Rearrangement of $N,N$-Dimethyl(1- or 2-naphthylmethyl)ammonium $N$-Methylylide

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$N,N$-Dimethyl(1- or 2-naphthylmethyl)ammonium $N$-methylylide (2a, b) produced from $N,N$-dimethyl-$N$-[(trimethylsilyl)methyl] (1- or 2-naphthylmethyl)ammonium iodide (1a, b) with CsF in $N,N$-dimethylformamide, was rearranged to 2-[(dimethylamino)methyl]-1,2-dihydro-1-naphtholidene (3a) or 1-[(dimethylamino)methyl]-1,2-dihydro-2-naphtholidene (3b), respectively, in high yield. Aromatization of 3a, b to the Sommelet–Hauser products (4a, b) occurred with the aid of KOH or heating.

Keywords ammonium ylide; Sommelet–Hauser rearrangement; Stevens rearrangement; organosilicon compound; [2,3]sigmatropic rearrangement

Sommelet–Hauser rearrangement of benzylammonium ylides is a useful method for synthesizing ortho-methylbenzylamines. However, base-promoted ylide formation, which is usually employed, often gives complex mixtures of amines because plural ylides are formed simultaneously.1,2) In fluoride ion-induced desilylation reaction of $N$-[1-(trimethylsilyl)alkyl]benzylammonium salts, the ylide-anions were located regioselectively on the carbons with which the silyl groups had been linked. Thus the yields of the products were remarkably improved.3–19) This paper reports the reaction of $N,N$-dimethyl-$N$-[(trimethylsilyl)methyl] (1- or 2-naphthylmethyl)ammonium iodides (1a, b) with cesium fluoride.

Ammonium iodides (1a, b) were prepared starting from $\alpha$- or $\beta$-naphthoyl chloride with $N$-methyl(trimethylsilyl)-methylamine followed by lithium aluminum hydride reduction, then quaternization with iodomethane. Treatment of 1a, b with cesium fluoride in $N,N$-dimethyl formamide (DMF) gave a high yield of 2-[(dimethylamino)methyl]-1,2-dihydro-1-naphtholidene (3a, [2,3]sigmatropic rearrangement product) or 1-[(dimethylamino)methyl]-1,2-dihydro-2-naphtholidene (3b) after 40 min of stirring at room temperature (Table I, entries 1 and 3). However, the product 3a changed to 1-methyl-2-[(dimethylamino)methyl]naphthalene (4a, Sommelet–Hauser rearrangement product) after 2 d (entry 2). Conversion of 3b to 2-methyl-1-[(dimethylamino)methyl]naphthalene (4b) was not completed after 3 d (entry 4). Pure 4b was obtained after 13 d but the yield was decreased by polymerization of 3b.

Hauser et al.20) obtained 4a (75%) and 4b (84%) from $N,N,N$-trimethyl(1-naphthylmethyl)ammonium chloride and a 1-naphthylmethyl analogue by treatment with sodium amide in liquid ammonia. The difference of the

![Chart 1](image)

**Table I.** Reaction of $N,N$-Dimethyl-$N$-[(trimethylsilyl)methyl] (1- or 2-naphthylmethyl)ammonium Iodides (1a, b) with CsF

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ammonium salt (1)</th>
<th>Reaction time</th>
<th>Total yield (%)</th>
<th>Ratio$^a$ of 3 : 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>40 min</td>
<td>85</td>
<td>91 : 9</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2 d</td>
<td>70</td>
<td>0 : 100</td>
</tr>
<tr>
<td>3</td>
<td>1b</td>
<td>40 min</td>
<td>92</td>
<td>98 : 2</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>3 d</td>
<td>79</td>
<td>35 : 65</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>13 d</td>
<td>26</td>
<td>0 : 100</td>
</tr>
</tbody>
</table>

$^a$ Determined from the integration of the signals in the $^1$H-NMR spectra.

**Table II.** Reaction of Naphtholidene Derivatives 3a and 3b

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction conditions</th>
<th>Ratio$^b$ of 4 : 5 : 6</th>
<th>Total yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a$^b$ 5% KOH/EtOH, r.t., 3 h</td>
<td>100 0 0</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>3a</td>
<td>Xylene, reflux, 6 h</td>
<td>78 22 0</td>
</tr>
<tr>
<td>3</td>
<td>3b$^b$ 5% KOH/EtOH, r.t., 5 h</td>
<td>100 0 0</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>3b</td>
<td>Xylene, reflux, 44 h</td>
<td>14 0 86</td>
</tr>
</tbody>
</table>

$^a$ Determined from the integration of the signals in the $^1$H-NMR spectra. $^b$ A mixture of 3a and 4a (91 : 9) was used. $^c$ A mixture of 3b and 4b (98 : 2) was used. r.t. = room temperature.
products between the two ylide reactions indicates that aromatization of 3 to 4 is slow in non-basic media but occurs quickly in the presence of a strong base. An antarafacial [1,3]hydrogen shift at the 2-position of 3a (or 1-position of 3b) to the exomethylene group is required in non-basic media. The π framework should be twisted far from planarity at the transition stage. Conjugation of the benzene ring with the triene portion may pose an obstacle to such a twisting conformation.

Indeed, 3a, 4b were respectively changed to 4a, 5b in 5% KOH solutions in high yields (Table II). Heating at 140°C in xylene, 3a converted to a mixture of 4a and N,N-dimethyl-2-(1-naphthyl)ethylamine (5a, Stevens rearrangement product), whereas 3b gave 1,2-bis[(1-dimethylamino)methyl]-2-naphthylmethane (6b) as the main product. The Stevens product 5a is formed as a result of [1,3] radical migration via a radical pair (7 in Chart 3). The dimerization product 6b may be formed from a β-naphthylmethyl radical (8) which is produced by elimination of the C1-hydrogen from 3b. However, it is still unclear what is the cause of the difference in thermal isomerization of 3a and 3b.

Experimental

All reactions were carried out in N2. DMF was dried over BaO and distilled under reduced pressure. Ether was distilled from Na benzophenone ketyl. CsF was dried over P2O5 at 180°C under reduced pressure. 1H-NMR spectra were recorded at 270 or 400 MHz. Mass spectra were obtained using electron impact (EI) ionization (70 eV). All melting and boiling points are uncorrected.

N,N-Dimethyl-N-(trimethylsilyl)methyl[1-naphthylmethyl]ammonium iodide (1a) A solution of N,N-dimethyl(trimethylsilyl)methylamine (2.45 g, 20.9 mmol) and 1-naphthyl chloride (8.56 g, 45.5 mmol) in benzene (130 ml) was stirred vigorously with 10% NaOH (30 ml) for 40 min at room temperature. The benzene layer was separated, washed with water, then dried (MgSO4), and the solvent was evaporated under reduced pressure to give a colorless oil. The oil was added to a suspension of LiAlH4 (1.50 g, 39.5 mmol) in ether (50 ml), and the mixture was heated at reflux for 2.5 h. The reaction was quenched with EtOAc (5 ml) and 5% HCl (50 ml), and then the mixture was extracted with ether. The extract was washed with water, dried (MgSO4), and concentrated under reduced pressure to give 14.8 g (86% yield).

A solution of the 1-naphthylmethylamine (0.71 g, 2.8 mmol) and iodomethane (3.26 g, 23 mmol) in MeCN (10 ml) was heated at reflux for 2.5 h and then concentrated. The residue was recrystallized from MeCN-ether to give 1a (2.22 g, 80%), mp 184–185°C. 1H-NMR (CDCl3) δ: 0.28 (9H, s), 3.34 (6H, s), 3.68 (2H, s), 5.61 (2H, s), 7.36–8.00 (7H, m). Anal. Caled for C13H14N2S: C, 74.65; H, 9.00; N, 5.44. Found: C, 74.59; H, 9.10; N, 5.35.

N,N-Dimethyl-N-(trimethylsilyl)methyl[2-naphthylmethyl]ammonium iodide (1b) A mixture similar to that described above, a mixture of N,N-dimethyl(trimethylsilyl)methylamine (2.67 g, 22.8 mmol) and 2-naphthyl chloride (3.64 g, 19.1 mmol) in benzene (60 ml) was stirred with 10% NaOH (10 ml) and treated with N,N-dimethyl(trimethylsilyl)methyl]-2-naphthamide (4.24, 82%), mp 51–52°C (hexane). 1H-NMR (CDCl3) δ: 0.20 (9H, s), 3.02 (3H, s), 3.15 (2H, s), 7.45–7.87 (7H, m). Anal. Caled for C19H16N2S: C, 70.80; H, 7.80; N, 5.16. Found: C, 70.56; H, 7.86; N, 4.99.

Reduction of the naphthamide (0.60 g, 22 mmol) with LiAlH4 (0.85 g, 22 mmol) in ether (40 ml) gave N,N-dimethyl-[2-[(trimethylsilyl)methyl][2- naphthylmethyl]amine (4.16 g, 73%), bp 140°C (2.5 mmHg, Kugelrohr). 1H-NMR (CDCl3) δ: 0.11 (9H, s), 2.02 (2H, s), 2.31 (3H, s), 3.70 (2H, s), 7.25–7.92 (7H, ArH). Anal. Caled for C19H22N2S: C, 74.65; H, 9.00; N, 5.44. Found: C, 74.48; H, 9.21; N, 5.20.

General Procedure for the Reduction of 1a or 1b with CsF The ammonium salt I (824 mg, 2.06 mmol) was placed in a 20-ml flask equipped with a magnetic stirrer, septum, and a test tube which was connected to the flask by a short piece of rubber tubing. CsF (1.52 g, 10 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and was flushed with N2. DMF (10 ml) was added to the flask by syringe. CsF was added from the test tube. The mixture was stirred at room temperature for the time listed in Table I. The reaction mixture was poured into 1% NaHCO3 (200 ml) and extracted with EtO (4 x 100 ml). The etheric extract was washed with 1% NaHCO3 (200 ml), dried (MgSO4), and concentrated under reduced pressure to give a pale yellow oil. The H-NMR spectrum of the oil from 1a showed the presence of 3a or 4a, and that of the oil from 1b revealed 3b and 4b. Samples were separated by HPLC (Merck, Hibar LiChrosorb NH2, 250 x 10 mm, hexane-ether). The results are listed in Table I.

1a. 1H-NMR (CDCl3, 200 MHz) δ: 2.21 (1H, dd, J = 7.2, 11.9 Hz, CH3N), 2.25 (6H, s, CH3N), 2.43 (1H, dd, J = 8.6, 11.9 Hz, CH2N), 3.28–3.33 (1H, m, 2-H), 5.07 (1H, s, CH2N), 5.49 (1H, s, CH3), 6.13 (1H, dd, J = 5.3, 9.6 Hz, 3-H), 6.40 (1H, d, J = 9.6 Hz, 4-H), 7.04 (1H, d, J = 7.2 Hz, 5-H), 7.16–7.26 (2H, m, 6-H, 7-H), 7.53 (1H, d, J = 7.5 Hz, 8-H). UV λmax nm (log e): 283 (3.77), 240 (4.43), 229 (4.45). Anal. Caled for C14H15N4: C, 84.37; H, 8.60; N, 6.92.

4a. 1H-NMR (CDCl3, 200 MHz) δ: 2.28 (6H, s, CH2N), 2.70 (3H, s, CH3), 3.60 (2H, s, CH2N), 7.41–8.09 (6H, m, ArH). Anal. Caled for C14H15N4: C, 84.37; H, 8.60; N, 6.79.

1b. 1H-NMR (CDCl3, 200 MHz) δ: 2.21 (1H, dd, J = 6.4, 12.3 Hz, CH3N), 2.25 (6H, s, CH2N), 2.45 (1H, dd, J = 8.9, 12.3 Hz, CH3N), 3.65 (1H, dd, J = 6.4, 8.9 Hz, CH2N), 5.15 (1H, s, CH3N), 6.28 (1H, d, J = 9.6 Hz, 3-H), 6.38 (1H, d, J = 9.6 Hz, 4-H), 7.06–7.17 (4H, m, ArH). UV λmax nm (log e): 301 (4.04), 221 (4.29). Anal. Caled for C14H15N4: C, 84.37; H, 8.60; N, 6.70.

3b. 1H-NMR (CDCl3, 200 MHz) δ: 2.33 (6H, s, CH2N), 2.56 (3H, s, CH3), 3.80 (2H, s, CH2N), 7.28 (1H, d, J = 8.6 Hz), 7.76 (1H, d, J = 8.6 Hz).
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\[ J = 8.6 \text{ Hz}, \quad 7.35 - 7.51 (2 \text{H}, \text{m}), \quad 7.76 (1 \text{H}, \text{d}, \text{J} = 10.7 \text{Hz}), \quad 8.23 (1 \text{H}, \text{d}, \text{J} = 8.6 \text{Hz}). \]
\[ \text{Anal. Calcd for C}_4\text{H}_8\text{N}: \text{C} = 84.37; \text{H} = 8.60; \text{N} = 7.03. \]
\[ \text{Found: C} = 84.21; \text{H} = 8.71; \text{N} = 6.83. \]

**Reaction of 3a and 3b in 5% KOH** A mixture of 3a and 4a (91:9, 384 mg) or 3b and 4b (98:2, 245 mg) was dissolved in 5% KOH in EtOH (3 ml) and stirred at room temperature. After 3a or 3b had disappeared (3 h for 3a, 5 h for 3b), the solution was mixed with water (20 ml) and extracted with ether (3 x 20 ml). The extract was dried (MgSO\(_4\)) and concentrated to give 4a (338 mg, 88%) and 4b (36 mg, 80%).

**Thermal Isomerization of 3a and 3b** A solution of 3a (451 mg, 2.26 mmol) or 3b (256 mg, 1.28 mmol) in xylene (5 ml) was heated at 140°C for 6 or 44 h and extracted with 10% HCl (4 x 5 ml). The aqueous extract was made alkaline with 10% NaOH and extracted with Et\(_2\)O (4 x 50 ml). The extract was washed with H\(_2\)O, dried (MgSO\(_4\)), and concentrated to give a mixture (473 mg) of 4a and 5a\(^{22}\) or a mixture (192 mg) of 4b and 6b. The product ratios were determined from the proton signal ratios in the \(^1\)H-NMR spectra.

**Compound 6b** was isolated by Al\(_2\)O\(_3\) column chromatography (Et\(_2\)O-hexane).

**6b** \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 1.58 - 1.67 (1H, m, C\(_7\)H\(_3\)CH\(_2\)), 1.71 - 1.82 (1H, m, CH\(_2\)CH\(_2\)), 2.61 (2H, d, J = 7.3 Hz, CH\(_2\)CH\(_3\)), 2.66 - 2.69 (1H, m), 2.88 - 3.00 (1H, m), 3.07 - 3.12 (1H, m), 3.81 (1H, s), 2.26 (6H, s, CH\(_3\)N), 2.29 (6H, s, CH\(_2\)N), 6.08 - 6.13 (1H, m), 6.54 (1H, d, J = 9.6 Hz, 4-H), 7.04 - 7.23 (4H, m), 7.28 (1H, d, J = 8.4 Hz, 4-H), 7.29 - 7.41 (1H, m), 7.44 - 7.50 (1H, m), 7.67 (1H, d, J = 8.4 Hz, 5-H), 7.75 (1H, d, J = 7.9 Hz, 5-H), 8.24 (1H, d, J = 8.6 Hz, 8-H).

**C-NMR (CDCl\(_3\)) \(\delta\):** 31.5, 31.7, 36.9, 38.6, 45.3, 46.2, 55.8, 59.2, 124.7, 124.8, 125.9, 125.9, 126.3, 126.4, 127.0, 127.7, 128.0, 128.2, 133.0, 131.1, 132.4, 133.5, 133.9, 136.9, 138.5, 139.9. \(\text{Anal. Calcd for C}_9\text{H}_8\text{N}: \text{C} = 84.37; \text{H} = 8.60; \text{N} = 7.03. \)

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**References**