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Formation of Dibenzo[*b,f*]azecines by the Reaction of 1-Halogenophenethyl-1*H*-2-benzazepines with Dimsylsodium[1]

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Treatment of 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-7,8-dimethoxy-2-methyl-1*H*-2-benzazepine (**7a**) with dimsylsodium afforded 5,6,7,8,13,14-hexahydro-*trans*-13,14-methano-2,3,10,11-tetramethoxy-5-methyldibenzo[*b,f*]azecine (**8**) and its *cis*-isomer (**9**). The structure of the former was confirmed by direct comparison with the authentic sample prepared by the Simmons-Smith reaction of the 13,14-*trans*-5,6,7,8-tetrahydrodibenzo[*b,f*]azecine (**11**). 5,6,7,8,13,14-Hexahydro-11-hydroxy-*cis*-13,14-methano-2,3,10-trimethoxy-5-methyldibenzo[*b,f*]azecine (**15**) was obtained by the reaction of 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-8-hydroxy-7-methoxy-2-methyl-1*H*-2-benzazepine (**7d**) with dimsylsodium. The same reaction by the use of 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-7-hydroxy-8-methoxy-2-methyl-1*H*-2-benzazepine (**7e**) afforded the 13-(methylsulfinyl)methyl-5*H*-dibenzo[*b,g*]azacycloundecine (**16**).

Keywords——benzyne reaction; ring expansion; dibenzo[*b,f*]azecine; dibenzo[*b,g*]-azacycloazaundecine; Simmons-Smith reaction

In continuation of our study focussed on the benzyne reaction of 1-halogenophenethylisoquinolines (**1**) using dimsylsodium[3] as a base, we found a novel ring expansion of 1-substituted isoquinolines leading to dibenzo[*b,g*]azecine system (**3**)[4,5] (Chart 1). Apparently, **3** was formed through the cleavage of the C–N bond of the intermediate (**2**) by dimsyl anion. We successively investigated the reaction of a series of 1-halogenophenethyl-1*H*-2-benzazepines, which were homologous of isoquinolines, with dimsylsodium as an extension of the previous works in order to examine whether the similar ring expansion occurred or not. These results were described in this paper.

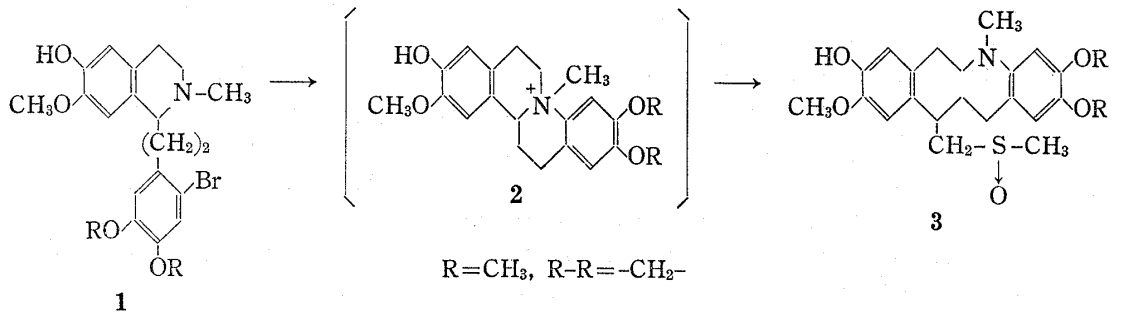
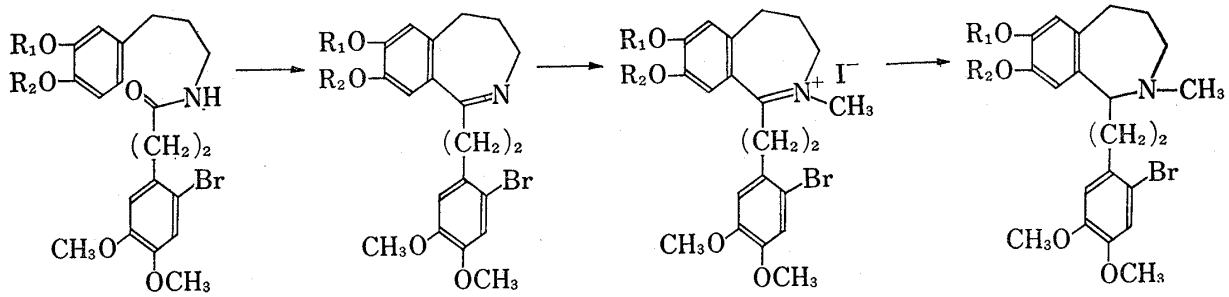


Chart 1

Firstly, a series of 1-halogenophenethyl-2,3,4,5-tetrahydro-2-methyl-1*H*-2-benzazepines were synthesized as follows. The Bischler-Napieralski type cyclization of the amide (**4a**),

1) Preliminary communication of this work appeared in *Heterocycles*, 3, 129 (1975).
2) Location: *1432–1 Horinouchi, Hachioji, Tokyo 192–03, Japan.*
3) E.J. Corey and M. Chaycovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).
4) S. Kano, E. Komiyama, T. Ogawa, Y. Takahagi, T. Yokomatsu, and S. Shibuya, *Chem. Pharm. Bull.* (Tokyo), **23**, 2058 (1975).
5) S. Kano, E. Komiyama, Y. Takahagi, and S. Shibuya, *Chem. Pharm. Bull.* (Tokyo), **24**, 648 (1976).

prepared from 3,4-dimethoxyphenylpropylamine[6] and 2-bromo-4,5-dimethoxyphenylpropionic acid yielded the 4,5-dihydro-3*H*-2-benzazepine (**5a**). Methylation of **5a** with methyl iodide, followed by reduction of the methiodide (**6a**) with sodium borohydride afforded 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-7,8-dimethoxy-2-methyl-1*H*-2-benzazepine (**7a**). Similarly, 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-8-hydroxy-7-methoxy-2-methyl-1*H*-2-benzazepine (**7d**) and 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-7-hydroxy-8-methoxy-2-methyl-1*H*-2-benzazepine (**7e**) were synthesized from the corresponding amides (**4b**) and (**4c**), respectively, by the usual manner, as shown in Chart 2 and described in the experimental section, (**4b**→**5b**→**6b**→**7b**→**7d**; **4c**→**5c**→**6c**→**7c**→**7e**).



4a: $R_1=R_2=CH_3$
4b: $R_1=CH_3$, $R_2=C_7H_7$
4c: $R_1=C_7H_7$, $R_2=CH_3$

5a: $R_1=R_2=CH_3$
5b: $R_1=CH_3$, $R_2=C_7H_7$
5c: $R_1=C_7H_7$, $R_2=CH_3$

6a: $R_1=R_2=CH_3$
6b: $R_1=CH_3$, $R_2=C_7H_7$
6c: $R_1=C_7H_7$, $R_2=CH_3$

7a: $R_1=R_2=CH_3$
7b: $R_1=CH_3$, $R_2=C_7H_7$
7c: $R_1=C_7H_7$, $R_2=CH_3$
7d: $R_1=CH_3$, $R_2=H$
7e: $R_1=H$, $R_2=CH_3$

Chart 2

The 1*H*-2-benzazepine (**7a**), thus obtained, was treated with dimsylsodium in dimethyl sulfoxide (DMSO) to give three products, which were separated by column chromatography on silica gel. The first product, $C_{23}H_{29}NO_4$ (MS *m/e*: M^+, 383), obtained from the benzene fraction, was assigned to 5,6,7,8,13,14-hexahydro-*trans*-13,14-methano-5-methyldibenzo-[*b*,*f*]-azecine (**8**) by direct comparison with the authentic sample prepared by the Simmons-Smith reaction of the 13,14-*trans*-5,6,7,8-tetrahydrodibenzo[*b*,*f*]azecine (11)[7]. The nuclear magnetic resonance (NMR) spectrum of **8** exhibited NCH_3 signal at δ 2.76 and four aromatic signals at δ 6.46, 6.53, 6.70 and 6.85 as singlets, respectively. Its ^{13}C–NMR spectrum[8] showed a methylene signal at δ 14.37 and two methine signals at δ 20.53 and 27.81, due to the *trans*-diphenylcyclopropane moiety, and three methylene signals were observed at δ 27.48, 30.60 and 52.85. Successively, the chloroform fraction afforded the second product (**9**). Its molecular formula was confirmed by elemental and mass spectral analysis (M^+, *m/e* 383) as $C_{23}H_{29}NO_4$. Its NMR spectrum showed NCH_3 signal at δ 2.58 and four aromatic signals at δ 6.38, 6.43, 6.47, and 6.57 as singlets, respectively. Its ^{13}C–NMR spectrum exhibited an extremely high methylene signal at δ 7.88 and two methine signal at δ 21.85 and 22.25, indicating a presence of *cis*-diphenylcyclopropane system as a partial structure, and three methylene signals at δ 25.75, 28.61 and 54.37. On the basis of these facts, the second product was assigned to 5,6,7,8,13,14-hexahydro-*cis*-13,14-methano-2,3,10,11-tetramethoxy-5-methyldibenzo[*b*,*f*]-azecine (**9**), *cis*-isomer of **8**. In addition to **8** and **9**, 2,3,4,5-tetrahydro-1-(2-hydroxy-3-methylthio-4,5-dimethoxyphenethyl)-7,8-dimethoxy-2-methyl-1*H*-2-benzazepine (**10**), formed by the reaction of dimsylsodium with benzyne intermediate, was obtained from 2% methanol–chloroform fraction. The 13,14-methanodibenzo[*b*,*f*]azecines (**8**) and (**9**) were also obtained by the reaction of the methiodide (**14**: $X^-=I^-$) with dimsylsodium. The methiodide (**14**:

6) I. Jirkovsky and M. Protiva, *Collect. Czech. Chem. Commun.*, **32**, 1197 (1967).
7) S. Kano, T. Yokomatsu, and S. Shibuya, *Heterocycles*, **4**, 933 (1976).
8) ^{13}C-NMR spectra were taken with a Varian NV-14 spectrometer in $CDCl_3$ using TMS as an internal standard operating at 15.1 MHz.

$X^-=I^-$) was prepared by methylation of the quino[2,1-*a*][2]benzazepine (**13**) obtained by cyclization of the tetrahydro-1*H*-2-benzazepine (**12**). This indicated that **8** and **9** were derived through the N-methyl quino[2,1-*a*][2]benzazepinium salt (**14**: X^-=appropriate anion) as an intermediate from **7a**.

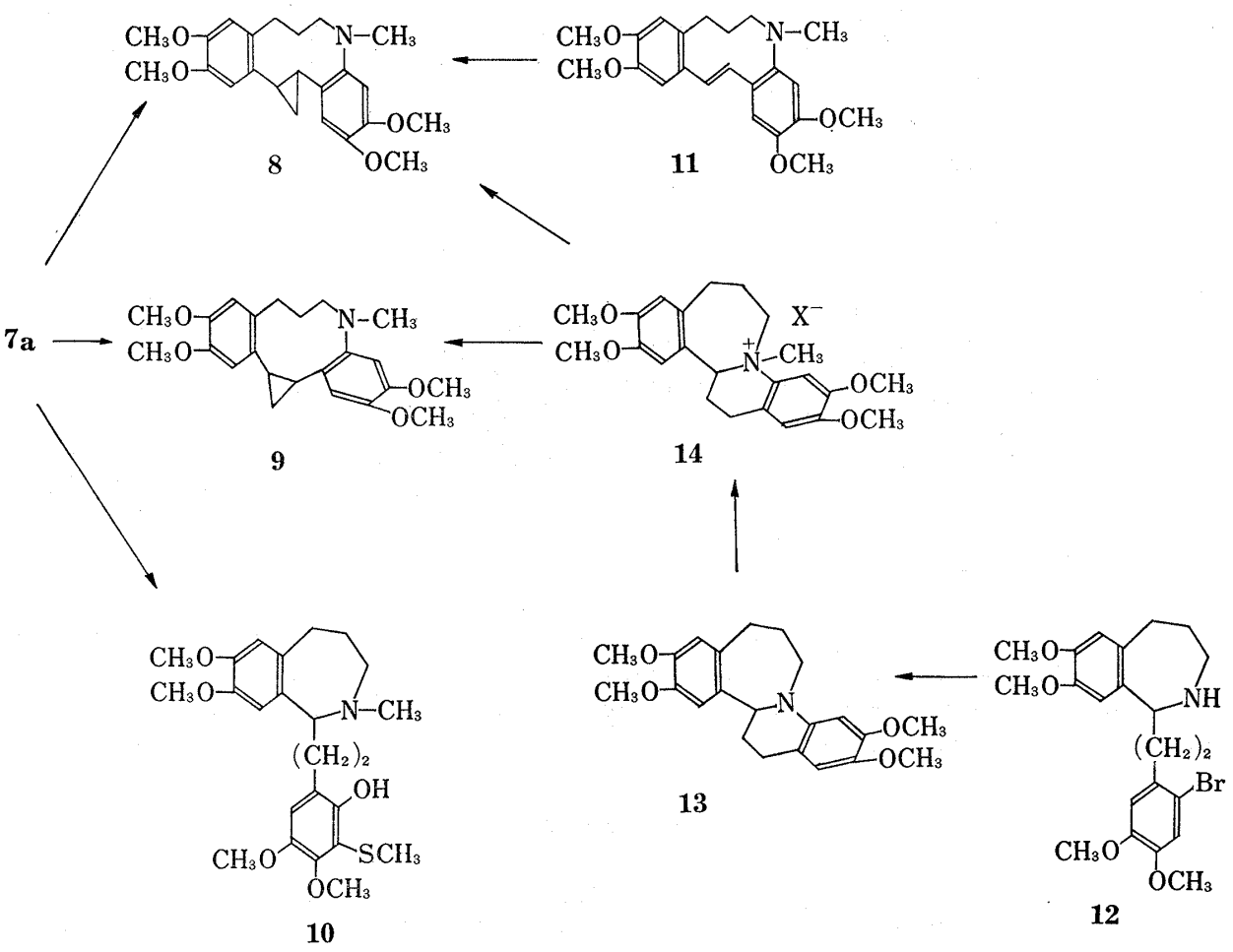


Chart 3

Similar reaction of the 2,3,4,5-tetrahydro-8-hydroxy-1*H*-2-benzazepine (**7d**) with dimsylsodium afforded the *cis*-13,14-methanodibenzo[*b*,*f*]azecine (**15**), in 35% yield. Its spectroscopic data were quite similar to those of **9**, and NCH_3 and four aromatic proton signals were observed at δ 2.58, 6.38, 6.43, 6.47 and 6.57 as singlets, respectively, in its NMR spectrum. Its ^{13}C–NMR spectrum exhibited a methylene signal at δ 7.75 and two methine signals at δ 20.05 and 22.25, attributable to diphenylcyclopropane moiety, and three methylene signals at δ 25.83, 28.81 and 54.64. O-Methylation of **15** with diazomethane gave **9**. Thus, the product from **7d** was assigned to 5,6,7,8,13,14-hexahydro-11-hydroxy-*cis*-13,14-methano-2,3,10-trimethoxy-5-methyldibenzo[*b*,*f*]azecine (**15**). On the other hand, in contrast to these results, the reaction of **7e** with dimsylsodium gave the dibenzo[*b*,*g*]azacycloundecine (**16**). Deoxygenation of **16** with zinc amalgam afforded the 13-(methylthio)methyl derivative (**17**), the NMR spectrum of which showed singlets attributable to SCH_3 and NCH_3 at δ 1.84 and 2.03, respectively. Desulfurization of **17** with Raney Ni catalyst yielded the corresponding 13-methyl derivative (**18**). The signals due to 13–CH_3 were observed at δ 1.40 as a doublet (J= 6.5 Hz) in its NMR spectrum. The NCH_3 protons resonated at δ 2.03 as a singlet. These abnormaly high aromatic NCH_3 signals in the NMR spectra of **17** and **18** would be caused by the anisotropy of the benzene-A ring. For a further proof of the structure of **16**, the reaction of the methiodide (**22**) of the quino[2,1-*a*][2]benzazepine (**21**) with dimsylsodium was

examined to give **16** in moderate yield. The quino[2,1-*a*][2]benzazepine (**21**) was prepared by cyclization of the 1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-1H-2-benzazepine (**19**), followed by debenzylation of the cyclized product (**20**).

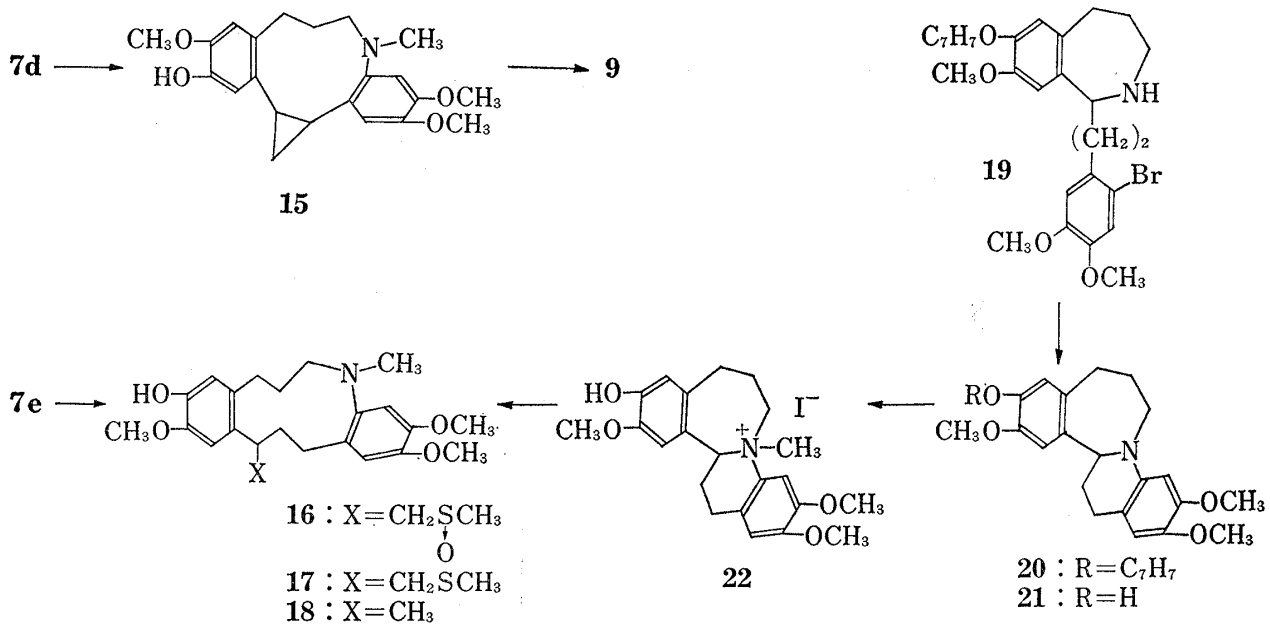


Chart 4

Thus, the reaction of 1-halogenophenethyl-1*H*-2-benzazepines with dimsylsodium was found to show an interesting ring expansion through the N-methyl quino[2,1-*a*][2]benzazepinium salts as the intermediate.

Experimental[9]

General Procedure for the Preparation of the Amides (**4**)——A mixture of 0.03 mol of 2-bromo-4,5-dimethoxyphenylpropionic acid and 0.03 mol of 3,4-dimethoxyphenylpropylamine[6] (for the preparation of **4b** and **4c**, 4-benzyloxy-3-methoxyphenylpropylamine[10] and 3-benzyloxy-4-methoxyphenylpropylamine[10] were used, respectively) was heated at 180° for 1.5 hr. After cooling, the mixture was recrystallized from benzene–ether to give **4** as colorless needles.

General Procedure for the Preparation of the 4,5-Dihydro-3*H*-2-benzazepine (**5**)——A mixture of 0.01 mol of **4**, 100 ml of CH_3CN and 0.03 mol of $POCl_3$ was refluxed for 4 hr. The solvent was evaporated and the resulting residue was made basic with NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to leave **5**.

General Procedure for the Preparation of 2,3,4,5-Tetrahydro-2-methyl-1*H*-2-benzazepine (**7**)——A mixture of 4 g of **5**, 40 ml of MeOH and 15 ml of CH_3I was refluxed for 5 hr. To a stirred solution of the remaining residue (**6**), obtained on removal of the solvent, in 150 ml of MeOH was added 2.5 g of $NaBH_4$ at room temperature. The mixture was worked up as usual to give **7** as a pale brownish oil. The phenolic bases (**7d, e**) were obtained from the corresponding O-benzyl derivatives by refluxing in EtOH–conc. HCl (1: 1) for 1.5 hr and usual work up.

General Procedure for the Reaction of 7a, d, e, 12, 14, 19, and 22 with Dimsylsodium——To a stirred solution of dimsylsodium (prepared from 15 equimolar amounts of NaH and DMSO) was added a solution of starting material (5 mmol) in DMSO at room temperature. After the stirring had been continued for 14 hr, the mixture was poured into H_2O and extracted with $CHCl_3$. For the phenolic base, excess NH_4Cl was added before extraction with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated. The resulting residue was purified by column chromatography on silica gel, in the cases of **7**, and **14**.

9) All melting points were uncorrected. NMR spectra were taken with a Varian T-60 spectrometer in $CDCl_3$ using TMS as an internal standard. Mass spectra were measured with a Hitachi RMU-7L spectrometer.

10) S. Kano, T. Yokomatsu, and S. Shibuya, *Chem. Pharm. Bull.* (Tokyo), **25**, 2401 (1977).

Table I. Elemental Analysis of **4**, **5**, and **7**

Compound	Formula	Yield(%)	mp(°C)	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
4a	$C_{22}H_{28}BrNO_5$	67	108—110 (Benzene–ether)	56.65	6.05	3.00	56.95	6.11	2.77
4b	$C_{28}H_{32}BrNO_5$	65	119—120 (Benzene–ether)	61.99	5.95	2.58	62.28	5.92	2.30
4c	$C_{28}H_{32}BrNO_5$	65	140—141 (Benzene–ether)	61.99	5.95	2.58	62.26	6.00	2.30
5a	$C_{28}H_{29}BrN_4O_{11}$ [a]	64	181—182 (EtOH)	49.64	4.31	8.27	49.58	4.43	8.07
5b	$C_{28}H_{30}BrNO_4$	67	Oil[b]						
5c	$C_{34}H_{33}BrN_4O_{11}$ [a]	67	207—208 (dec.) (EtOH–ether)	54.19	4.41	7.44	54.32	4.55	7.21
7a	$C_{23}H_{31}BrClNO_4$ [c]	87	202—204 (MeOH–ether)	55.15	6.24	2.80	55.01	6.23	2.65
7b	$C_{29}H_{35}BrClNO_4$ [c]	85	214—216 (dec.) (MeOH–ether)	60.36	6.11	2.43	60.13	6.20	2.22
7c	$C_{28}H_{37}BrN_4O_{11}$ [a]	85	100—101 (EtOH–ether)	54.84	4.47	7.31	54.64	4.62	7.03
7d	$C_{28}H_{31}BrN_4O_{11}$ [a]	72	179—180 (EtOH)	49.49	4.60	8.25	49.56	4.65	8.15
7e	$C_{28}H_{31}BrN_4O_{11}$ [a]	70	121—222 (EtOH)	49.49	4.60	8.25	49.13	4.80	8.09

a) Picrate.
b) Used for the following reaction because of difficulty of crystallization.
c) Hydrochloride.

Table II. Elemental Analysis of Reaction Products of **7a**, **d**, **e**, **12**, **14** ($X^-=I^-$), **19** and **22**

Starting material	Product	Formula	mp (°C)	Yield (%)	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
7a	**8**[a]	$C_{23}H_{29}NO_4$	138—140 (MeOH–ether)	19	72.03	7.62	3.65	72.08	7.63	3.26
	9[b]	$C_{23}H_{29}NO_4$	129—130 (MeOH–ether)	34	72.03	7.62	3.65	72.06	7.59	3.36
	10[c]	$C_{24}H_{33}NO_5S$	130—131 (MeOH–ether)	2.9	64.40	7.43	3.13	64.57	7.47	3.04
12	**13**	$C_{22}H_{27}NO_4$	117—118.5 (MeOH–ether)	60	71.52	7.37	3.79	71.55	7.57	3.84
14	**8**[d]	$C_{23}H_{23}NO_4$	138—140 (MeOH–ether)	8.7						
	9[d]	$C_{23}H_{29}NO_4$	129—130 (MeOH–ether)	17.5						
7d	**15**[b]	$C_{22}H_{27}NO_4$	133—135 (MeOH)	35	71.52	7.37	3.79	71.63	7.35	3.70
7e	**16**[c]	$C_{22}H_{33}NO_5S$	Oil[e]	46.8						
19	**20**	$C_{28}H_{31}NO_4$	143—144 (MeOH–ether)	77	75.48	7.01	3.14	75.35	6.98	3.05
22	**16**[f]	$C_{22}H_{33}NO_5S$	Oil	52						

a) Obtained from the benzene fraction.
b) Obtained from the $CHCl_3$ fraction.
c) Obtained from the 2% MeOH–$CHCl_3$ fraction.
d) Identical with the product obtained from **7a**.
e) Used for the following reaction because of difficulty of crystallization.
f) Identical with the product obtained from **7e**.

Table III. NMR Spectra of **5**, **7**, **8**, **9**, **10**, **13**, **15**, and **20**

No.	NMR (δ) in $CDCl_3$
5a	3.82 (6H, s, 2×OCH_3), 3.85, 3.93 (6H, each s, 2×OCH_3), 6.70, 6.75, 6.80, 6.95 (4H, each s, 4×Ar-H).
5b	3.80 (6H, s, 2×OCH_3), 3.88 (3H, s, OCH_3), 5.07 (2H, s, $PhCH_2O$), 6.67 (2H, s, 2×Ar-H), 6.78, 6.92 (2H, each s, 2×Ar-H).
5c	3.77, 3.81, 3.85 (9H, each s, 3×Ar-H), 5.10 (2H, s, $PhCH_2O$), 6.68, 6.72, 6.78, 6.91 (4H, each s, 4×Ar-H).
7a	2.18 (3H, s, NCH_3), 3.88 (12H, 4×OCH_3), 6.67 (2H, s, 2×Ar-H), 6.77, 7.00 (2H, each s, 2×Ar-H).
7b	2.10 (3H, s, NCH_3), 3.82 (6H, s, 2×OCH_3), 3.83 (3H, s, OCH_3), 5.07 (2H, s, $PhCH_2O$), 6.65 (2H, s, 2×Ar-H), 6.67, 6.95 (2H, each s, 2×Ar-H).
7c	2.18 (3H, s, NCH_3), 3.78, 3.83, 3.86 (9H, each s, 3×OCH_3), 5.04 (2H, s, $PhCH_2O$), 6.68 (2H, s, 2×Ar-H), 6.73, 6.94 (2H, each s, 2×Ar-H).
7d	2.13 (3H, s, NCH_3), 3.82 (9H, s, 3×OCH_3), 6.58 (1H, s, Ar-H), 6.70 (2H, s, 2×Ar-H),6.93 (1H, s, Ar-H).
7e	2.16 (3H, s, NCH_3), 3.84 (9H, s, 3×OCH_3), 6.57, 6.63, 6.69, 6.93 (4H, each s, 4×Ar-H).
8	2.76 (3H, s, NCH_3), 3.88 (12H, s, 4×OCH_3), 6.48, 6.53, 6.70, 6.85 (4H, each s, 4×Ar-H).
9	2.58 (3H, s, NCH_3), 3.67, 3.73, 3.77, 3.78 (12H, each s, 4×OCH_3), 6.30, 6.40, 6.52, 6.60 (4H, each s, 4×Ar-H).
10	2.23 (3H, NCH_3), 2.43 (3H, s, SCH_3), 6.50, 6.63, 6.67 (3H, each s, 3×Ar-H).
13	3.80 (3H, s, OCH_3), 3.90 (9H, s, 3×OCH_3), 6.27 (1H, s, Ar-H), 6.20 (2H, s, 2×Ar-H), 6.70 (1H, s, Ar-H).
15	2.58 (3H, s, NCH_3), 6.38, 6.43, 6.47, 6.57 (4H, each s, 4×Ar-H).
20	3.78 (3H, s, OCH_3), 3.87 (6H, s, 2×OCH_3), 5.09 (2H, s, $PhCH_2O$), 6.25, 6.58, 6.63, 6.71 (4H, each s, 4×Ar-H).

1-(2-Bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-7,8-dimethoxy-1*H*-2-benzazepine (12)——To a stirred solution of 5 g of the hydrochloride of **5a** in 150 ml of MeOH was added 2.5 g of $NaBH_4$ under ice-cooling. After the mixture was refluxed for 0.5 hr, the solvent was evaporated and the resulting residue was suspended in H_2O and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to leave 4 g of **12** as a colorless oil, picrate, mp 222—224° (MeOH–ether). *Anal.* Calcd. for $C_{28}H_{31}BrN_4O_{11}$: C, 49.49; H, 4.60; N, 8.25. Found: C, 49.69; H, 4.64; N, 7.97.

N-Methyl Quino[2,1-*a*][2]benzazepinium Iodide (14)——Treatment of **13** with CH_3I as usual afforded **14** ($X^-=I^-$), mp 227—228° (dec.) (MeOH). *Anal.* Calcd. for $C_{23}H_{30}INO_4$: C, 54.01; H, 5.91; N, 2.74. Found: C, 53.75; H, 5.81; N, 2.37.

The Simmons-Smith Reaction of 11——To a stirred solution of 0.4 g of **11** in 50 ml of dry dioxane was added 1.5 ml of 25% Et_2Zn hexane solution and 1.2 g of CH_2I_2. The mixture was warmed at 80° for 4 hr under stirring. The mixture was decomposed with excess NH_4Cl and H_2O, and extracted with $CHCl_3$. The extract was washed with $CHCl_3$, dried over Na_2SO_4 and evaporated. The resulting residue was chromatographed on 5 g of silica gel. Elution with $CHCl_3$ (20 ml) afforded 80 mg of colorless needles, which was identical with **8** in all respect.

6,7,8,13,14,15-Hexahydro-10-hydroxy-2,3,11-trimethoxy-5-methyl-13-(methylthio)methyl-5*H*-dibenzo-[*b*,*g*]azacycloundecine (17)——A mixture of 1.4 g of **16**, 40 ml of 50% AcOH–conc. HCl (1:1) and Zn–Hg (prepared from 5 g of Zn and 0.5 g of $HgCl_2$) was heated on a water bath for 1 hr. After removal of inorganic substance, the mixture was made basic with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to leave 1.1 g of **17** as colorless needles, mp 100—102° (ether–hexane). MS *m/e*: (M^+), NMR ($CDCl_3$) δ: 1.84 (3H, s, SCH_3), 2.03 (3H, s, NCH_3), 3.83 (6H, s, 2×OCH_3), 3.86 (3H, s, OCH_3), 6.55, 6.62, 6.68, 6.75 (4H, each s, 4×Ar–H). *Anal.* Calcd. for $C_{22}H_{33}NO_4S$: C, 66.79; H, 7.71; N, 3.25. Found: C, 67.02; H, 7.92; N, 3.16.

6,7,8,13,14,15-Hexahydro-10-hydroxy-2,3,11-trimethoxy-5,13-dimethyl-5*H*-dibenzo[*b*,*g*]azacycloundecine (18)——A solution of 1 g of **17** in 100 ml of EtOH was refluxed in the presence of 2 ml of Raney Ni catalyst for 10 hr. After removal of catalyst, the solvent was evaporated to give 0.5 g of **18** as a colorless oil. MS *m/e*: 385 (M^+), NMR ($CDCl_3$) δ: 1.40 (3H, d, J=6.5 Hz, 13-CH_3), 2.03 (3H, s, NCH_3), 3.85 (6H, s, 2×OCH_3), 3.87 (3H, s, OCH_3), 6.55, 6.62, 6.68, 6.75 (4H, each s, 4×Ar–H), picrate, mp 193—194° (EtOH). *Anal.* Calcd. for $C_{29}H_{34}N_4O_{11}$: C, 56.67; H, 5.68; N, 9.12. Found: C, 56.52; H, 5.67; N, 9.12.

7-Benzyloxy-1-(2-bromo-4,5-dimethoxyphenethyl)-2,3,4,5-tetrahydro-8-methyl-1*H*-2-benzazepine (19)——To a solution of 4 g of the hydrochloride of **20** in 150 ml of MeOH was added 3 g of $NaBH_4$ and

the mixture was worked up as usual to give 3.5 g of **19** as a colorless oil. NMR ($CDCl_3$) δ: 3.83 (9H, s, 3× OCH_3), 5.06 (2H, s, $PhCH_2O$), 6.67 (1H, s, Ar–H), 6.72 (2H, s, 2×Ar–H), 6.95 (1H, s, Ar–H), picrate, mp 100—102° (MeOH–ether). *Anal.* Calcd. for $C_{34}H_{35}BrN_4O_{11}$: C, 54.04; H, 4.67; N, 7.42. Found: C, 53.84; H, 4.85; N, 7.21.

Quino[2,1-*a*][2]benzazepine (21)——A mixture of 2 g of **20**, 9 ml of EtOH and 9 ml of conc. HCl was refluxed for 0.5 hr. The solvent was evaporated and the remaining residue was made basic with 28% NH_4OH and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to leave 1.5 g of **21** as a pale brownish oil. MS *m/e*: 355 (M^+); this was characterized as the methiodide (**22**), since it was unstable and difficult to crystallize, mp 195—197° (MeOH). *Anal.* Calcd. for $C_{28}H_{28}INO_4$: C, 53.12; H, 5.67; N, 2.82. Found: C, 53.05; H, 5.95; N, 2.63.

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