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

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(Received November 7, 1994)

When heated in an alcoholic solvent, such as ethylene glycol or butanol, 4-substituted 3-aroyl-1-alkylpyrrolidines, which are readily accessible via the condensation of an amino acid, paraformaldehyde, and 3-substituted 1-ary-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 aroylpyrrolidines obtained from the corresponding cyclic amino acids. A mechanism for the ring-transformation is proposed.

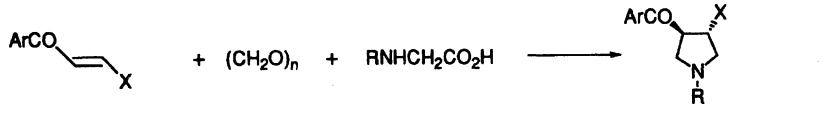
Since pyrroles present one of the most important classes of heterocycles, many preparative methods towards pyrrole rings have already been developed.[1,2] It was recently reported that when heated in an alcoholic solvent, 1-alkyl-3-aroylpyrrolidines give 1-alkyl-2-aryl-3-methylpyrroles via a novel dehydrative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

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

Results and Discussion

Preparation of Aroylpyrrolidines. 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-aroyl-2-arylethenes **2a**—**d**, and methyl 4-oxo-4-phenyl-2-butenoate (**3**)) with azomethine ylide generated in situ by the condensation of paraformaldehyde (**4a**) and N-substituted glycines **5a**—**c**. This method had been reported previously[4] (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 (2*R**, 3*S**, 4*S**)-isomer **13-A** gave a 4:1-mixture of **13-A** and (2*R**, 3*S**, 4*R**)-isomer **13-B**, while **13-B** was stable under the above-mentioned conditions. In the ^{1}H NMR of **13-B**, the methine proton of the 3-position was observed at a 0.59 ppm higher magnetic field than



1: X=COAr
2: X=Ar
3: X=CO_2Me, Ar=C_6H_5

4a

5a: R=Me
5b: R=$PhCH_2$
5c: R=Ph

8: X=COAr R=Me
9: X=COAr R=$PhCH_2$
10: X=COPh R=Ph
11: X=Ar R=Me
12: X=CO_2Me R=Me

Scheme 1.

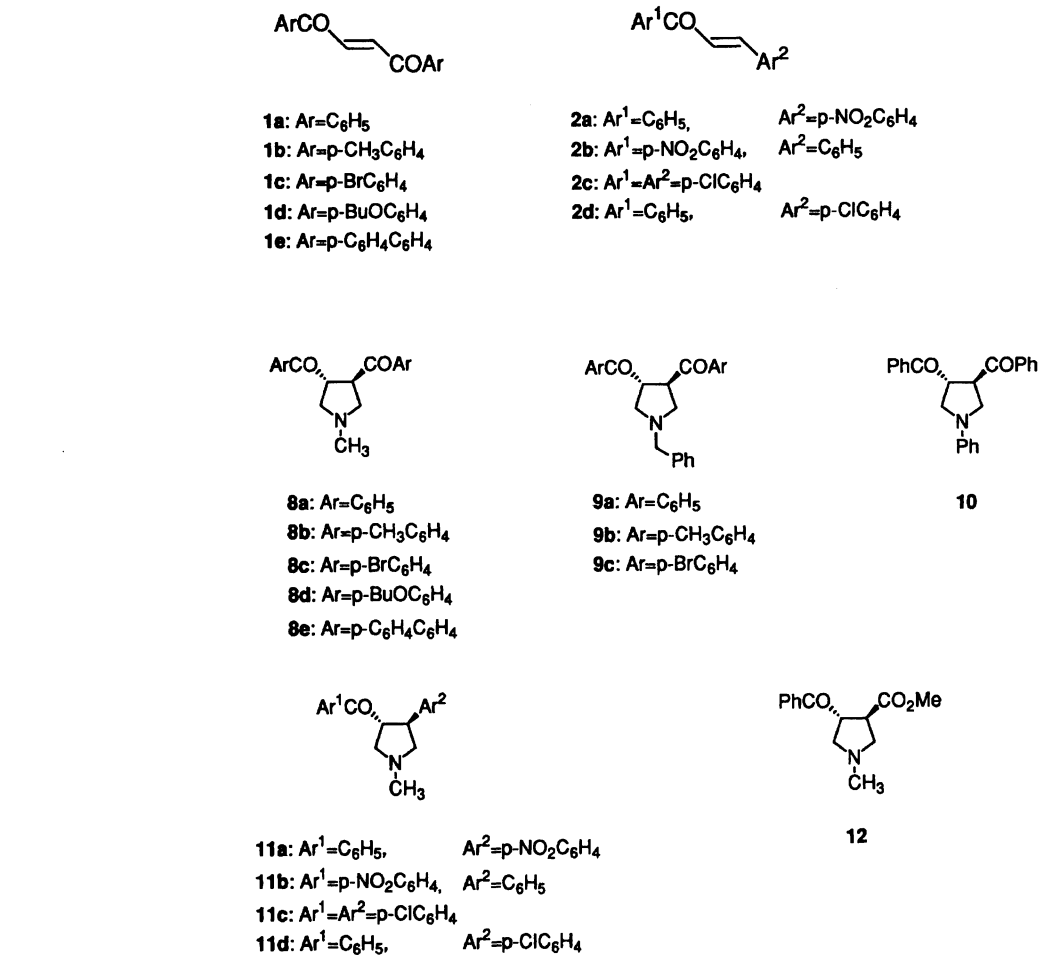
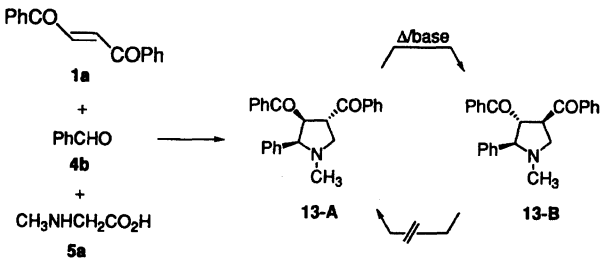


Chart 1.



Scheme 2.

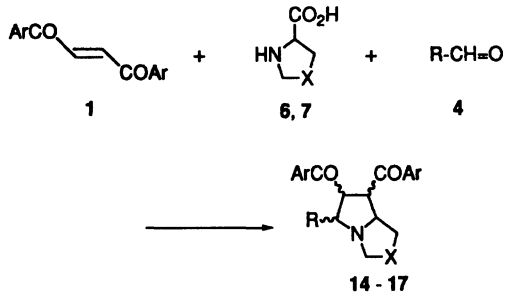
that of the 4-position, probably due to a shielding effect of the phenyl group at the 2-position. On the other hand, the corresponding two methine protons of **13-A** appeared between 4.93 and 5.03 ppm as complicated multiple peaks.

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 ($6R^*$, $7R^*$, $7aR^*$) configuration epimerized to the major isomer **14b-B** with ($6R^*$, $7R^*$, $7aS^*$) arrangement, while **14b-B** was stable under the same conditions. Bicyclic 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, ($1R^*$, $2R^*$, $7aS^*$)-isomer **15-A** and ($1R^*$, $2R^*$, $8aS^*$) 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 ($1R^*$, $2R^*$, $8aR^*$)-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 ($1R^*$, $2R^*$, $3S^*$, $7aR^*$) and ($1R^*$, $2R^*$, $3R^*$, $7aR^*$) 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



6: X=S
7a: X=CH_2
7b: X=CH_2CH_2

14a: X=S, Ar=C_6H_5, R=H
14b: X=S, Ar=p-BrC_6H_4, R=H
15a: X=CH_2, Ar=C_6H_5, R=H
15b: X=CH_2, Ar=p-$CH_3C_6H_4$, R=H

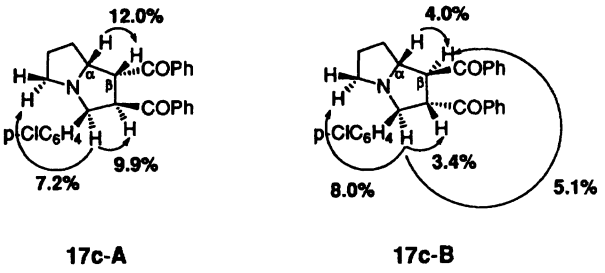
16a: X=CH_2CH_2, Ar=C_6H_5, R=H
16b: X=CH_2CH_2, Ar=p-$CH_3C_6H_4$, R=H
16c: X=CH_2CH_2, Ar=p-BrC_6H_4, R=H
17a: X=CH_2, Ar=C_6H_5, R=C_6H_5
17b: X=CH_2, Ar=C_6H_5, R=p-$CH_3C_6H_4$
17c: X=CH_2, Ar=C_6H_5, R=p-ClC_6H_4

Scheme 3.

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

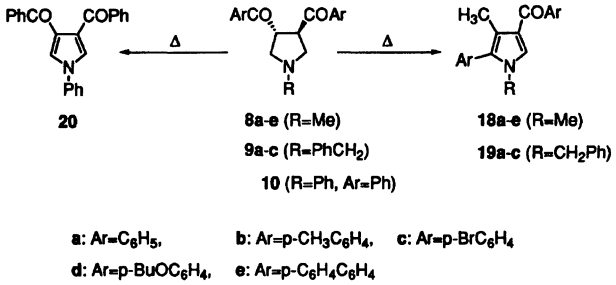
Pyrrolidine	Solvent[a)]	Additive	Time (h)	Temp (°C)	Pyrrole (%)
8a	EG	—	0.5	130	**18a** (96)
8a	BuOH	DBU	6	Reflux	**18a** (93)
8a	BuOH	—	24	Reflux	**18a** (71)
8a	BuOH	NEt_3	24	Reflux	**18a** (92)
8a	BuOH	TosOH	24	Reflux	**18a** (45)
8a	Toluene	DBU	32	Reflux	**18a** (41)
8a	Toluene	—	32	Reflux	**18a** (3)
8a	CF_3COOH	—	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



17c-A **17c-B**

Fig. 1. NOE of **17c**.



a: Ar=C_6H_5, **b**: Ar=p-$CH_3C_6H_4$, **c**: Ar=p-BrC_6H_4
d: Ar=p-$BuOC_6H_4$, **e**: Ar=p-$C_6H_4C_6H_4$

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-

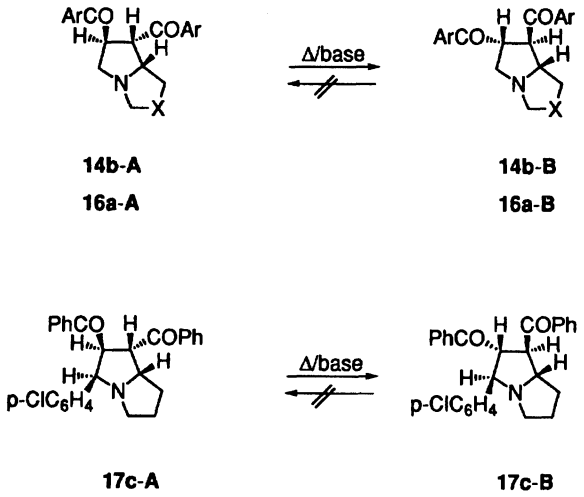


Fig. 2. Epimerization of **14b**, **16a**, and **17c**.

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).

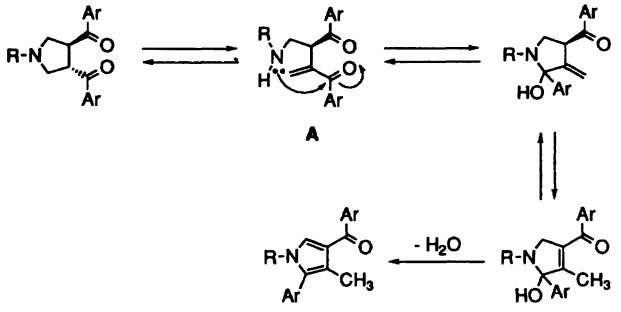
3-Aroyl-4-arylpyrrolidines **11** were transformed into air-labile 2,4-diaryl-1,3-dimethylpyrroles **21**, which decomposed or became dark-colored during a work-up. 3-Benzoyl-1-methyl-4-*p*-nitrophenylbenzoylpyrrolidine **11a** gave **21a** in 79% yield when heated in ethylene glycol at 130 °C. On the 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-withdrawing 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.

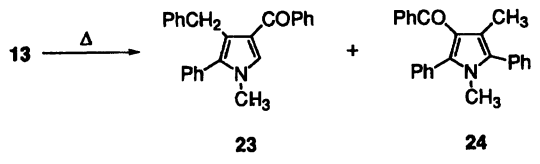
The ring-transformation reaction of **13** occurred in two directions, giving a 1 : 2-mixture (from ^{1}H NMR)[7] of the expected benzylpyrrole **23** and the methyl derivative **24** in low yields (Scheme 6). Unfortunately, the isolation of these pyrroles was unsuccessful.

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**.

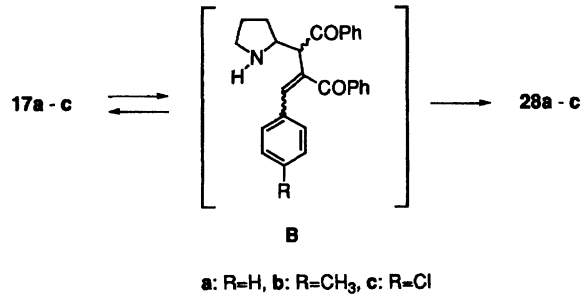
In summary, the above-mentioned ring-transformation of 3-aroylpyrrolidines is useful for preparing vari-



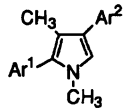
Scheme 5.



Scheme 6.

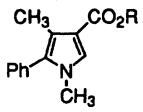


Scheme 7.



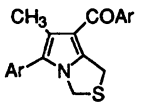
21

a: Ar^1=C_6H_5, Ar^2=p-$NO_2C_6H_4$
b: Ar^1=p-$NO_2C_6H_4$, Ar^2=C_6H_5
c: Ar^1=Ar^2=p-ClC_6H_4
d: Ar^1=C_6H_5, Ar^2=p-ClC_6H_4



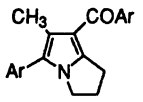
22

a: R=CH_3
b: R=CH_2CH_2OH
c: R=$CH_2CH_2OCH_3$



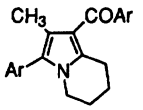
25

a: Ar=C_6H_5
b: Ar=p-BrC_6H_4



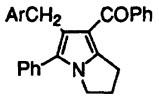
26

a: Ar=C_6H_5
b: Ar=p-$CH_3C_6H_4$



27

a: Ar=C_6H_5
b: Ar=p-$CH_3C_6H_4$
c: Ar=p-BrC_6H_4



28

a: Ar=C_6H_5
b: Ar=p-$CH_3C_6H_4$
c: Ar=p-ClC_6H_4

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 Mitamurariken Melt Thermo and are uncorrected. The IR spectra were measured on a Nippon-Bunko IR-700 as a KBr pellet, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer using Me_4Si as an internal reference in $CDCl_3$. 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}; ^{1}H 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 $C_{21}H_{23}NO_2$: 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}; ^{1}H 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 $C_{31}H_{27}NO_2$: 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}; ^{1}H 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 $C_{25}H_{23}NO_2$: 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}; ^{1}H 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); ^{13}C 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 $C_{27}H_{27}NO_2$: 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 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 $C_{25}H_{21}NO_2Br_2$: 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 $C_{18}H_{18}N_2O_3$: 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 $C_{18}H_{17}NOCl_2$: 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 $C_{18}H_{18}NOCl$: 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 $C_{14}H_{17}NO_3$: 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 $C_{24}H_{21}NO_2$: 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).

(2*R,3*S**,4*S**)-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 $C_{25}H_{23}NO_2$: C, 81.26; H, 6.28; N, 3.79%.

(2*R,3*R**,4*R**)-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 ($C_{25}H_{23}O_2N$+H^+): M, 370.1808.

6,7-Dibenzoyl-5,6,7,7a-tetrahydro-1*H*,3*H*-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 **(6*R**,7*R**,7a*S**)-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 $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68; N, 4.15%.

^1H NMR Data of (6*R,7*R**,7a*R**)-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-1*H*, 3*H*-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).

(6*R,7*R**,7a*R**)-Isomer 14b-A:** Colorless prisms (hexane–dichloromethane); mp 146—149 °C; IR 1673 cm^{-1}; ^{1}H 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 $C_{20}H_{17}NO_2SBr_2$: C, 48.51; H, 3.46; N, 2.83%.

(6*R,7*R**,7a*S**)-Isomer 14b-B:** Colorless prisms (hexane–dichloromethane); mp 193—194 °C; IR 1679 cm^{-1}; ^{1}H 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 $C_{20}H_{17}NO_2SBr_2$: C, 48.51; H, 3.46; N, 2.83%.

1,2-Dibenzoyl-2,3,5,6,7,7a-hexahydro-1*H*-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 descibed 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 **(1*R**, 2*R**,7a*S**)-Isomer 15a-A** (760 mg, 28%): Colorless needles (hexane–benzene); mp 165—167 °C: IR 1663 cm^{-1}; ^{1}H 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), ^{13}C 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 $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39%.

^{1}H NMR Data of (1*R,2*R**,7a*R**)-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- 1*H*-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 descrived 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 **(1*R**, 2*R**, 7a*S**)-Isomer 15b-A** (600 mg, 15%): Colorless prisms (hexane–benzene); mp 126—127 °C; IR 1671 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03%.

^{1}H NMR Data of (1*R,2*R**,7a*R**)-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%).

(1*R,2*R**,8a*S**)-Isomer 16a-A:** Colorless prisms (hexane–benzene); mp 140—141 °C; IR 1670 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20%.

(1*R,2*R**,8a*R**)-Isomer 16a-B:** Pale yellow oil; IR (NaCl) 1680 cm^{-1}; ^{1}H 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-1*H*-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%).

(1*R,2*R**,3*S**,7a*S**)-Isomer 17a-A:** Colorless prisms (hexane–benzene); mp 118.5—120 °C; IR 1665 cm^{-1}; ^{1}H 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 $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54%.

(1*R,2*R**,3*S**,7a*R**)-Isomer 17a-B:** Colorless prisms (hexane–benzene); mp 133—134 °C; IR 1669 cm^{-1}; ^{1}H 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-1*H*-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).

(1*R,2*R**,3*S**,7a*S**)-Isomer 17b-A:** Colorless prisms (hexane–dichloromethane); mp 117—118 °C; IR 1664 cm^{-1}; ^1H NMR δ=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%.

(1*R,2*R**,3*S**,7a*R**)-Isomer 17b-B:** Colorless prisms (hexane–dichloromethane); mp 91—93 °C; IR 1670 cm^{-1}; ^1H NMR δ=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-1*H*-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).

(1*R,2*R**,3*S**,7a*S**)-Isomer 17c-A:** Colorless prisms (hexane–benzene); mp 102—103 °C; IR 1669 cm^{-1}; ^1H NMR δ=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%.

(1*R,2*R**,3*S**,7a*R**)-Isomer 17c-B:** Colorless prisms (hexane–benzene); mp 142—144 °C; IR 1666 cm^{-1}; ^1H NMR δ=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 δ=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 δ=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 δ=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 δ=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 δ=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 δ=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-Biphenylyl)-1,3-dimethyl-4-*p*-phenylbenzoylpyrrole (18e). Yield 76%; colorless prisms (hexane–benzene); mp 187—189 °C; IR 1625 cm^{-1}; ^1H NMR δ=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-phenylprrole (19a). Yield 75%; pale yellow oil; IR (NaCl) 1632 cm^{-1}; ^1H NMR δ=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 δ=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 δ=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 $C_{25}H_{19}NOBr_2$: 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 $C_{24}H_{17}NO_2$: 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 $C_{18}H_{16}N_2O_2$: 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 $C_{18}H_{16}N_2O_2$: 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 $C_{18}H_{15}NCl_2$: 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 $C_{18}H_{16}NCl$: 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 $C_{14}H_{15}NO_2$: 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 $C_{15}H_{17}NO_3$: 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 $C_{16}H_{19}NO_3$: 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 ($C_{20}H_{17}ONS+H^+$): 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 ($C_{20}H_{15}NOSBr_2+0.25H_2O$): 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 $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65%.

2,3-Dihydro-6-methyl-7-*p*-toluoyl-5-*p*-tolyl-1*H*-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 $C_{23}H_{23}NO$: 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 $C_{22}H_{21}NO$: 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 $C_{24}H_{25}NO$: 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 $C_{22}H_{19}NOBr_2$: C, 55.84; H, 4.05; N, 2.96%.

7-Benzoyl-6-benzyl-2,3-dihydro-5-phenyl-1*H*-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 $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71%.

7-Benzoyl-2,3-dihydro-6-*p*-methylbenzyl-5-phenyl-1*H*-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 $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58%.

7-Benzoyl-6-*p*-chlorophenyl-2,3-dihydro-5-phenyl-1*H*-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 $C_{27}H_{22}NOCl$: C, 78.73; H, 5.38; N, 3.40%.

References

1) R. J. Sundberg, "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford (1984), Vol. 4, pp. 313—376.

2) R. J. Sundberg, "Progress in Heterocyclic Chemistry," ed by H. Suschitzky and E. F. V. Scriven, Pergamon Press, Oxford (1889—1993), Vol. 1—5.

3) S. Mataka, H. Kitagawa, O. Misumi, M. Tashiro, and K. Kamata, *J. Chem. Soc., Chem. Commun.*, **1993**, 671.
4) O. Tsuge, S. Kanemasa, M. Ohe, and S. Takenaka, *Bull. Chem. Soc. Jpn.*, **60**, 4079 (1987).
5) H. Junek and H. Sterk, *Tetrahedron Lett.*, **1968**, 430.
6) S. Danishefsky and G. Rovnyak, *J. Org. Chem.*, **39**, 2924 (1974).
7) Of the ^{1}H NMR data of this mixture, signals at 3.49 (3H, s), 4.15 (2H, s), 7.04—7.49 (m), and 7.76 (2H, dd, J=8.2 and 1.3 Hz) are assignable to the benzylpyrrole **23** and those at 2.15 (3H, s), 3.36 (3H, s), 7.04—7.49 (m), and 7.61 (2H, dd, J=8.5 and 1.3 Hz) to the methylpyrrole **24**.