A Novel Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) with Benzyl Halides in the Presence of Water

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1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) reacted with benzyl halides in CH_2Cl_2/H_2O 1:1 (*v*/*v*) to afford a mixture of eleven-membered cyclic amide **1** and seven-membered cyclic amide **2**. When the reaction was carried out in $EtOH/H_2O$ 1:1 (*v*/*v*), product **2** was obtained as the major product. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) gave the five-membered cyclic amide **3** as the sole product under the same reaction conditions.

Introduction. – 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) are well-known organic bases and play very important roles in organic synthesis. However, reactions with DBU or DBN as the starting material in organic synthesis are rare. So far, *Yuji et al.* reported that DBU can react with primary alkyl halides to give the corresponding quaternary ammonium salts [1]. *Yamamoto* and *Maruoka* disclosed that the reduction of DBU by DIBAL gives a large cyclic diamine in high yield [2]. Recently, the nucleophilic behavior of DBU and DBN has gradually attracted much attention. For example, *Juneja* and *Garg*, and *Alder et al.* independently employed DBU to react with alkyl halides producing the corresponding large cyclic compounds [3][4]. *Alder et al.* further disclosed that the DBU ring can be opened in the reaction with nucleophile [5]. *Kraft* and *Hesse* and co-workers also showed that the DBU ring can be opened to give a seven-membered ring product [6][7]. Moreover, *Chakrabarty et al.* investigated in 1996 the reaction of DBU with ethyl 3-bromopropanoate to furnish an *N*-substituted caprolactam derivative [8]. Herein, we wish to report another novel reaction in which DBU and DBN are used as starting materials to give the *N*,*N*-dibenzylated ring-opened product in the presence of benzyl halides and H_2O. Especially, we disclose here that two kinds of *N*,*N*-dibenzylated products (product **1** is a ring-enlargement product and product **2** is a ring-opened product) were obtained at the same time in the reaction of DBU with benzyl halides under special reaction conditions.

Results and Discussion. – In the course of preparing mixed carbonates ($ROC(O)OCH_2Ar$) with DBU as a base *via* a three-component coupling reaction of alcohols, benzyl chloride, and CO_2, we incidentally found that two dibenzylated compounds **1** and **2**, an eleven-membered and a seven-membered cyclic amide, respectively, were formed in low yields as the by-products. We assume that the formation of **1** and **2** is due to a hydrolysis process along with an *N*-benzylation

Scheme 1

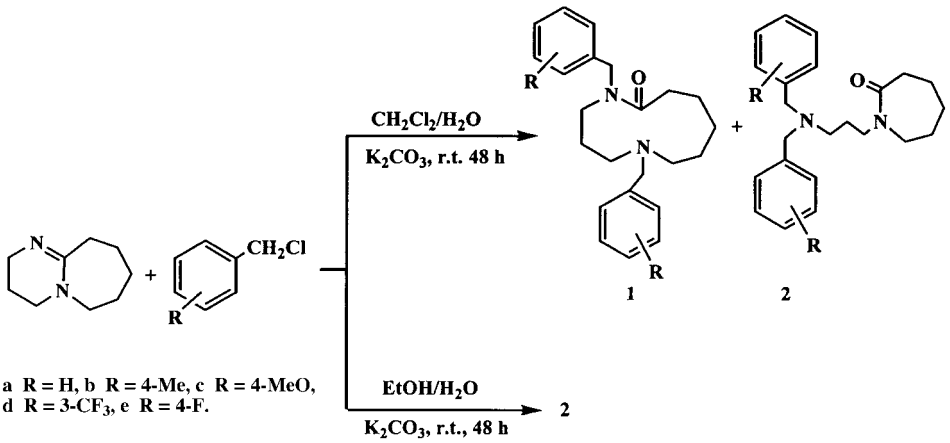


Table 1. *Reaction of DBU with Benzyl Halides in CH_2Cl_2/H_2O 1:1*

Entry	Compound	Benzyl halides	Yield [%][a])	
			1	**2**
1	**a**	$C_6H_4CH_2Cl$	60	30
2	**b**	4-Me–$C_6H_4CH_2Cl$	50	40
3	**c**	4-MeO–$C_6H_4CH_2Cl$	22	34
4	**d**	3-CF_3–$C_6H_4CH_2Cl$	27	21
5	**e**	4-F–$C_6H_4CH_2Cl$	42	44

[a]) Yields of isolated products.

reaction. Thus, we carried out the reactions of DBU with various benzyl halides in CH_2Cl_2/H_2O 1:1 (*v*/*v*) in the presence of K_2CO_3 as a base (*Scheme 1*). We found the two products were obtained in very high yields (*Table 1*). Their structures were determined by ^{1}H- and ^{13}C-NMR-spectral data, high-resolution mass spectrometry (HR-MS), and elemental analyses. Furthermore, the structures of **1a** and **2e** were established by X-ray analyses (*Figs. 1* and *2*). The substituent effects of benzyl halides on the yields of **1** and **2** were also elucidated. In general, neither electron-donating groups nor electron-withdrawing groups significantly affect the total yields of **1** and **2** (*Table 1*, *Entries 1–5*). The reaction with $PhCH_2Br$ under the same conditions gave similar results, while other alkyl halides, such as BuBr or allyl chloride, did not react, and $Ph(CH_2)_3Br$ reacted with DBU to give the corresponding products **1** and **2** in only trace amounts. Raising the reaction temperature accelerates the rate of the reaction of these aliphatic halides with DBU. For example, in the reaction of BuBr with DBU 40°, the corresponding product **2f** could be isolated in 30% yield (*Scheme 2*). The bases used for this reaction, including inorganic bases such as K_2CO_3, Na_2CO_3, or KOH, and organic bases such as Et_3N or DBU, do not affect the total yields of **1** and **2**. In general, the yields of **1** and **2** are up to 90%. It should be emphasized here that the solvents play a decisive role in this novel reaction, as the yields of **1** and **2** are very similar in toluene,

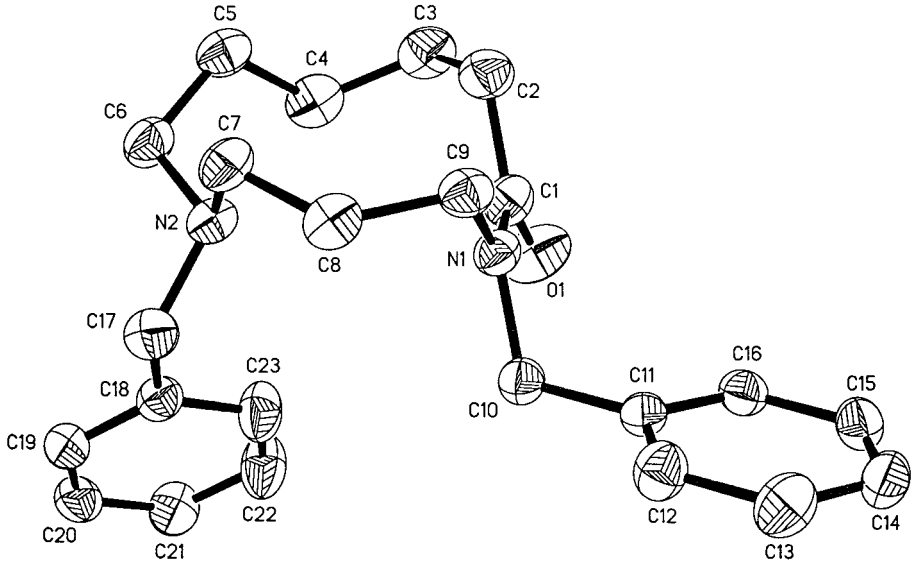


Fig. 1. *The crystal structure of* **1a**

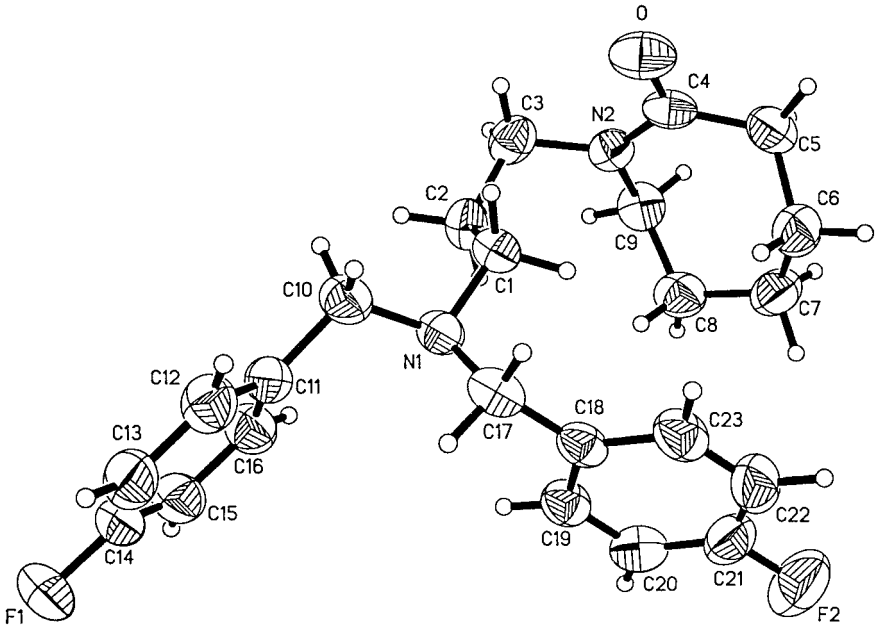
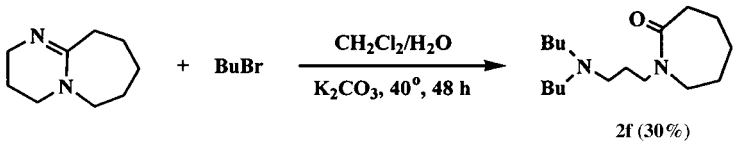


Fig. 2. *The crystal structure of* **2e**

MeCN, THF, Et_2O or AcOEt. On the other hand, the yield of **1** in CH_2Cl_2 or $ClCH_2CH_2Cl$ is much higher than in toluene, MeCN, THF, Et_2O, or AcOEt (*Table 2*). We also found that, in the reaction of DBU with $PhCH_2Cl$ in $EtOH/H_2O$ 1:1, **1a** and **2a** were formed at the same time in very high yield (*Table 3*, *Entry 1*). However, in the

Scheme 2



2f (30%)

Table 2. *Reactions of DBU with Benzyl Halides in Various Organic Solvents/H_2O 1 : 1*

Entry	Organic solvent	Yield [%][a])	
		1a	**2a**
1	Toluene	23	50
2	MeCN	10	80
3	THF	10	75
4	Et_2O	10	40
5	AcOEt	15	75

[a]) Yields of isolated products.

Table 3. *Reactions of DBU with Benzyl Halides in EtOH/H_2O 1 : 1*

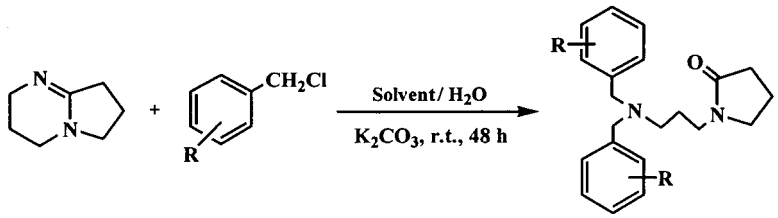
Entry	Compound	Benzyl halides	Yield [%][a])	
			1	**2**
1	**a**	$C_6H_5CH_2Cl$	30	50
2	**b**	4-Me–$C_6H_4CH_2Cl$	trace	66
3	**c**	4-MeO–$C_6H_4CH_2Cl$	–	–
4	**d**	4-CF_3–$C_6H_4CH_2Cl$	trace	30
5	**e**	4-F–$C_6H_4CH_2Cl$	trace	72

[a]) Yields of isolated products.

reaction with other benzyl chlorides shown in *Scheme 1*, compounds **2b**–**e** were obtained as the sole products in only moderate yields (*Scheme 1*, and *Table 3*, *Entries 2*, *4*, and *5*). It is especially worth mentioning that no reaction occurred with 4-MeO-$C_6H_4CH_2Cl$ (*Table 3*, *Entry 3*). At present, we cannot offer a reasonable explanation for the solvent effects in this reaction. However, we assume that the very strong electron-donating group such as 4-MeO of benzyl halides would impair the nucleophilic attack of DBU. *Chakrabarty et al.* suggested that the eleven-membered cyclic amide cannot be obtained in his reaction system [8]. We have unambiguously shown that the eleven-membered cyclic amides **1** are indeed formed in the reaction of benzyl halides with DBU.

On the other hand, in the reaction of DBN with benzyl halides, the five-membered cyclic amides of type **3** were obtained as the sole products when the reactions were carried out in CH_2Cl_2/H_2O 1:1 or in EtOH/H_2O 1:1 (*Scheme 3* and *Table 4*). Their structures were determined by comparison of the ^1H- and ^{13}C-NMR spectra data with those of **2**. With 4-MeO-$C_6H_4CH_2Cl$, **3c** was obtained in only very low yield in CH_2Cl_2/H_2O 1:1, but no reaction occurred in EtOH/H_2O 1:1 (*Table 4*, *Entries 3* and *8*). By

Scheme 3



3

a R = H, b R = 4-Me, c R = 4-MeO, d R = 3-CF_3, e R = 4-F.

Table 4. *Reaction of DBN with Benzyl Halides in CH_2Cl_2/H_2O 1 : 1*

Entry	Compound	Benzyl halides	Solvent	Yield of **3** [%][a])
1	**a**	$PhCH_2Cl$	CH_2Cl_2/H_2O	86
2	**b**	4-Me–$C_6H_4CH_2Cl$	CH_2Cl_2/H_2O	85
3	**c**	4-MeO–$C_6H_4CH_2Cl$	CH_2Cl_2/H_2O	4
4	**d**	3-CF_3–$C_6H_4CH_2Cl$	CH_2Cl_2/H_2O	72
5	**e**	4-F–$C_6H_4CH_2Cl$	CH_2Cl_2/H_2O	83
6	**a**	$PhCH_2Cl$	$EtOH/H_2O$	93
7	**b**	4-Me–$C_6H_4CH_2Cl$	$EtOH/H_2O$	86
8	**c**	4-MeO–$C_6H_4CH_2Cl$	–	–
9	**d**	3-CF_3–$C_6H_4CH_2Cl$	$EtOH/H_2O$	25
10	**e**	4-F–$C_6H_4CH_2Cl$	$EtOH/H_2O$	81

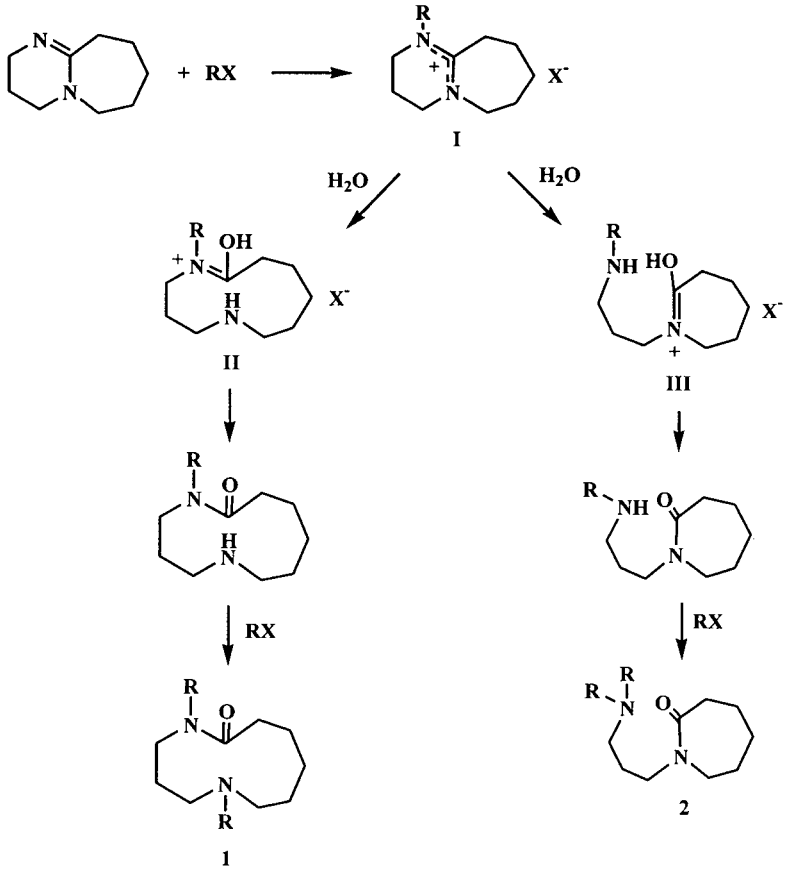
[a]) Yields of isolated products.

comparison of the structures between DBU and DBN, we assume that, for DBN, the corresponding nine-membered cyclic lactam is generally difficult to be formed, and, thus, the six-membered ring of DBN is easily opened by nucleophilic attack of H_2O. This is why exclusively compound **3** was formed.

We propose a plausible mechanism in *Scheme 4*. The first step is the *N*-benzylation of DBU to give a quaternary ammonium salt **I**. A nucleophilic attack of H_2O leads to the two intermediates **II** and **III**. The two intermediates then isomerize to the corresponding lactams, which further react with benzyl halides to give **1** and **2**, respectively. This is a novel tandem reaction, because both benzyl halide and H_2O are required to obtain the cyclic ketone.

Conclusions. – We have found a novel reaction of DBU and DBN with benzyl halides in the presence of H_2O and proposed a plausible mechanism for the formation of the dibenzylated cyclic amides. Efforts are underway to elucidate the mechanistic details of this reaction and to identify systems enabling similar reactions of other substrates and their subsequent transformations.

Scheme 4



Experimental Part

General. Org. solvents were dried by standard methods when necessary. Commercial reagents were used without further purification. All reactions were monitored by TLC with *Huanghai GF$_{254}$* silica-gel-coated plates. Flash column chromatography (CC): with 200–300 mesh silica gel. M.p.: *Yanagimoto* micromelting-point apparatus; uncorrected. ^{1}H-NMR Spectra: *Bruker AM-300* spectrometer in $CDCl_3$; TMS as internal standard; *J* values in Hz. MS: *HP-5989* instrument; HR-MS: *Finnigan MA+* mass spectrometer. Elemental analyses: *Carlo-Erba 1106* analyzer.

General Procedure for the Reactions of DBU or DBN with Benzyl Halides in the Presence of H_2O and Base. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 152 mg, 1.0 mmol) in CH_2Cl_2 (10 ml), $PhCH_2Cl$ (280 mg, 2.2 mmol), K_2CO_3 (304 mg, 2.2 mmol), and H_2O (2.0 ml) were added into a 50-ml round-bottom flask with a magnetic stir bar. The mixture was stirred at r.t. for 48 h. The H_2O layer was separated, and the org. layer was dried (Na_2SO_4). After filtration, the solvent was removed under reduced pressure, and the residue was purified by CC (SiO_2; petroleum ether/AcOEt 2:1) to give *1,5-dibenzyl-1,5-diazacycloundecan-6-one* (**1a**; 210 mg, 60%). White solid. M.p. 81–84°. IR ($CHCl_3$): 1627 (C=O). ^{1}H-NMR ($CDCl_3$): 1.26–1.40 (*m*, CH_2); 1.46–1.52 (*m*, CH_2); 1.68–1.71 (*m*, CH_2); 1.77–1.83 (*m*, CH_2); 2.26–2.29 (*m*, CH_2); 2.39–2.43 (*m*, CH_2); 2.50–2.62 (*m*, CH_2); 3.40–3.50 (*m*, 1 H, CH_2); 3.42 (*s*, 2 CH_2); 4.60–4.70 (*m*, 1 H, CH_2); 7.13–7.38 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.01; 25.17; 26.78; 32.40; 43.50; 46.25; 50.09; 53.91; 59.78; 126.92; 127.12; 128.14;

128.19; 128.45; 129.24; 137.81; 139.35; 175.20 (C=O). EI-MS: 350 ($M^{+\bullet}$). HR-EI-MS: 350.2360 ($C_{23}H_{30}N_2O^+$, M^+, calc. 350.2358). Anal. calc. for $C_{23}H_{30}N_2O$: C 78.82, H 8.62, N 7.99; found: C 78.47, H 8.23, N 7.62.

Data of 1-[3-(Dibenzylamino)propyl]azepan-2-one (**2a**): 175 mg (50%). A colorless liquid. IR ($CHCl_3$): 1638 (C=O). ^{1}H-NMR ($CDCl_3$): 1.44–1.73 (*m*, 4 CH_2); 2.42–2.47 (*m*, 2 CH_2); 3.12–3.15 (*m*, CH_2); 3.31–3.36 (*m*, CH_2); 3.55 (*s*, 2 CH_2); 7.20–7.38 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.24; 25.91; 28.58; 29.87; 37.20; 46.44; 49.53; 51.03; 58.57; 126.72; 128.08; 128.76; 139.73; 175.48 (C=O). EI-MS: 350 ($M^{+\bullet}$). HR-EI-MS: 350.2346 ($C_{23}H_{30}N_2O^+$, M^+; calc. 350.2358).

Data of 1,5-Bis(4-methylbenzyl)-1,5-diazacycloundecan-6-one (**1b**): 249 mg (66%). A colorless liquid. IR ($CHCl_3$): 1634 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15–1.19 (*m*, CH_2); 1.29–1.31 (*m*, CH_2); 1.35–1.39 (*m*, CH_2); 1.40–1.43 (*m*, CH_2); 1.65–1.71 (*m*, CH_2); 2.15–2.19 (*m*, CH_2); 2.23 (*s*, 2 Me); 2.27–2.31 (*m*, CH_2); 2.44–2.47 (*m*, CH_2); 3.26–3.32 (*m*, 1 H, CH_2); 3.30 (*s*, 2 CH_2); 4.46–4.61 (*m*, 1 H, CH_2); 6.87–8.18 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.84; 23.72; 24.86; 26.51; 32.21; 43.09; 45.61; 49.70; 53.43; 59.08; 126.20; 127.91; 128.63; 128.90; 134.39; 135.93; 136.16; 136.48; 175.00 (C=O). EI-MS: 378 ($M^{+\bullet}$). HR-EI-MS: 378.2685 ($C_{25}H_{34}N_2O^+$, M^+; calc. 378.2671).

Data of 1-[3-[Bis(4-methylbenzyl)amino]propyl]azepan-2-one (**2b**): 151 mg (40%). A colorless oil. IR ($CHCl_3$): 1636 (C=O). ^{1}H-NMR ($CDCl_3$): 1.43–1.73 (*m*, 4 CH_2); 2.31 (*s*, 2 Me); 2.39–2.41 (*m*, 2 CH_2); 3.08–3.11 (*m*, 2 CH_2); 3.30–3.35 (*m*, 2 CH_2); 3.50 (*s*, 2 CH_2); 7.09–7.12 (*m*, 4 arom. H); 7.24–7.26 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.74; 22.94; 25.66; 28.31; 29.59; 36.89; 46.15; 49.18; 50.52; 57.93; 128.46; 128.48; 135.78; 136.35; 175.03 (C=O). EI-MS: 378 ($M^{+\bullet}$). HR-EI-MS: 378.2668 ($C_{25}H_{34}N_2O^+$, $M^{+\bullet}$, calc. 378.2671).

Data of 1,5-Bis(4-methoxybenzyl)-1,5-diazacycloundecan-6-one (**1c**): 90 mg (22%). A colorless liquid. IR ($CHCl_3$): 1631 (C=O). ^{1}H-NMR ($CDCl_3$): 1.22–1.27 (*m*, CH_2); 1.41–1.45 (*m*, CH_2); 1.60–1.70 (*m*, CH_2); 1.72–1.80 (*m*, CH_2); 2.21–2.24 (*m*, CH_2); 2.34–2.38 (*m*, CH_2); 2.60–2.68 (*m*, CH_2); 3.50–3.56 (*m*, 1 H, CH_2);3.53 (*s*, 2 CH_2); 3.77 (*s*, MeO); 3.78 (*s*, MeO); 4.56–4.60 (*m*, 1 H, CH_2); 6.80–6.85 (*m*, 4 arom. H); 7.16–7.27 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.12; 25.23; 26.88; 32.58; 43.52; 45.74; 50.13; 53.74; 55.34; 59.08; 113.68; 113.97; 127.94; 129.64; 130.45; 131.46; 158.67; 158.88; 175.35 (C=O). EI-MS: 410 ($M^{+\bullet}$). HR-EI-MS: 410.2577 ($C_{25}H_{34}N_2O_3^+$, $M^{+\bullet}$; calc. 410.2569).

Data of 1-[3-[Bis(4-methoxybenzyl)amino]propyl]azepan-2-one (**2c**): 139 mg (34%). A colorless liquid. IR ($CHCl_3$): 1640 (C=O). ^{1}H-NMR ($CDCl_3$): 1.26–1.70 (*m*, 4 CH_2); 2.38–2.45 (*m*, 2 CH_2); 3.14–3.17 (*m*, CH_2); 3.29–3.34 (*m*, CH_2); 3.47 (*s*, 2 CH_2); 3.78 (*s*, 2 MeO); 6.83–6.86 (*m*, 4 arom. H); 7.24–7.27 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.45; 26.02; 28.78; 30.12; 37.41; 46.68; 49.78; 50.73; 55.37; 57.84; 113.68; 130.15; 131.78; 158.66; 175.80 (C=O). EI-MS: 410 ($M^{+\bullet}$). HR-EI-MS: 410.2562 ($C_{25}H_{34}N_2O_3^+$, M^+; calc. 410.2569).

Data of 1,5-Bis[3-(trifluoromethyl)benzyl]-1,5-diazacycloundecan-6-one (**1d**): 131 mg (27%). A colorless liquid. IR ($CHCl_3$): 1633 (C=O). ^{1}H-NMR ($CDCl_3$): 1.38–1.45 (*m*, 2 CH_2); 1.70–180 (*m*, CH_2); 2.24–2.25 (*m*, CH_2); 2.40–2.41 (*m*, CH_2); 2.66–2.70 (*m*, CH_2); 3.53 (*s*, 2 CH_2); 3.50–3.56 (*m*, 1 H, CH_2); 4.71–4.76 (*m*, 1 H, CH_2); 7.41–7.55 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.07; 25.07; 25.21; 26.87; 32.37; 44.05; 46.30; 50.09; 54.13; 59.38; 123.72 (*q*, *J*(C,F) = 3.4); 123.95 (*q*, *J*(C,F) = 3.4); 124.13 (*q*, *J*(C,F) = 267.0); 124.34 (*q*, *J*(C,F) = 267.0); 128.66; 128.94; 130.41 (*q*, *J*(C,F) = 32.9); 130.77; 130.86 (*q*, *J*(C,F) = 32.9); 131.28; 131.36; 138.76; 140.34; 175.36 (C=O). EI-MS: 486 ($M^{+\bullet}$). HR-EI-MS: 486.2103 ($C_{24}H_{28}F_6N_2O^+$, M^+; calc. 486.2106).

Data of 1-(3-[Bis[3-(trifluoromethyl)benzyl]amino]propyl)azepan-2-one (**2d**): 102 mg (21%). A colorless liquid. IR ($CHCl_3$): 1643 (C=O). ^{1}H-NMR ($CDCl_3$): 1.20–1.73 (*m*, 4 CH_2); 2.36–2.45 (*m*, 2 CH_2); 3.12–3.15 (*m*, CH_2); 3.28–3.32 (*m*, CH_2); 3.56 (*s*, 2 CH_2); 7.34–7.57 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.20; 25.92; 28.51; 29.72; 37.09; 46.28; 49.51; 51.38; 58.12; 123.70 (*q*, *J*(C,F) = 3.5); 124.13 (*q*, *J*(C,F) = 270.7); 125.20 (*q*, *J*(C,F) = 3.5); 128.66, 130.48 (*q*, *J*(C,F) = 31.9); 131.99, 140.59, 175.50 (C=O). EI-MS: 487 ($[M+1]^{+\bullet}$). HR-EI-MS: 486.2111 ($C_{24}H_{28}F_6N_2O^+$, M^+; calc. 486.2106).

Data of 1,5-Bis(4-fluorobenzyl)-1,5-diazacycloundecan-6-one (**1e**): 278 mg (72%). A colorless liquid. IR ($CHCl_3$): 1633 (C=O). ^{1}H-NMR ($CDCl_3$): 1.30–1.40 (*m*, CH_2); 1.40–1.46 (*m*, CH_2); 1.62–1.74 (*m*, CH_2); 1.75–1.81 (*m*, CH_2); 2.20–2.28 (*m*, CH_2); 1.26–1.40 (*m*, CH_2); 2.21–2.27 (*s*, 2 CH_2); 2.35–2.42 (*m*, CH_2); 2.52–2.65 (*m*, CH_2); 3.43 (*s*, CH_2); 3.41–3.46 (*m*, 1 H, CH_2); 4.60–4.66 (*m*, 1 H, CH_2); 6.92–7.01 (*m*, 4 arom. H); 7.03–7.32 (*m*, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.11; 25.16; 26.72; 32.35; 43.85; 45.80; 50.27; 53.85; 59.02; 115.15 (*m*, *J*(C,F) = 20.5); 115.43 (*d*, *J*(C,F) = 20.5); 129.92 (*d*, *J*(C,F) = 8.0); 130.80 (*d*, *J*(C,F) = 8.0); 133.70 (*d*, *J*(C,F) = 2.9); 135.10 (*d*, *J*(C,F) = 2.9); 162.0 (*d*, *J*(C,F) = 242.9); 162.10 (*d*, *J*(C,F) = 242.9); 175.31 (C=O). EI-MS: 386 ($M^{+\bullet}$). HR-EI-MS: 386.2177 ($C_{23}H_{28}F_2N_2O^+$, M^+, calc. 386.2170).

Data of 1-[3-[Bis(4-fluorobenzyl)amino]propyl]azepan-2-one (**2e**): 170 mg (44%). A white solid. M.p. 97–99°. IR ($CHCl_3$): 1639 (C=O). ^{1}H-NMR ($CDCl_3$): 1.55–1.69 (*m*, 4 CH_2); 2.37–2.43 (*m*, 2 CH_2); 3.15–3.17 (*m*, CH_2); 3.29–3.33 (*m*, CH_2); 3.47 (*s*, 2 CH_2); 6.95–7.00 (*m*, 4 arom. H); 7.26–7.28 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.39; 26.03; 28.77; 30.00; 37.35; 46.57; 49.70; 51.02; 57.79; 115.04 (*d*, *J*(C,F) = 21.1); 130.30

(*d*, *J*(C,F) = 7.9); 135.43; 162.0 (*d*, *J*(C,F) = 243); 175.62 (C=O). EI-MS: 387 ($[M+1]^{+\cdot}$). Anal. calc. for $C_{23}H_{28}F_2N_2O$: C 71.48, H 7.30, N 7.25; found: C 71.65, H 7.19, N 7.32.

Data of 1-[3-(Dibutylamino)propyl]azepan-2-one (**2f**): 85 mg (30%). A colorless oil. IR ($CHCl_3$): 1634 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.4, 2 Me); 1.20–1.45 (*m*, 4 CH_2); 1.60–1.82 (*m*, 4 CH_2); 2.29–2.33 (*m*, 3 CH_2); 2.34–2.45 (*m*, CH_2); 3.30–3.42 (*m*, 2 CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.18; 20.80; 23.54; 26.07; 28.80; 29.19; 30.09; 37.40; 46.75; 49.72; 51.60; 53.94; 175.77 (C=O). EI-MS: 239 ($[M-43]^{+\cdot}$). HR-EI-MS: 282.2677 ($C_{17}H_{34}N_2O^+$, M^+; calc. 282.2671).

Data of 1-[3-(Dibenzylamino)propyl]pyrrolidin-2-one (**3a**): 299 mg (93%). A colorless liquid. IR ($CHCl_3$): 1677 (C=O). ^{1}H-NMR ($CDCl_3$): 1.68 (*quint.*, *J* = 7.1, CH_2); 1.80 (*quint.*, *J* = 7.5, CH_2); 2.23 (*t*, *J* = 8.1, CH_2); 2.40 (*t*, *J* = 7.0, CH_2); 3.11 (*t*, *J* = 7.0, CH_2); 3.22 (*t*, *J* = 7.2, CH_2); 3.54 (*s*, 2 CH_2); 7.18–7.37 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.20; 24.37; 30.40; 39.82; 46.29; 49.99; 57.99; 126.29; 127.61; 128.25; 139.08; 174.09 (C=O). EI-MS: 323 ($[M+1]^{+\cdot}$). HR-EI-MS: 322.2033 ($C_{21}H_{26}N_2O^+$, M^+; calc. 322.2045).

Data of 1-{3-[Bis(4-methylbenzyl)amino]propyl}pyrrolidin-2-one (**3b**): 301 mg (86%). A colorless liquid. IR ($CHCl_3$): 1681 (C=O). ^{1}H-NMR ($CDCl_3$): 1.69 (*quint.*, *J* = 7.3, CH_2); 1.87 (*quint.*, *J* = 7.7, CH_2); 2.28 (*t*, *J* = 8.1, CH_2); 2.31 (*s*, 2 Me); 2.40 (*t*, *J* = 7.0, CH_2); 3.16–3.26 (*m*, 2 CH_2); 3.50 (*s*, 2 CH_2); 7.10–7.13 (*m*, 4 arom. H), 7.25–7.26 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.84; 21.08; 25.04; 31.02; 40.59; 47.05; 50.43; 58.18; 128.86; 136.37; 174.81 (C=O). EI-MS: 351 ($[M+1]^{+\cdot}$). HR-EI-MS: 350.2354 ($C_{23}H_{30}N_2O^+$, M^+; calc. 350.2358).

Data of 1-{3-[Bis(4-methoxybenzyl)amino]propyl}pyrrolidin-2-one (**3c**): 15 mg (4%). A colorless liquid. IR ($CHCl_3$): 1681 (C=O). ^{1}H-NMR ($CDCl_3$): 1.68 (*quint.*, *J* = 7.2, CH_2); 1.88 (*quint.*, *J* = 7.6, CH_2); 2.29 (*t*, *J* = 8.3, CH_2); 2.38 (*t*, *J* = 8.3, CH_2); 3.17–3.25 (*m*, 2 CH_2); 3.47 (*s*, 4 CH_2); 3.83 (*s*, 2 Me); 6.83–6.86 (*m*, 4 arom. H); 7.23–7.26 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.98; 25.07; 31.08; 40.71; 47.21; 50.32; 55.40; 57.79; 113.69; 130.16; 131.56; 158.70; 175.08 (C=O). EI-MS: 382 ($M^{+\cdot}$). HR-EI-MS: 382.2254 ($C_{23}H_{30}N_2O_3^+$, M^+; calc. 382.2256).

Data of 1-(3-{Bis[3-(trifluoromethyl)benzyl]amino}propyl)pyrrolidin-2-one (**3d**): 115 mg (25%). A colorless liquid. IR ($CHCl_3$): 1684 (C=O). ^{1}H-NMR ($CDCl_3$): 1.73 (*quint.*, *J* = 7.2, CH_2); 1.90 (*quint.*, *J* = 6.2, CH_2); 2.27 (*t*, *J* = 8.2, CH_2); 2.44 (*t*, *J* = 6.9, CH_2); 3.18–3.26 (*m*, 2 CH_2); 3.60 (*s*, 2 Me); 7.26–7.59 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.79; 25.11; 30.89; 40.40; 46.96; 51.15; 58.20; 123.90 (*q*, *J*(C,F) = 3.6); 124.10 (*q*, *J*(C,F) = 270); 125.27 (*q*, *J*(C,F) = 3.8); 128.78, 130.62 (*q*, *J*(C,F) = 31.9); 132.03; 140.43, 174.88 (C=O). EI-MS: 459 ($[M+1]^{+\cdot}$). HR-EI-MS: 458.1780 ($C_{23}H_{24}F_6N_2O^+$, M^+; calc. 458.1793).

Data of 1-{3-[Bis(4-fluorobenzyl)amino]propyl}pyrrolidin-2-one (**3e**): 297 mg (83%). A colorless liquid. IR ($CHCl_3$): 1676 (C=O). ^{1}H-NMR ($CDCl_3$): 1.67 (*quint.*, *J* = 7.2, CH_2); 1.88 (*quint.*, *J* = 7.3, CH_2); 2.27 (*t*, *J* = 8.1, CH_2); 2.37 (*t*, *J* = 7.0); 3.16–3.24 (*m*, 2 CH_2); 3.46 (*s*, 2 Me); 6.94–7.00 (*m*, 4 arom. H); 7.25–7.30 (*m*, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.69; 24.83; 30.84; 40.33; 46.83; 50.41; 57.51; 114.83 (*d*, *J*(C,F) = 21.0); 130.10 (*d*, *J*(C,F) = 7.8); 130.06 (*d*, *J*(C,F) = 3.0); 161.74 (*d*, *J*(C,F) = 243.0); 174.66 (C=O). EI-MS: 359 ($[M+1]^{+\cdot}$). HR-EI-MS: 358.1854 ($C_{21}H_{24}N_2OF_2^+$, M^+; calc. 358.1857).

X-Ray Crystal-Structure Analysis. The Crystal Data of **1a**: Empirical formula: $C_{23}H_{30}N_2O$; M_r 350.49; crystal system, space group: monoclinic, *P*2(1)/*c*; unit-cell dimensions: *a* = 15.7298(11), *b* = 7.7129(5), *c* = 16.9212(12) Å, $\alpha = 90^\circ$, $\beta = 103.7780^\circ$, $\gamma = 90^\circ$, *V* = 1993.8(2) Å^3; *Z*, calculated density: 4, 1.168 mg/m^3; absorption coefficient: 0.071 mm^{-1}; *F*(000) = 760. The data have been deposited in *CCDC* with CCDC No. 168002.

The Crystal Data of **2e**: Empirical formula: $C_{23}H_{28}F_2N_2O$; M_r: 386.47; crystal system, space group: monoclinic, *P*2(1)/*n*; unit-cell dimensions: *a* = 10.0887(7), *b* = 10.1110(6), *c* = 20.3206(13) Å, $\alpha = 90^\circ$, $\beta = 90.6640(10)^\circ$, $\gamma = 90^\circ$, *V* = 2072(2) Å^3; *Z*, calculated density: 4, 1.238 mg/m^3; absorption coefficient: 0.088 mm^{-1}; *F*(000) = 824. The data have been deposited in *CCDC* with CCDC No. 168003.

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