Substituent Effects on the Benzyl Groups in Sommelet–Hauser Rearrangement

Tetsuya TANAKA, Naohiro SHIRAI, and Yoshiro SATO*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan. *Received July 18, 1991*

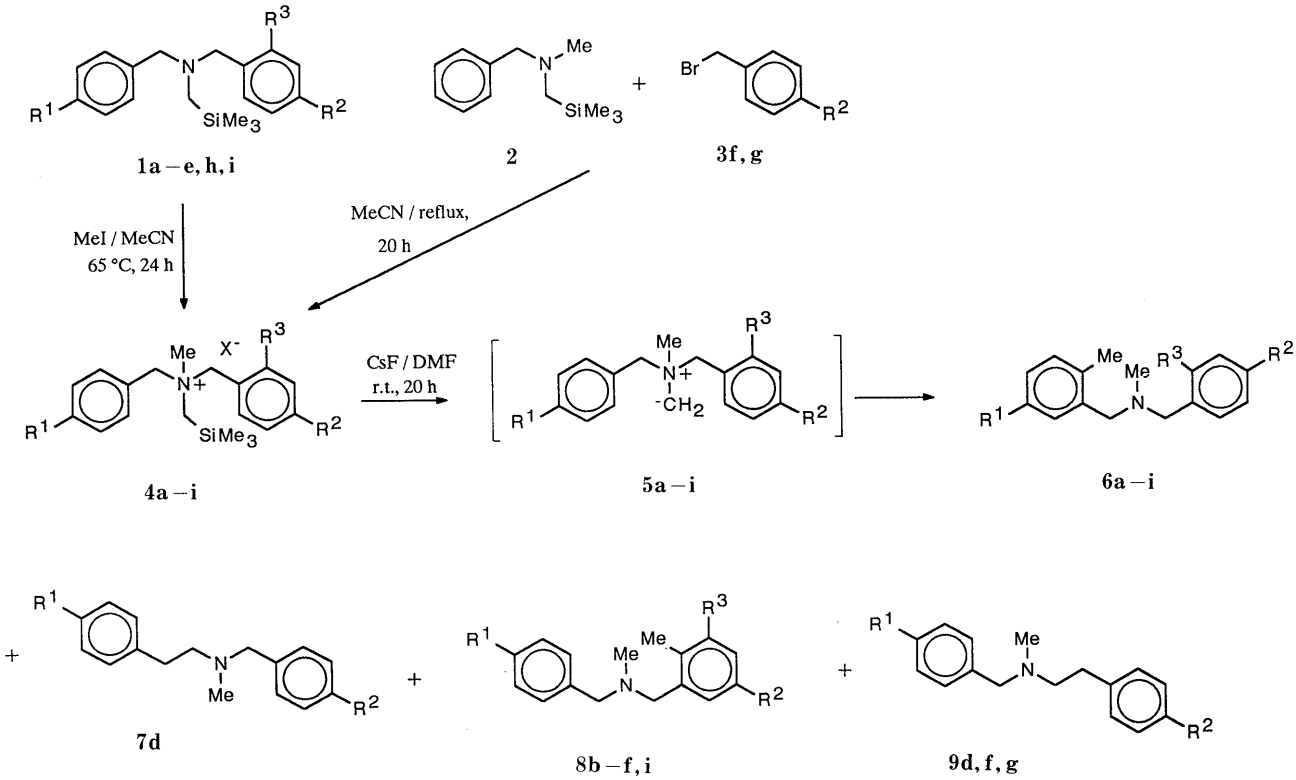
The effects of substituents (MeO, Me, H, Br, CN, NO_2) of the benzyl groups in the Sommelet–Hauser rearrangement of *N,N*-bis(substituted benzyl)-*N*-methyl(trimethylsilyl)methylammonium halides with cesium fluoride in *N,N*-dimethylformamide were examined.

Keywords ylide; Sommelet–Hauser rearrangement; desilylation; fluoride; sigmatropic rearrangement; substituent effect

We previously reported that the fluoride ion-induced desilylation of *N*-(substituted benzyl)-*N,N*-dimethyl(trimethylsilyl)methylammonium halides regioselectively provides *N*-methylide intermediates, which are isomerized to Sommelet–Hauser and/or Stevens rearrangement products.[1,2] The Sommelet–Hauser rearrangement products are formed predominantly from the ylides having electron-donating or weakly electron-withdrawing substituents (MeO, Me, H, Br, Cl, AcO) on the benzene ring; however, electron-withdrawing substituents (CN, NO_2) facilitate the Stevens products. In this paper, we deal with the substituent effects in the reaction of *N,N*-bis(substituted benzyl)-*N*-methyl(trimethylsilyl)methylammonium halides with CsF in *N,N*-dimethylformamide (DMF).[3]

Starting amines, *N,N*-bis(substituted benzyl)(trimethylsilyl)methylamines (**1a—e**, **1h**, and **1i**), were synthesized by reaction of *N*-benzyl(trimethylsilyl)methylamine with substituted benzyl bromides or by lithium aluminum hydride reduction of *N*-benzyl-*N*-(4-substituted benzoyl)(trimethylsilyl)methylamines (see the experimental section). Although *N,N*-dibenzyl-*N*-methyl(trimethylsilyl)methylammonium iodide (**4d**) was isolated from the reaction of **1d** with iodomethane, other ammonium iodides **4a—c**, **4e**, **4h**, **4i** prepared from **1a—c**, **1e**, **1h**, **1i** were subjected to the next desilylation reaction without being taken out of the flasks, because of their high purity and their hygroscopicity. *N*-Benzyl-*N*-(4-cyanobenzyl)-*N*-methyl(trimethylsilyl)methylammonium (**4f**) and *N*-benzyl-*N*-(4-nitrobenzyl)-*N*-methyl(trimethylsilyl)methylammonium bromides (**4g**) were prepared from *N*-benzyl-*N*-methyl(trimethylsilyl)methylamine (**2**) by treatment with 4-cyano- or 4-nitrobenzyl bromide (**3f** or **3g**) and used for the next reaction.

The reaction of **4** with CsF was quenched after 20 h at room temperature in DMF (Table I). Sommelet–Hauser rearrangement of *N*-benzyl-*N*-(4-methoxybenzyl)methylammonium *N*-methylide (**5a**) occurred selectively toward the non-substituted benzyl group to give *N*-methyl-*N*-(2-methylbenzyl)-4-methoxybenzylamine (**6a**). In the reaction of the 4-methyl-, 2-methyl-, or 4-bromo-substituted ammonium *N*-methylide (**5b**, **5c**, or **5e**), competitive rearrangement to both benzene rings occurred and two Sommelet–Hauser products were formed in a ratio of



1a–e, h, i **2** **3f, g**

4a–i **5a–i** **6a–i**

7d **8b–f, i** **9d, f, g**

Chart 1

TABLE I. Reaction of *N*,*N*-Bis(4-substituted benzyl)-*N*-methyl(trimethylsilyl)methylammonium Halides **4** with CsF

Ammonium salts (**4**)	R^1	R^2	R^3	X	Hammett constant (σ_{para}) of R^2	Yield of amines[a] (**6**—**9**) (%)	Ratio of **6**:**7**:**8**:**9**[b]
4a	H	MeO	H	I	−0.27	75	100:0: 0: 0
4b	H	Me	H	I	−0.17	63	60:0:40: 0
4c	H	H	Me	I	—	62	61:0:39: 0
4d	H	H	H	I	0	95[c]	49:1:49: 1
4e	H	Br	H	I	0.23	76	39:0:61: 0
4f	H	CN	H	Br	0.66	67	15:0:25:60
4g	H	NO_2	H	Br	0.78	68	6:0: 0:94
4h	Me	MeO	H	I	−0.27	65	100:0: 0: 0
4i	Me	Br	H	I	0.23	63	33:0:67: 0

a) Yield from **1**. *b*) Determined from the integration ratios of the proton signals in the ^{1}H-NMR spectra. *c*) Yield from **4d**.

6b:**8b** and **6c**:**8c** = 6:4 or **6e**:**8e** = 4:6. The product ratios from *N*-(4-methoxybenzyl)-*N*-(4-methylbenzyl)ammonium (**4h**) and *N*-(4-bromobenzyl)-*N*-(4-methylbenzyl)ammonium salts (**4i**) were similar to those of **4a** and **4e**, respectively. Apparently [2,3] sigmatropic rearrangement of the ylide occurs predominantly with a relatively non-electron-rich benzene ring and the selectivity decreases with increase of the values of Hammett's *para* substituent constant, σ_{para}.

Thus, the ylide rearrangement is favored by electron-deficient benzene rings. However, when the substituents are strongly electron-withdrawing groups (CN and NO_2), Stevens rearrangement predominates over Sommelet–Hauser rearrangement to give *N*-[2-(4-cyanophenyl)ethyl]-*N*-methylbenzylamine (**9f**) or *N*-[2-(4-nitrophenyl)ethyl]-*N*-methylbenzylamine (**9g**).

Experimental

Acetonitrile (CH_3CN) was dried by distillation from P_2O_5 and DMF by distillation from BaO under reduced pressure. CsF was dried over P_2O_5 at 190 °C under reduced pressure. ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL FX-100 or a GSX-400 spectrometer using tetramethylsilane as an internal standard. Aluminum oxide (Merck, Aluminumoxide 90, 70—230 mesh) was used for column chromatographies. All melting and boiling points are uncorrected. Distillation was performed by using a Büchi Kugelrohr distillation apparatus.

***N*-(4-Methylbenzyl)(trimethylsilyl)methylamine** A mixture of (chloromethyl)trimethylsilane (6.8 g, 55 mmol) and 4-methylbenzylamine (20.0 g, 165 mmol) was heated at 200 °C for 2.5 h in a sealed tube. After the addition of 20% NaOH (50 ml), the mixture was extracted with Et_2O (4 × 100 ml). The extract was dried ($MgSO_4$), concentrated, and distilled; yield, 8.2 g (72%); bp 106—107 °C (6 Torr). ^{1}H-NMR ($CDCl_3$) δ: 0.30 (9H, s, $SiCH_3$), 1.30 (1H, s, NH), 2.05 (2H, s, CH_2Si), 2.35 (3H, s, $ArCH_3$), 3.75 (2H, s, CH_2N), 7.05—7.30 (4H, m). *Anal.* Calcd for $C_{12}H_{21}NSi$: C, 69.50; H, 10.21; N, 6.75. Found: C, 69.55; H, 10.09; N, 6.62.

***N*-Benzyl-*N*-(4-methoxybenzyl)(trimethylsilyl)methylamine (1a)** A mixture of *N*-benzyl(trimethylsilyl)methylamine[4] (2.9 g, 15 mmol) and 4-methoxybenzoyl chloride (2.6 g, 15 mmol) in 10% NaOH was stirred at room temperature for 20 min. The mixture was poured into H_2O (100 ml) and extracted with AcOEt (4 × 50 ml). The extract was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed on an aluminum oxide column (AcOEt:hexane = 1:4) to give *N*-benzyl-*N*-(4-methoxybenzoyl)(trimethylsilyl)methylamine; yield, 4.75 g (97%); mp 39—40.5 °C. IR ν_{max}^{film} cm^{-1}: 1620 (CO–N), 1250 (Si–C, CH_3–O–C). ^{1}H-NMR ($CDCl_3$) δ: 0.10 (9H, s, $SiCH_3$), 2.90 (2H, s, $SiCH_2$), 3.80 (3H, s, OCH_3), 4.55 (2H, s, $ArCH_2$), 6.80—7.50 (9H, m). *Anal.* Calcd for $C_{19}H_{25}NO_2Si$: C, 69.68; H, 7.69; N, 4.28. Found: C, 69.51; H, 7.62; N, 3.99.

A mixture of *N*-benzyl-*N*-(4-methoxybenzoyl)(trimethylsilyl)methylamine (3.3 g, 10 mmol) and $LiAlH_4$ (0.57 g, 15 mmol) in Et_2O (40 ml) was heated at reflux for 5 h. The mixture was quenched with saturated sodium potassium tartrate (50 ml) and extracted with Et_2O (4 × 40 ml). The ether layer was extracted with 10% HCl (2 × 40 ml) and H_2O (40 ml). The combined aqueous extract was made alkaline with 20% NaOH and extracted with Et_2O (4 × 100 ml). The ethereal extract was dried ($MgSO_4$), concentrated, and distilled to give **1a**; yield, 2.91 g (92%); bp 165 °C (0.9 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1245, 850. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (9H, s), 1.95 (2H, s), 3.40 (2H, s), 3.50 (2H, s), 3.75 (3H, s), 6.70—7.40 (9H, m). *Anal.* Calcd for $C_{19}H_{27}NOSi$: C, 72.29; H, 8.68; N, 4.47. Found: C, 72.98; H, 8.98; N, 4.55.

***N*-Benzyl-*N*-(substituted benzyl)benzyl(trimethylsilyl)methylamine (1b—e): General Procedure** A solution of *N*-benzyl(trimethylsilyl)methylamine (3.9 g, 20 mmol) and substituted benzyl bromide (10 mmol) in MeCN (20 ml) was stirred at room temperature overnight. The mixture was poured into H_2O (100 ml) and extracted with Et_2O (4 × 50 ml). The extract was dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified on a silica gel column (hexane:Et_2O = 24:1 or 33:1) and by distillation.

***N*-Benzyl-*N*-(4-methylbenzyl)(trimethylsilyl)methylamine (1b)** Yield, 92%; bp 210 °C (20 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1248, 857. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (9H, s), 1.95 (2H, s), 2.34 (3H, s), 3.45 (4H, s), 6.95—7.44 (9H, m). *Anal.* Calcd for $C_{19}H_{27}NSi$: C, 76.71; H, 9.15; N, 4.71. Found: C, 76.46; H, 9.14; N, 4.59.

***N*-Benzyl-*N*-(2-methylbenzyl)(trimethylsilyl)methylamine (1c)** Yield, 86%; bp 190—195 °C (15 Torr, oven temperature). ^{1}H-NMR ($CDCl_3$) δ: 0.04 (9H, s), 1.94 (2H, s), 2.30 (3H, s), 3.45 (2H, s), 3.48 (2H, s), 7.09—7.46 (9H, m). *Anal.* Calcd for $C_{19}H_{27}NSi$: C, 76.71; H, 9.15; N, 4.71. Found: C, 76.72; H, 9.35; N, 4.54.

***N*,*N*-Dibenzyl(trimethylsilyl)methylamine (1d)** Yield, 98%; bp 200 °C (19 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1250, 860. ^{1}H-NMR ($CDCl_3$) δ: 0.01 (9H, s), 1.86 (2H, s), 3.44 (4H, s), 7.04—7.44 (10H, m). *Anal.* Calcd for $C_{18}H_{25}NSi$: C, 76.26; H, 8.89; N, 4.94. Found: C, 76.24; H, 8.81; N, 4.68.

***N*-Benzyl-*N*-(4-bromobenzyl)(trimethylsilyl)methylamine (1e)** Yield, 94%; bp 160 °C (1.0 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1245, 850, ^{1}H-NMR ($CDCl_3$) δ: 0.03 (9H, s), 1.95 (2H, s), 3.38 (2H, s), 3.45 (2H, s), 7.10—7.45 (9H, m). *Anal.* Calcd for $C_{18}H_{24}BrNSi$: C, 59.66; H, 6.68; N, 3.87. Found: C, 59.64; H, 6.85; N, 3.68.

***N*-(4-Methoxybenzyl)-*N*-(4-methylbenzyl)(trimethylsilyl)methylamine (1h)** In a manner similar to that described for **1a**, *N*-(4-methylbenzyl)-(trimethylsilyl)methylamine (3.1 g, 15 mmol) was treated with 4-methoxybenzoyl chloride (2.6 g, 15 mmol) to give *N*-(methoxybenzoyl)-*N*-(4-methylbenzyl)(trimethylsilyl)methylamine; yield, 4.8 g (94%); mp 55—56 °C. IR ν_{max}^{film} cm^{-1}: 1625 (CO–N), 1250 (Si–C, CH_3–O–C). ^{1}H-NMR ($CDCl_3$) δ: 0.10 (9H, s, $SiCH_3$), 2.35 (3H, s, $ArCH_3$), 2.90 (2H, s, $SiCH_2$), 3.80 (3H, s, OCH_3), 4.50 (2H, s, $ArCH_2$), 6.75—7.45 (8H, m). *Anal.* Calcd for $C_{20}H_{27}NO_2Si$: C, 70.34; H, 7.97; N, 4.10. Found: C, 70.10; H, 8.17; N, 3.92.

Treatment of *N*-(4-methoxybenzoyl)-*N*-(4-methylbenzyl)(trimethylsilyl)-methylamine (3.4 g, 10 mmol) with $LiAlH_4$ (0.57 g, 15 mmol) gave **1h**; yield, 2.74 g (84%); bp 165 °C (0.4 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1250, 860. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (9H, s), 1.95 (2H, s), 2.35 (3H, s), 3.40 (2H, s), 3.45 (2H, s), 3.85 (3H, s), 6.70—7.40 (8H, m). *Anal.* Calcd for $C_{20}H_{29}NOSi$: C, 73.34; H, 8.92; N, 4.28. Found: C, 73.26; H, 8.99; N, 4.03.

***N*-(4-Bromobenzyl)-*N*-(4-methylbenzyl)(trimethylsilyl)methylamine (1i)** *N*-(4-Methylbenzyl)(trimethylsilyl)methylamine (4.1 g, 20 mmol) was treated with 4-bromobenzyl bromide (2.5 g, 10 mmol) in a manner similar to that described for **1b**. Yield, 94%; bp 175 °C (1.0 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1250, 855. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (9H, s), 1.95 (2H, s), 2.35 (3H, s), 3.35 (2H, s), 3.45 (2H, s), 7.00—7.55 (8H, m). *Anal.* Calcd for: $C_{19}H_{26}BrNSi$: C, 60.63; H, 6.96; N, 3.72. Found: C, 60.55; H, 7.02; N, 3.47.

***N*,*N*-Dibenzyl-*N*-methyl(trimethylsilyl)methylammonium Iodide (4d)** A solution of **1d** (1.9 g, 6.7 mmol) and MeI (5.2 g, 37 mmol) in MeCN (10 ml) was heated at 50 °C for 24 h. The solvent was evaporated off and the residue was recrystallized from a mixture of AcOEt and EtOH to gave **4d**; yield, 1.89 g (66%); mp 137—138 °C. ^{1}H-NMR ($CDCl_3$) δ: 0.35 (9H, s, $SiCH_3$), 2.95 (3H, s, NCH_3), 3.35 (2H, s, $SiCH_2$), 4.90 and 5.01 (4H, ABq, J = 12.8 Hz, NCH_2), 7.25—7.75 (10H, m). *Anal.* Calcd for $C_{19}H_{28}INSi$: C, 53.64; H, 6.63; N, 3.29. Found: C, 53.43; H, 6.57; N, 3.11.

Reaction of Bis(4-substituted benzyl)methyl[(trimethylsilyl)methyl]ammonium Iodides (4a—c, e, h—i) with CsF: General Procedure A mixture

of **1a**, **1b**, **1c**, **1e**, **1h**, or **1i** (3 mmol) and MeI (more than 27 mmol) in MeCN (10 ml) was stirred at 65 °C for 24 h (**1a**, **1b**, **1e**, **1h**, or **1i**) or 48 h (**1c**). After removal of the solvent and the excess MeI under reduced pressure, anhydrous DMF (30 ml) was added. Then about 20 ml of DMF was distilled away under reduced pressure in order to remove the remaining CH_3CN. CsF (2.2 g, 14 mmol) was added to the mixture, and the whole was stirred at room temperature for 20 h then poured into 1% $NaHCO_3$ (200 ml) and extracted with Et_2O (4 × 100 ml). The ethereal extract was washed with 1% $NaHCO_3$ (2 × 100 ml), dried ($MgSO_4$), and concentrated to determine the total weight of the products and for measurement of the spectra. The residual oil was dissolved in Et_2O (50 ml) and extracted with 10% HCl (3 × 40 ml) and H_2O (40 ml). The acid layer was made alkaline with 20% NaOH and extracted with Et_2O (4 × 100 ml). Then the ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was chromatographed on an aluminum oxide column (hexane–Et_2O) to separate the Sommelet–Hauser products (**6** and **8**) and **1**. The ratios of **6** to **8** were determined from the integration ratios of proton signals in the ^{1}H-NMR spectra of the mixtures (see Table I).

***N*-Methyl-*N*-(2-methylbenzyl)-4-methoxybenzylamine (6a)** Yield, 75%; bp 120 °C (0.18 Torr, oven temperature). ^{1}H-NMR ($CDCl_3$) δ: 2.12 (3H, s), 2.34 (3H, s), 3.46 (2H, s), 3.47 (2H, s), 3.80 (3H, s), 6.85 (2H, d, J=8.8 Hz), 7.13—7.16 (3H, m), 7.24 (2H, d, J=8.8 Hz), 7.29—7.34 (m, 1H). *Anal.* Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.06; H, 8.50; N, 5.39.

***N*-Methyl-*N*-(2-methylbenzyl)-4-methylbenzylamine (6b) and *N*-Benzyl-*N*-methyl-2,5-dimethylbenzylamine (8b)** These compounds could not be separated by either chromatography or distillation. Yield, 63%; bp 125 °C (0.7 Torr, oven temperature). *Anal.* Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.43; H, 9.11; N, 5.82. **6b**: ^{1}H-NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.33 (3H, s), 2.35 (3H, s), 3.47 (2H, s), 3.48 (2H, s), 7.11 (2H, d, J=7.7 Hz), 7.22 (2H, d, J=7.7 Hz), 7.12—7.16 (4H, m). **8b**: ^{1}H-NMR ($CDCl_3$) δ: 2.14 (3H, s), 2.31 (6H, s), 3.46 (2H, s), 3.51 (2H, s), 6.96 (1H, dd, J=1.8, 7.7 Hz), 7.03 (1H, d, J=7.7 Hz), 7.14 (1H, d, J=1.8 Hz), 7.21—7.35 (5H, m).

***N*,*N*-Di(2-methylbenzyl)methylamine (6c) and *N*-Benzyl-*N*-methyl-2,3-dimethylbenzylamine (8c)** Yield, 62%; bp 120 °C (0.4 Torr, oven temperature). *Anal.* Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.18; H, 8.62; N, 5.64. After distillation, these compounds were separated by aluminum oxide column chromatography (*n*-hexane). **6c**: ^{1}H-NMR ($CDCl_3$) δ: 2.12 (3H, s), 2.30 (6H, s), 3.49 (4H, s), 7.10—7.17 (6H, m), 7.28—7.31 (2H, m). **8c**: ^{1}H-NMR ($CDCl_3$) δ: 2.12 (3H, s), 2.26 (3H, s), 2.28 (3H, s), 3.50 (2H, s), 3.51 (2H, s), 7.01—7.24 (4H, m), 7.27—7.34 (4H, m).

***N*-Methyl-*N*-(2-methylbenzyl)-4-bromobenzylamine (6e) and *N*-Benzyl-*N*-methyl-5-bromo-2-methylbenzylamine (8e)** These compounds could not be separated by either chromatography or distillation. Yield, 76%; bp 100 °C (0.5 Torr, oven temperature). *Anal.* Calcd for $C_{16}H_{18}BrN$: C, 63.17; H, 5.96; N, 4.60. Found: C, 63.19; H, 6.10; N, 4.28. **6e**: ^{1}H-NMR ($CDCl_3$) δ: 2.15 (3H, s), 2.35 (3H, s), 3.44 (2H, s), 3.53 (2H, s), 7.21 (2H, d, J=8.3 Hz), 7.13—7.18 (3H, m), 7.23—7.34 (1H, m), 7.42 (2H, d, J=8.3 Hz). **8e**: ^{1}H-NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.28 (3H, s), 3.48 (2H, s), 3.49 (2H, s), 7.00 (1H, d, J=7.9 Hz), 7.23—7.34 (5H, m), 7.28 (1H, dd, J=2.2, 7.9 Hz), 7.50 (1H, d, J=2.2 Hz).

***N*-Methyl-*N*-(4-methoxybenzyl)-2,5-dimethylbenzylamine (6h)** Yield, 65%; bp 115 °C (0.5 Torr, oven temperature). *Anal.* Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20. Found: C, 80.19; H, 8.82; N, 4.89. ^{1}H-NMR ($CDCl_3$) δ: 2.11 (3H, s), 2.30 (3H, s), 2.31 (3H, s), 3.43 (2H, s), 3.45 (2H, s), 3.80 (3H, s), 6.84 (2H, d, J=8.7 Hz), 6.96 (1H, dd, J=7.5, 1.7 Hz), 7.03 (1H, d, J=7.5 Hz), 7.12 (1H, br s), 7.24 (2H, d, J=8.7 Hz).

***N*-(4-Bromobenzyl)-*N*-methyl-2,5-dimethylbenzylamine (6i) and *N*-Methyl-*N*-(4-methylbenzyl)-5-bromo-2-methylbenzylamine (8i)** These compounds could not be separated by either chromatography or distillation. Yield, 63%; bp 130 °C (0.7 Torr, oven temperature). *Anal.* Calcd for $C_{17}H_{20}BrN$: C, 64.16; H, 6.33; N, 4.40. Found: C, 64.07; H, 6.19; N, 4.35. **6i**: ^{1}H-NMR ($CDCl_3$) δ: 2.12 (3H, s), 2.31 (6H, s), 3.45 (4H, s), 6.97 (1H, dd, J=1.8, 7.5 Hz), 7.00 (2H, d, J=8.3 Hz), 7.03 (1H, d, J=7.5 Hz), 7.12 (1H, br s), 7.42 (2H, d, J=8.3 Hz). **8i**: ^{1}H-NMR ($CDCl_3$) δ: 2.13 (3H, s), 2.27 (3H, s), 2.33 (3H, s), 3.42 (2H, s), 3.49 (2H, s), 7.12 (2H, d, J=8.0 Hz), 7.20 (1H, d, J=8.1 Hz), 7.21 (2H, d, J=8.0 Hz), 7.26 (1H, dd, J=2.1, 8.1 Hz), 7.49 (1H, d, J=2.1 Hz).

Reaction of 4d with CsF Compound **4d** (1.28 g, 3 mmol) and CsF (2.2 g, 14 mmol) were placed in a 30-ml flask equipped with a magnetic stirrer and a septum. The flask was dried under reduced pressure and flushed with N_2. Anhydrous DMF (10 ml) was added to the flask with a syringe and the mixture was stirred at room temperature for 20 h, then poured into 1% $NaHCO_3$ and extracted with Et_2O (4 × 100 ml). The ethereal extract was washed with 1% $NaHCO_3$ (2 × 100 ml), dried ($MgSO_4$), concentrated under reduced pressure, and distilled to give **6d** (same as **8d**) and **7d** (same as **9d**). The amount of **7d** was too small to allow its purification by either chromatography or distillation. The ratios of the products were determined from the integration ratios of the proton signals in the ^{1}H-NMR spectra of the mixtures. Yield, 0.64 g (95%); bp 115 °C (0.35 Torr, oven temperature). *Anal.* Calcd for $C_{16}H_{19}N$: C, 85.29; H, 8.50; N, 6.22. Found: C, 85.33; H, 8.62; N, 6.27. **6d**: ^{1}H-NMR ($CDCl_3$) δ: 2.14 (3H, s), 2.36 (3H, s), 3.49 (2H, s), 3.52 (2H, s), 7.12—7.35 (9H, m). **7d** (lit.[5]): ^{1}H-NMR ($CDCl_3$) δ: 2.66 (2H, t, J=7.8 Hz), 2.84 (2H, t, J=7.8 Hz). Other proton signals were overlapped by signals of **6d** and could not be recognized.

Reaction of *N*-Benzyl-*N*-(4-cyanobenzyl)-*N*-methyl(trimethylsilyl)methylammonium (4f) or *N*-Benzyl-*N*-(4-nitrobenzyl)-*N*-methyl(trimethylsilyl)-methylammonium Bromide (4g) with CsF A mixture of *N*-benzyl-*N*-methyl(trimethylsilyl)methylamine[6] (**2**, 0.64 g, 3.1 mmol) and 4-cyanobenzyl bromide (**3f**, 0.59 g, 3.0 mmol) or 4-nitrobenzyl bromide (**3g**, 0.65 g, 3.0 mmol) in MeCN (10 ml) was heated at reflux for 20 h. After removal of the solvent under reduced pressure, DMF (20 ml) was added. Then about 10 ml of DMF was distilled away under reduced pressure in order to remove the remaining MeCN. CsF (2.2 g, 14 mmol) was added to the mixture. After 20 h of stirring at room temperature, the mixture was poured into 1% $NaHCO_3$ (200 ml) and extracted with Et_2O (4 × 100 ml). The ethereal extract was washed with 1% $NaHCO_3$ (2 × 100 ml), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on an aluminum oxide column (hexane : Et_2O = 33 : 1) to separate **6f**, **g** (or **8f**), **9f**, **g**, and **2**. The ratios of the products were determined from the integration ratios of the proton signals in the ^{1}H-NMR spectra of the mixtures (Table I).

***N*-Methyl-*N*-(2-methylbenzyl)-4-cyanobenzylamine (6f) and *N*-Benzyl-*N*-methyl-5-cyano-2-methylbenzylamine (8f)** These compounds could not be separated by either chromatography or distillation. Yield, 27%; bp 120 °C (0.07 Torr, oven temperature). *Anal.* Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.81; H, 7.33; N, 10.89. **6f**: ^{1}H-NMR ($CDCl_3$) δ: 2.14 (3H, s), 2.37 (3H, s), 3.52 (2H, s), 3.55 (2H, s), 7.15—7.18 (3H, m), 7.22 (2H, d, J=7.9 Hz), 7.25—7.34 (1H, m), 7.43 (2H, d, J=7.9 Hz). **8f**: ^{1}H-NMR ($CDCl_3$) δ: 2.15 (3H, s), 2.38 (3H, s), 3.47 (2H, s), 3.55 (2H, s), 7.25—7.34 (5H, m), 7.44 (1H, dd, J=1.5, 8.4 Hz), 7.58 (1H, d, J=8.4 Hz), 7.67 (1H, d, J=1.5 Hz).

***N*-[2-(4-Cyanophenyl)ethyl]-*N*-methylbenzylamine (9f)** Yield, 40%; bp 130 °C (0.09 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 2300. ^{1}H-NMR ($CDCl_3$) δ: 2.28 (3H, s), 2.64 (2H, t, J=7.5 Hz), 2.86 (2H, t, J=7.5 Hz), 3.53 (2H, s), 7.21—7.31 (5H, m), 7.27 (2H, d, J=8.4 Hz), 7.55 (2H, d, J=8.4 Hz). *Anal.* Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.44; H, 7.10; N, 11.00

***N*-Methyl-*N*-(2-methylbenzyl)-4-nitrobenzylamine (6g)** Yield, 64%; bp 120 °C (0.2 Torr, oven temperature). IR ν_{max}^{film} cm^{-1}: 1515, 1345 (NO_2). ^{1}H-NMR ($CDCl_3$) δ: 2.16 (3H, s), 2.38 (3H, s), 3.54 (2H, s), 3.59 (2H, s), 7.13—7.20 (4H, m), 7.49 (2H, d, J=8.8 Hz), 8.16 (2H, d, J=8.8 Hz). *Anal.* Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.31; H, 6.92; N, 10.28.

***N*-[2-(4-Nitrophenyl)ethyl]-*N*-methylbenzylamine (9g)** Yield, 4%. The yield of this compound was too little to allow distillation or microanalysis. ^{1}H-NMR ($CDCl_3$) δ: 2.29 (3H, s), 2.67 (2H, t, J=7.4 Hz), 2.91 (2H, t, J=7.4 Hz), 3.54 (2H, s), 7.22—7.30 (5H, m), 7.31 (2H, d, J=8.8 Hz), 8.12 (2H, d, J=8.8 Hz).

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References and Notes

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