HETEROCYCLES, Vol. 53, No. 9, 2000, pp. 2009 - 2018, Received, 22nd June, 2000

A SYNTHESIS OF 2,3,4,5-TETRAHYDRO-1*H*-3-BENZAZEPINES *VIA* PUMMERER-TYPE CYCLIZATION OF *N*-(2-ARYLETHYL)-*N*-(2-PHENYLSULFINYLETHYL)FORMAMIDES

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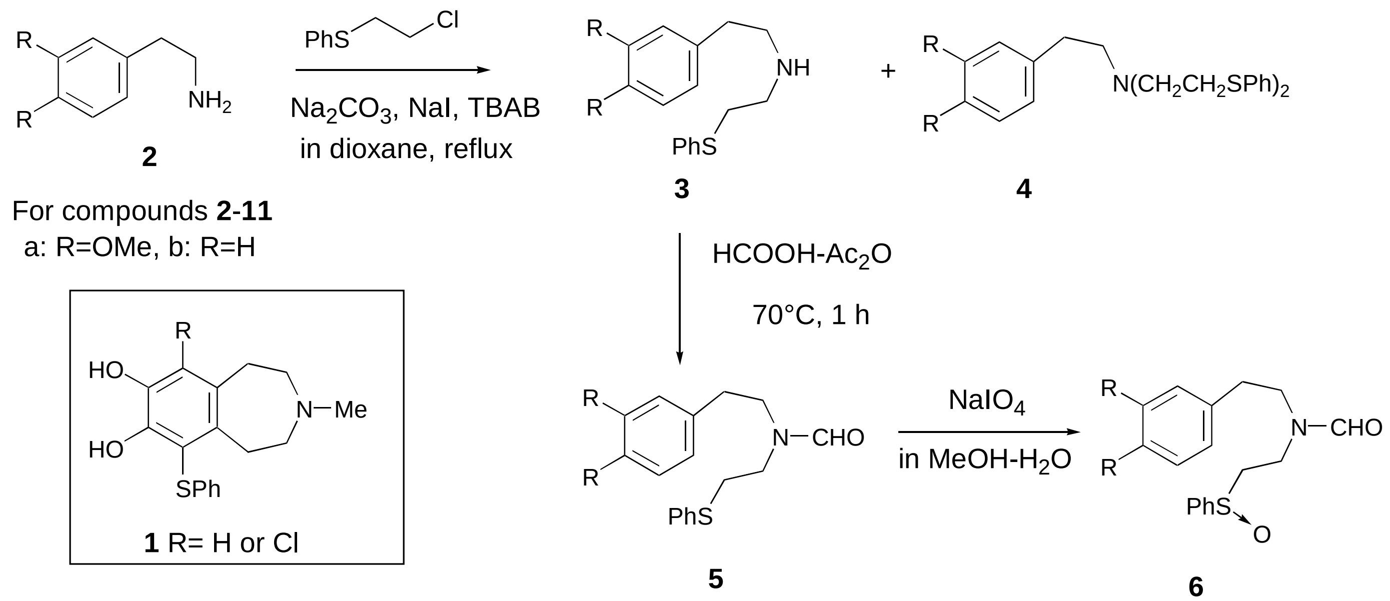
Abstract - A construction of 2,3,4,5-tetrahydro-1*H*-3-benzazepine ring system (**7**) was achieved *via* Pummerer-type cyclization of *N*-(2-arylethyl)-*N*-2-(phenylsulfinylethyl)formamides (**6**). This route produced the benzazepines (**10**) and (**11**) in six steps starting from readily available 2-arylethylamines (**2**) and 2-chloroethyl phenyl sulfide.

2,3,4,5-Tetrahydro–1*H*-3-benzazepine derivatives have received considerable attention, in part due to their interesting pharmacological activities observed in the compounds (**1**), a class of dopamine receptor antagonists and neuroleptics.[1] In a series of paper we reported the synthesis of 1,2,3,4-tetrahydroisoquinolines,[2] and 1,2,3,4-tetrahydroquinolines[3] using an aromatic cyclization of the *in situ* formed thionium ion generated under the acidic conditions from a sulfinyl precursor (Pummerer reaction).[4] We now describe a further extension of this method to the synthesis of 2,3,4,5-tetrahydro-1*H*-3-benzazepines.[5]

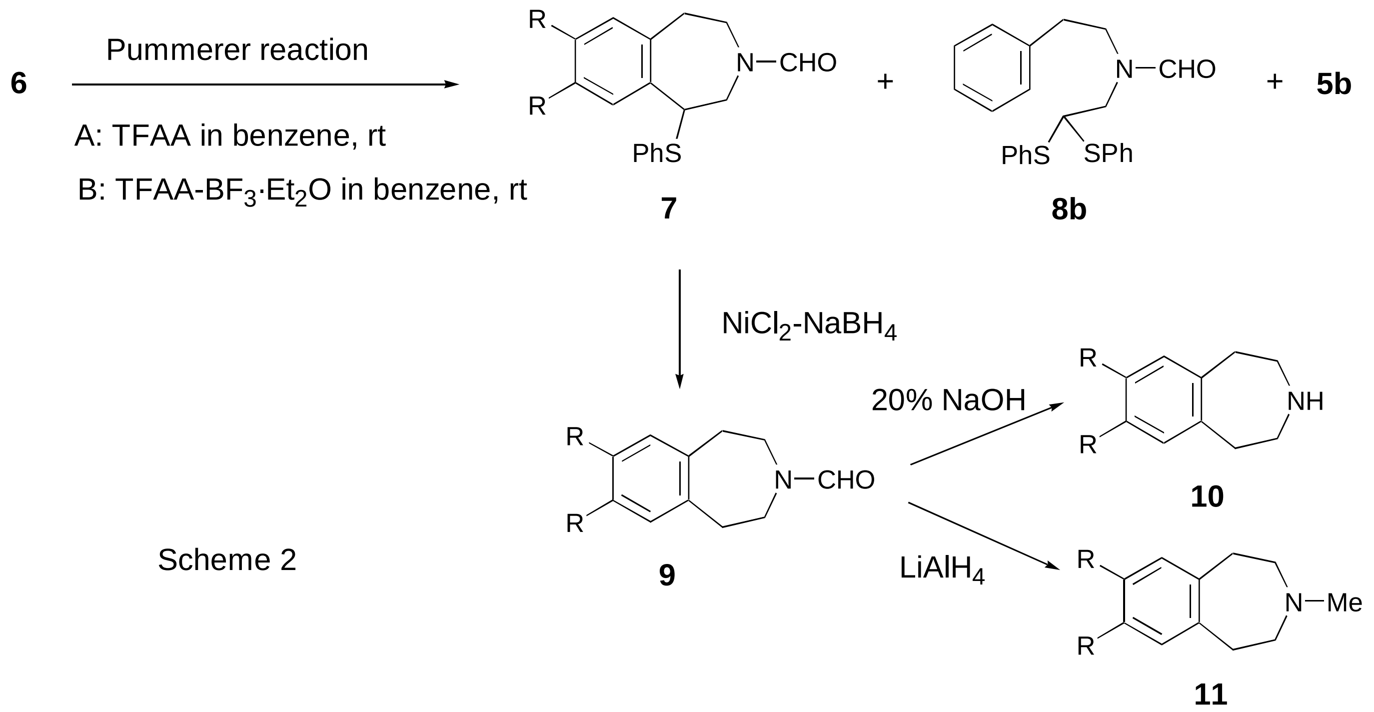
Preparation of Sulfoxides *N*-(2-Arylethyl)-*N*-(2-phenylsulfinylethyl)formamides (**6a-b**), substrates of the Pummerer-type cyclization, were prepared from 2-arylethylamines (**2a-b**) *via* the route shown in Scheme 1. A mixture of **2a-b** and 2-chloroethyl phenyl sulfide in dioxane was heated under reflux for 3 days in the presence of a phase transfer catalyst to afford secondary amines (**3a-b**) in good yields, although the undesired dialkyl derivatives (**4a-b**) were accompanied as a minor product. The amines (**3a-b**) were then treated with formic acid-acetic anhydride to give *N*-formyl derivatives (**5a-b**). Oxidation of **5a-b** with sodium metaperiodate in aqueous methanol gave sulfoxides (**6a-b**) in good overall yields.



Scheme 1

Pummerer Reaction. The sulfoxide (**6a**), on treatment with trifluoroacetic anhydride (TFAA) in benzene at room temperature for 24 h (method A), readily induced the cyclization to afford 3-formyl-7,8-dimethoxy-1-phenylsulfanyl-1*H*-3-benzazepine (**7a**) in 80% yield. On the other hand, the sulfoxide (**6b**) lacking an OMe group in the benzene ring, when treated as described above, did not induce the cyclization and merely produced a disulfide (**8b**) in 38 % yield. In our previous investigations,[2] we found that a similar cyclization, in the presence of BF_3•Et_2O used as an additive reagent proceeded in a highly effective manner, particularly in the cases of the aromatic ring with weak nucleophilicity. In fact, application of this reaction (method B) for the sulfoxide (**6b**) induced the cyclization to afford 3-formyl-1-phenylsulphanyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (**7b**) in 47% yield, although **8b** and a sulfide (**5b**) were accompanied as minor products. The reaction of **6a** under the method B condition only decreased the yield of **7a** (63%), although the reaction was much accelerated.

The results demonstrated that the Pummerer reaction is applicable for the construction of the 3-benzazepine ring even in the substrate whose nucleophilic aromatic ring is not activated by electron donating group such as OMe. However, this cyclization is less effective than that achieved in the 1,2,3,4-tetrahydroisoquinoline synthesis *via* this reaction.[2]



Scheme 2

Preparation of 2,3,4,5-Tetrahydro-1*H*-3-benzazepines. Reductive removal of the phenylsulfanyl group of **7a-b** proceeded by treatment with $NiCl_2$-$NaBH_4$ in MeOH-THF to give *N*-formyl-3-benzazepines **(9a-b)** in good yields. Deprotection of the *N*-formyl group was readily achieved by conventional methods. Alkaline hydrolysis of **9a-b** gave 3-benzazepines (**10a-b**). Reduction of **9a-b** with $LiAlH_4$ gave *N*-methylbenzazepines (**11a-b**).

Thus, this route produces the benzazepines (**10a**) and (**11a**) in 38 and 24% overall yields, respectively, from commercially available homoveratrylamine (**2a**) and 2-chloroethyl phenyl sulfide, thus providing a convenient and general method of 3-benzazepine synthesis. The benzazepines (**10a**) and (**11a**) are the synthetic intermediates of biologically important 3-benzazepines (**1**).[1, 6]

EXPERIMENTAL

General Notes. Melting points were taken on a Yanagimoto SP-M1 hot-stage melting point apparatus. TLC was performed on Merck precoated Silica gel 60 F_{254} plates (Merck). Column chromatography was carried out with silica gel (Wakogel C-200). Medium pressure liquid chromatography (MPLC) was performed on Kusano CIG prepacked column. IR spectra were obtained as KBr disks with a HORIBA FT-710 spectrophotometer and are given in cm^{-1}. NMR spectra were measured on a JEOL JNM-EX90 (^{1}H-NMR 90 MHz, ^{13}C-NMR 22.5 MHz) or JEOL JMS-AL 300 (^{1}H-NMR 300 MHz, ^{13}C-NMR 75.0 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, and the chemical shifts are given in δ values. Low-resolution MS spectra (LR-MS) and high-resolution MS spectra (HR-MS) were determined on a JEOL JMS-HX110A or JMS-D300 spectrometer at 30 eV with a direct inlet system. The organic extract from each reaction mixture was washed with brine, dried over anhydrous Na_2SO_4 before concentration *in vacuo*.

Alkylation of 1 with 2-Chloroethyl Phenyl Sulfide. Typical Procedure. A mixture of **2a** (1.0 g, 5.5 mmol), 2-chloroethyl phenyl sulfide (1.15 g, 6.6 mmol), Na_2CO_3 (0.88 g, 8.3 mmol), NaI (0.83 g, 5.5 mmol), and tetrabutylammonium bromide (TBAB) (0.89 g, 2.8 mmol) in dioxane (25 mL) was refluxed for 72 h under argon atmosphere. After removal of inorganic precipitates by filtration, the residual oil was concentrated *in vacuo*, and the residue after dilution with H_2O was extracted with $CHCl_3$. The residual oil was chromatographed with hexane/ethyl acetate (1:2) to give **4a** (0.38 g, 15%). Further elution with MeOH gave **3a** (1.4 g, 80%).

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-2-phenylsulfanylethylamine (3a)**: Pale yellow oil. IR (film): 3312, 1518. ^{1}H-NMR (90 MHz): 1.73 (1H, br s, >NH), 2.7-3.1 (8H, m, $ArCH_2CH_2$-, $PhSCH_2CH_2$-), 3.86 (6H, s, OCH_3x2), 6.7-6.8 (3H, m, ArH), 7.1-7.4 (5H, m, PhH). ^{13}C-NMR (22.5 MHz): 34.0 (t), 35.7 (t), 48.0 (t), 50.6 (t), 55.7 (q), 55.8 (q), 111.3 (d), 111.9 (d), 120.4 (d), 126.0 (d), 128.7 (dx2), 129.5 (dx2), 132.3 (s), 135.6 (s), 147.4 (s), 148.8 (s). LR-MS *m/z*: 317 (M^+, 4), 137 (100). HR-MS *m/z* (M^+): Calcd for $C_{18}H_{23}NO_2S$: 317.1449. Found: 317.1484.

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-di[2-(phenylsulfanyl)ethyl]amine (4a)**: Yellow gum. IR (film): 1518. ^{1}H-NMR (90 MHz): 2.6-3.1 (12H, m, $ArCH_2CH_2$-, $PhSCH_2CH_2$-x2), 3.85, 3.86 (each 3H, s, OCH_3x2), 6.6-6.9

(3H, m, ArH), 7.0-7.4 (10H, m, PhHx2). ^{13}C-NMR (22.5 MHz): 31.6 (tx2), 33.6 (t), 53.3 (tx2), 55.8 (qx2), 56.3 (t), 111.3 (d), 112.2 (d), 120.5 (d), 125.8 (dx2), 128.8 (dx4), 129.0 (dx4), 132.8 (s), 136.3 (sx2), 147.3 (s), 148.8 (s). FAB-LRMS *m/z*: 454 (MH^+, 28), 137 (100). HR-MS *m/z* (M^+): Calcd for $C_{26}H_{31}NO_2S_2$: 453.1796. Found: 453.1799.

***N*-(2-Phenylethyl)-2-phenylsulfanylethylamine (3b)**: From 2-phenylethylamine (**2b**) (8 g, 66 mmol), 2-chloroethyl phenyl sulfide (12.0 g, 72.8 mmol), Na_2CO_3 (10.6 g, 100 mmol), NaI (10.0 g, 66 mmol), and TBAB (5.4 g, 33 mmol) in dioxane (200 mL); column chromatography (hexane/ethyl acetate 1:4) gave **3b** (10.7 g, 63%) as pale yellow oil; IR (film): 3303, 1583. ^{1}H-NMR (90 MHz): 1.54 (1H, br s, >NH), 2.6-3.2 (8H, m, $PhCH_2CH_2$-, $PhSCH_2CH_2$-), 6.9-7.5 (10H, m, PhHx2). ^{13}C-NMR (75 MHz): 34.1 (t), 36.3 (t), 48.1 (t), 50.7 (t), 126.16 (d), 126.20 (d), 128.4 (dx2), 128.7 (dx2), 128.9 (dx2), 129.7 (dx2), 135.6 (s), 139.8 (s). CI-MS *m/z*: 258 (MH^+, 100). HR-MS *m/z* (M^+): Calcd for $C_{16}H_{19}NS$: 257.1236. Found: 257.1219.

***N*-(2-Phenylethyl)-di[2-(phenylsulfanyl)ethyl]amine (4b)**: Elution of hexane/ethyl acetate (20:1) gave **4b** (1.5 g, 6%) as yellow oil. IR (film): 1583. ^{1}H-NMR (90 MHz): 2.5-3.2 (12H, m, $PhCH_2CH_2$-, $PhSCH_2CH_2$-x2), 6.9-7.5 (10H, m, PhHx2). ^{13}C-NMR (22.5 MHz): 31.6 (tx2), 34.0 (t), 53.4 (tx2), 56.1 (t), 125.9 (dx2), 126.0 (dx2), 128.3 (dx2), 128.6 (dx2), 128.8 (dx3), 129.1 (dx4), 136.3 (sx2), 140.1 (s). CI-MS *m/z*: 394 (MH^+, 100). HR-MS *m/z* (M^+): Calcd for $C_{24}H_{27}NS_2$: 393.1585. Found: 393.1586.

Formylation of 3. Typical Procedure. To a solution of **3a** (11 g, 34.7 mmol) in formic acid (10 mL) was added slowly the mixed anhydride prepared from formic acid (25 mL, 0.66 mol) and acetic anhydride (33 mL, 0.35 mol) at 0 °C, and the mixture was heated at 60°C for 1 h. The reaction mixture was concentrated *in vacuo* and extracted with $CHCl_3$. The residue was chromatographed with $CHCl_3$ to give **5a** (11.9 g, 99%) as yellow gum.

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-*N*-(2-phenylsulfanylethyl)formamide (5a)**: IR (film): 1671, 1518. ^{1}H-NMR (90 MHz): 2.6-3.7 (8H, m, $ArCH_2CH_2$-, $PhSCH_2CH_2$-), 3.85 (6H, s, OCH_3x2), 6.5-6.8 (3H, m, ArH), 7.2-7.4 (5H, m, PhH), 7.83, 8.00 (total 1H, each s, CHO). LR-MS *m/z*: 345 (M^+, 7), 164 (100). HR-MS *m/z*

(M^+): Calcd for $C_{19}H_{23}NO_3S$: 345.1399. Found: 345.1407.

***N*-(2-Phenylethyl)-*N*-(2-phenylsulfanylethyl)formamide (5b)**: From **3b** (8.5 g, 33.1 mmol); column chromatography (hexane/ethyl acetate 5:4) gave **5b** (9.3 g, 99 %) as yellow gum. IR (film): 1668. ^{1}H-NMR (90 MHz): 2.6-3.7 (8H, m, $PhCH_2CH_2$-, $PhSCH_2CH_2$-), 6.9-7.6 (10H, m, PhHx2), 7.82, 7.99 (total 1H, eachs,CHO). LR-MS *m/z*: 285 (M^+, 6), 136 (100). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{19}NOS$: 285.1186. Found: 285.1216.

Oxidation of 5a with $NaIO_4$. Typical Procedure. A solution of **5a** (5 g, 14.5 mmol) and $NaIO_4$ (4.65 g, 21.75 mmol) in MeOH (60 mL) and H_2O (30 mL) was stirred at rt for 1.5 h. After removal of inorganic precipitates by filtration, the filtrate was concentrated *in vacuo*. The residue was extracted with $CHCl_3$. The product was chromatographed with hexane/ethyl acetate (1:2) to give **6a** (4.9 g, 93%) as yellow gum.

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-*N*-(2-phenylsulfinylethyl)formamide (6a)**: IR (film): 1669, 1518. ^{1}H-NMR (90 MHz): 2.7-3.8 (8H, m, $ArCH_2CH_2$-, $PhS(O)CH_2CH_2$-), 3.86 (6H, s, OCH_3x2), 6.6-6.9 (3H, m, ArH), 7.4-7.7 (5H, m, PhH), 7.81, 8.10 (total 1H, each s, CHO). CI-MS *m/z*: 362 (MH^+, 91). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{23}NO_4S$: 361.1347. Found: 361.1347.

***N*-(2-Phenylethyl)-*N*-(2-phenylsulfinylethyl)formamide (6b)**: From **5b** (9 g, 31.6 mmol); column chromatography (hexane/ethyl acetate 2:1) gave **6b** (8.7 g, 92%) as yellow gum. IR (film): 1668. ^{1}H-NMR (90 MHz): 2.6-3.8 (8H, m, Ph-CH_2CH_2-, PhS(O)-CH_2CH_2-), 7.0-7.7 (10H, m, PhHx2), 7.78, 8.10 (total 1H, each s, CHO). CI-MS *m/z*: 302 (MH^+, 92). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{19}NO_2S$: 301.1137. Found: 301.1173.

Pummerer Reaction of 6a.

i) Method A: TFAA (580 mg, 2.76 mmol) in benzene (5 mL) was added to a solution of **6a** (200 mg, 0.55 mmol) in benzene (15 mL) at rt under argon atmosphere, and the mixture was stirred for 24 h at the same temperature. After concentration of the mixture *in vacuo*, the residue was chromatographed with hexane/ethyl acetate (3:1) to give **7a** (153 mg, 80%) as pale yellow gum.

ii) Method B: A solution of TFAA (1.45 g, 6.9 mmol) in benzene (5 mL) was added to a solution of **6a** (500 mg, 1.39 mmol) at rt under argon atmosphere, and the mixture was stirred for 30 min. To this mixture was added

BF_3•Et_2O (600 mg, 4.2 mmol) and the mixture was further stirred at rt for 1.5 h. After concentration of the mixture *in vacuo*, the residue was treated with 5% $NaHCO_3$, and extracted with $CHCl_3$. The product was chromatographed with hexane/ethyl acetate (3:1) to give **7a** (300 mg, 63%).

3-Formyl-7,8-dimethoxy-1-phenylsulfanyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (7a): IR (film): 1667,1520. ^{1}H-NMR (90 MHz): 2.6-4.7 (7H, m, H-1, 2, 4, 5), 3.64, 3.72, 3.87 (total 6H, each s, OCH_3x2), 6.31, 6.45, 6.62, 6.65 (total 2H, each s, H-6, 9), 7.1-7.5 (5H, m, PhH), 7.95, 8.17 (total 1H, each s, CHO). LR-MS *m/z*: 343 (M^+, 10), 206 (100). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{21}NO_3S$: 343.1243. Found: 343.1265.

Pummerer Reaction of 6b.

i) Method A: TFAA (719 mg, 3.42 mmol) in benzene (5 mL) was added to a solution of **6b** (206 mg, 0.68 mmol) at rt under argon atmosphere, and the mixture was stirred for 48 h at the same temperature. After concentration of the mixture *in vacuo*, the residue was chromatographed with hexane/ethyl acetate (5:1) to give **8b** (47 mg, 36%) as pale yellow gum.

***N*-(2-Phenylethyl)-*N*-(2,2-diphenylsulfanylethyl)formamide (8b)**

IR (film): 1673. ^{1}H-NMR (90 MHz): 2.5-2.9 (2H, m, $PhCH_2CH_2$-), 3.3-3.8 (4H, m,$PhCH_2CH_2$-,$(PhS)_2CHCH_2$-), 4.27, 4.89 (total 1H, each t, *J*=7 Hz, $(PhS)_2CHCH_2$-), 6.9-7.6 (15H, m, PhHx3), 7.81, 8.04 (total 1H, each s, CHO). CI-MS *m/z*: 394 (MH^+, 19), 284 (100). HR-MS *m/z* (M^+): Calcd for $C_{23}H_{23}NOS_2$: 393.1218. Found: 393.1207.

ii) Method B: TFAA (1.74 g, 8.3 mmol) in benzene (5 mL) was added to a solution of **6b** (500 mg, 1.66 mmol) at rt under argon atmosphere, and the mixture was stirred for 30 min. To the mixture was added BF_3•Et_2O (700 mg, 5 mmol) and the mixture was further stirred at rt for 1.5 h. After concentration of the mixture *in vacuo*, the residue was basified with 5% $NaHCO_3$, and extracted with $CHCl_3$. The product was chromatographed with hexane/ethyl acetate (5:1) to give **8b** (37 mg, 9%), **5b** (41 mg, 11%), and **7b**. Further purification of the crude **7b** by MPLC with hexane/ethyl acetate (5:1) gave **7b** (220 mg, 47%) as colorless gum.

3-Formyl-1-phenylsulfanyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (7b): IR (film): 1668. ^{1}H-NMR (90 MHz):

2.6-4.8 (7H, m, H-1, 2, 4, 5), 6.8-7.5 (9H, m, H-6, 7, 8, 9, PhH), 7.98, 8.19 (total 1H, each s, CHO). LR-MS *m/z*: 283 (M^+, 3), 115 (100). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{17}NOS$: 283.1031. Found: 283.1068.

Reductive Desulfurization of 7a. General Procedure. To a stirred solution of **7** (**a** or **b**) (1 mol eq) $NiCl_2$•$6H_2O$ (7 mol eq) in MeOH-THF (3:1) was added $NaBH_4$ (21 mol eq) by portions at 0°C. After the addition was complete, stirring was continued at rt for 20 min. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The products were purified by column chromatography.

3-Formyl-7,8-dimethoxy-2,3,4,5-tetrahydro-1*H*-3-benzazepine (9a): From **7a** (218 mg, 0.64 mmol); column chromatography (hexane/$CHCl_3$ 1:2) gave **9a** (131 mg, 88%) as colorless prisms from Et_2O, mp 101-103 °C.IR: 1665. ^{1}H-NMR (300 MHz): 2.8-2.9 (4H, m, H-1, 5), 3.46, 3.66 (each 2H, each t, *J*=5 Hz, H-2, 4), 3.87 (6H, s, OCH_3x2), 6.66, 6.69 (each 1H, s, H-6, 9), 8.14 (1H, s, CHO). LR-MS *m/z*: 235 (M^+, 100). *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.58; H, 7.35; N, 5.88.

3-Formyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (9b): From **7b** (200 mg, 0.7 mmol); column chromatography (hexane/ethyl acetate 2:3) gave **9b** (95 mg, 77%) as colorless plates from Et_2O, mp 71-73 °C. IR: 1654. ^{1}H-NMR: 2.7-3.0 (4H, m, H-1, 5), 3.3-3.8 (4H, m, H-2, 4), 7.0-7.4 (2H, m, H-6, 7, 8, 9), 8.14 (1H, s, CHO). LR-MS *m/z*: 175 (M^+, 59), 117 (100). *Anal.* Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.36; H, 7.35; N, 7.93.

Hydrolysis of 9a. Typical Procedure. A solution of **9a** (207 mg, 0.88 mmol) in EtOH (10 mL) and 10% NaOH (10 mL) was refluxed for 1 h. The mixture was concentrated *in vacuo*, and the residue after diluted with H_2O was extracted with $CHCl_3$. The product was recrystallized from Et_2O to give **10a** (147 mg, 81%) as colorless prisms, mp 93-95 °C (lit.,[7] mp 94-95 °C).

7,8-Dimethoxy-2,3,4,5-terahydro-1*H*-3-benzazepine (10a): IR: 3550, 1520. ^{1}H-NMR (300 MHz): 1.99 (1H, br s, >NH), 2.8-2.9 (4H, m, H-1, 5), 2.9-3.0 (4H, m, H-2, 4), 3.85, 3.86 (each 3H, s, OCH_3x2), 6.64 (2H, s, H-6, 9). ^{13}C-NMR: 39.9 (tx2), 48.8 (tx2), 56.0 (qx2), 113.4 (dx2), 134.4 (sx2), 146.5 (sx2). LR-MS *m/z*: 207 (M^+,71), 165 (100). HR-MS *m/z* (M^+): Calcd for $C_{12}H_{17}NO_2$: 207.1257. Found: 207.1249.

2,3,4,5-Terahydro-1*H*-3-benzazepine (10b): From **9b** (200 mg, 1.14 mmol); column chromatography ($CHCl_3$/MeOH 9:1) gave **10b** (130 mg, 77%) as colorless prisms from Et_2O-hexane, mp 157-159 °C (lit.,[8] bp $_{18}$ 126-127 °C). IR: 3272. ^{1}H-NMR (90 MHz): 1.82 (1H, br s, >NH), 2.60 (8H, s, H-1, 2, 4, 5), 6.6-7.0 (4H, m, H-6, 7, 8, 9). ^{13}C-NMR: 40.3 (tx2), 48.6 (tx2), 126.1 (dx2), 129.2 (dx2), 142.3 (sx2). LR-MS *m/z*: 147 (M^+, 98), 117 (100). HR-MS *m/z* (M^+): Calcd for $C_{10}H_{13}N$: 147.1046. Found: 147.1046.

Reduction of 9a with $LiAlH_4$. Typical Procedure. $LiAlH_4$ (50 mg, 1.3 mmol) was added to a solution of **9a** (150 mg, 0.64 mmol) in dry THF (30 mL) under ice-cooling, and the mixture was refluxed for 1 h. Et_2O saturated with water was added to the reaction mixture, and insoluble material was filtered off. The product was chromatographed with $CHCl_3$/ethyl acetate (1:1) to give **11a** (71 mg, 50%) as colorless prisms from hexane, mp 37-39 °C (lit.,[9] mp 262-263 °C as HCl salt).

7,8-Dimethoxy-3-methyl-2,3,4,5-terahydro-1*H*-3-benzazepine (11a): IR: 1517. ^{1}H-NMR: 2.37 (3H, s, >NCH_3), 2.4-2.7 (4H, m, H-1, 5), 2.7-3.0 (4H, m, H-2, 4), 3.85 (6H, s, OCH_3x2), 6.64 (2H, s, H-6, 9). ^{13}C-NMR: 36.1 (tx2), 47.5 (q), 56.0 (qx2), 57.7 (tx2), 113.0 (dx2), 134.1 (sx2), 146.8 (sx2). LR-MS m/z: 221 (M^+, 69), 165 (100). HR-MS m/z (M^+): Calcd for $C_{13}H_{19}NO_2$: 221.1416. Found: 221.1417.

3-Methyl-2,3,4,5-terahydro-1*H*-3-benzazepine (11b): From **9b** (400 mg, 2.3 mmol); column chromatography (ethyl acetate) gave **11b** (300 mg, 82%) as colorless gum. IR (film): 1494. ^{1}H-NMR (90 MHz): 2.37 (3H, s, >NCH_3), 2.4-2.7 (4H, m, H-1, 5), 2.7-3.2 (4H, m, H-2, 4), 7.0-7.3 (4H, m, H-6, 7, 8, 9). ^{13}C-NMR: 36.5 (tx2), 47.5 (q), 57.4 (tx2), 126.2 (dx2), 128.8 (dx2), 141.9 (sx2). FAB-LRMS *m/z*: 162 (MH^+, 100). FAB-HRMS *m/z* (MH^+): Calcd for $C_{11}H_{16}N$: 162.1283. Found: 162.1284.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research (No 11672115) from the Ministry of Education, Science, Sports and Culture of Japan.

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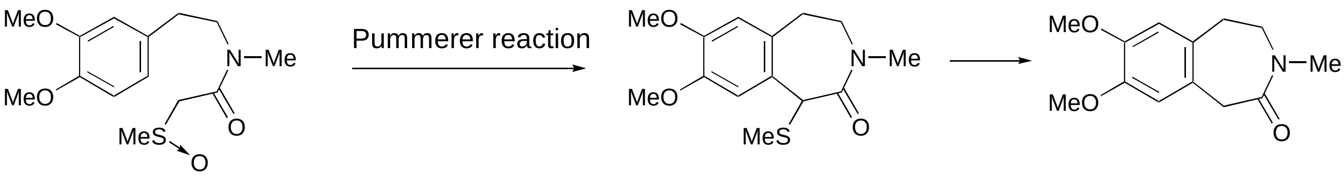

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