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SYNTHESIS OF ANNULATED 4-ALKYLIDENEBUTENOLIDES FROM NATURAL OCCURRING DIOSPHENOLS

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Abstract: Diosphenol (3) and Ψ -diosphenol (4), two constituents of the essential oil from the buchu plant, *Borosma betulina* (Bartl.), were utilized for the synthesis of the anulated 4-ylidenebutenolides (5) and (6).

Natural products which contain the 4-alkylidenebutenolide (1) structural moiety are frequently encountered, and many of these compounds display notable organoleptic or biological activity.^{1,2} This group of natural products include members like patulin and neopatulin,³ protoanemonin,⁴ peridenin, the principle carotenoid pigment of dinoflagellates,⁵ jolkinolide A,⁶ benthocyanin, a free radical scavenger of microbial origin,⁷ piperolide,⁸ and lettucenin which inhibits spore germination of *Ceratocystis fimbriata*.⁹ Since 4-alkylidenebutenolides (1) can furthermore be rearranged under basic conditions to cyclopentene-1,3-diones¹⁰ or reduced to the corresponding furans (2),¹¹ it is therefore not surprizing that much

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work has been devoted to the synthesis of these compounds.^{2,6,12} Despite previous efforts, the need for more convenient and generally applicable methods, especially for the synthesis of annulated 4-alkylidenebutenolides (1), still remains. In this communication we report on simple, generally applicable synthetic routes to annulated 4-ylidenebutenolides by utilizing natural occurring diosphenols (3) and (4) as starting materials for the synthesis of butenolides (5) and (6).



Diosphenol (3) and its isomer Ψ -diosphenol (4) are constituents of the essential oil of the indigenous buchu plant, *Borosma betulina* (Bartl.), that grows freely in some high lying areas of the Western Cape.¹³ Substantial quantities of pure, crystalline diosphenol (3) can be separated from the essential oil by fractional crystallization, but no convenient method for the isolation of Ψ -diosphenol in useful quantities appears to exist.

Gradual addition of a THF solution of the enolate of diosphenol (3) to bromoacetyl bromide in ether yielded the bromoester (7) which contained only trace amounts of the corresponding isomer (8). The order and speed of addition of the reagents are crucial for the successful outcome of the reaction since substantial coupling between the bromoester (7) and the enolate of diosphenol can otherwise take place. Treatment of the phosphonate (9), which was synthesized in 68% yield

from the pure bromoester (7), with sodium methoxide in methanol gave the butenolide (6) in low yield, as well as quantities of the ketoester (10) and the isomeric diosphenols (3) and (4). The outcome of this reaction is an indication that the phosphonate (9) is cleaved upon treatment with methoxide in methanol. This is followed by intermolecular condensation between the resulting trimethyl phosphonoacetate and the sterically less hindered Ψ -diosphenol (4), the base-catalyzed rearrangement product of diosphenol (3), to yield the butenolide (6) and ketoester (10) via enol lactonization and double bond migration of the initial condensation product, respectively.



The validity of the proposed cleavage reaction was furthermore substantiated by the formation of methyl cinnamate (72%), diosphenol (3) (51%), and Ψ -

diosphenol (4) (19%) when the phosphonate (9) was treated with methanolic sodium methoxide in the presence of one molar equivalent of benzaldehyde. Reaction of the phosphonate (9) with the weakly nucleophilic base, potassium *tert* butoxide, led to the desired intramolecular Horner condensation⁶ and the resulting formation of the butenolide (5) in good yield.

In order to develop a chemoselective synthesis for the isomeric butenolide (6), diosphenol (3) was treated with sodium carbonate in benzene to produce an oily, 55:45 equilibrium mixture of (3) and Ψ -diosphenol (4), respectively. Diosphenol (3) was largely removed from the equilibrium mixture by fractional crystallization from small quantities of hexane to yield an oily residue, which comprised Ψ -diosphenol (4) (86%) and diosphenol (3) (14%).



This product was treated with sodium hydride and bromoacetyl bromide under the usual reaction conditions to produce a mixture of the bromoesters (8) and (7), from which the desired product (8) could almost quantitatively be separated by crystallization. The phosphonate (11), which was synthesized from the pure bromoester (8) in 62% yield, smoothly underwent an intramolecular Horner

condensation in the presence of potassium *tert* butoxide to yield the desired isomeric butenolide (6).

EXPERIMENTAL

All operations were carried out in an argon atmosphere. Merck silica gel 60 (particle size 0.063 - 0.200 mm) and 60 PF 254 with calcium sulphate were used for column chromatography and separations on the chromatotron, respectively. Mass spectra were taken on a Varian MAT 311 A spectrometer, while NMR spectra were recorded for solutions in deuteriochloroform on a Varian VXR 300 instrument. COSY, HETCOR, and DEPT experiments were performed to interpret the more complex NMR spectra.

1. Diosphenol (3)

The essential oil from the buchu plant, *Borosma betulina* (Bartl.), was collected by steam distillation of dried buchu leaves. Subsequent cooling of the oil at 0°-4°C for 48 h gave substantial quantities of crystalline material which were recrystallized from hexane to yield pure *diosphenol* (3), m.p. 81.7°C (lit.² 82-83°C); $\delta_{\rm H}$ 0.96 (d, J 7.02 Hz, 3H), 0.86 (d, J 6.84, 3H), 1.78 (dddd, J 13.26, 11.64, 8.76, and 6.13 Hz, 1 H), 1.89 (t, J 1.20 Hz, 3H), 1.94 (dq, J 13.16 and 4.53 Hz, 1H), 2.20 (dt, J 11.52 and 4.51 Hz, 1H), 2.32-2.37 (m, 2H), and 2.40 (h, J 6.89 and 4.51 Hz, 1H); $\delta_{\rm C}$ 16.84 (q, CH₃), 18.47 (q, CH₃), 20.44 (q, CH₃), 22.70 (t, CH₂), 26.40 (d, CH), 29.32 (t, CH₂), 50.67 (d, CH), 129.51 (s, =C<), 143.82 (s, ≥C-OH), 196.05 (s, C=O).

2. 6-Isopropyl-3-methylcyclohex-2-enon-2-yl bromoacetate (7)

Pure recrystallized diosphenol (12.01 g; 71.0 mmol) in dry THF (50 cm³)

was added dropwise during 40 min to an oil-free suspension of sodium hydride (1.79 g; 74.0 mmol) in THF (20 cm³) at 0°C, and stirring was maintained for a further 90 min at 0°C and 15 min at 20°C. The resulting suspension of the enolate was then slowly added via a peristaltic pump (flow rate 1.0 cm³/min) to bromoacetyl bromide (14.43 g; 71 mmol) in ether (20 cm³) at 0°C and the mixture stirred for an additional 90 min at 0°C. After removal of the solvent by distillation, the residue was treated with water, extracted with ether, and the residue from the dried (MgSO₄) extract distilled to yield the bromoester (7) (16.0 g; 77%), b.p. 110°C (airbath temp.)/0.02 mm Hg; $\delta_{\rm H}$ 0.87 (d, J 6.77 Hz, 3 H), 0.95 (d, J 6.97 Hz, 3 H), 1.89 (t, 0.92 Hz, 3 H), 1.92 (m, 1 H), 2.02 (m, 1 H), 2.22 (dt, J 10.94 and 4.81 Hz, 1 H), 2.40 (m, 1 H), 2.49 (m, 2 H), and 4.04 (s, 2 H); $\delta_{\rm C}$ 17.52 (q, CH₃), 18.49 (q, CH₃), 20.48 (q, CH₃), 22.24 (t, CH₂), 25.02 (t, CH₂), 26.19 (d, CH), 30,00 (t, CH₂), 52.01 (d, CH), 141.52 (s, C), 146.93 (s, C), 164.97 (s, C=O), and 192.36 (s, ring C=O); M⁺, 290,0297 and 288.0317. Calc. for C₁₂H₁₇BrO₃: M, 290.0342 and 288.0362. The bromo-ester (7) contained according to ¹H NMR analysis < 1% of the isomeric bromoester (8) as an impurity.

Dimethyl 6-isopropyl-3-methylcyclohex-2-enon-2-ylphosphonoacetate (9)

Trimethylphosphite (6.90 g; 55.60 mmol) was added dropwise during 30 min to the bromoester (7) (15.60 g; 50.0 mmol) in dry toluene (30 cm³) at 70°C. The reaction mixture was heated under reflux for 24 h, whereupon the solvent was removed by distillation and the residue purified by chromatography on the chromatotron with THF as eluent to yield the pure *phosphonate* (9) (13.0 g; 68%), b.p. 150°C (air-bath temp.)/0.024 mm Hg; $\delta_{\rm H}$ 0.86 (d, J 6.81 Hz, 3 H), 0.95 (d, J 6.92 Hz, 3 H), 1.87 (m, 1 H), 1.91 (t, J 0.9 Hz, 3 H), 1.99 (m, 1 H), 2.21 (dt, J 11.0 and 4.8 Hz, 1 H), 2.38

(m, 1 H), 2.48 (m, 2 H), 3.19 (d, $J_{PH} 21.7$ Hz, 2 H), and 3.84 (d, $J_{PH} 11.3$ Hz, 2 x OCH₃); $\delta_{C} 17.50$ (q, CH₃), 18.53 (q, CH₃), 20.77 (q, CH₃), 22.32 (t, CH₂), 29.99 (t, CH₂), 32.65 (dt, $J_{PC} 134.10$ Hz, CH₂), 26.19 (d, CH), 52.15 (d, CH), 53.24 (dq, $J_{PC} 5.9$ Hz, 2 x OCH₃), 141.60 (s, =C<), 146.93 (s, \geq C-O), 163.23 (s, C=O), and 192.32 (s, ring C=O); M⁺, 318.1233. Calc. for C₁₄H₂₃O₆P : M, 318.1232.

4. Treatment of dimethyl 6-isopropyl-3-methylcyclohex-2-enon-2ylphosphonoacetate (9) with sodium methoxide

A freshly prepared solution of sodium (0,41 g; 17,60 mmol) in methanol (30 cm^3) was added dropwise to a stirred solution of the phosphonate (9) (5.10 g; 16.03 mmol) in methanol (5.0 cm³). The reaction mixture was stirred for 18 h at room temp and for an additional 3 h at 50°C. After evaporation of the solvent under vac, the residue was treated with water (60 cm³), and the aqueous mixture repeatedly extracted with ether. The residue from the dried (MgSO₄) ether extract was chromatographed on silica gel with ether-petroleum ether (3:17) as eluent to yield *diosphenol* (3)(0.19 g; 7.4%), *Y-diosphenol* (4) (0.14 g; 5.2%), m.p. 34.5°C (from hexane), δ_H 1.04 (d, J 6.91 Hz, 3 H), 1.07 (d, J 6.95 Hz, 3 H), 1.18 (d, 6.88 Hz, 3 H), 1.57-1.70 (m, 1 H), 2.04 (h, J 4.42 Hz, 1 H), 2.29-2.34 (m, 2 H), 2.36-2.49 (m, 1 H), 3.13 (h, J 6.91 Hz, 1 H), and 6.14 (s, OH); δ_C 15.53 (q, CH₃), 19.74 (q, >CH-<u>CH₃</u>), 20.04 (q, >CH-<u>CH₃</u>), 22.44 (t, CH₂), 28.06 (d, CH), 30.94 (t, CH₂), 39.91 (d, ring CH), 138.48 (s, =C<), 141.68 (s, \geq C-OH), and 197.54 (s, C=O). Elution with ether-petroleum ether (1:3) yielded 5,6-dihydro-7-isopropyl-4-methylbenzo [2,3-b] furan-2(5H)-one (6) (0.34 g; 11.0 %), b.p. 75°C (air-bath temp.) / 0.01 mm Hg; $\delta_{\rm H}$ 1.08 (d, J 7.14 Hz, 3 H), 1.10 (d, J 7.16 Hz, 3 H), 1.27 (d, J 6.85, 3 H), 1.48 (dddd, J 13.14, 11.64, 10.30, and 5.20 Hz, 1 H), 1.95 (ddd, J 13.20, 8.76, and 4.50 Hz, 1 H), 2.25 (dddt, J 17.70, 10.38, 4.38, and 0.86 Hz, 1 H), 2.37

(dt, J 17.70 and 4.66 Hz, 1 H), 2.70 (m, 1 H), 3.10 (p, J 6.98 Hz, 1 H), and 5.72 (d, J 1.78 Hz, 1 H); $\delta_{\rm C}$ 18.35 (q, CH₃), 19.93 (q, CH₃), 20.27 (q, CH₃), 23.05 (t, CH₂), 28.61 (d, CH), 30.37 (d, CH), 31.48 (t, CH₂) 108.58 (d, CH), 131.93 (s, =C<), 144.30 (s, =C<), 161.40 (s, \geq C-O), and 170.48 (s, C=O); M⁺, 192.1150. Calc. for C₁₂H₁₆O₂ : M, 192.1150. Elution with ether-petroleum ether (3:7) yielded *2-carbo-methoxymethyl-6-isopropyl-3-methylcyclohex-2-enone* (10) (1.21 g; 33%), b.p. 70°C (airbath temp.) / 0.056 mm Hg; $\delta_{\rm H}$ 0.85 (d, J 6.79 Hz, 3 H), 0.93 (d, J 7.0 Hz, 3 H), 1.82 (m, 1 H), 1.93 (t, J 0.75 Hz, 3 H), 1.97 (m, 1 H), 2.09 (dt, J 10.69 and 4.82 Hz, 1 H), 2.36 (m, 1 H), 2.44 (m, 2 H), 3.35 (d, J 16.55, 2 H), and 3.65 (s, 3 H); $\delta_{\rm C}$ 18.64 (q, CH₃), 20.62 (q, CH₃), 20.62 (q, CH₃), 22.42 (t, CH₂), 26.21 (q, CH₃), 30.95 (t, CH₂), 31.74 (t, ring CH₂), 51.56 (t, ring CH₂), 51.76 (d, CH), 129.24 (s, =C<), 156.69 (s, =C<), 171.92 (s, C=O), and 199.48 (s, ring C=O); M⁺, 224.1412. Calc. for C₁₃H₂₀O₃: M, 224.1412.

5. 5,6-Dihydro-4-isopropyl-7-methylbenzo[2,3-b]furan-2(5 H)-one (5)

The phosphonate (9) (7.15 g; 22.50 mmol) in dry THF (20 cm³) was added dropwise to a stirred suspension of potassium *tert* butoxide (2.77 g; 24.70 mmol) in dry THF (30 cm³) at 0°C during 40 min. Stirring was maintained for an additional 5 h at 0°C, whereafter the solvent was evaporated under vac, the residue treated with water (60 cm³), and the aqueous mixture repeatedly extracted with ether. The combined ether extracts were dried (MgSO₄) and the residue from the ether extract chromatographed on silica gel. Elution with ether-petroleum ether (1:4) yielded the pure *butenolide* (5) (3.28 g; 76%), b.p. 105°C (air-bath temp.) / 0.015 mm Hg; $\delta_{\rm H}$ 0.94 (d, J 6.86 Hz, 3 H), 1.03 (d, J 6.88 Hz, 3 H), 1.67 (dddd, J 13.36, 10.39, 8.38, and 5.76 Hz, 1 H), 1.85 (dq, J 13.36 and 4.76 Hz, 1 H), 1.95 (t, J 1.20 Hz, 3 H), 2.03-2.17 (m, 1 H), 2.28-2.36 (m, 2 H), 2.49-2.57 (m, 1 H), and 5.70 (dd, J 1.77 and 0.62 Hz); δ_{C} 16.76 (q, CH₃), 18.17 (q, CH₃), 20.52 (q, CH₃), 23.49 (t, CH₂), 28.87 (d, CH), 29.21 (t, CH₂), 41.48 (d, CH), 109.07 (d, =CH-), 122.81 (s, =C<), 146.29 (s, =C<), 158.86 (s, \geq C-O), and 170.50 (s, C=O); M⁺, 192.1150. Calc. for C₁₂H₁₆O₂: M, 192.1150.

6. 3-Isopropyl-6-methylcyclohex-2-enon-2-yl bromoacetate (8)

A suspension of diosphenol (3) (10.0 g; 59.0 mmol), anhydrous sodium carbonate (12,62 g; 119.0 mmol), and triethylbenzylammonium chloride (3.37 g; 14.90 mmol) in benzene (500 cm³) was refluxed for 10 h, filtered, and the solvent evaporated to yield upon cooling (4°C) a semi-crystalline residue which comprised an equilibrium mixture (55:45) of (3) and Ψ -diosphenol (4), respectively, according to ¹H NMR analysis. Diosphenol (3) was largely removed from the equilibrium mixture by fractional crystallization from small quantities of hexane to yield an oily residue (3.97g; 39.7%) which consisted of Ψ -diosphenol (4) (86%) and diosphenol (3) (14%). A product mixture from consecutive experiments (10.57 g; 62.9 mmol) in dry THF (60 cm³) was added dropwise during 50 min to an oil-free suspension of sodium hydride (1.67 g; 69.0 mmol) in THF (15 cm³) at 0°C, and stirring was continued for an additional 90 min at 0°C followed by 15 min at room temp. The resulting suspension was slowly added as in 2 to freshly distilled bromoacetyl bromide (12.70 g; 62.9 mmol) in dry ether (30 cm³) at 0°C and the mixture stirred for an additional 2 h at 0°C, filtered, the residue from the filtrate treated with water (60 cm³), and repeatedly extracted with ether. Recrystallization of the residue from the dried $(MgSO_4)$ ether extracts, which contained the bromoesters (8) (57%) and (7) (16%), from hexane-ether (9:1) and separation of the mother liquors on the chromatotron with ether-petroleumether (1:4) as eluent yielded the pure bromoester (8) (9.94 g; 57,0%), m.p. 59.5°C; δ_H 1.05 (d, J 5.11 Hz, 3 H),

1.08 (d, J 5.04 Hz, 3 H), 1.16 (d, J 6.79 Hz, 3 H), 1.73 (dddd, J 13.39, 12.04, 8.76, and 6.60 Hz, 1 H), 2.10 (dq, J 13.37 and 4.45 Hz, 1 H), 2.45 (m, 2 H), 2.95 (h, J 6.91 Hz, 1 H), and 4.03 (s, 2 H); $\delta_{\rm C}$ 14.98 (q, CH₃), 19.52 (q, CH₃), 19.92 (q, CH₃), 23.26 (t, CH₂), 25.00 (t, CH₂Br), 28.61 (d, CH), 30.07 (t, CH₂), 41.20 (d, ring CH), 139.54 (s, =C<), 155,40 (s, \geq C-O), 165.12 (s, C=O), and 193.55 (s, ring C=O); M⁺, 290.0297 and 288.0317. Calc. for C₁₂H₁₇BrO₃ : M, 290.0342 and 288.0363.

Dimethyl 3 - isopropyl - 6 - methylcyclohex - 2 - enon - 2 -ylphosphonoacetate (11)

Trimethyl phosphite (2.70 g; 21.80 mmol) in dry toluene (10 cm³) was added dropwise during 30 min to the pure bromoester (8) (6.30 g, 21.80 mmol) in toluene (20 cm³) at 60°C, whereupon the reaction mixture was refluxed for 27 h. Evaporation of the solvent under vac produced an oily residue which was rapidly separated on the chromatotron to minimize hydrolysis on the chromatodisc. Elution with ether, which vielded diosphenol (3) (0.20 g; 5.4%) and unreacted bromoester (8) (1.08; 17.3%), was followed by elution with THF to yield the pure phosphonate (11) (4.69 g; 67.7%), b.p. 105°C (air-bath temp.) / 0.025 mm Hg; $\delta_{\rm H}$ 1.05 (d, J 6.88 Hz, 3 H), 1.07 (d, J 6.89 Hz, 3 H), 1.16 (d, J 6.85 Hz, 3 H), 1.66-1.79 (m, 1 H), 2.09 (dq, J 13.39 and 4.46 Hz, 1H), 2.29-2.39 (m, 1 H), 2.40-2.53 (m, 2 H), 3.03 (h, J 6.91 Hz, 1 H), 3.19 (d, J_{PH} 21.52 Hz, 2 H), and 3.84 (d, JPH 11.26 Hz, 2 x OCH3); Sc 17.46 (q, CH3), 20.63 (q, CH3), 19.49 (q, CH3), 23.00 (t, CH2), 28.32 (d, CH), 30.11 (t, CH2), 32.65 (dt, J_{PC} 133.5 Hz, CH₂), 41.20 (d, CH), 53.24 (dq, J_{PC} 6.40 Hz, 2 x OCH₃), 139.56 (s, =C<), 155.32 (s, ≥C-O), 163.57 (s, C=O), and 193.63 (s, ring C=O); M^+ , 318.1233. Calc. for $C_{14}H_{23}O_6P$: M, 318.1232.

8. 5,6-Dihydro-7-isopropyl-4-methylbenzo [2,3-b]furan-2(5H)-one (6)

The phosphonate (11) (4.40 g; 13.80 mmol) in dry THF (30 cm³) was added dropwise to a stirred suspension of potassium *tert* butoxide (1.70 g; 15.0 mmol) in dry THF (30 cm³) at 0°C during 1 h. Stirring was maintained for an additional 1 h at room temp whereafter the solvent was evaporated under vac, the residue treated with water (70 cm³), and the aqueous reaction mixture repeatedly extracted with ether. The combined ether extracts were dried (MgSO₄) and the residue from the ether extract chromatographed on silica gel to yield the pure *butenolide* (6) (1.70 g; 65%) upon elution with ether-petroleum ether (1:4).

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References

- Dean, F.M., "Naturally Occurring Oxygen Ring Compounds", Butterworths, London, 1963; Pattenden, G., Fortsch. Chem. Org. Naturst., 1978, 35, 133.
- Asaoka, M., Yanagida, N., Ishibashi, K., and Takei, H., Tetrahedron Lett., 1981, 22, 4269.
- Bennett, M., Gill, G.B., Pattenden, G., Shuker, A.J., and Stapleton, A., J. Chem. Soc. Perkin. Trans. I, 1991, 929.
- 4. Grundmann, C. and Kober, E., J. Amer. Chem. Soc., 1955, 77, 2332.
- Strain, H.H., Svec, W.A., Aizetmuller, A., Grandolfo, M.C., Katz, J.J., Kjøsen, H., Norgård, S., Liaaen-Jensen, S., Haxo, F.T., Wegfahrt, P., and Rapoport, H., J. Amer. Chem. Soc., 1971, 93, 1823.

- Katsumura, S., Kimura, A., and Isoe, S., J. Chem. Soc. Chem. Commun., 1983, 330.
- Shin-ya, K., Furihata, K., Hayakawa, Y., and Seto, H., Tetrahedron Lett., 1991, 32, 943.
- 8. Stachel, H.-D. and Dandl, K., Tetrahedron Lett., 1980, 21, 2891.
- 9. Brooks, C.J.W. and Watson, D.G., Nat. Prod. Rep., 1991, 8, 367.
- Gedge, D.R. and Pattenden, G., J. Chem. Soc. Chem. Commun., 1978, 880.
- Boegman, N., During, F., and Garbers, C.F., Chem. Comm., 1966, 600; Minato, H. and Nagasaki, T., J. Chem. Soc. (C), 1966, 377; Gedge, D.R. and Pattenden, G., Tetrahedron Lett., 1977, 4443.
- Nakano, T. and Nagai, Y., J. Chem. Soc. Chem. Commun., 1981, 815;
 Rao, Y.S., Chem. Rev., 1976, 76, 625; Knight D.W. and Pattenden, G., J. Chem. Soc. Perkin Trans. I, 1975, 635.
- Kaiser, R., Lamparsky, D. and Schudel, P., J. Agric. Food Chem., 1975, 23, 943.

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