the corresponding epoxide in essentially quantitative yield; no detectable amounts of the ketone or ring-opened products formed. The oxide was readily identified by a comparison with authentic material prepared via the intermediate bromohydrin. Thus, this two-phase procedure appears superior to the previously described direct epoxidation.

The above results establish that this two-phase procedure enables one to prepare by direct epoxidation a number of reactive aryl oxiranes. The procedure has proven to be invaluable for the preparation of *cis*- or *trans*-oxiranes where other methods have yielded mixtures.

Experimental Section

Synthesis of Epoxides Using *m*-CPBA in a Two-Phase System. To a stirred solution of 1.16 g of indene in dichloromethane–phosphate buffer (the buffer was prepared by adding sufficient aqueous 0.1 M Na_2HPO_4 to 0.1 M NaH_2PO_4 until the pH was 8.0) (200 mL; 1:1) was added *m*-CPBA (1.73 g) in small portions over a 10-min period at 0 °C. After stirring for 5 h at room temperature, 1.73 g of *m*-CPBA was added in small portions to the mixture at 0 °C over a second 10-min period. The mixture was stirred at room temperature for 5 h and the organic layer was separated, washed with saturated sodium thiosulfate and water, and dried over anhydrous sodium sulfate. The NMR spectrum of the crude reaction product showed that indene epoxide (4) was produced in ~100% yield. A pure sample of 4 (1.26 g 91% yield, mp 30 °C (lit.[4] mp 29–30 °C)) was prepared by crystallization from petroleum ether. The NMR and mass spectra of this sample were identical with that of an authentic sample prepared from *trans*-1-hydroxy-2-bromoindane. The same yield of oxirane formed when a sodium bicarbonate solution (pH 8.0) was substituted for the phosphate buffer.

This procedure was also used to prepare the epoxides listed in Table I.

(*E*)-1-Phenyl-2-methylethylene oxide (1): colorless oil; MS 134 (M^+); NMR ($CDCl_3$) δ 1.43 (3 H, d, J = 5.0 Hz), 3.00 (1 H, m), 3.55 (1 H, d, J = 1.8 Hz), 7.20–7.32 (5 H, m).

(*E*)-1-Phenyl-2-ethylethylene oxide (2): colorless oil; MS 148 (M^+); NMR ($CDCl_3$) δ 1.06 (3 H, t, J = 7.5 Hz), 1.71 (2 H, qd, J = 7.5, 5.6 Hz), 2.94 (1 H, td, J = 5.6, 1.7 Hz), 3.62 (1 H, d, J = 1.7 Hz), 7.28–7.36 (5 H, m).

1,2-Epoxyacenaphthene (5): mp 83–84 °C (lit.[8] mp 83–84 °C); MS 168 (M^+); NMR ($CDCl_3$) δ 4.81 (2 H, s), 7.39–7.77 (6 H, m).

1,2-Epoxy-1,2,3,4-tetrahydronaphthalene (6): colorless oil; bp 89–91 °C/1 mm Hg (lit.[13] bp 73–75 °C/0.4 mm Hg); NMR ($CDCl_3$) δ 1.73 (1 H, m), 2.40 (1 H, m), 2.53 (1 H, m), 2.78 (1 H, m), 3.72 (1 H, m), 3.84 (1 H, d, J = 4.0 Hz), 7.09–7.40 (4 H, m).

(2-Naphthyl)ethylene oxide (7): mp 55–56 °C (lit.[10] mp 54–56 °C); MS 170 (M^+); NMR ($CDCl_3$) δ 2.89 (1 H, dd, J = 5.0, 2.5 Hz), 3.21 (1 H, dd, J = 5.0, 4.0 Hz), 4.00 (1 H, dd, J = 4.0, 2.5 Hz), 7.27–7.84 (7 H, m).

Synthesis of Epoxides via the Trans Halohydrins. (*E*)-1-Phenyl-2-methylethylene Oxide (1). When *trans*-β-methylstyrene was converted to a halohydrin and treated with 2 N KOH as described for acenaphthene, a mixture of trans and cis epoxides in the ratio of 5:2 (determined by NMR) was obtained. Because of their instabilities the two isomers were not separated. Cis epoxide: NMR ($CDCl_3$) δ 1.05 (3 H, d, J = 5.0 Hz), 3.29 (1 H, m), 4.02 (1 H, d, J = 4.8 Hz), 7.17–7.36 (5 H, m).

(*Z*)-1-Phenyl-2-ethylethylene Oxide. When *trans*-β-ethylstyrene was subjected to the above procedure a mixture of trans and cis epoxides formed (ratio of 5:3 (determined by NMR)). Cis epoxide: NMR ($CDCl_3$) δ 0.89 (3 H, t, J = 7.5 Hz), 1.00 (1 H, m), 1.23 (1 H, m), 3.09 (1 H, m), 4.05 (1 H, d, J = 4.6 Hz), 7.23–7.36 (5 H, m).

1,2-Epoxyacenaphthene (5). To a solution of acenaphthene (152 mg) in THF (100 mL) and H_2O (25 mL) was added freshly purified NBS (213 mg) and the solution was stirred overnight at room temperature. The reaction mixture was poured into cold water, extracted with ether, dried over anhydrous sodium sulfate, and concentrated. The crude *trans*-1-bromo-2-hydroxyacenaphthene was isolated by thick-layer chromatography (silica gel, ethyl acetate–hexane, 1:4) and the NMR ($CDCl_3$) spectrum of this compound showed resonances at δ 2.81 (1 H, broad s, OH), 5.46 (1 H, s), 5.81 (1 H, s), and 7.45–7.79 (6 H, m). The bromohydrin thus obtained without further purification was treated with 2 N KOH (100 mL) in $CHCl_3$ (100 mL) at 50 °C for 2 h. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by recrystallization (ether–petroleum ether (1:1)) to give 1,2-epoxyacenaphthene (5), mp 83–84 °C, 89 mg (53% overall yield). The NMR and mass spectra of this compound were identical with those of a sample prepared by a two-phase system using *m*-CPBA.

1,2-Epoxyacenaphthene was converted to 1-acenaphthenol by $LiAlH_4$ reduction. To a slurry of $LiAlH_4$ (18 mg) in 10 mL of dry THF was added 20 mg of 1,2-epoxyacenaphthene and the solution was stirred overnight at room temperature under N_2. The reaction mixture was decomposed using cold water and worked up as usual to yield 1-acenaphthenol, mp 147–148 °C, 16 mg (80% yield). The NMR spectrum of this compound was identical with that of an authentic sample.

Registry No.—*cis*-1-Phenyl-2-methylethylene oxide, 4541-87-1; *cis*-1-phenyl-2-ethylethylene oxide, 69140-51-8; *trans*-1-bromo-2-hydroxyacenaphthene, 69140-52-9; 1-acenaphthenol, 6306-07-6.

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Bis(phenylthio)methaneboronic Esters as Sources of Carbanions and Ketene Thioacetals

Abel Mendoza and Donald S. Matteson*

Department of Chemistry, Washington State University, Pullman, Washington 99164

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Boron-substituted carbanions show considerable promise as synthetic intermediates and have proved especially effective in Wittig-type condensations with carbonyl compounds to form substituted alkenes.[1–5] The synthesis of bis(phenylthio)methaneboronic esters from the readily available bis(phenylthio)methyllithium[6] was undertaken as a logical extension of this work.

Reaction of trimethyl borate with bis(phenylthio)methyllithium followed by workup with aqueous acid yielded bis(phenylthio)methaneboronic acid (1), which proved unstable to storage and was not fully purified, but was readily converted to the cyclic esters 2 by treatment with pinacol, 1,3-propanediol, or 2,2-dimethyl-1,3-propanediol.

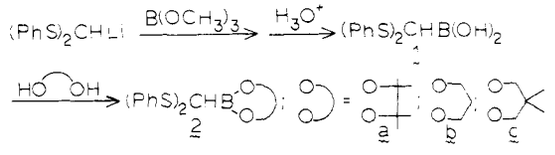

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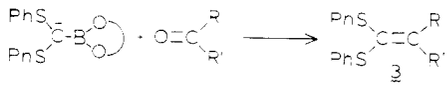
Table I. Ketene Thioacetals from Carbonyl Compounds and Bis(phenylthio)methide Anions Substituted with Boryl or Silyl Groups

registry no.	carbonyl compd	Z of $(PhS)_2\bar{C}Z$	product	registry no.	yield, %	bp (0.1 mm), °C
108-94-1	cyclohexanone	$-BO_2C_2(CH_3)_4$ (**2a**)	$(CH_2)_5C{=}C(SPh)_2$	69190-57-4	78	162–164
	cyclohexanone	$-BO_2(CH_2)_2C(CH_3)_2$ (**2c**)	$(CH_2)_5C{=}C(SPh)_2$		76	162–164
	cyclohexanone	$-BO_2(CH_2)_3$ (**2b**)	$(CH_2)_5C{=}C(SPh)_2$		78	162–164
	cyclohexanone	$-Si(CH_3)_3$	$(CH_2)_5C{=}C(SPh)_2$		10[a]	
67-64-1	acetone	$-BO_2(CH_2)_3$ (**2b**)	$(CH_3)_2C{=}C(SPh)_2$	41563-50-2	79	148–154[b]
	acetone	$-Si(CH_3)_3$	$(CH_3)_2C{=}C(SPh)_2$		0	
119-61-9	benzophenone	$-BO_2(CH_2)_3$ (**2b**)	$Ph_2C{=}C(SPh)_2$	41563-48-8	75	*c*
	benzophenone	$-Si(CH_3)_3$	$Ph_2C{=}C(SPh)_2$		75	*c*
30525-89-4	paraformaldehyde	$-BO_2(CH_2)_3$ (**2b**)	$H_2C{=}C(SPh)_2$	18889-01-5	73	139–142[d]
93-53-8	$PhCH(CH_3)CHO$	$-BO_2C_2(CH_3)_4$ (**2a**)	$PhCH(CH_3)CH{=}C(SPh)_2$	37891-69-3	70	210–222[e]

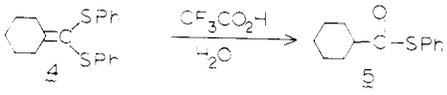
[a] Impure. [b] Lit.[14] bp 169 °C (0.8 mm). [c] mp 110–111 °C (lit.[14] mp 111–111.5 °C). [d] Lit.[15] bp 144–145 °C (0.2 mm). [e] Lit.[8] bp 210 °C (0.005 mm).

Ketene Thioacetals. All three of the esters **2** tested were readily deprotonated by lithium diisopropylamide, and condensations with aldehydes and ketones to form 1,1-bis(phenylthio)-1-alkenes (ketene thioacetals) **3** proved generally efficient. Results are summarized in Table I.

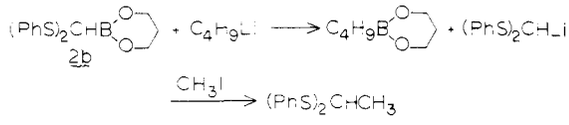


Analogues of **2** having silicon[7–9] or phosphorus[10,11] in place of boron, and in most cases a dithiane ring in place of $-CH(SPh)_2$, have been used previously to make ketene thioacetals by homologation of carbonyl compounds. The dithiane-type ketene thioacetals can also be made from esters and $(Me_2AlSCH_2)_2CH_2$[12] and are useful for a variety of synthetic operations.[12,13] However, acyclic ketene thioacetals are uniquely useful as sources of thiol esters.[9] We have found that the boron reagents **2** work much better than the trimethylsilyl analogue, $(PhS)_2CH{-}Si(CH_3)_3$,[8] which fails to homologate ketones having acidic α-hydrogens (Table I). The trimethylsilyl compound does homologate benzophenone (Table I), but $(PhS)_2CHLi$ followed by acid dehydration is effective in this particular case.[8] Generally, only the dimethoxyphosphoryl leaving group[11] appears to be as effective as the boronic ester leaving group in these homologations.

Since the previously reported hydrolysis of thiol esters utilized the methylthio series,[9] we demonstrated that similar trifluoroacetic acid treatment hydrolyzes [bis(phenylthio)methylene]cyclohexane **4** to phenyl cyclohexanecarbothioate **5**.

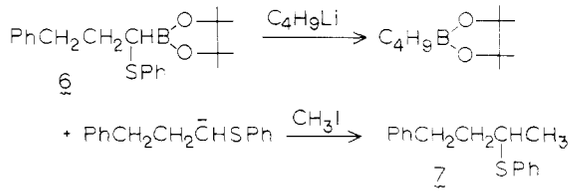


Cleavage to Phenylthio Carbanions. A second reason for investigating the chemistry of bis(phenylthio)methaneboronic esters **2** was the hope that homologation reactions similar to those reported for bis(phenylthio)methyllithium–trialkylboronate complexes[16–18] might be possible. However, treatment of **2b** with butyllithium followed by methyl iodide



yielded only the cleavage products, propanediol butaneboronate and bis(phenylthio)methyllithium, which was methylated to form bis(phenylthio)ethane. The relatively low Lewis acidity of the boronic ester function may fail to hold the required intermediate ate complex together long enough to permit rearrangement. We tried methylating the **2b** with methyl fluorosulfonate prior to the treatment with butyllithium in one experiment and obtained about 30% of what appeared to be propanediol 1-(phenylthio)-1-pentaneboronate, $C_4H_9CH(SPh)BO_2C_3H_6$, based on the ^1H NMR spectrum (and comparison with the known pinacol ester analogue),[5] in a mixture with diphenylmethane, in addition to a similar yield of propanediol butaneboronate, but these results did not seem sufficiently encouraging to justify further work with the toxic methyl fluorosulfonate.

The ease of cleavage of the bis(phenylthio)methaneboronic ester **2b** by butyllithium prompted us to try to generate a carbanion from a mono(phenylthio)alkaneboronic ester. Treatment of pinacol 1-(phenylthio)-2-phenylethane-1-boronate[5] with butyllithium at −75 °C in tetrahydrofuran followed by excess methyl iodide at 25 °C for 17 h failed to yield any anion methylation product, but after aqueous workup it gave the products of hydrolysis of the ate complex, 2-phenylethyl phenyl sulfide and pinacol butaneboronate. However, addition of butyllithium to pinacol 1-(phenylthio)-3-phenylpropane-1-boronate (**6**)[18] in tetrahydrofuran followed by excess methyl iodide and refluxing for 12 h did yield 75% of the product from methylation of the carbanion, 3-phenylthio-1-phenylbutane (**7**).



Experimental Section

General. For reactions involving carbanions, all glassware was dried at 120 °C and flushed with argon during assembly, and an argon atmosphere was maintained during the reactions. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Amines were distilled from potassium hydroxide. Other reagent grade chemicals were used as purchased. Reagents were transferred by syringe, using hypodermic needles and rubber-capped injection ports. ^1H NMR spectra (60 MHz) were measured with a Varian EM-360 spectrometer and calibrated with internal tetramethylsilane. Infrared spectra were recorded with a Beckman IR-18A instrument. Melting and boiling points are uncorrected. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

Bis(phenylthio)methaneboronic Acid (1). *n*-Butyllithium (83 mL; 0.20 mol; 2.4 *M*) in hexane was added to a solution of 47 g (0.20 mol) of bis(phenylthio)methane[6] in 250 mL of THF and stirred at 0 °C. After 0.5 h at 0 °C, the mixture was cooled to −78 °C and 21 g (0.2 mol) of trimethyl borate was added. The mixture was warmed to 25 °C and stirred 2 h, then cooled to −60 °C and treated with 30 mL of concentrated hydrochloric acid. Dilution with water, extraction with ether, and crystallization of the ether-soluble material from ether/pentane yielded 28–33 g (50–60%) of crude bis(phenylthio)methane-

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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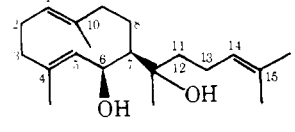
The family of brown seaweeds Dictyotaceae are unusually prolific producers of biologically active secondary metabolites. Within this family there seem to be, on chemical grounds, several more closely related genera, specifically *Pachydictyon*,[1] *Dictyota*,[2-7] *Dilophus*,[8] and *Glossophora*,[9] 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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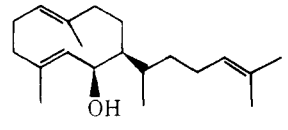

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