12-Acyloxy[4.4.2]propellanones (1a,b) and *endo*-8-Acetoxybicyclo[4.2.0]octan-7-one (8). Propellanones 1a,b and bicyclic cyclobutanone 8 were prepared as described previously.[2i]

General Irradiation Procedure. Methanol solutions (0.01 M) of 1a,b and 8 in Pyrex tubes were degassed, sealed, and irradiated with a high-pressure Hg lamp (500 W) for 0.5–4 h at 20 °C until the cyclobutanones were almost consumed (monitored by GLC; >98%). After removal of methanol, the residue was analyzed by GLC (columns A–C) and the products were isolated by preparative GLC (columns D–F). The yields of the products were calculated from the area percentages of GLC data based on the reacted cyclobutanones.

Irradiation of 1a. Irradiation of 1a (175 mg, 0.74 mmol) for 3 h (100% conversion) gave 184 mg of the product mixture composed of **5a** (a mixture of two epimers, 52%), **6** (a mixture of two epimers, 37%), and acetic acid (27%). **5a**: IR (neat) 1730, 1370, 1220, 1110, 1050 cm^{-1}; mass spectrum, *m/e* 268 (M^+, no peak), 236, 194 (base), 134; ^1H NMR (CCl_4) δ 1.00–1.96 (m, 16 H), 2.02 (s, 3 H), 3.30 (s, 3 H), 4.80 (d, J = 5 Hz, 0.8 H), and 5.50 (d, J = 5 Hz, 0.8 H) [major epimer], 4.88 (d, J = 7 Hz, 0.2 H) and 5.06 (d, J = 7 Hz, 0.2 H) [minor epimer]. Although the two epimers could not be separated by preparative GLC (columns D and F), the ratio was determined to be 4:1 by NMR analysis. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 66.96; H, 9.26. **6**: IR (neat) 1380, 1110, 990 cm^{-1}; mass spectrum, *m/e* 240 (M^+), 209, 180, 148 (base); ^1H NMR (CCl_4) δ 1.10–1.72 (m, 16 H), 3.36 (s, 6 H), and 4.52 (s, 1.6 H) [major epimer], 4.92 (s, 0.4 H) [minor epimer]. Although the two epimers could not be separated by preparative GLC (columns D and E), their ratio was determined to be 4:1 by NMR analysis. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.17. Found: C, 69.73; H, 10.20.

Irradiation of 1b. Irradiation of 1b (360 mg, 1.44 mmol) for 4 h (98% conversion) gave 400 mg of the product mixture composed of **5b** (a mixture of two epimers, 42%), **6** (a mixture of two epimers, 48%, 2:1), and propionic acid (45%). **5b**: IR (neat) 1730, 1170, 1010 cm^{-1}; mass spectrum, *m/e* 282 (M^+, no peak), 222, 194, 148 (base); ^1H NMR (CCl_4) δ 1.00–2.02 (m, 16 H), 1.12 (t, J = 8 Hz, 3 H), 2.28 (q, J = 8 Hz, 2 H), 3.30 (s, 3 H), 4.80 (d, J = 5 Hz, 0.8 H), and 5.54 (d, J = 5 Hz, 0.8 H) [major epimer], 4.90 (d, J = 7 Hz, 0.2 H) and 5.06 (d, J = 7 Hz, 0.2 H) [minor epimer]. Although the two epimers could not be separated by preparative GLC (columns D and F), the ratio was determined to be 4:1 by NMR analysis. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.05; H, 9.28. Found: C, 67.72; H, 9.45.

Irradiation of 8. Irradiation of 8 (319 mg, 1.75 mmol) for 0.5 h (99% conversion) gave 365 mg of the product mixture composed of **9** (a mixture of two epimers, 24%), **10** (a mixture of two epimers, 40%), **11** (a mixture of two epimers, 19%), **12** (12%), and acetic acid (22%). **9**: IR (neat) 1380, 1080, 960 cm^{-1}; mass spectrum, *m/e* 186 (M^+), 154, 122 (base); ^1H NMR (CCl_4) δ 1.04–2.08 (m, 8 H), 2.88 (m, 2 H), 3.22 (s, 3 H), 3.32 (s, 3 H), 4.58 (s, 0.8 H), and 4.82 (d, 0.8 H) [major epimer], 4.60 (s, 0.4 H) [minor epimer]. The NMR analysis shows that the major epimer and the minor epimer may be the anti and exo-syn forms, respectively. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found (major epimer): C, 64.58; H, 9.74. Found (minor epimer): C, 64.23; H, 9.81. **10**: IR (neat) 1730, 1360, 1220, 990 cm^{-1}; mass spectrum, *m/e* 214 (M^+, no peak), 154, 125, 122 (base); ^1H NMR (CCl_4) δ 1.00–1.88 (m, 8 H), 2.00 (s, 3 H), 2.22 (m, 1 H), 2.52 (m, 1 H), 3.26 (s, 3 H), 4.68 (s, 0.9 H), and 6.20 (d, 0.9 H) [major epimer], 4.64 (d, 0.1 H) and 5.90 (d, 0.1 H) [minor epimer]. The NMR analysis shows that the major epimer and the minor epimer (ratio 88:12 determined by GLC analysis) may be the anti and endo-syn forms, respectively. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found (Major epimer): C, 61.86; H, 8.73. Found (minor epimer): C, 61.37; H, 8.26. **11**: IR (neat) 1730, 1360, 1220, 1010, 940 cm^{-1}; mass spectrum, *m/e* 214 (M^+, no peak), 183, 154, 140, 112 (base); ^1H NMR (CCl_4) δ 1.02–1.88 (m, 8 H), 2.02 (s, 3 H), 2.28 (m, 1 H), 2.42 (m, 1 H), 3.34 (s, 3 H), 4.08 (d, 0.7 H) and 4.84 (m, 0.7 H) [major epimer], 3.88 (d, 0.3 H) and 4.84 (m, 0.3 H) [minor epimer]. The NMR analysis shows that the major epimer and the minor epimer may be the trans and cis forms, respectively. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found (major epimer): C, 61.91; H, 8.69. Found (minor epimer): C, 61.52; H, 8.56. **12**: IR (neat) 1740, 1730, 1660, 1360, 1200, 1030 cm^{-1}; mass spectrum, *m/e* 214 (M^+), 170, 154, 131, 112 (base); ^1H NMR (CCl_4) δ 1.24–1.80 (m, 6 H), 2.10 (s, 3 H), 2.14 (m, 2 H), 2.22 (dd, J = 8, 6 Hz, 2 H), 3.60 (s, 3 H), 4.76 (dd, J = 8, 7 Hz, 1 H), 6.96 (d, J = 7 Hz, 1 H). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.39; H, 8.65.

Irradiation and Dark Reactions of 10 in Methanol. Irradiation and dark reactions of the isolated **10** (a mixture of two epimers) in methanol were undertaken and monitored by GLC analysis (columns A and C). For example, after irradiation for 2 h, 33% of **10** was converted into the dimethoxy homologue **9** and 24% of **10** was also converted into **9** in the dark reaction for 3 days.

Baeyer–Villiger Oxidation of 1a. The Baeyer–Villiger oxidation of 1a (400 mg, 1.69 mmol) was undertaken in $CHCl_3$ (50 mL), using *m*-chloroperbenzoic acid (MCPBA) as previously reported,[1] and gave 425 mg of two isomers (4:1) of the propellane lactones **13** and **14** in 98% total yield. The two isomers were separated by preparative GLC (columns E and F, column temperature 200 °C). The spectral data on the major isomer **13** were reported previously.[1] **14**: mp 87–88 °C; IR (KBr) 1775, 1735, 1220, 1085, 960 cm^{-1}; mass spectrum, *m/e* 252 (M^+), 208, 193, 148 (base); ^1H NMR (CCl_4) δ 1.00–1.92 (m, 16 H), 2.12 (s, 3 H), 6.38 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.01 (t), 20.79 (t and q), 21.12 (t), 21.83 (t), 28.13 (t), 28.85 (t), 30.08 (t), 36.39 (t), 42.56 (s), 45.87 (s), 96.48 (d), 169.32 (s), 178.35 (s). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.74; H, 7.86.

Registry No. 1a, 71987-75-2; 1b, 71987-76-3; **5a** (isomer 1), 77551-84-9; **5a** (isomer 2), 77551-85-0; **5b** (isomer 1), 77551-86-1; **5b** (isomer 2), 77551-87-2; **6** (isomer 1), 77551-88-3; **6** (isomer 2), 77551-89-4; **8**, 71987-81-0; **9** (isomer 1), 77551-90-7; **9** (isomer 2), 77551-91-8; **10** (isomer 1), 77551-92-9; **10** (isomer 2), 77610-84-5; **11** (isomer 1), 77551-93-0; **11** (isomer 2), 77551-94-1; **12**, 77551-95-2; **13**, 71987-80-9; **14**, 77551-96-3.

A New Synthesis of the Antitumor 6*H*-Pyrido[4,3-*b*]carbazole Alkaloid Ellipticine

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Several 6*H*-pyrido[4,3-*b*]carbazoles, notably ellipticine (1a) and related compounds, have aroused widespread interest owing to their significant antitumor activity.[1] Although many synthetic routes to them have been devised,[2] most of these methods are not satisfactory for accesss to a variety of derivatives, despite their apparent simplicity. Thus, general and facile synthetic approaches are still required to obtain analogues for pharmacological evaluation. We report our own efforts toward a short-step synthesis of ellipticine and 11-demethylellipticine starting from 3-ethyl- and 3-methylindole, respectively. Our proposed synthesis is based on C–C bond formation between the alkyl carbon at the 3-position of indole and the carbon at the 3-position of pyridine through an *o*-quinodimethane intermediate[3,4] formed via a [1,5] sigmatropic shift of a

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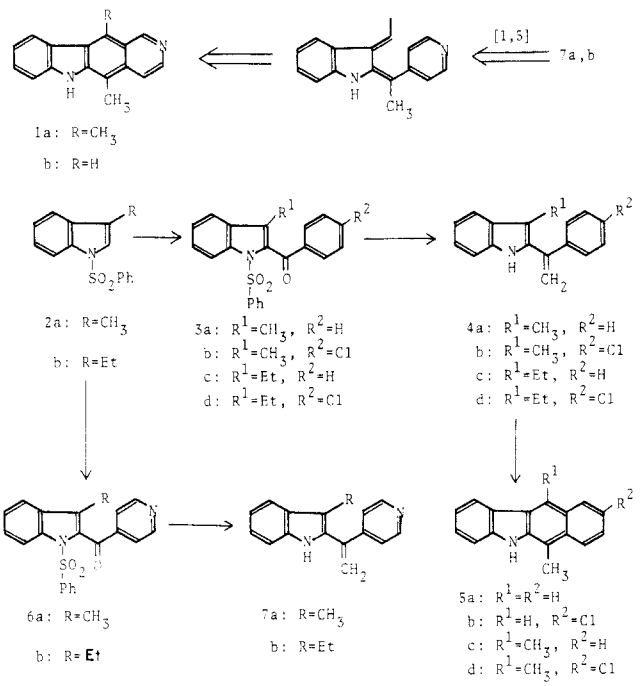
0022-3263/81/1946-2979$01.25/0

Scheme I



3-alkyl-2-vinylindole as shown in Scheme I.

As a model experiment, the ability of the 3-methyl- and 3-ethyl-2-(α-phenylvinyl)indoles **4a–d** to undergo cyclization to the benzo[*b*]carbazoles was examined. The indoles **4a–d** were conveniently prepared by the following procedure. Condensation of 1-(benzenesulfonyl)-3-methylindole (**2a**) [lithium diisopropylamide (LDA), tetrahydrofuran (THF), −78 °C, **2a**][5] with benzoic anhydride afforded the 2-benzoylindole **3a**. Methylenation of **3a** with methylenetriphenylphosphorane, followed by basic hydrolysis of the mixture,[6] gave **4a**. In a similar way, *p*-chlorobenzoylation of **2a** afforded **3b**, which was converted to **4b**. Furthermore, 1-(benzenesulfonyl)-3-ethylindole (**2b**) was also transformed to the 3-ethyl-2-(α-phenylvinyl)indoles **4c** and **4d** through **3c** and **3d**, respectively. Thermal cyclization of **4a** (490–500 °C, 3 min) gave **5a** (26%). Heating of **4b** at 490–500 °C gave **5b**. For the 3-ethyl analogues, cyclization proceeded at somewhat lower temperatures; **4c** (410 °C, 5 min) and **4d** (400 °C, 5 min) afforded **5c** (25%) and **5d** (24%), respectively.

This benzo[*b*]carbazole synthesis was applied to a preparation of ellipticine and 11-demethylellipticine. Treatment of the lithio salt of **2a** and **2b** with isonicotinic anhydride[7] gave the 2-isonicotinoyl derivatives **6a** (70.5%) and **6b** (74.6%), respectively. Methylenation of **6a** and **6b**, followed by hydrolysis of the reaction mixture as above, yielded **7a** (68.5%) and **7b** (66.7%), respectively. Thermal reaction of **7a** (500 °C, 3 min) afforded 11-demethylellipticine (**1b**).[8] Compound **7b** was heated at 500 °C for 7 min to give ellipticine (**1a**)[9] (50.2%), whose spectral and physical properties were in accord with those reported for the natural product.

Although the yields in the thermal cyclization of **4a–d** are somewhat low, the synthesis of ellipticine and 11-demethylellipticine was efficiently completed by heating **7a** and **7b** in high overall yield. Owing to the simplicity of the overall scheme, this procedure may have significant advantage over the other existing methods.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried and distilled from $LiAlH_4$ before use. ^1H NMR spectra were recorded on a Varian T-60 and JEOL PS-100 spectrometers with Me_4Si as an internal standard in $CDCl_3$ as a solvent. Mass spectra were determined on a Hitachi RMU-7L instrument.

1-(Benzenesulfonyl)-3-methylindole (2a). To a stirred solution of dimsylsodium [prepared from 8.4 g (0.21 mol) of NaH (60% dispersion in oil) and Me_2SO (85 mL)] was added a solution of 3-methylindole (26.2 g, 0.2 mol) in THF (130 mL) under ice cooling. After the stirring had been continued at room temperature for 1 h, to this solution was added a solution of benzenesulfonyl chloride (37 g, 0.21 mol) in THF (150 mL) under ice cooling. After being stirred at room temperature for 2 h, the mixture was poured into water and extracted with ethyl acetate. The extract was washed with water, dried over Na_2SO_4, and evaporated. The remaining residue was recrystallized from ethanol to give 50.5 g of **2a** (93.2%): mp 121–122.5 °C; mass spectrum, *m/e* 271 (M^+); ^1H NMR δ 2.28 (3 H, d, J = 2 Hz). Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.26; H, 4.77; N, 5.25.

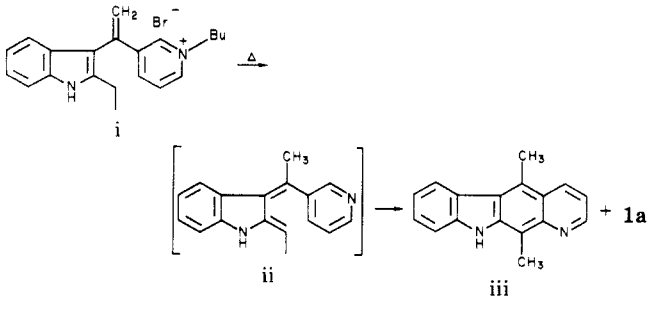
1-(Benzenesulfonyl)-3-ethylindole (2b). To a stirred solution of dimsylsodium [prepared from 8.4 g (0.21 mol) of NaH (60% dispersion in oil) and Me_2SO (85 mL)] was added a solution of 3-ethylindole (29 g, 0.2 mol) in THF (130 mL) under ice cooling. The mixture was stirred at room temperature for 1 h and then a solution of benzenesulfonyl chloride (37 g, 0.21 mol) in THF (150 mL) was added under ice cooling. The reaction mixture was worked up as above to give 47.7 g of **2b** (83.8%): mp 125–125.5 °C (ethanol); mass spectrum, *m/e* 285 (M^+); ^1H NMR δ 1.28 (3 H, t, J = 7 Hz), 2.66 (2 H, q, J = 7 Hz). Anal. Calcd for $C_{16}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.61; H, 5.39; N, 4.79.

General Procedure for the Preparation of 3 and 6. To a solution of LDA [prepared from diisopropylamine (3.89 g, 38.5 mmol) and *n*-BuLi (25.7 mL of 1.5 M hexane solution, 38.5 mmol) in THF] was added a solution of **2** (35 mmol) in THF (60 mL) under ice cooling. The mixture was stirred at room temperature for 1 h and then a solution of acid anhydride (42 mmol) in THF (60–100 mL) was added at −78 °C. The mixture was gradually warmed to room temperature. After the stirring had been continued at the same temperature for 10–14 h, the mixture was poured into water and extracted with ethyl acetate. The extract was washed with water, dried over Na_2SO_4, and evaporated to give **3** (and **6**). Yields and physical properties are as follows.

3a: 50% yield; mp 139–140 °C; ^1H NMR δ 2.14 (3 H, s). Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.27; H, 4.49; N, 3.44.

3b: 75% yield; mp 131–132 °C; ^1H NMR δ 2.17 (3 H, s); mass spectrum, *m/e* 411 (M^+ + 2), 409 (M^+). Anal. Calcd for

(4) Thermolysis of the 2-ethyl-3-[α-(3-pyridyl)vinyl]indole i gave ellipticine accompanied with formation of the 10*H*-pyrido[2,3-*b*]carbazole iii as a byproduct[3a] through cyclization of *o*-quinodimethane intermediate ii.



(5) Cf. R. J. Sundberg and H. F. Russel, *J. Org. Chem.*, **38**, 3324 (1973). This method was improved by using LDA instead of *t*-BuLi.

(6) Although the benzenesulfonyl group was removed during methylenylation, since small amounts remained without cleavage, the reaction mixture was subjected to hydrolysis without separation.

(7) A. W. Shrecker and P. W. Maurry, *J. Am. Chem. Soc.*, **76**, 5803 (1954).

(8) F. Le Goffic, A. Gouyette, and A. Ahonol, *Tetrahedron*, **29**, 3357 (1973).

(9) K. N. Kilminster and M. Sainsbury, *J. Chem. Soc., Perkin Trans. 1*, 2264 (1972).

$C_{22}H_{16}ClNO_3S$: C, 64.46; H, 3.93; N, 3.42. Found: C, 64.22; H, 3.88; N, 3.46.

3c: 76.5% yield; mp 143–144 °C; mass spectrum, *m/e* 389 (M^+); ^1H NMR δ 1.09 (3 H, t, *J* = 7 Hz), 2.62 (2 H, q, *J* = 7 Hz). Anal. Calcd for $C_{23}H_{19}NO_3S$: C, 70.93; H, 4.92; N, 3.60. Found: C, 70.96; H, 4.83; N, 3.38.

3d: 80.5% yield; mp 139–141 °C; mass spectrum, *m/e* 425 (M^+ + 2), 423 (M^+); ^1H NMR δ 1.10 (3 H, t, *J* = 8 Hz), 2.62 (2 H, t, *J* = 8 Hz). Anal. Calcd for $C_{23}H_{18}ClNO_3S$: C, 65.16; H, 3.80; N, 3.30. Found: C, 65.03; H, 4.07; N, 3.19.

6a: 70.5% yield; mp 159–160 °C; mass spectrum, *m/e* 376 (M^+); ^1H NMR δ 2.18 (3 H, s). Anal. Calcd for $C_{21}H_{16}N_2O_3S$: C, 67.00; H, 4.28; N, 7.49. Found: C, 66.97; H, 4.18; N, 7.58.

6b: 74.6% yield; mp 161–163 °C; mass spectrum, *m/e* 390 (M^+); ^1H NMR δ 1.19 (3 H, t, *J* = 7.5 Hz), 2.74 (2 H, q, *J* = 7.5 Hz). Anal. Calcd for $C_{22}H_{18}N_2O_3S$: C, 67.67; H, 4.65; N, 7.18. Found: C, 67.48; H, 4.56; N, 7.08.

General Procedure for the Preparation of 4 and 7. To a stirred solution of methylenetriphenylphosphorane [prepared from methyltriphenylphosphonium bromide (5.71 g, 16 mmol) and *n*-BuLi (10.67 mL of 1.5 M hexane solution, 16 mmol) in THF under ice cooling] was added a solution of **3** (or **6**) (13.6 mmol) in THF (30–60 mL) under ice cooling. The mixture was warmed to room temperature and kept under stirring for 14 h at the same temperature. The mixture was poured into water and extracted with ethyl acetate. The extract was washed with water, dried over Na_2SO_4, and evaporated. A mixture of the remaining residue, 10% NaOH (30 mL), and ethanol (100 mL) was refluxed for 14 h. The solvent was evaporated and the resulting residue was extracted with ethyl acetate. The extract was washed with water, dried over Na_2SO_4, and evaporated to give **4** (or **7**). Yields and physical properties are as follows.

4a: 74.5% yield; mp 73–75 °C; ^1H NMR δ 2.17 (3 H, s), 5.41 (1 H, d, *J* = 1.6 Hz), 5.59 (1 H, d, *J* = 1.6 Hz). Anal. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00. Found: C, 87.36; H, 6.31; N, 5.90.

4b: 71.5% yield; mp 102–104 °C; mass spectrum, *m/e* 269 (M^+ + 2), 267 (M^+); ^1H NMR δ 2.17 (3 H, s), 5.53 (1 H, s), 5.68 (1 H, s). Anal. Calcd for $C_{17}H_{14}ClN$: C, 76.25; H, 5.27; H, 5.27; N, 5.23. Found: C, 76.39; H, 5.39; N, 5.27.

4c: 72% yield; mp 115–117 °C; mass spectrum, *m/e* 247 (M^+); ^1H NMR δ 1.17 (3 H, t, *J* = 7 Hz), 2.68 (2 H, q, *J* = 7 Hz), 5.42 (1 H, d, *J* = 1.5 Hz), 5.61 (1 H, d, *J* = 1.5 Hz). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.17; H, 6.87; N, 5.90.

4d: 69.5% yield; mp 139–140 °C; mass spectrum, *m/e* 283 (M^+ + 2), 281 (M^+); ^1H NMR δ 1.17 (3 H, t, *J* = 7 Hz), 2.68 (2 H, q, *J* = 7 Hz), 5.44 (1 H, d, *J* = 1.5 Hz), 5.64 (1 H, d, *J* = 1.5 Hz). Anal. Calcd for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.56; H, 5.72; N, 4.70.

7a: 68.5% yield; mp 192–194 °C; mass spectrum, *m/e* 234 (M^+); ^1H NMR δ 2.18 (3 H, s), 5.74 (1 H, s), 5.58 (1 H, s). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.14; H, 5.96; N, 11.90.

7b: 66.7% yield; mp 140–142 °C; mass spectrum, *m/e* 248 (M^+); ^1H NMR δ 1.23 (3 H, t, *J* = 7 Hz), 2.68 (2 H, q, *J* = 7 Hz), 5.60 (1 H, s), 5.78 (1 H, s). Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 81.98; H, 6.36; N, 10.99.

6-Methyl-5*H*-benzo[*b*]carbazole (5a). **4a** (100 mg) was heated at 490–510 °C for 3 min and the reaction mixture was purified by preparative TLC on silica gel. Development with 15% ethyl acetate–*n*-hexane gave **5a** (25.8 mg, 26.0%): mp 210–211 °C; ^1H NMR δ 2.37 (3 H, s); mass spectrum, *m/e* 231.1032 (M^+) (calcd for $C_{17}H_{13}N$ 231.1047).

9-Chloro-6-methyl-5*H*-benzo[*b*]carbazole (5b). **4b** (100 mg) was heated at 490–500 °C for 3 min and the mixture was purified by preparative TLC on silica gel. Development with 10% ethyl acetate–*n*-hexane gave **5b** (26.1 mg, 26.3%): mp 150–152 °C; ^1H NMR δ 2.73 (3 H, s); mass spectrum, *m/e* 265.0635 (M^+) (calcd for $C_{17}H_{12}ClN$ 265.0656).

6,11-Dimethyl-5*H*-benzo[*b*]carbazole (5c). **4c** (100 mg) was heated at 410–420 °C for 5 min. The reaction mixture was purified by preparative TLC on silica gel. Development with 15% ethyl acetate–*n*-hexane gave **5c** (24.8 mg, 25%): mp 209–211 °C; ^1H NMR δ 2.77 (3 H, s), 3.19 (3 H, s); mass spectrum, *m/e* 245.1185 (M^+) (calcd for $C_{18}H_{15}N$ 245.1167).

9-Chloro-6,11-dimethyl-5*H*-benzo[*b*]carbazole (5d). **4d** (100 mg) was heated at 400 °C for 5 min and the reaction mixture was purified by preparative TLC on silica gel. Development with 15% ethyl acetate–*n*-hexane gave **5d** (23.8 mg, 24.0%) as an amorphous solid: ^1H NMR δ 2.77 (3 H, s), 3.14 (3 H, s); mass spectrum, *m/e* 279.0781 (M^+) (calcd for $C_{18}H_{14}ClN$ 279.0760).

5-Methylpyrido[4,3-*b*]carbazole (1b). **7a** (100 mg) was heated at 500 °C for 3 min and the reaction mixture was purified by preparative TLC on silica gel. Development with 10% methanol–chloroform gave **1b** (59.9 mg, 60.4%): mp 290–291 °C dec (lit.[8] mp 291–292 °C dec); ^1H NMR δ 2.73 (3 H, s); mass spectrum, *m/e* 232.1020 (M^+) (calcd for $C_{16}H_{12}N_2$ 232.1001).

Ellipticine (1a). **7a** (100 mg) was heated at 500 °C for 7 min and the reaction mixture was purified by preparative TLC on silica gel. Development with 5% methanol–chloroform afforded ellipticine (49.8 mg, 50.2%): mp 309–312 °C (lit.[9] mp 309–312 °C); ^1H NMR δ 2.71 (3 H, s), 3.22 (3 H, s); mass spectrum, *m/e* 246.1134 (M^+) (calcd for $C_{17}H_{14}N$ 246.1113).

Registry No. **1a**, 519-23-3; **1b**, 4238-66-8; **2a**, 58550-84-8; **2b**, 77507-52-9; **3a**, 77507-53-0; **3b**, 77507-54-1; **3c**, 77507-55-2; **3d**, 77507-56-3; **4a**, 77507-57-4; **4b**, 77507-58-5; **4c**, 77507-59-6; **4d**, 77507-60-9; **5a**, 77507-61-0; **5b**, 77507-62-1; **5c**, 73326-97-3; **5d**, 77507-63-2; **6a**, 77507-64-3; **6b**, 77507-65-4; **7a**, 77507-66-5; **7b**, 77507-67-6; 3-methylindole, 83-34-1; 3-ethylindole, 1484-19-1; benzoic anhydride, 93-97-0; *p*-chlorobenzoic anhydride, 790-41-0; isonicotinic anhydride, 7082-71-5.

Preparation of Formaldehyde and Acetaldehyde Acetals[1]

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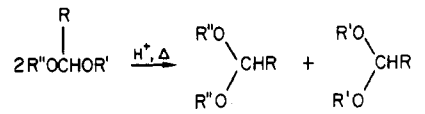
Acetals are useful as protecting groups for both carbonyl compounds and alcohols.[2] The preparation of symmetrical acetals derived from formaldehyde or acetaldehyde is not always easy.[3] We report a new method for accomplishing this goal based on an acetal interchange reaction with loss of a volatile symmetrical acetal (eq 1).



(1)

There are many examples of acetal interchange between an alcohol or diol and an acetal;[4a] however, there are few cases of acetal–acetal interchange[4b-d] even though this seems mechanistically straightforward. Consequently, in order to test the viability of the reaction of eq 1, a variety of methoxymethyl (MOM)[5] and ethoxyethyl (EE)[6] ethers were prepared and allowed to react with acid under anhydrous conditions.

Indeed, good yields of formaldehyde[7] and acetaldehyde acetals were obtained from MOM and EE ethers, respectively (see Tables I and II). For example, when the MOM ether of 1-hexanol is allowed to react with a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in refluxing benzene for 36 h, a 78% isolated yield of the formaldehyde acetal of 1-hexanol is obtained.[8,9] Even MOM ethers derived from acid-sensitive alcohols such as citronellol and nopol give the formaldehyde acetals but the weaker acid pyridinium *p*-toluenesulfonate[10] must be used. Ethoxy-

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