boronic acid, which decomposed in a few days at 25 °C. Recrystallization from ether/pentane yielded a sample which was not analytically pure: mp 66–69 °C; NMR ($CDCl_3$) δ 4.30 (s, 1, S_2CHB), 5.9 (broad, s, 2, OH), 7.1–7.8 (m, 10, C_6H_5).

Esters of Bis(phenylthio)methaneboronic Acid 2a,b,c. A solution of 10 g (36 mmol) of crude bis(phenylthio)methaneboronic acid 1 and 36 mmol of the diol in 50 mL of THF was kept at 25 °C for 2 h, then distilled. The pinacol ester **2a** was obtained in 8 yield: bp 180–184 °C (0.1 mm); NMR ($CDCl_3$) δ 1.10 (s, 12, CCH_3), 4.24 (s, 1, S_2CHB), 7.2–7.8 (m, 10, C_6H_5). Anal. Calcd for $C_{19}H_{23}BO_2S_2$: C, 63.69; H, 6.47; B, 3.02; S, 17.90. Found: C, 63.71; H, 6.33; B, 3.07; S, 17.74. The 1,3-propanediol ester **2b** was obtained in 91% yield: bp 182–186 °C (0.1 mm); NMR ($CDCl_3$) δ 1.62 (m, 2, CH_2), 3.83 (t, 4, OCH_2), 4.20 (s, 1, S_2CHB), 7.2–7.8 (m, 10, C_6H_5). Anal. Calcd for $C_{16}H_{17}BO_2S_2$: C, 60.77; H, 5.42; B, 3.42; S, 20.28. Found: C, 60.98; H, 5.30; B, 3.26; S, 20.45. The 2,2-dimethyl-1,3-propanediol ester **2c** was recrystallized from chloroform/pentane, 83%: mp 50–51 °C; NMR ($CDCl_3$) δ 0.90 (s, 6, CH_3), 3.64 (s, 4, OCH_2), 4.20 (s, 1, S_2CHB), 7.2–7.8 (m, 10, C_6H_5). Anal. Calcd for $C_{18}H_{21}BO_2S_2$: C, 62.79; H, 6.15; B, 3.14; S, 18.61. Found: C, 62.66; H, 6.11; B, 3.25; S, 18.79.

1,1-Bis(phenylthio)alkenes. A solution of 6.3 mmol of lithium diisopropylamide was prepared from 0.65 g (6.4 mmol) of diisopropylamine in 5 mL of THF and 2.9 mL (6.3 mmol) of 2.17 M butyllithium in hexane and was added at 0 °C to a stirred solution of 6.3 mmol of the bis(phenylthio)methaneboronic ester **2a,b,c** (or 6.3 mmol of trimethylsilylbis(phenylthio)methane) in 20 mL of THF. After 0.5 h at 0 °C, the mixture was cooled at −78 °C and 6.3 mmol of the aldehyde or ketone was added. The mixture was stirred 1 h at 25 °C. Workup with aqueous acid, extraction with ether, drying with magnesium sulfate, and distillation yielded the 1,1-bis(phenylthio)-1-alkene as summarized in Table I. One of these, [bis(phenylthio)-methylene]cyclohexane (**4**), has not been reported previously: NMR ($CDCl_3$) δ 1.64 (m, 6, CH_2), 2.7–3.0 (m, 4, $C{=}CCH_2$), 7.28 (s, 10, C_6H_5). Anal. Calcd for $C_{19}H_{20}S_2$: C, 73.03; H, 6.45; S, 20.52. Found: C, 72.93; H, 6.52; S, 20.35. The others had physical constants and NMR spectra the same as previously reported[8,14,15] except that the C_6H_5 peak of $(PhS)_2C{=}C(CH_3)_2$[14] should be corrected to δ 7.2 (CH_3 at δ 2.2), and for $(PhS)_2C{=}CH_2$ NMR ($CDCl_3$) δ 5.56 (s, 2, $=CH_2$), 7.2–7.8 (m, 10, C_6H_5). Our sample of $(PhS)_2C{=}CH_2$ contained 5–7% of $(PhS)_2CH_2$ and failed to crystallize (lit.[15] mp 56 °C).

***S*-Phenyl Cyclohexanecarbothioate (5).** A mixture of 1.84 g (5.9 mmol) of bis(phenylthio)methylenecyclohexane (**4**) and 4.5 mL of trifluoroacetic acid was stirred 20 min at 25 °C, treated with 1 mL of water, and stirred an additional 4 h. The mixture was poured into water and extracted with dichloromethane. The organic phase was washed with sodium bicarbonate, dried over sodium sulfate, and distilled to yield 1.09 g (85%) of **5**, bp 120–124 °C (0.1 mm). The analytical sample was redistilled: NMR ($CDCl_3$) δ 1.1–2.2 (m, 10, CH_2), 2.3–2.8 (m, 1, CH), 7.5 (s, 5, C_6H_5); IR (neat) C=O at 1690 cm^{-1}. Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. Found: C, 71.00; H, 7.39; S, 14.73.

Cleavage of Propanediol Bis(phenylthio)methaneboronate (2b) with Butyllithium. Treatment of 2.0 g (6.3 mmol) of **2b** in 25 mL of THF at −75 °C with 6.3 mmol of butyllithium was followed by being stirred 1 h at −75 °C, by adding 2.7 g (19 mmol) of methyl iodide, and by being stirred 4 h at 25 °C. Concentration under vacuum, addition of chloroform, filtration, and distillation led to isolation of 0.24 g (27%) of propanediol 1-butaneboronate [bp 38–40 °C (0.1 mm) lit.[19] bp 94 °C] and 1.50 g (92%) of 1,1-bis(phenylthio)ethane [bp 144–146 °C (0.1 mm)]; the ^1H NMR spectrum was same as published data.[6] An authentic sample of propanediol butaneboronate was prepared from dimethyl butaneboronate (Alfa Chemical Co.) and 1,3-propanediol and compared by ^1H NMR.

Cleavage of Pinacol 1-Phenylthio-2-phenylethane-1-boronate. A 5-mmol sample of the title compound in 40 mL of THF at −75 °C was treated with 5 mmol of butyllithium, followed after 1 h by 15 mmol of methyl iodide, and then stirred 17 h at 25 °C. Workup with aqueous acid followed by distillation yielded 0.50 g (55%) of pinacol butaneboronate [bp 35–36 °C (0.1 mm), NMR compared with authentic sample (see below)] and 0.72 g (67-) of 2-phenylethyl phenyl sulfide [bp 122–126 °C (0.1 mm) (lit.[20] bp 185 °C (13 mm))], bp, NMR, and IR were the same as the authentic sample prepared from phenylthiomethyllithium and benzyl bromide.

Pinacol Butaneboronate. Treatment of 10 g of dimethyl butaneboronate with 8.55 g of pinacol in 20 mL of THF for 3 h at 25 °C followed by distillation gave pinacol butaneboronate, $C_4H_9BO_2C_2(CH_3)_4$: bp 32–34 °C (0.1 mm); NMR ($CDCl_3$) δ 0.6–1.6 (m, 9, C_4H_9), 1.24 (s, 12, CH_3). Anal. Calcd for $C_{10}H_{21}BO_2$: C, 65.24; H, 11.50; B, 5.87. Found: C, 64.92; H, 11.39; B, 5.57. This compound was partially characterized previously.[21]

3-(Phenylthio)-1-phenylbutane (7). A solution of 3.54 g (10 mmol) of pinacol 1-phenylthio-3-phenylpropane-1-boronate (**6**)[18] in 30 mL of THF was treated with 10 mmol of *n*-butyllithium in hexane (2 M) at 25 °C, 5.7 g (40 mmol) of methyl iodide was added, and the solution was refluxed 12 h. Distillation yielded pinacol butaneboronate and 1.90 g (75%) of 3-phenylthio-1-phenylbutane (**7**): bp 124–126 °C (0.1 mm); NMR ($CDCl_3$) δ 1.28 (d, 3, $CHCH_3$), 1.6–2.2 (m, 2, CH_2), 2.5–3.4 (m, 3, SCH and $PhCH_2$), 7.0–7.6 (m, 10, C_6H_5). Anal. Calcd for $C_{16}H_{18}S$: S, 79.29; H, 7.48; S, 13.23. Found: C, 79.11; H, 7.48; S, 12.99.

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Registry No.—**1**, 69190-58-5; **2a**, 69190-59-6; **2b**, 69190-60-9; **2c**, 69190-61-0; **5**, 58587-03-4; **6**, 66080-31-7; **7**, 61836-03-1; pinacol, 76-09-5; 1,3-propanediol, 504-63-2; 2,2-dimethyl-1,3-propanediol, 126-30-7; trimethyl borate, 121-43-7; bis(phenylthio)methane, 3561-67-9; trimethylsilylbis(phenylthio)methane, 37891-39-7; propanediol 1-butaneboronate, 30169-71-2; 1,1-bis(phenylthio)ethane, 13307-56-7; pinacol 1-(phenylthio)-2-phenylethane-1-boronate, 66080-30-6; pinacol butaneboronate, 69190-62-1; 2-phenylethyl phenyl sulfide, 13865-49-1; dimethyl butaneboronate, 2117-94-4.

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Hydroxydilophol, a New Monocyclic Diterpenoid from the Brown Alga *Dictyota masonii*

Hao H. Sun and William Fenical*

Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, California 92093

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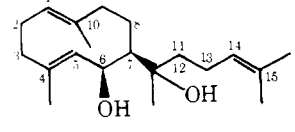
The family of brown seaweeds Dictyotaceae are unusually prolific producers of biologically active secondary metabolites. Within this family there seem to be, on chemical grounds, several more closely related genera, specifically *Pachydictyon*,[1] *Dictyota*,[2-7] *Dilophus*,[8] and *Glossophora*,[9] which produce oxygenated diterpenoids of new skeletal types. We wish to report here the isolation and structure elucidation of a new monocyclic diterpenoid, hydroxydilophol (**1**), isolated from *Dictyota masonii* Setchell and Gardner collected at Isla



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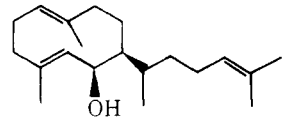

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Guadalupe in Pacific Mexico. This new metabolite is related by hydroxylation to dilophol (**2**), a metabolite recently isolated from the Mediterranean alga *Dilophus ligulatus*,[8] and its isolation here supports the intimate phylogenesis of this aforementioned subgroup.

Silica gel column chromatography of the crude chloroform–methanol extract (1:1) of *Dictyota masonii* yielded hydroxydilophol (**1**), an oil, as the sole terpenoid constituent of the alga. A molecular composition of $C_{20}H_{34}O_2$ was established for **1** based upon proton counts from ^1H NMR and ^{13}C off-resonance NMR studies, along with the elemental composition of $C_{20}H_{32}O$ established for the highest mass fragment ($M^+ - H_2O$) by high resolution mass spectrometry. Hydroxydilophol was recognized as a diol by intense infrared absorptions at 3400 cm^{-1}, and by the appearance of two oxygen-bearing carbons (δ 68.8 d and 76.7 s) in the ^{13}C NMR spectrum, and the production of a monoacetate **3** upon treatment with Ac_2O in pyridine (25 °C) established that **1** contains one secondary and one tertiary hydroxyl group.

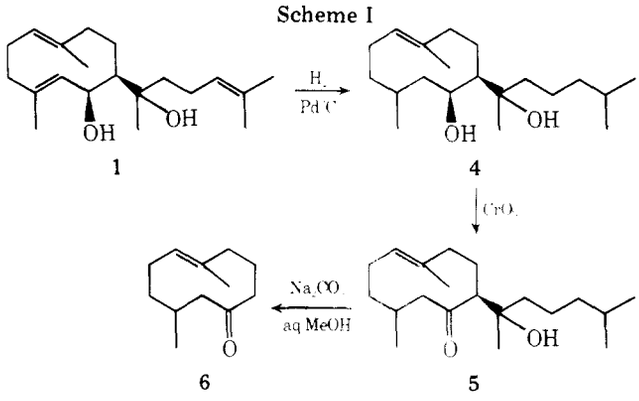
The ^1H NMR spectrum of hydroxydilophol (220 MHz, C_6D_6) shows three resolved olefin protons at δ 5.26 (bt, J = 6 Hz), 5.07 (bd, J = 8 Hz), and 4.86 (bm) and the secondary alcohol methine proton at δ 4.87 (bd, J = 8 Hz). This latter band was shifted to δ 5.77 in the corresponding acetate **3**. In $CDCl_3$, the methyl region was more highly resolved illustrating four singlet olefin methyl groups at δ 1.68, 1.60, 1.58, and 1.47 and a tertiary alcohol substituted methyl singlet at δ 1.10. Irradiation of the broadened olefin protons showed each was allylically coupled (~1 Hz) to one or more of the four vinyl methyls. Irradiation of the δ 5.26 triplet sharpened the two methyl groups at δ 1.68 and 1.60, thus establishing the familiar isopropylidene group which is common in metabolites from this family of algae. Irradiation of the δ 5.07 olefin band sharpened the δ 1.58 methyl group but also collapsed the alcohol methine band to a broad singlet, confirming that the secondary alcohol is allylic.

As the molecular formula for this compound requires four degrees of unsaturation, and three olefins are present by NMR, hydroxydilophol must be monocyclic. Oxidative ozonolysis of **1** gave levulinic acid, as determined by comparison with a commercial standard, and no other isolable degradation products. Hence, hydroxydilophol contains a terpenoid 1,5-diene system, and since one of these olefins is further coupled to an alcohol constellation, the ring must be at least nine-membered. In view, however, of the similar spectral features of dilophol (**2**), the structure of **1** was assigned as the more plausible two-membered ring analogue.

To rigorously establish ring size and sites of hydroxyl substitution, **1** was degraded as shown in Scheme I. As the sequence outlined in the scheme failed with hydroxydilophol itself, the tetrahydro derivative **4** was first produced by hydrogenation in methanol with Pd/C catalyst. Jones' oxidation gave the keto alcohol **5**, which when treated with sodium carbonate in methanol underwent a facile retro–aldol condensation yielding the cyclodecenone **6**. The ketone **6** analyzed for $C_{12}H_{20}O$ by mass spectrometry and showed infrared carbonyl absorptions at 1700 cm^{-1}. Its ^1H NMR spectrum (220 MHz, $CDCl_3$) contains bands for two methyl groups [δ 1.83 (s) and δ 0.88 (d, J = 6 Hz)] and a single olefin proton [δ 5.36 (dd, J = 11, 5 Hz)], as well as other features clearly assignable to this molecule (see Experimental Section). This sequence firmly established hydroxydilophol as formulated in structure **1**, however, without relative stereochemistry.

The subsequent assignment of both endocyclic olefins as E, and the secondary hydroxyl side chain stereochemistry as cis, was facilitated by a detailed spectral comparison with dilophol (**2**), and by the cyclization chemistry of **1**. The unusually high field vinyl methyl group in **1** is known in (E,E)-germacrene derivatives to be assignable to the C-10 methyl

Scheme I



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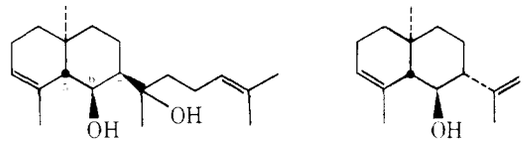
and to arise via shielding from the C-4–C-5 double bond. Further, the small unresolved coupling between the hydroxyl methine proton (C-6) and the methine proton at the side chain bearing carbon (C-7) are in close agreement with the values for the cis relationship known in dilophol.

Further evidence to support these spectral assignments was obtained by refluxing hydroxydilophol in dioxane, which served to produce the selinene-type diol **7**. Sesquiterpenoids of the germacrene skeleton are known to undergo transannular cyclizations to yield selinene derivatives, and transformations have been shown to require the E,E olefin configuration.[11,12] Analysis of the ^1H NMR characteristics of **7** also furnished



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evidence to support the proposed cis stereochemistry at C-6–C-7 in both this compound and in **1**. A useful NMR model is found in the sesquiterpenoid **8**, which possesses axial protons at C-5, C-6, and C-7. In this molecule the alcohol methine proton shows two axial–axial coupling constants of 9.5 Hz each. In **7** the C-6 methine is also axial but is observed as a broadened doublet with J = 8 Hz at δ 3.91. This multiplicity supports an axial–axial coupling between C-5 and C-6 and much smaller axial–equatorial coupling between C-6–C-7, in support of the cis arrangement of hydroxyl and side chain substituents.

Experimental Section

^1H-NMR spectra were recorded on a Varian HR-220 spectrometer with computerized Fourier transform and spin-decoupling capabilities. ^{13}C-NMR spectra were recorded on a Varian CFT-20 spectrometer. Chemical shifts are expressed as δ values in ppm relative to Me_4Si = 0. Infrared spectra were obtained on a Perkin-Elmer 137 sodium chloride spectrophotometer, UV spectra were recorded on a Perkin-Elmer 124 spectrophotometer, and optical rotations were measured on a Perkin-Elmer 1410 polarimeter. Low-resolution mass spectra and high-resolution mass measurements were supplied by the Analytical Facility at the California Institute of Technology. Low-resolution GC–mass spectra were obtained using a Hewlett-Packard 5930A mass spectrometer interfaced with a Hewlett-Packard 5910 gas chromatograph. All high-pressure liquid chromatographic separations were performed using a Waters Model 6000 liquid chromatograph with μ-Porasil columns.

Isolation of Hydroxydilophol (1). *Dictyota masonii* was collected at −20 ft using SCUBA at Isla Guadalupe, Pacific Mexico, September 12, 1977. The algae were air dried (1.2 kg) and extracted with $CHCl_3$–methanol (1:1) to yield, after solvent removal in vacuo, 45 g of crude extract. Silica gel column chromatography of the major portion of the extract (35 g) yielded fractions containing hydroxydilophol (**1**, 2.1 g) on elution with 2% diethyl ether in benzene. Further purification by repeated column chromatography of these combined fractions gave pure hydroxydilophol as a viscous, colorless oil, with the following spectral features: $[\alpha]^{20}_D$ −35.0° (c 1.44, $CHCl_3$); UV λ_{max}^{MeOH} 208 nm (ε 7000); IR (neat) ν_{max} 3400, 2940, 2870, 1670, 1440,

1380, 1090, 1030, 915, and 735 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.10 (3 H, s), 1.47 (3 H, s), 1.58 (3 H, s), 1.60 (3 H, s), 1.68 (3 H, s), 5.01 (1 H, br d, J = 8 Hz), 5.14 (2 H, br m), and 5.31 (1 H, br t, J = 6 Hz); ^1H NMR (benzene-d_6, 220 MHz) δ 1.15 (3 H, s), 1.34 (3 H, s), 1.49 (3 H, s), 1.61 (3 H, s), 1.69 (3 H, s), 4.86 (1 H, br m), 4.87 (1 H, br d, J = 8 Hz), 5.07 (1 H, br d, J = 8 Hz), and 5.26 (1 H, br t, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 16.6, 17.7, 23.5, 24.4, 24.7, 25.7, 41.5, 68.8 (d), 76.6 (s), 124.4 (d), 131.7 (s), and 133.3 (s); MS m/e 288 ($M^+ - H_2O$), 273, 270, 255, 219, 207, 187, 177, 167, 147, 135, 121, 119, 109, 94, 83, 81, 79, 69, 55, 43, and 41; calculated for $C_{20}H_{32}O$ ($M^+ - H_2O$) 288.245, found 288.245.

Acetylation of Hydroxydilophol (1). A solution of 28 mg (0.096 mmol) of 1 and excess acetic anhydride in 2 mL of anhydrous pyridine was allowed to react at room temperature for 24 h. Approximately 2 mL of distilled water was added, and the mixture was extracted with three 5-mL portions of CCl_4. After drying with anhydrous $MgSO_4$, concentrating, and TLC in 5:5:1 hexane–dichloromethane–ethyl acetate, 10 mg (30%) of 3 was obtained as an oil: IR (CCl_4) ν_{max} 3600, 2950, 2870, 1730, 1450, 1380, 1250, 1220, 1025, 985, and 855 cm^{-1}; ^1H NMR (CCl_4) δ 1.06 (3 H, s), 1.56 (6 H, s), 1.61 (3 H, s), 1.68 (3 H, s), 1.99 (3 H, s), 4.79 (1 H, br d, J = 8 Hz), 4.89 (1 H, br dd, J = 14, 7 Hz), 5.08 (1 H, br t, J = 6 Hz), and 5.77 (1 H, br d, J = 8 Hz); MS m/e 288 (M^+ – AcOH), 270, 255, 227, 203, 185, 173, 161, 159, 147, 133, 119, 109, 105, 93, 91, 81, 79, 69, 55, 43, and 41.

Ozonolysis of Hydroxydilophol (1). Ozone was bubbled through a solution of 1 (170 mg, 0.56 mmol) in 20 mL of CH_2Cl_2 at −78 °C until the solution became blue. The solvent was removed in vacuo, the residue taken up in acetone, and Jones' reagent added until an orange color persisted. The solution was stirred an additional 10 min, then diluted with water and extracted with diethyl ether. The ether extract was dried with $MgSO_4$ and concentrated in vacuo to give a brown oil. Preparative silica gel TLC of this oil in ethyl acetate gave 20 mg of levulinic acid (31%) as a colorless oil. ^1H NMR, infrared, and mass spectra obtained from this product were identical with those obtained from a commercial sample.

Tetrahydrohydroxydilophol (4). A solution of 183 mg (0.598 mmol) of 1 in 10 mL of CH_3OH and 40 mg of 10% palladium on carbon catalyst, was stirred for 48 h under an atmosphere of hydrogen. The catalyst was filtered off and the solvent was removed in vacuo to yield a yellow oil which when purified by LC (μ-Porasil, 20% EtOAc–hexanes) gave 69 mg (37%) of the tetrahydro derivative 4 as a colorless oil: IR (CCl_4) ν_{max} 3380, 2960, 1470, 1380, 1105, 1020, 935, 910, and 850 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.86 (3 H, d, J = 7 Hz), 0.88 (3 H, d, J = 7 Hz), 1.00 (3 H, d, J = 7 Hz), 1.20 (3 H, s), 1.71 (3 H, s), 2.09 (1 H, br dd, J = 13, 6 Hz), 2.59 (1 H, dddd, J = 13, 13, 13, 4 Hz), 2.66 (1 H, br s, D_2O exch), 2.76 (1 H, br dd, J = 13, 13 Hz), 3.41 (1 H, br s, D_2O exch), 4.50 (1 H, br dd, J = 13, 6 Hz), and 5.17 (1 H, br dd, J = 13, 4 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 19.9, 22.4, 22.5, 22.8, 23.8, 24.9, 25.9, 26.4, 27.2, 28.0, 36.5, 37.7, 38.1, 39.7, 40.2, 42.7, 69.6 (d), 77.1 (s), 127.9 (d), and 131.3 (s); MS m/e 310 (M^+), 292, 277, 274, 225, 207, 189, 179, 161, 149, 137, 121, 111, 109, 95, 81, 71, 69, 57, 55, 43, and 41.

Jones' Oxidation of Tetrahydrohydroxydilophol (4). Jones' reagent was cautiously added to an ice-cooled solution of 60 mg (0.194 mmol) of 4 in 5 mL of acetone until the orange color persisted. After stirring for an additional 15 min, the mixture was diluted with water and extracted with diethyl ether. The ether extract was dried (anhydrous $MgSO_4$) and reduced in vacuo to give the ketone 5 (84%) as a colorless oil: IR (CCl_4) ν_{max} 3350, 2960, 1700, 1540, 1460, 1370, and 980 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.87 (6 H, d, J = 6 Hz), 0.90 (3 H, d, J = 6 Hz), 1.16 (3 H, s), 1.89 (3 H, s), 2.17 (1 H, dddd, J = 12, 12, 12, 4 Hz), 2.40 (1 H, br s, D_2O exch), 2.82 (1 H, br d, J = 18 Hz), 3.14 (1 H, dd, J = 12, 3 Hz), 3.37 (1 H, br d, J = 18 Hz), and 5.38 (1 H, br dd, J = 12, 4 Hz); MS m/e 308 (M^+), 290, 275, 265, 237, 223, 205, 180, 155, 137, 123, 111, 109, 95, 81, 69, 55, 45, 43.

1,5-Dimethylcyclodecen-7-one (6). Two milliliters of an aqueous saturated Na_2CO_3 solution was combined with a solution of 5 (44 mg, 0.143 mmol) in 5 mL of methanol and stirred for 24 h. The solution was diluted with water and extracted with 3 × 5 mL portions of pentane. The combined pentane extracts were dried (anhydrous $MgSO_4$) and concentrated in vacuo to yield a colorless oil: IR (CCl_4) ν_{max} 2950, 1700, 1460, and 1125 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.88 (3 H, d, J = 6 Hz), 1.83 (3 H, s), 2.28 (1 H, dddd, J = 11, 11, 11, 5 Hz), 2.70 (1 H, br d, J = 17 Hz), 2.79 (1 H, ddd, J = 12, 12, 3 Hz), 3.47 (1 H, br d, J = 17 Hz), 5.36 (1 H, br dd, J = 11, 5 Hz); MS m/e 180 (M^+), 165, 149, 137, 121, 109, 105, 97, 95, 93, 81, 79, 69, 67, 55, 43, and 41.

Transannular Cyclization of 1. A solution of 1 (40 mg, 0.131 mmol) in 3 mL of dioxane was heated to reflux for 8 h. The dioxane was removed in vacuo and the residue was purified by preparative silica gel TLC (2:2:1, hexanes–CH_2Cl_2–EtOAc). Starting material (15 mg, 37%) was recovered, along with the diol 7 (12 mg, 30%) which illustrated the following spectral features: IR (CCl_4) ν_{max} 3450, 2940, 2870, 1450, 1370, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.19 (3 H, s), 1.23 (3 H, s), 1.60 (3 H, s), 1.68 (6 H, s), 2.67 (1 H, br d, J = 8 Hz), 3.19 (1 H, br s, D_2O exch), 3.45 (1 H, br s, D_2O exch), 3.91 (1 H, br d, J = 8 Hz), 5.08 (1 H, t, J = 6 Hz), and 5.25 (1 H, br t, J = 6 Hz); MS m/e 306 (M^+), 288, 270, 237, 221, 203, 179, 161, 145, 135, 120, 109, 93, 81, 69, 55, 43, and 41.

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Registry No.—1, 69204-66-6; 3, 69204-67-7; 4, 69204-68-8; 5, 69204-69-9; 6, 69204-70-2; 7, 69204-71-3; levulinic acid, 123-76-2.

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Platinacyclobutanes. Cyclopropane Exchange vs. Rearrangement

Thomas H. Johnson

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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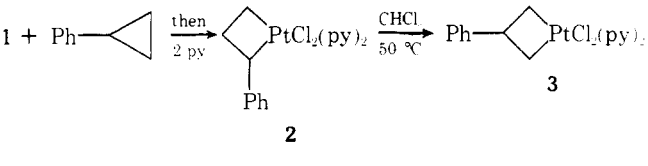
The reaction of Zeise's dimer[1a] (1) with most monosubstituted cyclopropanes was reported to occur with platinum insertion into the least substituted bond of the cyclopropane.[1b] Thus, the reaction of phenylcyclopropane with 1 followed by treatment with 2 equiv of pyridine was reported to give 3.[1] The structure of 3 was based upon its ^1H NMR spectrum. However, Puddephatt and Tipper established that the initial product was not 3 but 2 which resulted from platinum insertion into the substituted bond.[2] Furthermore, they established that 2 could be partially converted into 3 by heating at 50 °C for 45 min in chloroform.[3] The structures 2 and 3 were easily distinguished by ^{13}C NMR.[2]



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