Chemical Behavior of *N*-Alkyl-*N*-methylbenzylammonium *N*-Alkylide

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N-Alkyl-*N*-methyl(4-substituted benzyl)ammonium *N*-alkylides (**3**), produced by fluoride ion induced desilylation of *N*-alkyl-*N*-methyl-*N*-(4-substituted benzyl)-1-(trimethylsilyl)alkylammonium iodides (**2**), were mainly converted into *N*-alkyl-*N*-methyl-1-(4-substituted benzyl)alkylamines (**5**, Stevens rearrangement products) and 4-substituted toluenes (**8**). Both compounds were produced via radical-forming and -destroying pathways from 2-substituted-6-[1-(*N*-alkylmethylamino)alkyl]-5-methylene-1,3-cyclohexadienes (**4**), which were initially formed from **3** by [2,3] sigmatropic rearrangement. There is no direct [1,2] migration pathway from **3** to **5**.

Introduction

When an *N*-alkyl-*N*-benzyldimethylammonium salt is treated with a strong base, a hydrogen atom at the benzylic position or of the methyl group is abstracted to give a mixture of ammonium ylide intermediates; these are isomerized to tertiary amines by Stevens and/or Sommelet–Hauser rearrangements. It is difficult to form *N*-alkylides by selective deprotonation of an α-proton of the *N*-alkyl group.[1]

Fluoride ion induced desilylation[2] of *N*-benzyl-*N*,*N*-dialkyl(trimethylsilyl)methylammonium halides affords *N*-methylide intermediates,[3] which are isomerized preferentially to *N*,*N*-dialkyl(2-methylbenzyl)amines (Sommelet–Hauser rearrangement products) without Hofmann elimination by intramolecular proton transfer.[4] In this reaction the ylide anion locates selectively on the carbon that had been bonded to the silyl group. The desilylation reaction of *N*-benzyl-*N*,*N*-dialkyl-1-(trimethylsilyl)alkylammonium salts (**2**) apparently gives *N*-alkylide intermediates that isomerize to *N*,*N*-dialkyl-1-(2-methylbenzyl)alkylamines (**6**, Sommelet–Hauser rearrangement products).

Result and Discussion

N-Alkyl-*N*-(4-substituted benzyl)[1-(trimethylsilyl)alkyl]amines (**1**, Scheme I) were prepared by reaction of 2-(*N*-methyl-4-substituted benzylamino)-2-(trimethylsilyl)acetonitriles with Grignard reagents.[5] They were easily quaternized to *N*-alkyl-*N*-methyl-*N*-(4-substituted benzyl)-1-(trimethylsilyl)alkylammonium iodides (**2**) by refluxing with iodomethane in acetonitrile, whereas refluxing with iodoethane required considerable time. The yields and results are listed in Table I.

When the reaction of *N*-benzyl-*N*,*N*-dimethyl-1-(trimethylsilyl)ethylammonium iodide (**2a**) with cesium fluoride was carried out in hexamethylphosphoramide (HMPA) at room temperature, three amines were obtained in a ratio of 88:8:4 (total yield 32%) from the acid extract of the reaction mixture (entry 1 in Table II). The structure of the major amine was confirmed as *N*,*N*-dimethyl(1-benzylethyl)amine (**5a**, Stevens rearrangement product) by spectral analyses. Two minor amines were identical with the authentic samples of *N*,*N*-dimethyl-1-(2-methylphenyl)ethylamine (**6a**, Sommelet–Hauser rearrangement product) and *N*,*N*-dimethyl-1-(4-methylphenyl)ethylamine (**7a**), respectively. The two authentic samples were independently synthesized by dimethylamination of 2- or 4-methylacetophenone. The presence of 50% yield of toluene (**8a**) and a trace amount of bibenzyl (**9a**) was confirmed by GLC and GC mass spectral analyses in the organic layer after the acid extraction.

Table I. *N*,*N*-Dialkyl-*N*-(substituted benzyl)-1-(trimethylsilyl)alkylammonium Iodides (2)

entry	R^1	R^2	R^3	R^4	rctn time, h	yield, %
1, **2a**	H	Me	Me	Me	4	93
2, **2b**	H	Me	Me	Et	45	44[a]
3, **2b**	H	Me	Et	Me	4	83
4, **2c**	H	Et	Me	Me	4	94
5, **2d**	H	*n*-Bu	Me	Me	4	97
6, **2e**	MeO	Me	Me	Me	5	80

[a] Considerable amounts of the starting materials remained in the reaction mixture.

Table II. Reaction of *N*,*N*-Dialkyl-*N*-(substituted benzyl)-1-(trimethylsilyl)alkylammonium Iodides (2) with CsF

			amines 5, 6, and 7		
entry	solvent	time, h	total yield, %	ratio 5:6:7	toluenes (8), %
1, **a**	HMPA	16	32	88:8:4	50
2, **a**	DMF	22	39	92:4:4	32
3, **b**	HMPA	22	34	98:1:1	55
4, **b**	DMF	21	43	96:1:3	35
5, **c**	HMPA	17	43	98:1:1	35
6, **c**	DMF	22	46	98:1:1	18
7, **d**	HMPA	21	57	98:1:1	38
8, **d**	DMF	23	58	98:1:1	27
9, **e**	HMPA	75	53	99:1	37
10, **e**	DMF	63	51	99:1	13

Similar results were obtained from analogous ammonium salts **2b–e** (Table II). High selectivity of the Stevens products **5b–e** was observed, and minor product **7e** was not formed from para-substituted analogue **2e** (entry 9). When these reactions were carried out in dimethylformamide (DMF), the yield of amines was somewhat increased and the yield of toluenes decreased; however, the ratio of the three amines was not affected.

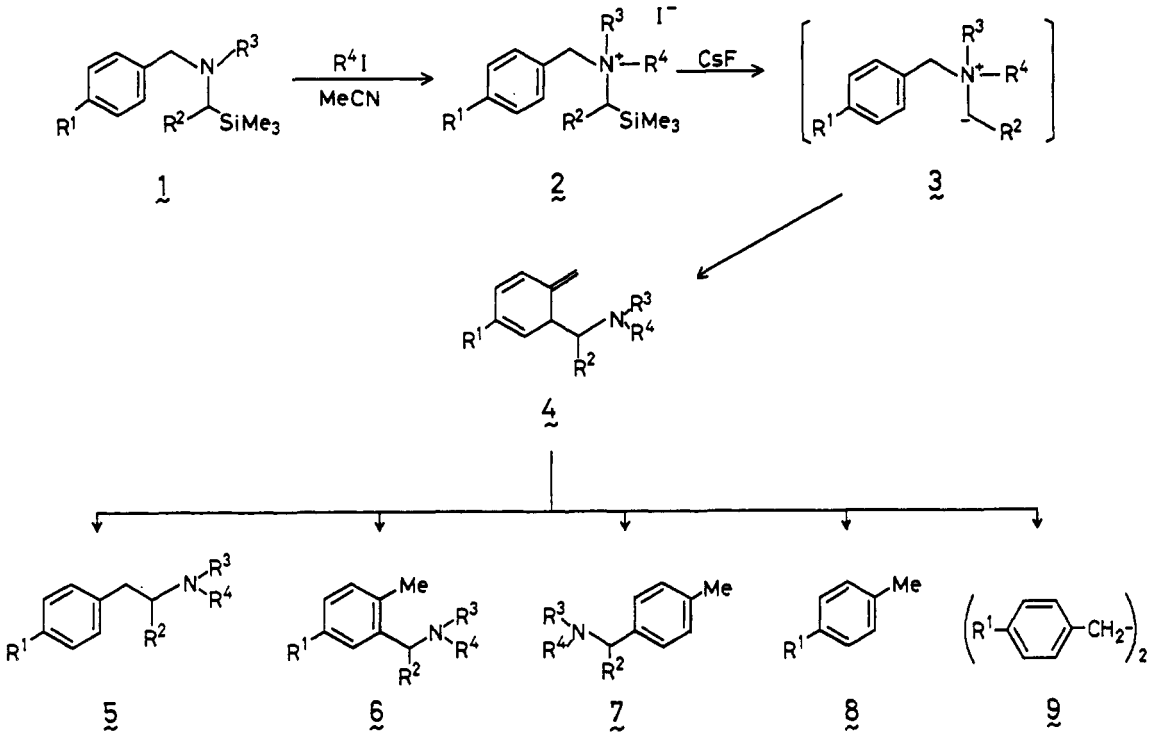
We previously reported that *N*-benzyl-*N*,*N*-dimethylammonium *N*-methylide, similarly produced from *N*-benzyl-*N*,*N*-dimethyl(trimethylsilyl)methylammonium bromide, is isomerized to *N*,*N*-dimethyl(2-methylbenzyl)amine (Sommelet–Hauser rearrangement product) and *N*,*N*-dimethyl(2-phenylethyl)amine (Stevens rearrangement product) in the ratios 97:3 (total yield 84%) in HMPA and 98:2 (total yield 61%) in DMF.[3]

Thus, the ratio of Sommelet–Hauser and Stevens products is just the reverse between *N*-methylide and *N*-alkylide **3**. The yields of amines from **3** are low, however, compared with those from the *N*-methylide, although

(1) Pine, S. H. *Org. React.* (*N.Y.*) **1970**, *18*, 403.
(2) For a review of fluoride ion induced desilylation reaction, see: Furin, G. G.; Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675.
(3) Nakano, M.; Sato, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1684; *J. Org. Chem.* **1987**, *52*, 1844.
(4) Shirai, N.; Sato, Y. *J. Org. Chem.* **1988**, *53*, 194.
(5) Okazaki, S.; Sato, Y. *Synthesis*, in press.

0022-3263/90/1955-0334$02.50/0

Scheme I



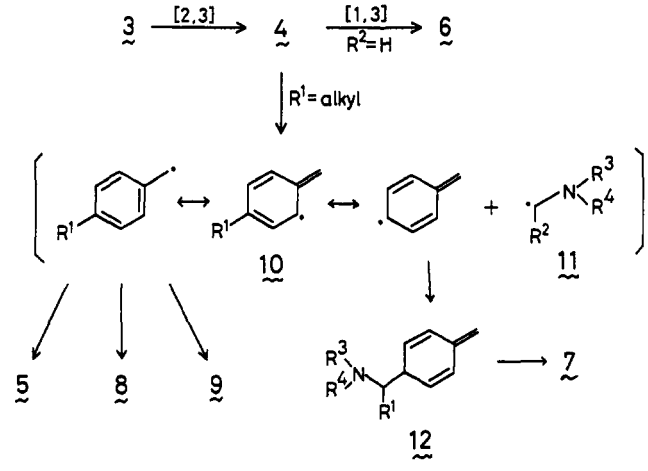
the total yield of the products (**5**–**8**, 64–90%) is the same as with the latter.

Stevens rearrangement of ylides results in the [1,2] migration of the alkyl group via radical cage intermediates, and Sommelet–Hauser rearrangement is the result of [2,3] sigmatropic shift.[1] It is unlikely there is a distinguishable difference between the *N*-methylide and the *N*-alkylide as to which pathway is favorable.

We previously revealed that an intermediate in the Sommelet–Hauser rearrangement, 5-[(dialkylamino)-methyl]-6-methylene-1,3-cyclohexadiene (isotoluene derivative), is an isolable compound with characteristic UV absorption in the region 310–320 nm.[6,7] When the reaction of **2a** with cesium fluoride in HMPA was carried out at 10 °C and quenched after 0.5 h, the ethereal extract of the reaction mixture exhibited characteristic UV absorption at 311 nm. The high-performance liquid chromatography (HPLC) and ^{1}H NMR analyses of the residual oil revealed the presence of 6-[1-(dimethylamino)ethyl]-5-methylene-1,3-cyclohexadiene (**4a**) and **5a** in the ratio 57:43. Purification of **4a** on a HPLC column, however, failed due to insufficient stability. Stability of the isotoluene compounds is affected by the nature of a substituent on the conjugated bonds. An electron-donating group (e.g., methoxy) stabilizes the isotoluene ring.[7] Actually, a similar treatment of **2e** gave 6-[1-(dimethylamino)ethyl]-2-methoxy-5-methylene-1,3-cyclohexadiene (**4e**) in 73% yield, and the contamination by **5e** was less than 1%.

When a mixture of **4a** and **5a** or of **4e** and **5e** was dissolved again in HMPA and allowed to stand at room temperature, the former was converted into a mixture of **5a**, **6a**, **7a** (total 20%; ratio 90:5:5), **8a** (36%), and **9a** (trace) after 19 h, and the latter to a mixture of **5e**, **6e** (total 30%; ratio 99:1), **8e** (33%), and **9e** (trace) after 66 h. These results are fairly comparable to those in the ylide formation reaction of **2a** and **2e** (compare to entries 1 and 9 in Table II). Thus, all reaction products **5**–**9** in the reaction of **2** with cesium fluoride are apparently produced via only intermediate **4**. Compound **5** is formed in two sequential rearrangement steps: the [2,3] sigmatropic rearrangement from **3** to **4** and then the [1,3] rearrangement from **4** to **5**. There is no direct [1,2] migration from **3** to **5**.

Scheme II



Although [1,3] sigmatropic migration of alkyl group is allowed suprafacially (with inversion of the configuration) or antarafacially,[8] both are extremely difficult in **4**. Stevens rearrangement has been known to occur via radical cage intermediates in which a CIDNP enhancement of the NMR signal is observed and radical coupling products are formed.[9]

The carbon–carbon bond of **4** may be cleaved homolytically to give a radical pair **10** and **11** in Scheme II.

(6) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Chem. Soc., Chem. Commun.* **1988**, 370; *J. Org. Chem.* **1989**, *54*, 836.
(7) Shirai, N.; Watanabe, Y.; Sato, Y. Unpublished results.
(8) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, 1987; p 1155.
(9) (a) Lepley, A. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1460. (b) Dolling, U. H.; Closs, G. L.; Cohen, A. H. *J. Chem. Soc., Chem. Commun.* **1975**, 545.

Table III. *N,N*-Dialkyl-*N*-(substituted benzyl)-1-(trimethylsilyl)alkylammonium Iodides (2)[a]

	mp, °C	IR (Nujol), cm^{-1}	^{1}H NMR ($CDCl_3$),[e] δ
2a	169–170[b]	1265, 860, 735, 705	0.40 (s, 9 H), 1.70 (d, 3 H, *J* = 8), 3.22 (s, 6 H), 3.90 (q, 1 H, *J* = 8), 4.92 (s, 2 H), 7.38–7.85 (m, 5 H)
2b	147–148[c,d]	1255, 850, 765, 710	0.38 (s, 9 H), 1.56 (t, 3 H, *J* = 7.2), 1.66 (d, 3 H, *J* = 7.5), 3.09 (s, 3 H), 3.16–3.25 (m, 1 H), 3.53–3.61 (m, 2 H), 4.71 and 4.74 (AB q, 2 H, *J* = 13.1), 7.45–7.51 (m, 3 H), 7.65 (m, 2 H) 0.42 (s, 9 H), 1.44 (t, 3 H, *J* = 7.1), 1.69 (d, 3 H, *J* = 7.5), 3.11 (s, 3 H), 3.05–3.25 (m, 1 H), 3.53–3.81 (m, 2 H), 4.35 and 4.91 (AB q, 2 H, *J* = 12.8), 7.45–7.51 (m, 3 H), 7.61 (m, 2 H)
2c	153–154[c]	1260, 850, 760, 730	0.40 (s, 9 H), 1.24 (t, 3 H, *N* = 7), 0.65–1.65 (m, 2 H), 3.17 (s, 6 H), 3.60–3.90 (m, 1 H), 4.86 (b s, 2 H), 7.30–7.80 (m, 5 H)
2d	182–182.5[c]	1255, 850, 770, 735	0.41 (s, 9 H), 0.94 (t, 3 H, *J* = 7.2), 1.37–1.57 (m, 3 H), 1.65–1.73 (m, 1 H), 1.81–1.90 (m, 1 H), 2.09–2.17 (m, 1 H), 3.15 (s, 3 H), 3.20 (s, 3 H), 3.84 (t, 1 H, *J* = 4.7), 4.86 and 4.91 (AB q, 2 H, *J* = 12.6), 7.45–7.53 (m, 3 H), 7.69 (d, 2 H, *J* = 6.4)
2e	139–140[c]	1250, 1030, 1260, 850	0.34 (s, 9 H), 1.63 (d, 3 H, *J* = 8), 3.13 (s, 6 H), 3.72 (q, 1 H, *J* = 8), 3.76 (s, 3 H), 4.79 (s, 2 H), 6.87 (d, 2 H, *J* = 9), 7.52 (d, 2 H, *J* = 9)

[a] Satisfactory analytical data (±0.3% for C, H, and N) were submitted for review. [b] Recrystallized from EtOH. [c] Recrystallized from a mixture of acetone and hexane. [d] A mixture of diastereomers (the ratio 4:1 was determined from the proton ratios in ^{1}H NMR after recrystallization). [e] *J* values are in herz.

Table IV. *N,N*-Dialkyl-1-alkyl-2-(4-substituted phenyl)ethylamines (5)[a]

	bp,[b] °C (press., mmHg)	IR (film), cm^{-1}	^{1}H NMR ($CDCl_3$),[c] δ
5a	110 (21)	740, 700	0.92 (d, 3 H, *J* = 6.6), 2.33 (s, 6 H), 2.38 (dd, 1 H, *J* = 9.8 and 12.9), 2.79 (ddq, *J* = 4.0, 9.9, and 6.6), 2.98 (dd, *J* = 4.0 and 12.8), 7.15–7.20 (m, 3 H), 7.25–7.29 (m, 2 H)
5b	155 (45)	735, 700	0.97 (t, 3 H, *J* = 7), 1.15 (d, 3 H, *J* = 8), 2.26 (s, 3 H), 2.03–3.20 (m, 5 H), 7.13 (s, 5 H)
5c	130 (36)	730, 700	0.84 (t, 3 H, *J* = 7.5), 1.32–1.45 (m, 2 H), 2.32 (s, 6 H), 2.34 (dd, 1 H, *J* = 9.0 and 13.2), 2.50–2.57 (m, 1 H), 2.92 (dd, 1 H, *J* = 4.4 and 13.2), 7.15–7.29 (m, 5 H)
5d	115 (10)	745, 700	0.82 (t, 3 H, *J* = 7.2), 1.10–1.44 (m, 6 H), 2.31 (s, 6 H), 2.32 (dd, 1 H, *J* = 9.0 and 13.2), 2.58–2.65 (m, 1 H), 2.92 (dd, 1 H, *J* = 4.4 and 13.2), 7.15–7.19 (m, 3 H), 7.25–7.28 (m, 2 H)
5e	150 (24)	1250, 1040, 750	0.90 (d, 3 H, *J* = 6.6), 2.32 (s, 6 H), 2.33 (dd, 1 H, *J* = 9.7 and 13.1), 2.68–2.77 (m, 1 H), 2.90 (dd, 1 H, *J* = 4.1 and 13.1), 3.79 (s, 3 H), 6.82 (d, 2 H, *J* = 8.6), 7.08 (d, 2 H, *J* = 8.6)

[a] Satisfactory analytical data (±0.3 for C, H, and N) were submitted for review. [b] Oven temperature of a Büchi Kugelrohr distillation apparatus. [c] *J* values are in hertz.

Recombination of these radicals affords **5** and **12**; the latter is subsequently isomerized to **7** by the [1,5] migration of a hydrogen. Toluenes **8** may be formed from **11** or the solvent. Dimerization of **10** forms **9**. Since bond dissociation energy between two tertiary carbons (71 kcal/mol) is lower than that between tertiary carbon and secondary carbon (76 kcal/mol),[10] the homolysis of the C–C bond may occur smoothly on **4** rather than on the intermediate (**4**, R^2 = H) from *N*-methylide. It is still unclear whether the [1,3] shift of hydrogen in the isomerization of **4** to **6** is an antarafacial sigmatropic movement or is a proton transfer in a proton dissociation–recombination pathway induced by its own basicity.

Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere. Hexamethylphosphoramide (HMPA) was dried by distillation under reduced pressure from sodium. Dimethylformamide (DMF) was distilled under reduced pressure from barium oxide. Acetonitrile was dried by distillation from P_2O_5. Cesium fluoride was dried at 190 °C under reduced pressure. ^{1}H NMR spectra were recorded on a JEOL JNM MH-100, FX-100, or GSX-400 spectrometer with Me_4Si as internal standard. IR spectra were obtained by using a JASCO IRA-2 spectrometer. Mass spectra were obtained by using a JEOL JMS-DX-300 GC mass spectrometer with either EI or CI ionization. Gas–liquid chromatographic analyses were carried out on a Gasukuro Kogyo Model 370 chromatograph with flame ionization detector using a 2-m, 10% Tergitol NP-35 on Uniport HP column. All melting points and boiling points are uncorrected.

***N*-Alkyl-*N*-methyl-*N*-(4-substituted benzyl)-1-(trimethylsilyl)alkylammonium Iodides (2a–e). General Procedure.** A solution of *N*-alkyl-*N*-(4-substituted benzyl)-1-(trimethylsilyl)alkylamine[5] (**1**, 10 mmol) and iodomethane or iodoethane (30 mmol) in acetonitrile (20 mL) was heated at reflux (the reaction time is shown in Table I). The solution was concentrated under reduced pressure, and the residue was recrystallized to give **2**. The solvents used for the recrystallization, the yields, and the characteristic data are summarized in Table III.

Reaction of 2a–e with CsF. General Procedure. Into a 20-mL flask equipped with a magnetic stirrer and a septum was placed **2a–e** (2 mmol) and CsF (1.5 g, 10 mmol). The flask was dried under reduced pressure and was flushed with an inert gas. HMPA or DMF (10 mL) was added to the flask with a syringe. The mixture was stirred at room temperature for the time shown in Table II and was then poured into 1.5% aqueous $NaHCO_3$ (200 mL) and extracted with ether (4 × 100 mL). The ethereal extract was washed with 1.5% aqueous $NaHCO_3$ (2 × 100 mL), concentrated to about 20 mL, and was then extracted with 10% HCl (3 × 10 mL). The acid extract was made alkaline with 30% NaOH and extracted with ether (3 × 10 mL). The ether layer was dried ($MgSO_4$) and concentrated under reduced pressure. Kugelrohr distillation of the residual oil gave a mixture of three amines, *N*-alkyl-*N*-methyl-1-(4-substituted benzyl)alkylamine (**5a–e**), *N*-alkyl-*N*-methyl-1-(2-methyl-5-substituted phenyl)alkylamine (**6a–e**), and *N*-alkyl-*N*-methyl-1-(4-methylphenyl)alkylamine (**7a–d**). The ratio of the products was calculated on the basis of the integrated values of the GLC. The yield and ratio are shown in Table II.

The ether layer remaining after extraction with 10% HCl was analyzed on a GLC column (10% Tergitol NP-35) and indicated the presence of 4-substituted toluenes (**8**) and bibenzyls (**9**). Identification of **6–9** was accomplished by comparison of the GC mass spectra with those of authentic samples. The yield of **8** was calculated by comparison of the integrated values of GLC with internal standard (propylbenzene). The spectral data of **5** are listed in Table IV.

6-[1-(Dimethylamino)ethyl]-5-methylene-1,3-cyclohexadiene (4a) and 6-[1-(Dimethylamino)ethyl]-2-methoxy-5-methylene-1,3-cyclohexadiene (4e). A mixture of **2a** or **2e** (2 mmol), CsF (1.5 g, 10 mmol), and HMPA (10 mL), prepared in a manner similar to that described above, was stirred at 10 °C for 30 min. The mixture was poured into 1.5% aqueous $NaHCO_3$

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Table V. Elemental Analysis of the New Compounds

compd	calcd C	calcd H	calcd N	found C	found H	found N
2a	46.28	7.21	3.85	46.13	7.03	3.52
2b	47.74	7.48	3.71	47.77	7.51	3.34
2c	47.74	7.48	3.71	47.50	7.25	3.64
2d	50.36	7.96	3.45	50.14	7.78	3.37
2e	45.80	7.17	3.56	45.51	7.17	3.28
5a	80.93	10.49	8.58	80.68	10.59	8.61
5b	81.30	10.80	7.90	81.34	11.01	7.88
5c	81.30	10.80	7.90	81.21	10.74	7.88
5d	81.89	11.29	6.82	81.68	11.33	6.70
5e	74.57	9.91	7.25	74.45	10.01	7.22

(200 mL) and was extracted with ether (4 × 100 mL). The ether layer was washed with 1.5% aqueous $NaHCO_3$ (2 × 100 mL), dried ($MgSO_4$), and concentrated. HPLC and ^1H NMR analyses of the residual oils indicated the presence of two isomeric amines, **4a** and **5a** or **4e** and **5e**. Their structures were confirmed by ^1H NMR and UV spectra. The yield of each compound was calculated from the mole ratio based on the proton ratios in ^1H NMR.

4a: ^1H NMR (C_6D_6) δ 1.08 (d, 3 H, J = 6.6 Hz, CH_3), 2.12 (s, 6 H, NCH_3), 2.35–2.40 (m, 1 H, CH), 3.53 (m, 1 H, CH), 4.80 (s, 1 H, $=CH_2$), 5.06 (s, 1 H, $=CH_2$), 5.63–5.66 (m, 1 H, —CH=), 5.90–5.95 (m, 2 H, —CH= × 2), 6.05 (d, 1 H, J = 10.3 Hz, —CH=); UV λ_{max} 311 nm (log ϵ was not determined due to insufficient purity).

4e: ^1H NMR ($CDCl_3$) δ 0.98 (d, 3 H, J = 6.5 Hz, CH_3), 2.14 (m, 1 H, CH), 2.34 (s, 6 H, NCH_3), 3.58 (s, 3 H, OCH_3), 3.63 (m, 1 H, CH), 4.72 (dd, 1 H, J = 4.9 and 2.2 Hz, —CH=), 4.90 (s, 1 H, $=CH_2$), 5.12 (s, 1 H, $=CH_2$), 5.64 (m, 1 H, —CH=), 6.14 (dd, 1 H, J = 0.7 and 9.9 Hz, —CH=); UV λ_{max} 318 nm (log ϵ 3.58).

Chemical Behavior of 4a and 4e in HMPA. A mixture of **4a** and **5a** or of **4e** and **5e**, obtained in a manner similar to that described above, was dissolved in HMPA (10 mL) and stirred at room temperature. After 19 h for **4a** or 66 h for **4e**, the UV absorption (λ_{max} 310–320 nm) of the solution had disappeared. The solution was poured into 1.5% aqueous $NaHCO_3$ (200 mL), and the mixture was extracted with ether (4 × 100 mL). The ethereal extract was washed with 1.5% aqueous $NaHCO_3$ (2 × 100 mL), concentrated to about 20 mL, and then extracted with 10% HCl (3 × 10 mL). The acid layer was made alkaline with 30% NaOH and extracted with ether (3 × 10 mL). The ether layer was dried ($MgSO_4$), concentrated, and distilled to give a mixture of **5**, **6**, and **7**. The ether layer remaining after the acid extraction was analyzed by GLC and GC mass spectra to determine the presence of **8** and **9**. The yields and ratio of the products were determined in a manner similar described above: **5a**, **6a**, and **7a** (total yield 20%; ratio 90:5:5), **8a** (36%), and **9a** (trace); **5e** and **6e** (total yield 30%; ratio 99:1), **8e** (33%), and **9e** (trace).

***N*,*N*-Dimethyl-1-(2-methylphenyl)ethylamine[11] (6a) and *N*,*N*-Dimethyl-1-(4-methylphenyl)ethylamine[11] (7a).** A mixture of dimethylamine hydrochloride (675 mg, 10 mmol), KOH (450 mg, 8 mmol), and MeOH (5 mL) was stirred for a few minutes. After the addition of 3A molecular sieves (about 1 g), the mixture was allowed to stand for 0.5 h. The supernatant of the above mixture was transferred to another flask, followed by addition of 2- (or 4-) methylacetophenone (268 mg, 2 mmol) and a solution of $NaBH_3CN$ (100 mg, 1.6 mmol) in MeOH (1 mL). After being stirred for 7 days at room temperature, the solution was mixed with 10% HCl (20 mL), and the mixture was washed with ether (2 × 10 mL). The acid layer was neutralized and extracted with ether. The extract was dried ($MgSO_4$), concentrated, and distilled to give **6a** (88 mg, 27%) or **7a** (235 mg, 72%).

6a: bp 115 °C (30 mmHg); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 6 Hz, CH_3), 2.16 (s, 6 H, NCH_3), 2.30 (s, 3 H, $PhCH_3$), 3.37 (q, 1 H, J = 6 Hz, CH), 6.99–7.47 (m, 4 H, Ar H).

7a: bp 115–102 °C (20 mmHg); ^1H NMR ($CDCl_3$) δ 1.33 (d, 3 H, J = 7 Hz, CH_3), 2.15 (s, 6 H, NCH_3), 2.29 (s, 3 H, $PhCH_3$), 3.18 (q, 1 H, J = 7 Hz, CH), 7.01 (s, 4 H, Ar H).

Elemental analyses of **2a–e** and **5a–e** are found in Table V.

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Registry No. **1** (R^1 = H, R^2 = R^3 = Me), 123701-29-1; **1** (R^1 = H, R^2 = Me, R^3 = Et), 123701-30-4; **1** (R^1 = H, R^2 = Et, R^3 = Me), 123701-31-5; **1** (R^1 = H, R^2 = Bu, R^3 = Me), 123701-32-6; **1** (R^1 = MeO, R^2 = R^3 = Me), 123701-33-7; **2a**, 123701-34-8; **2b** (diastereoisomer 1), 123701-35-9; **2b** (diastereoisomer 2), 123701-36-0; **2c**, 123701-37-1; **2d**, 123701-38-2; **2e**, 123701-39-3; **4a**, 123701-46-2; **4e**, 123701-47-3; **5a**, 4075-96-1; **5b**, 119290-77-6; **5c**, 2576-14-9; **5d**, 100874-84-8; **5e**, 26070-48-4; **6a**, 42142-24-5; **6b**, 123701-40-6; **6c**, 123701-42-8; **6d**, 123701-44-0; **6e**, 91553-19-4; **7a**, 42142-19-8; **7b**, 123701-41-7; **7c**, 123701-43-9; **7d**, 123701-45-1; **8a**, 108-88-3; **8e**, 104-93-8; 2-methylacetophenone, 577-16-2; 4-methylacetophenone, 122-00-9.

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α-Silyl Sulfones as Latent α-Sulfonyl Anions. Fluoride-Promoted Intramolecular 1,2-Additions to Aldehydes as the Basis of a New Cyclopentenylation Strategy[1]

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Conjugate addition of allylpotassium to vinyl sulfones **8** and **23** followed by carbon silylation provides α-silyl sulfones **9d** and **24b**. These materials are transformed to aldehydes **11** and **26**, which subsequently undergo smooth fluoride-induced cyclopentannulation giving β-hydroxy sulfones **13a** and **27**. Reductive cleavage of these alcohols affords cyclopentenyl-annulated compounds **14** and **28**.

Introduction

Utilization of the vinyl sulfone moiety as the focal point in a sequence involving conjugate addition (A to B, Scheme I) followed by electrophilic functionalization of the α-sulfonyl anion (B to C) represents a useful strategy for the rapid construction of complex substrates. Recent examples of this protocol are found in the total syntheses of PGE_2,[2] carbacyclin,[3] morphine,[4] and cephalotaxine.[5]

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