$CDCl_3$ (7.24 ppm). Guest stock solutions were prepared in volumetric flasks (2 mL) with deuteriochloroform. Concentrations of host and guest were quantified separately via NMR integrations against a standardized solution of a carefully tared amount of adamantyltrimethylammonium iodide (1) in $CDCl_3$ (2 mL, 19.1 mM). Volumetric measurements were made using Hamilton microliter syringes. Volumes were corrected for thermal expansion of solvent according to: $v_t = v_o(1 + \alpha t_o)$; where v_t = volume at the corrected probe temperature; t_o = difference between probe and room temperatures; v_o = volume measured at room temperature; and $\alpha = 0.001\,26$ cm^3/deg, the coefficient of thermal expansion for $CHCl_3$.[33]

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Aqueous VT Binding Studies. Aqueous binding spectra were referenced at all temperatures to internal 3,3-dimethylglutarate (DMG, 1.09 ppm vs TSP) in a standard 10 mM deuterated cesium borate buffer[17] at pD ~9 (borate-*d*). Concentrations of host and guest stock solutions were determined via NMR integrations against a stock solution of DMG (4.20–4.23 mM). Volumeric measurements were made using adjustable volumetric pipets. Volumes were corrected for density changes from a plot of densities of H_2O versus temperature (10–65 °C),[33] which fit the following equation: $y = a + bx + cx^2$; where y = density at corrected probe temperature, x (°C); $a = 1.0011$; $b = -6.7589 \times 10^{-5}$; $c = -3.8471 \times 10^{-6}$.

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Intermediate in Sommelet–Hauser Rearrangement of *N,N*-Dimethylbenzylammonium *N*-Methylides

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Formation of benzylammonium *N*-methylides by fluoride anion induced desilylation of dimethyl(4-substituted benzyl)[(trimethylsilyl)methyl]ammonium halides (**1**) and 3-substituted benzyl analogues (**6**) was examined to isolate 5-[(dimethylamino)methyl]-6-methylene-1,3-cyclohexadienes (isotoluene intermediates, **3**, **8**, and **10**) in the Sommelet–Hauser rearrangement. Some isotoluenes were isolated and their structures were confirmed by ^{1}H NMR analysis. The stability of the isotoluenes was dependent on the electron-donating effects of the substituents on the conjugated bonds, and 3-methoxy-substituted isotoluene **3a** was the most stable compound studied.

Introduction

The base-induced ylide formation reaction of (substituted benzyl)trimethylammonium halides gives mainly *N,N*-dimethyl-2-methylbenzylamine derivatives (Sommelet–Hauser rearrangement). This rearrangement has been thought to proceed via unstable intermediates, 5-[(dimethylamino)methyl]-6-methylene-1,3-cyclohexadienes (isotoluene derivatives), which are difficult to isolate because they are easily aromatized to the final products.[1] Hauser and Van Eenam isolated 5-[(dimethylamino)methyl]-1,3,5-trialkyl-6-methylene-1,3-cyclohexadienes from *N,N*-dimethyl-2,4,6-trialkylbenzylammonium *N*-methylide; however, these compounds do not have the hydrogen atom needed to restore ring resonance by proton migration.[2]

We previously reported that the fluoride anion induced desilylation of (substituted benzyl)dimethyl[(trimethylsilyl)methyl]ammonium halides gives the *N*-methylide intermediates exclusively and that they are isomerized to *N,N*-dimethyl-2-methylbenzylamines (Sommelet–Hauser rearrangement products) in high yields.[3] Similar desilylation of *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-phenylpiperidinium iodide, however, gave 2-methyl-1,3,4,5,6,11a-hexahydro-2*H*-2-benzazonine (an isotoluene derivative) instead of the expected 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine (Sommelet–Hauser rearrangement product).[4] This isotoluene derivative is unexpectedly stable in a neutral medium and is aromatized to the Sommelet–Hauser rearrangement product only in the presence of a strong base. This result suggests that 5-[(dimethylamino)methyl]-6-methylene-1,3-cyclohexadienes (isotoluene intermediates) might also be stable in a nonbasic medium. Here, we report the reexamination of the ylide formation reaction from benzyldimethyl[(trimethylsilyl)methyl]ammonium halides in order to determine the possible isolation of 5-[(dimethylamino)-

Scheme I

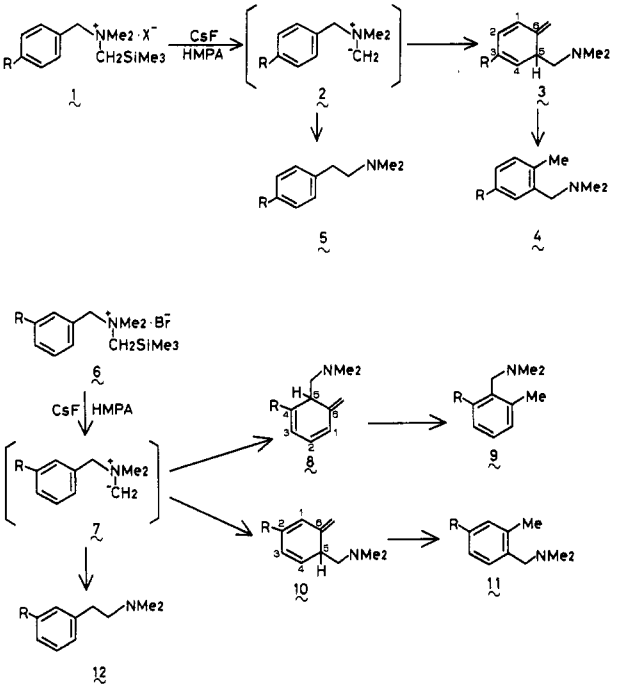

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Table I. Reaction of Dimethyl(4-substituted benzyl)[(trimethylsilyl)methyl]ammonium Bromide (1) with Cesium Fluoride in HMPA

				reaction products, 3, 4, and 5				
				after 0.5 h at 10 °C			after 24 h at room temp	
entry		R	Hammett constant σ_p	total yield, %	ratio[a] 3:(4 + 5)	UV λ_{max}, nm (log ϵ)	total yield, %	ratio[b] 4:5
1	a[c]	MeO	−0.27	58	100:0	318 (3.5)[d]	66[e]	
2	b	Me	−0.17	70	77:23	308 (*f*)	77	96:4[g]
3	c	AcO	0.31	32	46:54	302 (*f*)	72	99:1[g]
4	d	H	0	80	40:60	304 (*f*)	84	97:3[g]
5	e	$COOCMe_3$	0.45	41	0:100		79	86:14
6	f	NO_2	0.78	73	0:100		77	12:88[g]

[a] Determined from the proton ratios of ^1H NMR. [b] Determined from the integrated values of GLC analyses. [c] Iodide. [d] Determined on isolated **3a**. [e] Compound **3a**. [f] Not determined. [g] Reference 3.

Table II. Reaction of Dimethyl(3-substituted benzyl)[(trimethylsilyl)methyl]ammonium Bromides (6) with Cesium Fluoride in HMPA

			reaction products, 8–12				
			after 0.5 h at 10 °C			after 44 h at room temp	
entry		R	total yield, %	ratio[a] 8:9:10:11[c]	UV λ_{max}, nm (log ϵ)	total yield, %	ratio[b] 9:11:12
1	a	MeO	46	68:16:0:16	318 (*d*)	86	57:41:2
2	b	Me	75	39:11:22:28	307 (*d*)	76	55:44:1
3	c	AcO	52	0:0:0:100		52	0:98:2
4	e	$COOCMe_3$	16	55:0:0:45	328 (3.7)[e]	71	45:55:0
5	f	NO_2	0			22	0:88:12

[a] Determined from the proton ratios of ^1H NMR. [b] Determined from the integrated values of GLC analyses. [c] Small amounts of **12** were not detected by ^1H NMR analysis. [d] Not determined. [e] Determined on isolated **8e**.

methyl]-6-methylene-1,3-cyclohexadiene.

Results and Discussion

The reaction of benzyldimethyl[(trimethylsilyl)-methyl]ammonium bromide (**1d**) and (4-methoxybenzyl)- (**1a**), (4-methylbenzyl)- (**1b**), (4-acetoxybenzyl)- (**1c**), (4-(*tert*-butoxycarbonyl)benzyl)- (**1e**), and (4-nitrobenzyl)-ammonium salts (**1f**) with cesium fluoride in hexamethylphosphoramide (HMPA) gave mixtures of two isomeric products, *N,N*-dimethyl-2-methyl-5-substituted-benzylamines (Sommelet–Hauser rearrangement products, **4b–f**) and *N,N*-dimethyl-2-(4-substituted phenyl)ethylamines (Stevens rearrangement products, **5b–f**), after 24 h of stirring at room temperature,[3] except for **1a** (Table I).

When the same reaction was carried out at 10 °C and quenched after 30 min, characteristic strong UV absorption (λ_{max} 302–318 nm) was observed in the ethereal extracts of the reaction mixtures of **1a–d**. Their maximum values are similar to that of 5-[(dimethylamino)methyl]-1,3,5-trimethyl-6-methylene-1,3-cyclohexadiene (λ_{max} 313 nm).[2] However, no maximum appeared in the 300–320-nm region in the UV spectra of the products from **1e** and **1f**. Structures of the products were determined by ^1H NMR spectral analysis. The reaction product from **1a** was almost pure 5-[(dimethylamino)methyl]-3-methoxy-6-methylene-1,3-cyclohexadiene (an isotoluene derivative, **3a**) (entry 1), and the products from **1b–d** were mixtures of the 5-[(dimethylamino)methyl]-3-substituted-6-methylene-1,3-cyclohexadiene derivatives (**3b–d**) and **4b–d** (entries 2–4). However, from **1e,f**, the corresponding **3e,f** were not detected but **4e,f** and **5e,f** were formed in similar ratios to those after 24 h at room temperature (entries 5 and 6). These results are summarized in Table I in decreasing order of the 3:(4 + 5) ratio. This order is roughly similar to the increasing order of the σ_p value in Hammett para substituent constants. In other words, the 3:(4 + 5) ratio in the products decreases in decreasing order of the electron-donating effect of the substituents.

Methoxy-substituted compound **3a** is the most stable of those under study. It was isolated in 66% yield from the reaction mixture after 24 h of stirring at room temperature (entry 1) and purified on a HPLC column without isomerization. Purification of **3b–d** on the same HPLC column was difficult because they were partially isomerized to **4b–d** during elution. Isotoluenes **3e** and **3f** with electron-withdrawing substituents were not detectable under this reaction condition.

N,N-Dimethyl(3-substituted benzyl)ammonium *N*-methylides (**7**) can be converted into two types of Sommelet–Hauser rearrangement products, *N,N*-dimethyl-2-methyl-6-substituted-benzylamine (**9**) and *N,N*-dimethyl-2-methyl-4-substituted-benzylamine (**11**). The desilylation reaction of (3-methoxybenzyl)-, (3-methylbenzyl)-, or (3-(*tert*-butyoxycarbonyl)benzyl)ammonium bromides (**6a,b,e**) gave mixtures of the two isomers **9a,b,e** and **11a,b,e** in similar ratios, accompanied by small amounts of *N,N*-dimethyl-2-(3-substituted phenyl)ethylamines (Stevens rearrangement products, **12a,b**) after 44 h of stirring at room temperature (entries 1, 2, and 4 in Table II). From (3-acetoxybenzyl)- or (3-nitrobenzyl)-ammonium salt (**6c,f**), 4-substituted amine **11c,f** was obtained as the main product (entries 3 and 5).

When these reactions were also quenched after 30 min at 10 °C and treated in a manner similar to that described for **1**, strong UV absorption was observed in the extract from **6a**, **6b**, and **6e**, but not from **6c** and **6f**. The NMR spectra of the extracts revealed that the extract from **6a** was a mixture of 4-methoxy-5-[(dimethylamino)-methyl]-6-methylene-1,3-cyclohexadiene (**8a**), **9a**, and **11a**, but 2-methoxy-5-[(dimethylamino)methyl]-6-methylene-1,3-cyclohexadiene (**10a**) was not detected (entry 1). Four possible products, **8b**, **9b**, **10b**, and **11b**, were confirmed among the reaction products of **6b**. However, the extract from **6e** consisted of 4-(*tert*-butoxycarbonyl)-5-[(dimethylamino)methyl]-6-methylene-1,3-cyclohexadiene (**8e**)

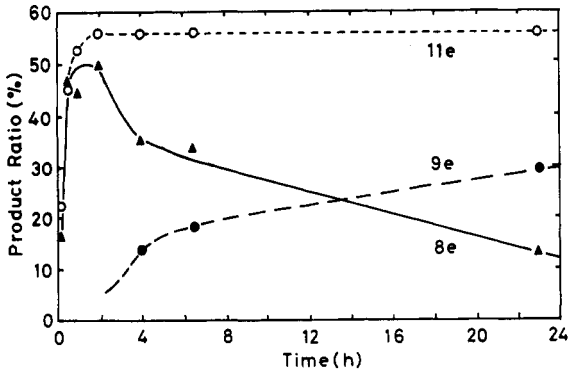

Figure 1. Plot of the product distribution vs time of the reaction of **6e** with CsF in HMPA at room temperature.

and **11e**. The result from **6c** was the same after 44 h; however, it is interesting that the rearrangement of (3-acetoxybenzyl)ammonium *N*-methylide **7c** proceeded only toward the 6-position of the benzene ring followed by quick aromatization to **11c**. The reaction of **6f** was very slow and gave almost no product after 0.5 h.

These results suggest that of the two isomers 8 is more stable than **10**. However, attempts to separate **8a**, **8b**, and **10b** failed because they were aromatized during elution on the HPLC column; **8e**, in contrast, was unexpectedly stable and purified on the column without isomerization.

Change in the mole ratios of the components in the reaction mixture of **6e** was measured at appropriate intervals by HPLC (Figure 1). Slow conversion of **8e** to **9e** can be seen. The unusual stability of **8e** compared with **3e** and **10e** may be due to its crowded structure.

Experimental Section

Hexamethylphosphoramide (HMPA) was dried by distillation under reduced pressure from sodium prior to use. Cesium fluoride was dried over P_2O_5 at 180 °C under reduced pressure. ^1H NMR spectra were recorded on a JEOL JNM-GSX-400 spectrometer using Me_4Si as internal standard. IR spectra were recorded on a Jasco IRA-2 spectrometer. Mass spectra were measured on a JEOL JMS-DX 300 GC–MS system (70 eV). GLC analyses were performed on a Hitachi Model 263-30 gas chromatograph with an FID detector using a 2-m, 5% PEG 20M on Uniport HP column. Preparative and analytical HPLC were carried out on a TOSOH CCP 8000 system. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer. Melting points and boiling points are uncorrected.

Dimethyl(4-methoxybenzyl)[(trimethylsilyl)methyl]ammonium Iodide (1a). A mixture of methyl(4-methoxybenzyl)amine (5.96 g, 39 mmol), (chloromethyl)trimethylsilane (2.42 g, 20 mmol), and dimethyl sulfoxide (10 mL) was heated at 140 °C for 8 h. The mixture was poured into water and extracted with ether. The extract was washed with water, dried ($MgSO_4$), concentrated, and distilled to give 3.295 g (70%) of methyl(4-methoxybenzyl)[(trimethylsilyl)methyl]amine: bp 110–115 °C (4 mmHg); ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 1.84 (s, 2 H), 2.12 (s, 3 H), 3.31 (s, 2 H), 3.72 (s, 3 H), 6.77 (d, 2 H, J = 8 Hz), 7.14 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.98; H, 9.63; N, 5.93.

A solution of methyl(4-methoxybenzyl)[(trimethylsilyl)methyl]amine (9.5 g, 40 mmol) and iodomethane (6.7 g, 47 mmol) in acetonitrile (40 mL) was heated at 60 °C for 2 h. The precipitated crystals were filtered, washed with ether, and dried to give **1a** (54%): mp 162–163 °C; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H), 3.28 (s, 6 H), 3.40 (s, 2 H), 3.81 (s, 3 H), 5.01 (s, 2 H), 6.92 (d, 2 H, J = 8 Hz), 7.62 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{14}H_{26}INOSi$: C, 44.33; H, 6.91; N, 3.69. Found: C, 44.29; H, 6.72; N, 3.67.

Dimethyl[4-(*tert*-butoxycarbonyl)benzyl][(trimethylsilyl)methyl]ammonium Bromide (1e) and Dimethyl(3-substituted benzyl)ammonium Bromides (6a–e). A mixture of [(dimethylamino)methyl]trimethylsilane (16 mmol), the 4- or 3-substituted benzyl bromide (18 mmol), and acetone (10 mL) was heated at reflux for 2 h. The precipitated crystals were filtered, washed with ether, and dried.

1e (yield 76%): mp 133–135 °C; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 1.60 (s, 9 H), 3.36 (s, 8 H), 5.24 (s, 2 H), 7.80 (d, 2 H, J = 8 Hz), 8.02 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{18}H_{32}BrNO_2Si$: C, 53.72; H, 8.01; N, 3.48. Found: C, 53.61; H, 7.80; N, 3.39.

6a (yield 89%): mp 175 °C; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 3.23 (s, 8 H), 3.72 (s, 3 H), 4.95 (s, 2 H), 7.10–7.23 (m, 4 H). Anal. Calcd for $C_{14}H_{26}BrNOSi$: C, 50.59; H, 7.88; N, 4.21. Found: C, 50.72; H, 7.70; N, 4.25.

6b (yield 78%): mp 140–141 °C; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 2.36 (s, 3 H), 3.33 (s, 6 H), 3.37 (s, 2 H), 5.00 (s, 2 H), 7.30–7.45 (m, 4 H). Anal. Calcd for $C_{14}H_{26}BrNSi$: C, 53.15; H, 8.28; N, 4.43. Found: C, 52.98; H, 8.06; N, 4.20.

6c (yield 86%): mp 165 °C; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 2.31 (s, 3 H), 3.33 (s, 8 H), 5.20 (s, 2 H), 7.21–7.61 (m, 4 H). Anal. Calcd for $C_{15}H_{26}BrNO_2Si$: C, 49.99; H, 7.27; N, 3.89. Found: C, 50.15; H, 7.21; N, 3.95.

6e (yield 98%): mp 206 °C; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9 H), 1.58 (s, 9 H), 3.38 (s, 8 H), 5.12 (s, 2 H), 7.49–8.08 (m, 4 H). Anal. Calcd for $C_{18}H_{32}BrNO_2Si$: C, 53.72; H, 8.01; N, 3.48. Found: C, 53.35; H, 8.04; N, 3.37.

Reaction of 1a–e or 6a–e with CsF at 10 °C. General Procedure. Ammonium halide (4 mmol) was placed in a 50-mL flask equipped with a septum, a magnetic stirrer, and a test tube connected with a short rubber tube. CsF (3.0 g, 20 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with high-purity nitrogen. HMPA (20 mL) was added to the flask by syringe, and then CsF was added from the test tube. The reaction mixture was stirred at 10 °C for 0.5 h, poured into 1.5% Na_2CO_3 (200 mL), and extracted with ether (100 mL × 4). The extract was washed with 1.5% Na_2CO_3 (100 mL × 2), dried ($MgSO_4$), and concentrated under reduced pressure. UV and ^1H NMR spectra of the residual oils were measured immediately. The maximum values of the UV spectra are listed in Tables I and II. Analyses of the NMR spectra indicated that the mixture consisted of **3–5** or **8–12**. The results are summarized in Tables I and II.

The ^1H NMR spectrum of the extract from **1a** exhibited there was almost pure **3a**. A part of the extract was further purified on a HPLC column (Merck Hibar LiChrosorb NH_2, 250 mm × 10 mm). The mobile phase was a mixture of 5% ether in hexane for 3 min at flow rate of 5 mL/min and increased linearly to 15% in 7 min. The eluent was monitored at a 235-nm UV detector. A fraction of retention time 8.2 min was collected and concentrated to give **3a** (an undistillable oil, the purity was judged to be >98% by HPLC): ^1H NMR ($CDCl_3$) δ 2.14 (dd, 1 H, J = 5.9 and 11.9 Hz), 2.27 (s, 6 H), 2.52 (dd, 1 H, J = 9.4 and 11.9 Hz), 3.33 (m, 1 H), 3.57 (s, 3 H), 4.89 (d, 1 H, J = 5.2 Hz), 4.95 (s, 1 H), 5.08 (s, 1 H), 5.68 (d, 1 H, J = 9.9 Hz), 6.13 (d, 1 H, J = 9.9 Hz).

Forty milligrams of the extract from **6e** was dissolved in hexane (1 mL), and 0.2 mL of the solution was injected into the same HPLC column and monitored at 235 nm. The mobile phase was a mixture of 2% ether in hexane for 8 min at flow rate of 5 mL/min, increased linearly to 15% in 3 min and then to 40% in 1 min. After this level was maintained for 5 min, the condition was returned to the initial in 1 min. Fractions of **8e** (9 min) and **11e** (11.5 min) were corrected. The same chromatography was repeated four times and the combined fractions were concentrated under reduced puressure to give **8e** (16 mg) and **11e** (11 mg).

8e (an undistillable oil, the purity was judged to be >98% by HPLC): ^1H NMR ($CDCl_3$) δ 1.51 (s, 9 H), 2.16 (dd, 1 H, J = 5.0 and 11.0 Hz), 2.25 (s, 6 H), 2.32 (dd, 1 H, J = 9.0 and 11.0 Hz), 3.67 (dd, 1 H, J = 5.0 and 9.0 Hz), 5.12 (s, 1 H), 5.23 (s, 1 H), 5.95 (dd, 1 H, J = 6.0 and 9.5 Hz), 6.32 (d, 1 H, J = 9.5 Hz), 6.95 (d, 1 H, J = 6.0 Hz).

11e: ^1H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 2.23 (s, 6 H), 2.39 (s, 3 H), 3.40 (s, 2 H), 7.32 (d, 1 H, J = 8 Hz), 7.76 (d, 1 H, J = 8 Hz), 7.77 (br s, 1 H).

Attempts to isolate the other isotoluenes failed because of their lack of stability. Their ^1H NMR data were read in those of the mixtures.

3b: ^1H NMR ($CDCl_3$) δ 1.78 (s, 3 H), 2.09 (dd, 1 H, J = 6.0 and 11.7 Hz), 2.26 (s, 6 H), 2.57 (dd, 1 H, J = 9.7 and 11.7 Hz), 3.22 (m, 1 H), 4.88 (s, 1 H), 5.04 (s, 1 H), 5.68 (d, 1 H, J = 9.5

Hz), 5.69 (br s, 1 H), 6.08 (d, 1 H, J = 9.5 Hz).

3c: ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3 H), 3.43 (m, 1 H), 4.97 (s, 1 H), 5.12 (s, 1 H), 5.62 (m, 2 H), 6.15 (d, 1 H, J = 10.4 Hz); signals of the CH_2N and $N(CH_3)_2$ groups could not be assigned due to overlaps with signals of **4c**.

3d: ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6 H), 3.31 (m, 1 H), 4.89 (s, 1 H), 5.04 (s, 1 H), 5.81 (dd, 1 H, J = 5.3 and 9.5 Hz), 6.00 (m, 2 H), 6.09 (d, 1 H, J = 9.5 Hz); signals of the CH_2N group could not be assigned due to an overlap with signals of **4d**.

8a: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6 H), 2.35 (dd, 1 H, J = 5.1 and 12.1 Hz), 2.47 (dd, 1 H, J = 8.6 and 12.1 Hz), 3.11 (dd, 1 H, J = 5.1 and 8.6 Hz), 3.60 (s, 3 H), 4.86 (s, 1 H), 5.01 (d, 1 H, J = 6.0 Hz), 5.03 (s, 1 H), 5.82 (d, 1 H, J = 9.4 Hz), 5.85 (dd, 1 H, J = 6.0 and 9.4 Hz).

8b: ^{1}H NMR ($CDCl_3$) δ 1.89 (s, 3 H), 2.24 (s, 6 H), 2.25 (dd, 1 H, J = 5.7 and 11.5 Hz), 2.34 (dd, 1 H, J = 8.1 and 11.5 Hz), 2.97 (br t, 1 H, J = 6.8 Hz), 4.89 (s, 1 H), 5.05 (s, 1 H), 5.73 (d, 1 H, J = 5.7 Hz), 5.81 (dd, 1 H, J = 5.7 and 9.3 Hz), 5.98 (d, 1 H, J = 9.3 Hz).

10b: ^{1}H NMR ($CDCl_3$) δ 3.23 (m, 1 H), 4.76 (s, 1 H), 4.92 (s, 1 H), 5.86 (d, 1 H, J = 9.5 Hz), 5.87 (s, 1 H), 6.02 (dd, 1 H, J = 4.9 and 9.5 Hz); signals of CCH_3, $N(CH_3)_2$, and CH_2N could not be assigned due to overlaps with signals of **9b** and **11b**.

Reaction of 1a, 1e, or 6a–e with CsF at Room Temperature. The reaction mixtures, prepared in the manner described above, were stirred at room temperature and treated after 24 h for 1 and 44 h for **6**. The ethereal extracts were distilled by a Büchi Kugelrohr distillation apparatus to give mixtures of **4** and **5** or of **9**, **11**, and **12**, except for the extract from **1a**. The product ratios were calculated from the integrated values of GLC of the distilled oils. ^{1}H NMR of the extract from **1a** showed that the product consisted of almost pure **3a**. The results are summarized in Tables I and II.

A mixture of **4e** and **5e**: bp 125 °C (7 mmHg). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.05; H, 9.29; N, 5.64. A mixture of **9a**,[5] **11a**,[5] and **12a**: bp 150 °C (14 mmHg). A mixture of **9b**,[5] **11b**,[5] and **12b**: bp 130 °C (20 mmHg). A mixture of **11c** and **12c**: bp 170 °C (17 mmHg). A mixture of **9e** and **11e**: bp 180 °C (7 mmHg). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 71.99; H, 9.39; N, 5.64.

A part of the distilled oils was chromatographed on an HPLC column (LiChrosorb NH_2, hexane/ether) to give pure samples.

4e: ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 2.23 (s, 6 H), 2.41 (s, 3 H), 3.39 (s, 2 H), 7.19 (d, 1 H, J = 8 Hz), 7.77 (dd, 1 H, J = 2 and 8 Hz), 7.83 (d, 1 H, J = 2 Hz).

5e: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 9 H), 2.29 (s, 6 H), 2.53 (t, 2 H, J = 8 Hz), 2.83 (t, 2 H, J = 8 Hz), 7.24 (d, 2 H, J = 8 Hz), 7.91 (d, 2 H, J = 8 Hz).

9a:[5] ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6 H), 2.38 (s, 3 H), 3.44 (s, 2 H), 3.80 (s, 3 H), 6.73 (d, 1 H, J = 8 Hz), 6.78 (d, 1 H, J = 8 Hz), 7.12 (t, 1 H, J = 8 Hz).

11a:[5] ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 6 H), 2.34 (s, 3 H), 3.31 (s, 2 H), 3.78 (s, 3 H), 6.68 (dd, 1 H, J = 2 and 8 Hz), 6.72 (d, 1 H, J = 2 Hz), 7.13 (d, 1 H, J = 8 Hz).

9b:[5] ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 6 H), 2.39 (s, 6 H), 3.39 (s, 2 H), 7.00 (d, 2 H, J = 7 Hz), 7.05 (t, 1 H, J = 7 Hz).

11b:[5] ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 6 H), 2.30 (s, 3 H), 2.32 (s, 3 H), 3.34 (s, 2 H), 6.96 (d, 1 H, J = 8 Hz), 6.97 (br s, 1 H), 7.12 (d, 1 H, J = 8 Hz).

11c: ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 6 H), 2.27 (s, 3 H), 2.35 (s, 3 H), 3.34 (s, 2 H), 6.86 (dd, 1 H, J = 2 and 9 Hz), 6.87 (d, 1 H, J = 2 Hz), 7.25 (d, 1 H, J = 9 Hz); exact mass spectrum, m/z 207.1269 (M^+; calcd for $C_{12}H_{17}NO_2$, 207.1258).

9e: ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 2.16 (s, 6 H), 2.39 (s, 3 H), 3.62 (s, 2 H), 7.14 (t, 1 H, J = 7 Hz), 7.18 (d, 1 H, J = 7 Hz), 7.32 (d, 1 H, J = 7 Hz).

Reaction of 1f or 6f with CsF. 3- or 4-Nitrobenzyl bromide (864 mg, 4 mmol) was placed in a 50-mL flask equipped with a magnetic stirrer, a reflux condenser, and a test tube in which CsF (3.0 g, 20 mmol) was placed. The apparatus was dried under reduced pressure and flushed with high-purity nitrogen. THF (10 mL) and [(dimethylamino)methyl]trimethylsilane (606 mg, 4.6 mmol) were added to the flask by syringe, and the mixture was heated at 50 °C for 2 h. After the mixture was cooled at 10 °C or room temperature, HMPA (20 mL) and CsF were added. The mixture was stirred at 10 °C for 0.5 h or at room temperature for 44 h. The reaction mixture was worked up in a manner similar to that described in the general procedure to give a mixture of **4f**[3] and **5f**,[3] bp 130 °C (20 mmHg, Kugelrohr), or of **11f** and **12f**, bp 140 °C (20 mmHg, Kugelrohr). The yields are calculated on the basis of the amount of nitrobenzyl bromide used. Results are shown in Tables I and II. Their ^{1}H NMR data were read in that of the mixture.

11f: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6 H), 2.42 (s, 3 H), 3.42 (s, 2 H), 7.40 (d, 1 H, J = 9 Hz), 7.92 (dd, 1 H, J = 2 and 9 Hz), 7.96 (d, 1 H, J = 2 Hz); exact mass spectrum, m/z 194.1037 (M^+; calcd for $C_{10}H_{14}N_2O_2$, 194.1054).

12f: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.55 (m, 2 H), 2.88 (m, 2 H), 7.40–7.60 (m, 2 H), 7.94–8.14 (m, 2 H).

HPLC Analysis of the Reaction of 6e with CsF. To a solution of **6e** (808 mg, 2 mmol) and CsF (1.5 g, 10 mmol) in HMPA (10 mL) was added isopropyl benzoate (180 mg) as an internal standard, and the mixture was stirred at room temperature. At appropriate time intervals, 2 μL of the reaction mixture was withdrawn, diluted with hexane (200 μL), and filtered. A part of the filtrate (4 μL) was analyzed on a Merck Hibar LiChrosorb NH_2 HPLC column (250 mm × 4 mm; ether/hexane; flow rate, 1 mL/min). The relative intensitites of the products were determined from the integrated values corrected with the correlation curve of each compound at 235 and 328 nm.

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Registry No. **1a**, 126062-57-5; **1b**, 102101-48-4; **1c**, 102101-52-0; **1d**, 72443-52-8; **1e**, 126062-58-6; **3a**, 126062-64-4; **3b**, 126062-65-5; **3c**, 126062-66-6; **3d**, 126062-67-7; **4b**, 60760-00-1; **4c**, 102101-54-2; **4d**, 4525-48-8; **4e**, 126062-68-8; **4f**, 107600-23-7; **5b**, 2358-90-9; **5c**, 95469-40-2; **5d**, 1126-71-2; **5e**, 126062-69-9; **5f**, 5339-05-9; **6a**, 126062-59-7; **66**, 126062-60-0; **6c**, 126062-61-1; **6e**, 126062-62-2; **8a**, 126062-70-2; **8b**, 126062-71-3; **8e**, 126062-74-6; **9a**, 104178-99-6; **9b**, 54521-25-4; **9e**, 126062-77-9; **10b**, 126062-72-4; **11a**, 104178-07-6; **11b**, 30489-76-0; **11c**, 107600-19-1; **11e**, 126082-42-6; **11f**, 126062-75-7; **12a**, 61134-88-1; **12c**, 126062-73-5; **12f**, 126062-76-8; $MeNHCH_2C_6H_4$-*p*-OMe, 702-24-9; $ClCH_2SiMe_3$, 2344-80-1; $MeN(CH_2SiMe_3)CH_2C_6H_4$-*p*-OMe, 126062-56-4; $Me_2NCH_2SiMe_3$, 18182-40-6; $BrCH_2C_6H_4$-*p*-CO_2Me_3, 108052-76-2; $MeOC_6H_4$-*m*-CH_2Br, 874-98-6; MeC_6H_4-*m*-CH_2Br, 620-13-3; $AcOC_6H_4$-*m*-CH_2Br, 49617-80-3; $BrCH_2C_6H_4$-*m*-CO_2CMe_3, 126062-63-3; $BrCH_2C_6H_4$-*m*-NO_2, 3958-57-4; $BrCH_2C_6H_4$-*p*-NO_2, 100-11-8.

Supplementary Material Available: ^{1}H NMR spectra of **3a** and **8e** (4 pages). Ordering information is given on any current masthead page.

(5) Beard, W. Q.; Van Eenam, D. N., Jr.; Hauser, C. R. *J. Org. Chem.* **1961**, *26*, 2310 (no ^{1}H NMR data were reported).