# THE SYNTHESIS OF 3*H*-AZEPINES : THERMAL REORGANIZATION OF 2,4- AND 3,5-DI-*t*-BUTYL-3a,5a-DIHYDRO-3*H*-CYCLOBUTA[*b*]PYRROLES TO 2,5- AND 3,6-DI-*t*-BUTYL-3*H*-AZEPINES

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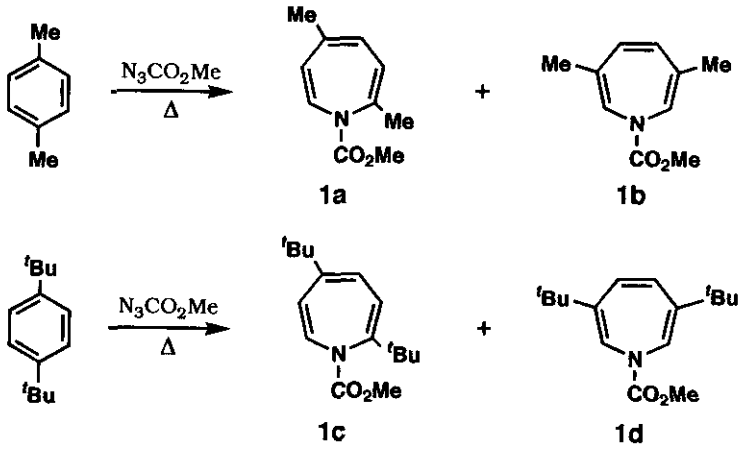
***Abstract*** - Thermal reaction of cyclobuta[*b*]pyrroles, which derived by photochemical cyclization of methyl 2,5- and 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylate gave di-*t*-butyl substituted 3*H*-azepines. The kinetics of the reaction were measured and the activation energy of the reorganization to 3*H*-azepines was estimated.

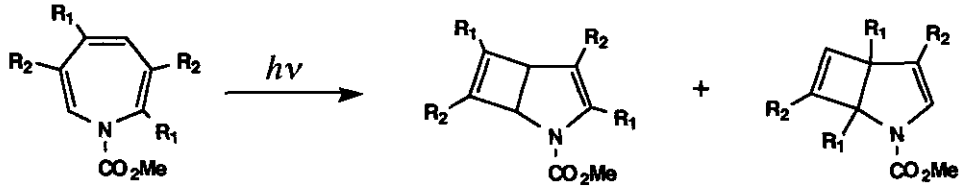
The intramolecular insertion reaction to the benzene ring of phenylnitrene in nucleophilic media has been considered a general synthetic method for 3*H*-azepine derivatives having 2-azatriene conjugated π-system.[1] However, the resulting 3*H*-azepines possess necessarily a strong electron donating functional group on the ring which may disturb study of native property of 3*H*-azepine system. E. Vogel *et al.* reported that the demethoxycarbonylation reaction of methyl 1*H*-azepine-1-carboxylate using iodotrimethylsilane gave labile parent 3*H*-azepine.[2] We report here a synthesis of 2,5- and 3,6-di-*t*-butyl-3*H*-azepines from methyl 2,5- and 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylate *via* thermal isomerization of corresponding 3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrrole derivatives which were prepared photochemically from 1*H*-azepines and the kinetics of the thermal reaction.[3]

## RESULT and DISCUSSION

Starting methyl 2,5- and 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylates (**1c** and **1d**) were prepared by the thermal decomposition of methyl azidoformate at 130°C in a media of molten *p*-di-*t*-butylbenzene (mp 110°C).[4] Methyl 2,5- and 3,6-dimethyl-1*H*-azepine-1-carboxylates (**1a** and **1b**) were obtained by reported method.[5]




The photoreaction of 1*H*-azepines was performed by using Paquette's procedure.[6] Thus, methyl 2,5-dimethyl-1*H*-azepine-1-carboxylate (**1a**) gave methyl 2,4-dimethyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**2a**) and methyl 3a,5a-dimethyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**3a**). Symmetrically substituted methyl 3,6-dimethyl-1*H*-azepine-1-carboxylate (**1b**) gave only methyl 3,5-dimethyl-3a,5a-dihydro-1*H*-pyrrole-1-carboxylate (**2b**) under the similar conditions. Similar photoreaction of methyl 2,5-di-*t*-butyl- and 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylates (**1c** and **1d**) gave methyl 2,4-di-*t*-butyl- and 3,5-di-*t*-butyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylates (**2c** and **2d**), respectively.

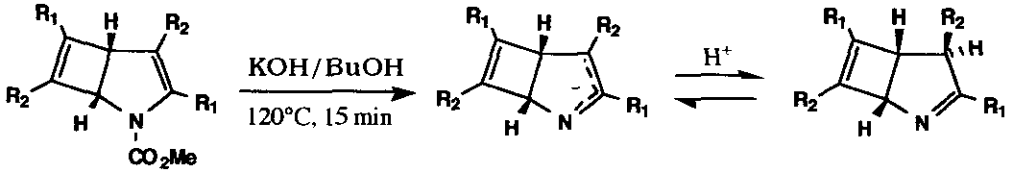



**1a-d** **2a-d** **3a**

a : $R_1$ = Me, $R_2$ = H
b : $R_1$ = H , $R_2$ = Me
c : $R_1$ = $^t$Bu, $R_2$ = H
d : $R_1$ = H, $R_2$ = $^t$Bu

Di-*t*-butyl substituted cyclobuta[*b*]pyrroles (**2c** and **2d**), thus obtained, were demethoxycarbonylated in *n*-butanol with potassium hydroxide as follows, although, dimethyl substituted derivatives (**2a**, **2b** and **3a**) did not give

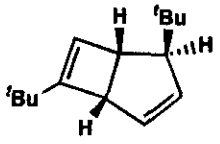
any assignable products under similar conditions. When a solution of an equimolar mixture of potassium hydroxide and the methyl 2,4-di-*t*-butyl- or 3,5-di-*t*-butyl-3a,5a-dihydro-1*H*-pyrrole-1-carboxylate (**2c** or **2d**) in the *n*-butanol was heated for 15 min at 120°C, carbon dioxide was liberated. When the reaction was complete, the solvent was evaporated off. Extraction of the alkaline reaction mixture diluted with water with ether provided 2,4-di-*t*-butyl-3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrrole (**5c**) as a pale yellow oil. On the other hand, 3,5-di-*t*-butyl-3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrrole (**5d**) was obtained from the ethereal extract of the neutralized reaction mixture with dilute hydrochloric acid as colorless prisms (mp 46-47°C). The difference in extractability between **5c** and **5d** suggests a greater acidity of the C-3 proton of **5d** than that of **5c**. On the basis of Karplus equation for the torsion angles of vicinal protons,[7] the observed coupling constant (3.3 Hz) between the C-3 and C-3a protons in **5d** supports the view that the *t*-butyl group is *cis*-oriented with respect to the C-3a proton. The stereochemistry of C-3 *t*-butyl group was also estimated by MM2[8] calculation for model hydrocarbons (**6** and **7**) of **5d** (Table 1). Although the vicinal steric repulsion between bridge-head proton and *t*-butyl group was expected, the MM2 calculation suggested that the structure (**6**) is more stable form than **7** by 1.8 kcal/mol. The measured vicinal coupling constant is in fairly good accord with the value expected for **6**. In other words, the corresponding anion (**4d**) may be stabilized due to the avoidance of steric repulsion between the large *t*-butyl group and the *cis*-vicinal C-3a proton. The energy of stabilization appears to be an important factor in increasing the acidity of the C-3 proton. The structures of these compounds were further confirmed as imines by ir spectra ($\nu_{max}$ 1615 for **5c** and 1605 $cm^{-1}$ for **5d**; N=C stretching).



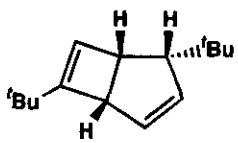

**2c-d** **4c-d** **5c-d**

c : $R_1$ = $^t$Bu, $R_2$ = H
d : $R_1$ = H, $R_2$ = $^t$Bu

Table 1. MM2 calculated torsion angles (C3H-C3-C3a-C3aH) and total steric energies and estimated coupling constants by Karplus' equation.




**6**

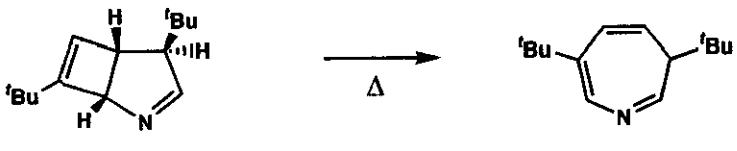



**7**

| | **6** | **7** |
|---|---|---|
| Torsion angle (degrees) $C_3H$-$C_3$-$C_{3a}$-$C_{3a}H$ | 110.4 | 24.8 |
| Calcd vicinal coupling constant (Hz) | 2.5 | 6.4 |
| MM2 calcd steric energy (kcal/mol) | 47.94 | 49.71 |

When a benzene solution of the imine (**5c**) or (**5d**) was heated for 12 h at 120°C in a sealed glass tube, ring opening occurred to give 2,5-di-*t*-butyl-3*H*-azepine (**8**), or 3,6-di-*t*-butyl-3*H*-azepine (**9**). A kinetic study of the thermal isomerization of cyclobuta[*b*]pyrroles (**5c**) and (**5d**) was carried out in $C_6D_6$ by using $^1H$ nmr. Good first-order plots were obtained in both cases in the range of 393 K to 423 K for **5c** and 373 K to 413 K for **5d**. Determined rates for **5c** and **5d** are listed on Table 2 along with half-life periods and the Arrhenius' plots showed on Figure 1. Rates measured for **5c** were treated in the usual fashion to give the rate expression $k_{5c} = 10^{11.1} e^{-28{,}720/RT}$. Although the Arrhenius' plot for **5c** gave good linear correlation, that of **5d** gave two linear lines obtained from respective temperature zone 373 - 393 K (lower temperature zone) and 393 - 413 K (higher temperature zone). Accordingly, the rate expression of **5d** was represented as $k_{5d(l)} = 10^{20.7} e^{-43{,}700/RT}$ for lower temperature zone and $k_{5d(h)} = 10^{2.5} e^{-11{,}000/RT}$ for higher temperature zone.


**5c** **8**




**5d** **9**

Table 2. First-order reaction rates and half-life periods of thermal isomerization of **5c** and **5d** in $C_6D_6$.

| Temp. (K) | Reaction of (5c) Rate ($\times10^{-5}$sec$^{-1}$) | Reaction of (5c) Half-life (min) | Reaction of (5d) Rate ($\times10^{-4}$sec$^{-1}$) | Reaction of (5d) Half-life (min) |
|---|---|---|---|---|
| 373 | - | - | 0.13±0.01 | 865 |
| 378 | - | - | 0.24±0.01 | 485 |
| 383 | - | - | 0.48±0.02 | 243 |
| 388 | - | - | 1.30±0.02 | 89 |
| 393 | 1.50±0.04 | 771 | 2.30±0.06 | 50 |
| 403 | 4.46±0.07 | 259 | 3.06±0.11 | 38 |
| 408 | 6.89±0.17 | 168 | 3.87±0.05 | 30 |
| 413 | 9.11±0.02 | 127 | 4.51±0.20 | 26 |
| 423 | 21.30±0.50 | 54 | - | - |

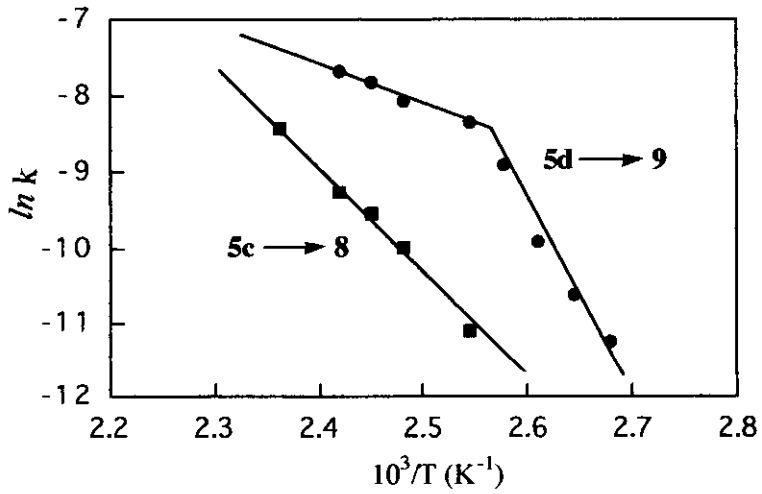
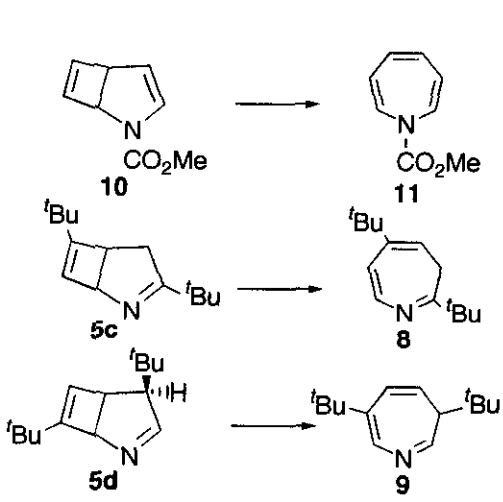



Figure 1. Arrhenius' plot of thermal reorganization of 2,4- and 3,5-di-*t*-butyl-3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrroles (**5c** and **5d**) in $C_6D_6$.

For the sake of comparison, the activation energy values of the present reaction were listed on Table 3 along with that of methyl 3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**10**).[9] It is interesting to note that the activation energy profile of **5c** is similar to that of **10** which has ene-amide structure in the molecule. In the case of **5d**, extremely small activation energy (11.0 kcal/mol) and frequency factor ($10^{2.5}$) were observed at higher temperature zone compared to values observed at lower temperature zone. In such a case, the reaction may be

"successive reaction". At present, further details of the characteristic kinetic behavior of **5d** are not so clear and are under investigation including the kinetic behavior of carboxylate esters **2c** and **2d**.

Table 3. Activation energy in thermal reorganization of **5c** , **5d** and methyl 3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**10**).




a) temperature range from 373 to 393 K b) temperature range from 393 to 413 K

## EXPERIMENTAL

Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. Silica gel $HF_{254}$ (Merck) for thin layer chromatography and silica gel Woelm 32-63 for preparative medium-pressure liquid chromatography (mplc) were used. Ir spectra were recorded on a JASCO FT-IR 5000 spectrophotometer. $^1H$ Nmr were measured on JEOL PMX-60 spectrometer or a Varian XL-500 spectrometer. Electronic Spectra were recorded on a Hitachi 288 spectrophotometer. Elemental analysis were performed on a Yanagimoto MT-2 CHN-corder. The molecular mechanics (MM2) calculation was carried out on NEC ACOS-2000 computer of Okayama University Computer Center.

### Synthesis of methyl 2,5-di-*t*-butyl-1*H*-azepine-1-carboxylate (1c) and methyl 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylate (1d)

To a heating (130°C) molten *p*-di-*t*-butylbenzene (145 g, 0.74 mol) was added dropwise methyl azidoformate (43 g, 0.42 mol) with efficiently stirring within 90 min, and the resulting solution was stirred at the temperature until stopping the evolution of nitrogen. After cooling, to the solidified reaction mixture was added 100 ml of cold

methyl alcohol to remove the unreacted excess *p*-di-*t*-butylbenzene by filtration. The brownish oil (75 g) was obtained from the filtrate by distillation of methyl alcohol under reduced pressure. The residue was chromatographed (ethyl acetate : hexane = 2 : 8 v/v) on silica gel to give 48.8 g of yellow oil. From 5 g of the yellow oil, methyl 2,5-di-*t*-butyl-1*H*-azepine-1-carboxylate (**1c**, 0.66 g, 5.9% based on methyl azidoformate) and methyl 3,6-di-*t*-butyl-1*H*-azepine-1-carboxylate (**1d**, 0.93 g, 8.2%) were obtained by means of mplc method using a mixed solvent (ethyl acetate : hexane = 1 : 9 v/v) as an eluent.

**1c:** colorless needles. mp 56 - 57°C. Ms m/z (%): 263 ($M^+$,100), 248 (55), 204 (84). Ir $\nu_{max}$ (KBr, $cm^{-1}$): 1716, 1623. Uv $\lambda_{max}$ (cyclohexane, nm): 208 (ε 14130), 245 (sh, 3800). $^1H$ Nmr (200 MHz, $CDCl_3$): δ 1.12 (s, 9H), 1.17 (s, 9H), 3.49 (s, 3H), 6.0 (m, 4H). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 72.90; H, 9.70; N, 5.59.

**1d:** pale yellow oil. Ms m/z (%): 263 ($M^+$,100), 248 (48), 204 (20). Ir $\nu_{max}$ (film, $cm^{-1}$): 1720, 1655, 1625. Uv $\lambda_{max}$ (cyclohexane, nm): 212 (ε 19500), 233 (sh, 4570). $^1H$ Nmr (200 MHz, $CDCl_3$): δ 1.09 (s, 18H), 3.66(s, 3H), 5.79 (s, 2H), 6.29 (s, 2H). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 72.83; H, 9.41; N, 5.19.

**General procedure: Preparation of dihydro-1*H*-cyclobuta[*b*]pyrroles (2a-d) and (3a)**

A methyl alcohol (110 ml) solution of 1*H*-azepine derivative (25 mmol) was irradiated with a 450 W high-pressure mercury lamp through a Pyrex filter at room temperature for 24 h. The solution was evaporated *in vacuo*, and the residue was chromatographed on silica gel (ethyl acetate : hexane = 2 : 8 v/v) to give bicyclic dihydro-1*H*-cyclobuta[*b*]pyrrole derivative. The following compounds (**2a-d**) and (**3a**) were prepared *via* this general procedure.

**Methyl 2,4-dimethyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (2a) and methyl 3a,5a-dimethyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (3a)**

**2a:** colorless prisms. mp 65 - 67°C. 24% yield: Ir $\nu_{max}$ (KBr, $cm^{-1}$): 1720, 1638. Uv $\lambda_{max}$ (EtOH, nm): 243 (*log* ε 3.69). $^1H$ Nmr (60 MHz, $CCl_4$): δ 1.65 (s, 3H), 1.97 (s, 3H), 3.45 (br s, 1H), 3.55 (s, 3H), 4.6 (m, 2H), 5.6 (m, 1H). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.89; H, 7.29; N, 7.90.

**3a:** pale yellow oil. 3% yield: Ir $\nu_{max}$ (film, $cm^{-1}$): 1695, 1598. Uv $\lambda_{max}$ (EtOH, nm): 221 (*log* ε 3.73), 251 (3.84). $^1H$ Nmr (60 MHz, $CCl_4$): δ 1.10 (s, 3H), 1.50 (s, 3H), 3.63 (s, 3H), 4.8 (m, 1H), 6.0 (m, 1H), 6.20

(d, J = 5.5 Hz, 1H), 6.4 (m 1H). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.77; H, 7.35; N, 7.94.

**Methyl 3,5-dimethyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (2b)**

pale yellow oil. 65% yield: Ir $\nu_{max}$ (film, $cm^{-1}$): 1700, 1620. Uv $\lambda_{max}$ (EtOH, nm): 238 (*log* ε 3.85). $^1H$ Nmr (60 MHz, $CCl_4$): δ 1.70 (s, 6H), 3.50 (br s, 1H), 3.63 (s, 3H), 4.7 (m, 1H), 6.05 (br s, 1H). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.21; H, 7.18; N, 7.68.

**Methyl 2,4-di-*t*-butyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (2c)**

colorless oil. 87% yield: Ir $\nu_{max}$ (film, $cm^{-1}$): 1720, 1630. Uv $\lambda_{max}$ (EtOH, nm): 230 (*log* ε 3.96). $^1H$ Nmr (60 MHz, $CCl_4$): δ 1.03 (s, 9H), 1.23 (s, 9H), 3.5 (m, 1H), 3.65 (s, 3H), 4.65 (d, J = 5.0 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 5.65 (s, 1H). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 72.76; H, 9.39; N, 5.21.

**Methyl 3,5-di-*t*-butyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (2d)**

pale yellow oil. 81% yield: Ir $\nu_{max}$ (film, $cm^{-1}$): 1710, 1610. Uv $\lambda_{max}$ (EtOH, nm): 245 (*log* ε 3.97). $^1H$ Nmr (60 MHz, $CCl_4$): δ 1.05 (s, 9H), 1.10 (s, 9H), 3.67 (s, 4H), 4.85 (br s, 1H), 6.0 (m, 2H). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 72.81; H, 9.34; N, 5.48.

**Synthesis of 2,4-di-*t*-butyl-3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrrole (5c)**

A solution of methyl 2,4-di-*t*-butyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**2c**, 310 mg, 1.18 mmol) in 5 ml of *n*-butanolic-KOH (1.43 N) was heated at 120°C for 15 min. The evolution of carbon dioxide was observed. After cooling, *n*-butanol was evaporated under reduced pressure. The residue was dissolved in water and extracted with ether. The bicyclic imine (**5c**, 109 mg) was obtained in 45% yield by mplc (ethyl acetate : hexane = 2 : 8) purification of crude product which came from the ether layer.

yellow oil: Ir $\nu_{max}$ (film, $cm^{-1}$): 1615. Uv $\lambda_{max}$ (EtOH, nm): 222.5 (sh *log* ε 2.87). $^1H$ Nmr (500 MHz, $CDCl_3$): δ 1.02 (s, 9H), 1.10 (s, 9H), 2.49 (ddd, J = 18.0, 10.2, and 2.0 Hz, 1H), 2.57 (dt, J = 18.0 and 3.5 Hz, 1H), 3.20 (ddt, J = 10.2, 3.5, and 1.2 Hz, 1H), 4.7 (m, 1H), 6.05 (s, 1H). $^{13}C$ Nmr (50 MHz, $CDCl_3$): δ 28.0 (q), 28.4 (q), 33.5 (s), 34.8 (t), 35.9 (s), 42.1 (d), 74.4 (d), 132.2 (d), 162.8 (s), 183.7 (s). Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.72; H, 11.15; N, 6.67.

**Synthesis of 3,5-di-*t*-butyl-3a,5a-dihydro-3*H*-cyclobuta[*b*]pyrrole (5d)**

A solution of methyl 3,5-di-*t*-butyl-3a,5a-dihydro-1*H*-cyclobuta[*b*]pyrrole-1-carboxylate (**2d**, 1.0 g, 3.8 mmol) in 5 ml of *n*-butanolic-KOH (1.43 N) was heated at 120°C for 30 min. After cooling, butanol was removed under reduced pressure. The residue was dissolved in water and the alkaline aqueous solution was extracted with ether. Unreacted material (**2d**, 572 mg) was recovered from the ethereal layer. The alkaline aqueous layer was neutralized by adding a dilute hydrochloric acid (1 N) and extracted with ether. The mplc purification of the extract gave bicyclic imine (**5d**, 140 mg) in 42% yield.

colorless needle. mp 46 - 47°C: Ir $\nu_{max}$ (KBr, $cm^{-1}$): 1605. Uv $\lambda_{max}$ (EtOH, nm): 255 (*log* ε 2.44). $^1$H Nmr (500 MHz, $CDCl_3$): δ 0.89 (s, 9H), 1.04 (s, 9H), 2.27 (dd, J = 3.3 and 2.5 Hz, 1H), 2.69 (t, J = 3.3 Hz, 1H), 4.9 (m, 1H), 5.72 (s, 1H), 7.43 (s, 1H). $^{13}$C Nmr (50 MHz, $CDCl_3$): δ 27.7 (q), 28.2 (q), 28.5 (s), 33.1 (d), 40.3 (d), 62.1 (d), 128.1 (d), 168.3 (s), 168.6 (d). Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.78; H, 11.21; N, 6.99.

**2,5-Di-*t*-butyl-3*H*-azepine (8)**

A solution of **5c** (250 mg, 1.22 mmol) in 10 ml of benzene was heated for 12 h at 120°C in a nitrogen purged Pyrex sealed tube. Benzene was evaporated under reduced pressure and the residue was chromatographed on silica gel with ethyl acetate : hexane = 2 : 8 v/v as an eluent. 2,5-Di-*t*-butyl-3*H*-azepine (**8**, 138 mg) was obtained in 55% yield.

colorless needles. mp 20.5 - 21°C: Ms m/z (%): 205 ($M^+$,54), 190 (57), 163 (81), 107 (100). Ir $\nu_{max}$ (film, $cm^{-1}$): 1600. $^1$H Nmr (500 MHz, $CDCl_3$): δ 1.07 (s, 9H), 1.10 (br s, 1H), 1.14 (s, 9H), 3.57 (br s, 2H), 5.03 (t, J = 7.0 Hz, 1H), 6.28 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H). $^{13}$C Nmr (125 MHz, $CDCl_3$): δ 28.7 (d), 30.3 (q), 32.4 (s), 34.4 (s), 38.1(s), 110.0 (d), 115.9 (d), 139.7 (d), 147.3 (s), 164.0 (s). Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.78; H, 11.35; N, 6.47.

**3,6-Di-*t*-butyl-3*H*-azepine (9)**

A solution of **5d** (320 mg, 1.56 mmol) in 10 ml of benzene was heated for 12 h at 120°C in a nitrogen purged Pyrex sealed tube. Benzene was evaporated under reduced pressure and the residue was chromatographed on silica gel with ethyl acetate : hexane = 2 : 8 v/v as an eluent. 3,6-Di-*t*-butyl-3*H*-azepine (**9**, 272 mg) was obtained in 85% yield.

colorless needles. mp 57.5 - 58.5°C: Ms m/z (%): 205 ($M^+$, 18), 190 (48), 148 (100). Ir $\nu_{max}$ (KBr, $cm^{-1}$): 1587. $^1$H Nmr (500 MHz, $CDCl_3$): δ 0.79 (ddd, J = 5.4, 4.8, and 1.7 Hz, 1H), 1.10 (s, 9H), 1.21 (s, 9H), 5.18 (dd, J = 9.6 and 5.4 Hz, 1H), 6.43 (dt, J = 9.6 and 1.7 Hz, 1H), 6.46 (d, J = 4.8 Hz, 1H), 7.43 (d, J =

1.7 Hz, 1H). $^{13}C$ Nmr (125 MHz, $CDCl_3$): δ 27.6 (q), 30.0 (s), 30.8 (q), 34.7 (s), 54.3 (d), 116.5 (d), 125.5 (d), 135.4 (d), 139.0 (s), 139.6 (d). Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.71; H, 11.17; N, 7.09.

**Kinetic measurements of thermal isomerization of 8 and 9**

A sealed nmr tube containing a solution of **5c** (15 mg, 0.073 mmol) in $C_6D_6$ (0.2 ml) was heated in a thermostat at the temperature of 393, 403, 408, 413 and 423 K, independently. The rate at the each temperature was determined by first-order analysis of the time depending decreasing of peak area at the nmr signal of C-5 proton (δ 5.98). A solution of **5d** (10 mg, 0.0487 mmol) in $C_6D_6$ (0.2 ml) was also treated in a similar manner at the temperature of 373, 378, 383, 388, 393, 403, 408, 413 and 423 K on the basis of measurement of time depending peak area shrinking at the nmr signal of C-4 proton (δ 6.63).

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