a nitrogen atmosphere was added 1.88 mL (2.54 mmol, 1.35 M solution) of *n*-butyllithium. The resultant deep red solution was stirred 30 min at 0 °C and cooled to -78 °C. After 5 min bis-(silyloxy) ketone **7** (507.2 mg, 1.62 mmol) in 3 mL of THF was added over a period of 5 min. The red mixture was stirred 2 h, and then 675.5 mg (3.67 mmol) of aldehyde **12a** in 1 mL of THF was added over a 50-s period. The color of the reaction mixture changed to orange-brown; stirring was continued for 2 min, and then saturated ammonium chloride (2 mL) was added. The mixture was diluted with 3 mL of water and extracted thoroughly with ether. The combined organic extracts were washed with water and dried. Removal of the solvent in vacuo gave 767 mg of yellow oil which was employed in the next step without purification.

To a solution of 5.6 mL (68.6 mmol) of pyridine in 65 mL of methylene chloride was added 3.25 g (32.5 mmol) of chromium trioxide (CrO_3). After the mixture was stirred 20 min at room temperature under a nitrogen atmosphere, the above hydroxy ketone (767 mg) in 5 mL of CH_2Cl_2 was then added and the stirring continued for 3 h. The organic layer was decanted from the dark residue, and the latter was washed with ether. A conventional workup and removal of solvent in vacuo gave 585 mg of a light brown oil, which was taken up in 40 mL of THF with 20 mL of 5% aqueous HCl and stirred at room temperature under a nitrogen atmosphere for 5 days. The mixture was then saturated with solid NaCl and diluted with ether. The organic layer was washed and dried, and the solvent was removed in vacuo to give 355 mg of a viscous yellow oil, which was purified via medium-pressure liquid chromatography [hexane/ethyl acetate (2:1)] to afford 241.3 mg (45% from **7**) of **14c** as a pale yellow oil: IR ($CHCl_3$) 2980, 2930 (s), 1700, 1630 (s), 1200, 1300 (br), 1040 (s), 920, 840 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.12 (s, 6 H), 1.20 (t, J = 7.25 Hz, 3 H), 1.66 (s, 3 H), 2.10 (m, 1 H), 2.35 (m, 1 H), 2.51 (d, J = 10.25 Hz, 2 H), 2.81 (m, 2 H), 4.20 (q, J = 7.25 Hz, 2 H), 5.75 (d, J = 16.2 Hz, 1 H), 6.94 (d, J = 16.2 Hz, 1 H), 7.20 (t, J = 1.5 Hz, 1 H), 9.61 (s, 1 H); mass spectrum, m/e 332.1615 (M^+; calcd for $C_{19}H_{24}O_5$ 332.1693).

Preparation of Spirofuranone 14b. To a mixture of 4-mL of methanol and 290 mg (0.873 mmol) of spirofuranone **14c** under a nitrogen atmosphere at -23 °C (CCl_4/CO_2) was added 33.78 mg (0.893 mmol) of sodium borohydride. The mixture was stirred for 15 min at 23 °C before the pH was adjusted to 7 with dilute aqueous HCl. The mixture was extracted extensively with ether. The organic material was then dried and concentrated in vacuo to afford 275.3 mg of a viscous colorless oil which was purified via medium-pressure liquid chromatography [hexane/ethyl acetate (2:1)] to give 231.3 mg (79.5%) of **14b** as a colorless oil: IR ($CHCl_3$) 3450, 3400 (br), 2980, 2930 (s), 1700, 1625 (s), 1480 (m), 1200 (br), 1040 (s) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 6 H), 1.22 (t, J = 7.8 Hz, 3 H), 1.72 (s, 3 H), 2.10 (m, 1 H), 2.35 (m, 1 H), 2.60 (br m, 4 H), 3.96 (br d, J = 2 Hz, 2 H), 4.22 (q, J = 7.8 Hz, 2 H), 5.75 (d, J = 16.3 Hz, 1 H), 6.20 (br s, 1 H), 7.03 (d, J = 16.3 Hz, 1 H); mass spectrum, m/e 334.1746 (M^+; calcd for $C_{19}H_{26}O_5$ 334.1781).

Preparation of Spirofuranone 14a. To a solution of 8 mL of MeOH, 2 mL of H_2O, and 250 mg (0.748 mmol) of spirofuranone **14b** at room temperature was added a concentrated aqueous K_2CO_3 solution, adjusting the pH of the reaction mixture to 10.5–11.0. The mixture was stirred 12 h at room temperature under nitrogen and then diluted with 5 mL of H_2O, and the pH was adjusted to 7. The mixture was extracted extensively with ether, and the organic fraction was dried and concentrated in vacuo to afford 231.3 mg (91.5%) of **14a**: IR ($CHCl_3$) 3450–2500 (br) 2980–2930 (s) 1700 (s), 1450 (br), 1080 (m), 850 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 3 H), 1.20 (s, 3 H) 1.65 (s, 3 H), 2.1 (m, 1 H), 2.35 (m, 2 H), 2.55 (m, 2 H), 2.70 (m, 1 H), 3.59 (br s, 1 H), 3.95 (m, 2 H), 5.18 (br s, 1 H), 5.75 (d, J = 16.2 Hz, 1 H), 6.10 (s, 1 H), 6.50 (d, J = 16.2 Hz, 1 H).

Preparation of *trans*-Normethyljatropholactone (3). To a solution consisting of 654 mg (2.55 mmol) of 1-methyl-2-chloropyridinium iodide in 65 mL of acetonitrile held at reflux was continuously and uniformly added a solution of 195 mg (0.64 mmol) of spirofuranone **14a** and 0.72 mL (5.12 mmol) of triethylamine in 55 mL of dry acetonitrile over a period of 9 h. After one additional hour at reflux evaporation of the solvent under reduced pressure followed via silica gel column chromatography afforded 138 mg of a viscous colorless oil that crystallized upon standing. Recrystallization [hexane/ethyl ether (10:1)] gave 104.0 mg (56.8%) of **3** as a white crystalline solid: mp 168–170 °C; IR 2980, 2930 (s), 1700, 1630 (s), 1460 (m), 1210 (m), 720 (br) cm^{-1}; NMR (250 MHz, $CDCL_3$) δ 1.21 (s, 3 H), 1.34 (s, 3 H), 1.75 (s, 3 H), 1.15 (m, 1 H) 2.28 (m, 1 H), 2.33 (d, J = 13 Hz, 1 H), 2.60 (m, 2 H), 2.80 (d, J = 13 Hz, 1 H), 4.31 (d, J = 14 Hz, 1 H), 4.75 (m, 1 H), 5.95 (d, J = 16.1 Hz, 1 H), 6.50 (d, J = 16.1 Hz, 1 H) 6.51 (t, J = 1.5 Hz, 1 H); mass spectrum, m/e 288.1359 (M^+; calcd for $C_{17}H_{20}O_4$ 288.1362).

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health (National Cancer Institute) through Grant Ca-22807. In addition, we thank Mr. S. T. Bella of the Rockefeller University for the microanalyses and Drs. G. Furst and T. Terwilliger of the University of Pennsylvania Spectroscopic Service Centers for aid in recording and interpertation of the high-field NMR and mass spectra, respectively.

Registry No. **2**, 82351-40-4; **3**, 82398-40-1; **5**, 82351-41-5; **6a**, 82351-42-6; **6b**, 82351-43-7; **6c**, 82351-44-8; **7**, 76445-18-6; **8**, 82351-45-9; **10a**, 67099-40-5; **10b**, 67099-41-6; **10c**, 82351-46-0; **10d**, 82351-47-1; **12a**, 82351-48-2; **12b**, 82351-49-3; **12c**, 82351-50-6; **14a**, 82351-51-7; **14b**, 82351-52-8; **14c**, 82351-53-9.

Cobalt-Mediated [2 + 2 + 2] Cycloadditions En Route to Natural Products: A Novel Total Synthesis of Steroids via the One-Step Construction of the B,C,D Framework from an A-Ring Precursor

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The first application of the cobalt-mediated intramolecular cyclization of α,δ,ω-diynenes to annulated cyclohexadienes in natural product synthesis is described by demonstrating its feasibility in a versatile and efficient steroid synthesis, including a new total synthesis of the Torgov intermediate, 3-methoxyestra-1,3,5(10),8,14-pentaen-17-one, via a new steroid, 3-methoxyestra-1,3,5(10),8(14),9-pentaen-17-one ethylene ketal. Several model reactions en route to *B*-homo-7-oxa steroids allow the delineation of some stereochemical details of the transition-metal-catalyzed [2 + 2 + 2] cycloaddition reaction.

We have recently developed methodology based on cobalt-mediated [2 + 2 + 2] cycloadditions of unsaturated substrates which yields annulated and complexed five-[1] and six-membered[2] rings. We believe that this strategy

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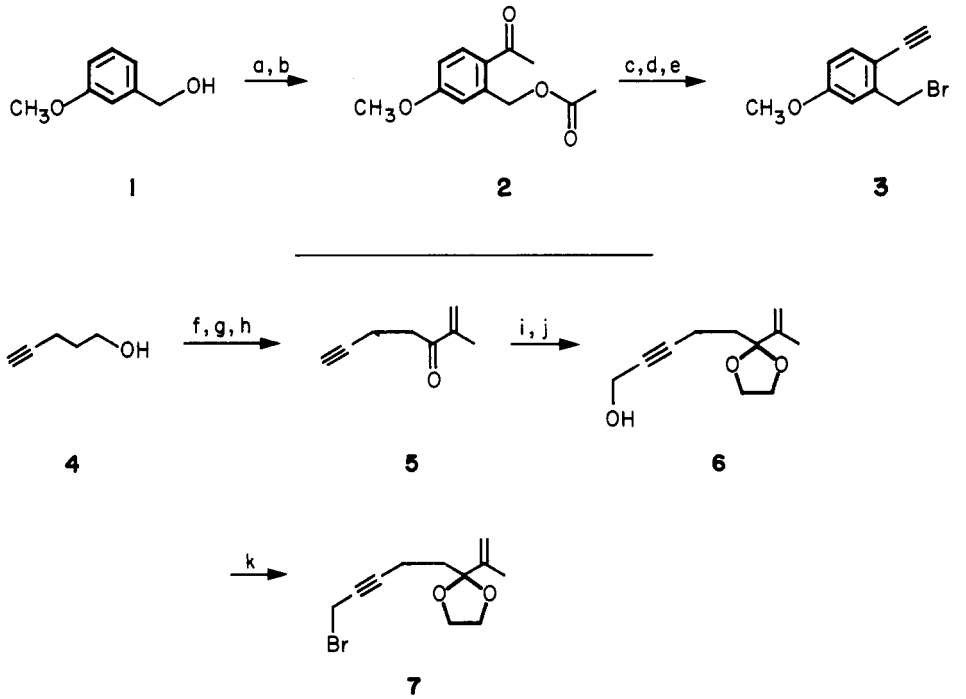
Scheme I. Synthesis of Intermediates 3 and 7[a]



[a] (a) Ac_2O, py, 21 °C, 12 h, 100%; (b) AcCl, CS_2, 0 °C, 68%; (c) PCl_5-$POCl_3$, 40–50 °C, 2 h, 92%; (d) $NaNH_2$, HMPA, THF, 40–50 °C, 88%; (e) $P(C_6H_5)_3 \cdot Br_2$, collidine, CH_2Cl_2, 21 °C, 5 h, 94%; (f) PCC, NaOAc, CH_2Cl_2, (g) 2-propenylmagnesium bromide, THF, 85% overall; (h) PCC, NaOAc, CH_2Cl_2, 80%; (i) $(CH_2OH)_2$, C_6H_6, *p*-TsOH, 52%; (j) *n*-butyllithium, *p*-formaldehyde, THF, −78 to 21 °C, 94%; (k) $P(C_6H_5)_3 \cdot Br_2$, collidine, CH_2Cl_2, 0 °C, 15 min, 54%.

has strong potential as a versatile alternative to the more conventional [4 + 2] (Diels–Alder)[3] or [3 + 2][4] approach to polycycles in organic synthesis. This report describes a novel total synthesis of the steroid nucleus[5] in which the advantage of the method becomes apparent through its ability to simultaneously construct the B,C,D framework attached to the A ring in one step starting from a monocyclic A-ring precursor. We chose this target because steroids continue to command synthetic attention as moderately complex targets with which to demonstrate the utility of new synthetic methods and strategies,[6] and because of their varied physiological activity, making the development of alternative syntheses an attractive proposition.[7]

A convergent approach to the crucial intermediates **3** and **7** is shown in Scheme I.[8] Alcohol **1** was protected and then subjected to Friedel–Crafts acylation, generating mainly the *p*-methoxyacetophenone **2** (mp 69.5–71 °C), contaminated by only small quantities of the ortho isomer. Conversion to **3** (mp 56–58 °C) followed standard procedures via the intermediacy of the *o*-ethynylbenzyl alcohol (mp 71–72.5 °C). Concomitantly, 4-pentynol (**4**) was first

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(4) See: J. J. Tufariello, *Acc. Chem. Res.*, **12**, 396 (1979), and the references therein.

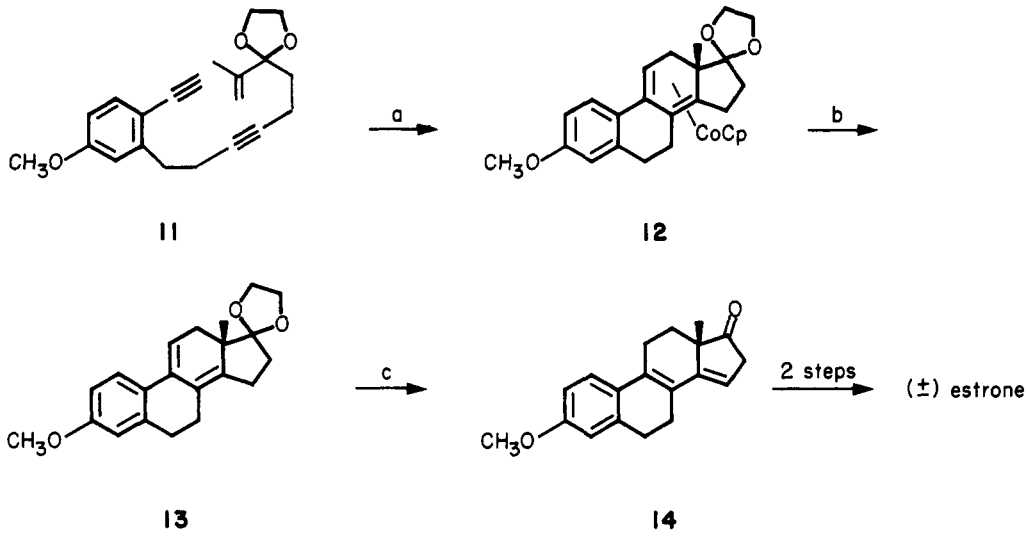
(5) This is to our knowledge the first successful A → BCD approach to A-ring aromatic steroids: A. A. Akhrem and Y. A. Titov, "Total Steroid Synthesis", Plenum Press, New York, 1970; R. T. Blickenstaff, A. C. Ghosh, and G. C. Wolf, "Total Synthesis of Steroids", Academic Press, New York, 1974. For a biomimetic A → BCD construction of steroids, see W. S. Johnson, C. E. Ward, S. G. Boots, M. B. Gravestock, R. L. Markezich, B. E. McCarry, D. A. Okorie, and R. J. Parry, *J. Am. Chem. Soc.*, **103**, 88 (1981), and the references therein.

(6) For a recent report addressing this point: L. N. Mander and J. V. Turner, *Tetrahedron Lett.*, 3683 (1981); See also *R. Soc. Chem., Spec. Per. Rep.*, **10**, 199 (1981).

(7) See, *Ann. Rep. Med. Chem.*, **16** (1981), and earlier volumes.

(8) Yields are not optimized. All new compounds gave satisfactory analytical and/or spectral data. Selected data for **9a**: red crystals, mp 210–212 °C; MS, *m/e* (relative intensity) 464.1392 (calcd 464.1400, M^+, 100), 294 (88), 124 (73); ^1H NMR (250 MHz, C_6D_6) δ 7.15 (d, *J* = 8.4 Hz, 1 H), 6.89 (dd, *J* = 8.4, 2.7 Hz, 1 H), 6.84 (d, *J* = 2.7 Hz, 1 H), 5.02 (d, *J* = 11 Hz, 1 H, ring B), 4.98 (d, *J* = 11.9 Hz, 1 H, ring B), 4.80 (d, *J* = 11.7 Hz, 1 H, ring B), 4.57 (d, *J* = 11.9 Hz, 1 H, ring B), 4.51 (s, 5 H), 3.69 (t, *J* = 6.1 Hz, 2 H, ketal), 3.44 (m, 3 H, ketal + vinyl), 3.40 (s, 3 H), 2.53 (dd, *J* = 15.0, 3.4 Hz, 1 H, ring C *endo*-CH_2), 2.10 (m, 2 H, ring D), 1.83 (ddd, *J* = 15.6, 10.8, 6.3 Hz, 1 H, ring D), 1.40 (m, 1 H, ring D), 1.08 (dd, *J* = 15.0, 3.1 Hz, 1 H, ring C *exo*-CH_2), 1.06 (s, 3 H). **9b**: red crystals, mp 172–175 °C; ^1H NMR (200 MHz, C_6D_6) δ 4.84 (s, 5 H), 3.38 (s, 3 H), 0.83 (s, 3 H). **10a**: orange oil; ^1H NMR (250 MHz, C_6D_6) δ 4.44 (s, 5 H), 3.40 (s, 3 H), 1.64 (s, 3 H). **10c**: yellow crystals, mp 139–142 °C; ^1H NMR (250 MHz, C_6D_6) δ 4.36 (s, 5 H), 3.38 (s, 3 H), 3.20 (dd, *J* = 5.6, 1.4 Hz, 1 H, vinyl), 1.33 (s, 3 H), 1.03 (dd, *J* = 13.6, 5.5 Hz, 1 H, ring C *endo*-CH_2), 0.69 (dd, *J* = 13.5, 1.2 Hz, 1 H, ring C *exo*-CH_2). **11**: colorless oil; ^1H NMR (250 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1 H), 6.77 (d, *J* = 3.8 Hz, 1 H), 6.48 (dd, *J* = 8.8, 3.8 Hz, 1 H), 5.26 (q, *J* = 1.5 Hz, 1 H), 4.84 (q, *J* = 2.0 Hz, 1 H), 3.43 (br s, 4 H), 3.26 (s, 3 H), 3.09 (t, *J* = 8.7 Hz, 2 H), 2.90 (s, 1 H), 2.55 (m, 4 H), 2.22 (br t, *J* = 8.7 Hz, 2 H), 1.71 (br s, 3 H); IR (neat) 3285, 2104 cm^{-1}. **12**: orange crystals, mp 108–110 °C; MS, *m/e* (relative intensity) 448.1447 (calcd 448.1448, M^+, 100), 310 (70); ^1H NMR (250 MHz, C_6D_6) δ 7.28 (d, *J* = 8.5 Hz, 1 H), 6.93 (d, *J* = 3.6 Hz, 1 H), 6.74 (dd, *J* = 8.5, 3.6 Hz, 1 H), 4.58 (s, 5 H), 3.74 (t, *J* = 7.5 Hz, 2 H, ketal), 3.52 (m, 3 H, ketal + vinyl), 3.46 (s, 3 H), 2.90 (ddd, *J* = 16.0, 5.3, 2.0 Hz, 1 H), 2.67 (dd, *J* = 14.5, 4.7 Hz, 1 H, ring C *endo*-CH_2), 2.35 (m, 3 H), 2.19 (t, *J* = 9.6 Hz, 2 H), 1.75 (ddd, *J* = 17.0, 8.5, 8.5 Hz, 1 H), 1.50 (ddd, *J* = 17.0, 7.4, 7.4 Hz, 1 H), 1.14 (dd, *J* = 14.5, 4.7 Hz, 1 H, ring C *exo*-CH_2), 0.96 (s, 3 H), all assignments were corroborated by complete decoupling experiments. **13**: colorless oil; ^1H NMR (200 MHz, C_6D_6) δ 7.60 (d, *J* = 8.6 Hz, 1 H), 6.84 (dd, *J* = 8.6, 2.5, 1 H), 6.70 (d, *J* = 2.5 Hz, 1 H), 6.11 (dd, *J* = 6.8, 3.0 Hz, 1 H, vinyl), 3.56 (m, 4 H, ketal), 3.14 (br d, *J* = 17 Hz, 1 H), 2.60 (t, *J* = 6.4 Hz, 2 H), 2.35 (m, 5 H), 2.08 (dd, *J* = 17. 6.8 Hz, 1 H), 1.37 (s, 3 H), the position of the vinyl proton was corroborated by NOE experiments involving H_1 (20% mutual enhancement).

Scheme II. Synthesis of Torgov Diene[a]

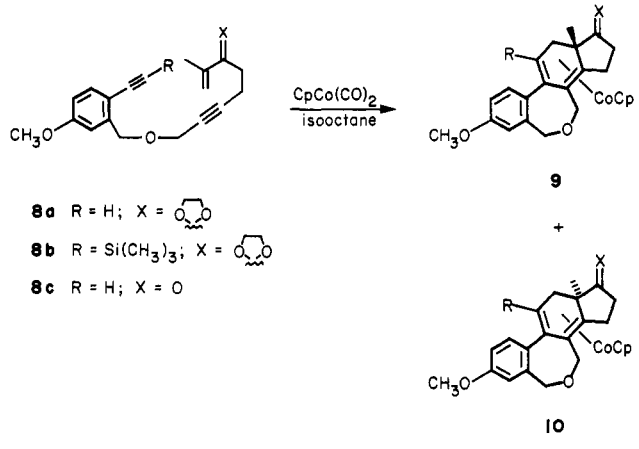


11 12 13 14

[a] (a) $CpCo(CO)_2$, isooctane, Δ, 65%; (b) $FeCl_3$ (1.1 equiv), CH_3CN, 0 °C, 1 h, 78%; (c) *p*-TsOH, THF, H_2O, 23 h, 95%.

converted to ketone **5** in a straightforward manner (Scheme I). Ketalization was difficult to drive to completion, some starting material (~20%) being recovered on workup. Homologation and bromination furnished **7**. The stage was now set to attempt a reductive coupling of the two bromides **3** and **7** with organometallic reagents,[9] a task that proved predictably problematic due to competitive random radical couplings and SN_2' processes. *tert*-Butyllithium (THF, −78 °C) gave optimum (25%) but nonetheless only mediocre quantities of the target substrate **11**.

Because of this obstacle and in order to probe the basic feasibility of our approach the more readily accesible ether **8a** was prepared from **3** and **6** (*n*-butyllithium, THF, HMPA, 2 h, 21 °C, 66%).[8] Trimethylsilylation [*n*-butyllithium, $(CH_3)_3SiCl$, 21 °C, 14 h, 71%] gave **8b**, whereas hydrolysis (5% aqueous HCl, THF, 1 h, 63%) resulted in **8c**.[8] Treatment of **8** with excess $CpCo(CO)_2$ in refluxing octane effected the desired intramolecular [2 + 2 + 2] cycloaddition to give in ca. 60% yield the two isomeric 7-oxa-*B*-homo steroid complexes **9** and **10** in varying proportions:[8] **9a**/**10a** = 2.6:1, **9b**/**10b** = 1:0, **9c**/**10c** = 1:2.

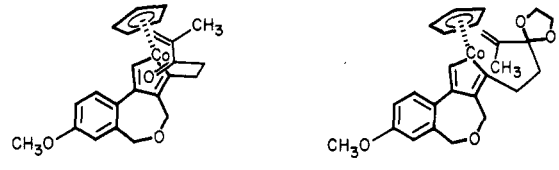


8a R = H; X = ⟨O,O⟩
8b R = Si(CH3)3; X = ⟨O,O⟩
8c R = H; X = O

9 + **10**

The assigned structures were in accord with spectral and analytical data. The high-field NMR spectra exhibited the characteristic pattern for a 1,2,4-substituted steroidal benzene, doublets for each of the B-ring protons, a relatively high field shifted terminal η^4-diene proton,[2] a ring-C *exo*-methylene absorption at high field, and the corresponding *endo*-methylene hydrogen at low field,[2] in addition to singlets for the methyl groups and (occasionally) more complex patterns for the remainder of the protons. The relative assignments of **9** and **10** was based on the finding that 5-methyl groups endo to (η^4-1,3-cyclohexadiene)cobalt appear deshielded when compared to their exo counterparts.[2d]

The changes in the observed stereochemistry along the series are interesting. We had noted earlier[2a] that trimethylsilyl substitution can have a profound effect on the stereochemical outcome of the cyclization reaction, but the origin of this phenomenon is still obscure. If one supposes that product formation proceeds through a Diels–Alder-type transition state in which the appended vinyl group functions as a dienophile with respect to a cobaltacyclopentadiene formed by oxidative coupling of the two alkyne units,[2] then the endo arrangement A would account for the preferred generation of **10c**, whereas steric effects due to the bulky ketal would enforce B, providing mainly **9a,b** in this case.



A B

The originally desired steroid precursor **11** was finally prepared[8] in 65% yield from **3** and **7** by the coupling procedure of Hirai[10] employing Al–Hg as the desulfurizing agent. Cyclization (Scheme II) gave the steoid complex **12** stereospecifically[8] which on oxidative demetalation[2] resulted in the very air sensitive *and hitherto unknown* steroid diene **13**.[8] Treatment with wet acid initially rearranged **13** to the 8,13-diene [δ 5.56 (dd, *J* = 2.7, 2.7 Hz, vinyl)], followed by hydrolysis to give **14**, identical in all respects with the racemic Torgov intermediate en route to estrone.[6,11]

(9) E. Negishi, "Organometallics in Organic Synthesis", Wiley, New York, 1980.

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The reported method should allow versatile access to many B,C,D-ring-modified steroids which are presently inaccessible. Moreover, it employs a transition-metal complex in a step that generates the first chiral center in the target natural product, suggesting future experiments aimed at utilizing optically active metal systems to obtain enantioselectivity. This prospect is under active scrutiny.

Acknowledgment. This work was supported by the National Institutes of Health (GM22479). We thank Dr. K. Hirai, Sankyo Co. Ltd., Tokyo for his helpful comments. K.P.C.V. is a Camille and Henry Dreyfus Teacher-Scholar (1978-1983).

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Registry No. 1, 6971-51-3; 2, 82064-54-8; 3, 82064-55-9; 4, 5390-04-5; 5, 82064-56-0; 6, 82064-57-1; 7, 82064-58-2; 8a, 82064-59-3; 8b, 82064-60-6; 8c, 82064-61-7; 9a, 82064-51-5; 9b, 82064-52-6; 9c, 82064-53-7; 10a, 82110-02-9; 10b, 82110-03-0; 10c, 82110-96-1; 11, 82064-62-8; 12, 82064-50-4; (±)-13, 82064-63-9; (±)-14, 1456-50-4.

Diels-Alder Reactions of Piperylenes

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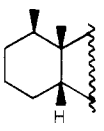
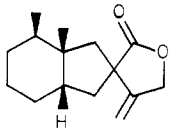
The synthesis of bakkenolide (2) and eremophilane (3) sesquiterpenes entails the construction of a *cis*-1,2-dimethylcyclohexane unit, 1, which can be synthesized by Diels-Alder reaction of *cis*-piperylene (4) and citraconic anhydride (**5a**). The use of a cuprous chloride/ammonium chloride catalyst led to very low yields of the desired adduct **7a** together with the other structural and stereoisomers (**8a-10a**), which made this route impractical. However, as part of a more general study we have compared the reactions of *cis*- and *trans*-piperylene (6) with five different maleic and citraconic dienophiles, **5a-e**, and obtained reasonable yields of the adducts **7c** and **7d** directly, thus demonstrating the utility of the $CuCl/NH_4Cl$ catalyst for sensitive dienes. The adducts **7a-10a** were transformed separately into the corresponding dimethyl esters **12-15** and then analyzed by NMR spectroscopy, which permitted the definition of their relative configurations and preferred conformations.

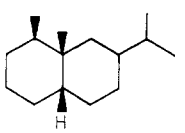
In our synthetic work on bakkenolide (2) and eremophilane (3) sesquiterpenes we have proposed[1] the preparation of a *cis*-1,2-dimethylcyclohexane unit, 1, as a possible



1



2



3

common intermediate. One approach would involve a Diels-Alder reaction[2] between *cis*-piperylene (4) and citraconic anhydride (**5a**) or *N*-phenylcitraconimide (**5b**). However, *cis*-piperylene (4) is known[2-6] to be very unreactive to cycloaddition under the conditions usually employed. Therefore, we initiated our study using the more reactive dienophiles maleic anhydride (**5c**) and *N*-phenylmaleimide (**5d**) in the presence of catalysts and then compared the reactions of the dienophiles **5a-e** with both *cis*-piperylene (4) and *trans*-piperylene (6). Fleming and Murray[7] have described the use of 2*H*-thiopyran (11) as a substitute for *cis*-piperylene (4) in reaction with maleic dienophiles **5c** and **5d**. As we obtained the pure adduct **7d** in 35% yield and the adduct **7c** in 49% yield (together with its epimer **9c**) directly from simple starting materials, we are prompted to report these and other related results.

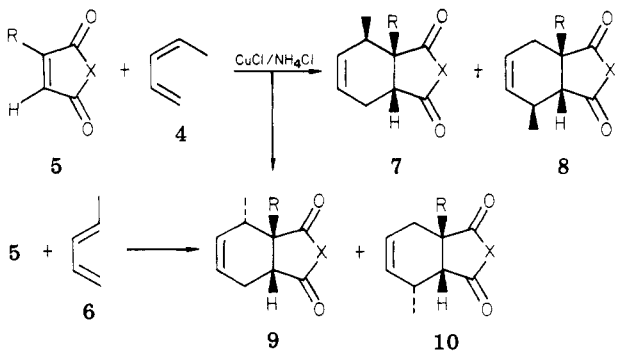
Results and Discussion

cis-Piperylene (4) is very prone to self polymerization and copolymerization with dienophiles. In our hands anhydrous aluminium chloride[2] only increases the polymerization rate at the expense of Diels-Alder reaction, as shown by the rapid formation of dark tars. On the other

Table I. Reactions of Piperylenes with Dienophiles 5a-e

diene	dienophile	products (yields, %)
6	5c	9c (81)
6	5d	9d (71)
4	5c	7c (49), 9c (9)
4	5d	7d (35)
6	5a	9a (67), 10a (26)
4	5a	9a (14), 10a (7), 7a (3), 8a (3.5)
6	5b	very slow reaction
6	5e	9e/10e (~3:1)
4	5e	9e + 10e + 7e + 8e

Scheme I[a]



[a] a, R = CH_3, X = O; b, R = CH_3, X = NPh; c, R = H, X = O; d, R = H, X = NPh; e, R = CH_2Cl, X = O.

†UFSCar.
‡USP.

(1) T. J. Brocksom, M. G. Constantino, and H. M. C. Ferraz, *Synth. Commun.*, 7, 483 (1977).

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