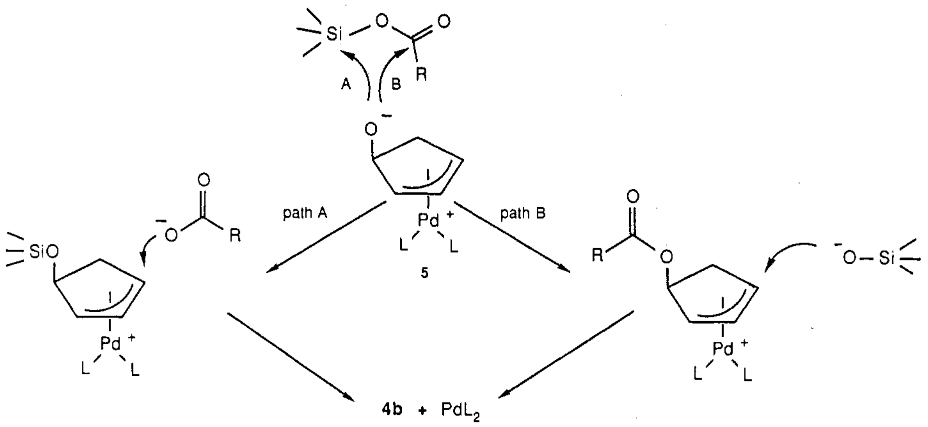
Scheme II



methylsiloxy)nitrobenzene were purchased from Petrarch Systems, Inc. and distilled prior to use. Cyclopentadiene monoepoxide[9] and trimethylsilyl benzoate[10] were prepared according to literature procedures. Tetrakis(triphenylphosphine)palladium was purchased from Aldrich and used without further purification. All reactions were carried out under anhydrous conditions with an inert blanket of nitrogen or argon.

General Procedure for the Preparation of Differentially Protected *cis*-2-Cyclopentene-1,4-diols. To a stirred, ice-cooled solution of trimethylsilyl acetate (463 mg, 3.50 mmol) and tetrakis(triphenylphosphine)palladium(0) (33 mg, 0.029 mmol, 0.95 mol %) in 3 mL of dry tetrahydrofuran was added dropwise over 10 min 250 mg (3.05 mmol) of cyclopentadiene monoepoxide. When addition was complete, the ice bath was removed, and the reaction progress was monitored via TLC (SiO_2, 4:1 hexane–ethyl acetate, R_f 0.53). Complete consumption of starting material generally takes less than 15 min. The reaction was terminated by passing the yellowish solution through a plug of SiO_2 (4.5 g) with absolute ether. The filtrate was carefully concentrated under aspirator pressure, and the residue was chromatographed over SiO_2 (28 g) with pentane–ether (9:1) as the eluent. Removal of the solvent afforded 0.539 (83%) of trimethylsilyl acetate **6a** as a clear, colorless oil: ^1H NMR (60 MHz) δ 0.0 (s, 9 H, Me_3Si), 1.61 (dt, J = 5 and 14 Hz, 1 H, β-CH_2), 2.03 (s, 3 H, Ac), 2.79 (overlapping dt, J = 7 and 14 Hz, 1 H, α-CH_2), 4.54–4.84 (m, 1 H, CHOSi), 5.31–5.61 (m, 1 H, CHOAc), 5.95 (br s, 2 H, CH=CH); IR (neat) 2970, 1735 (CO), 1373, 1250 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3Si$: C, 56.02; H, 8.47. Found: C, 56.01; H, 8.59.

Silyl ethers **6b–f** were prepared under essentially the same conditions.

Triethylsilyl acetate 6b: oil; 62% yield; R_f 0.64 (4:1 hexane–ethyl acetate); ^1H NMR (200 MHz) δ 0.60 (q, 6 H, CH_2Si), 0.94 (t, 9 H, CH_3CSi), 1.60 (dt, J = 4.9 and 13.9 Hz, 1 H, β-CH_2), 2.03 (s, 3 H, Ac), 2.78 (overlapping dt, J = 7.3 and 13.9 Hz, 1 H, α-CH_2), 4.67 (m, 1 H, CHOSi), 5.45 (m, 1 H, CHOAc), 5.87 (m, 1 H, CH=CH), 5.96 (m, 1 H, CH=CH); IR (neat) 2960, 1735, (CO), 1370, 1240 cm^{-1}; MS, m/z (relative intensity) 197 (1), 145 (100), 103 (26); HRMS calcd for $C_{13}H_{24}O_3Si$ (M^+) 256.1495, found 256.1500.

Dimethylphenylsilyl acetate 6c: oil; 65% yield; R_f 0.51 (4:1 hexane–ethyl acetate); ^1H NMR (60 MHz) δ 0.0 (br s, 6 H, Me_2Si), 1.65 (dt, J = 4.2 and 14 Hz, 1 H, β-CH_2), 2.04 (s, 3 H, Ac), 2.72 (overlapping dt, J = 7 and 14 Hz, 1 H, α-CH_2), 4.52–4.82 (m, 1 H, CHOSi), 5.27–5.57 (m, 1 H, CHOAc), 5.91 (br s, 2 H, CH=CH), 7.25–7.75 (m, 5 H, Ph); IR (neat) 1735 (CO), 1370, 1245 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_3Si$: C, 65.16; H, 7.30. Found: C, 65.11; H, 7.35.

Trimethylsilyl benzoate 6d: oil; 76% yield; R_f 0.64 (4:1 hexane–ethyl acetate); ^1H NMR (60 MHz) δ 0.0 (s, 9 H, Me_3Si), 1.64 (dt, J = 5 and 14 Hz, 1 H, α-CH_2), 2.74 (overlapping dt, J = 7 and 14 Hz, 1 H, β-CH_2), 4.43–4.83 (m, 1 H, CHOSi), 5.40–5.79 (m, 1 H, CHOBz), 5.81 (br s, 2 H, CH=CH), 7.08–7.56 (m, 3 H, Ar), and 7.73–8.05 (m, 2 H, Ar); IR (neat) 3160, 1815 (CO), 1375, 1205 cm^{-1}; MS, m/z (relative intensity) 276 (M^+, 0.71), 179 (28), 154 (48), 122 (7), 105 (100); HRMS calcd for $C_{15}H_{20}O_3Si$ (M^+) 276.1182, found 276.1180.

Trimethylsilyl phenyl ether 6e: oil; 23% yield; R_f 0.70 (4:1 hexane–ethyl acetate); ^1H NMR (200 MHz) δ 0.01 (s, 9 H, Me_3Si), 1.79 (dt, J = 5.0 and 13.7 Hz, 1 H β-CH_2), 2.86 (overlapping dt, J = 7.1 and 13.7 Hz, 1 H, α-CH_2), 4.74 (m, 1 H, CHOSi), 5.11 (m, 1 H, CHOPh), 6.15 (br s, 2 H, CH=CH), 6.93 (m, 3 H, Ar), 7.29 (m, 2 H, Ar); IR (neat) 2960, 1600, 1495, 1375 cm^{-1}; MS, m/z (relative intensity) 176 ($M^+ - Me_3Si$, 4), 95 (7), 94 (100), 82 (13); HRMS calcd for $C_{11}H_{12}O_2$ ($M^+ - Me_3Si$) 176.0832, found 176.0844.

Trimethylsilyl *p*-nitrophenyl ether 6f: oil; 87% yield; R_f 0.51 (4:1 hexane–ethyl acetate); ^1H NMR (200 MHz) δ 0.12 (br s, 9 H, Me_3Si), 1.79 (dt, J = 4.6 and 13.9 Hz, 1 H, β-CH_2), 2.91 (overlapping dt, J = 7.2 and 13.9 Hz, 1 H, α-CH_2), 4.78 (m, 1 H, CHOSi), 5.18 (m, 1 H, CHOAr), 6.06 (m, 2 H, CH=CH), 6.95 (m, 2 H, Ar), 8.16 (m, 2 H, Ar); IR (neat) 1514 (NO_2), 1374, 1343 (NO_2), 1255 cm^{-1}; MS, m/z (relative intensity) 293 (M^+, 0.1), 278 (4), 196 (12), 155 (81), 73 (100); HRMS calcd for $C_{14}H_{19}NO_4Si$ (M^+) 293.1083, found 293.1075.

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Registry No. 1, 7129-41-1; **3a**, 2754-27-0; **3b**, 5290-29-9; **3c**, 17887-60-4; **3d**, 2078-12-8; **3e**, 1529-17-5; **3f**, 1014-66-0; **6a**, 111001-25-3; **6b**, 111001-26-4; **6c**, 110874-60-7; **6d**, 110874-61-8; **6e**, 110874-62-9; **6f**, 110874-63-0; $Pd(PPh_3)_4$, 14221-01-3.

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Dual Resonance Functionality in Pyridine 1-Oxides. A Double Multinuclear NMR Approach

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Pyridine 1-oxides have a characteristic N–O functionality that can act as both a π-electron donor and a π-

Table I. ^{15}N and ^{17}O NMR Substituent Chemical Shifts (ppm) of 3- and 4-Substituted Pyridine 1-Oxides (PYNO) in DMSO

subst	^{15}N SCS PYNO	^{17}O SCS[a,b] PYNO	^{13}C SCS[c] MSB
4-NO_2	13.3	65	6.95
4-CN	9.2	52	5.01
4-COOMe	9.4	40	4.94
4-COMe	8.7	39	4.83
4-COPh	8.1	36	4.36
4-Cl	−2.5	6	−1.30
4-Ph	−2.4	2	−0.88
4-Me	−6.6	−13	−3.01
4-MeO	−18.0	−33	−7.85
4-NHAc	−14.0	(−38)	−5.31
4-NH_2	−34.6	−58	−12.55
H	0.0[d]	0	0.00
3-CN	2.0	19	1.19
3-COOMe	0.8	9	0.42
3-COMe	0.3	7	0.21
3-F	3.9	17	2.08
3-Cl	3.8	15	1.98
3,5-Cl_2	5.6	29	
3-Br	4.0	14	2.34
3-Ph	0.9	3	0.64
3-Me	0.0	−3	−0.11
3,5-Me_2	−0.7	−8	
3-OH	−0.1	−6	1.08
3-MeO	2.0	4	1.17
3-NHAc	−0.5	(3)	0.36
3-NH_2	−1.5	−12	0.50

[a] Reference 12a,b. [b] Numbers slightly different from those in the literature come from averaging more measurements. [c] MSB: monosubstituted benzene; reference 14e. [d] Absolute resonance frequency = 36.502 982 MHz.

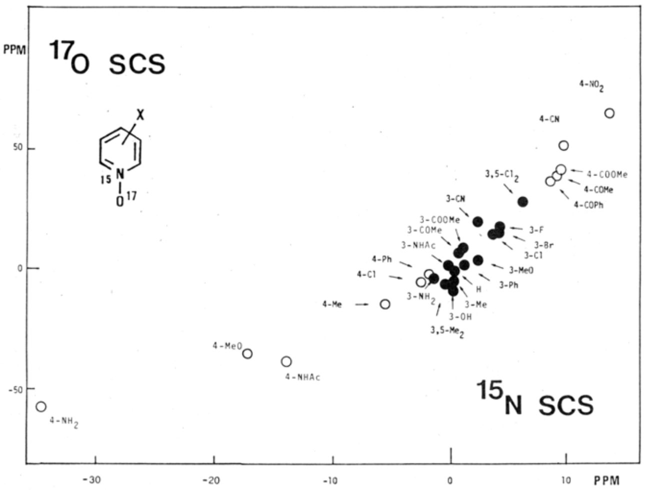

Figure 1. A plot of ^{17}O SCS against ^{15}N SCS of 3- and 4-substituted pyridine 1-oxides in DMSO.

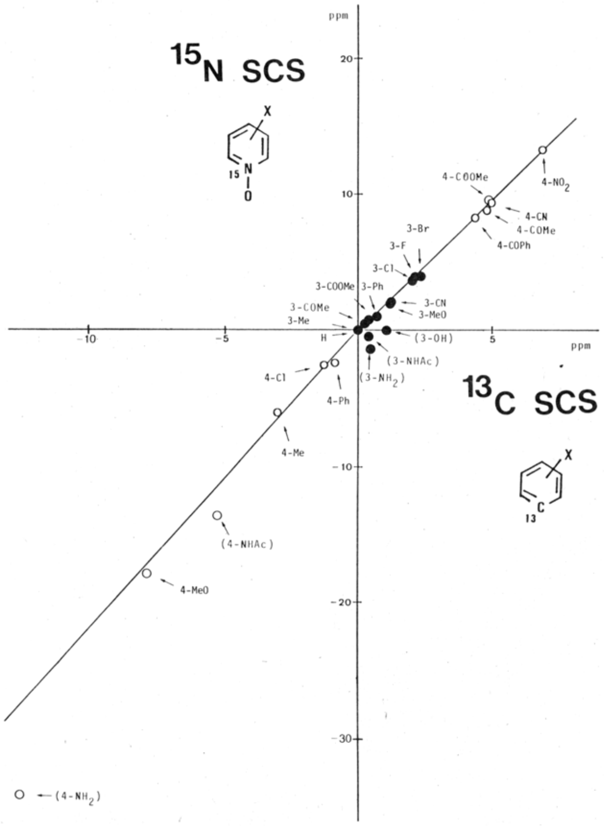

Figure 2. A plot of ^{15}N SCS of substituted pyridine 1-oxides against ^{13}C SCS of monosubstituted benzenes in DMSO.

electron acceptor.[2–7] However, there are few compounds of this class for which this dual functionality has been described by an LFER equation.[8–10] The scarcity of such quantitative expressions may be due to lack of adequate data or to limitations of conventional LFER treatments.

We have measured ^{15}N NMR spectra of several 3- and 4-substituted pyridine 1-oxides at natural abundance in DMSO. The ^{15}N substituent chemical shifts (SCS) were compared with previously measured ^{17}O SCS[11,12] as pair sets to determine whether the dual resonance functionality could be detected at the ring nitrogen and the side-chain oxygen with internal consistency. This technique may be called a double multinuclear NMR approach to studying resonance effects in a heteroaromatic system.[13] The LFER analysis was carried out by an advanced Yukawa–Tsuno equation (LSFE)[14] and by a Taft equation (DSP).[15]

The ^{15}N and ^{17}O NMR SCS for the substituted pyridine 1-oxides are summarized in Table I together with ^{13}C NMR SCS for the corresponding substituted benzenes.[14e] Although some ^{15}N SCS data for substituted pyridine 1-oxides have been reported, the measurement conditions

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Table II. LSFE Results for ^{15}N SCS and ^{17}O SCS of Pyridine 1-Oxides[a]

$$\mathrm{SCS} = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^-$$

set	ρ_i	ρ_π^+	ρ_π^-	ρ_π^+/ρ_π^-	note
^{15}N SCS (4-subst)	5	50	37	1.4	*b*
^{15}N SCS (3-subst)	(8)	(−3)	(−3)		*b*
^{17}O SCS (4-subst)	57	150	110	1.4	*c*
^{17}O SCS (3-subst)	48				*d*

[a] Linear substituent free energy (LSFE) equation. σ_i is the inductive substituent constant. σ_π^+ or σ_π^- is the substituent constants measuring the capability of substituents to donate or withdraw electrons through π-electronic delocalization, respectively, independent of substituent position and π-electronic framework in a given system. The numerical values are defined as follows: $\sigma_i = 0.74\sigma_I$, $\sigma_\pi^+ = 0.42\Delta\bar{\sigma}_R^+$, $\sigma_\pi^- = 0.73\Delta\bar{\sigma}_R^-$, $\sigma^\circ = \sigma_i + \sigma_\pi^+ + \sigma_\pi^-$. Linear aromatic substituent reactivity (LArSR) equation is a generalized Yukawa–Tsuno equation: $\log (k/k_o)$ or $P - P_o = \rho(\sigma^\circ + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-)$, where $\Delta\bar{\sigma}_R^+ = \sigma^+ - \sigma^\circ$ and $\Delta\bar{\sigma}_R^- = \sigma^- - \sigma^\circ$. [b] Derived from the bilinear relation in Figure 2.[14e,21] [c] Interconverted from the LArSR result.[22] [d] Derived from the σ_I treatment.[22]

were slightly different from ours.[16,17] Both ^{15}N and ^{17}O SCS are shifted downfield by acceptor substituents,[18] but the nonlinear relationship of the two shifts (Figure 1) suggests that the nitrogen and the oxygen are not affected to the same degree by the substituents.

On the other hand, there is a linear relationship between the ^{15}N SCS in pyridine 1-oxides and the ^{13}C SCS for the corresponding substituted benzenes (Figure 2). Only hydrogen-bonding substituents such as OH, NH_2, and NHAc fall off the straight-line plot, probably because of solute–solute interactions at the relatively high concentration (10–20 w/v %) in our sample solutions. The bilinear relationship for electron-attracting substituents (Figure 2, upper right-hand quadrant) can be expressed as

$$(^{15}\mathrm{N\ SCS}) = 1.90(^{13}\mathrm{C\ SCS}) - 0.16$$

$$r = 0.9990,\ s = \pm 0.19,\ n = 14$$

and that for electron-donating substituents (Figure 2, lower left-hand quadrant) as

$$(^{15}\mathrm{N\ SCS}) = 2.30(^{13}\mathrm{C\ SCS}) + 0.12$$

$$r = 0.9988,\ s = \pm 0.34,\ n = 6$$

This bilinearity, separated by the unsubstituted derivatives, is consistent with the relationship between ^{13}C SCS of monosubstituted benzenes and the corresponding 1,4-disubstituted benzenes.[19] The two slopes of 1.9 and 2.3 indicate that the ^{15}N SCS is about twice as sensitive as the ^{13}C SCS to a given substituent. Electron-donating substituents exert slightly more influence on the SCS (2.30/1.90 = 1.21) than do electron-accepting substituents. A similar ratio, 3.07 (n = 5)/2.49 (n = 4) = 1.23, has been observed in the plot on the ^{15}N SCS of the present 4-substituted pyridine 1-oxides against ^{13}C (C-1 position) SCS of the corresponding anisoles.[20]

We used an indirect LSFE analysis because of the limited number of well-behaved substituents studied.[14] By combining the reported LSFE results on ^{13}C SCS of monosubstituted benzenes[14e,21] with our present bilinear results, we derived the LSFE parameters for the ^{15}N SCS of pyridine 1-oxides (Table II). In addition, the LSFE ones for the ^{17}O SCS of pyridine 1-oxides were derived from our LArSR results.[14,22]

It is apparent that the ^{15}N SCS of 4-substituted pyridine 1-oxides are controlled mainly by π-electronic effects and negligibly by inductive effects. This finding is in contrast to the ^{17}O SCS, which are governed by both effects. Moreover, despite the different contributions of the inductive effect to ^{15}N and ^{17}O SCS, the ratio of the π-electronic effects of electron-attracting and electron-donating substituents (ρ_π^+/ρ_π^-) is constant for the 4-substituted pyridine 1-oxides.

It appears that the LSFE treatment can describe the dual functionality of the N–O bond in 4-substituted pyridine 1-oxides in terms of electron-donating and electron-accepting π-electronic contributions. The internal consistency of the ratio of the π-electronic effects (ρ_π^+/ρ_π^-), which has been first detected in the ^{15}N and ^{17}O SCS by using LSFE treatment, is taken as evidence for justification of the dual functionality of pyridine 1-oxides and then for rationalization of the LSFE treatment. The alternative DSP treatment is not satisfactory, probably because of oversimplifications.[23] The narrow range of the ^{15}N SCS for the 3-substituted pyridine 1-oxides does not permit meaningful conclusions.

Experimental Section

Most 3- and 4-substituted pyridine 1-oxides were prepared from the respective pyridines by oxidation in acetic acid.[24] The prepared and commercial pyridine 1-oxides were purified by recrystallization from appropriate solvents or distillation under reduced pressure. Melting points of 3- or 4-substituted (X) pyridine 1-oxides utilized were as follows [X, mp (°C) or bp (°C/mmHg)]: 4-NO_2, 162–163;[2,25] 4-CN, 221–223;[25] 4-COOMe, 115–117;[26] 4-COMe, 130–133;[27] 4-COC_6H_5, 125–126; 4-Cl, 166–170 dec;[2,25] 4-C_6H_5, 155–156;[28] 4-Me, 183–184;[25] 4-MeO, 82–83;[2,25,29] 4-NHAc, 265–268;[25,30] 4-NH_2, 221–223;[29] H, ca. 45 (hygroscopic);[2,25] 3-CN, 174–175;[25,31] 3-COOMe, ca. 85 (hygroscopic);[32] 3-COMe, 146–148;[33] 3-F, 100–102/5 (64–65);[25] 3-Cl, 120/3;[31,34] 3,5-Cl_2, 105–108;[35,36] 3-Br, 141–144/5;[34] 3-C_6H_5, 113–115;[28] 3-Me, 107/2;[31]

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(21) Derived from (1) $^{13}\mathrm{C}$(4-subst) SCS = $2.41\sigma_i + 21.68\sigma_\pi^+ + 19.37\sigma_\pi^- - 0.90$ (r = 0.992, s = ±0.81, n = 24) and (2) $^{13}\mathrm{C}$(3-subst) = $4.00\sigma_i - 1.41\sigma_\pi^+ - 1.41\sigma_\pi^- - 0.03$ (r = 0.92, s = ±0.31, n = 24).[14e]

(22) Derived from (1) $^{17}\mathrm{O}$(4-subst) SCS = $57.2(\sigma^\circ + 0.69\Delta\bar{\sigma}_R^+ + 0.64\Delta\bar{\sigma}_R^-)$ (r = 0.9926, s = ±3.8, n = 10) and (2) $^{17}\mathrm{O}$(3-subst) SCS = $35.2\sigma_I - 2.3$ (r = 0.9797, s = ±2.1, n = 12). The four equations ($\sigma^\circ = \sigma_i + \sigma_\pi^+ + \sigma_\pi^-$; $\sigma_i = 0.74\sigma_I$; $\sigma_\pi^+ = 0.415\Delta\bar{\sigma}_R^+$; $\sigma_\pi^- = 0.73\Delta\bar{\sigma}_R^-$)[14] are employed for the interconversion.

(23) $^{15}\mathrm{N}$(4-subst) SCS = $12.6\sigma_I + 34.5\sigma_R(\mathrm{BA}) - 0.6$ (r = 0.9922, s = ±1.2, n = 9). $^{15}\mathrm{N}$(3-subst) SCS = $5.8\sigma_I - 3.9\sigma_R^\circ - 0.3$ (r = 0.920, s = ±0.6, n = 10). $^{17}\mathrm{O}$(4-subst) SCS = $65\sigma_I + 117\sigma_R^\circ + 3$ (r = 0.9959, s = ±0.30, n = 9). $^{17}\mathrm{O}$(3-subst) SCS = $35\sigma_I + 3\sigma_R^\circ - 1.4$ (r = 0.975, s = ±1.7, n = 10). The substituent parameters are taken from ref 15a.

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3,5-Me_2, bulb-to-bulb distillation;[37] 3-OH, 190–191; 3-MeO, 100–102;[25] 3-NHAc, 209–214;[8a,25,30,38] 3-NH_2, 120–121.[38,39]

The ^{15}N INEPT measurements[40,41] were made on a Bruker AM360 NMR spectrometer at 36.50 MHz at ambient temperature with a 10 mm i.d. tube for solutions of ca. 10–20 w/v % in a mixture of DMSO (2.5 mL) and DMSO-d_6 (0.5 mL for internal deuterium lock). ^{15}N SCS values were calculated from absolute frequencies. Typical experimental conditions were 31-μs pulse width (90° flip angle), acquisition time of 0.56 s, spectral width of 14.7 kHz, 16K data points, and $\Delta_t = 0.25/(J_{NH}) = 0.050$ s. Digital resolution was 0.05 ppm (1.8 Hz), and reproducibility was ±0.1 ppm.

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Registry No. ^{15}N, 14390-96-6; ^{17}O, 13968-48-4; 4-NO_2-PYNO, 1124-33-0; 4-CN-PYNO, 14906-59-3; 4-CO_2Me-PYNO, 3783-38-8; 4-Ac-PYNO, 2402-96-2; 4-PHCO-PYNO, 14178-29-1; 4-Cl-PYNO, 1121-76-2; 4-Ph-PYNO, 1131-61-9; 4-Me-PYNO, 1003-67-4; 4-OMe-PYNO, 1122-96-9; 4-AcNH-PYNO, 14906-56-0; 4-NH_2-PYNO, 3535-75-9; PYNO, 694-59-7; 3-CN-PYNO, 14906-64-0; 3-CO_2Me-PYNO, 15905-18-7; 3-Ac-PYNO, 14188-94-4; 3-F-PYNO, 695-37-4; 3-Cl-PYNO, 1851-22-5; 3,5-Cl_2-PYNO, 15177-57-8; 3-Br-PYNO, 2402-97-3; 3-Ph-PYNO, 1131-48-2; 3-Me-PYNO, 1003-73-2; 3,5-Me_2-PYNO, 3718-65-8; 3-OH-PYNO, 6602-28-4; 3-OMe-PYNO, 14906-61-7; 3-AcNH-PYNO, 15010-23-8; 3-NH_2-PYNO, 1657-32-5.

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Ylide Rearrangement of Benzyltrialkylammonium Salts: The Improved Sommelet–Hauser Rearrangement. 2

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When a tetraalkylammonium salt is treated with a base, a hydrogen atom α to the nitrogen atom is removed to give an ammonium ylide intermediate.[1] Since an alkylbenzyldimethylammonium salt contains different kinds of α-hydrogen atoms, different ylides may be formed simultaneously, and they are isomerized to the tertiary amines via the Sommelet–Hauser rearrangement and/or the Stevens rearrangement, respectively. If the salt contains a β-hydrogen to the nitrogen, elimination of the alkyl group is usually important (Hofmann elimination). Thus the base-promoted reaction of alkylbenzyldimethylammonium salts leads to usually complex mixtures of tertiary amines.[2]

Table I. Benzyldialkyl[(trimethylsilyl)methyl]ammonium Halides 3

entry		R^1	R^2	X^-	condition temp[c]/time, h	% yield from 1
1	**a**	Me	Et	I	reflux/18	94
2	**b**	*i*-Pr	Me	I	rt/20	62
3	**c**	*t*-Bu	Me	I	rt/90[a]	78
4	**d**	c-Hx	Me	I	rt/20	74
5	**e**	Et	Et	I	reflux/44	62
6	**f**	$(CH_2)_4$		Br	reflux/2	87[b]
7	**g**	$(CH_2)_5$		Br	reflux/2	95[b]

[a] *N,N*-Dimethylformamide was used as the solvent. [b] Yield from 2. [c] rt = room temperature.

Table II. Reaction of Benzyldialkyl[(trimethylsilyl)methyl]ammonium Halides 3 with Cesium Fluoride

entry		reactn time, h	bp,[a] °C (mmHg)	products 5 and 6 yield,[b] %	products 5 and 6 ratio[c] 5/6	ref of 5
1	**a**	23	155 (160)	86	97:3	2, 8
2	**b**	27	165 (110)	86	93:7	2, 8
3	**c**	24	140 (120)	83	*d*	2
4	**d**	27	190 (40)	88	89:11	2
5	**e**	24	100 (140)	82	91:9	9
6	**f**	43	165 (65)	69	98:2	10
7	**g**	43	180 (90)	74	97:3	11

[a] Oven temperature of a Buchi Kugelrohr distillation apparatus. [b] Total yield of **5** and **6**. [c] The ratio was determined by GLC analysis (10% PEG 20M). [d] **5c**/**7**/**8** = 65:33:2.

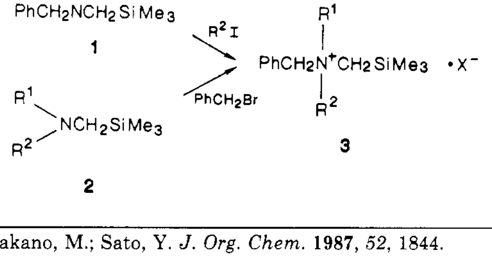
Table III. *N*-Alkyl-*N*-[(trimethylsilyl)methyl]benzylamine 1[a]

	bp °C (mmHg)	^1H NMR ($CDCl_3$), δ $SiCH_3$	$SiCH_2N$	NCH_2Ph
1a	111–114 (16)[b]			
1b	140 (20)[c]	0.00	1.86	3.44
1c	140 (25)[c]	−0.11	2.08	3.64
1d	180–195 (20)[c]	0.00	1.97	3.44
1e	79–83 (1.5)	0.00	1.89	3.44

[a] Satisfactory analytical data or high-resolution mass spectra were submitted for reviews. [b] Reference 5; bp 132–134 °C (14 mmHg). [c] Oven temperature of a Buchi Kugelrohr distillation apparatus.

Previously we reported that fluoride anion induced desilylation of substituted benzyldimethyl[(trimethylsilyl)methyl]ammonium halides gives the methyl ylide intermediates exclusively, and leads to high yields of the Sommelet–Hauser rearrangement products, *N,N*-dimethyl-2-methylbenzylamines.[3] This paper describes the desilylation reaction of benzyldialkyl[(trimethylsilyl)methyl]ammonium salts having hydrogens β to the nitrogen.

Seven benzyldialkyl[(trimethylsilyl)methyl]ammonium halides (**3**) were synthesized by quaternization of *N*-alkyl-*N*-[(trimethylsilyl)methyl]benzylamines (**1**) or *N,N*-dialkyl[(trimethylsilyl)methyl]amines (**2**) with alkyl halides (Tables I and III).



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