

A Novel Dehydrative Ring-Transformation of 1-Alkyl-3-aroypyrrolidines into 1-Alkyl-2-aryl-3-methylpyrroles

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When heated in an alcoholic solvent, such as ethylene glycol or butanol, 4-substituted 3-aryl-1-alkylpyrrolidines, which are readily accessible via the condensation of an amino acid, paraformaldehyde, and 3-substituted 1-aryl-2-propen-1-one, afforded 4-substituted 1-alkyl-2-aryl-3-methylpyrrole derivatives in good yields. The ring-transformation of 3,4-dibenzoyl-1-methyl-2-phenylpyrrolidine occurred in two directions, giving the corresponding 3-benzyl- and 3-methylpyrrole derivative. Also, bicyclic pyrroles, such as 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole, 2,3-dihydro-1*H*-pyrrolizine, and 5,6,7,8-tetrahydroindolizine, were prepared by the ring-transformation of bicyclic aroypyrrolidines obtained from the corresponding cyclic amino acids. A mechanism for the ring-transformation is proposed.

Since pyrroles present one of the most important classes of heterocycles, many preparative methods towards pyrrole rings have already been developed.^{1,2)} It was recently reported that when heated in an alcoholic solvent, 1-alkyl-3-aroypyrrolidines give 1-alkyl-2-aryl-3-methylpyrroles via a novel dehydrative ring-transformation reaction.³⁾

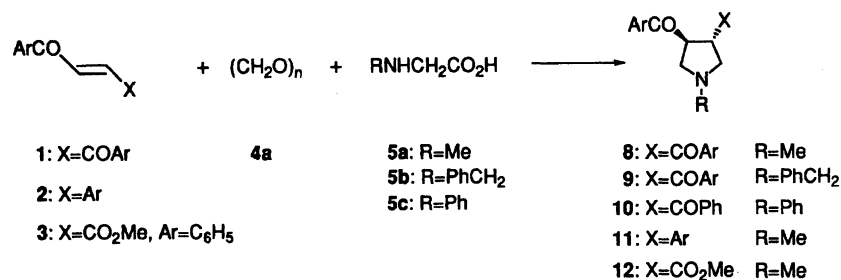
Here, the results of a detailed investigation on the ring-transformation reactions of various types of 1-alkyl-3-aroypyrrolidines are described, including the full details of our earlier communication.³⁾

Results and Discussion

Preparation of Aroypyrrolidines. Aroyl-substituted pyrrolidine derivatives **8**—**12** were prepared by reactions of the corresponding (*E*)-1-aryl-2-propen-1-ones (1,2-diaroylethenes **1a**—**e**, 1-aroyle-2-aryl-

ethenes **2a**—**d**, and methyl 4-oxo-4-phenyl-2-butenolate (**3**) with azomethine ylide generated in situ by the condensation of paraformaldehyde (**4a**) and *N*-substituted glycines **5a**—**c**. This method had been reported previously⁴⁾ (Scheme 1 and Chart 1).

The condensation reaction of **1a**, *N*-methylglycine (**5a**), and benzaldehyde (**4b**) produced two stereoisomers, **13-A** and **13-B**, of 3,4-dibenzoyl-1-methyl-2-phenylpyrrolidine (**13**) (Scheme 2). The stereostructures of **13-A** and **13-B** were assigned based on an epimerization reaction. When heated in ethanol under reflux for 24 h in the presence of NEt_3 , pure ($2R^*$, $3S^*$, $4S^*$)-isomer **13-A** gave a 4:1-mixture of **13-A** and ($2R^*$, $3S^*$, $4R^*$)-isomer **13-B**, while **13-B** was stable under the above-mentioned conditions. In the ^1H NMR of **13-B**, the methine proton of the 3-position was observed at a 0.59 ppm higher magnetic field than



Scheme 1.

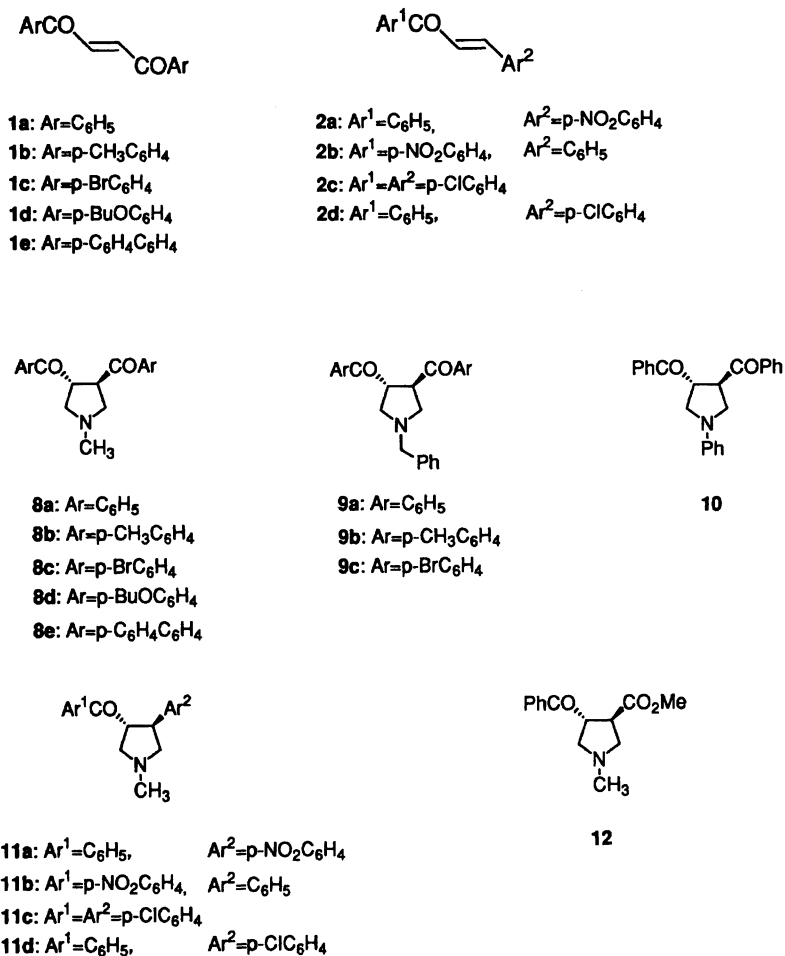
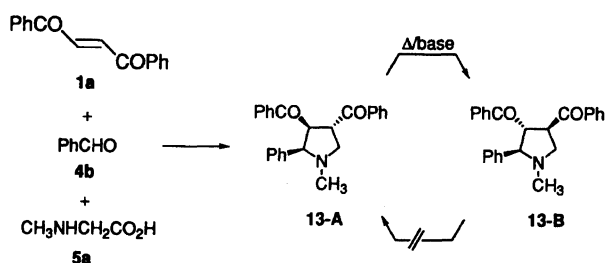


Chart 1.



Scheme 2.

that of the 4-position, probably due to a shielding effect of the phenyl group at the 2-position. On the other hand, the corresponding two methine protons of **13-A** appeared between 4.93 and 5.03 ppm as complicated multiple peaks.

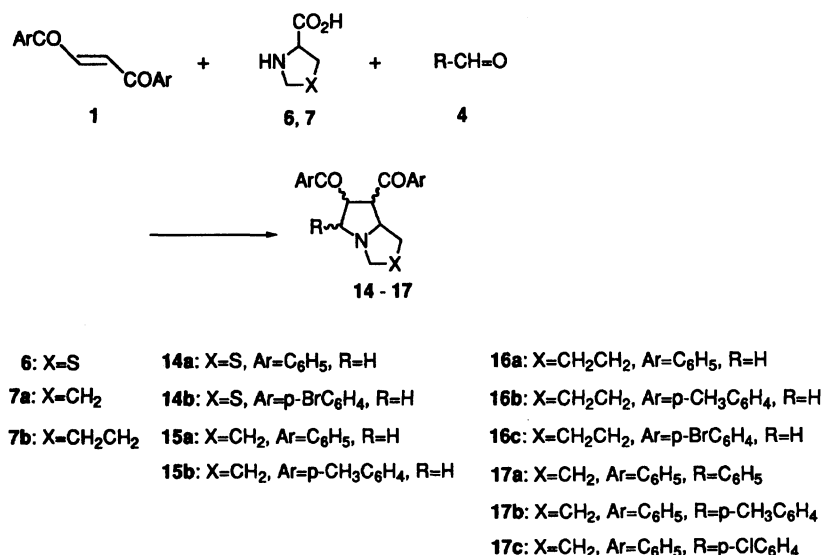
Using cyclic amino acids, the corresponding bicyclic derivatives **14**–**17** were prepared (Scheme 3).

Pyrrolothiazolizine **14** was obtained from thiazolidine-4-carboxylic acid (**6**) as a mixture of two stereoisomers. Upon a treatment with DBU in ethanol under reflux for 24 h, the minor isomer **14b-A** with the (6*R**, 7*R**, 7*aR**) configuration epimerized to the major isomer **14b-B** with (6*R**, 7*R**, 7*aS**) arrangement, while **14b-B** was stable under the same conditions. Bi-

cyclic pyrrolidines **15** and **16** were similarly obtained using L-proline (**7a**) and DL-pipecolic acid (**7b**), respectively, each as a mixture of the corresponding two stereoisomers. From the mixtures, (1*R**, 2*R**, 7*aS**)-isomer **15-A** and (1*R**, 2*R**, 8*aS**) derivative **16a-A** were obtained in pure forms. When heated in ethanol under reflux for 24 h in the presence of DBU, pure **16a-A** epimerized to give a mixture with (1*R**, 2*R**, 8*aR**)-isomer **16a-B**.

The hexahydro-1*H*-pyrrolizines **17** with an aryl group on the 3-position possess a further stereocenter. The condensation of **1a**, **7a**, and benzaldehydes led to two isomers **17-A** and **17-B**, which in each case separated into pure forms. NOE studies of **17c** (Fig. 1) revealed the stereochemistry of isomers **17-A** and **17-B** as being the (1*R**, 2*R**, 3*S**, 7*aR**) and (1*R**, 2*R**, 3*R**, 7*aR**) configurations, respectively. When treated with DBU in ethanol under reflux, **17c-A** epimerized into **17c-B**, which was stable under the above-mentioned conditions (Fig. 2).

Dehydrative Ring-transformation. When *trans*-3, 4-dibenzoyl-1-methylpyrrolidine (**8a**) was heated under the conditions listed in Table 1, 4-benzoyl-1,3-dimethyl-2-phenylpyrrole (**18a**) was produced. It was found that this reaction is greatly dependent on



Scheme 3.

Table 1. Transformation of 8 and 9 into 18 and 19

Pyrrolidine	Solvent ^{a)}	Additive	Time (h)	Temp (°C)	Pyrrole (%)
8a	EG	—	0.5	130	18a (96)
8a	BuOH	DBU	6	Reflux	18a (93)
8a	BuOH	—	24	Reflux	18a (71)
8a	BuOH	NEt ₃	24	Reflux	18a (92)
8a	BuOH	TosOH	24	Reflux	18a (45)
8a	Toluene	DBU	32	Reflux	18a (41)
8a	Toluene	—	32	Reflux	18a (3)
8a	CF ₃ COOH	—	32	Reflux	18a (53)
8a	DEG	—	2.5	130	18a (69)
8a	Methoxyethanol	—	13	Reflux	18a (69)
8b	EG	—	0.75	130	18b (79)
8c	EG	—	0.5	130	18c (73)
8d	EG	—	1.5	130	18d (63)
8e	EG	—	0.75	130	18e (76)
9a	EG	—	2	130	19a (75)
9b	EG	—	3.75	130	19b (75)
9c	EG	—	1.75	130	19c (77)

a) EG: Ethylene glycol; DEG: Diethylene glycol

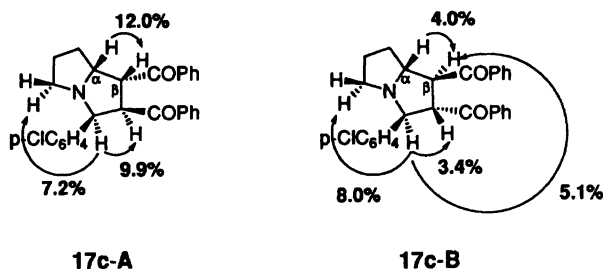
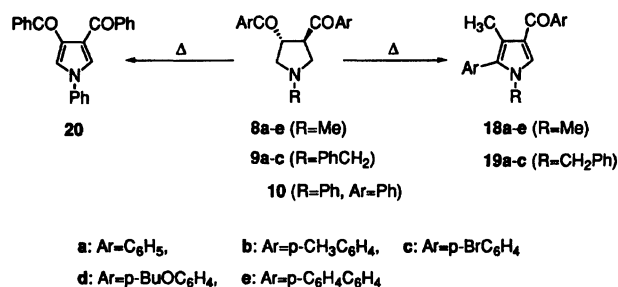


Fig. 1. NOE of 17c.



Scheme 4.

the nature of the substituent on the ring-nitrogen of **8**—**10** and the solvent used. The *N*-benzylpyrrolidine **9a** also gave pyrrole **19a**, while the *N*-phenyl derivative **10** produced an air-oxidized product, 3,4-dibenzoylpyrrole (**20**), in 48% yield, but not the expected pyrrole (Scheme 4). This reaction is promoted by a solvent having a high E_T -30 value, such as ethylene

glycol. A base promotes the reaction, while the reaction proceeded more slowly under acidic conditions. A ring-transformation of 3,4-bis(*p*-substituted benzoyl)pyrrolidines **8b**—**e** and **9b**—**c** proceeded smoothly in ethylene glycol, and gave **18b**—**e** and **19b**—**c**, respectively, in satisfactory yields. An electron-donating group tends to make the transformation slow. Surpris-

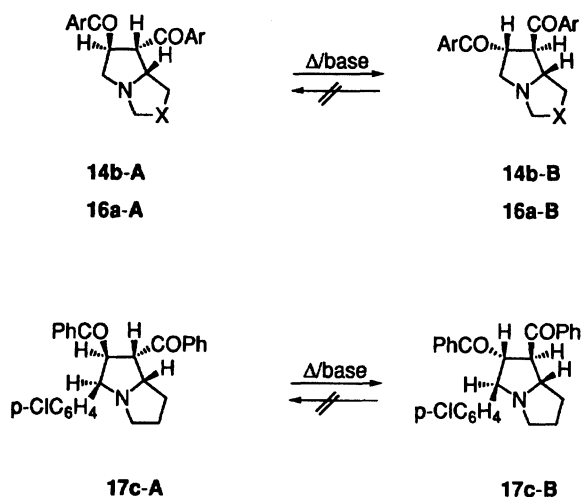


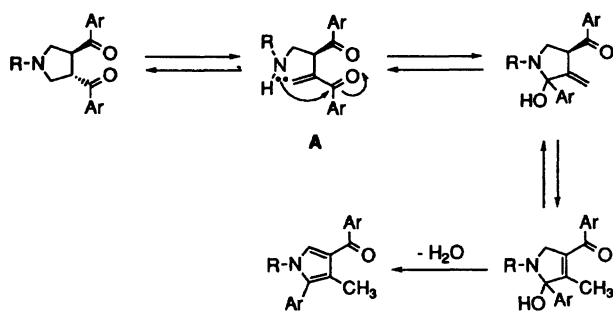
Fig. 2. Epimerization of 14b, 16a, and 17c.

ingly, upon heating **8a** above its melting point (130 °C) for 30 min without any solvent, no reaction occurred and **8a** was recovered quantitatively. From the above-mentioned results, the reaction mechanism via a thermally induced retro-Michael addition,^{5,6)} as shown in Scheme 5, is proposed. Intermediate **A** might be made disfavored by the electron-withdrawing phenyl group on the 1-position of **10**.

In the following, the transformation of various types of benzoylpyrrolidines is described. In all cases, the expected pyrroles would be isolated (Chart 2).

3-Aroyl-4-arylprrrolidines **11** were transformed into air-labile 2,4-diaryl-1,3-dimethylpyrroles **21**, which decomposed or became dark-colored during a work-up. 3-Benzoyl-1-methyl-4-*p*-nitrophenylbenzoylpyrrolidine **11a** gave **21a** in 79% yield when heated in ethylene glycol at 130 °C. On the other hand, 3-*p*-nitrobenzoyl-4-phenyl derivative **11b** gave unstable **21b** in 18% yield under similar conditions. However, yield of **21b** could be improved to 25% when the reaction was carried out in refluxing butanol in the presence of DBU. 3-*p*-Chlorobenzoyl-4-*p*-chlorophenyl derivative **11c** gave **21c** in 41% yield. The transformation of mono chloro-substituted derivative **11d** took a prolonged reaction time (48 h) and gave unstable pyrrole **21d** (53%) under the conditions mentioned above.

The ring-transformation of **12** with an electron-with-



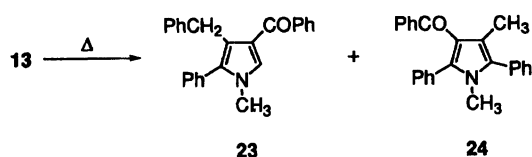
Scheme 5.

drawing ester functionality proceeded smoothly in ethylene glycol, though it was accompanied by transesterification, giving methyl pyrrolecarboxylate **22a** and 2-hydroxyethyl ester **22b** in 28% and 62% yields, respectively. When the reaction was carried out in 2-methoxyethanol under reflux for 24 h, 2-methoxyethyl ester **22c** was selectively obtained in 55% yield, together with **22a** in 3% yield. In dimethoxyethane, which has a low E_T -30 value and a low boiling point, the transformation did not proceed, and unchanged **12** was recovered.

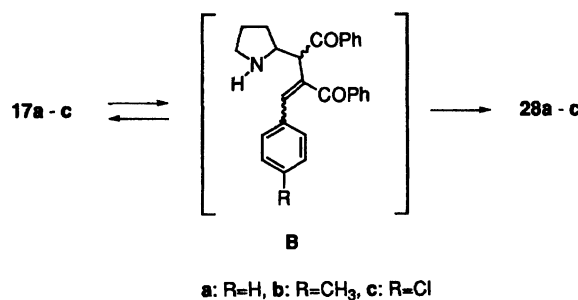
The ring-transformation reaction of **13** occurred in two directions, giving a 1:2-mixture (from ^1H NMR)⁷⁾ of the expected benzylpyrrole **23** and the methyl derivative **24** in low yields (Scheme 6). Unfortunately, the isolation of these pyrroles was unsuccessful.

Tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole **14a** and **14b** gave unstable 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole **25a** and **25b** in 62 and 57% yields, respectively, when the reaction was carried out in the presence of DBU. A part of **25** was found to decompose during the work-up of the reaction mixture. The ring-transformation of **15** and **16** gave the expected 2,3-dihydro-1*H*-pyrrolizine **26** and 5,6,7,8-tetrahydroindolizine **27**, respectively, in good yields. Aryl-substituted derivative **17** produced the expected **28** in a reaction carried out in the presence of DBU. Remarkably, it took 48 h to complete the reaction of the *p*-chlorophenyl derivative **17c** to give **28c** in 55% yield, while the reactions of **17a** and **17b** completed in 2 h, producing **28a** and **28b** in 52 and 66% yields, respectively. This remarkable substituent effect is tentatively explained as follows (Scheme 7): The electron-withdrawing *p*-chlorophenyl group of the intermediate **B** makes an attack on the cyclic amine-subunit on the carbon-carbon double bond, a more favorable pathway than an attack on the benzoyl carbon, which leads to the final product **28**.

In summary, the above-mentioned ring-transformation of 3-arylprrrolidines is useful for preparing vari-

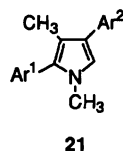


Scheme 6.

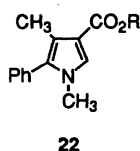


a: R=H, **b:** R=CH₃, **c:** R=Cl

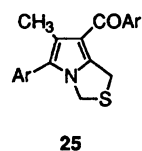
Scheme 7.



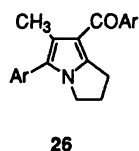
- a: Ar¹=C₆H₅, Ar²=p-NO₂C₆H₄
 b: Ar¹=p-NO₂C₆H₄, Ar²=C₆H₅
 c: Ar¹=Ar²=p-ClC₆H₄
 d: Ar¹=C₆H₅, Ar²=p-ClC₆H₄



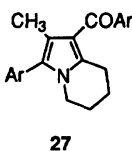
- a: R=CH₃
 b: R=CH₂CH₂OH
 c: R=CH₂CH₂OCH₃



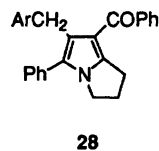
- a: Ar=C₆H₅
 b: Ar=p-BrC₆H₄



- a: Ar=C₆H₅
 b: Ar=p-CH₃C₆H₄



- a: Ar=C₆H₅
 b: Ar=p-CH₃C₆H₄
 c: Ar=p-BrC₆H₄



- a: Ar=C₆H₅
 b: Ar=p-CH₃C₆H₄
 c: Ar=p-ClC₆H₄

Chart 2.

ous types of 2-arylpyrroles. The ring-transformation of alkanoyl derivatives might suffer disadvantages due to side-reactions and an instability of the produced alkylpyrroles, although it was not investigated in this study.

Experimental

General. All of the melting points were measured on a Mitamura Melt Thermo and are uncorrected. The IR spectra were measured on a Nippon-Bunko IR-700 as a KBr pellet, unless otherwise stated. ¹H and ¹³C NMR spectra were recorded on a JEOL EX-270 spectrometer using Me₄Si as an internal reference in CDCl₃. The mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer. Elemental analyses were carried out on Yanako MT-5 CHN recorder. Column chromatography was carried out on silica gel (Wako-gel, C-300).

Typical Procedure for the Preparation of 8,9,11, and 12. A mixture of **1b** (2.00 g, 7.56 mmol), **4a** (1.13 g, 37.8 mmol), and **5a** (1.35 g, 15.1 mmol) in toluene (100 ml) was heated under reflux for 1 h. After being cooled to room temperature, insoluble materials were filtered off. The filtrate was evaporated in vacuo, leaving a residue. Chromatography (benzene/ethyl acetate=1/1) of this residue gave **trans-1-methyl-3,4-di-p-toluoylpyrrolidine (8b)** (1.80 g, 74%): Colorless needles (hexane-benzene); mp 116–117 °C; IR 1669 cm⁻¹; ¹H NMR δ=2.32 (3H, s), 2.38 (6H, s), 2.76 (2H, dd, *J*=9.2, 5.8 Hz), 3.02–3.12 (2H, m), 4.57–4.65 (2H, m), 7.23 (4H, d, *J*=8.2 Hz), 7.87 (4H, d, *J*=8.2 Hz); MS *m/z* 321 (M⁺). Found: C, 78.57; H, 7.27; N, 4.30%. Calcd for C₂₁H₂₃NO₂: C, 78.47; H, 7.21; N, 4.36%.

trans-1-Methyl-3,4-bis(p-phenylbenzoyl)pyrrolidine (8e). A mixture of **1e** (2.00 g, 5.15 mmol), **4a** (0.77 g, 25.7 mmol), and **5a** (0.92 g, 10.3 mmol) in toluene (100 ml) was heated under reflux for 1.5 h and worked up as described above. Chromatography (benzene/ethyl acetate=1/9) gave **8e** (1.24 g, 54%): Colorless prisms (hexane-benzene); mp 161–162 °C; IR 1673 cm⁻¹; ¹H NMR δ=2.36 (3H, s), 2.84 (2H, dd, *J*=8.8, 5.6 Hz), 3.14 (2H, dd, *J*=8.8, 8.2 Hz), 4.66–4.74 (2H, m), 7.32–7.62 (10H, m), 7.65–7.70 (4H, m), 8.06 (4H, dd, *J*=8.6, 2.0 Hz); MS *m/z* 445 (M⁺). Found: C, 83.79; H, 6.25; N, 2.99%. Calcd for C₃₁H₂₇NO₂: C, 83.57; H, 6.11; N, 3.14%.

trans-3,4-Dibenzoyl-1-benzylpyrrolidine (9a). A mixture of **1a** (3.00 g, 12.7 mmol), **4a** (1.91 g, 63.5 mmol), and **5b** (4.19 g, 25.4 mmol) in toluene (150 ml) was heated under reflux for 3 h and worked up as described above. Chromatography gave **1a** (700 mg, 23%) (benzene) and **9a** (2.76 g, 66%) (benzene/ethyl acetate=1/9): Colorless plates (hexane-benzene); mp 109–110 °C; IR 1680 cm⁻¹; ¹H NMR δ=2.79–2.85 (2H, m), 3.10–3.18 (2H, m), 3.63 (2H, s), 4.61–4.70 (2H, m), 7.17–7.29 (5H, m), 7.35–7.55 (6H, m), 7.94–8.00 (4H, m); MS *m/z* 369 (M⁺). Found: C, 81.36; H, 6.29; N, 3.52%. Calcd for C₂₅H₂₃NO₂: C, 81.27; H, 6.27; N, 3.79%.

trans-1-Benzyl-3,4-di-p-toluoylpyrrolidine (9b). A mixture of **1b** (2.00 g, 7.56 mmol), **4a** (1.13 g, 37.8 mmol), and **5b** (2.48 g, 15.0 mmol) in toluene (100 ml) was heated under reflux for 6 h and worked up as described above. Chromatography gave **1b** (700 mg, 35%) (benzene) and **9b** (840 mg, 28%) (benzene/ethyl acetate=95/5): Colorless prisms (hexane-benzene); mp 106–107 °C; IR 1671 cm⁻¹; ¹H NMR δ=2.37 (6H, s), 2.80 (2H, dd, *J*=9.1, 5.8 Hz), 3.06–3.16 (2H, m), 3.62 (2H, s), 4.58–4.66 (2H, m), 7.20–7.35 (9H, m), 7.86 (4H, d, *J*=8.4 Hz); ¹³C NMR δ=21.60, 47.28, 57.79, 59.39, 127.02, 128.26, 128.57, 128.82, 129.36, 133.69, 138.33, 144.08, 199.22; MS *m/z* 397 (M⁺). Found: C, 81.44; H, 6.74; N, 3.54%. Calcd for C₂₇H₂₇NO₂: C, 81.58; H, 6.85; N, 3.52%.

trans-1-Benzyl-3,4-bis(p-bromobenzoyl)pyrrolidine (9c). A mixture of **1c** (2.00 g, 5.08 mmol), **4a** (0.76 g, 25.4 mmol), and **5b** (1.67 g, 10.1 mmol) in toluene (100 ml) was heated under reflux for 5 h and worked up as described above. Chromatography (benzene/ethyl acetate) gave **9c** (1.05 g, 39%): Colorless needles (hexane-benzene); mp 106–107 °C; IR 1671 cm⁻¹; ¹H NMR δ=2.37 (6H, s), 2.80 (2H, dd, *J*=9.1, 5.8 Hz), 3.06–3.16 (2H, m), 3.62 (2H, s), 4.58–4.66 (2H, m), 7.20–7.35 (9H, m), 7.86 (4H, d, *J*=8.4 Hz); ¹³C NMR δ=21.60, 47.28, 57.79, 59.39, 127.02, 128.26, 128.57, 128.82, 129.36, 133.69, 138.33, 144.08, 199.22; MS *m/z* 397 (M⁺). Found: C, 81.44; H, 6.74; N, 3.54%. Calcd for C₂₇H₂₇NO₂: C, 81.58; H, 6.85; N, 3.52%.

trans-1-Benzyl-3,4-bis(p-bromobenzoyl)pyrrolidine (9c). A mixture of **1c** (2.00 g, 5.08 mmol), **4a** (0.76 g, 25.4 mmol), and **5b** (1.67 g, 10.1 mmol) in toluene (100 ml) was heated under reflux for 5 h and worked up as described above. Chromatography (benzene/ethyl acetate) gave **9c** (1.05 g, 39%): Colorless needles (hexane-benzene); mp 106–107 °C; IR 1671 cm⁻¹; ¹H NMR δ=2.37 (6H, s), 2.80 (2H, dd, *J*=9.1, 5.8 Hz), 3.06–3.16 (2H, m), 3.62 (2H, s), 4.58–4.66 (2H, m), 7.20–7.35 (9H, m), 7.86 (4H, d, *J*=8.4 Hz); ¹³C NMR δ=21.60, 47.28, 57.79, 59.39, 127.02, 128.26, 128.57, 128.82, 129.36, 133.69, 138.33, 144.08, 199.22; MS *m/z* 397 (M⁺). Found: C, 81.44; H, 6.74; N, 3.54%. Calcd for C₂₇H₂₇NO₂: C, 81.58; H, 6.85; N, 3.52%.

mp 124–125 °C; IR 1681 cm^{-1} ; ^1H NMR δ =2.77 (2H, dd, J =9.2, 6.0 Hz), 3.06–3.16 (2H, m), 3.61 (2H, s), 4.53–4.61 (2H, m), 7.20–7.27 (5H, m), 7.57 (4H, dd, J =6.6, 2.0 Hz), and 7.81 (4H, dd, J =6.6, 2.0 Hz); ^{13}C NMR δ =47.26, 57.47, 59.24, 127.29, 128.33, 128.52, 128.62, 130.17, 132.06, 134.77, 138.02, 198.36; MS m/z (rel intensity) 529, 527, 525 (M^+ ; 11, 20, 11). Found: C, 57.10; H, 4.17; N, 2.63%. Calcd for $\text{C}_{25}\text{H}_{21}\text{NO}_2\text{Br}_2$: C, 56.95; H, 4.01; N, 2.66%.

trans-1-Methyl-3-(p-nitrobenzoyl)-4-phenylpyrrolidine (11b). A mixture of **2b** (1.50 g, 5.92 mmol), **5a** (1.05 g, 11.85 mmol), and **4a** (0.89 g, 29.6 mmol) in toluene (100 ml) was heated under reflux for 2 h and worked up as described above. Chromatography gave **2c** (470 mg, 31%) (benzene) and **11b** (913 mg, 50%) (ethyl acetate): Oil; IR (NaCl) 1692 cm^{-1} ; ^1H NMR δ =2.43 (3H, s), 2.76 (1H, dd, J =9.3, 7.1 Hz), 2.99–3.16 (3H, m), 3.70–4.02 (2H, m), 7.23–7.31 (5H, m), 7.89 (2H, m), 8.19 (2H, m); ^{13}C NMR δ =41.87, 42.23, 55.96, 59.49, 64.55, 123.98, 126.92, 127.57, 128.79, 129.61, 140.83, 143.54, 150.17, 198.24; MS m/z 310 (M^+). Found: C, 69.68; H, 6.06; N, 9.16%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$: C, 69.66; H, 5.85; N, 9.03%.

trans-3-(p-Chlorobenzoyl)-4-(p-chlorophenyl)-1-methylpyrrolidine (11c). A mixture of **2c** (1.00 g, 3.6 mmol), **5a** (643 mg, 7.2 mmol), and **4a** (541 mg, 18 mmol) in toluene (50 ml) was heated under reflux for 1 h and worked up as described above. Chromatography (ethyl acetate) gave **11c** (1.11 g, 93%): Pale yellow oil: IR (NaCl) 1685 cm^{-1} ; ^1H NMR δ =2.40 (3H, s), 2.76 (1H, dd, J =9.2, 6.1 Hz), 2.84 (1H, dd, J =9.2, 6.6 Hz), 3.01 (1H, dd, J =9.2, 7.9 Hz), 3.11 (1H, dd, J =9.2, 8.3 Hz), 3.77–3.91 (2H, m), 7.20–7.30 (4H, m), 7.34–7.38 (2H, m), 7.70–7.75 (2H, m); MS m/z (rel intensity) 337, 335, 333 (M^+ ; 2, 11, 18). Found: C, 64.26; H, 5.24; N, 4.46%. Calcd for $\text{C}_{18}\text{H}_{17}\text{NOCl}_2$: C, 64.68; H, 5.13; N, 4.19%.

trans-3-Benzoyl-4-(p-chlorophenyl)-1-methylpyrrolidine (11d). A mixture of **2d** (3.00 g, 12.36 mmol), **5a** (2.20 g, 24.7 mmol), and **4a** (1.85 g, 61.8 mmol) in toluene (150 ml) was heated under reflux for 5 h and worked up as described above. Chromatography gave **2d** (1.25 g, 42%) (hexane/dichloromethane=1/1) and **11d** (1.59 g, 43%) (hexane/ethyl acetate=1:1): Pale yellow oil; IR (NaCl) 1682 cm^{-1} ; ^1H NMR δ =2.40 (3H, s), 2.78 (1H, dd, J =9.2, 6.5 Hz), 2.82 (1H, dd, J =9.2, 6.5 Hz), 3.02 (1H, dd, J =9.2, 7.9 Hz), 3.15 (1H, t, J =9.2 Hz), 3.84–3.98 (2H, m), 7.25 (4H, s), 7.36–7.42 (2H, m), 7.49–7.56 (2H, m), 7.78–7.82 (2H, m); ^{13}C NMR δ =41.91, 45.84, 55.55, 60.24, 64.08, 128.54, 128.64, 128.95, 132.18, 133.14, 136.32, 143.04, 199.26; MS m/z (rel intensity) 301, 299 (M^+ ; 41, 100). Found: C, 71.88; H, 5.78; N, 4.73%. Calcd for $\text{C}_{18}\text{H}_{18}\text{NOCl}$: C, 72.11; H, 6.05; N, 4.67%.

Methyl trans-4-Benzoyl-1-methylpyrrolidine-3-carboxylate (12). After a mixture of **3** (1.50 g, 7.89 mmol), **5a** (1.41 g, 15.77 mmol), **4a** (1.19 g, 39.4 mmol) in toluene (75 ml) was heated under reflux for 3 h and worked up as described above. Chromatography (benzene/ethyl acetate=1/1) gave **12** (1.36 g, 70%): Colorless prisms (hexane); mp 62–63 °C; IR 1734 and 1686 cm^{-1} ; ^1H NMR δ =2.33 (3H, s), 2.59 (1H, dd, J =9.3, 6.6 Hz), 2.86 (1H, t, J =8.8 Hz), 2.96 (1H, dd, J =9.3, 5.5 Hz), 3.10 (1H, t, J =8.8 Hz), 3.72–3.79 (4H, m), 4.40 (1H, ddd, J =8.8, 6.6, 5.5 Hz), 7.45–7.62 (3H, m), and 7.96–8.01 (2H, m); ^{13}C NMR δ =41.60, 41.62, 48.95, 52.25, 59.01, 59.84, 128.71, 133.37,

136.04, 174.43, 198.61; MS m/z 247 (M^+). Found: C, 67.91; H, 6.85; N, 5.68%. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$: C, 68.00; H, 6.93; N, 5.66%.

trans-3,4-Dibenzoyl-1-phenylpyrrolidine (10). After a mixture of **5c** (1.28 g, 8.46 mmol) and **4a** (1.27 g, 42.3 mmol) in toluene (100 ml) was heated under reflux for 30 min, **1a** (2.00 g, 8.46 mmol) was added to it. The whole mixture was then heated under reflux for 48 h, and worked up as described above. Chromatography (hexane/dichloromethane=1/3) gave **10** (2.15 g, 72%): Colorless prisms (hexane–ethyl acetate); mp 125–126 °C; IR 1674 cm^{-1} ; ^1H NMR δ =3.50 (2H, dd, J =8.9, 6.9 Hz), 3.93 (2H, t, J =8.9 Hz), 4.78 (2H, dd, J =8.9, 6.9 Hz), 6.53 (2H, d, J =8.3 Hz), 6.65–6.74 (1H, m), 7.16–7.24 (2H, m), 7.46–7.62 (6H, m), 8.02–8.04 (4H, m); ^{13}C NMR δ =47.40, 51.41, 112.31, 116.98, 128.86, 129.14, 133.64, 135.92, 147.04, 198.76; MS m/z 355 (M^+). Found: C, 81.37; H, 5.99; N, 3.68%. Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$: C, 81.10; H, 5.96; N, 3.94%.

3,4-Dibenzoyl-1-methyl-2-phenylpyrrolidine (13). A mixture of **1a** (3.00 g, 12.7 mmol), **5a** (2.26 g, 25.4 mmol), **4b** (2.02 g, 19.0 mmol) in toluene (150 ml) was heated under reflux for 27 h and worked up as described above. The residue was triturated with ether and an insoluble white solid was filtered. Chromatography (benzene/hexane=1/1) of the solid gave a mixture of **13-A** and **13-B**, which was again chromatographed, giving **13-A** (406 mg, 9%) (dichloromethane) and **13-B** (876 mg, 19%) (ethyl acetate).

(2R*,3S*,4S*)-Isomer (13-A): Colorless plates (hexane–benzene); mp 148–149 °C; IR 1674 cm^{-1} ; ^1H NMR δ =2.19 (3H, s), 2.54–2.64 (1H, m), 3.71–3.88 (2H, m), 4.93–5.03 (2H, m), 6.95–7.36 (8H, m), 7.45–7.51 (4H, m), 7.55–7.61 (1H, m), 8.06–8.10 (2H, m); MS m/z 369 (M^+). Found: C, 81.40; H, 6.32; N, 3.70%. Calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_2$: C, 81.26; H, 6.28; N, 3.79%.

(2R*,3R*,4R*)-Isomer (13-B). Pale yellow prisms (hexane–benzene); mp 84–86 °C; IR 1679 cm^{-1} ; ^1H NMR δ =2.11 (3H, s), 3.01 (1H, t, J =9.4 Hz), 3.44 (1H, dd, J =9.4, 1.7 Hz), 3.54 (1H, d, J =8.6 Hz), 4.28 (1H, ddd, J =9.4, 4.8, 1.7 Hz), 4.87 (1H, dd, J =8.6, 4.8 Hz), 7.19–7.30 (5H, m), 7.36–7.48 (5H, m), 7.52–7.58 (1H, m), 7.62–7.67 (2H, m), 7.94–7.98 (2H, m). HRMS (FAB). Found: m/z 370.1803. Calcd for $(\text{C}_{25}\text{H}_{23}\text{O}_2\text{N}+\text{H}^+)$: M , 370.1808.

6,7-Dibenzoyl-5,6,7,7a-tetrahydro-1H,3H-pyrrolo-[1,2-c]thiazole (14a). A mixture of **1a** (2.00 g, 8.46 mmol), **6** (2.24 g, 16.9 mmol), and **4a** (1.27 g, 42.3 mmol) in toluene (100 ml) was heated under reflux for 0.5 h, and worked up as described above. The residue was chromatographed (hexane/ethyl acetate=3/2) and triturated with ether, giving **14a** (1.20 g, 42%) as a 1:9-mixture of two stereoisomers **14a-A** and **14a-B**. Recrystallization of the mixture from hexane–benzene gave an analytical sample of **(6R*,7R*,7aS*)-isomer 14a-B**: Colorless needles (hexane–benzene); mp 153–156 °C; IR 1672 cm^{-1} ; ^1H NMR δ =2.80 (1H, dd, J =10.5, 8.8 Hz), 2.98 (1H, dd, J =10.5, 8.8 Hz), 3.23 (1H, dd, J =10.5, 7.6 Hz), 3.52 (1H, t, J =8.8 Hz), 3.73–3.80 (1H, m), 4.08 (1H, d, J =10.4 Hz), 4.21 (1H, d, J =10.4 Hz), 4.64 (1H, dd, J =5.6, 2.3 Hz), 4.86 (1H, ddd, J =10.5, 8.8, 5.6 Hz), 7.42–7.61 (6H, m), 7.94–8.06 (4H, m); MS m/z 337 (M^+). Found: C, 71.32; H, 5.76; N, 4.00%. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{S}$: C, 71.19; H, 5.68; N, 4.15%.

^1H NMR Data of (6R*,7R*,7aR*)-Isomer 14a-A:

δ =2.43 (1H, dd, J =10.4, 7.1 Hz), 2.57 (1H, dd, J =10.1, 9.6 Hz), 3.16–3.21 (1H, m), 3.44–3.51 (1H, m), 3.95–4.10 (1H, m), 4.08 (1H, d, J =9.9 Hz), 4.28 (1H, d, J =9.9 Hz), 4.80–4.90 (1H, m), 5.15 (1H, t, J =6.9 Hz), 7.40–7.65 (6H, m), 7.90–8.10 (4H, m).

6,7-Bis(*p*-bromobenzoyl)-5,6,7,7a-tetrahydro-1H, 3H-pyrrolo[1,2-*c*]thiazole (14b). A mixture of **1c** (3.00 g, 7.61 mmol), **6** (2.01 g, 15.3 mmol), and **4a** (1.14 g, 38.1 mmol) in toluene (150 ml) was heated under reflux for 0.5 h and worked up as described above. Chromatography gave **14b-A** (0.68 g, 18%) (dichloromethane) and **14b-B** (2.22 g, 59%) (hexane/ethyl acetate=1:1).

(6R*,7R*,7aR*)-Isomer 14b-A: Colorless prisms (hexane-dichloromethane); mp 146–149 °C; IR 1673 cm⁻¹; ¹H NMR δ =2.44 (1H, dd, J =10.5, 7.3 Hz), 2.56 (1H, dd, J =10.5, 9.3 Hz), 3.16–3.21 (2H, m), 3.97 (1H, dt, J =9.3, 7.3 Hz), 4.08 (1H, d, J =10.0 Hz), 4.27 (1H, d, J =10.0 Hz), 4.68–4.82 (1H, m), 5.06 (1H, t, J =7.3 Hz), 7.63 (4H, tt, J =8.9, 2.1 Hz), 7.85 (2H, dt, J =8.9, 2.1 Hz), 7.91 (2H, dt, J =8.9, 2.1 Hz); MS m/z (rel intensity) 497, 495, 493 (M⁺; 22, 39, 20). Found: C, 48.66; H, 3.55; N, 2.95%. Calcd for C₂₀H₁₇NO₂SBr₂: C, 48.51; H, 3.46; N, 2.83%.

(6R*,7R*,7aS*)-Isomer 14b-B: Colorless prisms (hexane-dichloromethane); mp 193–194 °C; IR 1679 cm⁻¹; ¹H NMR δ =2.78 (1H, dd, J =11.2, 8.9 Hz), 2.94 (1H, dd, J =11.2, 7.8 Hz), 3.22 (1H, dd, J =11.2, 7.8 Hz), 3.52 (1H, t, J =8.9 Hz), 3.76 (1H, ddd, J =7.8, 7.6, 2.3 Hz), 4.06 (1H, d, J =10.0 Hz), 4.20 (1H, d, J =10.0 Hz), 4.54 (1H, dd, J =5.9, 2.3 Hz), 4.75 (1H, ddd, J =11.2, 8.9, 5.9 Hz), 7.59–7.65 (4H, m), 7.79–7.86 (4H, m); MS m/z (rel intensity) 497, 495, 493 (M⁺; 11, 20, 10). Found: C, 48.76; H, 3.37; N, 2.72%. Calcd for C₂₀H₁₇NO₂SBr₂: C, 48.51; H, 3.46; N, 2.83%.

1,2-Dibenzoyl-2,3,5,6,7,7a-hexahydro-1H-pyrrolizine (15a). A mixture of **1a** (2.00 g, 8.46 mmol), **7a** (1.95 g, 16.9 mmol), and **4a** (1.27 g, 42.3 mmol) in toluene (100 ml) was heated under reflux for 30 min and worked up as described above. Chromatography (benzene/ethyl acetate=1/1) gave viscous oil (2.15 g, 80%) of a 2:1-mixture of **15a-A** and **15a-B**. Trituration of the oil with ether gave **(1R*,2R*,7aS*)-Isomer 15a-A** (760 mg, 28%): Colorless needles (hexane-benzene); mp 165–167 °C; IR 1663 cm⁻¹; ¹H NMR δ =1.19–1.34 (1H, m), 1.45–1.60 (1H, m), 1.60–1.75 (1H, m), 1.75–1.88 (1H, m), 2.65 (1H, ddd, J =9.9, 9.9, 5.9 Hz), 3.12 (1H, dd, J =11.4, 9.9 Hz), 3.18–3.29 (2H, m), 4.08–4.20 (1H, m), 4.58–4.77 (2H, m), 7.44–7.61 (6H, m), 7.99 (1H, d, J =8.8 Hz), 8.00 (1H, d, J =8.1 Hz), 8.08 (1H, d, J =8.8 Hz), 8.09 (1H, d, J =8.1 Hz), ¹³C NMR δ =27.08, 29.85, 46.72, 55.81, 56.98, 59.25, 66.83, 129.29, 129.49, 129.56, 129.65, 134.20, 134.25, 137.59, 137.86, 199.37, 200.48; MS m/z 319 (M⁺). Found: C, 78.81; H, 6.76; N, 4.54%. Calcd for C₂₁H₂₁NO₂: C, 78.97; H, 6.63; N, 4.39%.

¹H NMR Data of (1R*,2R*,7aR*)-Isomer 15a-B: δ =1.77–1.89 (2H, m), 1.95–2.06 (2H, m), 2.63–2.76 (1H, m), 2.95–3.08 (2H, m), 3.66–3.70 (2H, m), 4.43 (1H, t, J =8.0 Hz), 4.65–4.77 (1H, m), 7.40–7.58 (6H, m), 7.93–8.09 (4H, m).

2,3,5,6,7,7a-Hexahydro-1,2-di-*p*-toluoyl-1H-pyrrolizine (15b). A mixture of **1b** (3.00 g, 11.35 mmol), **7a** (2.61 g, 22.7 mmol), and **4a** (1.70 g, 56.8 mmol) in toluene (150 ml) was heated under reflux for 30 min and worked

up as described above. Chromatography (ethyl acetate) gave a 2:1-mixture of **15b-A** and **15b-B** (2.90 g, 74%) as viscous oil. Trituration of the oil with ether afforded **(1R*,2R*,7aS*)-Isomer 15b-A** (600 mg, 15%): Colorless prisms (hexane-benzene); mp 126–127 °C; IR 1671 cm⁻¹; ¹H NMR δ =1.26–1.33 (1H, m), 1.42–1.54 (1H, m), 1.57–1.71 (1H, m), 1.74–1.87 (1H, m), 2.41 (6H, s), 2.59–2.65 (1H, m), 3.10 (1H, dd, J =11.4, 9.9 Hz), 3.17–3.26 (2H, m), 4.09–4.18 (1H, m), 4.56–4.72 (2H, m), 7.25–7.29 (4H, m), 7.86–7.91 (2H, m), 7.96–8.01 (2H, m); ¹³C NMR δ =21.67, 26.20, 28.95, 45.61, 54.82, 56.12, 58.44, 66.05, 128.34, 128.75, 129.34, 129.43, 134.30, 134.55, 144.11, 148.18, 198.11, 199.24; MS m/z 347 (M⁺). Found: C, 79.57; H, 7.32; N, 4.35%. Calcd for C₂₃H₂₅NO₂: C, 79.51; H, 7.25; N, 4.03%.

¹H NMR Data of (1R*,2R*,7aR*)-Isomer 15b-B: δ =1.75–1.90 (2H, m), 1.90–2.10 (2H, m), 2.38 (3H, s), 2.39 (3H, s), 2.60–2.75 (1H, m), 2.95–3.10 (2H, m), 3.60–3.80 (2H, m), 4.39 (1H, t, J =8.3 Hz), 4.60–4.75 (1H, m), 7.20–7.40 (4H, m), 7.85–8.00 (4H, m).

1,2-Dibenzoylperhydroindolizine (16a). A mixture of ethene **1a** (2.00 g, 8.46 mmol), **7b** (2.19 g, 16.9 mmol), and **4a** (1.27 g, 42.3 mmol) in toluene (100 ml) was heated under reflux for 1 h and worked up as described above. Chromatography (benzene/ethyl acetate=3/1) gave **16a-B** (0.58 g, 21%) and **16a-A** (1.56 g, 55%).

(1R*,2R*,8aR*)-Isomer 16a-A: Colorless prisms (hexane-benzene); mp 140–141 °C; IR 1670 cm⁻¹; ¹H NMR δ =0.88–1.21 (2H, m), 1.42–1.67 (4H, m), 1.94–2.05 (1H, m), 2.37 (1H, t, J =9.1 Hz), 2.51 (1H, td, J =6.6, 2.6), 3.10–3.15 (1H, m), 3.61 (1H, t, J =8.5 Hz), 4.68–4.79 (2H, m), 7.42–7.58 (6H, m), 7.96–8.01 (4H, m); ¹³C NMR δ =24.22, 24.38, 25.75, 46.36, 49.77, 52.87, 58.44, 66.94, 128.59, 128.62, 128.73, 133.13, 133.37, 136.39, 138.08, 200.09, 200.23; MS m/z 333 (M⁺). Found: C, 79.01; H, 6.74; N, 4.04%. Calcd for C₂₂H₂₃NO₂: C, 79.25; H, 6.95; N, 4.20%.

(1R*,2R*,8aR*)-Isomer 16a-B: Pale yellow oil; IR (NaCl) 1680 cm⁻¹; ¹H NMR δ =1.11–1.74 (6H, m), 1.99–2.09 (1H, m), 2.28 (1H, td, J =10.9, 2.6 Hz), 2.88 (1H, dd, J =10.9, 9.9 Hz), 3.01 (1H, td, J =10.9, 2.6 Hz), 3.28 (1H, dd, J =9.2, 2.6 Hz), 4.25 (1H, ddd, J =10.9, 6.6, 2.6 Hz), 4.50 (1H, dd, J =9.5, 6.6 Hz), 7.38–7.58 (6H, m), 7.86–8.91 (2H, m), 8.00–8.60 (2H, m); MS m/z 333 (M⁺).

1,2-Dibenzoyl-2,3,5,6,7,7a-hexahydro-3-phenyl-1H-pyrrolizine (17a). A mixture of **1a** (1.50 g, 6.35 mmol), **7a** (1.46 g, 12.7 mmol), and **4b** (1.01 g, 9.53 mmol) in toluene (75 ml) was heated under reflux for 30 min and worked up as described above. Chromatography (hexane/ethyl acetate=3/1) gave **17a-B** (1.82 g, 73%) and **17a-A** (0.54 g, 22%).

(1R*,2R*,3S*,7aS*)-Isomer 17a-A: Colorless prisms (hexane-benzene); mp 118.5–120 °C; IR 1665 cm⁻¹; ¹H NMR δ =1.76–2.16 (4H, m), 2.70–2.78 (1H, m), 2.89 (1H, td, J =6.8, 4.8 Hz), 3.87 (1H, q, J =6.8 Hz), 4.14 (1H, d, J =9.6 Hz), 4.40 (1H, dd, J =9.6, 6.8 Hz), 4.85 (1H, t, J =9.6 Hz), 7.16–7.46 (11H, m), 7.51–7.60 (2H, m), 7.91–7.95 (2H, m); MS m/z 395 (M⁺). Found: C, 82.27; H, 6.20; N, 3.36%. Calcd for C₂₇H₂₅NO₂: C, 82.00; H, 6.37; N, 3.54%.

(1R*,2R*,3S*,7aR*)-Isomer 17a-B: Colorless prisms (hexane-benzene); mp 133–134 °C; IR 1669 cm⁻¹; ¹H NMR δ =1.30–1.56 (2H, m), 1.71–2.00 (2H, m), 2.81 (1H, td, J =9.9, 6.2 Hz), 3.29–3.36 (1H, m), 4.30–4.40 (1H,

m), 4.52 (1H, d, $J=7.6$ Hz), 4.86–4.99 (2H, m), 6.98–7.01 (2H, m), 7.09–7.17 (3H, m), 7.36–7.62 (6H, m), 7.87–7.92 (2H, m), 8.02–8.06 (2H, m); MS m/z 395 (M^+). Found: C, 82.08; H, 6.41; N, 3.45%. Calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54%.

1,2-Dibenzoyl-2,3,5,6,7,7a-hexahydro-3-*p*-tolyl-1H-pyrrolizine (17b). A mixture of **1a** (5.00 g, 21.2 mmol), **7a** (4.87 g, 42.3 mmol), and **4c** (3.81 g, 31.7 mmol) in toluene (250 ml) was heated under reflux for 2 h and worked up as described above. Chromatography gave **17b-B** (4.06 g, 47%) (hexane/ethyl acetate=4/1) and **17b-A** (2.00 g, 23%) (hexane/ethyl acetate=3/1).

(1R*,2R*,3S*,7aS*)-Isomer 17b-A: Colorless prisms (hexane-dichloromethane); mp 117–118 °C; IR 1664 cm^{-1} ; 1H NMR $\delta=1.69$ –2.16 (4H, m), 2.26 (3H, s), 2.69–2.78 (1H, m), 2.87 (1H, dt, $J=10.9$, 6.4 Hz), 3.86 (1H, q, $J=6.7$ Hz), 4.12 (1H, d, $J=9.6$ Hz), 4.39 (1H, dd, $J=9.6$, 6.7 Hz), 4.84 (1H, t, $J=9.6$ Hz), 7.02 (2H, d, $J=8.0$ Hz), 7.16–7.27 (4H, m), 7.33–7.46 (3H, m), 7.50–7.56 (1H, m), 7.58–7.62 (2H, m), 7.90–7.93 (2H, m). Found: C, 82.16; H, 6.55; N, 3.73%. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42%.

(1R*,2R*,3S*,7aR*)-Isomer 17b-B: Colorless prisms (hexane-dichloromethane); mp 91–93 °C; IR 1670 cm^{-1} ; 1H NMR $\delta=1.32$ –1.56 (2H, m), 1.70–2.00 (2H, m), 2.22 (3H, s), 2.81 (1H, td, $J=9.8$, 6.1 Hz), 3.29–3.37 (1H, m), 4.29–4.31 (1H, m), 4.49 (1H, d, $J=7.0$ Hz), 4.83–4.95 (2H, m), 6.87 (2H, d, $J=8.0$ Hz), 6.94 (2H, d, $J=8.0$ Hz), 7.40–7.61 (6H, m), 7.88–7.93 (2H, m), 8.01–8.06 (2H, m). Found: C, 82.17; H, 6.69; N, 3.61%. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42%.

3-*p*-Chlorophenyl-1,2-dibenzoyl-2,3,5,7,7a-hexahydro-1H-pyrrolizine (17c). A mixture of **1a** (3.00 g, 12.7 mmol), **7a** (2.92 g, 25.4 mmol), and **4d** (2.68 g, 19.1 mmol) in toluene (150 ml) was heated under reflux for 1.5 h and worked up as described above. Chromatography gave **17c-B** (3.06 g, 47%) (hexane/ethyl acetate=5/1) and **17c-A** (0.68 g, 22%) (hexane/ethyl acetate=3/1).

(1R*,2R*,3S*,7aS*)-Isomer 17c-A: Colorless prisms (hexane-benzene); mp 102–103 °C; IR 1669 cm^{-1} ; 1H NMR $\delta=1.78$ –2.19 (4H, m), 2.64–2.73 (1H, m), 2.81–2.90 (1H, m), 3.85 (1H, q, $J=6.6$ Hz), 4.15 (1H, d, $J=9.4$ Hz), 4.36 (1H, dd, $J=9.4$, 6.6 Hz), 4.79 (1H, t, $J=9.4$ Hz), 7.15–7.64 (12H, m), 7.89–7.94 (2H, m); MS m/z 431, 429 (M^+). Found: C, 75.34; H, 5.71; N, 3.55%. Calcd for $C_{27}H_{24}NO_2Cl$: C, 75.43; H, 5.63; N, 3.26%.

(1R*,2R*,3S*,7aR*)-Isomer 17c-B: Colorless prisms (hexane-benzene); mp 142–144 °C; IR 1666 cm^{-1} ; 1H NMR $\delta=1.29$ –1.56 (2H, m), 1.69–1.85 (1H, m), 1.90–1.99 (1H, m), 2.78 (1H, td, $J=9.9$, 6.1 Hz), 3.29 (1H, ddd, $J=9.9$, 6.9, 2.6 Hz), 4.31 (1H, td, $J=8.6$, 6.6 Hz), 4.48 (1H, d, $J=7.8$ Hz), 4.84 (1H, dd, $J=9.8$, 8.6 Hz), 4.96 (1H, dd, $J=9.8$, 7.8 Hz), 6.93 (2H, dd, $J=8.2$, 2.0 Hz), 7.09 (2H, dd, $J=8.2$, 2.0 Hz), 7.40–7.62 (6H, m), 7.86–7.91 (2H, m), 8.01–8.05 (2H, m); MS m/z (rel intensity) 431, 429 (M^+ ; 19, 53). Found: C, 75.39; H, 5.68; N, 3.06. Calcd for $C_{27}H_{24}NO_2Cl$: C, 75.43; H, 5.63; N, 3.26%.

4-Benzoyl-1,3-dimethyl-2-phenylpyrrole (18a). Typical procedure. A solution of **8a** (200 mg, 0.68 mmol) in ethylene glycol (10 ml) was heated at 130 °C for 0.5 h. It was then cooled, poured into water, extracted with dichloromethane, dried ($MgSO_4$), and evaporated in vacuo, leaving

a residue. Chromatography (benzene) of the residue gave **18a** (180 mg, 96%): Colorless prisms (hexane-benzene); mp 131–134 °C; IR 1632 cm^{-1} ; 1H NMR $\delta=2.31$ (3H, s), 3.49 (3H, s), 7.02 (1H, s), 7.30–7.55 (8H, m), 7.79–7.83 (2H, m); ^{13}C NMR $\delta=11.62$, 35.29, 119.88, 122.01, 127.87, 128.06, 128.25, 128.46, 128.86, 130.64, 130.97, 131.26, 133.60, 141.16, 191.80; MS m/z 275 (M^+). Found: C, 82.92; H, 6.45; N, 5.22%. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09%.

1,3-Dimethyl-4-*p*-toluoyl-2-*p*-tolylpyrrole (18b). Yield 79%; colorless plates (hexane-benzene); mp 128–129 °C; IR 1626 cm^{-1} ; 1H NMR $\delta=2.28$ (3H, s), 2.41 (3H, s), 2.42 (3H, s), 3.47 (3H, s), 7.00 (1H, s), 7.18–7.78 (6H, m), 7.73 (2H, d, $J=7.9$ Hz); ^{13}C NMR $\delta=11.61$, 21.29, 21.51, 35.20, 119.57, 122.05, 128.32, 128.71, 129.07, 129.16, 130.19, 130.47, 133.49, 137.64, 138.42, 141.39, 191.59; MS m/z 303 (M^+). Found: C, 82.87; H, 6.95; N, 4.68%. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62%.

4-*p*-Bromobenzoyl-2-*p*-bromophenyl-1,3-dimethylpyrrole (18c). Yield 73%; colorless prisms (hexane-benzene); mp 154–155 °C; IR 1624 cm^{-1} ; 1H NMR $\delta=2.26$ (3H, s), 3.49 (3H, s), 6.99 (1H, s), 7.16–7.22 (2H, m), 7.58–7.63 (4H, m), 7.66–7.70 (2H, m); MS m/z (rel intensity) 435, 433, 431 (M^+ ; 48, 100, 53). Found: C, 52.95; H, 3.62; N, 3.09%. Calcd for $C_{19}H_{15}NOBr_2$: C, 52.69; H, 3.49; N, 3.23%.

4-*p*-Butoxybenzoyl-2-*p*-butoxyphenyl-1,3-dimethylpyrrole (18d). Yield 63%; colorless plates (hexane-benzene); mp 107–109 °C; IR 1620 cm^{-1} ; 1H NMR $\delta=0.99$ (3H, t, $J=7.3$ Hz), 1.00 (3H, t, $J=7.3$ Hz), 1.44–1.58 (4H, m), 1.75–1.85 (4H, m), 2.26 (3H, s), 3.46 (3H, s), 3.98–4.05 (4H, m), 6.93 (2H, d, $J=8.8$ Hz), 6.97 (2H, d, $J=8.8$ Hz), 7.00 (1H, s), 7.22 (2H, d, $J=8.8$ Hz), 7.82 (2H, d, $J=8.8$ Hz); MS m/z 419 (M^+). Found: C, 76.57; H, 7.94; N, 3.22%. Calcd for $(C_{27}H_{33}NO_3+0.25H_2O)$: C, 76.47; H, 7.96; N, 3.30%.

2-(4-Biphenyl)-1,3-dimethyl-4-*p*-phenylbenzoylpyrrole (18e). Yield 76%; colorless prisms (hexane-benzene); mp 187–189 °C; IR 1625 cm^{-1} ; 1H NMR $\delta=2.37$ (3H, s), 3.57 (3H, s), 7.11 (1H, s), 7.35–7.57 (8H, m), 7.63–7.72 (8H, m), 7.89–7.94 (2H, m); MS m/z 427 (M^+). Found: C, 86.94; H, 5.84; N, 3.14%. Calcd for $C_{31}H_{25}NO$: C, 87.09; H, 5.89; N, 3.28%.

4-Benzoyl-1-benzyl-3-methyl-2-phenylpyrrole (19a). Yield 75%; pale yellow oil; IR (NaCl) 1632 cm^{-1} ; 1H NMR $\delta=2.31$ (3H, s), 4.98 (2H, s), 6.86–6.89 (2H, m), 7.08 (1H, s), 7.19–7.26 (5H, m), 7.33–7.52 (6H, m), 7.79–7.83 (2H, m); MS m/z 351 (M^+). Found: C, 85.51; H, 6.03; N, 4.43%. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99%.

1-Benzyl-3-methyl-4-*p*-toluoyl-2-*p*-tolylpyrrole (19b). Yield 75%; colorless prisms (hexane); mp 100–101 °C; IR 1626 cm^{-1} ; 1H NMR $\delta=2.29$ (3H, s), 2.38 (3H, s), 2.40 (3H, s), 4.97 (2H, s), 6.89–6.92 (2H, s), 7.05 (1H, s), 7.11 (2H, d, $J=8.1$ Hz), 7.17–7.28 (7H, m), 7.72 (2H, d, $J=8.1$ Hz); ^{13}C NMR $\delta=11.54$, 21.28, 21.49, 51.03, 119.67, 122.60, 126.57, 127.56, 128.19, 128.66, 128.73, 129.14, 129.19, 129.41, 130.65, 133.78, 137.63, 137.77, 138.22, 141.54, 191.68; MS m/z 379 (M^+). Found: C, 85.19; H, 6.63; N, 3.76%. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69%.

1-Benzyl-4-*p*-bromobenzoyl-2-*p*-bromophenyl-3-methylpyrrole (19c). Yield 77%; colorless prisms (hex-

ane-benzene); mp 142–143 °C; IR 1631 cm^{-1} ; ^1H NMR δ =2.26 (3H, s), 4.96 (2H, s), 6.85–6.89 (2H, m), 7.06 (1H, s), 7.08–7.09 (2H, m), 7.24–7.26 (3H, m), 7.48–7.53 (1H, m), 7.56–7.58 (3H, m), 7.65–7.70 (1H, m); ^{13}C NMR δ =11.45, 51.30, 120.52, 122.30, 122.42, 125.93, 126.47, 127.85, 128.80, 129.92, 130.51, 131.35, 131.71, 132.29, 132.68, 137.02, 139.51, 190.47; MS (rel intensity) m/z 511, 509, 507 (M^+ ; 35, 67, 35). Found: C, 58.91; H, 3.77; N, 2.40%. Calcd for $\text{C}_{25}\text{H}_{19}\text{NOBr}_2$: C, 58.96; H, 3.76; N, 2.75%.

3,4-Dibenzoyl-1-phenylpyrrole (20). A solution of **10** (200 mg, 0.56 mmol) in ethylene glycol (10 ml) was heated at 130 °C for 24 h and worked up as described above. Chromatography gave **10** (46 mg, 23%) (benzene) and **20** (95 mg, 48%) (ethyl acetate): Colorless prisms (hexane-benzene); mp 214–216 °C; IR 1637 cm^{-1} ; ^1H NMR δ =7.24–7.56 (11H, m), 7.70–7.73 (4H, m); ^{13}C NMR 121.36, 125.50, 126.84, 127.87, 128.21, 129.02, 130.06, 132.20, 139.01, 139.08, 190.89; MS m/z 351 (M^+). Found: C, 82.22; H, 4.80; N, 3.85%. Calcd for $\text{C}_{24}\text{H}_{17}\text{NO}_2$: C, 82.03; H, 4.88; N, 3.99%.

1,3-Dimethyl-4-(*p*-nitrophenyl)-2-phenylpyrrole (21a). A mixture of **2a** (3.00 g, 11.8 mmol), **5a** (2.11 g, 23.7 mmol), and **4a** (1.77 g, 59.2 mmol) in toluene (150 ml) was heated under reflux for 5 h. After it was cooled to room temperature, insoluble materials were filtered off. The filtrate was evaporated in vacuo, leaving a residue. Chromatography gave unchanged **2a** (1.42 g, 47%) (hexane/dichloromethane=1/1) and **11a** (1.65 g, 45%) (hexane/ethyl acetate=1/1) as an oil. A solution of this oil (200 mg, 0.64 mmol) in ethylene glycol (10 ml) was heated at 130 °C for 2.5 h under argon and worked up as described above. Chromatography (hexane/dichloromethane=1/2) gave **21a** (148 mg, 79%): Unstable yellow prisms; mp 163–165 °C; ^1H NMR δ =2.18 (3H, s), 3.56 (3H, s), 6.95 (1H, s), 7.32–7.42 (3H, m), 7.44–7.50 (2H, m), 7.57–7.62 (2H, m), 8.19–8.25 (2H, m). HRMS Found: m/z 292.1201. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$: M, 292.1213.

1,3-Dimethyl-2-(*p*-nitrophenyl)-4-phenylpyrrole (21b). A mixture of **11b** (200 mg, 0.64 mmol) and DBU (98 mg, 0.64 mmol) in 1-butanol (10 ml) was heated under reflux for 2.5 h under argon. It was cooled and evaporated in vacuo, leaving a residue which, on chromatography (hexane/dichloromethane=1/1), gave **21b** (48 mg, 25%): Unstable yellow prisms; mp 175–176 °C; ^1H NMR δ =2.18 (3H, s), 3.60 (3H, s), 6.86 (1H, s), 7.22–7.28 (1H, s), 7.36–7.46 (4H, m), 7.48–7.52 (2H, m), 8.28–8.33 (2H, m), MS m/z 292 (M^+). Found: C, 74.20; H, 5.31; N, 9.56%. Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$: C, 73.95; H, 5.52; N, 9.58%.

2,4-Bis(*p*-chlorophenyl)-1,3-dimethylpyrrole (21c). After a mixture of **11c** (535 mg, 1.60 mmol) and DBU (243 mg, 1.60 mmol) in 1-butanol (20 ml) was heated under reflux for 12 h under argon, it was cooled and evaporated in vacuo, giving a residue. The residue was recrystallized from hexane-benzene, giving **21c** (204 mg, 41%): Colorless prisms; mp 178–181 °C; ^1H NMR δ =2.10 (3H, s), 3.52 (3H, s), 6.78 (1H, s), 7.25–7.44 (8H, m). Found: C, 68.20; H, 4.80; N, 4.21%. Calcd for $\text{C}_{18}\text{H}_{15}\text{NCl}_2$: C, 68.37; H, 4.78; N, 4.43%.

4-(*p*-Chlorophenyl)-1,3-dimethyl-2-phenylpyrrole (21d). After a solution of **11d** (202 mg, 0.67 mmol) and DBU (103 mg, 0.67 mmol) in 1-butanol (10 ml) was heated under reflux for 48 h under argon, it was cooled. The precipitates were collected by filtration and washed with

ether, giving **21d** (100 mg, 53%): Unstable colorless prisms; mp 139–140 °C; ^1H NMR δ =2.05 (3H, s), 3.46 (3H, s), 6.70 (1H, s), 7.30–7.48 (9H, m). HRMS Found: m/z 281.0960. Calcd for $\text{C}_{18}\text{H}_{16}\text{NCl}$: M, 281.0973.

1,4-Dimethyl-5-phenylpyrrole-3-carboxylate 22a and 22b. After a solution of **12** (200 mg, 0.81 mmol) in ethylene glycol (10 ml) was heated at 130 °C for 45 min, it was cooled and evaporated in vacuo, giving a residue which, on chromatography, gave methyl ester **22a** (51 mg, 28%) (benzene) and 2-hydroxyethyl ester **22b** (129 mg, 62%) (benzene/ethyl acetate).

Methyl 1,4-Dimethyl-5-phenylpyrrole-3-carboxylate (22a): Unstable pale yellow oil; IR (NaCl) 1708 cm^{-1} ; ^1H NMR δ =2.12 (3H, s), 3.39 (3H, s), 3.71 (3H, s), 7.16–7.20 (2H, m), 7.22 (1H, s), 7.28–7.38 (3H, m). HRMS Found: m/z 229.1112. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$: M, 229.1104.

2-Hydroxyethyl 1,4-Dimethyl-5-phenylpyrrole-3-carboxylate (22b): Unstable pale yellow oil; IR (NaCl) 3448, 1703 cm^{-1} ; ^1H NMR δ =2.11 (3H, s), 2.90 (1H, br), 3.26 (3H, s), 3.80 (2H, t, J =4.8 Hz), 4.26 (2H, t, J =4.8 Hz), 7.15 (2H, dd, J =7.8, 1.4 Hz), 7.23–7.36 (4H, m); ^{13}C NMR δ =11.13, 35.04, 61.44, 65.09, 112.81, 118.94, 127.58, 127.89, 128.25, 130.46, 131.21, 132.63, 165.68. HRMS Found: m/z 259.1204. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: M, 259.1209.

2-Methoxyethyl 1,4-Dimethyl-5-phenylpyrrole-3-carboxylate (22c). A mixture of **12** (500 mg, 2.02 mmol) and DBU (307 mg, 2.02 mmol) in 2-methoxyethanol (25 ml) was heated under reflux for 24 h and worked up as described above. Chromatography gave **22a** (14 mg, 3%) (hexane/dichloromethane=1/1) and **22c** (301 mg, 55%) (hexane/dichloromethane=2/3): Pale yellow oil; IR (NaCl) 1705 cm^{-1} ; ^1H NMR δ =2.21 (3H, s), 3.42 (3H, s), 3.48 (3H, s), 3.67–3.71 (2H, m), 4.37–4.40 (2H, m), 7.25–7.29 (2H, m), 7.38–7.44 (4H, m); MS m/z 273 (M^+). Anal. Found: C, 70.51; H, 6.91; N, 5.30%. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3$: C, 70.31; H, 7.01; N, 5.12%.

7-Benzoyl-6-methyl-5-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole (25a). A mixture of **14a-A** (200 mg, 0.59 mmol) and DBU (90 mg, 0.59 mmol) in degassed ethylene glycol (10 ml) was heated at 130 °C for 7 h under argon and worked up as described above. Chromatography (dichloromethane) gave **25a** (118 mg, 62%): Unstable colorless prisms; mp 164–167 °C; IR 1629 cm^{-1} ; ^1H NMR δ =2.16 (3H, s), 3.87 (2H, d, J =1.3 Hz), 4.94 (2H, d, J =1.3 Hz), 7.33–7.39 (2H, m), 7.43–7.49 (5H, m), 7.63–7.73 (2H, m). HRMS (FAB) Found: m/z 320.1107. Calcd for $(\text{C}_{20}\text{H}_{17}\text{ONS}+\text{H}^+)$: 320.1110.

7-*p*-Bromobenzoyl-5-*p*-bromophenyl-6-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole (25b). A mixture of **14b-A** (200 mg, 0.40 mmol) and DBU (61 mg, 0.40 mmol) in degassed ethylene glycol (10 ml) was heated at 130 °C for 5 h under argon and worked up as described above. Chromatography (dichloromethane) gave **25b** (110 mg, 57%): Unstable colorless prisms; mp 214–217 °C; IR 1619 cm^{-1} ; ^1H NMR δ =2.11 (3H, s), 3.90 (2H, t, J =1.5 Hz), 4.92 (2H, t, J =1.5 Hz), 7.18–7.24 (2H, m), 7.56–7.62 (6H, m); MS m/z (rel intensity) 479, 477, 475 (M^+ ; 54, 100, 50). Found: C, 49.79; H, 3.26; N, 2.86%. Calcd for $(\text{C}_{20}\text{H}_{15}\text{NOSBr}_2+0.25\text{H}_2\text{O})$: C, 49.87; H, 3.24; N, 2.91%.

7-Benzoyl-2,3-dihydro-6-methyl-5-phenyl-1*H*-pyrrolizine (26a). A solution of **15a-A** (200 mg, 0.63 mmol) in ethylene glycol (10 ml) was heated at 130 °C

for 1.5 h and worked up as described above. Chromatography (benzene) gave **26a** (124 mg, 66%): Colorless needles (hexane–benzene); mp 171–172 °C; IR 1623 cm^{-1} ; ^1H NMR δ =2.30–2.37 (2H, m), 2.34 (3H, s), 2.55 (2H, t, J =7.3 Hz), 3.92 (2H, t, J =7.3 Hz), 7.28–7.53 (8H, m), 7.68–7.72 (2H, m); ^{13}C NMR δ =12.26, 26.65, 26.87, 46.58, 116.50, 122.14, 126.88, 127.76, 128.00, 128.39, 128.82, 130.10, 131.79, 141.80, 144.42, 192.70; MS m/z 301 (M^+). Found: C, 83.53; H, 6.43; N, 4.58%. Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$: C, 83.69; H, 6.35; N, 4.65%.

2,3-Dihydro-6-methyl-7-*p*-toluoyl-5-*p*-tolyl-1H-pyrrolizine (26b). A solution of **15b-A** (200 mg, 0.58 mmol) in ethylene glycol (10 ml) was heated at 130 °C for 1.5 h and worked up as described above. Chromatography (dichloromethane) gave **26b** (120 mg, 64%): Colorless needles (hexane–benzene); mp 161–162 °C; IR 1627 cm^{-1} ; ^1H NMR δ =2.32 (3H, s), 2.33 (2H, t, J =7.1 Hz), 2.39 (3H, s), 2.41 (3H, s), 2.60 (2H, t, J =7.1 Hz), 3.90 (2H, t, J =7.1 Hz), 7.25–7.28 (6H, m), 7.60–7.64 (2H, m); ^{13}C NMR δ =12.33, 21.24, 21.55, 26.99, 46.56, 116.64, 121.81, 127.73, 128.62, 128.71, 129.04, 129.18, 136.69, 138.99, 141.11, 143.88, 192.65; MS m/z 329 (M^+). Found: C, 83.93; H, 7.07; N, 4.04%. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$: C, 83.85; H, 7.04; N, 4.25%.

1-Benzoyl-5,6,7,8-tetrahydro-2-methyl-3-phenylindolizine (27a). A solution of **16a-A** (150 mg, 0.45 mmol) in ethylene glycol (7.5 ml) was heated at 130 °C for 3 h and worked up as described above. Chromatography (dichloromethane) gave **27a** (95 mg, 67%): Colorless plates (hexane–benzene); mp 122–124 °C; IR 1625 cm^{-1} ; ^1H NMR δ =1.71–1.92 (4H, m), 1.89 (3H, s), 2.78 (2H, t, J =6.4 Hz), 3.73 (2H, t, J =6.4 Hz), 7.26–7.52 (8H, m), 7.72–7.76 (2H, m); MS m/z 315 (M^+). Found: C, 84.00; H, 6.51; N, 4.25%. Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}$: C, 83.78; H, 6.71; N, 4.44%.

5,6,7,8-Tetrahydro-2-methyl-1-*p*-toluoyl-3-*p*-tolylindolizine (27b). A mixture of **1b** (3.00 g, 11.35 mmol), **6b** (2.93 g, 22.7 mmol), and **4a** (1.70 g, 56.75 mmol) in toluene (150 ml) was heated under reflux for 30 min. It was cooled and evaporated in vacuo, leaving a residue which, on chromatography (benzene/ethyl acetate=3/1), gave **16b** (3.04 g) as a yellow solid. A solution of this solid (500 mg, 1.38 mmol) in ethylene glycol (20 ml) was heated at 130 °C for 7 h. Chromatography (benzene) gave **27b** (225 mg, 35% from **1b**): Colorless prisms (hexane); mp 113–114 °C; IR 1626 cm^{-1} ; ^1H NMR δ =1.71–1.78 (2H, m), 1.82–1.88 (2H, m), 1.89 (3H, s), 2.39 (3H, s), 2.40 (3H, s), 2.78 (2H, t, J =6.3 Hz), 3.72 (2H, t, J =6.3 Hz), 7.17–7.26 (6H, m), 7.66 (2H, dd, J =8.1, 1.7 Hz); ^{13}C NMR δ =11.69, 20.52, 21.26, 21.58, 23.27, 24.40, 44.55, 117.36, 119.93, 128.77, 128.89, 129.02, 129.13, 130.67, 135.47, 137.18, 139.08, 141.53, 193.79; MS m/z 343 (M^+). Found: C, 83.95; H, 7.40; N, 4.01%. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$: C, 83.93; H, 7.34; N, 4.08%.

1-*p*-Bromobenzoyl-3-*p*-bromophenyl-5,6,7,8-tetrahydro-2-methylindolizine (27c). A mixture of **1c** (3.00 g, 7.61 mmol), **6b** (1.97 g, 15.2 mmol), and **4a** (1.14 g, 38.06 mmol) in toluene (150 ml) was heated under reflux for 30 min. It was cooled and evaporated in vacuo, leaving a residue which, on chromatography (benzene/ethyl acetate=3/1), gave **16c** (1.55 g) as a yellow solid. A solution of this solid (500 mg, 1.02 mmol) in ethylene glycol (20 ml) was heated at 130 °C for 2.75 h. It was then cooled and evaporated in vacuo, leaving

a residue which, on chromatography (benzene), gave **27c** (200 mg, 17% from **1c**): Yellow prisms (hexane–benzene); mp 159.5–161 °C; IR 1626 cm^{-1} ; ^1H NMR δ =1.74–1.80 (2H, m), 1.86 (3H, s), 1.87–1.91 (2H, m), 2.77 (2H, t, J =6.3 Hz), 3.70 (2H, t, J =6.3 Hz), 7.14–7.19 (2H, m), 7.54–7.64 (6H, m); ^{13}C NMR δ =11.72, 20.32, 23.12, 24.46, 44.64, 117.91, 119.64, 121.78, 125.89, 129.77, 130.46, 130.55, 131.43, 131.61, 132.29, 136.51, 140.50, 192.56; MS m/z (rel intensity) 475, 473, 471 (M^+ ; 50, 100, 52). Found: C, 55.93; H, 4.09; N, 2.94%. Calcd for $\text{C}_{22}\text{H}_{19}\text{NOBr}_2$: C, 55.84; H, 4.05; N, 2.96%.

7-Benzoyl-6-benzyl-2,3-dihydro-5-phenyl-1H-pyrrolizine (28a). A mixture of **17a-A** (200 mg, 0.51 mmol) and DBU (77 mg, 0.51 mmol) in degassed ethylene glycol (10 ml) was heated at 130 °C for 2 h. It was cooled, evaporated, and chromatographed (dichloromethane), giving **28a** (103 mg, 52%): Colorless prisms (hexane–benzene); mp 132–133 °C; IR 1610 cm^{-1} ; ^1H NMR δ =2.34 (2H, quint, J =7.0 Hz), 2.54 (2H, t, J =7.0 Hz), 3.90 (2H, t, J =7.0 Hz), 4.20 (2H, s), 7.02–7.16 (5H, m), 7.28–7.49 (8H, m), 7.58–7.62 (2H, m); ^{13}C NMR δ =26.63, 26.97, 31.19, 46.50, 115.81, 125.01, 125.17, 127.40, 127.92, 128.01, 128.21, 128.55, 128.75, 129.18, 130.67, 131.80, 141.74, 142.78, 144.53, 192.63; MS m/z 377 (M^+). Found: C, 86.04; H, 6.19; N, 3.77%. Calcd for $\text{C}_{27}\text{H}_{23}\text{NO}$: C, 85.91; H, 6.14; N, 3.71%.

7-Benzoyl-2,3-dihydro-6-*p*-methylbenzyl-5-phenyl-1H-pyrrolizine (28b). A mixture of **17b-A** (200 mg, 0.49 mmol) and DBU (74 mg, 0.49 mmol) in degassed ethylene glycol (10 ml) was heated at 130 °C for 2 h and worked up as described above. Chromatography (dichloromethane) gave **28b** (126 mg, 66%): Colorless prisms (hexane–dichloromethane); mp 148–149 °C; IR 1621 cm^{-1} ; ^1H NMR δ =2.23 (3H, s), 2.34 (2H, quint, J =7.0 Hz), 2.53 (2H, t, J =7.0 Hz), 3.90 (2H, t, J =7.0 Hz), 4.16 (2H, s), 6.95 (4H, s), 7.28–7.49 (8H, m), 7.59–7.64 (2H, m); MS m/z 391 (M^+). Found: C, 85.85; H, 6.67; N, 3.50%. Calcd for $\text{C}_{28}\text{H}_{25}\text{NO}$: C, 85.90; H, 6.44; N, 3.58%.

7-Benzoyl-6-*p*-chlorophenyl-2,3-dihydro-5-phenyl-1H-pyrrolizine (28c). A mixture of **17c-A** (200 mg, 0.48 mmol) and DBU (74 mg, 0.49 mmol) in degassed ethylene glycol (10 ml) was heated at 130 °C for 48 h and worked up as described above. Chromatography (dichloromethane) gave **28c** (106 mg, 55%): Colorless needles (hexane–benzene); mp 165–167 °C; IR 1614 cm^{-1} ; ^1H NMR δ =2.34 (2H, quint, J =7.1 Hz), 2.53 (2H, t, J =7.1 Hz), 3.91 (2H, t, J =7.1 Hz), 4.15 (2H, s), 7.01 (2H, d, J =8.2 Hz), 7.10 (2H, d, J =8.2 Hz), 7.29–7.50 (8H, m), 7.58–7.61 (2H, m); ^{13}C NMR δ =26.65, 27.03, 30.67, 46.52, 115.67, 124.51, 127.56, 127.99, 128.07, 128.17, 128.64, 128.84, 129.11, 129.58, 130.76, 130.82, 131.59, 141.33, 141.63, 144.65, 192.52; MS m/z (rel intensity) 413, 411 (M^+ ; 37, 100). Found: C, 79.00; H, 5.37; N, 3.46%. Calcd for $\text{C}_{27}\text{H}_{22}\text{NOCl}$: C, 78.73; H, 5.38; N, 3.40%.

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