Synthesis of 5-Alkylidene-6-(dimethylamino)methyl-1,3-cyclohexadienes from α-Substituted Benzyldimethylammoniomethylides

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2-Substituted 5-alkylidene-6-(dimethylamino)methyl-1,3-cyclohexadienes (*E*)-**4** and (*Z*)-**4** were prepared by the reaction of α,4-disubstituted dimethyl[(trimethylsilyl)methyl]benzylammonium iodides **2** with cesium fluoride. Their *E*-isomers were stable at room temperature and could be used in the Diels–Alder reaction. Some related reactions are also described.

5-Methylene-1,3-cyclohexadienes (isotoluene derivatives), which are isomeric forms of toluene derivatives, were prepared by three independent routes by Baylouny,[1] Kopecky,[2] Pryor[3] and their co-workers, respectively, and investigations of properties were made by them and by Gajewski.[4] Although these compounds are useful in organic chemistry, their synthetic routes are very long, and application to synthetic chemistry is difficult.

We previously reported[5–8] that 6-[2-(dimethylamino)-alkyl]-5-methylene-1,3-cyclohexadienes which are intermediates in the Sommelet–Hauser rearrangement of benzyldimethylammoniomethanides were isolable at room temperature under non-basic conditions, and that their stabilities depend on the kinds of substituents on the triene bonds. Methoxy-substituted compounds were most stable and could be employed in further reactions (e.g. Diels–Alder reaction), however, the other compounds did not have the stability required for use in synthetic organic chemistry. We examined the synthesis of 5-alkylidene-6-(dimethylamino)methyl-1,3-cyclohexadiene **4** from 4,α-disubstituted benzyldimethylammoniomethanide **3** in the search of more stable isotoluenes.

The four required amines, 4 = substituted *N*-methyl-*N*-[(trimethylsilyl)methyl]-α-alkylbenzylamines **1a–d** were synthesized from the corresponding 4-substituted *N*-methyl-α-alkylbenzylamines with (iodomethyl)trimethylsilane. *N*-Methyl-*N*-(trimethylsilylmethyl)diphenylmethylamine (**1e**) was prepared starting from diphenylmethylamine. Quaternization of **1** to α,4-disubstituted benzyl dimethyl(trimethylsilylmethyl)ammonium iodides **2** was carried out by heating with iodomethane in acetonitrile (Tables 1 and 2).

Ammonium salts **2** were treated with cesium fluoride in dimethylformamide (DMF) or hexamethylphosphoric triamide (HMPT) (Table 3). When the reaction was quenched after 0.5 h of stirring at 10 °C, two geometrical isomers of 2-substituted 5-alkylidene-6-(dimethylamino)-methyl-1,3-cyclohexadienes, (*E*)-**4a–d** and (*Z*)-**4a–d**, were obtained together with 2-arylalkyl-*N*,*N*-dimethylamines (**5a–d**, Stevens rearrangement products) and (*E*)-1-aryl-1-alkenes (**6a–d**, Hofmann elimination products) from the reaction of the (α-alkylbenzyl)ammonium salts **2a–d** (entries 1, 5, 8, 11, 14). The (α-phenylbenzyl)ammonium salt **2e** gave (*E*)-5-benzylidene-6-(dimethylamino) methyl-1,3-cyclohexadiene (*E*)-**4e**, 2-benzyl-*N*,*N*-dimethylbenzylamine (**7e**, Sommelet–Hauser rearrangement product), *N*,*N*-dimethyl-2,2-diphenylethylamine (**5e**), and 4-benzyl-*N*,*N*-dimethylbenzylamine (**8**) (entry 17).

In the ^{1}H-NMR spectra of the two geometrical isomers (*E*)-**4** and (*Z*)-**4**, the chemical shifts of vinylic protons in the alkylidene groups appeared at lower magnetic field for the major isomers than for the minor isomers. However, observation of NOE for the vinylic protons failed, and we therefore temporarily assigned the major products to the *E*-isomers (*E*)-**4** and the minor to *Z*-isomers (*Z*)-**4** in this paper.

Table 1. 4-Substituted *N*-Methyl-*N*-(trimethylsilylmethyl)-α-alkylbenzylamines **1** Prepared

Product	Time (h)	Yield (%)	bp (°C)/Torr or mp (°C)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS δ, *J* (Hz)
1a	4	84	126–127.5/22	$C_{13}H_{23}NSi$ (221.4)	0.03 (s, 9H), 1.32 (d, 3H, *J* = 6.8), 1.78, 1.90 (AB-q, 2H, *J* = 14.3), 2.17 (s, 3H), 3.45 (q, 1H, *J* = 6.8), 7.20–7.34 (m, 5H)
1b	5	87	109.5–111/1.9	$C_{14}H_{25}NOSi$ (251.4)	0.02 (s, 9H), 1.29 (d, 3H, *J* = 6.8), 1.74, 1.88 (AB-q, 2H, *J* = 14.3), 2.14 (s, 3H), 3.43 (t, 1H, *J* = 6.8), 3.80 (s, 3H), 6.84 (d, 2H, *J* = 8.8), 7.23 (d, 2H, *J* = 8.8)
1c	7	71	132.5–133.5/19	$C_{14}H_{25}NSi$ (235.4)	0.02 (s, 9H), 0.86 (t, 3H, *J* = 7.3), 1.65–1.91 (m, 4H), 2.12 (s, 3H), 3.30 (dd, 1H, *J* = 5.7, 8.7), 7.19–7.45 (m, 5H)
1d	1	76	144–145/21	$C_{15}H_{27}NSi$ (249.5)	0.02 (s, 9H), 0.86 (t, 3H, *J* = 7.3), 1.08–1.29 (m, 2H), 1.57–1.95 (m, 4H), 2.12 (s, 3H), 3.30 (t, 1H, *J* = 7.0), 7.19–7.45 (m, 5H)
1e	2	63	59–60	$C_{18}H_{25}NSi$ (283.5)	0.05 (s, 9H), 1.84 (s, 2H), 2.14 (s, 3H), 4.18 (s, 1H), 7.10–7.48 (m, 10H)

[a] Satisfactory microanalyses obtained: C ±0.21, H +0.37, N +0.22.

Table 2. 4-Substituted Dimethyl(trimethylsilylmethyl)-α-alkylbenzylammonium Iodides **2** Prepared

Product	Time (h)	Yield (%)	mp (°C)[a]	Molecular Formula[b]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
2a	1	90	137–138.5	$C_{14}H_{26}INSi$ (363.2)	0.33 (s, 9H), 1.89 (d, 3H, J = 7.0), 3.21, 3.29 (AB-q, 2H, J = 14.5), 3.25 (s, 3H), 3.29 (s, 3H), 5.48 (q, 1H, J = 7.0), 7.44–7.48 (m, 3H), 7.70–7.71 (m, 2H)
2b	2	83	125–127	$C_{15}H_{28}INOSi$ (393.4)	0.33 (s, 9H), 1.87 (d, 3H, J = 6.9), 3.16, 3.26 (AB-q, 2H, J = 14.7), 3.21 (s, 3H), 3.26 (s, 3H), 3.83 (s, 3H), 5.41 (q, 1H, J = 6.9), 6.96 (d, 2H, J = 8.9)
2c	1	90	155–156	$C_{15}H_{28}INSi$ (377.2)	0.33 (s, 9H), 0.81 (t, 3H, J = 7.2), 2.04–2.29 (m, 1H), 2.37–2.45 (m, 1H), 3.24 (s, 3H), 3.26 (s, 2H), 3.30 (s, 3H), 5.23 (dd, 1H, J = 3.4, 12.2), 7.27–8.00 (m, 5H)
2d	1	88	158–158.5	$C_{16}H_{30}INSi$ (391.4)	0.33 (s, 9H), 0.94 (t, 3H, J = 7.2), 0.99–1.08 (m, 1H), 1.19–1.32 (m, 1H), 2.18–2.28 (m, 2H), 3.23 (s, 3H), 3.28 (s, 2H), 3.30 (s, 3H), 5.31 (dd, 1H, J = 4.6, 11.0), 7.28–7.90 (m, 5H)
2e	3	85	164–165.5	$C_{19}H_{28}INSi$ (425.2)	0.28 (s, 9H), 3.34 (s, 8H, $(CH_3)_2N$, CH_2Si), 7.02 (s, 1H), 7.30–8.18 (m, 10H)

[a] Recrystallized from a mixture of EtOAc and MeOH.
[b] Satisfactory microanalyses obtained: C ±0.31, H ±0.34, N ±0.38.

Table 3. Reaction of 4-Substituted Dimethyl(trimethylsilylmethyl)-α-alkylbenzylammonium Iodides **2** with CsF

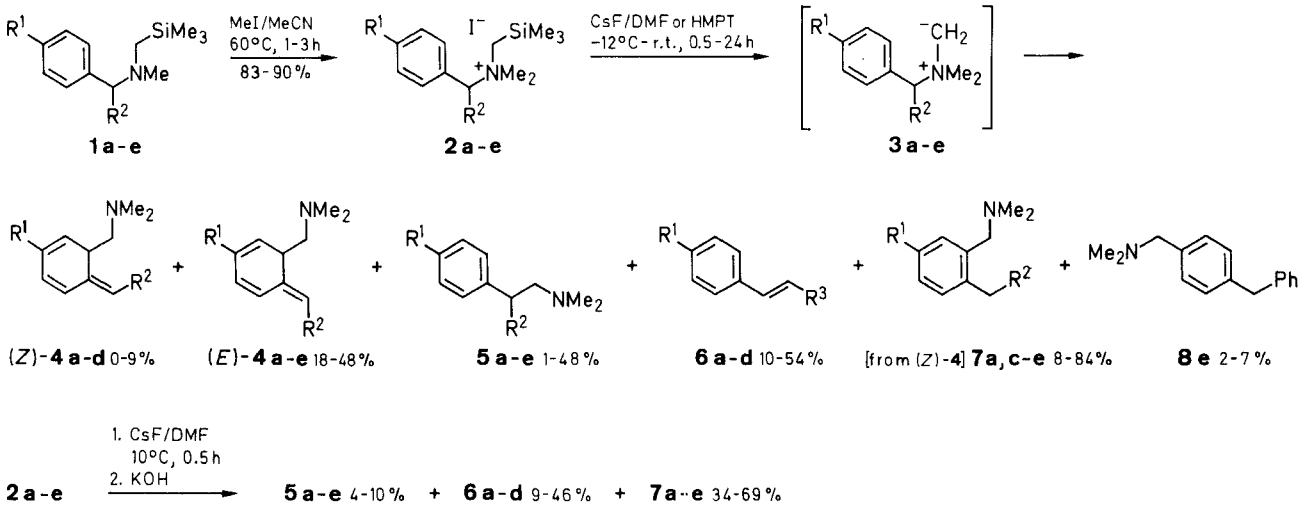
Entry	Reaction Conditions				Products Yield (%)[a]					Ratio
	Ammonium Salts, **2**		Temp. (°C)	Time (h)	(*E*)-**4**	(*Z*)-**4**	**7**	**5**	**6**	(*E*)-**4**/(*Z*)-**4**/**7**/**5**/**6**
1	**2a**	DMF	10	0.5	29	6	0	5	49	32:7:0:6:0:55
2	**2a**	DMF	r.t.	0.5	28	6	0	5	49	32:7:0:5:56
3	**2a**	DMF	r.t.	22	27	3	8	5	46	31:3:9:5:52
4	**2b**	DMF	−12	20	33	5	0	1	35	45:6:0:2:47
5	**2b**	DMF	10	0.5	30	7	0	4	37	39:9:0:5:47
6	**2b**	DMF	r.t.	0.5	24	8	0	7	39	31:10:0:9:50
7	**2b**	DMF	r.t.	24	22	7	0	7	41	28:9:0:9:54
8	**2b**	HMPT	10	0.5	34	9	0	5	30	44:11:0:7:38
9	**2b**	HMPT	r.t.	0.5	32	9	0	7	27	42:12:0:9:37
10	**2b**	HMPT	r.t.	22	18	7	0	6	54	21:8:0:7:64
11	**2c**	DMF	10	0.5	48	7	0	6	11	67:10:0:8:15
12	**2c**	DMF	r.t.	0.5	48	6	0	6	10	67:10:0:9:14
13	**2c**	DMF	r.t.	24	42	0	8	6	11	62:0:12:9:17
14	**2d**	DMF	10	0.5	45	6	0	7	14	63:8:0:9:20
15	**2d**	DMF	r.t.	0.5	45	6	0	7	15	62:8:0:9:21
16	**2d**	DMF	r.t.	24	48	0	9	7	11	64:0:12:9:15
17	**2e**	HMPT	10	0.5	43	0	30	10 + 2[b]	0	51:0:35:14[c]:0
18	**2e**	HMPT	r.t.	0.5	0	0	30	48 + 7[b]	0	0:0:35:65[c]:0
19	**2e**	HMPT[d]	r.t.	0.5	0	0	84	2	0	0:0:97:3:0

[a] Determined from the proton ratio of ^{1}H-NMR.
[b] 4-Benzyl-*N*,*N*-dimethylbenzylamine (**8**).
[c] Includes **8**.
[d] DBU (5 mole equivalents for **2e**) was added.

When the reactions were quenched after 0.5 h at room temperature, no appreciable changes were observed in the reaction products from **2a–d** (entries 2, 6, 9, 12, and 15); however, (*E*)-**4e** had disappeared and instead there was an increase of **5e** and **8** (entry 18). After 22–24 h of stirring, (*Z*)-**4a, c, d** were decreased and *N*,*N*-dimethyl-(2-alkylbenzyl)amines **7a, c, d** newly formed, though no change was observed in the amounts of (*E*)-**4a, c, d** (entries 3, 13, 16).

The Hofmann elimination process from the ylide **3a–d** having a β-hydrogen was a major reaction when the α-alkyl group (R^2) was methyl, although the [2,3]sigmatropic rearrangement process giving (*E*)-**4** and (*Z*)-**4** was preferable when R^2 was ethyl or propyl (entries 11–16). The rate of the two processes was not affected by changing the solvents or temperature (compare entries 4–10).

At room temperature, (*Z*)-**4a, c, d** were unstable and converted to the Sommelet–Hauser rearrangement products **7a, c, d**. (*Z*)-5-Benzylidene-6-(dimethylamino)methyl-1,3-cylcohexadiene (*Z*)-**4e** may be unstable and converted to **7e** at 10 °C. The *E*-isomers (*E*)-**4a–d** were stable at room temperature and extracted with 10% citric acid without appreciable isomerization, however, further purification was difficult because they were



1–7	R^1	R^2	R^3
a	H	Me	H
b	MeO	Me	H
c	H	Et	Me
d	H	Pr	Et
e	H	Ph	–

Scheme 1

Table 4. Reaction Products from **2** with CsF at 10°C for 0.5 h Followed by Treatment with KOH

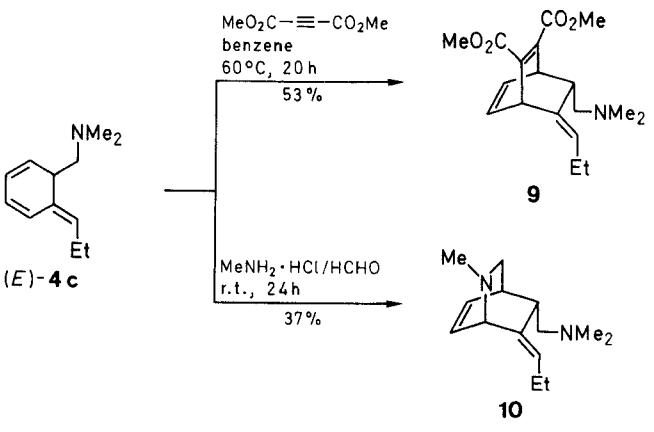
Entry	Ammonium Salts, **2**	Reaction Conditions		Products Yield (%)[a]					Ratio (*E*)-**4**/(*Z*)-**4**/**7**/**5**/**6**
		Temp. (°C)	Time (h)	(*E*)-**4**	(*Z*)-**4**	**7**	**5**	**6**	
1	**2a**	60	24	0	0	34	5	46	0:0:40:6:54
2	**2b**	60	72	0	0	37	4	34	0:0:50:5:45
3	**2c**	60	24	0	0	56	5	9	0:0:80:7:13
4	**2d**	60	24	0	0	50	6	13	0:0:73:8:19
5	**2e**	25	6	0	0	69	10 + 1[b]	0	0:0:86:14[c]:0

[a] Determined from the proton ratio in the ^{1}H-NMR.
[b] 4-Benzyl-*N*,*N*-dimethylbenzylamine **8**.
[c] Includes **8**.

partially isomerized on alumina columns during elution. It is interesting that (*E*)-**4e** was unstable at room temperature and converted to **5e** and **8**, but not to **7e**.

When the reaction mixtures after 0.5 h at 10°C were subsequently dissolved in 10% potassium hydroxide solution in ethanol and heated at 60°C, (*E*)-**4a–d** and (*Z*)-**4a–d** were slowly changed into **7a–d** (Table 4). The conversion of (*E*)-**4e** to **7e** occurred at room temperature. This result indicates that the presence of a base is essential in aromatization of (*E*)-**4e** to **7e**; under a non-basic condition, (*E*)-**4e** changed to **5e** and **8** apparently via radical dissociation and recombination process of the *C*,*C* bond.[5] Indeed, when the reaction of **2e** was carried out in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), **7e** was predominantly formed and the formation of **5e** and **8** was suppressed (entry 19 in Table 3).

Diels–Alder reaction of (*E*)-**4c** with dimethyl acetylenedicarboxylate or *N*-methylenemethylamine gave dimethyl 8-dimethylaminomethyl-7-propylidenebicyclo-[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**9**) or 8-dimethylaminomethyl-2-methyl-7-propylidene-2-azabicyclo-[2.2.2]octa-5-ene (**10**) (Scheme 2).



Scheme 2

Table 5. Mixtures of Three Isomers; **7**,**5** and **8**

Amines	Ratio[a]	bp (°C)[b]/Torr	Molecular Formula[c]
7a[d] + **5a**[e]	87:13	100/11	$C_{11}H_{17}N$ (163.3)
7b + **5b**	90:10	150/17	$C_{12}H_{19}NO$ (193.3)
7c + **5c**[f]	92:8	110/12	$C_{12}H_{19}N$ (177.3)
7d + **5d**[f]	89:11	105/18	$C_{13}H_{21}N$ (191.3)
7e + **5e**[h] + **8**	86:12:2	200/23	$C_{16}H_{19}N$ (225.3)

[a] Determined from the proton ratios of ^{1}H-NMR.
[b] Oven temperature of Büchi Kugelrohr distillation apparatus.
[c] Satisfactory microanalyses obtained: C ± 0.37, H ± 0.24, N ± 0.24.
[d] Ref. 10, bp was not reported.
[e] Ref. 11, bp 46–47 °C/2 Torr.
[f] Ref. 12, bp 94–95 °C/10 Torr.
[g] Ref. 13, bp 101–104 °C/5.3 Torr.
[h] Ref. 14, bp was not reported.

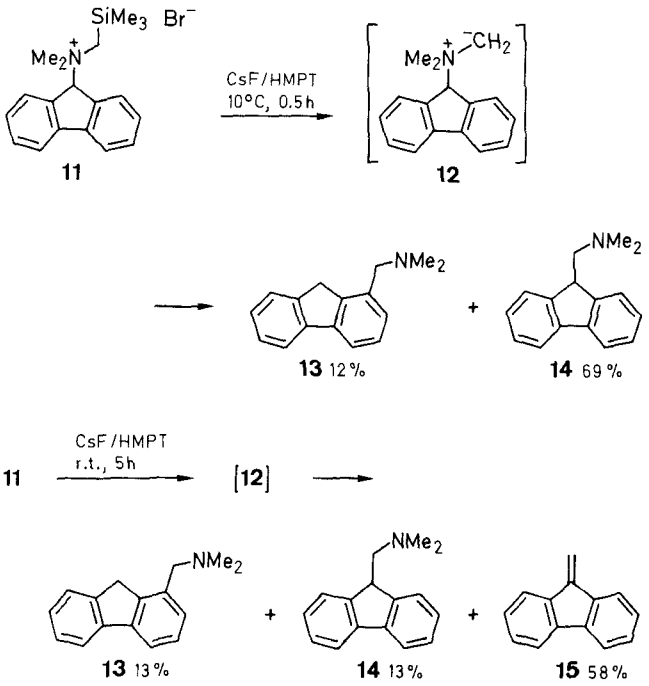
Table 6. ^{1}H-NMR Spectra of (*E*)-**4**, (*Z*)-**4**, **5**, **7**, and **8**

Compound	^{1}H-NMR ($CDCl_3$/TMS) δ, *J* (Hz)
(*E*)-**4a**	1.73 (d, 3H, *J* = 7.1, $CHC\underline{H}_3$), 1.98 (dd, 1H, *J* = 4.5, 11.4, CH_2N), 2.28 (s, 6H, NCH_3), 2.59 (dd, 1H, *J* = 11.4, 11.4, CH_2N), 3.55–3.59 (m, 1H, 6-H), 5.52–5.58 (m, 1H, $=C\underline{H}CH_3$), 5.68–5.71 (m, 1H, 3-H), 5.95–6.06 (m, 3H, 1-H, 2-H, 4-H)
(*Z*)-**4a**	1.74 (d, 3H, *J* = 7.2, $CHC\underline{H}_3$), 2.00 (dd, 1H, *J* = 5.7, 11.0, CH_2N), 2.25 (s, 6H, NCH_3), 2.66 (dd, 1H, *J* = 11.0, 11.0, CH_2N), 3.09–3.17 (m, 1H, 6-H), 5.30–5.38 (m, 1H, $=C\underline{H}CH_3$), 5.78–5.86 (m, 1H, 3-H), 6.00–6.06 (m, 2H, 1-H, 2-H), 6.34–6.36 (m, 1H, 4-H)
(*E*)-**4b**	1.72 (d, 3H, *J* = 7.1, $CHC\underline{H}_3$), 1.98 (dd, 1H, *J* = 4.0, 11.7, CH_2N), 2.28 (s, 6H, NCH_3), 2.47 (dd, 1H, *J* = 11.7, 11.7, CH_2N), 3.56–3.78 (m, 1H, 6-H), 3.58 (s, 3H, OCH_3), 4.96 (dd, 1H, *J* = 5.7, 2.4, 1-H), 5.54–5.60 (m, 2H, $=C\underline{H}CH_2$, 3-H), 6.04 (d, 1H, *J* = 9.4, 4-H)
(*Z*)-**4b**	1.75 (d, 3H, *J* = 7.1, $CHC\underline{H}_3$), 2.02 (dd, 1H, *J* = 5.5, 11.9 CH_2N), 2.25 (s, 6H, NCH_3), 2.52 (dd, 1H, *J* = 11.9, 11.9, CH_2N), 3.12–3.18 (m, 1H, 6-H), 3.56 (s, 3H, OCH_3), 4.91 (dd, 1H, *J* = 2.3, 5.7, 1-H), 5.37–5.43 (m, 1H, $=C\underline{H}CH_3$), 5.69 (d, 1H, *J* = 10.3, 3-H), 6.41 (d, 1H, *J* = 10.3, 4-H)
(*E*)-**4c**	1.03 (t, 3H, *J* = 7.5, $CH_2C\underline{H}_3$), 1.94 (dd, 1H, *J* = 4.6, 11.7, CH_2N), 2.05–2.20 (m, 2H, $C\underline{H}_2CH_3$), 2.27 (s, 6H, NCH_3), 2.62 (dd, 1H, *J* = 11.7, 11.7, CH_2N), 3.49–3.54 (m, 1H, 6-H), 5.43 (t, 1H, *J* = 7.9, $=C\underline{H}CH_2$), 5.70 (dd, 1H, *J* = 5.9, 9.4, 3-H), 5.95–6.05 (m, 3H, 1-H, 2-H, 4-H)
(*Z*)-**4c**	1.00 (t, 3H, *J* = 7.5, $CH_2C\underline{H}_3$), 2.05–2.20 (m, 2H, $C\underline{H}_2CH_3$), 1.96 (dd, 1H, *J* = 6.6, 11.3, CH_2N), 2.26 (s, 6H, NCH_3), 2.71 (dd, 1H, *J* = 11.3, 11.3, CH_2N), 3.08–3.15 (m, 1H, 6-H), 5.24–5.26 (m, 1H, $=C\underline{H}CH_2$), 5.79–5.82 (m, 1H, 3-H), 5.95–6.05 (m, 3H, 1-H, 2-H, 4-H)
(*E*)-**4d**	0.94 (t, 3H, *J* = 7.3, $CH_2C\underline{H}_3$), 1.41–1.47 (m, 2H, $C\underline{H}_2CH_3$), 1.95 (dd, 1H, *J* = 4.6, 11.6, CH_2N), 2.01–2.16 (m, 2H, $C\underline{H}_2Et$), 2.27 (s, 6H, NCH_3), 2.62 (dd, 1H, *J* = 11.6, 11.6, CH_2N), 3.49–3.56 (m, 1H, 6-H), 5.43–5.48 (m, 1H, $=C\underline{H}CH_2$), 5.67–5.72 (m, 1H, 3-H), 5.95–6.06 (m, 3H, 1-H, 2-H, 4-H)
(*Z*)-**4d**	0.91 (t, 3H, *J* = 7.3 $CH_2C\underline{H}_3$), 1.41–1.47 (m, 2H, $C\underline{H}_2CH_3$), 1.97 (dd, 1H, *J* = 6.0, 11.4, CH_2N), 2.01–2.16 (m, 2H, $C\underline{H}_2Et$), 2.26 (s, 6H, NCH_3), 2.72 (dd, 1H, *J* = 11.4, 11.4 CH_2N), 3.09–3.16 (m, 1H, 6-H), 5.24–5.28 (m, 1H, $=C\underline{H}CH_2$), 5.74–5.82 (m, 1H, 3-H), 5.95–6.05 (m, 3H, 1-H, 2-H, 4-H)
(*E*)-**4e**	2.14 (dd, 1H, *J* = 4.4, 11.9, CH_2N), 2.18 (s, 6H, NCH_3), 2.67 (dd, 1H, *J* = 11.9, 11.9, CH_2N), 4.02–4.07 (m, 1H, 6-H), 5.88–5.91 (m, 1H, 3-H), 6.04–6.11 (m, 2H, 1-H, 2-H), 6.16 (dd, 1H, *J* = 1.0, 9.5, 4-H), 6.45 (s, 1H, =CHPh), 7.10–7.73 (m, 5H)
5a	1.26(d, 3H, *J* = 6.1), 2.22 (s, 6H), 2.40 (m, 2H), 2.71–2.92 (m, 1H), 7.12–7.44 (m, 5H)
5b	1.23 (d, 3H, *J* = 7.0), 2.22 (s, 6H), 2.36–2.42 (m, 2H), 2.83–2.89 (m, 1H), 3.79 (s, 3H), 6.85 (d, 2H, *J* = 8.6), 7.13 (d, 2H, *J* = 8.6)
5c	0.76 (t, 3H, *J* = 7.3), 1.43–1.60 (m 1H), 1.76–187 (m, 1H), 2.20 (s, 6H), 2.43–2.47 (m, 2H), 2.54–2.67 (m, 1H), 7.11–7.31 (m, 5H)
5d	0.84 (t, 3H, *J* = 7.3), 1.05–1.21 (m, 2H), 1.67–1.78 (m, 2H), 2.20 (s, 6H), 2.49–2.62 (m, 2H), 2.77–2.85 (m, 1H), 7.12–7.46 (m, 5H)
5e	2.26 (s, 6H), 2.89 (d, 2H, *J* = 7.8), 4.16 (t, 1H, *J* = 7.8), 7.10–7.30 (m, 10H)
6d[a]	1.09 (t, 3H, *J* = 7.5), 2.16–2.26 (m, 2H), 6.27 (dt, 1H, *J* = 6.2, 15.8), 6.38 (d, 1H, *J* = 15.8), 7.10–7.52 (m 5H)
7a	1.21 (t, 3H, *J* = 7.5), 2.23 (s, 6H), 2.74 (q, 2H, *J* = 7.5), 3.40 (s, 2H), 7.12–7.28 (m, 4H)
7b	1.18 (t, 3H, *J* = 7.6), 2.24 (s, 6H), 2.66 (q, 2H, *J* = 7.6), 3.37 (s, 2H), 3.79 (s, 3H), 6.75 (dd, 1H, *J* = 2.8, 8.3), 6.86 (d, 1H, *J* = 2.8), 7.08 (d, 1H, *J* = 8.3)
7c	0.99 (t, 3H, *J* = 7.3), 1.56–1.67 (m, 2H), 2.24 (s, 6H), 2.67 (t, 2H, *J* = 7.9), 3.39 (s, 2H), 7.12–7.29 (m, 4H)
7d	0.95 (t, 3H, *J* = 7.3), 1.33–1.45 (m, 2H), 1.49–1.59 (m, 2H), 2.24 (s, 6H), 2.69 (t, 2H, *J* = 7.9), 3.42 (s, 2H), 7.12–7.52 (m, 4H)
7e	2.20 (s, 6H), 3.32 (s, 2H), 4.15 (2H), 7.10–7.29 (m, 9H)
8	2.22 (s, 6H), 3.38 (s, 2H), 3.97 (s, 2H), 7.13–7.30 (m, 9H)

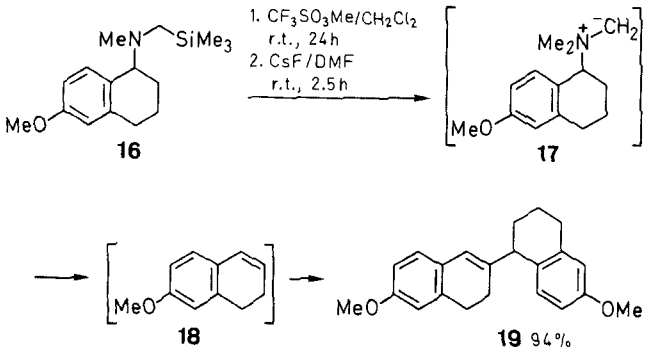
[a] Ref. 15.

Treatment of (9-fluorenyl)dimethyl(trimethylsilylmethyl)-ammonium bromide (**11**) with cesium fluoride at 10 °C for 0.5 h gave 1-(dimethylaminomethyl)fluorene (**13**, Sommelet–Hauser rearrangement product) and 9-(dimethylaminomethyl)fluorene (**14**, Stevens rearrangement product). The presence of an intermediate isotoluene was not detected. Compound **14** changed partially to dibenzofulvene (**15**)[6] when the reaction was quenched after 5 h at room temperature (Scheme **3**).

Dimethyl(6-methoxy-1,2,3,4-tetrahydronaphthyl)-ammoniomethanide (**17**), similarly produced from *N*-methyl-*N*-(trimethylsilyl)methyl-6-methoxy-1,2,3,4-tetrahydronaphthylamine (**16**), methyl trifluoromethanesulfonate, and cesium fluoride, changed to 7-methoxy-3-(6-methoxy-1,2,3,4-tetrahydronaphthyl)-1,2-dihydronaphthalene (**19**) in high yield. Compound **19** may be formed by dimerization of 7-methoxy-1,2-dihydronaphthalene (**18**), which is a Hofmann elimination product of **17** (Scheme **4**).



Scheme 3



Scheme 4

DMF was dried by distillation from BaO under reduced pressure. CsF was dried (P_2O_5) at 190°C under reduced pressure. Hexamethylphosphoric triamide (HMPT) was distilled under reduced pressure from sodium. ^{1}H-NMR spectra were recorded at 400 MHz. Aluminum oxide (Merck, Aluminum oxide 90, 70–230 mesh) was used for column chromatographies. All melting and boiling points are uncorrected.

4-Substituted *N*-Methyl-*N*-(trimethylsilylmethyl)-α-alkylbenzylamines 1a–d; General Procedure:

A mixture of 4-substituted *N*-methyl-α-alkylbenzylamines (20 mmol) and (iodomethyl)trimethylsilane (10 mmol) in DMSO (10 mL) is stirred at 100°C for the time listed in Table 1. The mixture is poured into H_2O (10 mL) and extracted with Et_2O (4 × 30 mL). The ethereal extract is washed with H_2O (2 × 50 mL), dried ($MgsO_4$), and concentrated under reduced pressure, and the crude product is purified on an aluminum oxide column (hexane/Et_2O, 49:1) (Table 1).

***N*-Methyl-*N*-(trimethylsilylmethyl)diphenylmethylamine (1e):**

A solution of diphenylmethylamine (21.6 g, 118 mmol) and (iodomethyl)trimethylsilane (11.8 g, 55 mmol) in DMSO (50 mL) is heated for 4 h and treated in a manner similar to that described for **1a–d** to give *N*-(trimethylsilylmethyl)diphenylmethylamine; yield: 13.7 g (92%); bp 111–114°C/0.45 Torr; mp 39.5–40°C.

$C_{17}H_{23}NSi$ (269.5) calc. C 75.78 H 8.60 N 5.20 found 75.74 8.60 5.18

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.03 (s, 9H, $SiCH_3$), 1.24 (s, 1H, NH), 2.98 (s, 2H, CH_2Si), 4.66 (s, 1H, CHN), 7.04–7.44 (m, 10H_{arom})

A mixture of *N*-(trimethylsilylmethyl)diphenylamine (4.0 g, 15 mmol), formaldehyde (15 mL, 35% solution in H_2O), and MeOH (40 mL) is heated at reflux for 2 h. After the addition of $NaBH_4$ (2.0 g, 53 mmol) to the mixture at 0°C, the mixture is stirred for 2 h at r.t. H_2O (30 mL) is added to the mixture, then MeOH is removed under reduced pressure. The aqueous residue is extracted with Et_2O (5 × 100 mL). The extract is dried ($MgSO_4$), filtered, and concentrated under reduced pressure, and the product is purified on an aluminum oxide column (hexane) (Table 1).

4-Substituted α-Alkylbenzyldimethyl(trimethylsilylmethyl)ammonium Iodides 2a–e; General Procedure:

A solution of **1** (10 mmol) and MeI (8.5 g, 60 mmol) in MeCN (10 mL) is stirred at 60°C for the time shown in Table 2. The solvent is removed and the residue is recrystallized from a mixture of AcOEt and MeOH to give **2a–e** (Table 2).

Reaction of Compounds 2a–e with Cesium Fluoride; General Procedure:

In a 30 mL flask equipped with a magnetic stirrer and a septum is placed **2** (2 mmol) and anhydrous CsF (1.52 g, 10 mmol). The flask is dried under reduced pressure and is flushed with N_2. Anhydrous DMF (10 mL) is added to the flask with a syringe and the mixture is stirred under the conditions listed in Table 3. The mixture is poured into 2% $NaHCO_3$ (200 mL) and extracted with Et_2O (4 × 50 mL). The ethereal extract is washed with 2% $NaHCO_3$ (2 × 100 mL), and is extracted with 5% citric acid (4 × 50 mL). The acid extract is made at pH 8 with 5% $NaHCO_3$ and extracted with Et_2O (4 × 100 mL). The extract is dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a mixture of the 2-substituted (*E*)- and (*Z*)-5-alkylidene-6-(dimethylamino)methyl-1,3-cyclohexadiene (*E*)-**4** and (*Z*)-**4**, 2-aryl-*N*,*N*-dimethylalkylamines **5**, 5-substituted 2-alkyl-*N*,*N*-dimethylbenzylamines **7**, and 4-benzyl-*N*,*N*-dimethylbenzylamine (**8**). The ether layer after the acid extraction is dried ($MgSO_4$) and concentrated to give the (*E*)-1-aryl-1-alkenes **6**. Ratios of the products are determined from the proton ratios of ^{1}H-NMR of the mixture (Table 3). ^{1}H-NMR data of **4**, **5**, **7**, and **8** are listed in Table 6. The structures of **6a**, **b**, **c** are determined by comparison with authentic samples on the market.

Reaction of 2e with CsF in the presence of DBU:

In a manner similar to that described above, **2e** (851 mg, 2.0 mmol) and CsF (1.52 g, 10 mmol) are placed in a flask and DBU (1.64 g, 10.8 mmol) and anhydrous HMPT (10 mL) are then added by syringe. After 0.5 h of stirring at r.t., the mixture is poured into 2% $NaHCO_3$ and extracted with Et_2O. The extract is washed with 2% $NaHCO_3$, dried ($MgSO_4$), filtered, concentrated, and distilled to give a mixture of **7e** and **5e**; bp 200°C/25 Torr (oven temperature of Kugelrohr distillation apparatus); yield: 390 mg (86%, **7e**/**5e**, 97:3).

Dimethyl 8-Dimethylaminomethyl-7-propylidenebicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (9):

A mixture of **2c** (1.0 g, 2.6 mmol) and CsF (1.5 g, 10 mmol) in DMF (10 mL) is treated at 10°C for 0.5 h according to the general procedure described above. The crude **4c** (233 mg, purity 90% (^{1}H-NMR)) obtained after the acid extraction, is mixed with dimethyl acetylenedicarboxylate (520 mg, 3.7 mmol) in benzene (10 mL). The mixture is stirred at 60°C for 20 h, then extracted wtih 10% HCl (2 × 10 mL) and with H_2O (10 mL). The aqueous extracts are combined and made alkaline with 20% NaOH and extracted with Et_2O (4 × 50 mL). The extract is dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue is chromatographed on an aluminum oxide column (hexane/Et_2O, 9:1) to give **9**; yield: 182 mg (53%); bp 140°C/0.06 Torr (Kugelrohr).

$C_{18}H_{25}NO_4$ calc. C 67.69 H 7.89 N 4.39
(319.4) found 67.63 8.00 4.34

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.94 (t, 3H, $J \approx 7.5$ Hz, CH_2CH_3), 1.87–2.06 (m, 2H, CH_2CH_3), 2.22 (s, 6H, NCH_3), 2.23 (d, 2H, J = 7.7 Hz, NCH_2), 2.48–2.50 (m, 1H, 8-H), 3.76 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.27–4.29 (m, 2H, 1-H, 4-H), 5.31 (t, 1H, J = 7.2 Hz, -CH=), 6.38 (t, 1H, J = 5.8 Hz, -CH=), 6.53 (t, 1H, J = 5.8 Hz, -CH=).

8-Dimethylaminomethyl-2-methyl-7-propylidene-2-azabicyclo-[2.2.2]octa-5-ene (10):

A solution of **4c** (purity 90%, 185 mg, 1.0 mmol), methylamine hydrochloride (2.5 M aq sol., 0.76 mL, 1.9 mmol), and HCHO (35% aq. sol., 0.16 mL, 1.9 mmol) is stirred at r.t. for 24 h. The mixture is poured into 20% NaOH (10 mL) and extracted with Et_2O (4 × 20 mL). The ethereal extract is dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue is purified on an aluminum oxide column (EtOAc/hexane, 4:1 to 100:0) to give **10**; yield: 84 mg (37%); bp 150°C/10 Torr (Kugelrohr).

$C_{14}H_{24}N_2$ calc. C 76.31 H 10.98 N 12.71
(220.4) found 76.53 11.09 12.34

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.00 (t, 3H, J = 7.4 Hz, CH_2CH_3), 2.00–2.18 (m, 4H, CH_2CH_3 and NCH_2), 2.21 (s, 6H, NCH_3), 2.22 (s, 3H, NCH_3), 2.35 (dd, 1H, J = 1.5 Hz, 9.8 Hz, 3-H), 2.46–2.49 (m, 1H, 8-H), 2.54 (dd, 1H, J = 3.1 Hz, 9.8 Hz, 3-H), 2.83–2.88 (m, 1H, 4-H), 3.30 (dd, 1H, J = 1.0 Hz, 5.7 Hz, 1-H), 5.16–5.20 (m, 1H, =CH-Et), 6.30 (t, 1H, J = 7.1 Hz, 5-H), 6.42–6.46 (m, 1H, 6-H).

(9-Fluorenyl)dimethyl(trimethylsilylmethyl)ammonium Bromide (11):

A mixture of 9-bromofluorene (4.90 g, 20 mmol) and (dimethylaminomethyl)trimethylsilane (4.65 g, 20 mmol) in MeCN (30 mL) is stirred at r.t. for 1 h. The solvent is removed under reduced pressure and the residue is recrystallized from a mixture of EtOAc and MeOH to give **11**; yield: 7.06 g (93.8%); mp 176–178°C.

$C_{19}H_{26}BrNSi$ calc. C 60.63 H 6.96 N 3.72
(376.4) found 60.29 6.87 3.65

^{1}H-NMR ($CDCl_3$/TMS): $\delta \approx 0.25$ (s, 9H, CH_3Si), 2.98 (s, 2H, CH_2Si), 3.51 (s, 6H, CH_3N), 6.61 (s, 1H, NCH), 7.18–7.88 (m, 8 H_{arom}).

Reaction of 11 with CsF:

In a manner similar to that described for the reaction of **2a–e** with CsF, a mixture of **11** (753 mg, 2 mmol) and CsF (1.52 g, 10 mmol) in HMPT (10 mL) is stirred at 10°C for 0.5 h. The ethereal extract is distilled under reduced pressure to give a mixture of 1-(dimethylaminomethyl)fluorene **(13)** and 9-(dimethylaminomethyl)-fluorene **(14)**[6]; yield: 352 mg (81%); bp 150°C/40 Torr; **13/14** (15:85) (determined from the proton ratio of ^{1}H-NMR).

$C_{16}H_{17}N$ calc. C 86.06 H 7.67 N 6.27
(223.3) found 86.37 7.79 6.04

The sample of **13** is isolated on an aluminum oxide column (Et_2O/hexane, 9:1).

13: ^{1}H-NMR ($CDCl_3$/TMS): δ = 2.28 (s, 6H, NCH_3), 3.55 (s, 2H, CH_2N), 3.92 (S, 2H), 7.25–7.79 (m, 7H).

A similar reaction is quenched after 5 h at r.t. and the ethereal extract is extracted with 10% HCl. The ether layer is dried, concentrated, and distilled to give dibenzofulvene (**15**), yield: 206 mg (58%). The acid extract is neutralized with NaOH and extracted with Et_2O. The extract is dried, concentrated, and distilled to give a mixture of **13** and **14**; yield: 118 mg (26%). Ratio: **13/14/15** (17:17:66) (determined by ^{1}H-NMR).

Reaction of Dimethyl(6-methoxy-1,2,3,4-tetrahydronaphthyl)-(trimethylsilylmethyl)ammonium Trifluoromethanesulfonate with Cesium Fluoride:

A mixture of 6-methoxy-*N*-methyl-*N*-trimetylsilylmethyl-1,2,3,4-tetrahydronaphthylamine (**16**; 975 mg, 3.5 mmol) and CF_3SO_3Me (603 mg, 3.7 mmol) in CH_2Cl_2 (20 mL) is stirred at r.t. for 24 h. The solvent is removed under reduced pressure. Anhydrous DMF (20 mL) and CsF (2.1 g, 14 mmol) are added to the mixture. The mixture is stirred at r.t. for 2.5 h, then poured into 1.5% Na_2CO_3 (200 mL) and extracted with Et_2O (4 × 100 mL). The ethereal extract is washed with 1.5% Na_2CO_3 2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue is chromatographed on an aluminum oxide column (hexane/Et_2O, 9:1) to give unreacted **16**, yield: 314 mg (32%) and 7-methoxy-3-(6-methoxy-1,2,3,4-tetrahydronaphthyl)-1,2-dihydronaphtharene **(19)**; yield: 358 mg (94%) (based on consumed **16**); mp 72–73°C.

$C_{22}H_{24}O_2$ calc. C 82.46 H 7.55
(320.4) found 82.18 7.42

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.69–1.82 (m, 2H, 3'-H), 1.91–1.93 (m, 2H, 2'-H), 2.06–2.17 (m, 2H, 2-H), 2.72–2.80 (m, 4H, 4'-H, 1-H), 3.59–3.62 (m, 1H, 1'-H), 3.78 (s, 6H, OCH_3), 6.14 (s, 1H, 4-H), 6.63–6.69 (m, 4H, 6-H, 8-H, 5'-H, 7'-H), 6.91–6.93 (m, 1H, 5-H), 7.09 (d, 1H, J = 8.0 Hz, 8'-H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 158.3 (s), 157.5 (s), 143.1 (s), 138.9 (s), 136.5 (s), 130.3 (s), 130.3 (d), 128.1 (s), 126.5 (d), 124.2 (d), 113.5 (d), 113.4 (d), 112.0 (d), 111.2 (d), 55.3 (q), 55.2 (q), 46.5 (d), 30.2 (t), 29.1 (28.8 (t), 25.0 (t), 21.5 (t).

MS (EI, 70 eV): m/z (%) = 320 (M^+, 61), 160 (100).

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