 (2H, t, J=6.26 Hz,

CH_2Cl), 6.55 (2H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.11 (t, CH_2), 29.66 (t, CH_2), 38.56 (q, Me), 44.36 (t, NCH_2), 51.74 (t, CH_2Cl), 110.50 (d, arom-C), 128.11 (s, arom-C), 133.90 (s, arom-C), 149.83 (s, arom-C); MS (EI) m/z 310 (20, M^+-1), 233 (100), 217 (2), 187 (33), 152 (12). Found: m/z 310.0023 Calcd for $C_{11}H_{13}O_2N_2Cl_3$: M, 310.0042.

1-Methyl-1-[4-(*N*-methyl-3,5-dichloro-4-nitroanilino)butyl]pyrrolidinium Chloride (36a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2987, 1599, 1508, 1487, 1462, 1354, 1323, 1263, 1151, 1127, 1051, 982, 811, 793, 687, and 655 cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.56 (2H, m, CH_2), 1.82 (2H, m, CH_2), 2.13 (4H, m, CH_2), 3.05 (3H, s, Me), 3.10 (3H, s, Me), 3.53 (2H, t, NCH_2), 3.56 (6H, m, N^+CH_2), 6.90 (2H, s, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.36 (t, CH_2), 21.09 (t, CH_2), 23.01 (t, CH_2), 38.33 (q, Me), 47.49 (q, Me), 50.86 (t, NCH_2), 62.54 (t, N^+CH_2), 63.35 (t, N^+CH_2), 110.39 (d, arom-C), 126.78 (s, arom-C), 135.69 (s, arom-C), 150.12 (s, arom-C). Found: C, 48.65; H, 5.94; N, 10.56%. Calcd for $C_{16}H_{24}O_2N_3Cl_3$: C, 48.44; H, 6.10; N, 10.59%.

2,6-Dichloro-4-piperidinonitrobenzene (33b): Yellow crystals (from benzene–heptane); mp 75.7—76.6 °C; IR (KBr) 2941, 2853, 1587, 1548, 1520, 1486, 1461, 1448, 1382, 1352, 1268, 1248, 1219, 1190, 1160, 1130, 1062, 1038, 1024, 963, 853, 818, 777, and 669 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.66 (6H, m, CH_2), 3.30 (4H, t, NCH_2), 6.73 (2H, s, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=23.87 (t, CH_2), 24.99 (t, CH_2), 48.41 (t, $^2J_{C-H}$=3.05 Hz, NCH_2), 113.03 (d, arom-C), 127.74 (s, arom-C), 137.93 (s, arom-C), 151.63 (s, arom-C); MS (EI) m/z (rel intensity) 274 (100, M^+), 258 (5), 244 (26), 227 (23), 218 (7), 192 (10), 172 (4), 160 (4), 136 (5), 109 (7), 97 (2). Found: C, 48.04; H, 4.41; N, 10.21%. Calcd for $C_{11}H_{12}O_2N_2Cl$: C, 48.02; H, 4.40; N, 10.18%.

2,3-Dichloro-4-(1-pyrrolidinyl)nitrobenzene (38a): Yellow crystals (from benzene–heptane); mp 83.4—84.3 °C; IR (KBr) 2987, 2845, 1576, 1546, 1491, 1476, 1460, 1387, 1369, 1302, 1287, 1166, 1123, 1080, 993, 868, 795, 786, 753, 738, and 702 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=2.00 (4H, m, CH_2), 3.60 (4H, m, NCH_2), 6.55 (1H, d, J=9.56 Hz, arom-H), 7.83 (1H, d, J=9.56 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=25.77 (t, CH_2), 51.77 (t, NCH_2), 111.94 (d, arom-C), 119.87 (s, arom-C), 125.30 (d, arom-C), 129.70 (s, arom-C), 138.56 (s, arom-C), 151.14 (s, arom-C); MS (EI) m/z (rel intensity) 259 (100, M^+-2), 244 (2), 225 (32), 213 (32), 204 (18), 179 (16), 151 (4), 144 (20), 136 (4), 123 (4), 109 (7), 97 (2), 75 (2, C_6H_2+1). Found: C, 46.14; H, 3.91; N, 10.66%. Calcd for $C_{10}H_{10}O_2N_2Cl_2$: C, 46.00; H, 3.86; N, 10.73%.

***N*-(4-Chlorobutyl)-*N*-methyl-2,3-dichloro-4-nitroaniline (39a):** Yellow oil; IR (neat) 2955, 2867, 1572, 1515, 1486, 1456, 1333, 1168, 1118, 1087, 985, 824, 764, and 736 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.79—1.84 (4H, m, CH_2), 2.91 (3H, s, Me), 3.21 (2H, t, J=6.93 Hz, NCH_2), 3.57 (2H, t, J=6.26 Hz, CH_2Cl), 6.98 (1H, d, J=8.91 Hz, arom-H), 7.80 (1H, d, J=8.91 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=24.66 (t, CH_2), 29.69 (t, CH_2), 40.42 (q, Me), 44.60 (t, NCH_2), 54.21 (t, CH_2Cl), 117.31 (d, arom-C), 124.29 (d, arom-C), 127.83 (s, arom-C), 128.54 (s, arom-C), 142.52 (s, arom-C), 155.03 (s, arom-C); MS (EI) m/z 310 (12, M^+), 233 (100), 217 (3), 187 (34), 152 (9). Found: m/z 310.0027. Calcd for $C_{11}H_{13}O_2N_2Cl_3$: M, 310.0042.

1-Methyl-1-[4-(*N*-methyl-2,3-dichloro-4-nitroanilino)butyl]pyrrolidinium Chloride (40a): Yellow crystals (from methanol–ethyl acetate); mp>250 °C; IR (KBr) 2963, 1607, 1589, 1563, 1516, 1492, 1314, 1272, 1245, 1143, 1036, 976, 812, 787, 767, 712, 709, and 656 cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ=1.67—1.78 (4H, m, CH_2), 2.13 (4H, m, CH_2), 2.93 (3H, s, Me), 3.08 (3H, s, Me), 3.28 (2H, t, NCH_2), 3.45—3.57 (6H, m, N^+CH_2), 7.34 (1H, d, J=9.24 Hz, arom-H), 8.03 (1H, d, J=9.24 Hz, arom-H); ^{13}C NMR (DMSO-d_6, 67.80 MHz) δ=20.24 (t, CH_2), 21.05 (t, CH_2), 23.71 (t, CH_2), 40.15 (q, Me), 47.44 (q, Me), 53.61 (t, NCH_2), 62.50 (t, N^+CH_2), 63.32 (t, N^+CH_2), 118.52 (d, arom-C), 124.84 (d, arom-C), 125.67 (s, arom-C), 126.52 (s, arom-C), 141.40 (s, arom-C), 154.70 (s, arom-C). Found: C, 48.36; H, 6.03; N, 10.79%. Calcd for $C_{16}H_{24}O_2N_3Cl_3$: C, 48.44; H, 6.10; N, 10.59%.

2,3-Dichloro-4-piperidinonitrobenzene (38b): Yellow crystals (from benzene–heptane); mp 85.1—85.9 °C; IR (KBr) 2937, 2855, 1570, 1560, 1500, 1456, 1444, 1374, 1335, 1322, 1243, 1153, 1134, 1112, 946, 853, 779, 710, and 662 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=1.64 (2H, m, CH_2), 1.77 (4H, m, CH_2), 3.10 (4H, t, J=5.61 Hz, NCH_2), 6.96 (1H, d, J=8.91 Hz, arom-H), 7.81 (1H, d, J=8.91 Hz, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=23.94 (t, CH_2), 25.83 (t, CH_2), 52.39 (t, NCH_2), 117.26 (d, arom-C), 124.44 (d, arom-C), 128.15 (s, arom-C), 128.84 (s, arom-C), 142.74 (s, arom-C), 155.66 (s, arom-C); MS (EI) m/z (rel intensity) 273 (100, M^+), 259 (2), 227 (23), 218 (8), 192 (5), 173 (2), 158 (7), 136 (4), 109 (5), 75 (2, C_6H_2+1). Found: C, 48.30; H, 4.48; N, 10.11%. Calcd for $C_{11}H_{12}O_2N_2Cl_2$: C, 48.02; H, 4.40; N, 10.18%.

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