A Regiospecific Synthesis of Iridoids Based on the Paterno–Büchi Enone Photoannulation Reaction

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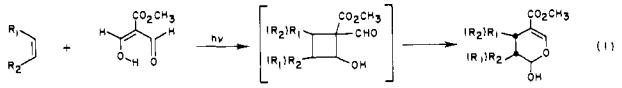
Abstract: The photochemical annulation reaction known as the Paterno–Büchi reaction is an efficient route to the total synthesis of cyclopentano monoterpenoids (iridoids) but heretofore has not been reported to be regiospecific when unsymmetrical olefins react with methyl diformylacetate (**1**). We have now found that 5-(trimethylsilyl)-1,3-cyclopentadiene (**4**) reacts with **1** in CH_3CN to give only one regio- and stereoisomer of the olefinic product (**6**). This compound contains the tetrahydrocoumalate ring system characteristic of iridoid aglucones and an allyl silane functionality, which can be transformed to several homologous compounds (**10a–c**) known to be valuable intermediates for the total synthesis of iridoids. Consequently, our findings provide an exceptionally efficient synthetic route to iridoid aglucones.

The total synthesis of cyclopentanoid monoterpenes (iridoids[1]) has been the objective of many research groups during the past two decades because of the wide occurrence,[2] biological activity,[3] and biosynthetic importance[4] of these natural products. Among the published syntheses,[5] the strategy of Büchi and coworkers,[6] in which a photoannulation reaction between an olefin and methyl diformylacetate (**1**) was used to construct the characteristic tetrahydrocoumalate ring system (**3**, eq 1), stands out for its simplicity and mechanistic novelty. Four different iridoids (loganin[6,7]), secoiridoid aglucones (secologanin,[8,9] sweroside,[8,9] sarracenin[10,11] or related compounds[8,12] have been synthesized by the approach since 1971.



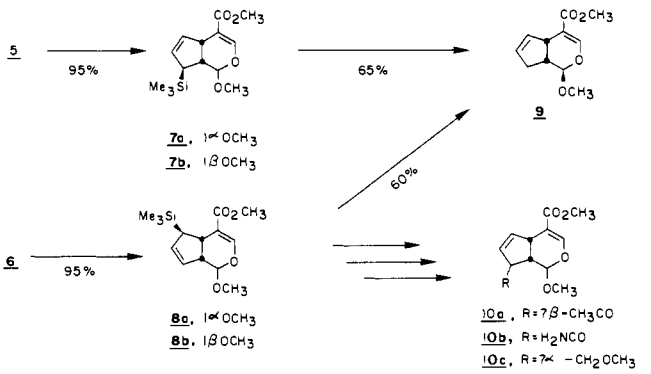
(1)

1 **2** **3**

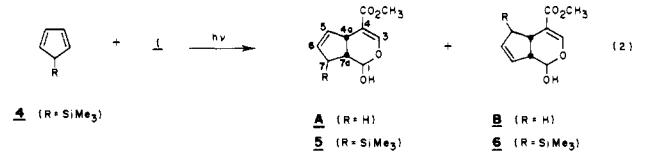
This photoannulation strategy has had one major limitation: poor regioselectivity when used with unsymmetrical olefins[7,10,11] although the stereoselectivity of the reaction is excellent.[6,11] Thus the formation of regioisomeric products has complicated its use for the total synthesis of optically active iridoids even when the amount of asymmetric induction was high.[7,10,11] We now have found a solution to the regiochemistry problem, as described below, which makes the Paterno–Büchi reaction (eq 1) an efficient and versatile strategy for the total synthesis of iridoids and their structural analogues.

We felt that the progression of likely intermediates of this reaction to the hypothetical 2,2,3,4-tetrasubstituted cyclobutanol (**2**, eq 1) could be influenced by steric and electronic parameters in the reaction between substituted cyclopentadienes or cyclopentenes and **1**. In particular, we reasoned that an allylsilane

Scheme I



functionality in these cyclic olefins might be an effective modulator of the course of the reaction and also would permit several different functional group interchanges within the product **3**. The photochemical reaction between cyclopentadiene and **1**[12] in CH_3CN gave an about 3:7 mixture of the two regioisomers, A and B (eq 2), but no products were obtained in the reaction using the



(2)

4 (R = $SiMe_3$) **A** (R = H) **B** (R = H)
5 (R = $SiMe_3$) **6** (R = $SiMe_3$)

ethyleneketal of 2-cyclopentenone. In contrast, the use of 5-(trimethylsilyl)-1,3-cyclopentadiene[13] (**4**) gave a 1:2 mixture of **5** and **6** in 60–65% yield on a preparative scale when the reaction was done in CH_2Cl_2 (0.15 M in **1**; 1.5 M in **4**) for 6 h at −35 to −50 °C using Corex-filtered irradiation from a 450-W Hanovia lamp but a 2:1 mixture of **5** and **6** when carried out in THF under similar conditions. Only **6** was produced in the same yields but at a slower rate when the solvent was CH_3CN. The allylsilane functionality, therefore, can be introduced regiospecifically and stereoselectively into the desired product, which overcomes the regiochemical problem observed in all other reports in the iridoid literature of the use of the Paterno–Büchi reaction with unsymmetrical olefins.[7,10,11]

The structures of **5** and **6** were deduced from the following key spectral and chemical experiments. (1) Treatment of either **5** or **6** with BF_3/OEt_2 in MeOH at room temperature gave a difficultly separable mixture of C-1 epimeric *O*-methylacetals **7a,b** or **8a,b**, respectively (Scheme I). The ^1H NMR spectrum of **7b** when analyzed by $^1H/^1H$ double irradiation experiments showed that H-7a (dt) was coupled to H-1 (d, J = 8.2 Hz), H-4a (m, J = 8.2 Hz), and H-7 (quin, J = 2 Hz). These data support the relative

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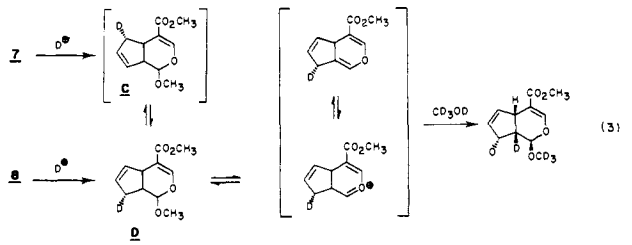
stereochemistry shown for **7b**. The regio- and relative stereochemistry of **8a,b** was also assigned by analysis of its partially degenerate 200-MHz ^{1}H NMR spectrum. The 22.5-MHz ^{13}C NMR spectral data when compared with **7a,b** and several other compounds prepared in our study rigorously supported the stereochemistry assigned to both regioisomers. (2) Treatment of **7a,b** or **8a,b** with *p*-TsOH (1 equiv) in refluxing benzene for 1.5 h gave only one protiodesilylated[14] product, **9** (Scheme I), whereas treatment of the mixture of **7a,b**/**8a,b** with *n*-$Bu_4N^+F^-$ in THF at 50 °C for 2 h produced a regioisomeric and C-1 epimeric mixture of desilylated olefins. This mixture gave only **9** when treated with *p*-TsOH in refluxing benzene. When the protiodesilylation of **7a,b** or **8a,b** was done with *p*-TsOD (10 equiv), **9** contained ^{2}H only at C-7 and C-7a. Likewise, in the presence of *p*-TsOD and CD_3OD (excess) **9** contained ^{2}H additionally at the C-1-*O*-methyl (3 mol equiv of ^{2}H). With CF_3CO_2D (2 equiv in CH_2Cl_2, 0–25 °C, 16 h), protiodesilylation of **7a,b** or **8a,b** gave *only* 7α-[7-$^2H_1$]-**9** as a mixture of C-1 epimers, which proves the stereochemistry of this process to be different from that observed by Young and Fleming for a closely related system.[17] These data together show that **9** is the thermodynamically stablest regioisomer and C-1 epimer and that its formation is consistent with the mechanism drawn in eq 3. This interpretation shows a β con-



(3)

figuration for the trimethylsilyl group at C-7 of **7** and C-5 of **8**, which directs the anti protonation (deuteration) of the allylsilane in **7** (→ C) and **8** (→ D).[14,15] Since ^{2}H was not introduced at C-5 of **9**, C, if actually formed (we could not prove this directly), must interconvert to D by the loss of ^{2}H from the α face of the molecules as drawn in eq 3. D is drawn with a 7α-^{2}H since this agrees with the stereochemistry of protiodesilylation of **7a,b** and **8a,b** at 0 °C. The incorporation of ^{2}H at C-7a is shown to occur after protiodesilylation on the basis of the observed relative exchange rates at 80 °C. (3) Reaction of **8** with $CH_3COCl/AlCl_3$ (1 equiv)[16] gave **10a** (10%),[18] with $ClSO_2NC$ (2 equiv), then with H_3O^+ according to the Fleming precedent[17] gave **10b** (30%), and with $ClCH_2OCH_3$ (1 equiv)[17,18] gave **10c** (45%) as shown in Scheme I. The spectral data (^{1}H and ^{13}C NMR and MS) for these three products of electrophilic attack on the β position of the allylsilane fully support their assigned structures and, thereby, the structure and expected reactivity of **8**.

The results of our brief study of the photochemical reaction between **1** and unsymmetrical pentacyclic olefins are valuable for two reasons. First they open the way to efficient, stereospecific syntheses of most of the known iridoids[2] starting from 6.[19] Asymmetric syntheses may also be possible depending on the asymmetric induction achievable with chiral silicon.[20] Second, they suggest that further study of the effect of olefin substitution via steric and electronic factors on the outcome of the Paterno–Büchi reaction with **1** may reveal more details about its mechanism than are known currently.[21] Such work must be done before we can explain fully the observations noted here about the reaction of **1** with **4**.

Experimental Section

Preparation of Compounds 5 and 6. Nitrogen was bubbled through a solution of **1**[12] (2 g, 15.4 mmol) and **4**[13] (20 mL) in CH_2Cl_2 (100 mL) at −35 to −50 °C while it was irradiated by a 450-W Hanovia mercury lamp fitted with a Corex filter sleeve. After 6 h, the solvent and excess **4** were removed under vacuum to give a yellow oil (ca. 4 g). A portion (ca. 1 g) of this residue was chromatographed on a silica gel column using EtOAc/*n*-hexane (1:2) as eluant, and three fractions were collected: **5** (55 mg), **5** plus **6** (350 mg), and **6** (107 mg). The combined yield of **5** and **6** based on **1** was ca. 50%, but direct *O*-methylation of the crude product followed by chromatographic purification gave a combined yield of their 1-*O*-methylacetals of 60–65%. The exact ratio of **5** and **6** was determined by gas chromatographic analysis of their 1-*O*-methylacetals on OV-101 at 170 °C.

Irradiation of **1** (1.5 g, 11.5 mmol) and **4** (15 mL) in CH_3CN (110 mL) at −5 to −25 °C for 14 h likewise gave a yellow oil (ca. 3 g), which contained only **6** by gas chromatographic and ^{13}C NMR analyses.

5: ^{1}H NMR ($CDCl_3$, 270 MHz) δ_H 7.51 (1 H, d, J = 1 Hz, H-3), 5.75–5.68, 5.68–5.61 (2 H, m, H-5 and H-6), 4.69 (1 H, dd, J = 5, 7.5 Hz, H-1), 3.73 (3 H, s, CO_2CH_3), 3.55 (1 H, m, H-4a), 2.05 (1 H, br s, H-7), 2.16 (1 H, dd, J = 7.5, 7.5 Hz, H-7a); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 153.2 (C-3), 130.8 (C-5 and C-6), 109.3 (C-4), 96.5 (C-1), 51.3 (CO_2CH_3), 43.4 (C-8), 43.3 (C-4a), 38.1 (C-7a); MS, m/z (rel abund) 268 (M^+, 0.5), 253 (0.2), 236 (0.5), 221 (1.2), 207 (1.1), 193 (1.3), 159 (6.7), 146 (4.2), 118 (5.1), 85 (15), 73 (100).

6: ^{1}H NMR ($CDCl_3$, 270 MHz) δ_H 7.53, 7.57 (1 H, br s, H-3), 5.81 (1 H, m, H-6), 5.63, 5.40 (1 H, br d, H-7), 5.48, 5.10 (1 H, br s, H-1), 3.73 (3 H, s, CO_2CH_3), 3.30–3.12 (2 H, m, H-4a and H-7a), 1.98 (1 H, br s, H-5); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 168.1 (CO_2CH_3), 153.4, 151.7 (C-3), 136.2, 135.7 (C-6), 51.1 (CO_2CH_3), 50.7, 49.5 (C-7a), 44.0, 43.6 (C-4a), 37.5, 33.7 (C-5); MS, m/z (rel abund) 268 (M^+, 0.6), 253 (0.2), 236 (0.5), 207 (1), 193 (1), 185 (1), 171 (1), 159 (7), 149 (4), 146 (4), 135 (4), 133 (3), 118 (5), 107 (5), 105 (4), 101 (4), 85 (29), 73 (100).

Preparation of the 1-*O*-Methylacetals (8). The crude hemiacetal (**6**, ca. 2 g) obtained from the photoannulation experiment using CH_3CN was treated with freshly distilled BF_3/OEt_2 (0.5 mL) in dry MeOH (10 mL) at room temperature with stirring for 2 h. Water (25 mL) was added to the reaction, and the mixture was extracted with EtOAc (3 × 35 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ and then brine and dried over anhydrous Na_2SO_4. Evaporation under vacuum gave a yellow oil that was purified by chromatography on a silica gel column using EtOAc/hexane (1:3) to give a mixture of C-1 epimers of **8** (1.3 g, ca. 60% yield based on **1**). A small amount (5 mg) of this mixture was separated into the two C-1 epimeric *O*-methylacetals by preparative thin-layer chromatography on silica gel TLC plates impregnated with 10% (w/w) $AgNO_3$ and developed with benzene/hexane (1:1) to give pure **8b** (2.0 mg, more polar) and **8a** (1.2 mg, less polar) as colorless solid films.

8b: ^{1}H NMR ($C_6D_6/CDCl_3$, 2.5:1, 270 MHz) δ_H 7.57 (1 H, s, H-3), 5.88–5.81 (1 H, q, J = 2.7 Hz, H-6 or H-7), 5.42–5.36 (1 H, br d, J = 5.4 Hz, H-6 or H-7), 4.90 (1 H, d, J = 1.4 Hz, H-1), 3.69 (3 H, s, CO_2CH_3), 3.52 (1 H, br d, J = 7 Hz, H-4a), 3.44 (3 H, s, OCH_3), 3.36–3.28 (1 H, m, H-7a), 2.41–2.34 (1 H, m, H-5), 0.48 (9 H, s, $Si(CH_3)_3$); MS, same as **8a**.

8a: ^{1}H NMR ($CDCl_3$, 270 MHz) δ_H 7.54 (1 H, d, J = 0.7 Hz, H-3), 5.91–5.80 (1 H, m, H-6 or H-7), 5.68–5.51 (1 H, br d, J = 6.8 Hz, H-6 or H-7), 4.73 (1 H br s, H-1), 3.73 (3 H, s, CO_2CH_3), 3.63 (3 H, s, OCH_3), 3.30–3.20 (2 H, m, H-4a and H-7a), 1.99 (1 H, hextet, J = 1.7 Hz, H-5), 0.09 (9 H, s, $Si(CH_3)_3$); MS, m/z (rel abund) 282 (2, M^+), 267 (0.6), 251 (0.5), 235 (3.5), 177 (3), 159 (2), 149 (4), 146 (4), 133 (14), 119 (6), 108 (8), 73 (100).

Reaction of 8a,b with Chloromethyl Methyl Ether. A magnetically stirred solution of **8a,b** (57 mg, 0.2 mmol) in dry CH_2Cl_2 (0.5 mL) under a N_2 atmosphere at −78 °C was treated with CH_3OCH_2Cl (0.2 mL, 2

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(18) The coupling constant between H-7 and H-7a (4.2 Hz) shows that the acetyl group has the C-7β configuration in **10a**, whereas the $-CH_2OCH_3$ in **10c** has the expected C-7α configuration ($J_{H_7H_{7a}}$ = 7.8 Hz). The configuration of the amide group at C-7 in **10b** was not determined, but we believe it is β, which would result from epimerization to the thermodynamically preferred isomer after the electrophile added to the allylsilane, like **10a**.

(19) We have synthesized 1-*O*-methyl-7-ketologanin aglucon from **8b**, for example (Chaudhuri, R. K., to be submitted for publication).

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mmol) and $SnCl_4$ (10 mg, 0.04 mmol). After 1 h at -78 °C, the reaction was stopped by the addition of saturated aqueous $NaHCO_3$ (0.5 mL) and extracted with EtOAc (3 × 3 mL). After the combined extracts were dried over anhydrous Na_2SO_4 and evaporated under vacuum, the resulting crude reaction product was purified by preparative thin layer silica gel chromatography using EtOAc/hexane (1:10) to give pure **10c** (23 mg, 45%).

10c: ^1H NMR ($CDCl_3$, 200 MHz) δ_H 7.41 (1 H, d, J = 1.7 Hz, H-3), 6.04 (1 H, ddd, J = 5.9, 1.8, 1.8 Hz, H-5 or H-6), 5.68 (1 H, ddd, J = 5.6, 1.9, 1.9 Hz, H-5 or H-6), 5.02 (1 H, d, J = 4.4 Hz, H-1), 3.73 (3 H, s, CO_2CH_3), 3.58-3.33 (10 H, m, two OCH_3, OCH_2CH, H-7 and H-4a), 2.62 (1 H, ddd, J = 8.0, 8.0, 4.2 Hz, H-7a): ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 167.6, 151.5, 134.6, 131.2, 110.6, 100.1, 75.8, 73.2, 58.9, 56.3, 51.3, 47.5, 42.5, 39.4 ppm; MS, m/z (rel abund) 254 (M^+, 4), 223 (10), 222 (10), 209 (8), 190 (3), 177 (67), 162 (17), 149 (51), 145 (16), 121 (30), 105 (13), 91 (25), 77 (21), 44 (100).

Preparation of the Olefin 9. The allylsilane **8a** (40 mg, 0.11 mmol) dissolved in benzene (0.5 mL) containing p-TsOH·H_2O (21 mg, 0.11 mmol) was refluxed for 1.5 h. The reaction mixture was poured into water, and then the organic phase was extracted with saturated aqueous $NaHCO_3$ and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent under vacuum gave a dark residue that was purified by preparative thin-layer chromatography on silica gel using hexane/EtOAc (3:1) to give **9** (20 mg, 73%).

9: ^1H NMR ($CDCl_3$, 270 MHz) δ_H 7.49 (1 H, d, J = 1.2 Hz, H-3), 5.93-5.85, 5.70-5.64, (2 H, m, H-5 and H-6), 4.43 (1 H, d, J = 6.1 Hz, H-1), 3.73 (3 H, s, CO_2CH_3), 3.54 (3 H, s, OCH_3), 2.51-2.41 (3 H, m, H-7, H-7a); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 168.0 (CO_2CH_3), 152.5 (C-3), 134.5 (C-6), 128.7 (C-5), 110.0 (C-4), 102.5 (C-1), 57.3 (C-1, OCH_3), 51.3 (CO_2CH_3), 40.9 (C-4a), 40.0 (C-8), 34.5 (C-7a); MS, m/z (rel abund) 210 (M^+, 36), 179 (29), 178 (44), 150 (22), 149 (26), 147 (36), 146 (44), 139 (44), 121 (30), 120 (20), 119 (36), 118 (44), 108 (44), 107 (40), 91 (65), 84 (44), 77 (32), 71 (43), 66 (60), 45 (100).

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Synthesis of Triannulanes via Intramolecular [2 + 1] Cyclizations of Large-Ring Cycloalkenes

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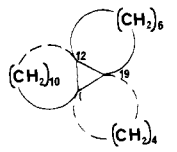
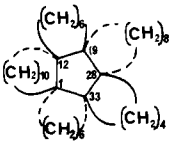
Abstract: Synthetic routes to *trans,cis,cis*-[10.4.3]- and *trans,cis,cis*-[10.4.4]triannulane-16,18-dione (**48** and **60**) are described. The former was prepared via intramolecular [2 + 1] cycloaddition of the carbene generated by photolysis of the α-diazo β-keto ester **43**, followed by Dieckmann cyclization of the derived diester **45**, and subsequent hydrolysis, decarboxylation, and oxidation. The [10.4.4] homologue **60** was prepared via analogous [2 + 1] cyclization of the carbene derived from photolysis of the [10.9]betweenanene α-diazo β-diketone **59**. This intermediate was secured from the acyloin cyclization product **56** of diester **55**, an intermediate in a previously reported synthesis of [10.10]betweenanene. The conversion to dione **58** entailed cyclopropanation of the ene diol bis(trimethylsilyl) ether **56** followed by periodate cleavage of the derived 1,2-cyclopropanediol intermediate. The foregoing sequence was also performed with optically active diester **55** to give optically active triannulanedione **60**. The structures of diones **48** and **60** were confirmed through single-crystal X-ray structure analysis.

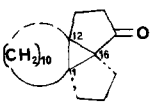
We recently formulated a new class of carbocyclic compounds, "perannulanes", consisting of a central ring whose every side is spanned by bridging chains so as to fashion a ring of fused rings.[1a] The number of bridging chains is indicated by the prefix "tri, tetr, pent, hex, etc.", and the length of each bridging chain is denoted by a bracketed numerical prefix as shown in the following examples. Since each side of the central ring is spanned by a bridging chain, the number of such chains is equal to the central ring size. Thus "triannulanes" have a central three-membered ring, "tetrannulanes" a central four-membered ring, and so forth.[1b] The bracketed chain length designators are arranged in order starting with the longest bridge and proceeding to the longer of the two adjacent bridges and thence to the next contiguous bridge until all bridges have been specified. The stereochemistry of each bridge is indicated by the prefix "cis" or "trans" arranged in the order corresponding to that of the numerical bridge length prefixes. Atoms are numbered starting at the bridgehead common to the longest bridge and the shorter of the two bridges immediately adjacent. Numbering proceeds along the longer bridge and then the next longer adjacent bridge in the order of the bracketed chain length designators until the first numbered position is reached. In the case of functionalized perannulenes, the aforementioned numbering protocol is observed but, if the bridges are symmetrically disposed, the direction of numbering is chosen to accord the lower number to the functional group.



trans, cis, cis-[10.6.4]triannulane
not
trans, cis, cis-[10.4.6]triannulane



trans, cis, cis, cis, cis-[10.6.8.4.6]pentannulane
not
trans, cis, cis, cis, cis-[10.6.4.8.6]pentannulane



trans, cis, cis-[10.3.3]triannulan-15-one
not
trans, cis, cis-[10.3.3]triannulan-17-one

(1) (a) Marshall, J. A.; Peterson, J. C.; Lebioda, L. *J. Am. Chem. Soc.* **1983**, *105*, 6515-6516. (b) Related polycyclic structures "coronanes" have recently been proposed by Fitjer et al. (Fitjer, L.; Giersig, M.; Clegg, W.; Schormann, N.; Sheldrick, G. M. *Tetrahedron Lett.* **1983**, *24*, 5351-5354). Their "[6.4]coronane" is equivalent to *all-cis*-[2.2.2.2.2.2]hexannulane. (c) *trans*-Bicyclo[5.1.0]octanes are relatively stable whereas *trans*-bicyclo-[4.1.0]heptanes are appreciably strained. Likewise, *trans*-cyclooctenes are considerably more stable than *trans*-cycloheptenes. For leading references, see: Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667-669. Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 4550-4555.

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