88–93 °C, $[\alpha]^{24}_D$ +542° (c 0.04, ethanol), ee ≳97%, by NMR chiral shift (below).

From 590 mg (1.7 mmol) of (−)-(hydroxymethyl)norvincadifformine **13a**, 360 mg (57%) of the chloride **16a** was obtained, $[\alpha]^{24}_D$ −370° (c 0.1, ethanol). Rearrangement and reduction of 350 mg (0.939 mmol) of this product gave 155 mg (49%) of total solid vincadifformine product with $[\alpha]^{24}_D$ −555° (c 0.14, ethanol), ee ≳98% by NMR chiral shift (below). Recrystallizations from ethanol and aqueous methanol provided an analytical sample with mp 98–99 °C: $[\alpha]^{24}_D$ −564° (c 0.14, ethanol). Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74; N, 8.28. Found: C, 74.62; H, 8.02; N, 8.19.

A sample of natural vincadifformine, recrystallized from ethanol, had mp 98–99 °C and $[\alpha]^{24}_D$ −563° (c 0.15, ethanol) and gave no depression on mixture melting point with the synthetic product.

For determination of enatiomeric excesses (ee) by the NMR chiral shift method, 0.1 molar ratios of $Eu(hfc)_3$ to vincadifformine were used. The methyl ester singlet at δ 3.76, when not complexed, is split into signals at δ 4.33 for the (+) enantiomer and δ 4.21 for the (−) enantiomer, when the racemic compound is complexed. In order to evaluate the asymmetric efficacy of the synthesis, the ee values were obtained for the respective total uncrystallized vincadifformine product. In each enantiomeric series only one enantiomeric ester peak could actually be seen and the 97% and 98% ee values are conservatively derived from assignment of base-line noise to a conceivable minor enantiomer.

Acknowledgment. We thank Dr. J. Hannart of OMNI CHEM for comparison samples of (−)-vincadifformine and (−)-tabersonine. Support for parts of this research project by the National Cancer Institute under National Institutes of Health Research Grant RO1 CA 12010 is gratefully acknowledged. We thank Mr. Tim Spitzer of our research group for mass spectra.

3,4,9,9a-Tetrahydro-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one Derivatives. 2.[1] Unusual Results from Eschweiler–Clarke Methylation

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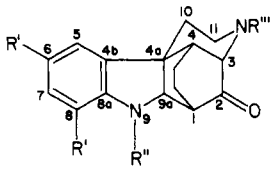
The N-methylation of 3,4,9,9a-tetrahydro-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (1) under Eschweiler–Clarke reaction conditions using excess formaldehyde gave 3,4,9,9a-tetrahydro-6,8,9,12-tetramethyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (**1b**). When an equivalent amount of formaldehyde was used, the main products were 3,4,9,9a-tetrahydro-12-methyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (**1c**) and 1,3,4,9a-tetrahydro-12-methyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazole-9(2*H*)-carboxaldehyde (**1d**).

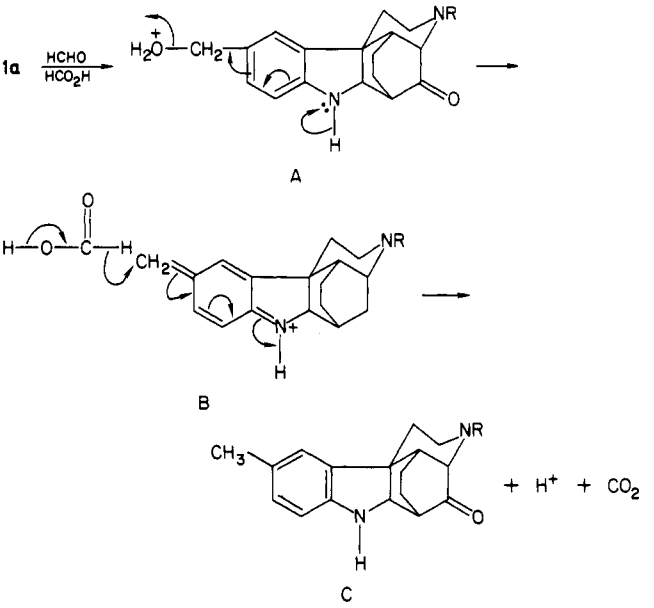
In an earlier paper,[1] we have reported the synthesis of 3,4,9,9a-tetrahydro-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (**1a**) and its hexacyclic derivatives. We now describe some unusual methylation results using a typical Eschweiler–Clarke procedure.[2]



1a, R′=R″=R‴=H
1b, R′=R″=R‴=CH_3
1c, R′=R″=H; R‴=CH_3
1d, R′=H; R″=CHO; R‴=CH_3
1e, R′=H; R″=R‴=CH_3
1f, R′=H; R″=$CONHCH_3$; R‴=CH_3

Refluxing a solution of **1a** with excess formaldehyde in 90% aqueous formic acid gave 3,4,9,9a-tetrahydro-6,8,9,12-tetramethyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (**1b**) as the sole isolable product. Analytical and spectral data are in full agreement with structure **1b** (see Experimental Section).

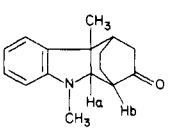
Mechanistically, a quinoid-like intermediate (B) can be proposed, which is reduced in situ to give C. A similar mechanism would operate for the introduction of the second (ortho) nuclear methyl group. Electron availability on the aniline nitrogen[3,4] is apparently necessary for the



(1) Part 1: Bobowski, G.; Morrison, G. C. *J. Org. Chem.* **1981**, *46*, 4927.

(2) (a) Icke, R. N.; Wisegarver, B. B. *Org. Synth.* **1946**, *25*, 89. (b) Eschweiler, W. *Chem. Ber.* **1905**, *38*, 880. (c) Decker, H.; Becker, P. *Liebigs Ann. Chem.* **1913**, *395*, 343; (d) **1913**, *395*, 360. (e) Decker, H.; Becker, P. *Chem. Ber.* **1912**, *45*, 2404. (f) Werner, E. A. *J. Chem. Soc.* **1917**, *111*, 844. (g) Clarke, H. T.; Gillespie, H. B.; Weisshaus, S. Z. *J. Am. Chem. Soc.* **1933**, *55*, 4571. (h) Wagner, E. C. *J. Am. Chem. Soc.* **1933**, *55*, 724. (i) Kametani, T.; Noguchi, I.; Saito, K. *J. Heterocycl. Chem.* **1969** *6*(6), 869.

(3) In a partly similar structure Cranwell and Saxton (Cranwell, P. A.; Saxton, J. E. *Tetrahedron* **1964**, *20*, 877) report NCH_3 at δ 2.77 and Ha as a doublet ($J_{a,b}$ = 4.5 Hz) at δ 3.40. In the parent compound **1a**[1] this proton (H-9a) resonates at δ 3.75. It is obvious that the neighboring *N*-methyl group causes considerable shielding.

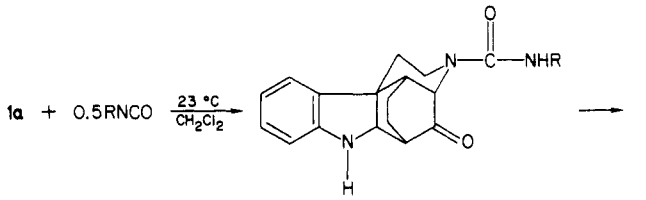


0022-3263/85/1950-0929$01.50/0

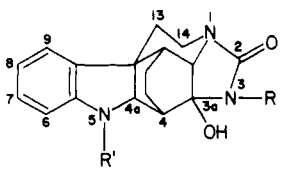
methylation of the aromatic ring. This is supported by derivatives **1d** and **1f** which lack these electrons. No nuclear methylation was observed when **1d** and **1f** were subjected to the same reaction conditions.

When only 1 equiv of formaldehyde was used to avoid nuclear methylation (other conditions being equal), only the monomethylated product **1c** was produced. Modification of the procedure by using 100% formic acid gave only the *N*-formyl(9-CHO) *N*-methyl(12) derivative **1d**. No *N,N'*-dimethyl derivative **1e** was observed under these conditions.

As shown by the formation of **1c**, **1d**, and **1f** under these reaction conditions, the aliphatic nitrogen, N-12, was always attacked first, followed by reaction at the aniline nitrogen. As further evidence that this is the case, the reaction was carried out under phase-transfer catalysis using 1 equiv of Me_2SO_4, **1a**, and catalytic amount of Adogen 464;[5] **1c** was the only product. Likewise, when 0.5 equiv of methyl isocyanate was allowed to react with **1a** at room temperature, addition to N-12 was quantitative. The intermediate urea **1g**[6] spontaneously cyclized to give **2a**.



1g, R=CH_3
1h, R=C_6H_{11}



2a, R'=H, R=CH_3
2b, R'=CNHCH$_3$, R=CH_3
2c, R'=H, R=C_6H_{11}
2d, R'=CNHC$_6$H$_{11}$, R=C_6H_{11}

Following the reaction of **2a** with an additional 0.5 equiv of MeNCO, addition to the dihydroindole nitrogen was effected to give the hexacyclic urea derivative **2b**.[1,6] In the reaction of **1a** with isocyanate having a bulky alkyl group like cyclohexyl, the intermediate urea derivative **1h** which was isolated was quite stable. It was cyclized irreversibly to the hexacyclic derivative **2c** on heating at 140 °C. Similarly, to **2b**, the urea derivative **2d** was formed on addition of 0.5 equiv of cyclohexyl isocyanate.[1,6]

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus which was calibrated against known standards. The UV and IR spectra were obtained, respectively, with a Cary 118 UV–vis recording spectrophotometer and a Nicolet FT-IR MX-1 spectrometer. The ^1H NMR spectra were recorded with a Varian EM390 and XL200 spectrometers with Me_4Si as an internal reference. The ^{13}C NMR were recorded on a Bruker WH90 with a 22.63-MHz operating frequency. The mass spectra were recorded on a Finnigan 1015 Quadrupole mass spectrometer. TLC was carried out on silica gel G (Stahl) by using a variety of solvents (specified individually), and the chromatograms were developed in an iodine chamber.

3,4,9,9a-Tetrahydro-6,8,9,12-tetramethyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (1b). Method A. A solution of 1.4 g (5.5 mmol) of 3,4,9,9a-tetrahydro-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (**1a**)[1] and 6 mL of 37% aqueous HCHO in 10 mL of 90% HCO_2H was refluxed for 3 h. TLC (silica gel; chloroform, ethanol, ammonia, 90:10:1) showed the absence of starting **1a** (R_f 0.2) and the presence of the main spot at R_f 0.5. A considerable amount of polymeric material close to the origin was also present. Hydrochloric acid (5 mL, 10%) was added and the solution was heated for 30 min at 100 °C and concentrated in vacuo to a low volume. The mixture was taken up with ice–water, neutralized with aqueous $NaHCO_3$, and extracted twice with 50 mL of CH_2Cl_2. The combined extracts were filtered through silica gel and evaporated to dryness. Trituration of the residue with acetonitrile gave 0.5 g of off-white crystals, mp 125–126 °C. Recrystallization from ethanol gave analytically and chromatographically pure **1b** as white crystals: mp 126–127 °C; UV (CH_3OH) λ_{max} 257 nm (ϵ 8640), 304 (2900); IR (KBr) 1724 (C=O); ^1H NMR ($CDCl_3$) δ 2.22 (s, 3 H, CH_3-6 or CH_3-8),[7] 2.32 (s, 3 H, CH_3-6 or CH_3-8),[7] 2.70 (s, 3 H, NCH_3-12),[8] 2.85 (s, 3 H, CH_3N-9),[9] 3.31 (d, 1 H, $J_{9a,1}$ = 4.2 Hz, H-9a),[3] 2.93 (d, 1 H, $J_{3,4}$ = 3.0 Hz, H-3), 6.60 (s, 1 H, H-5 or H-7), 6.71 (s, 1 H, H-5 or H-7); ^1H NMR (Me_2SO-d_6) δ 2.18 (s, 3 H, CH_3-6 or CH_3-8), 2.27 (s, 3 H, CH_3-6 or CH_3-8), 2.54 (s, 3 H, NCH_3-12), 2.82 (s, 3 H, NCH_3-9), 6.62 (s, 2 H, H-5 and H-7); ^{13}C NMR ($CDCl_3$) δ 148.7, 135.3, 131.9, 128.6, 120.1, 70.8, 67.3, 47.7, 47.1, 44.9, 44.4 (NCH_3-12),[10] 41.2, 39.7 (NCH_3-9),[10] 38.8, 20.6 (CH_3-6),[11] 20.1, 19.3 (CH_3-8),[11] 16.7; mass spectrum, *m/e* 310. Anal. Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.03. Found: C, 77.52; H, 8.30; N, 9.02.

3,4,9,9a-Tetrahydro-12-methyl-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazol-2(1*H*)-one (1c). Compound **1c** was prepared in a manner analogous to **1b** by utilizing 1 equiv of formaldehyde. An analytically pure **1c**, mp 151–152 °C, was obtained by recrystallization from isopropyl ether: UV (CH_3OH) λ_{max} 253 nm (ϵ 8450), 304 (2900); IR ($CHCl_3$) 3400 (NH), 1721 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (s, 3 H, CH_3-12), 2.97 (d, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 3.80 (br, 1 H, H-9, D_2O-exchangeable), 3.96 (m, 1 H, H-9a), 6.70 (m, 2 H, H-6, H-8), 7.00 (m, 2 H, H-5, H-7); ^1H NMR (Me_2SO-d_6) δ 2.54 (s, 3 H, NCH_3-12), 2.92 (d, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 3.98 (m, 1 H, H-9a; on D_2O-exchange collapses to d, J = 4.0 Hz), 5.65 (d, J = 4.0 Hz, NH), 6.45 (m, 2 H, H-6, H-8), 6.86 (m, 2 H, H-5, H-7); mass spectrum, *m/e* 268. Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.44. Found: C, 76.25; H, 7.58; N, 10.41.

Method B. With Phase-Transfer Catalyst (Adogen 464).[5] To a rapidly stirred mixture of 1.26 g (5 mmol) of **1a**, 1.39 g (11 mmol) of Me_2SO_4, and 10 mL of 30% aqueous KOH in 35 mL of CH_2Cl_2 was added 0.5 g of Adogen 464. After 2 h at room temperature, the ^1H NMR spectrum showed only one CH_3. After the mixture was stirred overnight at ambient temperature and the usual workup, the product (0.4 g, mp 151–152 °C) was identical in all respectes with **1c**.

(4) Lonquet-Higgins, H. C.; Coulson, C. A. *Trans. Faraday Soc.* **1947**, *43*, 87.
(5) Aldrich Chemical Company.
(6) Compounds **2b** and **2d** are identical in all respects with those obtained directly when equivalent amounts of respective isocyanates were used in ref 1.
(7) The ^1H NMR spectrum of 2,4,6-trimethylbenzenamine shows the 4-CH_3 signal at a slightly lower field (δ 2.16) than those of 2,6-dimethyl groups (δ 2.12) (Aldrich Company Catalog). However, in *N,N*,2,4,6-pentamethylbenzenamine (which has partial resemblance to **1b** in the aromatic part), this relationship is reversed; the 4-methyl group resonates at δ 2.23 and 2,6-dimethyl groups show the signal at δ 2.25.
(8) The low-field resonance as compared to 1-methylpiperidine (δ 2.10) is apparently due to the deshielding influence of the neighboring ketone function. The situation could roughly resemble that of 1-methyl-2-acylpiperidine or that of 1-methyl-3-piperidinone.
(9) Cf. ref 3. *N,N*,2,4,6-Pentamethylbenzenamine shows the *N,N*-dimethyl signal at δ 2.78. It is evident that a multiple substitution on the aromatic ring causes the *N*-methyl substituents to resonate at higher fields [cf. *N,N*-dimethylbenzenamine (δ 2.93)].
(10) The first (NCH_3-12) would generally compare with *N*,2-dimethylpiperidine (δ_{NCH_3} 42.45) and the latter with *N,N*-dimethylbenzenamine (δ 41.10). Ellis, G.; Jones, R. G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 437.
(11) This is in general agreement with the fact that 4-methyl group of *N,N*,4-trimethylbenzenamine resonates at a somewhat lower field (δ 21.30) than the 2-methyl analogue (δ 19.40).

1,3,4,9a-Tetrahydro-12-methyl-2-oxo-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazole-9(2*H*)-carboxaldehyde (1d). A solution of 1.26 g (5 mmol) of **1a** and 1 mL of 37% of formaldehyde in 6 mL of 100% formic acid was refluxed for 3 h and subsequently evaporated to dryness. The residue was taken up with cold aqueous K_2CO_3 and extracted with 50 mL of ethyl acetate. The organic extract was washed, dried (Na_2SO_4), and evaporated. Crystallization of the residue from ethyl acetate–diisopropyl ether gave 0.4 g of **1d**: mp 148–149 °C; UV (CH_3OH) λ_{max} 251 nm (ϵ 15 100), 280 (3500); IR (KBr) 1724 (ketone C=O), 1668 (anilide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (CH_3-12), 2.97 (d, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 4.36 (d, $J_{9a,1}$ = 4.0 Hz, 1 H, H-9a), 7.00–7.28 (m, 4 H, Ar), 9.95 (s, 1 H, CHO); mass spectrum, *m/e* 296. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.01; H, 6.49; N, 9.26.

1,3,4,9a-Tetrahydro-*N*,12-dimethyl-2-oxo-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazole-9(2*H*)-carboxamide (1f). A solution of 0.2 g of **1c**, 0.2 g of CH_3NCO, and 1 drop of *N,N*-diethylethanamine in 5 mL of CH_2Cl_2 was allowed to stand for 24 h at 23 °C. After the solution was evaporated, the solid residue was crystallized from ethyl acetate, giving 0.15 g of **1f** as white crystals, mp 211–212 °C; UV (CH_3OH) λ_{max} 250 nm (ϵ 15 150), 281 (3500); IR (KBr) 3450, 3330 (NH), 1723 (ketone C=O), 1658, 1533 (NHCO) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.52 (s, CH_3-12), 2.63 (d, J = 5.4 Hz, $NHCH_3$), 2.93 (d, $J_{3,4}$ = 3.0 Hz, 1 H, H-3), 4.41 (d, $J_{9a,1}$ = 3.5 Hz, 1 H, H-9a), 6.70 (q, J = 5.4 Hz, 1 H, D_2O-exchangeable, $NHCH_3$), 6.85 (m, 1 H, H-6), 7.07–7.18 (m, 2 H, H-5, H-7), 7.83 (d, J = 8.0 Hz, 1 H, H-8); mass spectrum, *m/e* 325. Anal. Calcd for $C_{19}H_{23}N_3O_2$: C, 70.13; H, 7.12; N, 12.91. Found: C, 70.25; H, 7.19; N, 12.95.

3a,4,4a,5,10,10a-Hexahydro-3a-hydroxy-3-methyl-1,9b:4,10-diethanoimidazo[4,5-*b*]carbazol-2(3*H*)-one (2a). Methyl isocyanate (0.29 g, 5 mmol) and 1 drop of *N,N*-diethylethanamine were added to a solution of 1.47 g (5 mmol) of **1a** in 10 mL of CH_2Cl_2 and allowed to stand at 23 °C for 4 days. The resulting white crystals (1.2 g) of **2a** of analytical purity were collected, mp 292–293 °C dec. Evaporation of the filtrate and trituration with ethanol gave additional product **2a** (total yield, 88%): mp 291–292 °C; UV (CH_3OH) λ_{max} 250 nm (ϵ 15 000), 290 (2770); IR (KBr) 3400, 3250 (OH, NH), 1673 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.59 (s, 3 H, CH_3), 5.54 (d, J = 1.6, 1 H, D_2O-exchangeable, NH), 6.15 (s, 1 H, D_2O-exchangeable, OH), 6.49 (m, 2 H, Ar), 6.88 (m, 2 H, Ar); mass spectrum, *m/e* 311. Anal. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.39; H, 6.94, N, 13.74.

3,3a,4,4a,10,10a-Hexahydro-3a-hydroxy-*N*,3-dimethyl-2-oxo-1,9b:4,10-diethanoimidazo[4,5-*b*]carbazole-5(2*H*)-carboxamide (2b). To a solution of 2 mmol of **2a** in 10 mL of dry tetrahydrofuran was added 2 mmol of MeNCO and 1 drop of Et_3N. After 2 days at 23 °C, the solution was evaporated in vacuo and the solid residue recrystallized from ethanol, giving 0.3 g of pure **2b**, mp 280–281 °C. The analytical and spectral data as well as a mixture of melting point are identical with product obtained directly when equivalent amounts of **1a** and MeNCO were employed.[1]

***N*-Cyclohexyl-1,2,3,4,9,9a-hexahydro-2-oxo-1,4-ethano-3,4a-(iminoethano)-4a*H*-carbazole-12-carboxamide (1h).** A solution of 2 mmol of **1a**, 1 mmol of cyclohexyl isocyanate, and 1 drop Et_3N in 15 mL of CH_2Cl_2 was allowed to stand overnight at 23 °C. After the solvent was removed under diminished pressure, the residue was crystallized from a mixture of 2-propanol–diisopropyl ether to give 0.4 g of **1h**: mp 155–156 °C; UV (CH_3OH) λ_{max} 249 nm (ϵ 16 800) 284 (3100); IR (KBr) 3440, 3330 (NH), 1726 (ketone C=O), 1655, 1528 (NHCO) cm^{-1}; mass spectrum, *m/e* 379. Anal. Calcd for $C_{23}H_{29}N_3O_2$: C, 72.79; H, 7.70; N, 11.07. Found: C, 72.53; H, 7.85; N, 10.86.

3-Cyclohexyl-3a,4,4a,5,10,10a-hexahydro-3a-hydroxy-1,9b:4,10-diethanoimidazo[4,5-*b*]carbazol-2(3*H*)-one (2c). A solution of 0.3 g of **1h** in 30 mL of xylene was refluxed for 2 h and subsequently evaporated under diminished pressure. The solid residue was crystallized from ethanol, giving 0.2 g of **2d**: mp 229–230 °C; UV (CH_3OH) λ_{max} 251 nm (ϵ 15 300), 291 (2780); IR (KBr) 3400, 3260 (OH, NH), 1671 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 5.70 (br, 1 H, D_2O-exchangeable, NH), 6.12 (s, 1 H, D_2O-exchangeable, OH); mass spectrum, *m/e* 379. Anal. Calcd for $C_{23}H_{29}N_3O_2$: C, 72.79; H, 7.70; N, 11.07. Found: C, 72.61; H, 7.73; N, 11.02.

On addition of 1 equiv of cyclohexyl isocyanate to a solution of **2c** in tetrahydrofuran, *N*-3-dicyclohexyl-3,3a,4,4a,10,10a-hexahydro-3a-hydroxy-2-oxo-1,9b:4,10-diethanoimidazole-5-(2*H*)-carboxamide (**2d**) was obtained, mp 203–204 °C dec. The analytical and spectral data of **2d** are identical with the product obtained by thermal cyclization of the dicyclohexylurea derivative.[1]

General Chiral Route to Irregular Monoterpenes via a Common Intermediate: Syntheses of (*S*)-Lavandulol, *cis*-(1*S*,3*R*)-Chrysanthemol, (1*S*,2*R*)-Rothrockene, and (*R*)-Santolinatriene

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Treatment of (*S*)-*O*-benzylglycidol (**6**) with senecioic acid in the presence of LDA, followed by acid workup, yielded a mixture of lactones **9** and **10**, whose enolate **11** on exposure to hydrochloric acid (10%) gave the α/γ-syn lactone **12** as a single product via stereo- and regioselective protonation. With lactone **12** as a common intermediate, four of five irregular monoterpenoid skeletons so far known have been synthesized. Thus, **12** afforded (*S*)-lavandulol (**16**) as the lavandulyl, *cis*-(1*S*,3*R*)-chrysanthemol (**21**) as the chrysanthemyl, (1*S*,2*R*)-rothrockene (**26**) as the rothrockyl, and (*R*)-santolinatriene (**33**) as the santolinyl groups, respectively, without difficulties.

Irregular monoterpenes which do not obey the isoprene rule have so far been found in nature in five skeletal systems divided into lavandulyl (1), chrysanthemyl (2), artemisyl (3), rothrockyl (4), and santolinyl (5) groups (Chart I).[1,2] These compounds are of particular interest since their generation via common chrysanthemyl pyrophosphate has been proposed for the biosynthetic pathway.[3,4] Although a number of synthetic entries into each skeletal type of these compounds has been reported,[5,6] no

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