Synthesis of the 3*H*-Azepines Utilizing the Thermolysis of Substituted Aryl Azides

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Thermolysis of several *p*-substituted aryl azides (*p*-R-$C_6H_4N_3$; R=$COCH_3$, CO_2CH_3, COPh) in methanol gave 5-substituted 2-methoxy-3*H*-azepines in moderate yields. Thermolysis of *m*-substituted aryl azides (*m*-R-$C_6H_4N_3$; R=$COCH_3$, CO_2CH_3, COPh, NO_2) gave 4-substituted 2-methoxy-3*H*-azepines and 6-substituted 2-methoxy-3*H*-azepines in good yields. In contrast, thermolysis of *p*-azidoacetophenone in piperidine gave 5-acetyl-2-piperidino-3*H*-azepine and an unusual product, 6-acetyl-2-piperidino-3*H*-azepine, and *p*-aminoacetophenone.

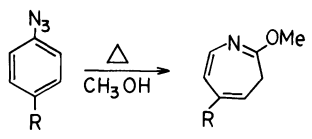
Formation of 3*H*-azepines by the thermolysis and photolysis of aryl azides in methanol is well documented.[1-3]

In general, however, many attempts at the synthesis of 3*H*-azepines by the thermolysis or photolysis of aryl azides have failed or given low yields of 3*H*-azepines. Only succeeded experiment was the photolysis of o-azidobenzoic acids[4a-c] in alcohols. It has been considered that an electron-withdrawing substituent at *m*-or *p*-position of azidobenzene apparently prevents the azepine formation by decreasing the electron density on the carbon center at which the electrophilic single nitrene attacks.[4a]

We have investigated the thermolysis of *m*-azidoacetophenone (**2a**) and *p*-azidoacetophenone (**1a**), and in a preliminary communication[5] we have shown that the thermolysis of these azides in methanol gives ring-expansion products, 3*H*-azepines, in excellent yields. We now report the thermolysis of *p*-substituted aryl azides (**1**; R=$COCH_3$, CO_2CH_3, COPh, NO_2) and *m*-substituted aryl azides (**2**; R=$COCH_3$, CO_2CH_3, COPh, NO_2) in methanol and the thermolysis of **1a** and **1c** in piperidine and morpholine.

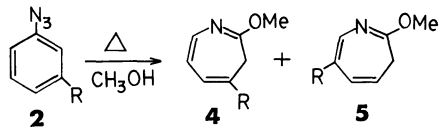
Results and Discussion

The thermolysis of methanol solution of **1a—c** in a sealed Pyrex tube at 170 °C gave 5-substituted 2-methoxy-3*H*-azepines (**3a—c**) in moderate yields. The results are shown in Table 1. The structure of all azepines (**3a—c**) was confirmed by ^1H NMR spectroscopy. The thermolysis of 1-azido-4-nitrobenzene (**1d**) at 190 °C for 2 h gave only tar.



1 **3**

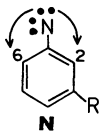
a: R=$COCH_3$
b: R=CO_2CH_3
c: R=COPh
d: R=NO_2



2 **4** **5**

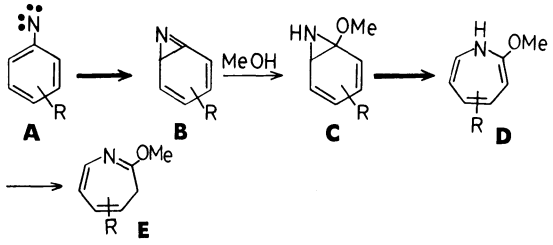
a: R=$COCH_3$
b: R=CO_2CH_3
c: R=COPh
d: R=NO_2

Thermolysis of *m*-substituted aryl azides (**2a—d**) under the similar conditions also gave 6-substituted 3*H*-azepines (**5a—d**) and 4-substituted 3*H*-azepines (**4a—d**). These results are also shown in Table 1. The observed ratio of **5a—c** to **4a—c** shows that electron-withdrawing *m*-substituent ($COCH_3$. CO_2CH_3, COPh) favor an intramolecular cycloaddition of nitrene (**N**) at C-2 position to give **5a—c**. It is



N

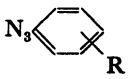
suggested from the failure to give 2-methoxy-3*H*-azepine in the thermolysis of azidobenzene in methanol that electron-withdrawing *m*- and *p*-substituents accelerate cycloaddition of singlet nitrene (**A**) to give azirne (**B**) and facilitate ring-expansion of (**C**) to 1*H*-azepine (**D**), which by prototropic migration yields 3*H*-azepine (**E**)(Scheme 1). In contrast with the thermolysis, the photolysis of **1a** and **2a** in methanol gave a low yields of 3*H*-azepines (**3a, 4a, 5a**). These results show that the thermolysis is superior to the photolysis for the formation of 3*H*-azepines from *m*-



Scheme 1.

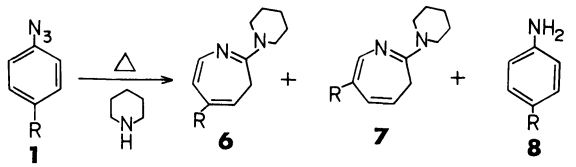
Table 1. Yieldes of 3*H*-Azepines

AZIDE	R[a]	Reaction Conditions Temp/°C	Time/h	Yield of Product/% 3	4	5
1a	*p*-$COCH_3$	170	4	60		
1b	*p*-CO_2CH_3	170	1.5	47		
1c	*p*-COPh	170	4	32		
1d	*p*-NO_2	190	2	—		
2a	*m*-$COCH_3$	170	4		25	58
2b	*m*-CO_2CH_3	170	2		35	63
2c	*m*-COPh	170	4		24	62
2d	*m*-NO_2	180	2		15	5

a) 

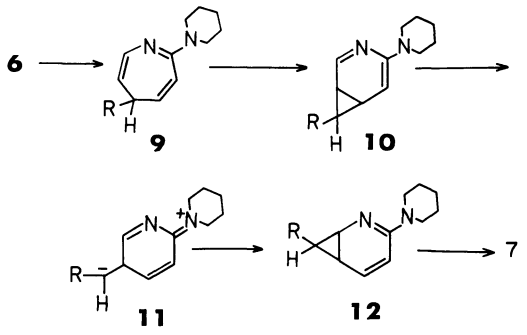
and *p*-substituted azidobenzenes.

The thermolysis of **1a** in piperidine at 170 °C for 2 h gave 5-acetyl-2-piperidino-3*H*-azepine (**6a**) (10%) and unexpected product, 6-acetyl-2-piperidino-3*H*-azepine (**7a**) (13%) and a triplet product,[7] *p*-aminoacetophenone (**8a**) (22%). The thermolysis of **1c** in piperidine at 170°C for 2 h gave 6-benozyl-2-piperidino-3*H*-azepine (**7c**) (18%) and *p*-aminobenzophenone (**8c**) (27%). The thermolysis of **1a** in morpholine at 170 °C for 2 h gave 5-acetyl-2-morpholino-3*H*-azepine (**13a**) (30%), 6-acetyl-2-morpholino-3*H*-azepine (**14a**) (22%) and *p*-aminoacetophenone (**8a**) (32%). The thermolysis of **1c** in morpholine at 170 °C for 6 h gave 6-benzoyl-2-



a: R=$COCH_3$
c: R=COPh

morpholino-3*H*-azepine (**14c**) (7%) and tar. The pathway to 6-acetyl-3*H*-azepine (**7a**) must involve the bicyclic valence isomers **10** and **11** (Scheme 2). Analogous step has been postulaed[8] for the formation of 1,3-diazepine by the thermal isomerzation of 1,2-diazepine. In support of the above mechanism, the thermal isomerzation of **6a** in piperidine at 170 °C for 6 h gave **7a** (85%). The thermal isomerization of **13a** in morpholine at 170 °C for 6 h gave **14a** in 75% yield. But the thermal isomerzation of **6a** in xylene at 170 °C for 6 h gave no **7a**, and **6a** was recovered in 91% yield. These results can be explained by the existence of the dipolar transition state or intermediae (**11**) for the formation of **7a** from **6a** in piperidine. Rate constant for this valence isomerization[9] was found to be 9.45×10^{-5} s^{-1}.



Scheme 2.

Experimental

Melting points were determined in a capillary tube. IR spectra were recorded for liquids as thin films and solids as KBr discs on a Japan Spectroscopic IR-G spectrometer. UV spectra were recorded in ethanol on a Hitachi 220A spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ at 60 MHz using a Hitachi R24-B spectrometer (Me_4Si as internal standard). Mass spectra were determined with a JEOL JMS-01SG-2 spectrometer (75 eV). Unless otherwise stated recorded yields are based on the material after separation by medium-pressure liquid chromatography (Silica-gel Woelm 32—63 μm or aluminium oxide 200—300 mesh).

Preparation of Azidobenzenes. All azides were prepared from the corresponding amines by diazotization, followed by azidation with sodium azide. Azidobenzenes (**1b, 1d, 2b,** and **2d**) were prepared according to literature.[11a-c]

***p*-Azidoacetophenone (1a)** To a solution of *p*-aminoacetophenoe (1.00 g, 7.41 mmol) in acetic acid (10 ml), concd sulfulic acid (3 ml) was added under cooling (0—5 °C), and a solution of sodium nitrite (3.00 g, 43 mmol) in water (15 ml) was added over 15 min and stirrd at 0—5 °C for 2 h. A solution of sodium azide (5.00 g, 77 mmol) in water (23 ml) was added over 2 h and stirred at 0—5 °C for 1 h and extracted with ether. The extract was washed with water and dried over Na_2SO_4. Evaporation of the extract to dryness and chromatography of residue with hexane/ethyl acetate=3:1 on silica-gel (Wako Q-22) gave 879 mg (75%) of *p*-azidoacetophenone (**1a**); Yellow needles; mp 43—44 C(lit,[11a] mp 44 °C); Anal. ($C_8H_7O_1N_3$) C, H, N. IR(KBr) 3030, 2929, 2130, 2100, 1670, and 1598 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.58 (3H, s), 7.10 (2H d, *J*=8 H), and 7.95 (2H, d, *J*=8 Hz).

Following azides were prepared similarly:

***p*-Azidobenzophenone (1c)** (90%): Yellow needles; Anal. ($C_{13}H_9O_1N_3$) C, H, N.; mp 73—74 °C(lit,[12] mp 74 °C); IR(KBr) 3040, 2900, 2130, 2100, 1658, and 1592 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.0—7.8 (9H, m).

***m*-Azidoacetophenone (2a)** (86%): Yellow oil; Anal. ($C_8H_7O_1N_3$) C, H, N.; IR(oil) 3050, 2910, 2125, 2120, 1685, and 1585 cm^{-1}: ^1H NMR ($CDCl_3$) δ=2.58 (3H, s), and 7.05—7.80 (4H, m).

***m*-Azidobenzophenone (2c)** (93%): Yellow oil; Anal.

($C_{13}H_9O_1N_3$) C, H, N.); IR(oil) 3040, 2150, 2110, 1658, 1598, and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.10—7.90 (9H, m).

Thermolysis of *p*-Azidoacetophenone (1a). General procedure. A solution of 319 mg (1.98 mmol) of **1a** in methanol (10 ml) was sealed in a Pyrex tube and heated at 170 °C for 2 h. Evaporation of the solution to dryness gave dark brown oil which was chromatographed on silica-gel (Wako-gel Q-22) with benzene:ethyl acetate=3:1 to give 196 mg(60%) of 5-acetyl-2-methoxy-3*H*-azepine (**3a**) as yellow oil; Anal. ($C_9H_{11}O_2N_1$) C, H, N.; UV (95% C_2H_5OH) 220.0 (ε 15400) and 290 nm (sh, 1960); IR (oil) 2980, 2930, 2840, 1670, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.38 (3H, s), 2.79 (2H, d, J=7.5 Hz), 3.73 (3H, s), 6.22 (1H, t, J=7.5 Hz), 6.52 (1H, d, J=8 Hz), 7.10 (1H, d, J=8 Hz), and 61 mg (23%) of *p*-aminoacetophenone.

Thermolysis of Methyl *p*-Azidobenzoate (1b). A solution of 102 mg (0.68 mmol) of **1b** in methanol (20 ml) was heated at 170 °C for 2 h to give 101 mg (97%) of methyl 2-methoxy-3*H*-azepine-5-carboxylate (**3b**)[4b] as yellow oil; Anal. ($C_9H_{11}O_3N_1$) C, H, N.; UV (95% C_2H_5OH) 285.0 nm (ε 2970); IR (oil) 2095, 2840, 1723, and 1627 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.74 (2H, d, J=7 Hz), 3.72 (3H, s), 3.79 (3H, s), 6.36 (1H, t, J=7 Hz), 6.48 (1H, d, J=8 Hz), 7.09 (1H, d, J=8 Hz).

Thermolysis of *p*-Azidobenzophenone (1c). Thermolysis of 256 mg (1.16 mmol) of **1c** in methanol (39 ml) at 170 °C for 4 h gave 84 mg of 5-benzoyl-2-methoxy-3*H*-azepine (**3c**) as yellow oil; Anal. ($C_{14}H_{13}O_2N_1$) C, H, N.; UV (95% C_2H_5OH) 251.0 nm (ε 15000); IR (oil) 3050, 2950, 2840, 1645, 1620, and 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.76 (2H, d, J=7 Hz), 3.76 (3H, s) 5.83 (1H, t, J=7 Hz), 6.47 (1H, d, J=8 Hz), 7.06 (1H, d, J=8 Hz), 7.24—7.75 (5H, m).

Thermolysis of 1-Azido-4-nitrobenzene (1d). A solution of 360 mg (2.20 mmol) of **1d** in methanol (20 ml) was heated at 190 °C for 2 h to give no 3*H*-azepine and some tar.

Thermolysis of *m*-Azidoacetophenone (2a). A solution of 530 mg of **2a** in methanol (20 ml) was heated at 170 °C for 2 h. After the similar procedure, described for the thermolysis of **1a**, a mixture of 330 mg (61%) of 6-acetyl-2-methoxy-3*H*-azepine (**5a**) and 122 mg (22%) of 4-acetyl-2-mehoxy-3*H*-azepine (**4a**) was obtained. The yields of **5a** and **4a** were determined by ^1H NMR. The analytical samples of **4a** and **5a** were obtained by HPLC (Dupont Zorbax ODS, 15.0 cm×4.6 mm; solvent, MeOH/H_2O=1:1), giving **5a** as yellow oil; Anal. ($C_9H_{11}O_2N_1$) C, H, N.; UV (95% C_2H_5OH) 217.0 (ε 18300) and 288.5 nm (13900); IR (oil) 2990, 2940, 2840, 1658, and 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 2.66 (2H, d, J=7 Hz), 3.73 (3H, s), 5.47 (1H, dt, J=9 and 7 Hz), 6.79 (1H, dd, J=9 and 1 Hz), 7.94 (1H, d, J=1 Hz) and **4a** as yellow; oil Anal. ($C_9H_{11}O_2N_1$) C, H, N.; UV (95% C_2H_5OH) 221.0 (ε 12800) and 313.0 nm (6400); IR (oil) 2990, 2940, 2840, 1658, and 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.37 (3H, s). 2.98 (2H, s), 3.70 (3H, s), 6.09 (1H, dd, J=8 and 6 Hz), 7.14 (1H, dd, J=6 and 1 H), 7.22 (1H, dd, J=8 and 1 Hz).

Thermolysis of Methyl *m*-Azidobenzoate (2b). A solution of 640 mg (3.62 mmol) of **2b** in methanol (20 ml) was heated a 170 °C for 2 h to give a mixture of 396 mg (60%) of methyl 2-methoxy-3*H*-azepine-6-carboxylate (**5b**) and 222 mg (34%) of methyl 2-methoxy-3*H*-azepine-4-carboxylate (**4b**). Analytical samples were obtained by HPLC under the same conditions used for **4a** and **5a**, giving **5b** as yellow oil; Anal. ($C_9H_{11}O_3N_1$) C, H, N.; UV (C_2H_5OH) 280.0 nm, (ε 6650); IR (oil) 2960, 2940, 2820, 1708, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.60 (2H, d, J=7 Hz), 3.75 (3H, s), 3.80 (3H, s), 5.40 (1H, dt, J=9 and 7 Hz), 6.74 (3H, s), 3.80 (3H, s), 5.40 (1H, dt, J=9 and 7 Hz), 6.74 (1H, dd, J=9 and 2 Hz), 8.05 (1H, d J=2 Hz) and **4b** as yellow oil; Anal. ($C_9H_{11}O_3N_1$) C, H, N.; UV (95% C_2H_5OH) 213.5 (ε 6610) and 308.0 nm (5430); IR (oil) 2960, 2910, 2825, 1704, and 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.01 (2H, s), 3.73 (3H, s), 3.80 (3H, s), 6.03 (1H, dd, J=6 and 8 Hz), 7.20 (1H, dd, J=8 and 1 Hz), 7.27 (1H, dd, J=6 and 1 Hz).

Thermolysis of *m*-Azidobenzophenone (2c). A solution of 241 mg (1.08 mmol) of **2c** in methanol (10 ml) was heated at 170 °C for 4 h to give the mixture of 152 mg (62%) of 6-benzoyl-2-methoxy-3*H*-azepine (**5c**) and 58 mg (24%) of 4-benzoyl-2-methoxy-3*H*-azepine (**4c**). Analytical samples were obtained similarly. **5c**; yellow oil; Anal. ($C_{14}H_{13}O_2N_1$) C, H, N.; UV (C_2H_5OH) 245.0 (ε 9300) and 296.0 nm (9620); IR (oil) 3050, 3000, 2940, 1640, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.80 (2H, d, J=6 Hz), 3.80 (3H, s), 5.60 (1H, dt, J=9 and 6 Hz), 6.94 (1H, dd, J=9 and 1 Hz), 7.70 (1H, d, J=1 Hz). **4c**; yellow oil; Anal. ($C_{14}H_{13}O_2N_1$) C, H, N.; UV (C_2H_5OH) ca. 240 (sh, ε 7430) and 318.0 nm (5330); IR (oil) 3020, 2930, 2850, 1640, and 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.16 (2H, s), 3.58 (3H, s), 6.06 (1H, dd, J=8 and 6 Hz), 6.94 (1H, d, J=6 Hz), 7.20 (1H, d, J=8 Hz), 7.3—7.8 (5H, m).

Thermolysis of 1-Azido-3-nitrobenzene (2d). A solution of 231 mg (1.41 mmol) of **2d** in methanol (20 ml) was heated at 180 °C for 2 h to give the mixture of 11 mg (5%) of 6-nitro-2-methoxy-3*H*-azepine (**5d**) and 36 mg (15%) of 4-nitro-2-methoxy-3*H*-azepine (**4d**). 5d; colorless oil; Anal. ($C_7H_8O_3N_2$) C, H, N.; UV (95% C_2H_5OH) 224.0 (ε 7030) and 323.0 nm (5990); IR (oil) 2980, 2940, 2850, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.75 (2H, d, J=7 Hz), 3.73 (3H, s), 5.48 (1H, dt, J=9 and 7 Hz), 7.00 (1H, dd, J=9 and 2 Hz), 8.43 (1H, d, J=2 Hz). **4d**; yellow oil; Anal. ($C_7H_8O_3N_2$) C, H, N.; UV (95% C_2H_5OH) 231.5 (ε 9900) and 347.5 nm (4910); IR (oil) 2980, 2930, 2840, and 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.33 (2H, s), 3.76 (3H, s), 6.00 (1H, dd, J=8 and 6 Hz), 7.31 (1H, dd, J=8 and 1 Hz), 7.64 (1H, dd, J=8 and 1 Hz).

Phtolysis of *p*-Azidoacetophenone (1a) in Methanol. A solution of 500 mg (3.11 mmol) of **1a** in methanol (400 ml) was irradiated (Ushio 100 W high pressure Hg lamp with Pyrex filter) for 5 h under nitrogen to give 40 mg (8%) of **3a** and intractable tar. The reaction was monitored using HPLC,[6] and **1a** was consumed completely.

Photolysis of *m*-Azidoacetophenone (2a) in Methanol. A solution of 425 mg (2.64 mmol) of **2a** in methanol (400 ml) was irradiated under the similar conditions to give 26 mg (8%) of the mixture of **4a** (2%) and **5a** (6%). An intractable tar was also obtained, and **2a** was consumed completely.

Thermolysis of *p*-Azidoacetophenone (1a) in Piperidine. A solution of 300 mg (1.86 mmol) of **1a** in piperidine (20 ml) was heated at 170 °C for 2 h. The reaction mixture was chromatographed by medium-pressure liquid chromatography (aluminium oxide 200—300 mesh) with ethyl acetate/hexane=1:3 to give 53 mg (13%) of 6-acetyl-2-piperidino-3*H*-azepine (**7a**) as brown oil; Found: M^+, 218.1395. Calcd for $C_{13}H_{18}O_1N_2$: M^+, 218.1418.[10] UV (95%

C_2H_5OH) 231.5 (ε 13400) and 335.0 nm (22700); IR (oil) 2980, 2920, 2850, 1638, and 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.46—1.78 (6H, m), 2.39 (3H, s), 2.70 (2H. d. J=7 Hz), 3.37—3.73 (4H, m), 5.23 (1H, dt, J=8 and 7 Hz), 6.88 (1H dd, J=8 and 1.5 Hz), 8.07 (1H, d, J=1.5 Hz) and 41 mg (10%) of 5-acetyl-2-piperidino-3*H*-azepine (**6a**) as brown oil; Found: N, 12.94%; Calcd for $C_{13}H_{18}O_1N_2$: N, 12.83%; UV (95% C_2H_5OH) 230.0 (sh, ε 15600) and 325.0 nm (4350); IR (oil) 2980, 2920, 2850, 1705, and 1668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.51—1.84 (6H, m), 2.36 (3H, s), 2.77 (2H, d, J=7.5 Hz), 3.34—3.70 (4H m), 5.93 (1H, dt, J=1 and 7.5 Hz), 6.23 (1H, dd, J=8 and 1 Hz), 7.20 (1H, d, J=8 Hz), and 54 mg (22%) of **8a**.

Thermolysis of 1a in Morpholine. Thermolysis of 272 mg (1.69 mmol) of **1a** in morpholine (20 ml) a 170 °C for 2 h gave 82 mg (22%) of 6-acetyl-2-morpholino-3*H*-azepine (**14a**) as yellow oil; Found: N, 12.94%; Calcd for $C_{12}H_{16}O_2N_2$; N, 12.72%; UV (95% C_2H_5OH) 231.5 (ε 6000) and 330.5 nm (9190); IR (oil) 2940, 2890, 2840, 1636, and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.42 (3H, s), 2.72 (2H, d, J=7 Hz), 3.25—4.11 (8H, m), 5.24 (1H, dt, J=9 and 7 Hz), 6.89 (1H, dd, J=9 and 1 Hz), 8.09 (1H, d, J=1 Hz), and 110 mg (30%) of 5-acetyl-2-morpholino-3*H*-azepine (**13a**) as yellow oil; Found: M^+, 220.1218. Calcd for $C_{12}H_{16}O_2N_2$: M^+, 220.1211.[10]; UV (95% C_2H_5OH) 233.0 (ε 7780) and 274.5 nm (6250); IR (oil) 2950, 2880, 2840, 1668, and 1563 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.37 (3H, s), 2.75 (2H, d, J=7 Hz), 3.23—3.79 (8H, m), 5.99 (1H, td, J=7 and 1 Hz), 6.32 (1H, dd, J=9 and 1 Hz), 7.22 (1H, d, J=9 Hz), and 72 mg (32%) of **8a**.

Thermolysis of 1c in Piperidine. A solution of 270 mg (1.21 mmol) of **1c** in piperidine (20 ml) was heated at 170 °C for 2 h to give 61 mg (18%) of 6-benzoyl-2-piperidino-3*H*-azepine (**7c**) as yellow oil; Found: M^+, 280.1577. Calcd for $C_{18}H_{20}O_1N_2$: M^+, 280.1575.[10]; UV (95% C_2H_5OH) 235.5 (ε 9270) and 347.0 nm (12200); IR (oil) 3010, 2930, 2850, 1625, and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.01—1.92 (6H, m), 2.81 (2H, d, J=7 Hz), 3.23—3.95 (4H, m), 5.27 (1H, dt, J=9 and 7 Hz), 7.04 (1H, dd, J=9 and 1.5 Hz), 7.23—7.85 (5H, m), 7.89 (1H, d, J=1.5 Hz), and 64 mg (27%) of **8c**.

Thermolysis of 1c in Morpholine. Thermolysis of 191 mg (0.86 mmol) of **1c** in morpholine (10 ml) at 170 °C for 2 h gave 16 mg (7%) of 6-benzoyl-2-morpholino-3*H*-azepine (**14c**) as brown oil; Found: M^+, 282.1361. Calcd for $C_{17}H_{18}O_2N_2$: M^+, 282.1367.[10]; UV (95% C_2H_5OH) 340.5 (ε 15100) and 237.0 nm (12200); IR (oil) 2940, 2890, 2840, 1626, and 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.79 (2H, d, J=7 Hz), 3.63 (8H m) 5.29 (1H, dt, J=9 and 7 Hz), 7.02 (1H, dd, J=9 and 1 Hz), 7.20—7.80 (5H, m), 7.85 (1H, d, J=1 Hz).

Thermolysis of 5-Acetyl-2-piperidino-3*H*-azepine (6a) in Piperidine. A solution of 44 mg (0.2 mmol) of **6a** in piperidine (4 ml) was heated at 170 °C for 6 h. The solution was evaporated and the residue was chromatographed by medium-pressure liquid chromatography (aluminium oxide 200—300 mesh, hexane/ethyl acetate=3:1) to give 35 mg (80%) of **7a** and no **6a**.

Thermolysis of 5-Acetyl-2-piperidino-3*H*-azepine (6a) in Xylene. A solution of 44 mg (0.2 mmol) of **6a** in xylene (4 ml) was heated at 170 °C for 6 h and the similar procedure gave 36 mg (82%) of recovered **6a** and no other products.

Thermolysis of 5-Acetyl-2-morpholino-3*H*-azepine (13a) in Morpholine. A solution of 54 mg (0.25 mmol) of **13a** in morpholine (4 ml) was heated at 170 °C for 6 h and the similar procedures described above gave 40 mg (74%) of 6-acetyl-2-morpholino-3*H*-azepine (**14a**).

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