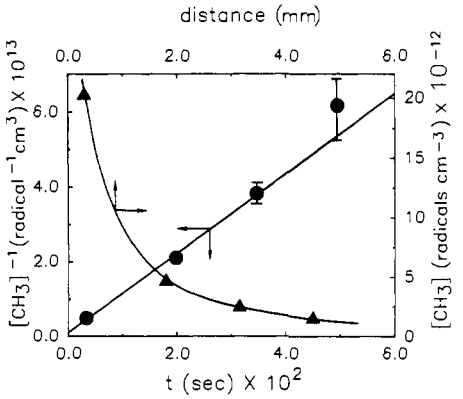

Figure 1. Plots of $[CH_3^{\bullet}]$ versus probe distance and $[CH_3^{\bullet}]^{-1}$ versus time (time for gas flow from catalyst bed to the probe).

Table I. Comparison of Gas-Phase Methyl Radicals and Ethane Production[a]

CH_4 molecules reacted (min^{-1})	1.4×10^{18}
CH_4 molecules to C_2's (min^{-1})	8.0×10^{17}
$CH_3^{\bullet}$ radicals exiting catalyst bed (min^{-1})[b]	3.2×10^{17}
($CH_3^{\bullet}$ radicals)/(CH_4 reacted)	0.23
($CH_3^{\bullet}$ radicals)/(CH_4 to C_2's)	0.40

[a] Reaction conditions: catalyst = 0.03 g of 7 wt% Li/MgO mixed with inert powdered quartz and supported in a thin layer of quartz wool. Temperature = 670 °C; atmospheric pressure; total flow = 880 cm^3 min^{-1} (STP); $Ar/CH_4/O_2$ = 219/9.3/1. [b] Radicals min^{-1} were detected, the collection efficiency in the sensitive region of the sapphire rod was 10%, and the percentage of molecules entering the leak was 0.28%.

low-pressure region where they are frozen on a sapphire rod maintained at 14 K. The sapphire rod with the matrix is then lowered into an ESR cavity where the spectrum is recorded. The original apparatus was converted into an atmospheric flow system through the construction of pressure leaks which allowed for the collection of ~2 cm^3 min^{-1} (STP) from the atmospheric stream. Moreover, the distance from the catalyst bed to the leak was adjustable. With this modification the gas-phase $CH_3^{\bullet}$ radical concentration at varying distances from the exit of the catalyst bed could be measured under atmospheric conditions. The radical collection efficiency was determined by carrying out a MIESR experiment with the stable NO_2 free radical.

Plots of $[CH_3^{\bullet}]$ versus distance and $[CH_3^{\bullet}]^{-1}$ versus time (time for gas flow from the catalyst bed to the probe) are shown in Figure 1. The slope of the $[CH_3^{\bullet}]^{-1}$ versus time plot should be the second-order rate constant for gas-phase $CH_3^{\bullet}$ radical coupling, and the intercept gives the gas-phase $CH_3^{\bullet}$ concentration at the exit of the catalyst bed. Analysis of the product stream was carried out with the use of standard GC techniques. From these results a direct comparison between the amounts of $CH_3^{\bullet}$ radicals and C_2 products was possible.

In establishing the slope of Figure 1 more weight was given to the greater concentrations obtained at short distances from the catalyst bed as these data were obtained at a much higher signal-to-noise ratio. A second-order rate constant for $CH_{3(g)}^{\bullet}$ coupling of 1.1×10^{-11} cm^3 $radical^{-1}$ s^{-1} at 670 °C compares favorably with a "best value" of $(2.6 \pm 1) \times 10^{-11}$ cm^3 $radical^{-1}$ s^{-1} reported in a review by Warnatz.[9] The comparison of gas-phase $CH_3^{\bullet}$ radicals and C_2H_6 production is summarized in Table I. The results show that at least 40% of the C_2H_6 produced can be accounted for by the coupling of gas-phase $CH_3^{\bullet}$ radicals. Additional experiments to substantiate this result were carried out by placing the leak directly in contact with the catalyst bed. These experiments showed that >45% of the C_2H_6 could be accounted for by the gas-phase $CH_3^{\bullet}$ radicals.

In view of the tortuous path that the radicals must follow in leaving the polycrystalline catalyst particles and the catalyst bed it is expected that considerable recombination would occur before the radicals reach the exterior region of the bed. Thus, the value of 40–45% is a lower limit on the gas-phase reaction. Also, because of the nature of the bed, it is unlikely that the gas–surface equilibrium would have been perturbed to the point where surface recombination reactions would have been negated.

(9) Warnatz, J. In *Combustion Chemistry*; Gardiner, W. C., Ed.; Springer-Verlag: New York, 1984; pp 197–360.

Table II. Experimental and Simple Collision Theory Rates for C_2H_6 Formation[a]

	conc $CH_{3(g)}$,[b] radical cm^{-3}	conc $CH_{3(s)}$,[c] radical cm^{-2}	rate C_2H_6 prod., s^{-1}
gas phase	1.1×10^{14}		2.5×10^{15}[d]
surface coupling	1.1×10^{14}	8.8×10^{7}	1.5×10^{15}[e]
Rideal–Eley	1.1×10^{14}	8.8×10^{7}	6.6×10^{13}[e]

[a] Calculations are for T = 670 °C. [b] Concentration is the value at the exit of the catalyst bed. [c] Value assumes that the virtual pressure at the surface is 20 times that of the gas phase. [d] Value obtained from Table I assumes all gas-phase radicals couple. [e] Results obtained by using a reaction efficiency of 0.06. This value was determined by comparing the coupling rate to the collision frequency.

It was of interest to compare the experimental results with results predicted from simple collision theory for the surface coupling of adsorbed $CH_3^{\bullet}$ radicals and also for C_2H_6 formation according to a Rideal–Eley mechanism; i.e., a gas-phase $CH_3^{\bullet}$ radical reacting with a surface radical. These results are summarized in Table II. The results indicate that a Rideal–Eley mechanism is probably not important for this process. As a result of the assumptions used the experimental gas-phase and surface-coupling rates are comparable; however, it should be realized that the surface coupling calculation assumes a two-dimensional perfect gas velocity to describe the mobility of the adsorbed $CH_3^{\bullet}$ radicals. The latter assumption ignores the fact that an adsorption process which would result in a high virtual pressure would also limit the mobility of the radicals across the surface.

In conclusion, the results presented here show that gas-phase coupling of methyl radicals during the catalytic oxidative coupling of CH_4 represents a major mechanistic pathway for the formation of C_2H_6.

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Expeditious Enantioselective Syntheses of Indole Alkaloids of *Aspidosperma*- and *Hunteria*-Type

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Indole alkaloids are known to possess a variety of physiological activities. The interest in *Aspidosperma* and *Hunteria* alkaloids is reflected in the numerous reports of syntheses of these alkaloids in the racemic and optically active forms.[1] The indole-2,3-quinodimethane strategy developed by Magnus[2] is among the most elegant racemic syntheses from the chemical point of view. The Pictet–Spengler or the Bischler–Napieralski condensation of tryptamine with the C_9 or C_{10} unit is the most widely accepted strategy because of the general applicability.[3] Here we describe

(1) (a) *Aspidosperma* alkaloids: Cordell, G. A. In *The Alkaloids*; Manske, R. H. F., Rodrigo, R. G. A., Eds.; Academic Press: New York, 1979; Vol. XVII, p 199. (b) *Hunteria* alkaloids: Döpke, W. In *The Alkaloid*; Manske, R. H. F., Rodrigo, R. G. A., Eds.; Academic Press: New York, 1981; Vol. XX, p 297. Atta-ur-Rahman; Sultana, M. *Heterocycles* **1984**, *22*, 841.

(2) (a) Magnus, P.; Gallagher, T.; Brown, P.; Pappalardo, P. *Acc. Chem Res.* **1984**, *17*, 35. (b) Magnus, P.; Pappalardo, P.; Southwell, I. *Tetrahedron* **1986**, *42*, 3215. (c) Magnus, P.; Pappalardo, P. *J. Am. Chem. Soc.* **1986**, *108*, 212 and references cited therein.

(3) Kutney, J. P. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; John-Wiley & Sons: New York, 1979; Vol. 3, p 273.

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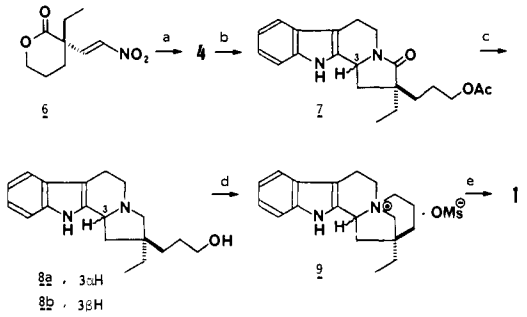
Scheme I[a]

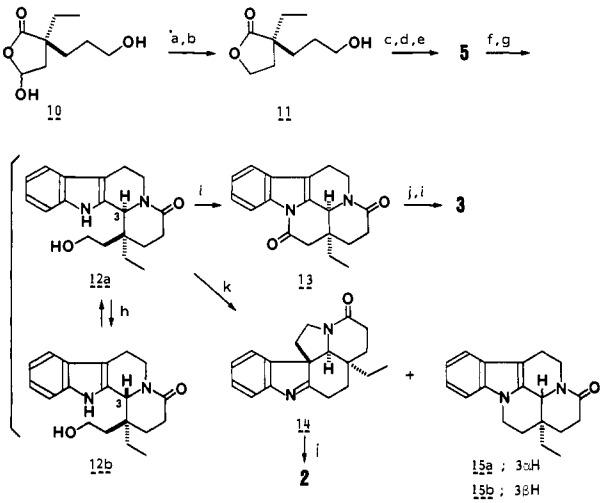


[a] (a) $TiCl_3$/MeOH/pH5; (b) tryptamine/AcOH/reflux; (c) $LiAlH_4$/THF/reflux; (d) $MsCl/Et_3N/CHCl_3$; (e) Na/EtOH/liquid NH_3.

short efficient chiral syntheses, based on the Pictet–Spengler condensation, of two *Aspidosperma* alkaloids (+)-quebrachamine (**1**)[4] and (−)-aspidospermidine (**2**),[5] and a *Hunteria* alkaloid, (−)-eburnamonine (**3**),[6] all of which possess the C_9 unit as a monoterpenoid unit.

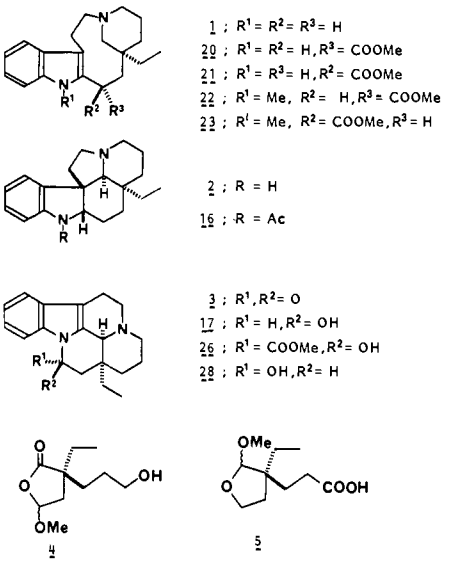
Synthesis of optically active alkaloids using the Pictet–Spengler condensation is difficult due to the lack of an efficient method for synthesizing the chiral C_9 unit. Compound **4** is an ideal chiral

Scheme II[a]



[a] (a) $NaBH_4$; (b) 5% HCl/reflux; (c) CrO_3/H_2SO_4/acetone; (d) $DIBAH/Et_2O$; (e) TsOH/MeOH/reflux; (f) tryptamine/AcOH/reflux; (g) NaOH/MeOH; (h) BF_3OEt_2; (i) CrO_3/pyridine; (j) $LiAlH_4/Et_2O$; (k) CF_3SO_3H.

C_9 building block for the synthesis of (+)-quebrachamine (**1**) and compound **5** for (−)-aspidospermidine (**2**) and (−)-eburnamonine (**3**), because they possess a quarternary carbon atom bearing C_1, C_2, and C_3 units in different oxidation stages as well as an ethyl group indispensable to the construction of those optically active alkaloids.



The nitro olefin **6** is an efficient starting material for chiral syntheses of these units, since it has a chiral quarternary carbon with an ethyl group and the functional groups feasible for the necessary transformations. Moreover, nitro olefin **6** has been easily prepared in high yield and with a high enantiomeric excess from 2-ethyl-δ-valerolactone through asymmetric induction via an addition–elimination process that we developed recently.[7] With use of the nitroolefin **6**, we prepared **4** in a single step and **5** in five steps. Thus, treatment of the chiral nitroolefin **6** of 85% ee with $TiCl_3$ in methanol at pH 5 gave **4**, which was immediately subjected to the Pictet–Spengler condensation with tryptamine in acetic acid to afford the tetracyclic lactam **7** (Scheme I) as a 1:1 mixture at C-3 in 84% yield in two steps. Exposure of **7** to $LiAlH_4$ in tetrahydrofuran (THF) gave the amino alcohols **8a** and **8b** in 83% combined yield. Separation by column chromatography over silica gel followed by recrystallization yielded pure

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(5) For the racemate, see: (a) Harley-Mason, J.; Kaplan, M.; *Chem. Commun.* **1967**, 915. (b) Laronze, J.-Y.; Laronze-Fontaine, J.; Lévy, J.; Le Man, J. *Tetrahedron Lett.* **1974**, 491. (c) Gallagher, T.; Magnus, P.; Huffman, J. C. *J. Am. Chem Soc.* **1982**, *104*, 1140. Gallagher, T.; Magnus, P.; Huffman, J. C. *Ibid.* **1983**, *105*, 4750. (d) *N*-Acetylaspidospermidine: Seki, K.; Ohnuma, T.; Oishi, T.; Ban, Y. *Tetrahedron Lett.* **1975**, 723, ref 4c and 4k. No chiral synthesis has been reported.

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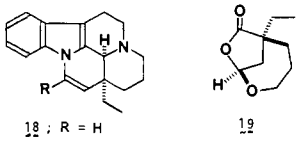
8a [mp 155-156 °C (AcOEt-MeOH); $[\alpha]^{22}_D$ - 70.4° (*c* 0.25, MeOH) [lit.[4m] mp 157-158 °C; $[\alpha]_D$ -62.37°]] and **8b** [mp 194.5-195.5 °C (AcOEt); $[\alpha]^{22}_D$ + 63.3° (*c* 0.07, MeOH) [lit.[4l] mp 193-194 °C; $[\alpha]_D$ + 61.14°]].

According to Kutney's procedure,[4c] quarternary ammonium salt **9** obtained on mesylation of a mixture of **8a** and **8b** was reduced with Na-EtOH in liquid ammonia to give crude (+)-quebrachamine (**1**). A single recrystallization from MeOH yielded optically pure (+)-quebrachamine [mp 144-146 °C; $[\alpha]^{22}_D$ + 117° (*c* 0.18, $CHCl_3$) [lit.[8] mp 147-149 °C; $[\alpha]_D$ + 111°]] in 53% overall yield from the lactam **7**. This revealed the absolute stereochemistry of **6**[7] to be *S*.

Hemiacetal **10** was obtained when reductive denitration of **6** with $TiCl_3$ was conducted in dimethoxyethane. Treatment of **10** with $NaBH_4$ followed by refluxing in aqueous 9% HCl afforded the lactone alcohol **11** in 75% overall yield from **6** (Scheme II). Conversion of **11** into the acetal **5** was accomplished in 76% overall yield through three steps involving the Jones oxidation and partial reduction with diisobutylaluminum hydride (DIBAH), followed by treatment with *p*-toluenesulfonic acid in methanol. Condensation of **5** with tryptamine proceeded in acetic acid to afford a 1:1 mixture of tetracyclic lactams **12a** and **12b** in 84% overall yield from **5** after hydrolysis. Enantiomeric enrichment of **12a** and **12b** was carried out after separation with short-path column chromatography on silica gel and gave optically pure lactams **12a** [mp 263-265 °C dec (aqueous MeOH); $[\alpha]^{22}_D$ -195.5° (*c* 0.16, MeOH)] and **12b** [mp 107-108.5 °C (aqueous MeOH); $[\alpha]^{22}_D$ +88.3° (*c* 0.13, MeOH)]. The Sarett oxidation of the optically pure lactam alcohol **12a** afforded dilactam **13** in 53% yield. (-)-Eburnamonine (**3**) [mp 171-172 °C (MeOH); $[\alpha]^{22}_D$ -88° (*c* 0.09, $CHCl_3$) [lit.[9] mp 173-174 °C; $[\alpha]_D$ -85°]] was obtained in 74% yield from **13** through reduction with $LiAlH_4$ followed by the Sarett oxidation.[10] This transformation confirmed the α-configuration of H(3) in **12a**. Since **12a** and **12b** were shown to establish an equilibrium in the approximate ratio of 1:1 in boron trifluoride-etherate at 35-40 °C after 10 h, the lactam **12a** necessary for the synthesis of (-)-eburnamonine (**3**) could be obtained from **12b**.

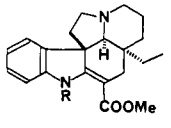
The behavior of **12a** against protic acids is totally different from boron trifluoride-etherate.[11] Thus, **12a** was converted into **14** in triflic acid at 100-110 °C for 45 min in 60% yield along with the eburnamine-type lactams **15a** (20%) and **15b** (12%). Reduction of **14** with $LiAlH_4$ afforded (-)-aspidospermidine (**2**), which was characterized as acetate **16** (81% from **14**) [$[\alpha]^{22}_D$ + 14.1° (*c* 0.31, $CHCl_3$) [lit.[12] $[\alpha]_D$ -15°]].

Recently, (-)-eburnamonine (**3**), (+)-eburnamine (**17**), and (-)-eburnamenine (**18**) were synthesized via the optically active bicyclic acetal **19** as a key intermediate. The latter was prepared

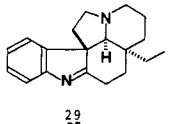


18 ; R = H
27 ; R = COOMe

19



24 ; R = H
25 ; R = Me



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in more than 10 steps and resulted in a 13% overall yield from L-glutaric acid.[6v] We prepared **19** [mp 89-90 °C (Et_2O); $[\alpha]^{22}_D$ + 5.4° (*c* 1.47, CH_2Cl_2) [lit.[6v] mp 82-85 °C, $[\alpha]_D$ + 6.7°]] from **6** in 74% yield with $TiCl_3$ in DME followed by treatment with *p*-toluenesulfonic acid in benzene. This completed an extremely short synthesis of these alkaloids in a formal sense. Since the quarternary salt **9** has been transformed into vincadine (**20**),[13] *epi*-vincadine (**21**),[13] vincaminoreine (**22**),[14] vincaminorine (**23**),[13] vincadifformine (**24**),[13] minovine (**25**),[13] vincamine (**26**),[15] and apovincamine (**27**),[16] the synthesis of optically active **9** constitutes the total syntheses of those alkaloids in optically active form though in a formal sense. Formal total syntheses of optically active isoeburnamine (**28**) and 1,2-dehydroaspidospermidine (**29**) could also be done, because these alkaloids had been derived from dilactam **13**[6a] and quebrachamine (**1**),[17] respectively.

Acknowledgment. We are grateful to Professor Seiichi Takano (Tohoku University, Japan) for providing us with ^1H NMR and IR spectra of (±)-quebrachamine and the authentic sample of optically active **19**. We are also grateful to Professor James P. Kutney (University of British Columbia, Canada) for sending us ^1H NMR and IR spectra of **8a** and **8b**.

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(9) Döpke, W.; Meisel, H. *Pharmazie* **1966**, *21*, 444.
(10) (+)-Dilactam **13** was converted into (+)-eburnamonine previously, see: ref 6a.
(11) In ref 5a, it is reported that a racemate of **12** (the relative configuration was not specified) afforded **14** on treatment with boron trifluoride etherate at 100 °C. However, poor yield of **14** was obtained with our hands.
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Assistance of Protodemercuration by Bis-Thiol Ligation and Nucleophilic Catalysis. A Model Study Which Relates to the Organomercurial Lyase Reaction

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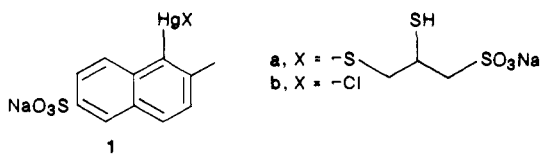
Received July 13, 1987

The first step in the microbial detoxification of organomercurial salts is the protonolytic cleavage of the carbon-mercury bond.[1] Organomercurial lyase enzymes that catalyze the protodemercuration of alkyl, aryl, allyl, and vinyl-mercury salts have been isolated from *Escherichia coli* and from *Pseudomonas*.[2-4] Neither enzyme possesses a cofactor. At least 2 × excess of thiol over substrate is required for activity. These enzymes show optimal activity at remarkably low $[H^+]$. The *E. coli* enzyme[2,3] shows optimal activity at pH 10 and the *Pseudomonas* enzyme[4] at pH 7. Aspects of the enzymatic reaction must, therefore, increase the susceptibility of the C-Hg bond to protonolysis. We establish in this preliminary report a plausible means by which the susceptibility of the C-Hg bond is enhanced in the organomercurial lyase reaction.

The water-soluble **1b** was obtained in >95% purity (^1H NMR, ^{13}CNMR, elemental analysis) by reacting sodium 2-methylnaphthalene 6-sulfonate (1 mM) with mercuric nitrate (1 mM)



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at 85 °C in 10 mL of 0.57 M HClO4 followed by reversed phase

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