

Chemical Behaviour of Trimethylammonium *N*-Methylides Substituted with Nitrogen-containing Heteroaromatic Rings. Rearrangement of *N,N*-Dimethyl-(pyridylmethyl)ammonium, *N,N*-Dimethyl-(1-methylpyrrolylmethyl)ammonium and *N,N*-Dimethyl-(1-methylindolylmethyl)ammonium *N*-Methylides

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N,N-Dimethyl(pyridylmethyl)ammonium *N*-methylides **2**, **6**, **11**, *N,N*-dimethyl(1-methylpyrrolylmethyl)ammonium *N*-methylides **15**, **20** and *N,N*-dimethyl(1-methylindolylmethyl)ammonium *N*-methylides **23**, **28** were generated by fluoride ion-induced desilylation of the corresponding (trimethylsilyl)methylammonium salts **1**, **5**, **10**, **14**, **19**, **22** and **27**, and the isomerization products of the ylides were investigated.

Although ammonium ylide intermediates are usually produced by treatment of tetraorganoammonium salts with strong bases (e.g., sodium amide in liquid ammonia), the resulting products are often complex because more than one ylide intermediate is produced under the basic reaction conditions.¹ In the ylide formation by desilylation of [(trimethylsilyl)methyl]ammonium salts with caesium fluoride in aprotic solvents, the products are simple because the ylide-anions locate regioselectively on the carbons with which the silyl groups had linked.^{2,3} However, the rearrangement products of the ylides are not always the same by the two methods. In the desilylation, for example, Sommelet-Hauser rearrangement of benzylammonium *N*-methylides stopped occasionally at the step of [2,3]-sigmatropic rearrangement to give the conjugated triene compounds.^{3d,f,g} We report herein the behaviour of trimethylammonium *N*-methylides substituted with nitrogen-containing heteroaromatic rings under non-basic conditions.

N-(2-Pyridylmethyl)-, *N*-(3-pyridylmethyl)- and *N*-(4-pyridylmethyl)-*N,N*-dimethyl[(trimethylsilyl)methyl]ammonium chlorides **1**, **5**, **10** were prepared by reaction of the corresponding 2-, 3-, or 4-(chloromethyl)pyridine with [(dimethylamino)methyl]trimethylsilane. Reaction of these ammonium chlorides with caesium fluoride at room temperature gave mixtures of the corresponding Sommelet-Hauser rearrangement products **3**, **7**, **8**, **12** and Stevens rearrangement products **4**, **9**, **13** in *N,N*-dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) (Scheme 1, Table 1). The total yields and selectivity of the Sommelet-Hauser products to the Stevens products were higher in HMPA than in DMF. However, completion of the reaction in HMPA required stirring for a long time (5 days) due to low solubility of the chlorides.

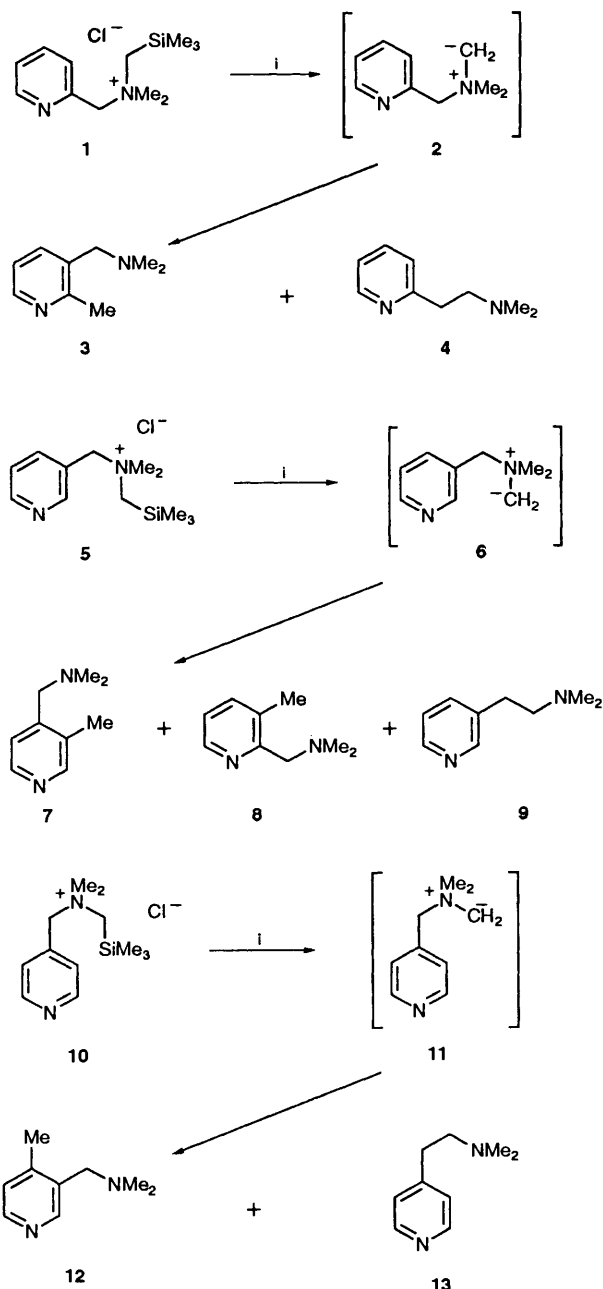
When *N,N*-dimethyl-*N*-[(trimethylsilyl)methyl](1-methylpyrrol-2-ylmethyl)ammonium triflate **14** was similarly treated with caesium fluoride in HMPA (Scheme 2), the product was a mixture of 3-(dimethylamino)methyl-1,2-dimethylpyrrole **16** (Sommelet-Hauser rearrangement product), 2-[2-(dimethylamino)ethyl]-1-methylpyrrole **17** (Stevens rearrangement product), and 1,2-dimethylpyrrole **18** (deamination product) in a ratio of 45:25:30 (total yield, 38%) (Table 2, entry 1). However, a similar treatment of *N,N*-dimethyl-*N*-[(trimethylsilyl)methyl](1-methylpyrrol-3-ylmethyl)ammonium triflate **19** gave only a low yield of 2-(dimethylamino)methyl-1,3-dimethylpyrrole **21** (Sommelet-Hauser product).

Paul and Tchelitcheff⁴ reported the reaction of *N,N,N*-trimethyl(pyrrolylmethyl)ammonium iodides and *N,N,N*-trimethyl(pyridylmethyl)ammonium chlorides with sodium amide in liquid ammonia. They isolated the Sommelet-Hauser products **16**, **21** from the (pyrrolylmethyl)ammonium salts, but various products were isolated from the (pyridylmethyl)ammonium salts: e.g., 2-[1-(dimethylamino)ethyl]pyridine (12%) from *N,N,N*-trimethyl(2-pyridylmethyl)ammonium chloride, 4-(dimethylamino)methyl-3-methylpyridine (22%) from the (3-pyridylmethyl)ammonium analogue, and no product from the (4-pyridylmethyl)ammonium analogue. Although the cause of these differences is still not clear, the formation of plural ylides under basic conditions may bring about the complicated results.

Reaction of *N,N*-dimethyl-*N*-[(trimethylsilyl)methyl](1-methylindol-2-ylmethyl)ammonium triflate **22** with caesium fluoride also gave a mixture of a Sommelet-Hauser rearrangement product **24**, a Stevens product **25**, and a deamination product **26** in a ratio of 18:36:46 (total yield, 76%) (Scheme 3

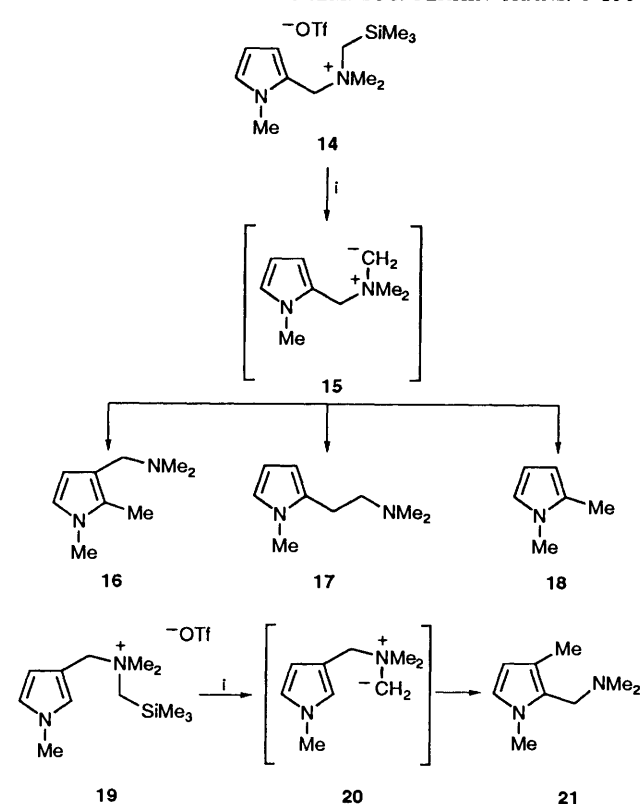
Table 1 Products and conditions for the reaction of *N*-(2-pyridylmethyl)-, *N*-(3-pyridylmethyl)- and *N*-(4-pyridylmethyl)-*N,N*-dimethyl[(trimethylsilyl)methyl]ammonium chlorides **1**, **5**, **10** with CsF at room temperature

Entry	Ammonium Salt	Solvent	Reaction time (d)	Products (ratio)		
				Total yield (%)	Sommelet-Hauser	Stevens
1	1	DMF	2	32	3 (78)	4 (22)
2	1	HMPA	2	49	3 (100)	4 (0)
3	1	HMPA	5	74	3 (100)	4 (0)
4	5	DMF	2	25	7 (58), 8 (40)	9 (2)
5	5	HMPA	2	35	7 (64), 8 (36)	9 (0)
6	5	HMPA	5	52	7 (61), 8 (39)	9 (0)
7	10	DMF	2	62	12 (88)	13 (12)
8	10	HMPA	2	75	12 (100)	13 (0)
9	10	HMPA	5	94	12 (100)	13 (0)



Scheme 1 Reagents and conditions: i, CsF, KI, DMF or HMPA, room temp., 2–5 d

and Table 2). However, treatment of *N,N*-dimethyl-*N*-[(trimethylsilyl)methyl](1-methylindol-3-ylmethyl)ammonium triflate **27** afforded 2-(dimethylamino)methyl-1-methyl-3-methylene-2,3-dihydroindole **29** in high yield.



Scheme 2 Reagents and conditions: i, CsF, HMPA, room temp., 2 d

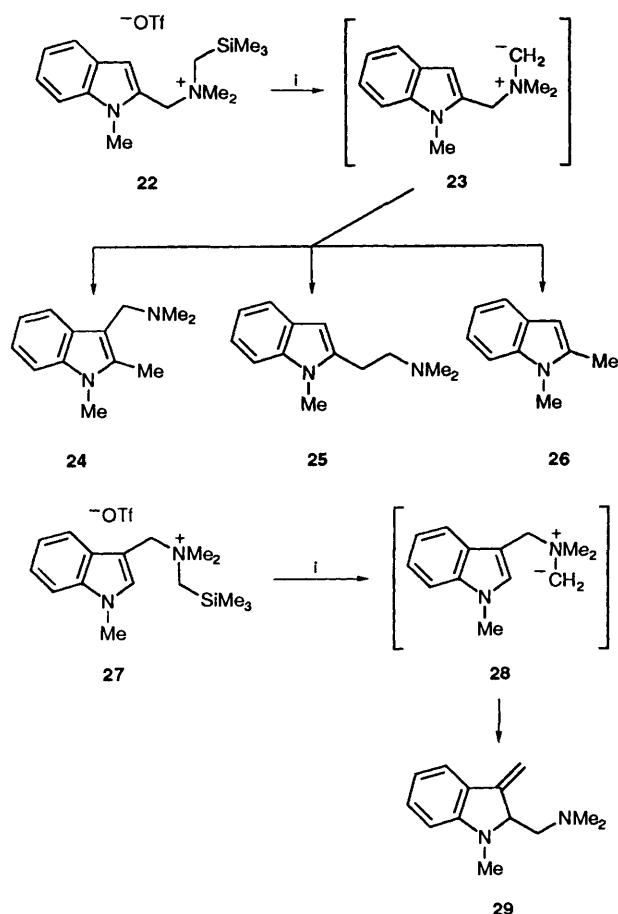
We found previously^{3e,1} that the Stevens products from benzylammonium ylides were not directly formed *via* a [1,2] radical migration pathway as had been stated,^{1,5} but were produced as a result of a [2,3] sigmatropic rearrangement followed by a [1,3] radical migration (Scheme 4). When the reaction was carried out in the presence of DBU, the amounts of the Stevens products decreased and the yields of Sommelet–Hauser products increased.^{3k,1,n,o}

The reaction of compounds **14** or **22** with caesium fluoride in HMPA was repeated in the presence of DBU. The amounts of the Stevens product **17** or **25** and the deamination product **18** or **26** decreased and the Sommelet–Hauser product **16** or **24** increased (compare entries 1 to 2 and 4 to 5 in Table 2). These results support the formation of the Stevens and the deamination products *via* [2,3] sigmatropic rearrangement products of the ylides, although the changes in the product ratios were smaller than we had expected from our previous work.^{3l} The [2,3] sigmatropic rearrangement product **29** from the (indol-3-ylmethyl)ammonium ylide **28** was stable at room temperature and no aromatization to the indole ring was observed in the presence of DBU (entry 7).

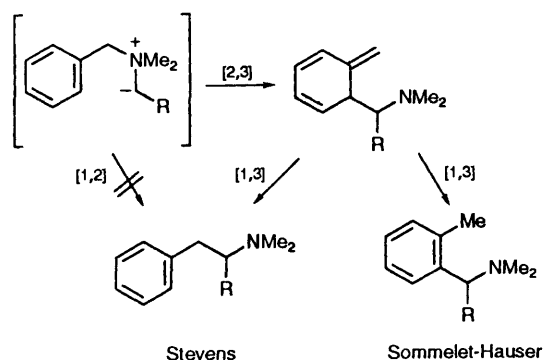
Rearrangement products of *N,N*-dimethyl(2-furylmethyl)-

Table 2 Products and conditions for the reaction of dimethyl[(trimethylsilyl)methyl]pyrrolylmethylammonium triflates **14**, **19** and dimethyl[(trimethylsilyl)methyl]indolylmethylammonium triflates **22**, **27** with CsF in HMPA

Entry	Ammonium salt	Conditions		Products (ratio)			
		Additive (5 mol equiv.)	Time (h)	Total yield (%)	Sommelet–Hauser	Stevens	Deamination
1	14		48	38	16 (45)	17 (25)	18 (30)
2	14	DBU	48	43	16 (61)	17 (21)	18 (18)
3	19		48	9	21 (100)		
4	22		3	76	24 (18)	25 (36)	26 (46)
5	22	DBU	3	83	24 (85)	25 (15)	26 (0)
6	27		3	81	[29 (100)]		
7	27	DBU	3	70	[29 (100)]		



Scheme 3 Reagents and conditions: i, CsF, HMPA, room temp., 3 h

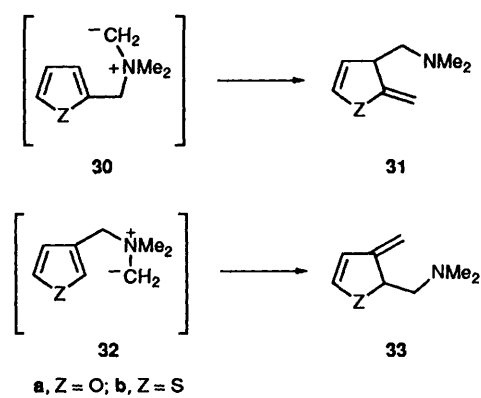


Scheme 4

ammonium *N*-methylide **30a**, *N,N*-dimethyl(3-furylmethyl)-ammonium *N*-methylide **32a**, and their thienylmethyl analogues **30b** and **32b** were 3-(dimethylamino)methyl-2-methylene-2,3-dihydrofuran **31a**, 2-(dimethylamino)methyl-3-methylene-2,3-dihydrofuran **33a**, and their thiophene analogues **31b**, **33b**, and their aromatization to the heterocyclic rings did not quickly occur at room temperature (Scheme 5).^{3m} The stability of **29** may be induced by conjugation of the *exo*-methylene group with the benzene ring. However, it is unclear what is the cause of the difference in chemical behaviour between the (furylmethyl)-ammonium or (thienylmethyl)ammonium ylides and the (pyrrolylmethyl)ammonium ylides.

Experimental

All reactions were carried out in N₂. HMPA was dried by distillation under reduced pressure from sodium prior to use.



Scheme 5

DMF was dried by distillation under reduced pressure from BaO. Dichloromethane was distilled from CaH₂. CsF and KI powder were dried over P₂O₅ at 180 °C under reduced pressure. GLC analyses were performed using a 2 m, 5% PEG-20M on Uniport HP column. Aluminium oxide (Merck, aluminium oxide 90, 70–230 mesh) was used for column chromatography. All m.p.s and b.p.s are uncorrected. *J* Values are given in Hz.

N,N-Dimethyl-*N*-[(trimethylsilyl)methyl](2-pyridylmethyl)-ammonium Chloride **1**.—A solution of 2-(chloromethyl)pyridine (4.13 g, 32.4 mmol) and [(dimethylamino)methyl]trimethylsilane (5.17 g, 39.5 mmol) in acetone (20 cm³) was heated at reflux for 2 h. The solvent was evaporated, and the residue was recrystallized from a mixture of acetonitrile and ether to give the *title salt 1* (6.26 g, 75%), m.p. 151–152 °C (Found: C, 55.9; H, 8.9; N, 10.8. C₁₂H₂₃ClN₂Si requires C, 55.7; H, 9.0; N, 10.8%); ν_{\max} (KBr)/cm⁻¹ 1260 and 850 (C-Si); δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.33 (9 H, s, SiMe₃), 3.42 (6 H, s, NMe₂), 3.45 (2 H, s, CH₂Si), 5.13 (2 H, s, CH₂N), 7.40 (1 H, ddd, *J* 1.0, 4.8, 7.7, 5-H), 7.85 (1 H, td, *J* 1.7, 7.7, 4-H), 8.21 (1 H, d, *J* 7.7, 3-H) and 8.65 (1 H, ddd, *J* 1.0, 1.7, 4.8, 6-H).

N,N-Dimethyl-*N*-[(trimethylsilyl)methyl](3-pyridylmethyl)-ammonium Chloride **5**.—A solution of 3-(chloromethyl)pyridine (4.64 g, 36.4 mmol) and [(dimethylamino)methyl]trimethylsilane (5.54 g, 42.3 mmol) in acetone (20 cm³) was heated at reflux for 1 h. The solvent was evaporated and the residue was recrystallized from acetonitrile–ether to give the *title salt 5* (6.13 g, 65%), m.p. 194–196 °C (Found: C, 55.45; H, 8.7; N, 10.6. C₁₂H₂₃ClN₂Si requires C, 55.7; H, 9.0; N, 10.8%); ν_{\max} (KBr)/cm⁻¹ 1260 and 860 (C-Si); δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.31 (9 H, s, SiMe₃), 3.29 (6 H, s, NMe₂), 3.39 (2 H, s, CH₂Si), 5.53 (2 H, s, CH₂N), 7.44 (1 H, dd, *J* 4.8, 7.9, 5-H), 8.41 (1 H, dt, *J* 1.8, 7.9, 4-H), 8.72 (1 H, br d, *J* 3.7, 6-H) and 8.82 (1 H, br s, 2-H).

N,N-Dimethyl-*N*-[(trimethylsilyl)methyl](4-pyridylmethyl)-ammonium Chloride **10**.—A solution of 4-(chloromethyl)pyridine (3.83 g, 30.0 mmol) and [(dimethylamino)methyl]trimethylsilane (5.17 g, 39.5 mmol) in acetone (20 cm³) was heated at reflux for 2.5 h. The solvent was evaporated, and the residue was recrystallized from acetonitrile–ether to give the *title salt 10* (5.50 g, 71%), m.p. 228–229 °C (Found: C, 55.4; H, 9.0; N, 10.9. C₁₂H₂₃ClN₂Si requires C, 55.7; H, 9.0; N, 10.8%); ν_{\max} (KBr)/cm⁻¹ 1250 and 850 (C-Si); δ_{H} (500 MHz; CDCl₃; Me₄Si) 0.29 (9 H, s, SiMe₃), 3.34 (2 H, s, CH₂Si), 3.40 (6 H, s, NMe₂), 5.36 (2 H, s, CH₂N), 7.75 (2 H, dd, *J* 1.8, 4.3, 3-H and 5-H) and 8.73 (2 H, dd, *J* 1.8, 4.3, 2-H and 6-H).

Reaction of 1 with CsF in DMF.—Ammonium salt **1** (517 mg, 2 mmol) and KI powder (1.10 g, 6.6 mmol) were placed in a 20-

cm³ flask equipped with a magnetic stirrer, a septum, and a test tube which was connected to the flask by a short piece of rubber tubing. CsF (1.52 g, 10 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and was flushed with N₂. DMF (10 cm³) was added to the flask with a syringe and then CsF was added from the test tube. The mixture was stirred for 2 days at room temperature, poured into 2 mol dm⁻³ NaOH (100 cm³), and extracted with ethyl acetate (4 × 50 cm³). The ethyl acetate layer was extracted with 10% HCl, and the acid extract was concentrated under reduced pressure. The residue was mixed with 2 mol dm⁻³ NaOH (80 cm³) and extracted with ether (4 × 50 cm³). The ethereal extract was dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was distilled at 120 °C/21 mmHg (oven temperature of Kugelrohr distillation apparatus) and the distillate (96 mg, 32%) was chromatographed on aluminium oxide with ether as the eluent to give 3-(dimethylamino)methyl-2-methylpyridine **3** and 2-[2-(dimethylamino)ethyl]pyridine⁶ **4**. The product ratio was determined from the integrated values of ¹H NMR of the mixture (see Table 1).

Compound **3**: (Found: C, 72.1; H, 9.5; N, 18.4. C₉H₁₄N₂ requires C, 72.0; H, 9.4; N, 18.65%); ν_{max}(film)/cm⁻¹ 2950, 2780, 1440 and 1030; δ_H(270 MHz; CDCl₃; Me₄Si) 2.24 (6 H, s, NMe₂), 2.58 (3 H, s, CMe), 3.37 (2 H, s, CH₂N), 7.08 (1 H, dd, *J* 4.8, 7.6, 5-H), 7.55 (1 H, dd, *J* 1.7, 7.6, 4-H) and 8.38 (1 H, dd, *J* 1.7, 4.8, 6-H).

Reaction of 1 with CsF in HMPA.—In a manner similar to that described above, CsF (1.52 g, 2.0 mmol) was added to a mixture of the ammonium salt **1** (517 mg, 2.0 mmol) and KI powder (1.10 g, 6.6 mmol) in HMPA (10 cm³). The mixture was stirred for 2 or 5 days at room temperature, poured into 2 mol dm⁻³ NaOH (100 cm³), and extracted with ethyl acetate (4 × 50 cm³). The extract was dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was chromatographed on aluminium oxide column (ether) to give the pyridine **3** (147 mg, 49% or 222 mg, 74%).

Reaction of 5 with CsF in DMF.—In the same way, a mixture of the ammonium salt **5** (517 mg, 2.0 mmol), KI powder (1.10 g, 6.6 mmol) and CsF (1.52 g, 2.0 mmol) in DMF (10 cm³) was stirred for 2 days at room temperature, then worked up. The distillate (74 mg, 25%) at 130 °C/29 mmHg (Kugelrohr) was chromatographed on aluminium oxide (ether) to give 4-(dimethylamino)methyl-3-methylpyridine⁴ **7**, 2-(dimethylamino)methyl-3-methylpyridine⁴ **8** and 3-[2-(dimethylamino)ethyl]pyridine⁶ **9**. The ratio of the products was determined from the integrated values of ¹H NMR of the mixture (Table 1).

Compounds **8**: δ_H(400 MHz; CDCl₃; Me₄Si) 2.28 (6H, s, NMe₂), 2.40 (3 H, s, Me), 3.55 (2 H, s, CH₂), 7.09 (1 H, dd, *J* 4.8, 7.5, 5-H), 7.43 (1 H, d, *J* 7.5, 4-H) and 8.39 (1 H, dd, *J* 1.5, 4.8, 6-H).

Reaction of 5 with CsF in HMPA.—In the same way, a mixture of the ammonium salt **5** (517 mg, 2.0 mmol), KI powder (1.10 g, 6.6 mmol) and CsF (1.52 g, 2.0 mmol) in HMPA (10 cm³) was stirred for 2 or 5 days at room temperature and then worked up to give the pyridines **7** and **8**. The result is shown in Table 1.

Reaction of 10 with CsF in DMF.—In the same way, a mixture of the ammonium salt **10** (517 mg, 2.0 mmol), KI powder (1.10 g, 6.6 mmol) and CsF (1.52 g, 2.0 mmol) in DMF (10 cm³) was stirred for 2 days at room temperature and worked up. The distillate (187 mg, 62%) at 125 °C/24 mmHg (Kugelrohr) was chromatographed on aluminium oxide (ether)

to give 3-(dimethylamino)methyl-4-methylpyridine **12** and 4-[2-(dimethylamino)ethyl]pyridine⁷ **13**.

Compound **12**: (Found: C, 71.8; H, 9.4; N, 18.6. C₉H₁₄N₂ requires C, 72.0; H, 9.4; N, 18.65%); ν_{max}(film)/cm⁻¹ 2950, 2780, 1600, 1460 and 1020; δ_H(270 MHz; CDCl₃; Me₄Si) 2.23 (6 H, s, NMe₂), 2.38 (3 H, s, Me), 3.38 (2 H, s, CH₂), 7.06 (1 H, d, *J* 4.1, 5-H), 8.36 (1 H, s, 2-H) and 8.3 (1 H, d, *J* 4.1, 6-H).

Compound **13**: δ_H(400 MHz; CDCl₃; Me₄Si) 2.31 (6 H, s, NMe₂), 2.56–2.60 (2 H, m, CH₂), 2.77–2.81 (2 H, m, CH₂), 7.14 (2 H, d, *J* 4.4, 3-H and 5-H) and 8.50 (2 H, d, *J* 4.4, 2-H and 6-H).

Reaction of 10 with CsF in HMPA.—In the same way, a mixture of the ammonium salt **10** (517 mg, 2.0 mmol), KI powder (1.10 g, 6.6 mmol) and CsF (1.52 g, 10.0 mmol) in HMPA (10 cm³) was stirred for 2 or 5 days at room temperature and then worked up to give the pyridine **12** (224 mg, 75% or 281 mg, 94%).

N,N-Dimethyl-N-[(trimethylsilyl)methyl](1-methylpyrrol-2-ylmethyl)ammonium Triflate 14.—A solution of 2-(dimethylamino)methyl-1-methylpyrrole⁸ (2.07 g, 15.0 mmol) and (trimethylsilyl)methyl triflate (2.41 g, 10.2 mmol) in dichloromethane (10 cm³) was stirred at room temperature for 0.5 h. The solvent was evaporated and the residue was recrystallized from methanol-ether to give the *title salt* **14** (2.76 g, 73%), m.p. 131–133 °C (Found: C, 41.7; H, 6.6; N, 7.25. C₁₃H₂₅F₃N₂O₃SSi requires C, 41.7; H, 6.7; N, 7.5%); ν_{max}(KBr)/cm⁻¹ 1260 and 840 (C–Si); δ_H(270 MHz; CD₃OD; Me₄Si) 0.30 (9 H, s, SiMe₃), 3.01 (6 H, s, NMe₂), 3.07 (2 H, s, CH₂Si), 3.72 (3 H, s, NMe), 4.52 (2 H, s, CH₂N), 6.18–6.21 (1 H, m, 3-H), 6.45–6.47 (1 H, m, 4-H) and 6.90–6.92 (1 H, m, 5-H).

N,N-Dimethyl-N-[(trimethylsilyl)methyl](1-methylpyrrol-3-ylmethyl)ammonium Triflate 19.—A solution of 3-(dimethylamino)methyl-1-methylpyrrole⁴ (1.52 g, 11.0 mmol) and (trimethylsilyl)methyl triflate (4.11 g, 17.4 mmol) in dichloromethane (15 cm³) was stirred at room temperature for 0.5 h. The solvent was evaporated and the residue was recrystallized from ethyl acetate-hexane to give the *title salt* **19** (3.26 g, 79%), m.p. 72–73 °C (Found: C, 41.7; H, 6.7; N, 7.75. C₁₃H₂₅F₃N₂O₃SSi requires C, 41.7; H, 6.7; N, 7.5%); ν_{max}(KBr)/cm⁻¹ 1260 and 850 (C–Si); δ_H(400 MHz; CDCl₃; Me₄Si) 0.28 (9 H, s, SiMe₃), 3.04 (2 H, s, CH₂Si), 3.06 (6 H, s, NMe₂), 3.67 (3 H, s, NMe), 4.38 (2 H, s, CH₂N), 6.15 (1 H, br s, 4-H), 6.62 (1 H, br s, 5-H) and 6.99 (1 H, br s, 2-H).

Reaction of 14 with CsF.—In a manner similar to that described for the reaction of compound **1** with CsF in DMF, the ammonium salt **14** (748 mg, 2 mmol) and CsF (1.52 g, 10 mmol) were placed in a flask and mixed with HMPA (10 cm³) and toluene (internal standard, 11 mg, 0.12 mmol). The mixture was stirred for 2 days at room temperature, poured into 1% NaHCO₃ (100 cm³), and extracted with ether (4 × 50 cm³). The extract was washed with water (4 × 100 cm³), dried (MgSO₄), filtered, and concentrated under reduced pressure. The distillate [80 °C/17 mmHg (Kugelrohr), 81 mg, 27%] of the residue was chromatographed on aluminium oxide (ether-hexane, 1:1) to yield 3-(dimethylamino)methyl-1,2-dimethylpyrrole⁴ **16** and 2-[2-(dimethylamino)ethyl]-1-methylpyrrole¹⁷ **17**. The ratio was determined from the integrated values of ¹H NMR of the distillate (Table 2). GC-mass analysis (5% PEG-20M, 70 eV) of the reaction mixture showed the presence of another reaction product which was identified as 1,2-dimethylpyrrole⁹ **18** (11%). The yield was determined by comparison with the internal standard.

Compound **17**: (Found: C, 70.9; H, 10.5; N, 18.35. C₉H₁₆N₂ requires C, 71.0; H, 10.6; N, 18.4%); ν_{max}(film)/cm⁻¹ 2950, 2820,

2770, 1490, 1460 and 700; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 2.30 (6 H, s, NMe_2), 2.53–2.57 (2 H, m, $\text{CH}_2\text{CH}_2\text{N}$ or $\text{CH}_2\text{CH}_2\text{N}$), 2.70–2.74 (2 H, m, $\text{CH}_2\text{CH}_2\text{N}$ or $\text{CH}_2\text{CH}_2\text{N}$), 3.55 (3 H, s, NMe), 5.88–5.90 (1 H, m, 3-H), 6.05 (1 H, dd, J 2.7, 3.0, 4-H) and 6.54 (1 H, dd, J 2.0, 2.7, 5-H).

Reaction of 14 with CsF in the presence of DBU.—In the same way, a mixture of the ammonium salt **14** (748 mg, 2 mmol), CsF (1.52 g, 10 mmol), DBU (1.52 g, 10 mmol) and toluene (48 mg, 0.52 mmol) in HMPA (10 cm^3) was similarly treated to give the pyrroles **16**, **17** and **18**. The results are listed in Table 2.

Reaction of 19 with CsF.—To a solution of the ammonium salt **19** (748 mg, 2.0 mmol) in HMPA (10 cm^3) prepared in a manner similar to that described for **14**, was added CsF (1.52 g, 10 mmol). The mixture was stirred for 48 h at room temperature, poured into 1% NaHCO_3 (100 cm^3), and extracted with ether (4 \times 50 cm^3). The extract was washed with water (4 \times 100 cm^3), dried (MgSO_4), filtered, and concentrated under reduced pressure. Distillation at 110 $^\circ\text{C}/45$ mmHg (Kugelrohr) of the residue gave 2-(dimethylamino)-methyl-1,3-dimethylpyrrole⁴ **21** (27 mg, 9%); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 2.05 (3 H, s, CMe), 2.18 (6 H, s, NMe_2), 3.21 (2 H, s, CH_2N), 3.59 (3 H, s, NMe), 5.88 (1 H, d, J 2.6, 4-H) and 6.49 (1 H, d, J 2.6, 5-H).

N,N-Dimethyl-N-[(trimethylsilyl)methyl](1-methylindol-2-ylmethyl)ammonium Triflate 22.—A solution of 1-methylisogramine¹⁰ (1.92 g, 10.2 mmol) and (trimethylsilyl)methyl triflate (3.01 g, 12.8 mmol) in dichloromethane (15 cm^3) was stirred at room temperature for 2 h. The solvent was evaporated and the residue was recrystallized from methanol–ether to give the title compound **22** (3.34 g, 77%), m.p. 141–142 $^\circ\text{C}$ (Found: C, 48.2; H, 6.4; N, 6.5. $\text{C}_{17}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_3\text{SSi}$ requires C, 48.1; H, 6.4; N, 6.6%); ν_{max} (KBr)/ cm^{-1} 1260 and 840 (C–Si); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.27 (9 H, s, SiMe_3), 3.17 (6 H, s, NMe_2), 3.21 (2 H, s, CH_2Si), 3.81 (3 H, s, NMe), 4.92 (2 H, s, CH_2N), 6.82 (1 H, s, 3-H), 7.13–7.32 (3 H, m, 4-H, 5-H, 6-H) and 7.61 (1 H, d, J 8, 7-H).

N,N-Dimethyl-N-[(trimethylsilyl)methyl](1-methylindol-3-ylmethyl)ammonium Triflate 27.—A solution of 1-methylgramine¹¹ (1.60 g, 8.5 mmol) and (trimethylsilyl)methyl triflate (2.51 g, 10.6 mmol) in dichloromethane (15 cm^3) was stirred at room temperature for 1.5 h. The solvent was evaporated and the residue was recrystallized from methanol–ether to give the title compound **27** (3.15 g, 87%), m.p. 141–142 $^\circ\text{C}$ (Found: C, 48.3; H, 6.4; N, 6.5. $\text{C}_{17}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_3\text{SSi}$ requires C, 48.1; H, 6.4; N, 6.6%); ν_{max} (KBr)/ cm^{-1} 1260 and 850 (C–Si); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.26 (9 H, s, SiMe_3), 3.09 (6 H, s, NMe_2), 3.14 (2 H, s, CH_2Si), 3.72 (3 H, s, NMe), 4.76 (2 H, s, CH_2N), 7.19–7.31 (3 H, m, 4-H, 5-H, 6-H), 7.54 (1 H, s, 2-H) and 7.64 (1 H, d, J 7.7, 7-H).

Reaction of 22 with CsF.—In a manner similar to that described for compound **14**, a mixture of the ammonium salt **22** (848 mg, 2 mmol) and CsF (1.52 g, 10 mmol) in HMPA (10 cm^3) was treated for 3 h at room temperature, poured into 1% NaHCO_3 (100 cm^3) and extracted with ether (4 \times 50 cm^3). The ether layer was extracted with 10% HCl (50 cm^3), and the acid layer was made alkaline (pH 11) with NaOH and extracted with ether (3 \times 20 cm^3). The extract was dried (MgSO_4), filtered, and concentrated under reduced pressure. The residue was distilled at 160 $^\circ\text{C}/1.5$ mmHg (Kugelrohr) to give a mixture (174 mg, 43%) of 1,2-dimethyl-3-[(dimethylamino)methyl]indole¹² **24** and 3-(dimethylamino)methyl-1,2-dimethylindole¹³ **25**. The ether layer, after the acid extraction, was dried (MgSO_4), filtered, and concentrated under reduced pressure to give 1,2-

dimethylindole **26** (95 mg, 33%). The ratio of the products was determined from the integrated values of ^1H NMR of the mixture before the acid extraction.

Reaction of 22 with CsF in the presence of DBU.—In the same way, to a solution of the ammonium salt **22** (848 mg, 2 mmol) in HMPA (10 cm^3) was added DBU (1.52 g, 10 mmol) and CsF (1.52 g, 10 mmol), and the mixture was worked up after 3 h stirring at room temperature. The results are shown in Table 2.

Reaction of 27 with CsF.—In the same way, the ammonium salt **27** (727 mg, 1.7 mmol) and CsF (1.52 g, 10 mmol) were treated in HMPA (10 cm^3) for 3 h at room temperature. The mixture was poured into 1% NaHCO_3 and extracted with ether. The extract was dried (MgSO_4), concentrated, and the residue was chromatographed on an aluminium oxide column (hexane) to give 2-(dimethylamino)methyl-1-methyl-3-methylene-2,3-dihydroindole **29** (281 mg, 81%), an undistillable oil (Found: C, 77.25; H, 9.0; N, 13.7. $\text{C}_{13}\text{H}_{18}\text{N}_2$ requires C, 77.2; H, 9.0; N, 13.85%); ν_{max} (film)/ cm^{-1} 1610, 1480, 1020 and 740; λ_{max} (hexane)/nm 230 ($\log \epsilon$ 4.37), 270 ($\log \epsilon$ 4.00) and 360 ($\log \epsilon$ 3.70); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 2.32 (6 H, s, NMe_2), 2.50 (1 H, dd, J 4.6, 12.8, CH_2N), 2.68 (1 H, dd, J 7.0, 12.8, CH_2N), 2.97 (3 H, s, NMe), 4.00–4.04 (1 H, m, 2-H), 5.00 (1 H, d, J 2.7, CCH_2), 5.40 (1 H, d, J 3.3, CCH_2), 6.54 (1 H, d, J 7.9, 4-H), 6.66 (1 H, ddd, J 0.9, 7.3, 7.5, 6-H), 7.15 (1 H, ddd, J 0.7, 7.3, 7.9, 5-H) and 7.31 (1 H, dd, J 0.7, 7.5, 7-H).

Reaction of 27 with CsF in the presence of DBU.—To a solution of the ammonium salt **27** (848 mg, 2 mmol) in HMPA (10 cm^3) was added DBU (1.52 g, 10 mmol) and CsF (1.52 g, 10 mmol), and the mixture was treated in the manner described above to give **29** (283 mg, 70%).

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