

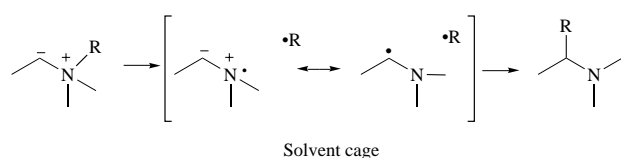
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Isomerization of trimethylammonium *N*-benzylide **2** failed to occur at room temperature in a non-basic medium (HMPA) or at $-78\text{ }^{\circ}\text{C}$ in the presence of butyllithium in THF. However, *N,N*-dimethyl-1-phenylethylamine **4** (Stevens rearrangement product) was formed when the temperature of the latter reaction was raised to room temperature. The mechanism of the Stevens rearrangement is discussed.

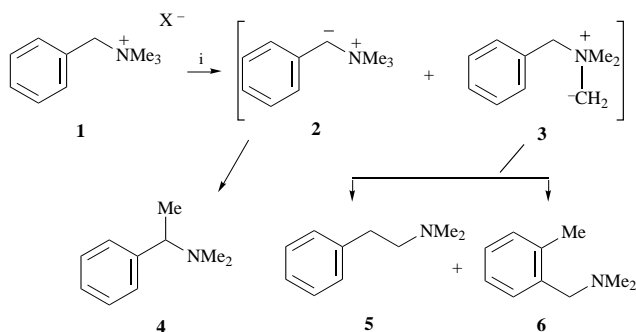
Introduction

The Stevens rearrangement is a typical reaction of ammonium and sulfonium ylides, and the mechanism has been the subject of considerable study.¹ This rearrangement represents an intramolecular [1,2] shift in which the configuration of a migrating group is retained.² Based on CIDNP spectra, it seems reasonable that the products are formed directly from a radical-pair precursor in which the radicals do not drift apart in a solvent cage.³



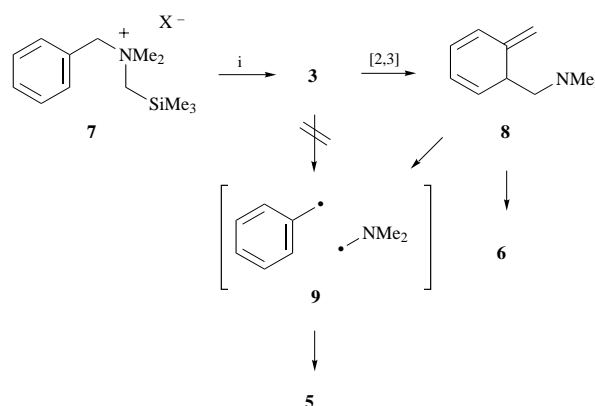
Scheme 1

For example, trimethylammonium *N*-benzylide **2** and *N,N*-dimethylbenzylammonium *N*-methylide **3** are competitively formed in the reaction of *N,N,N*-trimethylbenzylammonium halides **1** with butyllithium in diethyl ether–hexane, and they subsequently isomerize to Stevens rearrangement products **4** and **5**, respectively, accompanied by the formation of a Sommelet–Hauser rearrangement product **6** (Scheme 2).⁴



Scheme 2 Reagents and conditions: i, BuLi, Et₂O–hexane, RT

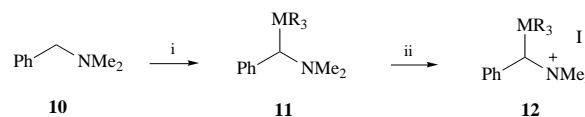
In our studies on benzylammonium *N*-alkylides in non-basic media, we found that **5** was not directly formed from **3** by the [1,2] shift mentioned above, but from an isotoluene-type compound **8** by way of a [1,3] migration pathway (Scheme 3).⁵ Thus, [2,3] sigmatropic rearrangement of **3** to **8** occurs more quickly than the C–C bond cleavage of **3** to give a radical pair **9**. The bond cleavage of **8** to give **9** competes with a [1,3] proton transfer which gives **6**. Here we report the chemical behaviour of **2** in a non-basic medium.



Scheme 3 Reagents and conditions: i, CsF, HMPA or DMF, RT

Results and discussion

α -Trimethylsilylbenzyl- and α -tributylstannylbenzyl-*N,N,N*-trimethylammonium iodides **12a,b** were prepared by quaternization of α -trimethylsilylbenzyl- and α -tributylstannylbenzyl-*N,N*-dimethylamines **11a,b**, which were synthesized by treating *N,N*-dimethylbenzylamine **10** with potassium *tert*-butoxide followed by chlorotrimethylsilane or chlorotributyltin (Scheme 4).



Scheme 4 Reagents and conditions: i, BuLi, KOBu^t, a: ClMR₃ = ClSiMe₃, b: ClMR₃ = ClSnBu₃, THF–hexane, RT; ii, MeI, THF or acetone, RT, 2 h

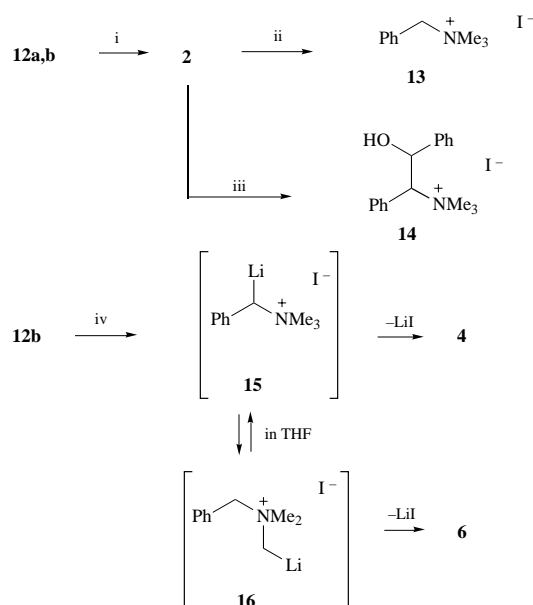
Surprisingly, no product was obtained from the ethereal extract of a reaction mixture of **12a,b** with caesium fluoride in HMPA for 3 h, while *N,N,N*-trimethylbenzylammonium iodide **13** was isolated from the aqueous layer after diethyl ether extraction (Table 1, entries 1, 4). When the same reactions were repeated in the presence of benzaldehyde, *N,N,N*-trimethyl(2-hydroxy-1,2-diphenylethyl)ammonium iodide **14** was obtained in good yields (entries 2, 5). Furthermore, **14** was also isolated in fairly good yield when benzaldehyde was added 1 h after the addition of caesium fluoride (entries 3, 6). These results indicate that **2** was generated in high yield and some remained in the reaction mixtures after 1 h at room temperature. Nevertheless, no Stevens rearrangement product was formed. Since **4** was formed in a base-induced ylide reaction⁴ (Scheme 2), the conversion of **2** into **4** should require the aid of a strong base.

Destannylation of organotin compounds with butyllithium is useful for regioselective ylide formation under basic conditions.⁶ The reaction of **12b** with butyllithium at $-78\text{ }^{\circ}\text{C}$ for

Table 1 Reaction of α -trimethylsilylbenzyl- and α -tributylstannylbenzyl-*N,N,N*-trimethylammonium iodides **12a,b** with CsF or BuLi for 3 h

		MR ₃	Reagent	Solvent	Additive	Reaction temp. (°C)	Yield of products (%)			
							4	6	13	14
1	12a	SiMe ₃	CsF	HMPA	—	RT	0	0	92	—
2	12a	SiMe ₃	CsF	HMPA	PhCHO ^a	RT	0	0	15	61
3	12a	SiMe ₃	CsF	HMPA	PhCHO ^b	RT	0	0	43	18
4	12b	SnBu ₃	CsF	HMPA	—	RT	0	0	91	—
5	12b	SnBu ₃	CsF	HMPA	PhCHO ^a	RT	0	0	29	51
6	12b	SnBu ₃	CsF	HMPA	PhCHO ^b	RT	0	0	31	31
7	12b	SnBu ₃	BuLi	THF	—	-78	0	0	75	—
8	12b	SnBu ₃	BuLi	THF	PhCHO ^c	-78	0	0	38	35
9	12b	SnBu ₃	BuLi	THF	—	RT ^d	28	32	<i>e</i>	—
10	12b	SnBu ₃	BuLi	Et ₂ O	—	RT ^d	67	4	<i>e</i>	—

^a Benzaldehyde was added before the addition of CsF. ^b Benzaldehyde was added 1 h after the addition of CsF. ^c Benzaldehyde was added 3 h after the addition of BuLi. ^d The reaction was carried out at -78 °C for 1 h, then at room temp. for 2 h. ^e Not determined.



Scheme 5 Reagents and conditions: i, (a) CsF, HMPA, RT, 3 h, (b) BuLi, THF, -78 °C, 3 h; ii, KI, H₂O; iii, PhCHO, KI, H₂O; iv, BuLi, THF or Et₂O, RT, 3 h

3 h in THF gave no rearrangement product but, instead, **13** was formed (entry 7). The addition of benzaldehyde before quenching resulted in the formation of **14** (entry 8). These results are similar to those of the reaction with caesium fluoride at room temperature. The ylide **2** was formed by destannylation, but no change occurred at -78 °C. However, when the reaction temperature was increased to 25 °C after the mixture had been stirred for 1 h, a mixture of **4** and **6** was formed (entry 9). Selective formation of **4** was obtained when the solvent was changed to diethyl ether (entry 10).

Thus, Stevens rearrangement of **2** occurs at room temperature in the presence of butyllithium. Organolithium intermediates such as **15** may be essential for the [1,2] shift of the methyl group. March⁷ noted that Stevens rearrangement is possible *via* an ion-pair intermediate instead of radical pairs in a solvent cage, however, experimental support has not been reported. Our results may be the first example supporting the ion-pair mechanism. The formation of **6** shows that there is significant conversion of **15** into **16** in THF, but very little in diethyl ether.

In conclusion, Stevens rearrangement of ammonium ylides may occur *via* one of the following three processes: (a) a [1,2] radical shift when the radical of the migrating group is stabilized by adjacent group(s), such as oxygen,⁸ cyano,⁹ or phenyl groups;¹⁰ (b) a [1,2] (ionic?) shift when the migrating group has no adjacent stabilizing group(s) and in the presence of a strong base; (c) a [1,3] shift from isotoluenes when a [2,3] sigmatropic rearrangement of ylides is allowed.⁵

Experimental

All reactions were carried out under N₂. HMPA was dried by distillation from sodium under reduced pressure. THF and Et₂O were distilled from sodium and benzophenone. CsF was dried over P₂O₅ at 180 °C under reduced pressure. Aluminium oxide (Merck, 70–230 mesh) was used for column chromatography. All melting points and boiling points are uncorrected.

N,N-Dimethyl- α -(trimethylsilyl)benzylamine **11a**

This compound was synthesized according to Kalinowski.¹¹ A mixture of *N,N*-dimethylbenzylamine **10** (9.5 g, 70 mmol), KOBu^t (7.8 g, 70 mmol) and BuLi (1.6 M in hexane; 44 cm³, 70 mmol) in hexane (35 cm³) was stirred at 0 °C for 0.5 h. After the addition of THF (70 cm³), chlorotrimethylsilane (7.6 g, 70 mmol) was added dropwise at -50 °C to the mixture. The mixture was then stirred at RT for 20 h, poured into water (150 cm³) and extracted under reduced pressure and distilled to give the *title amine* **11a** (12.8 g, 88%), bp 90–95 °C/11 mmHg (Found: C, 69.6; H, 10.15; N, 6.8. C₁₂H₂₁NSi requires C, 69.5; H, 10.2; N, 6.75%); δ_{H} (270 MHz; CDCl₃) -0.02 (9 H, s), 2.28 (6 H, s), 2.65 (1 H, s) and 7.15–7.24 (5 H, m); ν_{max} (film)/cm⁻¹ 2950, 1250, 870 and 840.

N,N,N-Trimethyl- α -(trimethylsilyl)benzylammonium iodide **12a**

A solution of **11a** (9.1 g, 44.0 mmol) and iodomethane (11.5 g, 80.6 mmol) in acetone (30 cm³) was stirred at RT for 2 h after which the solvent was removed under reduced pressure. The residue was recrystallized from MeOH–Et₂O to give the *title salt* **12a** (13.9 g, 90%), mp 180–184 °C (Found: C, 44.45; H, 6.9; N, 4.0. C₁₃H₂₄INSi requires C, 44.7; H, 6.9; N, 4.0%); δ_{H} (270 MHz; CDCl₃) 0.28 (9 H, s), 3.47 (9 H, s), 5.23 (1 H, s) and 7.33–7.77 (5 H, m); ν_{max} (KBr)/cm⁻¹ 2950, 1490, 1250 and 850.

N,N,N-Trimethyl- α -(tributylstannyl)benzylammonium iodide **12b**

A solution of *N,N*-dimethyl- α -(tributylstannyl)benzylamine¹¹ **11b** (10.6 g, 25.0 mmol) and iodomethane (7.9 g, 55.6 mmol) in THF (20 cm³) was stirred at RT for 2 h after which the solvent was removed under reduced pressure. The residue was recrystallized from acetone–hexane to give the *title salt* **12b** (11.3 g, 80%), mp 98–99 °C (Found: C, 46.4; H, 7.4; N, 2.7. C₂₂H₄₂INSn requires C, 46.7; H, 7.5; N, 2.5%); δ_{H} (400 MHz; CDCl₃) 0.85 (9 H, t, *J* 7.0), 0.98–1.48 (18 H, m), 3.44 (9 H, s), 5.12 (1 H, t, *J* 16.9), 7.28 (1 H, br s), 7.40–7.47 (3 H, m) and 7.67 (1 H, br s); ν_{max} (Nujol)/cm⁻¹ 1380, 1180, 870 and 690.

Reaction of **12a** with CsF

Method A. The ammonium salt **12a** (698 mg, 2 mmol) was placed in a 20 cm³ flask equipped with a septum and a test tube which was connected to the flask by a short, bent piece of

glass tubing. CsF (920 mg, 6 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and was flushed with N₂. HMPA (10 cm³) was added to the flask and then CsF was added from the test tube. The mixture was stirred at RT for 3 h, after which it was poured into water (40 cm³) and extracted with Et₂O. The extract was washed with water, dried (MgSO₄) and concentrated under reduced pressure but gave no product. The aqueous layer after Et₂O extraction was concentrated under reduced pressure and the residue was mixed with 10% aqueous MeOH (10 cm³) and saturated aqueous KI (15 cm³). The mixture was extracted with CHCl₃. The extract was concentrated under reduced pressure and the residue was recrystallized from MeOH–Et₂O to give *N,N,N*-trimethylbenzylammonium iodide **13** (509 mg, 92%), mp 177–179 °C (decomp.) [lit.,¹² mp 178–179 °C (decomp.)].

Method B. In a reaction similar to that described above, benzaldehyde (600 mg, 5.7 mmol) was added before the addition of CsF, and the reaction mixture was treated as above. The aqueous layer after Et₂O extraction was concentrated and the residue was recrystallized from MeOH–Et₂O to give *N,N,N*-trimethyl-(2-hydroxy-1,2-diphenylethyl)ammonium iodide **14** (467 mg, 61%). The mother liquor was concentrated to give **13** (83 mg, 15%).

Compound 14.—Mp 244 °C (Found: C, 53.2; H, 5.65; N, 3.7. C₁₇H₂₂INO requires C, 53.3; H, 5.8; N, 3.65%); δ_H(270 MHz; CDCl₃) 3.43 (9 H, s), 5.05 (1 H, d, *J* 10.6), 5.70 (1 H, d, *J* 10.6) and 7.06–7.68 (10 H, m); ν_{max}(KBr)/cm⁻¹ 3360, 1260, 1040 and 700.

Method C. In a similar reaction, benzaldehyde was added 1 h after the addition of CsF, and the reaction mixture was then treated to give **13** (238 mg, 43%) and **14** (138 mg, 18%).

Reaction of **12b** with CsF

Method A. In a manner similar to that described for **12a**, a mixture of **12b** (1.13 g, 2 mmol) and CsF (920 mg, 6 mmol) in HMPA (10 cm³) was prepared and stirred for 3 h at RT, after which it was quenched with water (40 cm³). Precipitated crystals of fluorotributyltin were filtered off on Celite and the filtrate was extracted with Et₂O. The aqueous layer after Et₂O extraction was concentrated to give **13** (413 mg, 91%).

Method B. In a reaction similar to that described above, benzaldehyde (600 mg, 5.7 mmol) was added before the addition of CsF; the reaction mixture was then treated as before. The aqueous layer after Et₂O extraction was concentrated and the residue was recrystallized from MeOH–Et₂O to give **13** (161 mg, 29%) and **14** (391 mg, 51%).

Method C. In a similar reaction, benzaldehyde was added 1 h after the addition of CsF, and the reaction mixture was treated as above to give **13** (172 mg, 31%) and **14** (237 mg, 31%).

Reaction of **12b** with BuLi

Method A. The salt **12b** (1.13 g, 2 mmol) was placed in a 20 cm³ flask equipped with a septum and magnetic stirrer. The apparatus was dried under reduced pressure and flushed with N₂. THF (10 cm³) was added to the flask by syringe and the mixture was cooled at –78 °C. BuLi (1.52 M in hexane; 1.3 cm³, 2 mmol) was added to the mixture which was then stirred for 3 h. After this, the mixture was poured into water (40 cm³) and extracted with Et₂O. No product was obtained from the Et₂O extract. The aqueous layer after Et₂O extraction was concentrated and the residue was mixed with 10% MeOH (10 cm³) and saturated aqueous KI (15 cm³). The mixture was extracted with CHCl₃. The extract was concentrated and the residue was recrystallized to give **13** (415 mg, 75%).

Method B. In the same way, **12b** (1.13 g, 2 mmol) and BuLi (1.52 M in hexane; 1.3 cm³, 2 mmol) were allowed to react in THF (10 cm³) at –78 °C for 3 h after which benzaldehyde (600 mg, 5.7 mmol) was added to the mixture. After being stirred at RT for 1 h, the reaction mixture was treated as above to give **13** (211 mg, 38%) and **14** (268 mg, 35%).

Method C. In the same way, a mixture of **12b** (1.13 g, 2 mmol) and BuLi (1.52 M in hexane; 1.3 cm³, 2 mmol) was allowed to react in THF or Et₂O (10 cm³) at –78 °C for 1 h and then at RT for 2 h. After this the mixture was poured into water (40 cm³) and extracted with Et₂O. The Et₂O layer was extracted with 1 M aqueous hydrochloric acid (3 × 50 cm³). The HCl layer was made alkaline with 5 M aqueous NaOH (50 cm³) and extracted with Et₂O. The Et₂O layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was distilled using a Kugelrohr distillation apparatus at 120 °C/50 mmHg. The distillate was chromatographed on an aluminium oxide column (Et₂O–hexane, 1:2) to yield *N,N*-dimethyl-1-phenylethylamine¹³ **4** (83 mg, 28% in THF or 199 mg, 67% in Et₂O) and *N,N*-dimethyl-2-methylbenzylamine¹⁴ **6** (95 mg, 32% in THF or 12 mg, 4% in Et₂O).

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