Ring Transformation of Oxazoles to Fused Imidazoles. New Synthetic Route for 6-Methyl-2,3-diphenyl-7,8-dihydroimidazo[1,2-*b*]pyridazine and 5-Methyl-2,3-diphenyl-6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole, and Their Perhydrobenzo Analogues

Tadashi Sasaki,* Masatomi Ohno, and Eikoh Ito
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Fused imidazoles were synthesized by an intramolecular ring transformation of γ-keto-oxazoles with hydrazine and by an intramolecular dehydration of γ-amino-oxazoles. γ-Keto-oxazoles (4) and (6) were prepared by the reaction of lithiated 2-methyl-4,5-diphenyloxazole (1) with the methyl enol ether of an α-bromo ketone, followed by hydrolysis. γ-Keto-oxazoles (4) and (6) gave the 7,8-dihydroimidazo-[1,2-*b*]pyridazine (7) and the 6,7,8,9,9a,10-hexahydroimidazo[1,2-*b*]cinnoline (8), respectively, on treatment with hydrazine hydrate in acetic acid. The transformed fused imidazoles (7) and (8) were further converted into the corresponding tetrahydroimidazo[1,2-*b*]pyridazine (9) and octahydroimidazo-[1,2-*b*]cinnoline (10), respectively, by reduction with $NaBH_4$. γ-Amino-oxazoles (11) and (12) were prepared from (4) and (6), respectively, on reduction with $NaBH_3CN$ in the presence of ammonium acetate. The pyrolysis of (11) and (12) provided the cyclodehydrated 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]-imidazole (13) and 5,6,7,8,8a,9-hexahydro-4a*H*-imidazo[1,2-*a*]indole (14), respectively.

A variety of ring transformations of heterocycles are known,[1] but few have been applied to the synthesis of bicyclic heterocycles.† An intramolecular ring transformation strategy could potentially provide an attractive route to a variety of bridgehead nitrogen heterocycles. We have recently applied this strategy to the synthesis of fused azoles.[2,3] This paper deals with the synthesis of fused imidazoles such as 7,8-dihydroimidazo[1,2-*b*]pyridazines [*e.g.* (7) and (8)] and 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazoles [*e.g.* (13) and (14)], in which the intramolecular replacement of the oxygen in an oxazole ring with nitrogen is the key step (see Scheme). Imidazopyridazines are obtained by the reaction of γ-keto-oxazoles with hydrazine. Pyrroloimidazoles are obtained by intramolecular dehydration of γ-amino-oxazoles.

Results and Discussion

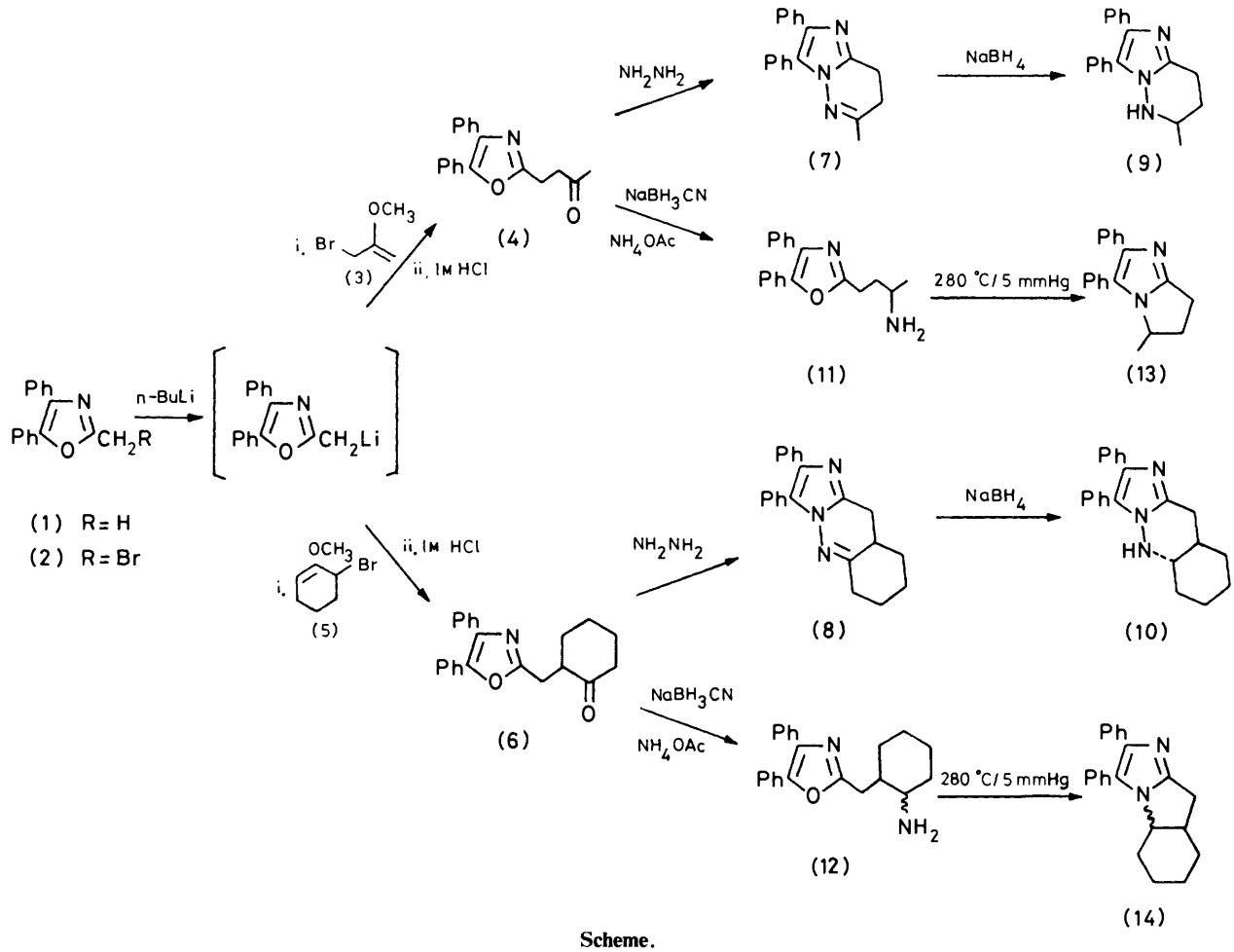
Preparation of Oxazoles (4) *and* (6).—The preparation of the γ-keto-oxazoles (4) and (6) was envisaged to occur *via* coupling of the bromide (2) with an enolate anion. However, compound (2) could not be obtained by bromination of the 2-methyloxazole (1) [4,5] or the lithium derivative of the 2-methyl-oxazole.[6] An alternative method involving the reaction of lithiated (1) with a suitable electrophile was more successful. The methyl enol ether of the α-bromo ketone solved the problem. Treatment of lithiated (1) ‡ with 2-methoxyallyl bromide (3) [7] in tetrahydrofuran (THF) at −78 °C, followed by hydrolysis of the resulting methyl enol ether with 1M HCl, provided the ketone (4) in 59% yield after purification on a silica gel column and subsequent recrystallisation. Similarly, 2-(2-oxocyclohexyl)methyl-4,5-diphenyloxazole (6) was prepared in 96% yield by treatment of lithiated (1) with 3-bromo-2-methoxycyclohexene (5).[8] The i.r. spectra showed a strong carbonyl absorption at 1 720 cm^{-1} for (4) and 1 710 cm^{-1} for (6), and the ^1H n.m.r. spectra exhibited methyl and methylene proton signals for (4) at δ 2.55 and 2.95—3.20, and complicated cyclohexane ring and methylene proton signals for (6) at δ 1.20—3.65.

Transformation of (4) *and* (6) *into Fused Imidazoles.*—Reaction of the γ-keto-oxazole (4) with hydrazine hydrate (5-fold excess) in acetic acid at room temperature for 3 days gave the 7,8-dihydroimidazo[1,2-*b*]pyridazine (7) in 80% yield. Similarly, (6) was transformed into the corresponding tricyclic hexahydroimidazo[1,2-*b*]cinnoline (8) in 76% yield. However, higher temperatures with shorter reaction times lowered the yields of both (7) and (8). The structures of (7) and (8) were based on elemental analyses and spectral data: the i.r. spectra of (7) and (8) showed no carbonyl absorption and the ^1H n.m.r. spectra exhibited methyl and methylene proton signals for (7) at δ 2.12 and 2.30—3.25, and complicated ring proton signals for (8) at δ 1.20—3.50. The mechanism for these transformations is considered to be that proposed previously, with cyclisation of the hydrazones to give the spiro derivatives (15 a and b), which collapse to the ketones (16 a and b). The final cyclisation of (16 a and b) provides the fused imidazoles (7) and (8) respectively [equation (1)].

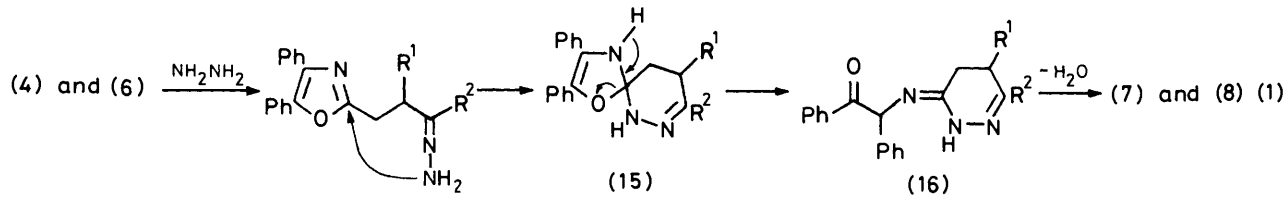
Compounds (7) and (8) underwent smooth reduction with $NaBH_4$ to give the corresponding tetrahydro derivative (9) and octahydro derivative (10) in 95 and 94% yield, respectively. The amino function in these products was indicated by the strong absorption at 3 180 cm^{-1} for (9) and 3 195 cm^{-1} for (10) in the i.r. spectra and the appearance of D_2O-exchangeable N–H signals at δ 4.00 for (9) and 3.80 for (10) in the ^1H n.m.r. spectra. The structure of (9) was further supported by a methyl doublet (*J* 6.8 Hz) at δ 1.20 and the chemical shift of the ring protons at δ 1.50—2.40 (2 H, m, 7-H_2) and 2.80—3.50 (3 H, m, 6-H and 8-H_2), being in good agreement with those of the 5,6,7,8-tetrahydroimidazo[1,2-*b*]pyridazine ring system reported in the literature.[9] The ^{13}C n.m.r. spectrum of (10) showed two doublets at δ_C 59.0 and 38.1 p.p.m. assignable to C-5a and C-9a, respectively, and five triplets due to C-6, -7, -8, -9, and -10. No other minor signals were observed, indicating that the product is a single stereoisomer. We tentatively

† One is the synthesis of cycloalkano[*a*]pyrroles by the dehydration of furylalkylamines: J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, 1962, **27**, 1652; F. Sorm and Z. Arnold, *Collect. Czech. Chem. Commun.*, 1947, **12**, 467. The other is the synthesis of pyrrolizines by the similar dehydration of 2-(3-aminoalkyl)tetrahydrofurans: A. A. Ponomarev and I. M. Skvortsov, *Zh. Obshch. Khim.*, 1962, **32**, 97 (*Chem. Abstr.*, 1962, **57**, 12409).

‡ Although Lipshutz recommended the reaction temperature to be −100 °C, we found that we could carry out the lithiation at −78 °C.



Scheme.



a; $R^1 = H$, $R^2 = CH_3$
b; $R^1R^2 = [CH_2]_4$

a; $R^1 = H$, $R^2 = CH_3$
b; $R^1R^2 = [CH_2]_4$

(4) ⟶ (15a) ⟶ (16a) ⟶ (7)
(6) ⟶ (15b) ⟶ (16b) ⟶ (8)

assigned the stereochemistry of (10) as *trans* because axial approach of hydride ion is commonly accepted in the reduction of cyclohexanone.[10]

Attempted aromatization of (7) and (8) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing methanol led to no reaction.

Treatment of (4) and (6) with ammonium acetate in refluxing acetic acid did not provide the desired pyrrolo[1,2-*a*]-imidazoles, but resulted in the recovery of the starting material. An alternative, two-step synthetic route was considered; first, conversion of the γ-keto-oxazole into a γ-amino-oxazole and second, cyclodehydration to a 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]-imidazole. The reduction of the oxime of the γ-keto-oxazole with $LiAlH_4$ in refluxing THF was examined first but gave a mixture of inseparable products. The desired conversion was achieved by treating compounds (4) and (6) with $NaBH_3CN$ in the presence of ammonium acetate in methanol.[11] After purification on an alumina column, γ-amino-oxazoles (11)

and (12) were obtained in 49 and 63% yield, respectively. Their structures were indicated by the appearance of broad N–H absorptions at 3 600—3 200 cm^{-1} for (11) and 3 500—3 200 cm^{-1} for (12) in the i.r. spectra and by D_2O-exchangeable N–H signals at δ 1.77 for (11) and 1.88 for (12) in the ^1H n.m.r. spectra. The ^{13}C n.m.r. spectrum of (12) revealed two pairs of doublets at δ_C 44.9 and 54.6 p.p.m. and at δ_C 40.3 and 49.1 p.p.m., suggesting (12) to be a mixture of stereoisomers. The former pair, observed at lower field, was characterized as due to C-1 and C-2 of the cyclohexane ring of the *trans* isomer and the latter as those of the *cis* isomer.* Thus the ratio of *cis* to *trans* isomers of (12) was determined by the integral ratio to be 1 : 4, but the isomers could not be separated by column chromatography.

For the cyclodehydration of γ-amino-oxazoles (11) and (12) to the dihydropyrroloimidazole (13) and the hexahydroimidazoindole (14), respectively, we examined various acidic conditions including treatment with (a) conc. H_2SO_4 at room temperature, (b) PPA (polyphosphoric acid) at 150 °C, (c) P_2O_5 in refluxing benzene, and (d) P_2O_5–CH_3SO_3H at 70 °C,[12] but these reactions resulted in the recovery of the starting material. No reaction was also observed under the anionic conditions using Bu^nLi in refluxing THF. However, pyrolysis accomplished the desired cyclodehydration. Crude (11), after the reductive amination, was directly heated at 280°C under reduced pressure (5 mmHg) to give the cyclodehydrated dihydropyrroloimidazole (13) in 46% overall yield from (4) after purification on an alumina column. Under the same conditions, crude (12) was transformed into the tricyclic hexahydroimidazoindole (14) in 23% overall yield from (6). The structures of (13) and (14) were determined from elemental and spectral analyses: the ^1H n.m.r. spectrum of (13) showed ring proton signals at δ 1.80—3.20 (4 H, m, 6- and 7-H_2) and 4.10—4.70 (1 H, m, 5-H). These chemical shifts are in accord with those of the 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazole ring system reported in the literature.[13] The ^1H n.m.r. spectrum of (14) exhibited two C-4a proton signals due to *cis* and *trans* isomers at δ 3.90—4.40 and 3.20—3.90, respectively. The ^{13}C n.m.r. spectrum of (14) revealed, as expected, two pairs of doublets due to C-4a and C-8a of each isomer at δ_C 64.1 and 50.8 p.p.m. (*trans*) and at δ_C 56.4 and 40.1 p.p.m. (*cis*). The intensity of these signals showed (14) to be a 1 : 5 mixture of *cis* and *trans* isomers, although the separation of these two isomers was not performed by column chromatography. The lack of appreciable change in the *cis* : *trans* ratio from (12) to (14) suggests that the cyclodehydration was not substantially affected by the stereochemistry of (12).

Experimental

M.p.s were measured with a Yanagimoto micromelting point apparatus and are uncorrected. I.r. spectra were obtained on a JASCO-IRA-1 spectrometer. ^1H N.m.r. and ^{13}C n.m.r. spectra were recorded on a JEOL JMN-C-60HL instrument at 60 MHz and a JEOL-FX-60 FT spectrometer at 15.04 MHz, respectively. Chemical shifts are reported in p.p.m. (δ) relative to Me_4Si as internal standard. Microanalyses were performed with a Perkin-Elmer 240B elemental analyser. Pyrolysis was carried out with Sibata Glass Tube Oven GTO-250.

2-(3-*Oxobutyl*)-4,5-*diphenyloxazole* (4).—To a stirred solution of (1)[4] (3.0 g, 12.8 mmol) in dry THF (40 ml) was added a solution of Bu^nLi in hexane (1.6M; 10 ml, 16.0 mmol) dropwise during 30 min at −78 °C under a current of N_2. After the resulting deep orange-red suspension had been stirred at −78 °C for an additional 15 min, compound (3)[7] (2.5 ml, 19 mmol) was added. The resulting mixture was slowly warmed to room temperature and quenched with phosphate buffer (70 ml; pH 7). The organic layer was extracted with $CHCl_3$ (3 × 50 ml). The combined extracts were washed in turn with 1M HCl (100 ml) and water (3 × 100 ml), and dried over $MgSO_4$. Removal of the solvent yielded an orange oil which was chromatographed on a silica gel column [AcOEt–n-hexane (1 : 2)] to give crude (4). Subsequent recrystallisation from ethanol gave pure *ketone* (4) (2.2 g, 59%), m.p. 69—71 °C (Found: C, 78.4; H, 5.95; N, 4.85. $C_{19}H_{17}NO_2$ requires C, 78.33; H, 5.88; N, 4.81%); $\nu_{max.}$ (KBr) 3 050, 2 930, 1 720, 1 600, 1 585, 1 500, 1 440, and 1 420 cm^{-1}; δ_H ($CDCl_3$) 2.25 (3 H, s, CH_3), 2.95—3.20 (4 H, m, 2 × CH_2), and 7.20—7.80 (10 H, m, Ar).

2-(2-*Oxocyclohexyl*)*methyl*-4,5-*diphenyloxazole* (6).—By the same procedure as employed for the preparation of (4), compound (6) was obtained from (1) and (5).[8] Purification was performed on a silica gel column using $CHCl_3$ as eluant: 96% yield; *yellow oil* (Found: C, 79.6; H, 6.5; N, 4.25. $C_{22}H_{21}NO_2$ requires C, 79.73; H, 6.39; N, 4.23%); $\nu_{max.}$ (film) 3 050, 2 940, 2 860, 1 710, 1 600, 1 565, 1 500, and 1 445 cm^{-1}; δ_H ($CDCl_3$) 1.20—3.65 (11 H, m), and 7.20—7.80 (10 H, m, Ar).

6-*Methyl*-2,3-*diphenyl*-7,8-*dihydroimidazo*[1,2-b]*pyridazine* (7).—A solution of compound (4) (1.5 g, 5.2 mmol) and hydrazine hydrate (1.3 g, 26 mmol) in acetic acid (20 ml) was stirred at room temperature for 3 d. Then the resulting mixture was poured into saturated brine (200 ml). Filtration of the precipitates gave *compound* (7) (1.2 g, 80%). An analytical sample was obtained by recrystallisation from ethanol, m.p. 173—176 °C (Found: C, 79.4; H, 6.05; N, 14.55. $C_{19}H_{17}N_3$ requires C, 79.41; H, 5.96; N, 14.62%); $\nu_{max.}$ (KBr) 3 070, 2 960, 1 650, 1 605, 1 530, 1 445, 1 385, and 1 350 cm^{-1}; δ_H ($CDCl_3$) 2.12 (3 H, s, CH_3), 2.30—3.25 (4 H, m, 7- and 8-H_2), and 7.10—7.70 (10 H, m, Ar).

2,3-*Diphenyl*-6,7,8,9,9a,10-*hexahydroimidazo*[1,2-b]*cinnoline* (8).—In a similar way to (7), compound (8) was obtained from (6) in 67% yield, m.p. 184—187 °C (from EtOH) (Found: C, 80.45; H, 6.5; N, 12.65. $C_{22}H_{21}N_3$ requires C, 80.70; H, 6.46; N, 12.83%); $\nu_{max.}$ (KBr) 3 100, 2 945, 2 850, 1 620, 1 600, 1 535, and 1 440 cm^{-1}; δ_H ($CDCl_3$) 1.20—3.50 (11 H, m) and 7.10—7.70 (10 H, m, Ar).

6-*Methyl*-2,3-*diphenyl*-5,6,7,8-*tetrahydroimidazo*[1,2-b]-*pyridazine* (9).—To a stirred solution of $NaBH_4$ (280 mg, 7.4 mmol) in dry ethanol (7 ml) was added dropwise a solution of compound (7) (210 mg, 0.7 mmol) in dry ethanol (20 ml). The mixture was stirred for an additional 20 h at room temperature and the unchanged $NaBH_4$ was then decomposed with 6M HCl solution (pH 2). The mixture was then made basic with 10% NaOH solution (pH 9) and evaporated to dryness under reduced pressure, and the residue was extracted with hot $CHCl_3$ (3 × 10 ml). The combined extracts were dried over $MgSO_4$ and concentrated to give crude (9), which was purified on a silica gel column using $CHCl_3$–EtOH (30 : 1) as eluant to give pure compound (9) (200 mg, 95%), m.p. 126—129 °C (Found: C, 79.15; H, 6.75; N, 14.15. $C_{19}H_{19}N_3$ requires C, 78.86; H, 6.61; N, 14.52%); $\nu_{max.}$ (KBr) 3 180, 3 000, 2 980, 2 940, 1 600, 1 505, 1 440, and 1 440 cm^{-1}; δ_H ($CDCl_3$) 1.20 (3 H, d, *J* 6.8 Hz, CH_3), 1.50—2.40 (2 H, m, 7-H_2), 2.80—3.50 (3 H, m, 6-H and 8-H_2), 4.00 (1 H, br s, D_2O-exchangeable, NH), and 7.05—7.62 (10 H, m, Ar).

* The ^{13}C n.m.r. chemical shifts of the ring carbons appear at higher field in *cis*-1,2-disubstituted cyclohexanes than in the *trans* isomers: H. B. Kagan, 'Stereochemistry,' Georg Thieme Publishers, Stuttgart, 1977, vol. 1, pp. 105—108.

2,3-*Diphenyl*-5,5a,6,7,8,9,9a,10-*octahydroimidazo*[1,2-b]*cinnoline* (10).—By the same reduction as above, compound (10) was obtained from (8). Purification was performed on a silica gel column using $CHCl_3$ as eluant: 94% yield, m.p. 200—201 °C (Found: C, 80.45; H, 7.05; N, 12.7. $C_{22}H_{23}N_3$ requires C, 80.21; H, 7.04; N, 12.76%); $\nu_{max.}$ (KBr) 3 195, 3 060, 2 925, 2 850, 1 600, 1 510, and 1 440 cm^{-1}; δ_H ($CDCl_3$) 1.00—3.50 (12 H, m), 3.80 (1 H, br s, D_2O-exchangeable, NH), and 7.10—7.50 (10 H, m, Ar); δ_C ($CDCl_3$) 24.9 (t), 25.4 (t), 30.0 (t), 30.2 (t), 32.1 (t), 38.1 (d, C-9a), 59.0 (d, C-5a), 125.1 (s), 126.1 (d), 126.9 (d), 127.7 (d), 128.0 (d), 128.4 (d), 129.9 (s), 130.5 (d), 134.6 (s), 134.9 (s), and 139.6 p.p.m. (s).

2-(3-*Aminobutyl*)-4,5-*diphenyloxazole* (11).—A solution of the ketone (4) (870 mg, 3 mmol), $NaBH_3CN$ (1.3 g, 21 mmol), and ammonium acetate (2.3 g, 30 mmol) in dry methanol (30 ml) was heated under reflux for 4 h. The resulting mixture was acidified with conc. HCl solution (pH 2) and then basified with 20% NaOH solution. After extraction with $CHCl_3$ (3 × 20 ml), the combined extracts were dried over $MgSO_4$. Removal of the solvent yielded crude (11) as a yellow oil, which was purified on an alumina column [$CHCl_3$—EtOH (30 : 1)] to give the *amine* (11) (430 mg, 49%) (Found: C, 78.15; H, 6.9; N, 9.5. $C_{19}H_{20}N_2O$ requires C, 78.05; H, 6.90; N, 9.58%); $\nu_{max.}$ (film) 3 600—3 200 br, 3 050, 2 960, 1 600, 1 570, 1 500, and 1 445 cm^{-1}; δ_H ($CDCl_3$) 1.13 (3 H, d, *J* 6.7 Hz, CH_3), 1.77 (2 H, br s, D_2O-exchangeable NH_2), 1.87 (2 H, q, *J* 7.5 Hz, CH_2), 2.70—3.20 (3 H, m), and 7.20—7.80 (10 H, m, Ar).

2-(2-*Aminocyclohexyl*)*methyl*-4,5-*diphenyloxazole* (12).—By the same reductive amination as above, compound (12) was obtained from (6): 63% yield; *yellow oil* (Found: C, 79.4; H, 7.7; N, 8.1. $C_{22}H_{24}N_2O$ requires C, 79.48; H, 7.28; N, 8.43%); $\nu_{max.}$ (film) 3 500—3 200br, 3 040, 2 920, 2 840, 1 600, 1 570, 1 500, and 1 445 cm^{-1}; δ_H ($CDCl_3$) 0.90—3.50 (12 H, m), 1.88 (2 H, br s, D_2O-exchangeable, NH_2), and 7.20—7.90 (10 H, m, Ar); δ_C ($CDCl_3$) *trans*: 25.6 (t), 25.9 (t), 31.5 (t), 32.0 (t), 37.1 (t), 44.9 (d, C-1 of cyclohexane), and 54.6 p.p.m. (d, C-2 of cyclohexane); *cis*: 20.7 (t), 24.7 (t), 26.8 (t), 28.2 (t), 33.3 (t), 40.3 (d, C-1 of cyclohexane), and 49.1 p.p.m. (d, C-2 of cyclohexane). The other complicated aromatic carbon signals were observed at δ_C 126.4—162.9 p.p.m.

5-*Methyl*-2,3-*diphenyl*-6,7-*dihydro*-5H-*pyrrolo*[1,2-a]*imidazole* (13).—Crude compound (11) obtained from (4) (1.0 g, 3.4 mmol) was heated at 280 °C under 5 mmHg pressure for 20 min in a glass tube oven with a trap bulb heated at 200 °C. The brown oil trapped in a bulb immediately solidified on being cooled. Purification on an alumina column with $CHCl_3$ as eluant gave compound (13) [430 mg, 46% from (4)], m.p. 141—143 °C (Found: C, 83.2; H, 6.75; N, 10.05. $C_{19}H_{18}N_2$ requires C, 83.18; H, 6.61; N, 10.21%); $\nu_{max.}$ (KBr) 3 040, 2 970, 1 602, 1 535, 1 500, and 1 445 cm^{-1}; δ_H ($CDCl_3$) 1.20 (3 H, d, *J* 6.7 Hz, CH_3), 1.80—3.20 (4 H, m, 6- and 7-H_2), 4.10—4.70 (1 H, m, 5-H), and 7.05—7.70 (10 H, m, Ar).

2,3-*Diphenyl*-5,6,7,8,8a,9-*hexahydro*-4aH-*imidazo*[1,2-a]*indole* (14).—In the same way as above, compound (14) was obtained by the pyrolysis of crude (12). Purification was performed on a silica gel column with AcOEt as eluant: 23% yield from (6), m.p. 160—163 °C (Found: C, 83.9; H, 7.25; N, 8.85. $C_{22}H_{22}N_2$ requires C, 84.04; H, 7.05; N, 8.91%); $\nu_{max.}$ (KBr) 3 050, 2 930, 2 850, 1 600, 1 535, and 1 445 cm^{-1}; δ_H ($CDCl_3$) 0.80—3.20 (11 H, m), 3.20—3.90 (m, 4a-H of *trans* isomer), 3.90—4.40 (m, 4a-H of *cis* isomer), and 7.00—7.75 (10 H, m, Ar); δ_C ($CDCl_3$) *trans*: 24.4 (t), 25.7 (t), 29.1 (t), 29.8 (t), 30.4 (t), 50.8 (d, C-8a), and 64.1 p.p.m. (d, C-4a); *cis*: 21.1 (t), 22.0 (t), 26.9 (t), 27.8 (t), 29.1 (t), 40.1 (d, C-8a), and 56.4 p.p.m. (d, C-4a). The other complicated aromatic signals were observed at δ_C 125.6—152.9 p.p.m.

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