

Application of ^{13}C NMR Spectroscopy and ^{13}C -Labeled Benzylammonium Salts to the Study of Rearrangements of Ammonium Benzylides

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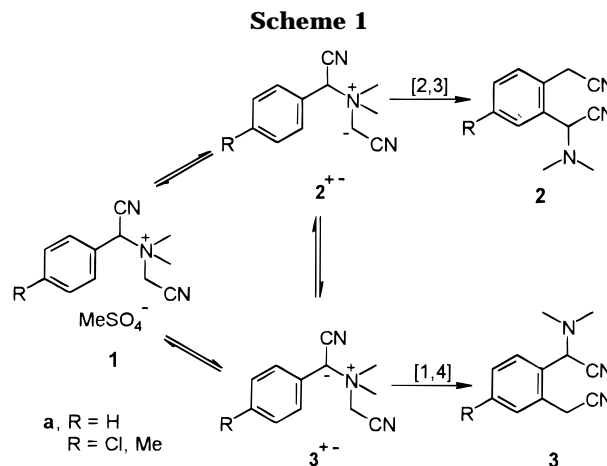
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Ylides generated from *N*-(cyanomethyl)-*N,N*-dimethyl-*N*-[α -(trimethylsilyl)benzyl]ammonium chloride (**4**) and fluoride anion afford the products of [1,2] shift **11** and [2,3] shift **13**. Formation of product **13** shows that, in the presence of water from TBAF, rearrangements and [1,3]H shift in ylide intermediates become competitive processes. The reaction of *N*-benzyl-*N,N*-dimethyl-*N*-[α -(trimethylsilyl)benzyl]ammonium bromide (**5**) and ^{13}C labeled (at the benzyl carbon) salt **5*** gave a mixture of **10**, **14**, and **15** as products of [1,4], [1,2], and [2,3] rearrangement, respectively. ^{13}C NMR spectra of products derived from salt **5*** exclude [1,3]H shift in ylide **9a⁺⁻**. Rearrangement of ylides generated from *N*-benzyl-*N,N*-dimethyl-*N*-[(dimethylphenylsilyl)methyl]ammonium bromide (**6***) (enriched in ^{13}C at benzyl carbon) and *n*-BuLi reveals that *N,N*-dimethyl-2-[(dimethylphenylsilyl)methyl]benzylamine (**20***) is not formed by a [1,4] shift but instead, via a [2,3] shift in silylmethylide followed by subsequent [1,4]Si and [1,2]H shift, as previously suggested in the literature. This mechanism is unique to some silyl-substituted ylides.

Recently, we have shown that ylides **2⁺⁻** and **3⁺⁻**, generated from benzylammonium salts **1** by means of suitable base-solvent systems, yield a mixture of products **2** and **3** via [2,3] (Sommelet–Hauser) and the hitherto unknown [1,4] (“reverse” Sommelet–Hauser) rearrangement, respectively (Scheme 1).¹

The use of salt **1a** enriched in ^{13}C at the benzyl cyano group allowed us to confirm this mechanism.² However, the salts **1** and some structurally related thienyl analogues are so far the only examples of ammonium salts that generate arylides prone to [1,4] shift.^{1–4} To collect more information on this rearrangement, we investigated ylides generated from silyl-substituted salts **4–6** and fluoride anion or *n*-BuLi and applied ^{13}C NMR technique and labeled benzylammonium salts. This method, already shortly described by us,² which allows us to distinguish the paths of rearrangements of ylides, is now developed and detailed. Regioselective generation of ylides via desilylation of ammonium salts by means of fluoride anion has been extensively studied.⁵



Results and Discussion

Rearrangements of Ylides Generated via Desilylation of Ammonium Salts. On the basis of the reactivity of ylide **3⁺⁻** (Scheme 1) benzylides **7⁺⁻** and **9⁺⁻**, regioselectively generated from the salts **4** and **5** by means of fluoride anion (tetra-*n*-butylammonium fluoride, TBAF, or cesium fluoride) in aprotic dipolar solvents, were expected to undergo [1,4] rearrangement to afford products **8** and **10**, respectively (Schemes 2 and 3).

Commercial hydrated TBAF is not suitable for desilylation of ammonium salts because it favors equilibration of the ylides formed.^{5,6} Furthermore, due to solvation of the fluoride anion by water, TBAF·3H₂O did not desilylate salt **5** effectively. Dehydration of molten TBAF·3H₂O in vacuo usually causes partial decomposition of this

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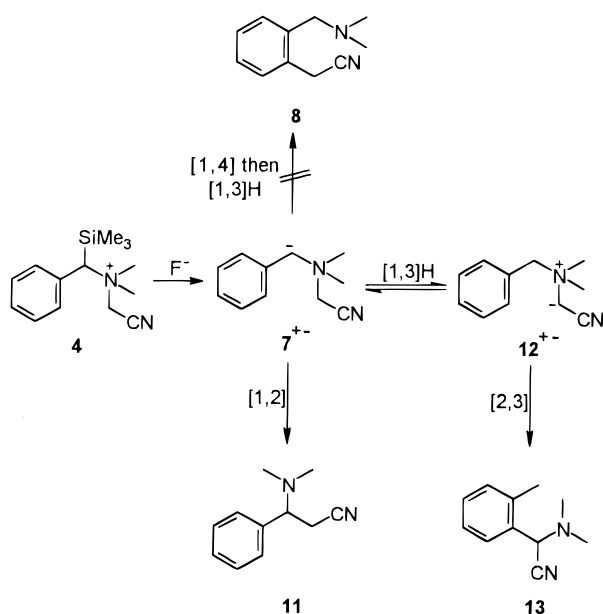
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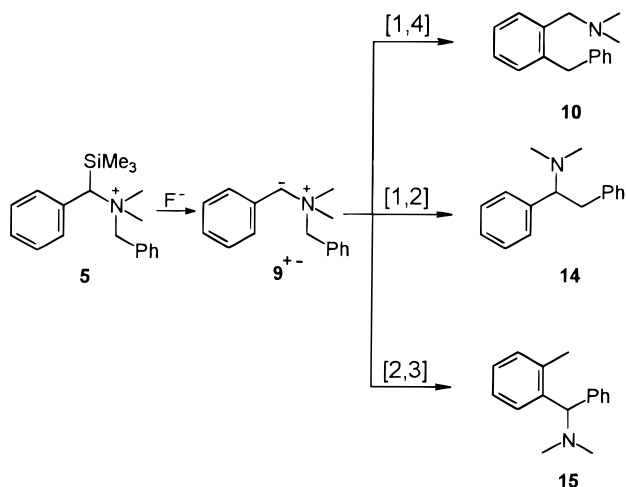
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Scheme 2



Scheme 3



material.⁷ Another procedure for drying this salt involves azeotropic removal of water with benzene or benzene-acetonitrile,⁸ followed by reduced pressure replacement of these solvents with dry DMF, DMSO, or HMPA.

However, if salt **4** was allowed to react with such "anhydrous" TBAF in DMSO or HMPA, it gave an equimolar mixture of products **11** (via 7^{+-}) and **13** (via 12^{+-}), in a total yield 80–90%. These results show that ylide 7^{+-} prefers reaction via a [1,2] instead of a [1,4] shift (for the reasons unknown at present) and that 7^{+-} equilibrates with ylide 12^{+-} , leading to formation of α -amino nitrile **13** (Table 1, Scheme 2) via [2,3] rearrangement.

Preferential [2,3] rearrangement of cyanomethylides is well documented, for example, in the products of *N*-aryl- or *N*-(hetarylmethyl)-*N*-(cyanomethyl)-*N,N*-dialkylammonium salts and a base.⁹

Table 1. Products **11** and **13** Formed from the Salt **4**

entry	source of F^-	solvent	ratio of the products ^a		total yield ca. (%)
			11	13	
1	TBAF	DMSO	50	50	86
2	TBAF	HMPA	55	45	80
3	CsF	DMF	96	4	80

^a Determined by GC and 1H NMR.

Table 2. Products **10**, **14**, and **15** from Salts **5** and **5*** and TBAF in DMSO

entry	salt	yield (%)	ratio of products			ratio of $^{13}C/^{13}C$ in products of rearrangement of 9^*a^{+-} and 9^*b^{+-} ^{a,b}		
			10	14	15	10*	14*	15*
1	5	80 ^c	12	35	53			
2	5	22 ^d	10	40	50			
3	5*	80 ^c	9	38	53	9.21	10.51	10.22
4	5*	20 ^d	10	40	50	10.03	10.46	9.71

^a Ratio of the concentrations of ^{13}C in positions marked by * (Scheme 4) in products **10***, **14***, and **15*** (s_a/s_b). ^b Estimated error is $\leq 10\%$ for **10**, and possibly lower in the case of products formed with high yields. ^c "Anhydrous" TBAF. ^d Reaction with CsF.

The same reaction carried out by using anhydrous CsF in DMF afforded mainly product **11** (yield 80%) and only a small amount of aminonitrile **13** (Table 1). Recently, salt **4** (with bromide counterion) has been rearranged under the same conditions to give only the product **11**.^{5c}

We attribute the generation of the more stable ylide 12^{+-} (precursor of the product **13**) to the presence of water remaining in the "anhydrous" TBAF, which facilitates the equilibration of ylides ($7^{+-} \rightleftharpoons 12^{+-}$). Indeed, the Karl Fischer method applied for water determination in "anhydrous" TBAF obtained according to above cited method⁸ indicated that the amount of water varies but does not drop below ca. 10% (what corresponds to the formula TBAF·1.6H₂O).

Reaction of salt **5** in DMSO either with "anhydrous" TBAF, or with CsF, afforded a mixture of products **10**, **14**, and **15** via [1,4], [1,2], and [2,3] shifts, respectively. A low yield was obtained using CsF, due to the poor solubility of CsF in DMSO. On the other hand, reaction of **5** with CsF in DMF led to formation of some unidentified products, apart from compounds **10**, **14**, and **15** (Scheme 3, Table 2).

Degenerate [1,3]H shift in the ylide 9^{+-} intermediate would have no consequence on the product distribution from an unlabeled precursor. Therefore, to determine whether rearrangements are preceded by [1,3]H shift in ylide 9^{+-} , the salt **5*** ^{13}C labeled at the benzylic carbon was synthesized and allowed to react with TBAF or CsF in DMSO, and the products were analyzed by ^{13}C NMR in a manner previously described by us.² In all cases studied the product mixture consisted of **10*a,b**, **14*a,b**, and **15*a,b** (Scheme 4).

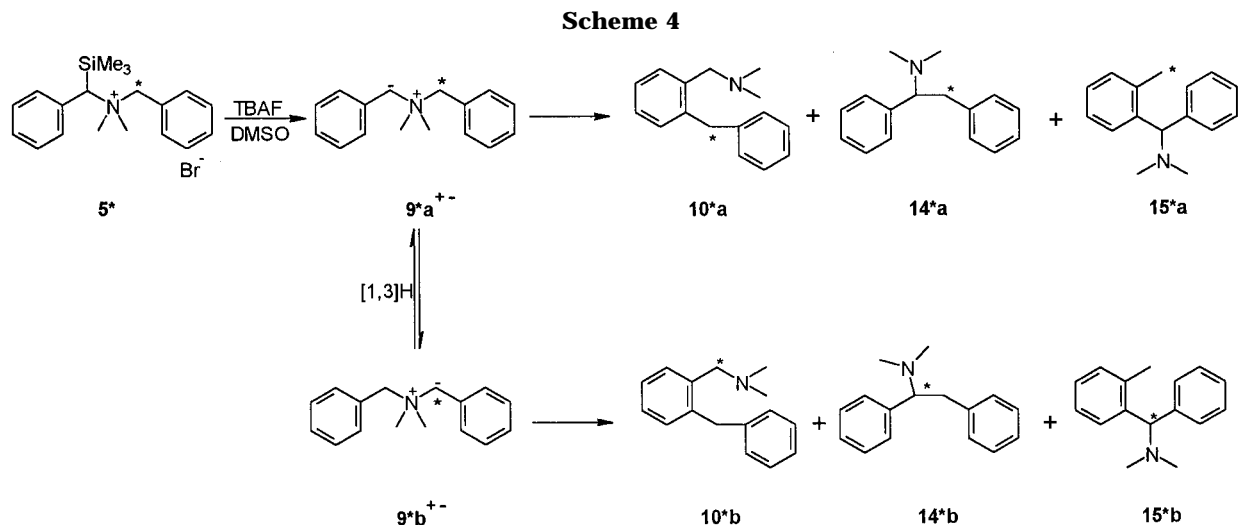
The ratio of $^{13}C/^{13}C$ in products derived from salt **5*** shows that very little if any [1,3]H shift in ylide intermediate 9^*a^{+-} occurred (Table 2), due to equal acidities of both benzylic positions. On the other hand, partial [1,3]H shift in ylide 7^{+-} leading to ylide 12^{+-} is well explained by better stabilization of the latter species (Scheme 2, Table 1).

Structure **5** is another example of a salt that generates ylides prone to [1,4] shift, although to only a small extent.

Rearrangements of Ylides Generated via Reaction of a Base with Ammonium Salts. Our earlier

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investigations indicated that concerted mechanisms with six-electron aromatic transition states and suprafacial-suprafacial characteristics are possibly involved in the [1,4] rearrangement of ammonium benzylides.¹ However, another explanation for the formation of the products of formal [1,4] shift of ammonium benzylides has been proposed.¹⁰ Thus, treating salt **6** with $\text{NaNH}_2/\text{NH}_3(\text{liq})$ or $n\text{-BuLi}/\text{THF}$ led to the formation of product **20**, as well as **19** and **21**.¹⁰ The formation of **20** was explained by sequential [1,4]Si and [1,2]H shifts from intermediate **18**, which in turn is a result of [2,3] rearrangement of silylmethylide **16**⁺⁻. These previous studies gave no experimental evidence that would support the suggested route a, **18** \rightarrow **20** (Scheme 5), but they referenced the precedence of anionic C–C shifts of silyl group during reactions of α - and β -silyl substituted amines.¹¹ Alternatively, product **20** may result via [1,4] rearrangement of benzylide **17**⁺⁻, which also appears as the precursor of amine **21** (route b, Scheme 5).

¹³C labeling (*) the salt **6** at the benzyl carbon should allow a choice between these two alternative mechanisms (Scheme 5). Thus, salts **6** and **6**^{*} (enriched up to ca. 10% in ¹³C at the benzyl carbon, Figure 1) were prepared and allowed to react with $n\text{-BuLi}$ following literature procedures,¹⁰ and the product mixtures were analyzed by ¹H and ¹³C NMR.

We found that this reaction afforded the three silyl-amines **19**–**21**, as described, in the ratio of ca. 1:5:1, with a yield of ca. 100%. The same reaction carried out with **6**^{*} resulted in a similar yield and product ratio. Determination of the abundance of ¹³C in both benzyl positions in **20**^{*} (by comparison with the natural abundance of ¹³C in **20**) from the ¹³C NMR spectra (Figure 2) indicated that all of the marker was located at the benzyl carbon α to Si (**20a**^{*} not **20b**^{*}, Scheme 5).

This result was consistent with product **20** being formed via the route suggested by Sato et al.¹⁰ (i.e., **16**⁺⁻ \rightarrow **18** \rightarrow **20** not **17**⁺⁻ \rightarrow **20**, Scheme 5).

At this point in our investigations the question arises whether product **3** might result from **1** via a mechanism similar to that which forms **20** from **6** (Scheme 6).

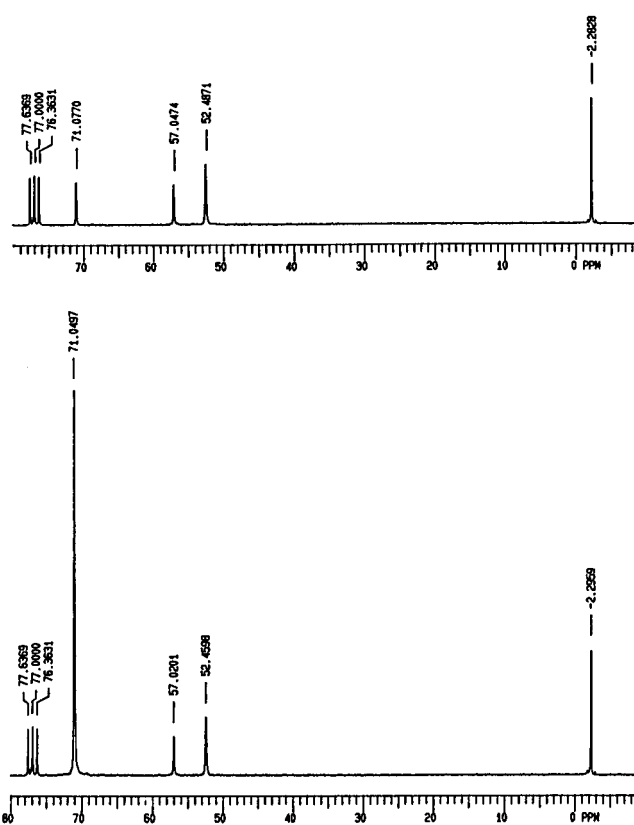


Figure 1. ¹³C NMR spectra (aliphatic carbons region) of salts **6** and **6**^{*} (enriched up to ca. 10% in ¹³C at the benzyl carbon). For full description of spectra see Experimental Section.

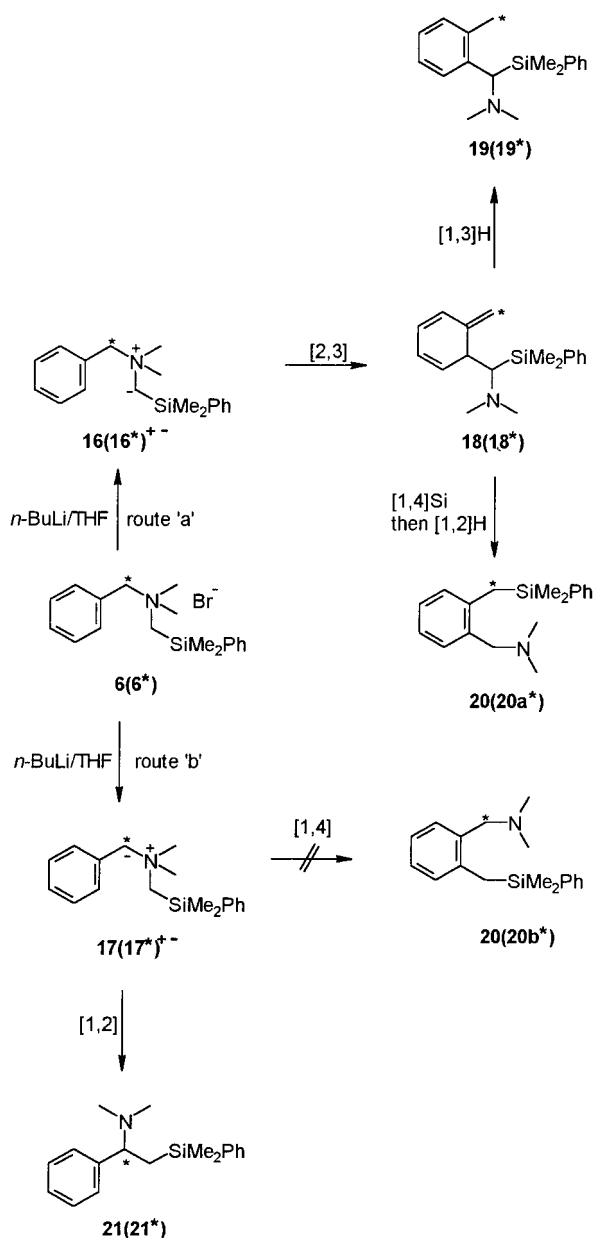
In this case, ¹³C labeling at the benzylic and/or either of the cyano groups in **1** does not lead to unequivocal results because identical structures are formed irrespective of [1,4] rearrangement or [2,3], then [1,4]NMe₂ and [1,2]H shifts. Assuming that the route leading to formation of **3**, visualized in Scheme 6, is valid, the amino groups in α -cyano amines should be susceptible to attack by nucleophiles (or electron pairs), which is against the

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Scheme 5



experimental facts indicating that the cyano group exhibits such reactivity.¹² Therefore, we should observe the formation of structure **22**, which, in fact, is not found. So route a in Scheme 5 is probably unique to some silyl-substituted ylides only.

Our data show that ylides generated from the salts of select structures (like **1** or **5**) in some base-solvent systems undergo [1,4] rearrangement. We have also demonstrated that ¹³C NMR spectroscopy of the products formed from reactions of a base with ammonium salts enriched in ¹³C at the benzyl carbon atom is a convenient tool to study rearrangements of ammonium ylides.

Experimental Section

General Methods. Commercial TBAF·3H₂O, Ph¹³CO₂H (99% ¹³C), (chloromethyl)dimethylphenylsilane, and a 2 M solution of *n*-BuLi in cyclohexane (all Aldrich) were used. Melting points (measured with a capillary melting point apparatus) and boiling points are uncorrected. Gas chromatography (GC) analyses were performed on a HP 50+ capillary

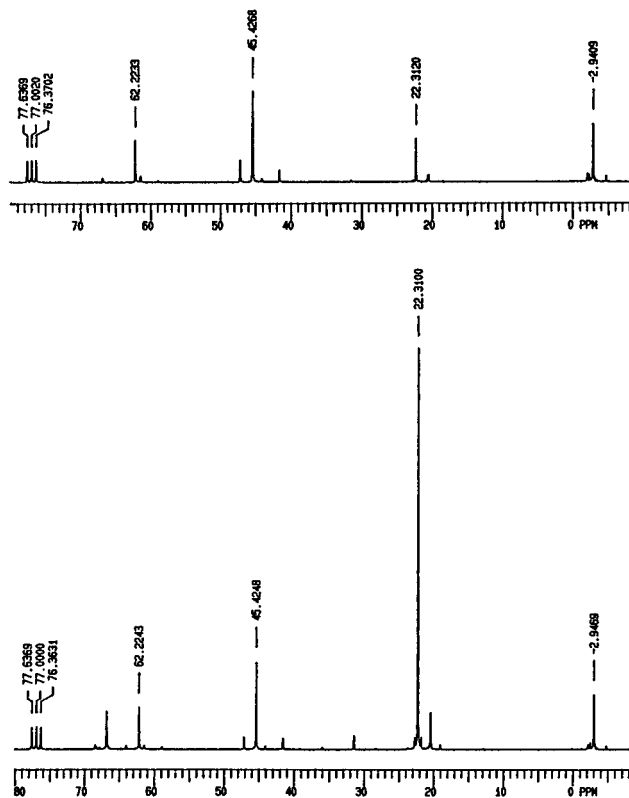
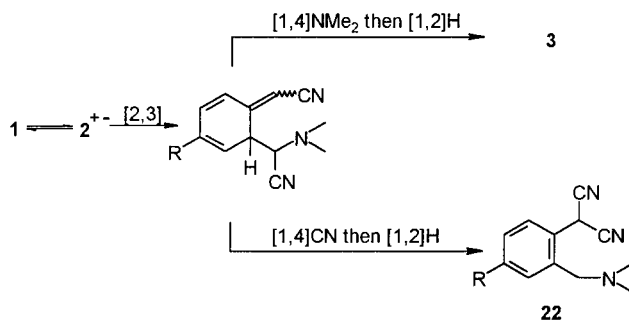


Figure 2. ¹³C NMR spectra (aliphatic carbons region) of the mixture of silylamines **19–21** (upper) and **19^{*}–21^{*}** (lower). Signals with reported shifts are ascribed to silylamine **20(20^{*})**, see Experimental Section for details.

Scheme 6



column. ¹H and ¹³C NMR spectra were measured at 200 and 50 MHz, respectively. Additionally, for carbon peak assignment the attached proton test (APT)¹³ was applied.

¹³C NMR spectra of compounds of natural and enriched in ¹³C isotopomers populations were measured (concentration 100 mg/mL; at 1 s; decoupler profile WALZ 16; nt 10000). The degree of enrichment in ¹³C isotopomers (*s*) was calculated from the following equation

$$s = \frac{I_A^* I_S}{I_S^* I_A} (1.108\%)$$

where *I_A*, *I_A^{*}* and *I_S*, *I_S^{*}* denote integral intensities of ¹³C signals of investigated carbon A and standard one (S) in spectra of compound of natural and enriched in ¹³C isotopomers population, respectively, and 1.108% means natural content of ¹³C isotopomers.²

The $^{13}\text{C}/^{13}\text{C}$ ratios of the concentrations of markers in the two considered positions A and B in salt **5*** and products **10***, **14***, and **15*** were calculated as follows

$$^{13}\text{C}/^{13}\text{C} = \frac{I_A^* I_B}{I_B^* I_A}$$

where I_A , I_A^* and I_B , I_B^* denote integral intensities of ^{13}C signals of investigated carbons A and B in spectra of compounds of natural and enriched in ^{13}C isotopomers population, respectively. The estimated error of this approach is 10%.

N-Cyanomethyl-N,N-dimethyl-N-[α -(trimethylsilyl)-benzyl]ammonium Chloride (4). A mixture of [α -(dimethylamino)benzyl]trimethylsilane¹⁴ (11.8 g, 56 mmol) and chloroacetonitrile (6.3 g, 84 mmol) was heated at ca. 40 °C for 24 h, diluted with the mixture of benzene and acetone (2:1), and thoroughly stirred, and the solid product was filtered to give **4** (10.0 g, 63%): mp 170–173 °C; ^1H NMR (DMSO- d_6) δ 0.17 (s, 9H), 3.27 (s, 3H), 3.38 (s, 3H), 4.75 and 4.89 (AB, $J = 16.3$ Hz, 2H), 4.92 (s, 1H), 7.45–7.65 (m, 5H); ^{13}C NMR (DMSO- d_6) δ 0.0, 51.7, 52.9, 53.7, 73.7, 112.1, 129.1, 129.4, 129.8, 130.6, 131.4, 133.8. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{ClN}_2\text{Si}$: C, 59.45; H, 8.20; N, 9.90. Found: C, 59.28; H, 7.98; N, 9.65.

N-Benzyl-N,N-dimethyl-N-[α -(trimethylsilyl)benzyl]ammonium Bromide (5). A solution of [α -(dimethylamino)benzyl]trimethylsilane¹⁴ (2.1 g, 1 mmol) and benzyl bromide (2.1 g, 1.2 mmol) in ethanol (3 mL) was heated at ca. 40 °C for 24 h and diluted with ethyl acetate (10 mL), and the solid product was filtered and washed with ethyl acetate to give **5** (3.6 g, 96%): mp 188–190 °C; ^1H NMR (DMSO- d_6) δ 0.23 (s, 9H), 2.85 (s, 3H), 2.94 (s, 3H), 4.47 and 4.67 (AB, $J = 12.3$ Hz, 2H), 5.11 (s, 1H), 7.45–7.75 (m, 10H); ^{13}C NMR (DMSO- d_6) δ 0.4 (SiMe₃), 49.7 (^+NMe), 49.8 (^+NMe), 67.4 (CH₂Ph), 74.2 (CHPh), 128.1, 128.7, 129.0, 129.3, 129.4, 130.3, 131.1, 132.6, 133.4, 134.0. Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{BrNSi}$: C, 60.03; H, 7.46; N, 3.70. Found: C, 60.11; H, 7.48; N, 3.58.

Salt 5*. Benzoic-carboxy- ^{13}C acid (1.0 g, 8.2 mmol) was added to benzoic acid (10.0 g, 82 mmol), and this mixture was converted to benzyl bromide via the following intermediates: Ph $^{13}\text{COCl}$ (with SOCl_2 , 90%), Ph $^{13}\text{CO}_2\text{Et}$ (with EtOH, 90%), Ph $^{13}\text{CH}_2\text{OH}$ (with LAH in Et₂O, 96%), and Ph $^{13}\text{CH}_2\text{Br}$ (with triphenylphosphine dibromide,¹⁵ 96%). Starting from this benzyl bromide and [α -(dimethylamino)benzyl]trimethylsilane,¹⁴ the salt **5*** (mp 187–190 °C) was prepared as described above for **5**.

5*: ^{13}C NMR (DMSO- d_6) δ 0.4 (SiMe₃), 49.7 ($^+\text{NMe}_2$), 67.5 ($^+\text{CH}_2\text{Ph}$), 74.1 (CHPh), 128.0, 128.7, 128.9, 129.2, 129.3, 130.2, 131.0, 132.5, 133.3, 134.0.

Calculated concentration of ^{13}C in both benzyl positions:

$\delta_{\text{CH}_2\text{Ph}} = 10.75\%$ (relative to integral intensity of signals of $^+\text{NMe}_2$) and 10.85% (relative to integral intensity of signal of SiMe₃);

$\delta_{\text{CHPh}} = 1.08\%$ (relative to $^+\text{NMe}_2$) and 1.09% (relative to SiMe₃).

Calculated ratio of $^{13}\text{C}/^{13}\text{C}$ in both benzyl positions: 9.95.

General Procedure for the Reactions of 4, 5, and 5* with TBAF in DMSO. Commercial TBAF·3H₂O (4.0 g, 12.5 mmol) was dissolved in the mixture of benzene/acetonitrile (1/1 v/v, ca. 50 mL), and water was removed with these solvents on a rotary evaporator. The procedure was repeated twice, and the residual sticky oil was evaporated at 40 °C/0.01 Torr for 30 min to obtain a white semisolid containing ca. 10% water (Karl Fischer titration) that was dissolved in dry DMSO (15 mL). This solution was placed in an ice bath, and during stirring the salt **4**, **5**, or **5*** (2.5 mmol) was added. The mixture was stirred at 20–25 °C for 24 h, poured into water (100 mL), and extracted with benzene (3 × 10 mL), the organic extracts were washed once with water and twice with brine and dried (Na₂SO₄). The solvent was evaporated, and the residue was

analyzed by means of GC and NMR spectroscopy. The yields of crude products were 80–100%.

Salt 4. The product mixture consisted of equimolar amounts of **11** and **13** (Table 1). A benzene solution of the products, obtained after extraction, was shaken with 3% aqueous HCl (3 × 10 mL), the phases were separated, the combined water phases were made alkaline with solid NaHCO₃ and extracted with benzene (3 × 10 mL), and the organic extracts were washed with brine, and dried (Na₂SO₄). The solvent was evaporated, and the residue was distilled to give **11** (0.2 g, 46%): bp 80 °C (0.075 Torr); mp 56–58 °C (cyclohexane–hexane); ^1H NMR (CDCl₃) δ 2.22 (s, 6H), 2.78 and 2.83 (part AB of ABX, $J_{AB} = 16.77$, $J_{AX} = 7.65$, $J_{BX} = 5.37$ Hz, 2H), 3.54 (part X of ABX, 1H), 7.30–7.45 (m, 5H); ^{13}C NMR (CDCl₃) δ 22.9, 42.7, 66.6, 117.9, 127.6, 128.2, 128.6, 138.3. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.69; H, 8.30; N, 16.07. The organic phase, after being shaken with aqueous HCl, was washed with aqueous NaHCO₃ and dried (Na₂SO₄), the solvent was evaporated, and the residue was distilled to give **13** (0.15 g, 35%): bp 70 °C (0.075 Torr) [lit.^{9c} bp 105–107 °C (5 Torr)]; ^1H NMR (CDCl₃) δ 2.29 (s, 6H), 2.39 (s, 3H), 4.87 (s, 1H), 7.16–7.32 (m, 3H), 7.50–7.57 (m, 1H); ^{13}C NMR (CDCl₃) δ 18.3, 41.1, 60.8, 114.9, 125.5, 128.0, 128.7, 130.7, 131.5, 137.1. An authentic sample of **13** was prepared from 2-methylbenzaldehyde, aqueous dimethylamine, and sodium cyanide [yield 65%, bp 79 °C (0.1 Torr)], as described for α -(dimethylamino)phenylacetonitrile.¹⁶

Salt 5. Treating salt **5** or **5*** with “anhydrous” TBAF in DMSO afforded the mixtures of **10** (**10***), **14** (**14***), and **15** (**15***) (Table 2, entries 1 and 3), ratios of which were determined by GC and ^1H NMR spectroscopy. These mixtures were also analyzed by ^{13}C NMR to determine the $^{13}\text{C}/^{13}\text{C}$ ratios of the concentration of marker in both benzylic positions (Scheme 4). Reference samples of the products **10**, **14**, and **15** were prepared as follows.

N,N-Dimethyl-2-benzylbenzylamine (10) via rearrangement of ylide generated from benzhydryltrimethylammonium iodide by means of NaNH₂ in NH₃(liq):¹⁷ bp 189–191 °C (33 Torr) [lit.¹⁷ bp 189–191 °C (33 Torr)]; ^1H NMR (CDCl₃) δ 2.29 (s, 6H), 3.42 (s, 2H), 4.25 (s, 2H), 7.18–7.40 (m, 9H); ^{13}C NMR (CDCl₃) δ 38.3 (CH₂Ph), 45.5, 62.0 (CH₂N), 125.8, 126.0, 127.2, 128.2, 128.8, 130.3, 130.5, 137.2, 139.8, 141.0.

1,2-Diphenyl-1-(dimethylamino)ethane (14) was obtained by reduction of 1,2-diphenyl-1-(dimethylamino)ethene¹⁸ with NaBH₄ in methanol: bp 140–142 °C (0.4 Torr) [lit.¹⁹ bp 142 °C (1 Torr)]; ^1H NMR (CDCl₃) δ 2.33 (s, 6H), 3.02 (dd, $^2J = 13.1$, $^3J = 9.55$ Hz, 1H), 3.38 (dd, $^2J = 13.1$, $^3J = 5.0$ Hz, 1H), 3.52 (dd, $^3J = 9.55$, $^3J = 5.0$ Hz, 1H), 7.00–7.35 (m, 10H); ^{13}C NMR δ 39.9 (CH₂), 42.9, 72.6 (CHN), 125.6, 126.9, 127.7, 127.8, 128.6, 129.2, 139.4, 139.6.

2-Methyl-N,N-dimethylbenzhydrylamine (15) was obtained from 2-methylbenzhydryl chloride²⁰ with an excess of aqueous dimethylamine: mp 47–49 °C (lit.²¹ mp 46 °C); ^1H NMR (CDCl₃) δ 2.22 (s, 6H), 2.38 (s, 3H), 4.29 (s, 1H), 7.00–7.10 (m, 2H), 7.18–7.32 (m, 4H), 7.40–7.50 (m, 2H), 7.83 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (CDCl₃) δ 19.9 (CH₃Ar), 44.9, 72.8 (CHN), 126.2, 126.3, 126.8, 127.0, 128.3, 128.4, 130.4, 135.4, 141.5, 142.4.

Reaction of Salt 4 with CsF in DMF. Dried (180 °C, reduced pressure) CsF (0.76 g, 5 mmol) was suspended in freshly dried DMF (5 mL), the mixture was stirred and cooled to ca. 0 °C, and salt **4** (0.28 g, 1 mmol) was added in one portion. The cooling bath was removed, stirring was continued for 24 h, and the mixture was worked up as described in the General Procedure. The crude oil (0.20 g) was analyzed by GC to show 86% of **11** and ca. 3% of **13** (Table 1, entry 3) and

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solidified when degassed in vacuo. Recrystallization afforded **11** (0.14 g, 80%), mp 56–58 °C (cyclohexane–hexane).

Reaction of Salt 5 or 5* with CsF in DMSO. The suspension of dried CsF (0.76 g, 5 mmol) in dry DMSO (6 mL) was stirred while salt **5** or **5*** (0.38 g, 1 mmol) was added in one portion. The mixture was stirred at rt for 48 h and worked up as described in the General Procedure to give a mixture of amines **10**, **14**, and **15** or **10***, **14***, and **15*** (Table 2, entries 2 and 4), which were analyzed by GC (purity ca. 90%) and ¹H and ¹³C NMR spectroscopy in the manner already described above.

Reactions of Salts 6 and 6* with *n*-BuLi. Salt **6** was prepared via reaction of *N,N*-dimethyl-*N*-(dimethylphenylsilyl)methylamine [synthesized in turn from (chloromethyl)-dimethylphenylsilane and dimethylamine^{11c}] with benzyl bromide by literature procedure.¹⁰ The salt **6*** was obtained similarly using benzyl bromide enriched in ¹³C at benzyl carbon to ca. 10%.

6*: yield 90%; mp 157–159 °C; ¹H NMR (CDCl₃) δ 0.51 (s, 6H), 3.00 (s, 6H), 3.65 (s, 2H), 4.96 (s and d, *J*_{C–H} = 145.7 Hz, 2H, *CH₂), 7.20–7.30 and 7.45–7.55 (m, 10H); ¹³C NMR (CDCl₃) δ –2.3 (SiMe₂, *J*_{Si–C} = 55.2 Hz), 52.5 (⁺NMe₂), 57.0 (SiCH₂, *s* = 1.09%, concentration of ¹³C relative to integral intensity of signal of ⁺NMe₂), 71.0 (Ph*CH₂, *s* = 10.15%, concentration of ¹³C relative to integral intensity of signal of ⁺NMe₂), 127.6 (*J*_{Si–C} = 45.9 Hz), 128.3, 128.5, 130.1, 130.2, 133.0, 133.7.

Treating of the salt **6** with a 2 M solution of *n*-BuLi in cyclohexane according to literature procedure¹⁰ led to formation of the mixture of **19**, **20**, and **21** (ca. 100%) in a ratio of

1:5:1. Distillation of this mixture gave a fraction of bp 150–155 °C (2 Torr) containing silylamines **19**, **20**, and **21** in the ratio of 1:6:1 (¹H NMR).

The salt **6*** (1.82 g, 5 mmol) was treated with a 2 M solution of *n*-BuLi in cyclohexane in the same manner as salt **6**. The crude products (yield ca. 100%) were distilled, and the fraction of bp 150–155 °C (2 Torr) was collected and analyzed by ¹H NMR to show silylamines **19***, **20***, and **21*** in the ratio of 1:8:1.

Both mixtures (**19**, **20**, **21** and **19***, **20***, **21***) were analyzed by ¹³C NMR. The large excess of amine **20** (**20***) in the samples [relative to **19** (**19***) and **21** (**21***)] allowed the separation of individual resonance signals of **20** and **20***.

20: δ –2.9 (SiMe₂), 22.3 (SiCH₂, *J*_{Si–C} = 47.6 Hz), 45.4 (NMe₂), 62.2 (CH₂N), 124.0, 126.7, 127.7, 128.9, 129.3, 130.2, 133.6, 135.7, 139.0, 139.1.

20*: δ –2.9 (SiMe₂), 22.3 (SiCH₂, *J*_{Si–C} = 47.6 Hz), 45.4 (NMe₂), 62.2 (CH₂N), 124.0, 126.7, 127.7, 129.0, 129.4, 130.2, 133.6, 135.7, 139.0, 139.1.

The determined degree of enrichment in ¹³C (*s*) at both benzyl carbons in **20*** gave the following results:

*s*_{CH₂Si} = 10.31% and *s*_{CH₂N} = 1.23% (both relative to NMe₂).

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