1*H*-pyrido[4,3,2-*mn*]thiazolo[5,4-*b*]acridine-9-ethanamine for dercitin (**1**). This is the first report of a pentacylic aromatic alkaloid bearing the thiazole functionality.

Acknowledgment. This is Harbor Branch Oceanographic Institution Contribution No. 648. We thank Dr. S. Pomponi for identification of the sponge, Drs. S. S. Cross, R. Longley, M. Lui, and J. Clement for biological assays, and Dr. Kurt L. Loening, Director of Nomenclature, Chemical Abstracts Service, Columbus, OH, for the IUPAC nomenclature of dercitin.

Supplementary Material Available: Isolation procedure, UV and MS data of **1**, spectral data of **3**, and ^{1}H and ^{13}C NMR data of dercitin (**1**) (3 pages). Ordering information is available on any current masthead page.

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Synthetic Studies on Arene–Olefin Cycloadditions. 10.[1] A Concise, Stereocontrolled Total Synthesis of (±)-Laurenene

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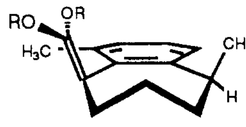
Received January 27, 1988

The term fenestrane was introduced in 1972 by Georgian and Saltzman[3] for tetracyclo$[3.3.1.0^{3,9}.0^{7,9}]$nonane, a hydrocarbon of considerable theoretical interest due to the expected planar geometry of its central carbon atom. The novel synthetic problems posed by this tetracycle and, more generally, by other rosettanes[4] have attracted much attention,[5] which has been further stimulated by the 1979 report of the first naturally occurring member of this novel class, lauren-1-ene (**1**).[6,7] We describe herein a total synthesis of **1**, which represents an unprecedentedly concise and stereocontrolled solution to this problem. This synthesis is based on the most complex example of an arene–olefin meta photocycloaddition reported to date and provides a novel and general strategy for the synthesis of analogous rosettanes.

Previous studies from these[1] and other laboratories[8] have established a set of selection rules which allows for the prediction of mode, regio, facial, and stereoselectivities for photoinduced cyclizations of 5-arylpent-1-enes. For the application of this methodology to lauren-1-ene, however, two previously unexplored but significant issues arise. First, in contrast to previous studies, the tether between the alkene and arene subunits in this application (**3**→**2**; Scheme I) would be subjected to an untested rotational restriction (about C-8,C-9), potentially disfavoring the conformation required for cycloaddition.[1] Moreover, for all three modes of meta cycloaddition (i.e., alkene addition to C-5, C-8, to C-4, C-1, or to C-8, C-2), the alkene substituents would be forced into a potentially adverse steric interaction with a non-arene ring. Models suggested that of these three possibilities, alkene addition to C-5,C-8 (**3**→**2**) would encounter the least steric hindrance, but it was not clear whether even this approach trajectory would have sufficient clearance and whether this steric problem would be exacerbated by rotational restrictions and the conflicting directing effects of the donor groups at C-1, C-4, and C-8. Second, the success of this plan would require that the photoaddition proceed with the formation of three contiguous quaternary centers (**2**: C-4,C-8,C-9), a sterically demanding process which could be superseded by energy transfer.[9]

The substrate required to test these points was prepared as illustrated in Scheme II.[10] Thus, Diels–Alder reaction of cyclohepta-1,3-diene and toluyne[11] allowed for the 5C + 2C construction of the target seven-membered ring, providing direct access to arene **4** (65% yield; 84% based on recovered starting material). Alternatively, this tricycle was also obtained, albeit in six steps (37% overall yield), by using a similar cycloaddition strategy involving an initial Diels–Alder reaction of benzoquinone and cyclohepta-1,3-diene.[12] Subsequent elaboration of arene **4** required that carbons C-17 and C-16, present in the alkene subunit, be differentiated and modified such that the former could be employed to assist the introduction of the homoprenyl chain at C-9, while the latter could be parlayed into the requisite C-16 methyl group. This differentiation was achieved efficiently through ozonolysis of **4**, which proceeded with in situ aldolization to afford only one set of aldol isomers **5**. The regiospecificity and facility of this aldol reaction are attributable to the peri-methyl group (C-20), which sterically inhibits enolization at C-9 and enforces C-15,C-17 propinquity. Exploitation of this result—involving selective formation and Grob fragmentation of keto tosylate **8** and hydrogenation of the fragmentation product **9**—allowed for the elaboration of **14**, possessing the requisite differentiated appendages at C-9 and C-15. Unfortunately, all attempts to use ester **14** or ester derivatives (CO_2H, CN, CHO, etc.) for introduction of the homoprenyl chain at C-9 were unsuccessful. The once-beneficial peri-methyl presumably served at this point to cant the enolate out of the arene plane (by 68° as calculated by Macromodel) and thereby block electrophilic attack on the only accessible enolate face.



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The problem with alkylative introduction of the C-9 homoprenyl chain was finally solved through the use of lactone **10**, in which the previously troublesome C-20, C-17 nonbonded interaction is

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(10) All new compounds furnished appropriate spectroscopic data and combustion analyses or exact mass. Partial spectroscopic data for key intermediates is as follows: **4**, PMR 7.02 (m, 2 H), 6.94 (m, 1 H), 3.72 (m, 1 H), 3.41 (m, 1 H), 2.32 (s, 3 H), 1.60 (m, 3 H), 1.50 (m, 2 H), 1.30 (m, 1 H). **3**, 7.18 (t, 1 H, J = 7.5), 7.10 (d, 1 H, J = 7.5), 6.87 (d, 1 H, J = 7.5), 5.14 (d, 1 H, J = 5.5), 5.05 (tm, 1 H, J = 7), 5.02 (d, 1 H, J = 15), 4.78 (d, 1 H, J = 15), 3.19 (m, 1 H, J = 7.5), 2.43 (d, 1 H, J = 5.5), 2.06 (m, 2 H), 1.89 (dd, 1 H, J = 8.15), 1.65 (s, 3 H), 1.59 (s, 3 H), 1.34 (d, 3 H, J = 7). **2**, 5.35 (br t, 1 H, J = 2), 4.69 (d, 1 H, J = 5), 4.04 (d, 1 H, J = 11), 3.82 (d, 1 H, J = 11) 2.76 (d, 1 H, J = 5), 2.34 (dd, 1 H, J = 7, 13), 1.29 (d, 1 H, J = 7.5), 1.14 (d, 3 H, J = 7), 1.05 (s, 3 H), 1.02 (s, 3 H).

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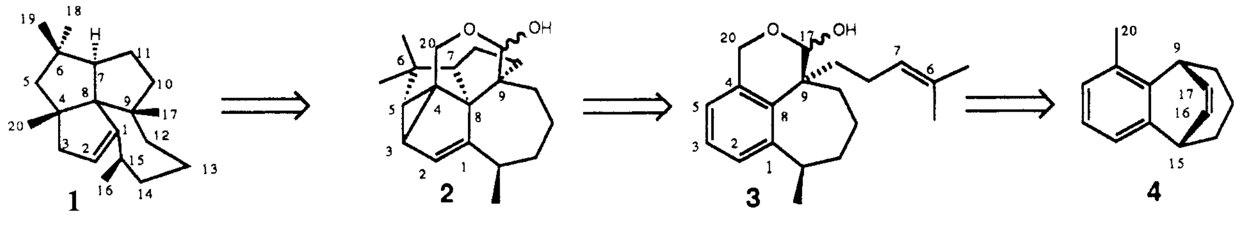
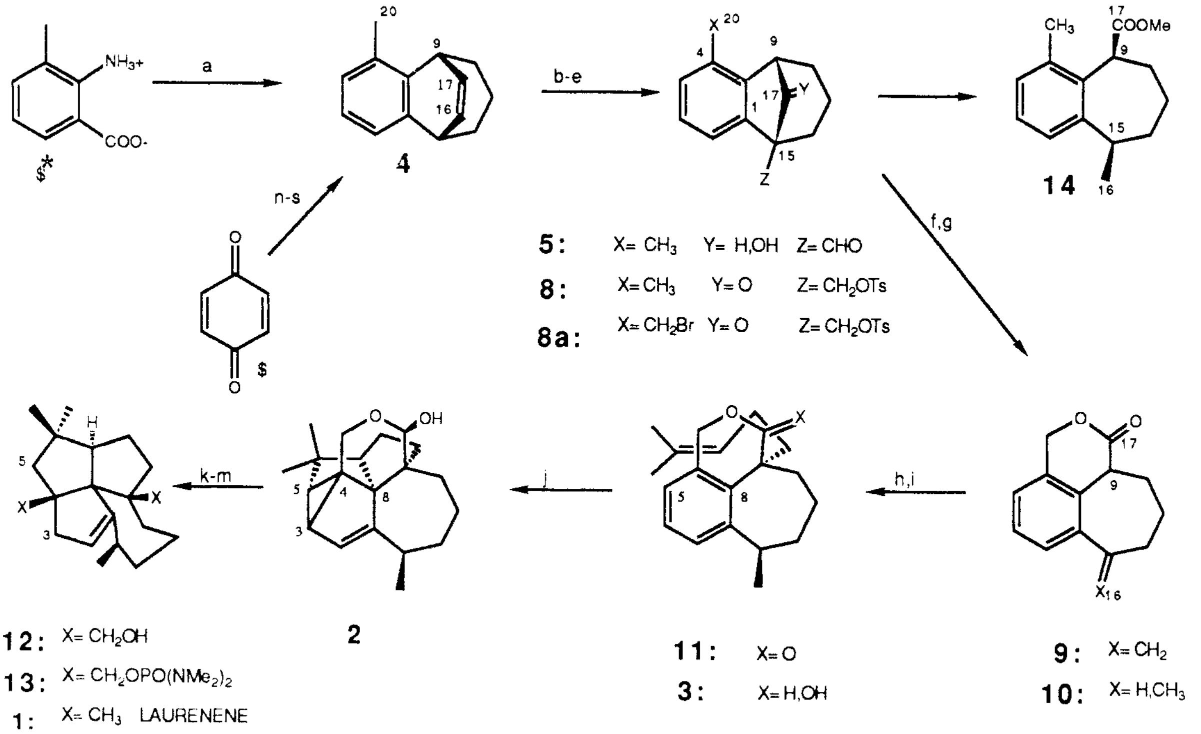
Scheme I



Scheme II[a,b]



[a] *\$ = Commercially available. [b] (a) Isopentyl nitrite, Cl_3CCO_2H; cyclohepta-1,3-diene, CH_2Cl_2, 34 °C (84% based on recovered starting material); (b) O_3, Me_2S, Et_3N (68%); (c) $Zn(BH_4)_2$, Et_2O (98%); (d) TsCl (72%); (e) PCC (98%); (f) i. NBS, AIBN; ii. KOH (72%); (g) H_2, Pt (96%); (h) LDA, DMPU, homoprenyliodide (48% (90% based on recovered starting material)); (i) LAH, THF (95%); (j) $h\nu$ (51%); (k) Li^0, $MeNH_2$, -6 °C (96%); (l) KHMDS, HMPA, $(Me_2N)_2POCl$ (55%); (m) Li^0, $EtNH_2$ (65%); (n) cyclohepta-1,3-diene, $BF_3{\cdot}Et_2O$; (o) Zn^0, HOAc (93%); (p) MeLi (72%); (q) Red-Al (99%); (r) $POCl_3$, DBU (92%); (s) DDQ (78%).

replaced by a lactone bond. For this purpose, **8** was converted with NBS to the bromomethyl adduct **8a** which, upon Grob fragmentation and hydrogenation of the fragmentation product, led to lactone **10**. Alkylation of this lactone (**10**) with homoprenyl iodide[13] proceeded now, according to plan, to give preferentially (8:1) the desired stereoisomer **11**. The stereochemical outcome of this alkylation step—a matter of critical importance to the success of this synthesis and one that has not been resolved thus far for this skeletal class—is that expected from models which reveal that one face of the lactone enolate is shielded from electrophile approach by the resident C-16 methyl group.

For the key step in our plan, the lactol **3**, prepared by LAH reduction of **11**, was submitted to photolysis (Hanovia medium pressure lamp, vycor filter), which proceeded smoothly to afford a single product at low conversion (ca. 30%). Further irradiation, however, produced increasingly complex mixtures due, in part, to product absorbance. In order to minimize this problem, photolysis of **3** was conducted through an aqueous bismuth trichloride filter solution[14] which allowed for higher (80%) conversion without complication and for the isolation of a single hexacyclic product **2** as a crystalline solid (51%; 64% based on recovered starting material). Unlike all previous reports, only a single vinylcyclopropane isomer was detected in this cycloaddition, a result attributable to the greater strain (as calculated by Macromodel) inherent in the alternative isomer. Verification of the structure assigned to this complex cycloadduct and completion of the synthesis was accomplished in three steps. Orbital overlap-controlled reductive cleavage of the C-3, C-5 cyclopropane bond[15] occurred with concomitant reduction of the lactol to form diol **12**. Deoxygenation of this product[16] then afforded (±)-lauren-1-ene (**1**).[17]

In summary, a synthesis of laurenene has been achieved in an unprecedentedly efficient (5% overall), concise (13 steps from commercially available materials), and stereocontrolled fashion. This synthesis establishes the strategic value of the arene–olefin meta photocycloaddition for a new skeletal class and augurs well for the broader application of this process in the synthesis of complex rosettanes. The successful cycloaddition of lactol **3** suggests that this key process can be extended to other highly congested substrates and that the vinyl cyclopropane product ratio can be predicted, in part, from strain considerations. Further studies are in progress.

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Acknowledgment. This work was supported by the National Science Foundation through Grant (5F32 CA07831-02) and through Grants CHE84-14329 and CHE81-09064 for the NMC-300 and XL-400 NMR spectrometers. We also thank Prof. Rex T. Weavers for the generous gift of natural laurenene.

Supplementary Material Available: Spectral and analytical data for **4**, **2**, and **1** (2 pages). Ordering information is given on any current masthead page.

An Ethylene Complex of Vanadium: Synthesis, Structure, and Reactivity of Cyclopentadienylbis(trimethylphosphine)(ethylene)vanadium(I)

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Received March 22, 1988

Although olefin complexes of the early transition metals are frequently named as intermediates in catalytic reactions such as olefin polymerization and hydrogenation,[1] very few complexes have actually been isolated, especially for the 3d-metals. For Ti the sole representative of this class of compounds is $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}$(ethylene),[2] while for V only two compounds are fully characterized: $\text{Cp}_2\text{V(EtO}_2\text{CCH=CHCO}_2\text{Et)}$[3] and $\text{V(CO)}_4[\text{PPh}_2$(2-alkenylphenyl)],[4] the latter stabilized by the chelate effect. Here we wish to report a simple olefin complex of V(I), $\text{CpV}(\eta^2$-ethylene)$(\text{PMe}_3)_2$, with some aspects of its reactivity.

When $\text{CpVCl}_2(\text{PMe}_3)_2$[5] (**1**) is reacted with 1 mol of 1,4-bis(bromomagnesio)butane in THF at 0 °C, the ethylene complex CpV(ethylene)$(\text{PMe}_3)_2$ (**2**) can be isolated in 38% yield, instead of a possibly anticipated vanadiocyclopentane product. The blue $\text{CpVCl(PMe}_3)_2$[6] was observed as an intermediate in the reaction.[7] **2** can also be obtained, in 49% overall yield, from the reaction of $\text{CpVCl(PMe}_3)_2$ (produced by reduction of **1** with 1 mol of Na/Hg) with 0.5 mol of the diGrignard. Thus it seems likely that **2** is not formed by elimination of ethylene from a vanadiocyclopentane intermediate but by rearrangement of a 1,4-divanadiobutane complex (eq 1). This behavior appears to be

$$\mathbf{1} \xrightarrow[\text{THF}]{\text{Na/Hg}} \text{CpVCl(PMe}_3)_2 \xrightarrow[\text{THF, 0 °C}]{{}^1\!/_2(\text{BrMg})_2(\text{CH}_2)_4} {}^1\!/_2[\text{Cp(PMe}_3)_2\text{VCH}_2(\text{CH}_2)_2\text{CH}_2\text{V(PMe}_3)_2\text{Cp}] \rightarrow \underset{(\mathbf{2})}{\text{CpV(ethylene)(PMe}_3)_2} \quad (1)$$

unprecedented for 1,4-dimetallabutanes. However, recently the production of ethylene from reduction of 1,4-dibromobutane by a nickel tetraazaannulene complex was reported.[9] One of the mechanisms suggested there (a concerted internal electron-transfer reaction) may well be applicable in our case.

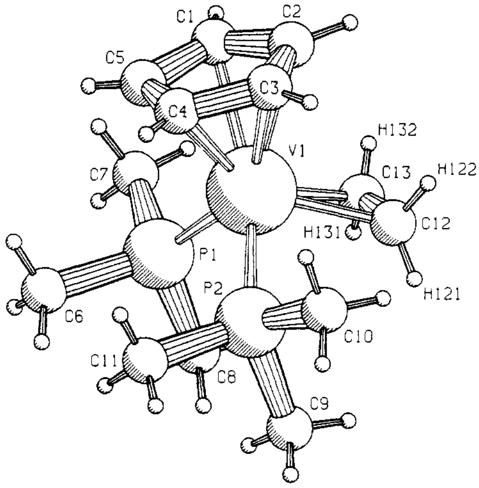

Figure 1. Molecular structure of $\text{CpV}(\eta^2$-ethylene)$(\text{PMe}_3)_2$ (**2**). Selected structural parameters are as follows: V(1)–P(1) = 2.429 (1) Å, V(1)–P(2) = 2.427 (1) Å, V(1)–C(12) = 2.153 (3) Å, V(1)–C(13) = 2.173 (3) Å, C(12)–C(13) = 1.365 (5) Å, ∠P(1)–V(1)–P(2) = 95.97 (3)°, ∠C(12)–V(1)–C(13) = 36.8 (1)°.

2 is a green crystalline paramagnetic (by NMR) 16-electron high spin complex, extremely air sensitive, but thermally stable in solution at 0 °C. An X-ray structure determination[10] shows (Figure 1) that **2** has a simple piano-stool geometry with the phosphine ligands in eclipsed conformation. The V–C(ethylene) distances are close to those in Cp*_2Ti(ethylene) (2.160 (4) Å[2]), but the amount of π-backdonation (and concomitantly the amount of metallacyclopropane character) is much smaller than in the latter compound. This can be seen from both the ethylene C–C distance and the sharp dihedral angle α between the two planes through each of the two CH_2 groups (both increase with increasing metallacyclopropane character[11]). **2**: C(12)–C(13) = 1.365 (5) Å, α = 47. (3)°; $(\text{C}_5\text{Me}_5)_2$Ti(ethylene):[2] C–C = 1.438 (5) Å, α = 70. (4)°; ethylene:[12] 1.337 (2) Å, α = 0°. The relatively small amount of π-backdonation into the ethylene π*-orbital in **2** (despite formally being a d^4-species) may be caused by competition from the two phosphine ligands.

The ethylene complex **2** exhibits a wide range of reactivity. With (hard or soft) Lewis bases displacement of the ethylene ligand can occur. E.g., **2** reacts with CO, diphenylacetylene, or 2,2′-bipyridine to form $\text{CpV(CO)}_2(\text{PMe}_3)_2$,[13] $\text{CpV}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{PMe}_3)_2$, and the paramagnetic CpV(bpy)PMe_3, respectively. Thus through **2** various CpV(I)-species that do not contain CO ligands can be synthesized under mild conditions (0 °C). Apart from CpV(arene) species,[14] all CpV(I) compounds known so far contain at least one carbonyl ligand. The ethylene ligand is retained in reaction with CO_2, where the 2-oxavanadacyclo-3-pentanone $\text{CpV}(\eta^1\text{-O}_2\text{CCH}_2\text{CH}_2)\text{PMe}_3$ (ν_{CO} = 1565 cm^{-1}) is formed. Oxidative addition to the low valent metal center can also be observed: **2** reacts with diphenyldisulfide to give the insoluble dimeric V(III) species $[\text{CpV}(\mu\text{-SPh})_2]_2$.[15] **2** is moderately active in the catalytic dimerization of olefins. For example, 38 mol/mol V of 1-hexene is transformed into $\text{C}_{12}\text{H}_{24}$ (three isomers, GCMS M^+ = 168) in 48 h (1-hexene, room temperature).

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[7] V(III) in **1** is reduced to V(II) by β-H containing alkyl Grignards like EtMgBr and *n*-PrMgBr, yielding $\text{CpVX(PMe}_3)_2$ (X = Cl, Br). Reaction of **1** with 2 mol of *n*-PrMgBr in THF produces a poorly soluble brown material. No formation of **2** was observed, making THF as an ethylene source[8] for **2** unlikely.

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[10] **2** crystallizes in the orthorhombic space group *Pbca*, *a* = 12.351 (3) Å, *b* = 15.526 (4) Å, *c* = 16.948 (3) Å (140 K), *Z* = 8. Reflections (2474) with 1.2° ≤ θ ≤ 26.0° were considered observed. All hydrogen atoms were located from the Fourier difference map and refined isotropically. *R* = 0.035, R_w = 0.041 ($w = 1/\sigma^2(F)$) for 254 refined parameters.

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