The high yield of the lactonization step coupled with the ease of preparation of the ethynes[9] makes this procedure a potentially useful approach to isocoumarins (1*H*-benzo-2-pyran-1-ones). The presence of bromine at the 4 position permits ready elaboration to more complex derivatives.

Experimental Section

4-Bromo-3-phenyl-1*H*-benzo-2-pyran-1-one (1). A solution of bromine (0.2 mL) in 10 mL of acetic acid was added dropwise to a mixture of 0.48 g of methyl 2-(2-phenylethynyl)benzoate,[9] (**5a**, 2.0 mmol) and 0.25 g of lithium bromide (2.9 mmol) in 10 mL of acetic acid, and the reaction was stirred overnight. The reaction mixture was added to 50 mL of water and the product filtered. The filter cake was washed with water, a sodium thiosulfate solution, and again with water and dried to give 0.47 g of **1**: mp (uncorr) 130–131.5 °C (recrystallized from cyclohexane) (lit.[3] 133 °C); mass spectrum, *m/e* (relative intensity) 302 (84), 300 (98), 274 (52), 272 (53), 221 (9), 193 (88), 165 (83), 164 (27), 105 (100), 88 (39), 77 (97); IR (KBr) 1742, 1623, 1603, 1478, 1403, 1236, 1090, 1080, 1058, 1035, 1025, 964, 761, 754, 692, 647 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.33–8.26 (m, 1 H), 7.94–7.87 (m, 1 H) 7.85–7.72 (m, 3 H) 7.60–7.50 (m, 1 H) 7.50–7.41 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHZ) δ 160.88 (s), 151.64 (s), 136.44 (s), 135.29 (d), 132.64 (s), 130.08 (d), 129.59 (d), 129.53 (d), 129.01 (d), 127.98 (d), 126.48 (d), 120.45 (s), 101.19 (s).

3-Phenyl-1*H*-benzo-2-pyran-1-one (4). Tributyltin hydride (45 mg) and **1** (32 mg) were stirred together (no solvent) at 145 °C for 14 h. The crude product was purified by TLC (silica gel, $CHCl_3$) to give 12 mg of **4** (51%) and 13 mg of **1** (41%): mp (uncorr) 91.5–92.5 °C (recrystallized from cyclohexane) (lit.[10] 91–92 °C; IR (KBr) 1719 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.36–8.27 (m, 1 H), 7.94–7.86 (m, 2 H), 7.78–7.67 (m, 1 H), 7.56–7.43 (m, 5 H), 6.96 (s 1 H).

Acknowledgment. We are most grateful to our colleagues Profs. George Newkome, Jim Traynham, and Klaus Fischer for their valuable comments and suggestions. This work is support by Grant GM29128 from the National Institutes of Health.

Registry No. 1, 22115-36-2; **4**, 4809-08-9; **5a**, 33578-05-1; **5b**, 88180-65-8.

(9) Castro, C. E.; Stephens, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 4358–4363.
(10) Gabriel, S. *Ber.* **1885**, *18*, 2445.

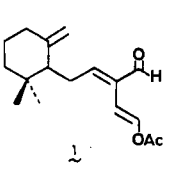
Ilikonapyrone Esters, Likely Defense Allomones of the Mollusc *Onchidium verruculatum*

Chris M. Ireland,*[†,⊥] Joseph E. Biskupiak,[†] Gilbert J. Hite,[†,‡] Michael Rapposch,[‡] Paul J. Scheuer,[§] and John R. Ruble[∥]

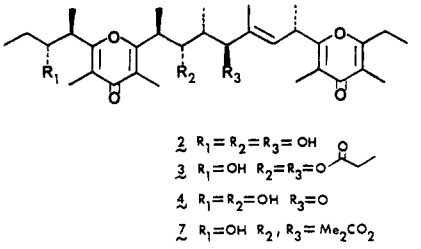
Section of Medicinal Chemistry and Pharmacognosy, School of Pharmacy, University of Connecticut, Storrs, Connecticut 06268, Institute of Material Sciences, University of Connecticut, Storrs, Connecticut 06268, Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, and Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received August 5, 1983

Naked gastropod molluscs belonging to the subclass *Opisthobranchia* have evolved various chemical defenses that include ingestion of functional coelenterate cnidoblasts from their prey and secretion of various repellents, including strong acids.[1] An observation[2] that the nudibranch *Phyllidia varicosa* secretes a defensive fluid led one of us (P.J.S.) to the first chemical elucidation of such an allomone, an isocyanosesquiterpene.[3] Members of the family Onchidacea are known to possess peripherally situated epidermal glands, described as "repugnatorial". The milky exudate from these glands reportedly deters predation and "when received upon one's tongue is found to sting like wild mustard".[4] Likewise this observation led one of use (C.M.I.) to the isolation of onchidal (**1**), the defensive allomone of *Onchidella binneyi*.[5] We now report the isolation of a mixture of esters, all based on the bispyrone alcohol ilikonapyrone (**2**),[6] as probable defense allomones of the Hawaiian onchid *Onchidium verruculatum* (Cuvier, 1830).



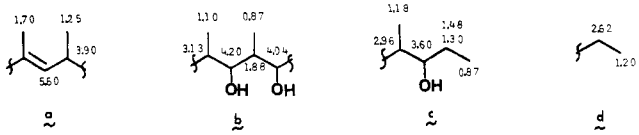
1



2 $R_1=R_2=R_3=OH$
3 $R_1=OH$ $R_2=R_3=O$
4 $R_1=R_2=OH$ $R_3=O$
7 $R_1=OH$ $R_2, R_3=Me_2CO_2$

O. verruculatum from Portlock, Oahu, HI were stored whole in acetone for 24 h. The acetone filtrate was evaporated and the residue partitioned between ether and H_2O to give 0.53 g of organic oil. Chromatography of the oil on Sephadex LH-20 (CH_2Cl_2/hexane, 4:1) and Bio-Sil A (EtOAc) gave a mixture of UV absorbing esters (IR 1735 cm^{-1}) that could only be partially resolved chromatographically to give small amounts of pure **3**. However, saponification greatly simplified the mixture, yielding a single alcohol **2**.

The triol **2** ($C_{32}H_{48}O_7$; HRMS obsd *m/z* 544.335, calcd 544.340) exhibited data for two fully substituted γ-pyrone rings bearing methyl groups at the β carbons [IR 1660, 1610 cm^{-1}; UV 260 nm (ϵ 12700); ^{13}C NMR ($CDCl_3$) δ 180.1 (s), 180.0 (s), 165.5 (s), 165.3 (s), 164.7 (s), 164.6 (s), 119.3 (s), 119.2 (s), 118.0 (s), 117.3 (s), 9.7 (q), 9.6 (q, 3 C); ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H), 1.92 (s, 3 H), 1.91 (s, 3 H), 1.89 (s, 3 H)] and the isolated spin systems a–d as defined by proton decoupling. The electron-impact mass spectrum of **2** (Scheme I) exhibited prominent ions at *m/z* 486 and 180, resulting from consecutive McLafferty rearrangements, indicating that b and c are attached to the same pyrone ring. Treatment of **2** with MnO_2 in CH_2Cl_2 furnished α,β-unsaturated ketone **4** [IR 1675, 1660, 1600 cm^{-1}; UV 242 nm (ϵ 13800), 257 (13300); ^1H NMR ($CDCl_3$) δ 1.76 (d, 3 H, J = 1 Hz), 6.43 (dd, 1 H, J = 9, 1 Hz)], indicating that a and b are also joined. Finally, treatment

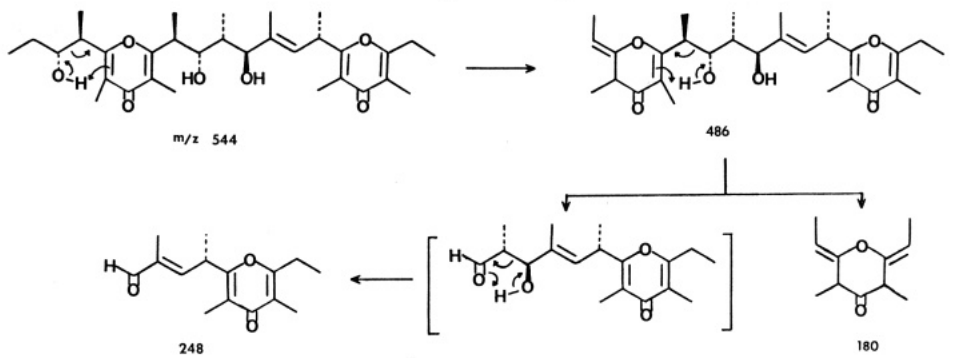


a b c d

(1) Thompson, T. E. *J. Mar. Biol. Assoc. U.K.* **1960**, *39*, 123–134.
(2) Johannes, R. E. *Veliger* **1963**, *5*, 104–105.
(3) Burreson, B. J.; Scheuer, P. J.; Finer, J.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 4763–4764. Hagadone, M. R.; Burreson, B. J.; Scheuer, P. J.; Finer, J. S.; Clardy, J. *Helv. Chim. Acta* **1979**, *62*, 2484–2494.
(4) Arey, L.; Crozier, W. J. *J. Exp. Zool.* **1921**, *32*, 433–502.
(5) Ireland, C.; Faulkner, D. J. *Bioorg. Chem.* **1978**, *7*, 125–131.
(6) Ilikona is the Hawaiian translation of the Latin *verrucula*, the specific name of the animal meaning "wart".

[†] School of Pharmacy, University of Connecticut.
[‡] Institute of Material Sciences, University of Connecticut.
[§] University of Hawaii at Manoa.
[∥] University of Pittsburgh.
[⊥] Present address: College of Pharmacy, University of Utah, Salt Lake City, UT 84112.

Scheme I. EI Mass Spectral Fragmentation of 2



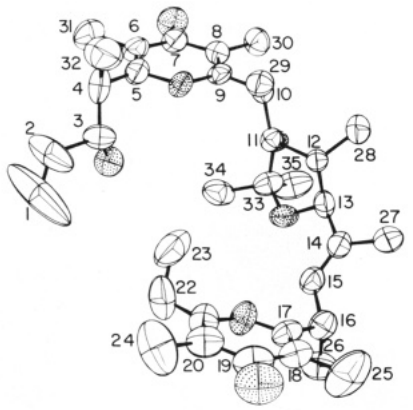
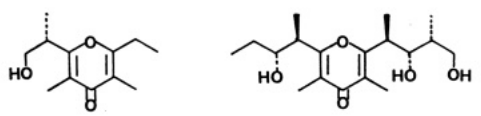


Figure 1. Numbering system and thermal ellipsoid plot, including 50% probability for ilikonapyrone acetonide.

of **2** with OsO_4–$NaIO_4$, followed by $NaBH_4$, gave the monopyrones **5** and **6**. Both **5** and **6** exhibited spectral



5 **6**

data (see Experimental Section) for a single pyrone ring and the side chains were identified by proton decoupling.

The relative stereochemistry of the seven asymmetric centers and of the trisubstituted olefin of **2** was determined by X-ray analysis (see Experimental Section) of the acetonide derivative **7**. Figure 1 shows the thermal ellipsoid plot for **7**. The X-ray solution did not distinguish between enantiomeric structures. The 3*R*,4*R*,10*S*,11*S*,12*S*,13*S*,16*S* enantiomer shown is an arbitary choice.

The predominant natural ester, $C_{38}H_{56}O_9$ (HRMS obsd m/z 656.391, calcd 656.392), was assigned structure **3** on the basis of mass spectral evidence. A strong $(M - CH_3CH_2CHO)^+$ peak at m/z 598 followed by peaks at 524 and 450 for consecutive losses of propionic acid indicate an alcohol at C-21 and propionate esters at C-11 and C-13.

Experimental Section

Infrared spectra were recorded on a Beckman 620 MX spectrophotometer. Electron-impact mass spectra were recorded on a Varian MAT 311 or AE1 MS-902 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL 100 or Bruker WM 500 spectrometer. Chemical shifts are reported relative to Me_4Si ($\delta = 0$). Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. UV spectra were recorded on a Cary 15 spectrophotometer. Melting points were recorded on a Hoover apparatus and are uncorrected. HPLC separations were performed on a Waters Model 201 system with 441 differential refractometer.

Onchidium verruculatum ($N = 400$) were collected at Portlock, Oahu, HI and stored in acetone at 5 °C for 24 h. The acetone extract was filtered through Whatman no. 1 paper and concentrated to a watery residue. The residue was suspended in H_2O (100 mL) and extracted with ether (3 × 100 mL). The combined ether layers were dried over $MgSO_4$ and evaporated to give 0.53 g of organic oil. The oil was chromatographed on Sephadex LH-20 (150 × 2 cm; CH_2Cl_2/hexane, 4:1) and Bio-Sil A (75 × 2 cm; EtOAc) to yield a mixture of esters (60 mg) and 2 mg of **3**. **3**: IR 3550, 1735, 1660, 1370 cm^{-1}; mass spectrum, m/z 656 $(M)^+$, 598 $(M - CH_3CH_2CHO)^+$, 524, 450; HRMS obsd m/z 656.391 calcd 656.392 for $C_{38}H_{56}O_9$.

Saponification of the Ester Mixture. The mixture of esters (60 mg) was stirred in 1% KOH/MeOH (25 mL) at room temperature for 2 h. Water (25 mL) was added to the reaction and the mixture extracted with $CHCl_3$ (3 × 50 mL). Evaporation of the $CHCl_3$ gave **2** (45 mg): $C_{32}H_{48}O_7$ (mass measurement; obsd 544.335, calcd 544.340); mp 96–98 °C; $[\alpha]_D$ −16° (*c* 1.5, CH_2Cl_2); IR (CH_2Cl_2) 3550, 1660, 1610 cm^{-1}; UV (MeOH) 260 nm (ϵ 12700); ^1H NMR ($CDCl_3$) δ 5.60 (1 H, dd, J = 9, 1 Hz), 4.20 (1 H, dd, J = 8, 1 Hz), 4.04 (1 H, d, J = 7 Hz), 3.90 (1 H, dq, J = 9, 7 Hz), 3.60 (1 H, m), 3.13 (1 H, dq, J = 8, 7 Hz), 2.96 (1 H, dq, J = 7, 7 Hz), 2.62 (2 H, q, J = 7 Hz), 1.93 (3 H, s), 1.92 (3 H, s), 1.91 (3 H, s), 1.89 (3 H, s), 1.70 (3 H, d, J = 1 Hz), 1.48 (1 H, ddq, J = 14, 3, 7 Hz), 1.30 (1 H, ddq, J = 14, 7, 7 Hz), 1.25 (3 H, d, J = 7 Hz), 1.20 (3 H, t, J = 7 Hz), 1.18 (3 H, d, J = 7 Hz), 1.10 (3 H, d, J = 7 Hz), 0.89 (3 H, t, J = 7 Hz), 0.87 (3 H, d, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 180.1 (s), 180.0 (s), 165.5 (s), 165.3 (s), 164.7 (s), 164.6 (s), 137.5 (s), 127.1 (d), 119.3 (s), 119.2 (s), 118.0 (s), 117.3 (s), 79.6 (d), 75.9 (d), 71.9 (d), 41.2 (d), 39.5 (d), 37.2 (d), 34.8 (d), 28.0 (t), 25.1 (t), 18.6 (q), 15.9 (q), 15.8 (q), 12.2 (q), 11.5 (q), 9.9 (q), 9.8 (q), 9.7 (q), 9.6 (q, 3 C).

MnO_2 Oxidation of 2 to 4. MnO_2 (30 mg) and **2** (10 mg) were stirred in CH_2Cl_2 (20 mL) at room temperature for 24 h. The reaction was filtered through Whatman no. 1 paper and the chloroform evaporated to give crude product. Silica HPLC (EtOAc) gave **4** (5 mg) as the only product: IR 3550, 1675, 1660, 1600, 1380 cm^{-1}; UV (MeOH) 242 nm (ϵ 13800), 275 (13300); ^1H NMR δ 6.34 (dd, 1 H, J = 9, 1 Hz), 4.0 (dd, 1 H, J = 8, 1 Hz), 3.90 (m, 1 H), 3.60 (m, 1 H), 3.05 (m, 2 H), 2.54 (q, 2 H, J = 7 Hz), 1.92 (s, 9 H), 1.88 (s, 3 H), 1.76 (d, 3 H, J = 1 Hz), 1.34 (d, 3 H, J = 7 Hz), 1.26 (d, 6 H, J = 7 Hz), 1.18 (d, 3 H, J = 7 Hz), 1.05 (m, 6 H).

OsO_4/$NaIO_4$ Oxidation of 3 to 5 and 6. The triol **2** (45 mg) was dissolved in dioxane (25 mL). OsO_4 (1 crystal) was added and the reaction stirred at room temperature. After 30 min $NaIO_4$ (100 mg) was added and stirring continued for 24 h. Water (25 mL) was added to the reaction and the mixture extracted with ether (25 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to give 30 mg of oil. The oil was dissolved in MeOH (20 mL) and $NaBH_4$ (50 mg) added. The mixture was stirred at room temperature for 1 h. The reaction was terminated by addition of H_2O (10 mL) and extracted with ether (3 × 25 mL). The combined ether layers were dried over $MgSO_4$ and concentrated to 25 mg of oil. Silica HPLC (EtOAc) gave **5** (8 mg) and **6** (12 mg).

5: $[\alpha]_D$ −16.7° (*c* 0.3, CH_2Cl_2); IR (CH_2Cl_2) 3610, 1660, 1610 cm^{-1}; UV (MeOH) 258 nm (ϵ 6000); ^1H NMR ($CDCl_3$) δ 3.78 (2 H, m), 3.23 (1 H, m), 2.61 (2 H, q, J = 7 Hz), 1.96 (3 H, s), 1.92 (3 H, s), 1.20 (6 H, m); MS, m/z 210 (M^+), 193, 179, 122.

6: $[\alpha]_D$ −6.7° (*c* 0.3, CH_2Cl_2); IR (CH_2Cl_2) 3610, 1660, 1610 cm^{-1}; UV (MeOH) 260 nm (ϵ 7200) ^1H NMR ($CDCl_3$) δ 4.12 (1 H, dd,

J = 9, 3 Hz), 3.68 (3 H, m) 3.14 (1 H, dq, J = 9, 7 Hz), 3.03 (1 H, dq, J = 7, 7 Hz), 1.96 (3 H, s), 1.95 (3 H, s), 1.94 (1 H, m), 1.60–1.44 (2 H, m), 1.26 (3 H, d, J = 7 Hz), 1.15 (3 H, d, J = 7 Hz), 0.99 (3 H, t, J = 7 Hz), 0.95 (3 H, d, J = 7 Hz); MS, m/z 326 (M^+), 268, 180.

Conversion of 2 to 7. The triol **2** (14 mg) was dissolved in 2,2-dimethoxypropane (4 mL). A crystal of TsOH was added and the reaction refluxed for 3 h. The reaction was diluted with dry benzene (10 mL). The organic layer was evaporated to give **7** (10 mg): crystals from hexane; mp 134–135 °C; high-resolution mass measurement, obsd 584.372, calcd 584.3715 for $C_{35}H_{52}O_7$.

X-ray Analysis of 7. Precession photographs of a single crystal (0.10 × 0.10 × 0.25 mm) of ilikonapyrone acetonide ($C_{35}H_{52}O_7$) revealed orthorhombic symmetry ($P2_12_12_1$). Latice translations, a = 19.380 (3), b = 23.031 (4), c = 7.831 (1) Å, were determined by least-squares fitting of 24 automatically centered (Picker FACS-I diffractmeter) reflections (39° < 2θ < 48°) measured with Ni-filtered Cu Kα radiation (λ = 1.5405 Å) at 291 K. Crystal density (1.108 g/cm^3, flotation, KI–H_2O), lattice parameters, and space group symmetry reveal that there are four molecules per unit cell and one per asymmetric crystallographic unit. Intensity data (2$\theta \leq$ 100°) were measured in the $\theta/2\theta$ scan mode. Of 2089 unique reflections, 1697 were considered observed by using the criterion $I_0 \geq 3\sigma(I_0)$ after correction for Lorentz, polarization, background, decay (6%), and absorption (ψ-scan, μ = 6.16 cm^{-1}, 8.2% maximum at 15,2,2) effects. The structure was solved by direct methods. Repeated cycles of structure factor and difference Fourier synthesis provided acceptable positional parameters for all 42 non-hydrogen atoms. Anisotropic refinement converged at R = 0.12, minimizing $\sum w[|F_o| - |F_c|]^2$ where $w = 1/\sigma^2$. Repeated cycles of refinement and difference Fourier synthesis revealed positions for 25 hydrogen atoms. Positional parameters for 20 additional hydrogen atoms could be calculated on the basis of geometrical constraints. In the final cycles of refinement, hydrogen atom positional parameters were fixed. Throughout, thermal parameters for hydrogen atoms were also fixed and were assigned values of $8\pi^2(\sum_{i=1}^{3} U_{ij}/3)$ of the atoms to which they were bonded. Hydrogen atoms of the hydroxyl group and the methyl groups C(1) and C(24) could not be satisfactorily located. Refinement converged (shift/error ≤ 0.5) at $R = 0.072$ ($R = \sum(||F_o| - |F_c||)/\sum|F_o|$) and $wR = 0.079$ ($wR = [\sum w(|F_o| - |F_c|^2/\sum w|F_o|^2]^{1/2}$. Additional crystallographic details (structure factor table, atomic positional and thermal parameters, bond distances, bond angles, and torsion angles) can be found in the supplementary material.

Calculations were performed on IBM 370/168 and DEC PDP-10 computers. Atomic scattering factors were taken from Cromer and Weber (Cromer, D. T.; Weber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109) and Stewart et al. (Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187). The principle programs used were the following: XRAY72, the X-ray system of crystallographic programs (Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. Technical Report TR-192, Computer Science Center, University of Maryland, College Park, MD, 1972); ORTEP-II, crystallographic illustration program (Johnson, K. C. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976); MULTAN, programs for solution of crystal structures from X-ray diffraction data (Declercq, J. P.; Germain, G.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1975**, *31*, 367–372); ORFLS, full-matrix least-squares program for refinement of crystal structures (Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962); and ABS, a locally modified absorption correction program (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351–359.

Acknowledgment. This study was supported in part by a grant from the National Institutes of Health to CMI (CA 29821). ^{1}H and ^{13}C NMR spectra were obtained on the Bruker WM-500 at the Northwest Regional NSF–NMR Facility, Yale University, partially supported by the National Science Foundation (Grant CHE 79-16210). We thank David Sesin for technical assistance in preparing ilikonapyrone acetonide and Deborah Roll for additional collections of *O. verruculatum*.

Registry No. **2**, 88130-78-3; **3**, 88130-79-4; **4**, 88130-80-7; **5**, 88130-81-8; **6**, 88130-82-9; **7**, 88130-83-0; 2,2-dimethoxypropane, 77-76-9.

Supplementary Material Available: Tables I and II listing structure factors, atomic positional and thermal parameters, bond distances, bond angles, and torsion angles (11 pages). Ordering information is given on any current masthead page.

Isolation of the Key Intermediate in the Formation of *cis*-Bicyclo[3.3.0]octane-3,7-diones from Dimethyl 3-Ketoglutarate and 1,2-Dicarbonyl Compounds

G. Kubiak and J. M. Cook*

Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

U. Weiss

Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, Digestive and Kidney Diseases, Bethesda, Maryland 20205

Received June 29, 1982

The reaction of 2 equiv of dimethyl 3-ketoglutarate (*1*) with 1 equiv of a 1,2-dicarbonyl compound **2**[1] provides a convenient approach to tetramethoxycarbonyl compounds,[2,3] which in turn yield *cis*-bicyclo[3.3.0]octane-3,7-diones on acid-catalyzed hydrolysis–decarboxylation. Examination of this process in our laboratories has resulted in a facile, general route for the preparation of more complex polyquinanes,[1-6] some of which are illustrated in Scheme I, as well as for compounds of pharmaceutical interest.[7] The versatility of this approach has been amply illustrated recently by reports of the syntheses of gymnomitrol,[8a] isocomene,[8b] and modhephene.[5]

The formation of the *cis*-bicyclo[3.3.0]octane-3,7-dione system from **1** and **2** can be easily rationalized[9] through the sequence of aldolization and Michael reactions shown in Scheme II. In agreement with this, Bertz has suggested that in mildly acidic media (pH 5) the aldol product **3** undergoes cyclization to **4**, which eventually leads to the *cis*-bicyclo[3.3.0] system,[10] while under less acidic conditions evidently elimination to a *trans*-olefin is observed.[10] We have now found that at pH >8 the 4-hydroxycyclo-

(1) Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885.
(2) Yang, S.; Cook, J. M. *J. Org. Chem.* **1976**, *41*, 1903. Weber, R. W.; Cook, J. M. *Can. J. Chem.* **1978**, *56*, 189.
(3) Bertz, S. H. Ph.D. Thesis, Harvard University, Cambridge, MA, 1978.
(4) Mitschka, R.; Oehldrich, J.; Takahashi, K.; Weiss, U.; Cook, J. M. *Tetrahedron* **1981**, *37*, 4521.
(5) Wrobel, J.; Takahashi, K.; Honkan, V.; Bertz, S.; Lannoye, G.; Cook, J. M. *J. Org. Chem.* **1983**, *48*, 139.
(6) Lannoye, G.; Honkan, V.; Weiss, U.; Bertz, S.; Cook, J. M. "Abstracts of Papers", 16th Annual Meeting, Great Lakes American Chemical Society Region, Illinois State University, Normal, IL, June 7–9, **1982**, No. 201.
(7) Nicolaou, K. C.; Sipio, W. J.; Magolda, R. L.; Seitz, S.; Barnett, W. E. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1067. Shibasaki, M.; Ueda, J.; Ikegami, S. *Tetrahedron Lett.* **1979**, 433.
(8) (a) Coates, R. M.; Shah, S. K.; Mason, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 6765. Han, Y.-K.; Paquette, L. *J. Org. Chem.* **1979**, *44*, 3731. (b) Dauben, W. G.; Walker, D. M. *Ibid.* **1981**, *46*, 1103.
(9) Yang-Lan, S.; Mueller-Johnson, M.; Oehldrich, J.; Wichman, D.; Weiss, U.; Cook, J. M. *J. Org. Chem.* **1976**, *41*, 4053.
(10) Bertz, S. H.; Adams, W. O.; Silverton, J. V. *J. Org. Chem.* **1981**, *46*, 2828.

0022-3263/84/1949-0561$01.50/0