by the subsequent reduction of available enono-lactone. A similar transfer hydrogenation has recently been observed with D-glucose and D-mannose over Pt, Pd, and Rh castalysts.[10]

L-Gulono-1,4-lactone has been prepared by the catalytic reduction of D-glucurono-6,3-lactone,[8] and D-mannono-1,4-lactone is available via either bromine or catalytic air oxidation of D-mannose.[9] As both L-ascorbic acid and erythorbic acid are items of commerce, their stereoselective reduction represents a convenient and economic alternative for the preparation of L-gulono- and D-mannono-1,4-lactone lactones.[11-13]

Experimental Section

L-Gulono-1,4-lactone (3). A solution of 23.1 g (0.13 mol) of L-ascorbic acid in 170 mL of H_2O was hydrogenated over 2.2 g of 10% Pd/C (Lot 21,005, Engelhard) in a Parr hydrogenator at 50 °C and 50 psi hydrogen pressure for 24 h. The catalyst was removed by filtration and the water removed in vacuo to afford 23.2 g (0.13 mol, 99%) of a white crystalline solid which was shown to be homogeneous by GLC and ^{13}C NMR analysis. On recrystallization of a sample from methanol–ethyl acetate, material which was identical with authentic L-gulono-1,4-lactone was obtained: mp 182–183.5 °C; mmp 182–184 °C; mp of authentic material 183.5–185.2 °C (lit.[8] mp 180–181 °C); $[\alpha]^{23}_D$ +55.3° (H_2O); $[\alpha]^{23}_D$ of authentic material +55.2° (H_2O);[8] IR (KBr) 1770 cm^{-1}; NMR (Me_2SO-d_6) δ 5.80 (d, 1, OH), 5.30 (d, 1, OH), 4.95 (d, 1, OH), 4.65 (t, 1, OH), 4.45–4.07 (m, 3), 4.00–3.35 (m, 3); ^{13}C NMR (Me_2SO-d_6) δ 177.8 (s), 81.3 (d), 70.8 (d), 70.1 (d), 69.6 (d), 61.6 (t).

D-Mannono-1,4-lactone (4). The above procedure was repeated, using 10 g (0.057 mol) of D-erythorbic acid (2) in 100 mL of H_2O at 50 °C, 7.0 g of 5% Pd/C, and 50 psi hydrogen pressure for 6h. Isolation as above afforded an oil which crystallized on standing and was shown to be >90% pure by GLC[7] analysis of a persilylated derivative and by ^{13}C NMR analysis of a neutralized sample. Crystallization from methanol–ethyl acetate afforded 4.8 g (50%) of the pure γ-lactone 4: mp 151–151.5 °C (lit.[9] mp 151 °C); $[\alpha]_D^{23}$ 50.3° (H_2O) [lit.[9] $[\alpha]^{23}_D$ 51.3° (H_2O)]; ^{13}C NMR (Me_2SO-d_6) δ 176.3 (s), 78.2 (d), 71.0 (d), 69.4 (d), 68.0 (d), 63.1 (t).

An additional 2.4 g of crystalline lactone was obtained from the mother liquor after concentration for a total yield of 71%.

Registry No. 1, 50-81-7; 2, 89-65-6; 3, 1128-23-0; 4, 26301-79-1.

(10) de Wit, G.; de Vlieger, J. J.; Kock-van Dalon, A. C.; Kieboom, A. P. G.; van Bekkum, H. *Tetrahedron Lett.* **1978**, 1327. Descotes, G.; Sabadie, J.; Sinore, D. *Ibid.* **1978**, 3351.

(11) These materials are now readily available and reasonably inexpensive chiral starting materials for use in synthesis. For a review on the chemistry of gulono-1,4-lactone, see: Crawford, T. C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *38*, 287.

(12) See ref 2b for an example in which ascorbic acid was used as the source of subsequent chirality.

(13) For an example in which erythorbic acid was used as the source of subsequent chirality, see: Cohen, N.; Banner, B. L.; Lopresti, R. J. *Tetrahedron Lett.* **1980**, 4163.

Oxacarbene Intermediates Generated by the Photolysis of 12-Acyloxy[4.4.2]propellan-11-ones

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Recently, the chemistry of propellanes has attracted much attention, especially in view of structure–reactivity relationships,[1] and we have been deeply interested in these relationships on [*m.n.*2]propellane derivatives.[2] In this connection, we have recently reported on the novel dimerization of oxacarbene intermediates generated by the photolysis of the cyclobutanone rings incorporated into 12-acyloxy[4.4.2]propellan-11-ones (**1a,b**), in an aprotic solvent[2i] (Scheme I).

In these reactions, the most significant feature is the regiospecific ring expansions via primary α-cleavages[3] to give the oxacarbene intermediates (**2a,b**) exclusively, judging from the structure of the obtainable oxacarbene dimers (**3a,b**). An essential question is whether or not the formation of the other oxacarbene intermediates (**4a,b**) is inhibited, probably by the electron-withdrawing α-acyloxyl substituent, in analogy with the cases of some cyclobutanones carrying the α-electron-withdrawing substituent, such as dichloro- and trifluoromethyl groups.[4] In order to solve the above problem, the present work has been done. The photoreaction of **1a,b** was examined in methanol, which is a good trapping agent for oxacarbene intermediates. Irradiation of **1a,b** in methanol (0.01 M) in a degassed Pyrex tube at 20 °C with a high-pressure Hg lamp gave the ring-expanded acetals (**5a,b**, Scheme II) along with a new type of ring-expanded 11,13-dimethoxy-12-oxatricyclo[4.4.3.$0^{1,6}$]tridecane (**6**). Significantly, the formation of acetic acid or propionic acid was also observed, which was nearly equivalent to the quantity of **6**. But, we have been unable to obtain any evidence for the formation of the ring-expanded acetals (**7a,b**) via **4a,b**.

In order to obtain instructive information about the relation between **6** and **7a,b**, similar irradiation of *endo*-8-acetoxybicyclo[4.2.0]octan-7-one (**8**) was undertaken[5] (Scheme III). Fortunately, three kinds of ring-expanded acetals (**9**, **10**, and **11**) were formed in good yields together with the cycloeliminated product **12** and acetic acid. With the lapse of reaction time, the quantity of **9** (a mixture of two epimers) increases gradually with decreasing **10** (a mixture of two epimers).[6] In addition, both irradiation and dark reactions of the isolated acetal **10** proceeded appreciably on irradiation, but slowly in the dark reaction. From the above facts, it is reasonable to assume that the generation of **4a,b** via a photochemical ring expansion of **1a,b** takes place smoothly to result in labile **7a,b** in methanol, followed by rapid replacement of an acyloxyl group of **7a,b** by a methoxyl group to give **6** as an isolable product. In an aprotic solvent, the dimerization of **4a,b** might be suppressed, because they have greatly hindered carbene sites owing to the steric requirement of the con-

(1) For a review see: Gisnburg, D. "Propellanes, Structure and Reactions"; Verlag Chemie: Weinheim/Bergstr., Germany, 1975. See also: Paquette, L. A.; Photis, J. M.; Micheli, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 7899 and references cited therein.

(2) (a) Kunai, A.; Yorihiro, K.; Hirata, T.; Odaira, Y. *Tetrahedron* **1973**, *29*, 1679. (b) Kunai, A.; Ishii, T.; Odaira, Y. *Chem. Lett.* **1974**, 315. (c) Tobe, Y.; Omura, H.; Kunai, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 319. (d) Tobe, Y.; Doi, A.; Kunai, A.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1977**, *42*, 2523. (e) Tobe, Y.; Kimura, K.; Odaira, Y. *Ibid.* **1978**, *43*, 3776. (f) Tobe, Y.; Hoshino, T.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *Ibid.* **1978**, *43*, 4334. (g) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 639. (h) Tobe, Y.; Kimura K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 639. (i) Fukuda, Y.; Negoro, T.; Tobe, Y.; Kimura, K.; Odaira, Y. *Ibid.* **1980**, *45*, 177. (j) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *Ibid.* **1980**, *45*, 637.

(3) The addition of 1,3-pentadiene has no influence on the present photoreaction. However, this result does not always mean that α-cleavage proceeds via the singlet state.

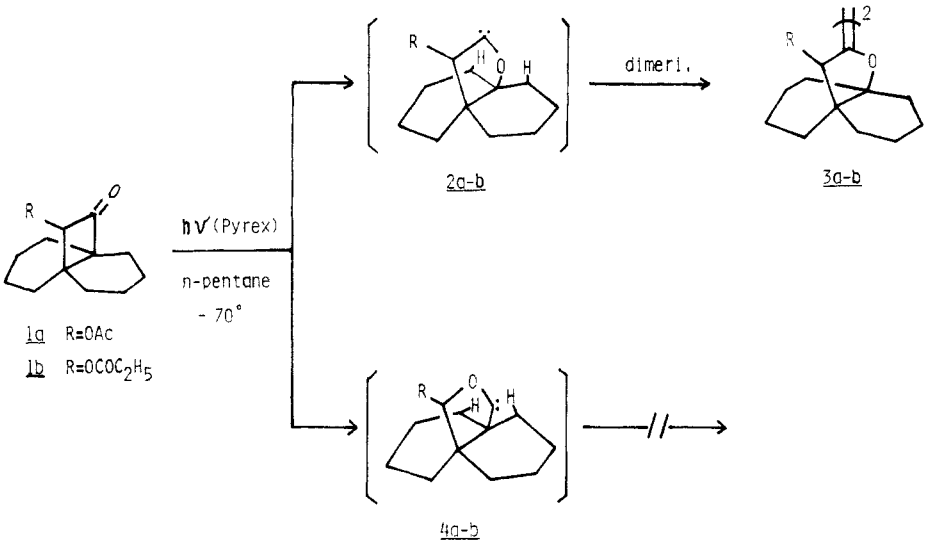
(4) (a) Morton, D. R.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3947. (b) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D. R.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92.

(5) Quantum yields for the disappearance of these ketones in methanol at 20 °C are observed as follows: **1a**, 0.08; **1b**, 0.06; **8**, 0.23.

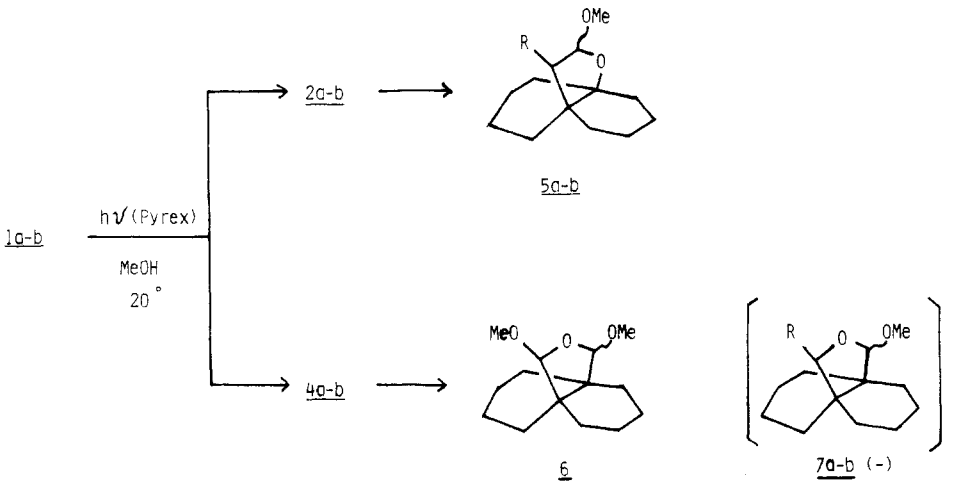
(6) For example, irradiation of **8** gave the following products at the indicated times: 1 h, **9** (30%), **10** (33%), **11** (19%), and **12** (11%); for 2 h, **9** (38%) and **10** (23%); for 3 h, **9** (45%) and **10** (17%); for 4 h, **9** (49%) and **10** (14%).

0022-3263/81/1946-2977$01.25/0

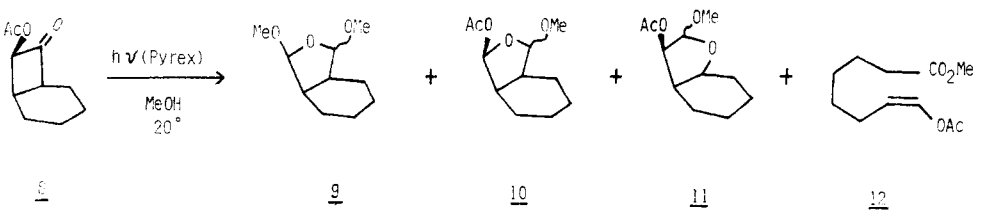
Scheme I



Scheme II



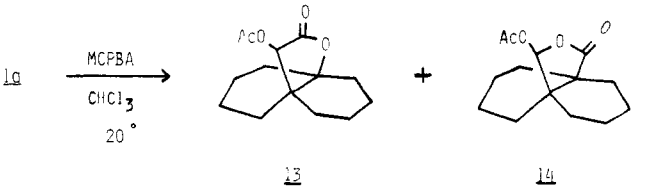
Scheme III



strained propellane ring system and the bulky acyloxyl substituents. Consequently, **4a,b** may revert to the starting propellanones **1a,b** without formation of any product.[7]

Furthermore, the reaction of **1a** with *m*-chloroperbenzoic acid in chloroform was attempted, paying attention to the similarity in migratory regiospecificity in the Baeyer–Villiger oxidation.[8] Interestingly, two propellane lactones (**13** and **14**) in a ratio of 4:1 were obtained quantitatively (Scheme IV).

Scheme IV



Experimental Section

General Methods. Melting points were measured in a sealed tube and are uncorrected. Infrared spectra were recorded on a JASCO IR-G spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on JEOL JNM-PS-100 and JEOL JNM-FX60S spectrometers, respectively, using CCl_4 or $CDCl_3$ as a solvent, and Me_4Si as an internal standard. Mass spectra were determined with a Hitachi RMU-6E spectrometer. UV spectra were recorded on a Hitachi 356 spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph (1 m × 3 mm columns: A, 10% FFAP; B, 5% SE-30; C, 5% OV-17), and preparative GLC separation was undertaken on a Varian Aerograph 90-P or 920 gas chromatograph (5 ft × 0.25 in. columns: D, 10% FFAP; E, 5% SE-30; F, 5% OV-17).

(7) Morton, D. R.; Turro, N. J. *Adv. Photochem.* **1974**, *9*, 197.
(8) Miller, R. D.; Dolce, D. L.; Merritt, V. Y. *Tetrahedron Lett.* **1974**, 3347.

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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