matography of the crude mixture on silica gel gave 54 mg of **6** and 73 mg (42%) of **15**. A second chromatography (ether 5% in benzene) gave 49 mg (28%) of pure **15**.

Quantum Yield Determinations. Solutions of different ketones **1–6** ($\sim 10^{-2}$ M) in spectrograde acetonitrile or in a 1 M solution of acetone in acetonitrile were subjected to three freeze–pump–thaw cycles and sealed at 10^{-4} mm in 10-mm o.d. quartz cells. Irradiations were carried out using a 313-nm line produced by a Bausch and Lomb monochromator. Light intensities were measured by ferrioxalate actinometry. Photolyses were run to <10% conversion, and the resulting solutions were analyzed by VPC.

Quenching Studies. Sample preparations and irradiations were the same as for the quantum yield determinations except that varying amounts of *cis*-1,3-pentadiene (10^{-3} to 0.6 M) were added to the solutions. Percentages of isomerization of *cis*-pentadiene were determined on column C (room temperature).

Acknowledgment. The authors are grateful to Dr. R. Beugelmans for bringing about this subject, and to Dr. N. Ivanoff for many helpful discussions.

Registry No.—12, 67271-53-8; **12** semicarbazone, 67271-56-11; **16**, 67271-54-9; *endo*-2-norbornanecarboxylic acid, 934-28-1; *endo*-3-phenylnorbornane-2-*exo*-carboxylic acid, 59286-05-4; *endo*-2-carboxy-*exo*-3-phenylnorbornene, 58800-36-5; *exo*-2-carboxy-*exo*-3-phenylnorbornane, 59286-12-3; cyclopentyl bromide, 137-43-9; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; *exo*-2-acetyl-*endo*-3-phenylnorbornene, 67271-55-0; 2-*endo*-carboxy-3-*endo*-phenylnorbornene, 59286-09-8.

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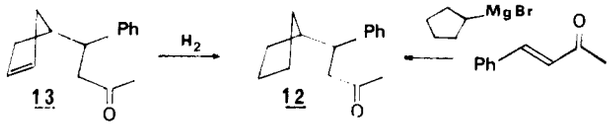

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Marine Natural Products: Sesquiterpene Alcohols and Ethers from the Sea Hare *Aplysia dactylomela*

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Received March 10, 1978

Three isomeric sesquiterpene ethers, dactyloxene-A, -B, and -C, as well as a related alcohol, dactylenol, and its acetate were isolated from the sea hare *Aplysia dactylomela*. Structure determinations involved ^{13}C NMR, ^{1}H NMR in the presence of shift reagent, and chemical degradation. All of the compounds have a common rearranged monocyclofarnesyl skeleton. Dactyloxene-B and -C are stereoisomers, each having a tetrahydrofuran ring spiro-fused on a substituted cylohexene ring. Dactyloxene-A possesses an oxadecalin skeleton. Dactylenol was converted by acid treatment to a mixture containing dactyloxene-A and -C.

Earlier we described[2] the isolation of dactyloxene-B (**5**), a sesquiterpene ether having a rearranged monocyclofarnesyl skeleton, from the sea hare *Aplysia dactylomela*. Since then, other investigators studying marine red algae have discovered two alcohols[3] having the same carbon skeleton as **5** as well as two monobromo alcohols[4] and a related ether,[5] each having an unrearranged monocyclofarnesyl skeleton. One of the bromo alcohols has been synthesized by a biomimetic route utilizing bromonium ion induced cyclization of a farnesyl derivative.[6] In this paper we report the isolation and structure determination of four new monocyclofarnesyl sesquiterpenoids from *A. dactylomela*, all of which have the rearranged skeleton of dactyloxene-B (**5**). Two of these compounds are ethers, dactyloxene-A (**12**) and -C (**10**). The remaining compounds are an alcohol, dactylenol (**1**), and its acetate **4**. In addition to these sesquiterpenoids, extracts of *A. dactylomela* have also yielded a new bicyclic sesquiterpene alcohol, dactylol,[7] and two halogenated straight-chain acetylenic ethers,[8] one of which has shown interesting central nervous system activity.[9]

The sesquiterpene ethers **5**, **10**, and **12**, the related alcohol **1**, and the acetate **4** were isolated from hexane extracts of whole dried animals or dichloromethane solubles of an alcohol extract of fresh digestive glands of the sea hare. Chromatography of the hexane extracts over Florisil using hexane as eluent provided fractions containing dactyloxene-A, -B, and -C.

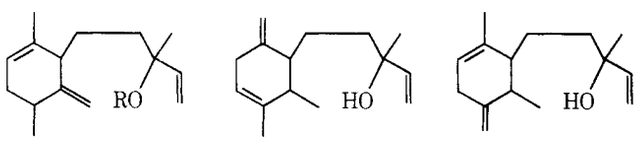
0022-3263/78/1943-4220$01.00/0

Repeated preparative layer chromatography (silica gel) of these fractions yielded the pure sesquiterpene ethers. Dactylenol (1) and its acetate (4) were eluted from the Florisil column with hexane–benzene in fractions that also contained dactylyne,[8a] isodactylyne,[8b] and dactylol.[7] Dactylenol (1) was isolated from these fractions by repeated silica gel chromatography followed by silver nitrate–silica gel preparative layer chromatography. Dactylenol acetate (4) was partially purified by silica gel chromatography, but final purification of this compound could be accomplished only by preparative gas chromatography.

Dactylenol (1) was obtained as a colorless oil: $[\alpha]_C$ +204°; $C_{15}H_{24}O$. Absorption in the infrared spectrum at 3400 cm^{-1} and the absence of signals in the ^1H NMR spectrum in the δ 3.0–4.5 region indicated that dactylenol was a tertiary alcohol.

The ^1H NMR spectrum revealed the presence of three methyl groups in **1**: a quaternary methyl most likely bonded to the carbinol carbon [δ 1.14 (s)], a secondary methyl [δ 1.08 (d)], and an olefinic methyl group [δ 1.68 (brd s)] on a trisubstituted double bond. The olefinic region possessed the following signals: a broad one-proton multiplet at δ 5.36 coupled to the olefinic methyl signal, a two-proton doublet at δ 4.73 (J = 2 Hz) corresponding to an exocyclic methylene group, and three one-proton signals that formed a clear AMX pattern [δ 5.06 (J = 10 and 2 Hz), 5.20 (J = 18 and 2 Hz), and 5.94 (J = 18 and 10 Hz)]. The last signals are indicative of a vinyl group attached to a quaternary center. Assuming that this group is attached to the quaternary carbinol carbon leads to formulation of the partial structure $-C(OH)(CH_3)-CH{=}CH_2$.

Three possible structures for dactylenol, **1**, **2**, and **3**, could be envisaged from the spectrally deduced structural fragments, the inclusion of a ring to account for the final degree of unsaturation required by the molecular formula, and consideration of the isoprene rule. Structure **1** was confirmed for dactylenol by extensive decoupling of the europium shifted ^1H NMR spectrum (0.45 mol ratio for $Eu(fod)_3$/dactylenol). Under these conditions the signal for each of the nonequivalent protons or sets of protons in dactylenol was distinctly resolved. The increments in chemical shifts for the quaternary methyl signal (δ 1.14→8.75) and the lowest field signal from the vinyl group (δ 5.94→12.5) confirmed that these groups are attached to the carbinol carbon. The methylene chain attached to the carbinol carbon was identified by the occurrence of a pair of one-proton doubled triplets at δ 9.27 and 9.63 (J = 13 and 4 Hz) coupled to another pair of one-proton signals at δ 6.82 (tt, J = 13 and 4 Hz) and 6.26 (ddt, J = 13, 10, and 4 Hz). The latter signals were further coupled only to a one-proton, broadened doublet at δ 4.36 (brd d, J = 10 Hz, small). Irradiation of this δ 4.36 signal revealed that it was coupled only to the two methylene protons in the side chain and slightly with one of the exocyclic methylene protons (δ 5.68), thus supporting structure **1**. Further decoupling showed that



1, R = H
4, R = Ac

2 3

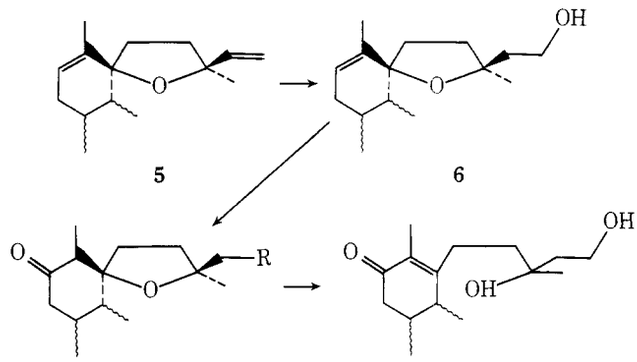
the methine proton signal at δ 3.66 (poorly resolved septet?), which was coupled to the secondary methyl group at δ 1.34, was coupled further only to two one-proton multiplets (δ 2.02 and 2.63). Both of the last signals were coupled to the olefinic proton (δ 5.80) of the trisubstituted double bond. This confirms all of the proton sequences in structure **1** and unambiguously confirms it as the structure for dactylenol.

Dactylenol acetate (**4**), an oil, $[\alpha]_D$ +168°, $C_{17}H_{26}O_2$, was correlated with dactylenol (**1**) by reductive removal of the acetate using lithium aluminum hydride. Conversely, dactylenol (**1**) was converted to the acetate **4** in approximately 10% yield (GC analysis) by reaction with acetic anhydride–pyridine at 50 °C for 8 h.

Dactyloxene-B (**5**), an oil, $[\alpha]_D$ +106°, $C_{15}H_{24}O$, exhibited infrared absorption indicative of double bonds [3080, 1640, 910 (vinyl) and 810 (trisubstituted double bonds) cm^{-1}] and an ether group (990 cm^{-1}), while being devoid of hydroxyl and carbonyl absorption. Only end absorption was noted in the UV spectrum. The ^{13}C NMR spectrum possessed singlet signals for two carbons attached to oxygen (δ 83.2 and 86.1), and this established the ditertiary ether nature of dactyloxene-B. The ^{13}C NMR spectrum further showed signals for only four unsaturated carbons, all sp^2: δ 145.6 (d), 136.9 (s), 124.2 (d), and 110.7 (t). Hence, dactyloxene-B must be bicyclic.

The ^1H NMR spectrum of dactyloxene-B exhibited signals for four methyl groups: δ 0.97 and 1.06 (doublets, secondary methyls), 1.34 (s, $-C(CH_3)-O-$), and 1.70 (olefinic methyl). Decoupling of the secondary methyl signals by irradiation at δ 1.77 and 1.52, respectively, demonstrated that the secondary methyl groups are attached to separate carbons and are not part of an isopropyl group. The olefinic region of the spectrum contained a broad multiplet at δ 5.44 that was reduced to a triplet upon irradiation at δ 1.70 (vinyl methyl position), thus indicating the partial structure $-CH_2CH{=}C(CH_3)-$. The remaining signals in the olefinic region were a set of three one-proton signals that formed a clear AMX pattern [δ 4.97 (J = 11 and 2 Hz), 5.12 (J = 17 and 2 Hz), and 6.09 (J = 17 and 11 Hz) indicative of a vinyl group attached to a quaternary center as in **1**.

By analogy with structure **1**, the above structural units are readily incorporated into formula **5** as a possible structure for dactyloxene-B. Compelling support for this formula was obtained from the mass spectral fragmentation pattern which contained a sizeable peak at m/e 164 (calcd for $C_{11}H_{16}$, 164.1201; found, 164.1199), corresponding to a facile loss of C_4H_8 in a retro-Diels–Alder fragmentation.



7, R = CH_2OAc
8, R = CO_2H

9

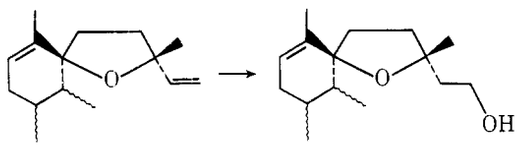
Additional confirmation for structure **5** was obtained by the conversions outlined below. Hydroboration of dactyloxene-B (**5**) with a hindered borane followed by oxidation yielded the alcohol **6**, which showed the same facile loss of C_4H_8 in its mass spectrum as did **5**. The acetate of **6** upon hydroboration followed by oxidation with chromic acid[10] afforded two products: keto acetate **7** and keto acid **8**. The keto acid **8** showed carbonyl absorption only at 1700 cm^{-1}, corresponding to both carboxyl and cyclohexanone carbonyl groups, thus confirming the carbocyclic ring size in dactyloxene-B (**5**). The keto acetate **7** upon treatment with sodium methoxide in methanol at room temperature underwent a facile elimination to give the α,β-unsaturated keto diol **9** (IR 1660 and 1650 cm^{-1}). The ^1H NMR spectrum of **9** possessed a signal for an olefinic methyl

Table I. Europium ^{1}H NMR Shift Data for Alcohols 6 and 11

	6				11			
	Eu(fod)$_3$/alcohol mole ratio (±5%)				Eu(fod)$_3$/alcohol mole ratio (±5%)			
protons	0	0.57	1.26	Δδ	0	0.57	1.26	Δδ
secondary Me	0.97	1.52	1.75	0.78	0.97	1.10	1.10	0.13
secondary Me	1.04	2.34	3.05	2.01	1.00	2.40	3.60	2.60
$CH_3C\lessdot O$	1.30	3.50	4.90	3.60	1.36	2.92	4.60	3.24
$-C=C(CH_3)-$	1.74	3.80	4.70	2.96	1.74	2.46	3.18	1.44
$-CH_2CH_2OH$	3.7	4.70	5.72		3.7	3.4	5.17	
		7.00	9.85			5.96	9.90	
		11.65	15.85			9.00	14.40	
		12.80	17.65			10.10	16.93	
-CH=C-	5.85	6.10	6.45	1.10	5.35	5.6	5.80	0.45

group (δ 1.78), but it clearly lacked any olefinic proton signals. This ring opening confirmed that one of the ether links is β to the carbonyl group in **7**, and hence allylic to the ring double bond as proposed in **5**. Thus, the overall structure for dactyloxene-B, disregarding stereochemistry, is given by **5**.

Dactyloxene-C (**10**), a colorless oil, $[\alpha]_D$ +45.8°, $C_{15}H_{24}O$, possessed the same diagnostic spectral features in its IR, ^{1}H NMR, ^{13}C NMR, and mass spectra as dactyloxene-B (**5**), and hence the two were judged to be stereoisomers. Both dactyloxene-C (**10**) and the derived alcohol **11** (selective hydroboration/oxidation) showed a facile loss of C_4H_8 in their mass spectra, corresponding to a retro-Diels–Alder loss of butene as observed for **5**. In the ^{1}H NMR spectrum of dactyloxene-C (**10**), the two secondary methyl resonances are superimposed to give a single doublet at δ 0.93 in carbon tetrachloride, but in benzene-*d* two doublets are observed. The stereochemical relationships of **5** and **10** are discussed below.

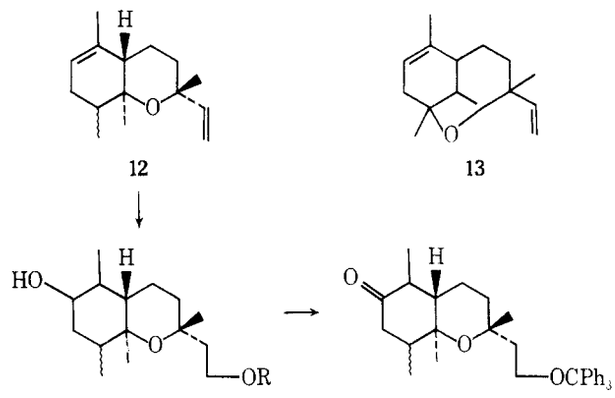


10 **11**

Dactyloxene-A (**12**), a colorless oil, $C_{15}H_{24}O$, exhibits a small negative rotation, $[\alpha]_D$ −5.9°, in contrast to the positive rotations found for the isomeric ethers. The infrared spectrum of **12** shows absorption for unsaturation (1630, 910, and 790 cm^{-1}) and an ether (990 cm^{-1}). The ^{13}C NMR spectrum contained signals corresponding to two quaternary carbons attached to oxygen [(δ 75.7 and 72.0) and four sp^2 carbons (144.2, 135.4, 118.7, and 109.7 (t)], thus characterizing dactyloxene-A also as a bicyclic ditertiary ether.

The ^{1}H NMR spectrum of dactyloxene-A (**12**) was significantly different from those of **5** and **10** in the methyl region. Two quaternary methyl groups were indicated in **12** (δ 1.04 and 1.23) and only one secondary methyl group (δ 0.97), in addition to one olefinic methyl (δ 1.68). The olefinic region exhibited signals for one proton on a trisubstituted double bond of the type $-CH_2CH=C(CH_3)-$ (δ 5.20) and three distinct multiplets corresponding to a vinyl group attached to a quaternary center (δ 4.94, 4.95, and 6.10).

Using compounds **1**, **5**, and **10** as models, the structures **12** and **13** were formulated as likely ones for dactyloxene-A based on the spectral data. The large peak in the mass spectrum corresponding to a reverse Diels–Alder fragmentation, prominent in the spectra of dactyloxene-B (**5**) and C (**10**), was completely absent in the spectrum of dactyloxene-A. A decision in favor of formula **12** was made on the basis of the chemical conversions outlined below. Hydroboration of dactyloxene-A with excess diborane followed by hydrogen peroxide oxidation afforded the diol **14**, which was selectively tritylated to give the ether alcohol **15**. Oxidation of **15** with chromium trioxide–pyridine complex[11] afforded in quantitative yield the keto trityl ether **16**, which showed carbonyl absorption at 1712 cm^{-1} in agreement with the postulated cyclohexene structure for dactyloxene-A. Treatment of the ketone **16** with sodium methoxide–methanol did not bring about the elimination and ether ring opening that would be expected for a ketone derived from structure **13** (cf. the ready opening observed for the keto acetate **7** derived from dactyloxene-B). Thus, the overall structure **12** is proposed for dactyloxene-A.



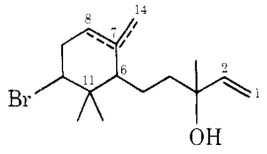
12 **13**

14, R = H
15, R = CPh_3

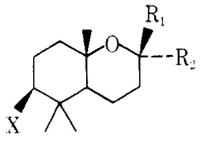
16

A tentative partial assignment of the relative stereochemistry of **5** and **10** was derived from analysis of the europium induced chemical shifts of the methyl group signals in the respective derived alcohols **6** and **11** (see Table I). The chemical shift changes in the protons of the hydroxyethyl side chain provide a convenient internal standard to show that comparable complexing with Eu(fod)$_3$ occurred with both alcohols. The signal for the olefinic methyl group in **6** was shifted downfield more than twice as much as the corresponding signal in **11**. Calculations using a graphical method[12] and assuming that the principal magnetic axis falls approximately parallel to and near the plane of the tetrahydrofuran ring predict a significantly larger shift for the vinyl methyl signal when that group and the hydroxyethyl side chain are cis oriented on the tetrahydrofuran ring. This leads to the conclusion that **5** and **10** differ in configurations at the tertiary ether carbons as shown.

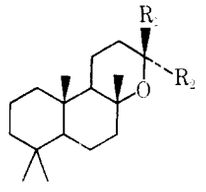
The partial relative stereochemistry shown for **12** is also based on ^{1}H NMR data. The chemical shifts for the quaternary methyl groups in **12** (δ 1.04 and 1.23) are very similar to those for the analogous methyl groups in 3β-bromo-8-*epi*-caparrapi oxide (**19**) (δ 1.12 and 1.14),[5] (+)-8-*epi*-caparrapi oxide (**21**) (δ 1.14 and 1.22),[13] and epimanoyl oxide (**23**) (δ 1.08 and 1.17)[14] all of which have the cis 1,3-diaxial quaternary methyl/vinyl group arrangement as proposed for **12**. On the other hand, in those cases where the two quaternary methyl groups are cis 1,3-diaxially oriented, i.e., caparrapi oxide (**20**)[13] and manoyl oxide (**22**),[14] the quaternary methyl group



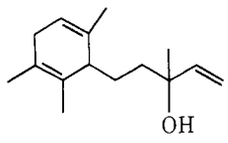
17, Δ^7
18, $\Delta^{7,14}$



19, X = Br; R_1 = CH=CH_2; R_2 = CH_3
20, X = H; R_1 = CH_3; R_2 = CH=CH_2
21, X = H; R_1 = CH_3; R_2 = CH=CH_2



22, R_1 = CH_3; R_2 = CH=CH_2
23, R_1 = CH=CH_2; R_2 = CH_3



24

chemical shifts differ by only 0.02 ppm or less. The signal for the -CH=CH_2 proton in **12** occurs at δ 6.10, close to where the corresponding protons in (+)-8-*epi*-caparrapi oxide (**21**) and epimanoyl oxide (**23**) absorb (δ 6.08 and 6.04, respectively). The trans ring juncture with the axial vinyl group in **12** is also supported by the fact that the -C**H**=CH_2 proton experiences long range coupling (~1 Hz). The W arrangement[15] of bonds between this proton and one of the ring methylene protons that is conducive to such coupling is best accommodated when the vinyl group is axial.

Treatment of **1** with toluenesulfonic acid or BF_3 etherate in ether afforded a complex mixture of products (at least 22 components) which contained **5** as one of the major components and **12** as a minor one. No attempts were made to optimize conditions for this conversion or to identify the remainder of the products. It is interesting to note that under these conditions the tetrahydrofuran derivative **5** is formed to a greater extent than the tetrahydropyran isomer **12**, even though formation of **5** requires isomerization of **1** prior to cyclization.

Dactylenol (**1**), its acetate **4**, and the ethers **5**, **10**, and **12** are closely related structurally to α- and β-snyderol (**17** and **18**),[4] 3β-bromo-8-*epi*-caparrapi oxide (**19**),[5] and nidifidienol (**24**),[3] all of which have been isolated from marine red algae. Three of these terpenoids, **17**, **18**, and **19**, retain an unrearranged monocyclofarnesyl skeleton, while the fourth, **24**, has the same rearranged skeleton that **1**, **4**, **5**, **10**, and **12** have. The biogenesis proposed for this group of compounds involves bromonium ion induced cyclization of farnesol.[16] Solvolytic loss of bromine from **17** followed by a methyl migration would produce an intermediate that could readily give rise to **1**, **4**, **5**, **10**, **12**, and **24**.

Experimental Section[17]

Isolation of Dactylenol (1), Dactylenol Acetate (4), and Dactyloxene-A (12), -B (5), and -C (10). Sea hares were collected and extracted as described previously.[8b] A portion (5.0 g) of the fourth hexane fraction (10.63 g) from the Florisil chromatography described earlier was chromatographed on a column using 40 g of silica gel H. The column was eluted with a benzene–hexane (15:85) mixture. An elution volume of 50–320 mL yielded a red oil (2.88 g, fraction A). The next 75 mL of eluate, fraction B, contained 0.51 g of a mixture consisting primarily of dactyloxene-A and -B with small amounts of dactyloxene-C. Further elution, 15-mL cuts, yielded four additional fractions containing sesquiterpene ether mixtures, fractions C (0.25 g), D (0.20 g), E (0.14 g), and F (0.10 g).

Pure dactyloxene-A (**12**) could be obtained from fraction B by thick-layer chromatography on silica gel–9% silver nitrate plates, 20 × 20 cm, 2 mm thick. A 100-mg amount of fraction B on a single plate eluted twice with ethyl acetate–diethyl ether–hexane (4:8:88) gave 25 mg of pure dactyloxene-A. (Bands were visualized by spraying the edges and a center strip with 2′,7′-dichlorofluorescein.) Alternatively, pure dactyloxene-A could be obtained by repeated chromatography of fractions enriched in this isomer over TLC mesh silica gel using a hexane–ether (98:2) mixture as eluent.

Dactyloxene-B and -C were each purified by repeated chromatography of fractions C–F over TLC mesh silica gel using a hexane–ether (98:2) mixture as eluent.

The combined yield of the dactyloxene-A, -B, and -C mixture from the original hexane extract was approximately 0.4%.

The sesquiterpene ethers were obtained from the alcohol extracts of freshly collected digestive glands somewhat more conveniently in the following manner. The concentrated alcohol extract was suspended in water and extracted with dichloromethane for 24 h. The dichloromethane solubles were dissolved in a methanol–water (9:1) mixture and extracted three times with hexane. A 33-g portion of the hexane extract was distilled at 53–67 °C and 5 μm of pressure to yield an orange distillate (9.58 g). Chromatography of this distillate over silicic acid (Bio-Sil A, 80 g; Bio-Rad Laboratories, Richmond, Calif.) with a hexane–benzene mixture (1:1) gave fractions containing dactyloxene-A, -B, and -C, quite free of other contaminants, and some fractions were nearly homogeneous with respect to individual isomers.

Dactyloxene-A (12): Colorless oil; $[\alpha]_D$ −5.9° (*c* 1.4, $CHCl_3$); n^{24}_D 1.4912; IR (film) 3090, 1630 (w), 1450, 1375, 990 (ether), 910 (vinyl), 790 cm^{-1}; UV, only end absorption; ^1H NMR (100 MHz, $CDCl_3$) δ 0.97 (3 H, d, J = 6 Hz), 1.04 and 1.23 (3 H each, s), 1.68 (3 H, m, vinyl methyl), 1.3–2.4 (8 H, m), 4.94 (1 H, dd, J = 11 and 1.5 Hz), 4.95 (1 H, d, J = 18 and 1.5 Hz), 5.20 (1 H, m), 6.10 (1 H, ddd, J = 18, 11, and 1.0 Hz). ^{13}C NMR ($CDCl_3$) (off-resonance mult): sp^2 δ 144.3 (d), 135.4 (s), 118.7 (d), 109.7 (t); sp^3 δ 75.7 (s), 72.0 (s), 47.4 (d), 33.3 (t), 32.3 (t), 31.5 (q), 28.3 (d), 22.4 (t), 21.4 (q), 20.8 (q), 14.3 (q). Mass spectrum, *m/e* 220.1838 (M^+; calcd for $C_{15}H_{24}O$, 220.1827), (70 eV) (relative intensity) 220 (M^+, 3), 202 (14), 187 (7), 177 (3), 173 (6), 159 (6), 152 (10), 145 (10), 133 (50), 121 (100), 120 (50), 109 (43), 105 (43), 91 (27).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.91; H, 10.99.

Dactyloxene-B (5): colorless oil; $[\alpha]_D$ +110.2° (*c* 0.74, $CHCl_3$); n^{25}_D 1.4925; IR (film) 3080, 1640, 990 (ether), 910 (vinyl), 810 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$), see text and ref 2. ^{13}C NMR ($CDCl_3$) (off-resonance mult): sp^2 δ 145.6 (d), 136.9 (d), 124.2 (d), 110.7 (t); sp^3 δ 86.1 (s), 83.2 (s), 45.6 (d), 38.0 (t), 34.9 (t), 32.6 (t), 32.1 (d), 27.8 (q), 20.9 (q), 20.0 (q), 15.0 (q). Mass spectrum, *m/e* 220.1814 (M^+; calcd for $C_{15}H_{24}O$, 220.1827), (70 eV) 220 (M^+, 1), 202 (78), 187 (41), 173 (61), 164 (19), 164.1199 (calcd for $C_{11}H_{16}O$, 164.1201), 145 (47), 133 (100), 132 (87), 121 (53), 119 (59), 105 (50), 91 (47), 79 (23), 77 (27), 54.0466 (calcd for C_4H_8, 54.0469).

Anal. Calcd for $C_{15}H_{24}O$; C, 81.76; H, 10.98. Found: C, 81.94; H, 11.04.

Dactyloxene-C (10): colorless oil; $[\alpha]_D$ +45.8° (*c* 0.9, $CHCl_3$); n_D 1.4941; IR (film) 3080, 1640, 1460, 1375, 1015 (ether), 910 (vinyl), 780 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.93 (6 H, d, J = 6 Hz, coincident methyl d), 1.40 (3 H, s, -C(CH_3)-O-), 1.80 (3 H, m, olefinic methyl), 5.0 (1 H, dd, J = 10 and 2 Hz, -CH=C**H**$_2$, cis H), 5.17 (1 H, dd, J = 17 and 2 Hz, -CH=C**H**$_2$, trans H), 5.41, (1 H, m, -CH=C(CH_3)-), 6.13 (1 H, dd, J = 17 and 10 Hz, -C**H**=CH_2); ^1H NMR (C_6D_6) δ 0.89 and 0.94 (3 H each, d, J = 7 Hz), 1.33 (3 H, s), 1.74 (3 H, m); ^1H NMR (decoupling in C_6D_6) irr δ 1.56 (collapse δ 0.89) and irr δ 1.78 (collapse δ 0.94). ^{13}C NMR ($CDCl_3$) (off-resonance mult): sp^2 δ 145.3 (d), 139.2 (s), 123.9 (d), 110.7 (t); sp^3 δ 89.2 (s), 83.8 (s), 45.7 (d), 37.9 (t), 34.9 (t), 32.9 (q), 31.5 (t), 28.7 (q), 20.1 (q), 19.9 (d), 13.3 (q). Mass spectrum, *m/e* 205.1586 (M^+ − 15; calcd for $C_{14}H_{21}O$, 205.1592), (70 eV) (relative intensity) 202 (M^+ − 18, 100), 137 (52), 173 (51), 164 (35), 164.1194 (calcd for $C_{11}H_{16}O$, 164.1201), 159 (20), 145 (61), 133 (95), 119 (75), 105 (57), 91 (39), 84 (56), 77 (27).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.91; H, 10.99.

Isolation of Dactylenol (1) and Dactylenol Acetate (4). A portion (2.62 g) of the material obtained in combined fractions 9–11 from the Florisil chromatography described earlier[8b] was chromatographed on TLC mesh silica gel (40 g) using benzene–hexane (1:1) as solvent. After initially collecting 31 15-mL fractions, many of which contained dactylyne,[8a] three 100-mL fractions were collected. The first of these contained predominantly (80–90%) dactylenol acetate (**4**) (61 mg).

Attempts to obtain pure **4** by further chromatography on silica gel or 9% silver nitrate impregnated silica gel were unsuccessful. Preparative gas chromatography on a 6 ft × 0.25 in 20% FFAP column at 169 °C yielded **4** as a colorless oil: $[\alpha]_D$ +168° (*c* 2.46, $CHCl_3$); bp (Kugelrohr) 75 °C yielded **4** as a colorless oil: $[\alpha]_D$ +168° (c 2.46, $CHCl_3$); bp (Kugelrohr) 75 °C (1 Torr); IR (neat) 3090, 2970, 2945, 2885, 2835, 1740, 1645, 1455, 1370, 1245, 1090, 915, 885 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.08 (3 H, d, *J* = 6 Hz), 1.48 (3 H, s, $CH_3CO_2C(CH_3)$–), 1.65 (3 H, brd s, –CH=C(CH_3)–, 1.95 (3 H, s, acetate), 2.6–~1.12 (8 H, m), 4.68 (2 H, brd d, *J* = 2 Hz, C=CH_2), 5.05 (1 H, dd, *J* = 10 and 2 Hz, –CH=CH_2, cis H), 5.08 (1 H, dd, *J* = 17 and 2 Hz, –CH=CH_2, trans H), 5.23 (1 H, brd t, *J* = 6 and <1 Hz, –C**H**=C(CH_3)–), 5.91 (1 H, dd, *J* = 17 and 10 Hz, –C**H**=CH_2); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion observed) 202 (M^+ − 60, 35), 187 (17), 173 (16), 159 (15), 145 (11), 134 (97), 121 (100), 105 (12), 81 (42).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.72; H, 9.95.

Chromatography of the material (6.3 g) obtained from the combined fractions 15–18 described earlier[8b] on 60 g of TLC mesh silica gel using benzene–hexane (7:3) as solvent and collecting 50-mL fractions yielded, in fractions 17–20 and a 100-mL 100% benzene flush, ~1.8 g of dactylenol (**1**), homogeneous by TLC analysis. Gas chromatographic analysis of this material on a 5 ft × ⅛ in 10% FFAP column indicated that this material was a mixture of at least five components. Pure **1** was obtained by chromatography on 9% $AgNO_3$ impregnated silica gel thick-layer plates (20 × 20 cm, 2 mm thick) employing ethyl acetate–cyclohexane (4:6) for development. From a 100-mg sample applied on a single plate, 40–50 mg of pure dactylenol was obtained.

Pure dactylenol (**1**) was a colorless oil: $[\alpha]_D$ +203.8°; IR (neat) 3400 (broad), 3080, 1640, 1150, 1100, 985, 910, 880, 800, 775 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.60–1.0 (8 H, m), see text for remainder; ^1H NMR (100 MHz, CCl_4, 0.45 mol ratio of Eu(fod)$_3$/dactylenol) (signals not discussed in text) δ 2.29 (3 H, m, vinyl methyl), 5.30 (1 H, d, *J* = 2 Hz), 7.81 (1 H, dd, *J* = 10 and 1 Hz, –CH=CH_2, cis H), 10.75 (1 H, dd, *J* = 18 and 1 Hz, –CH=CH_2, trans H); mass spectrum (70 eV), *m/e* (relative intensity) 220 (M^+, 3), 202 (13), 187 (12), 173 (10), 159 (8), 145 (8), 134 (100), 132 (23), 121 (80), 119 (32), 105 (12), 71 (10).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.94; H, 11.14.

Dactylenol (1) from Dactylenol Acetate (4). To a 25-mL round-bottom flask containing 57.3 mg of **4** and a magnetic stirring bar was added ~10 mL of dry ether (distilled directly from lithium aluminum hydride) and then 20 mg of lithium aluminum hydride ($LiAlH_4$). After the reaction mixture had stirred at room temperature for 30 min, excess $LiAlH_4$ was destroyed by the addition of ethyl acetate followed by water. The water layer was extracted twice with ethyl acetate and twice with ether. The organic layers were combined, dried (Na_2SO_4), and evaporated under reduced pressure, leaving 49.5 mg of a colorless oil. The reaction product was chromatographed on 10 g of thin-layer mesh silica gel using ether–hexane (1:9) as solvent and collecting 7-mL fractions. Fractions 14–17 contained a single compound (TLC, GC) which was identical with naturally occurring **1** based on the following criteria: $[\alpha]_D$ +204° (*c* 0.25, $CHCl_3$); IR, ^1H NMR (60 MHz), and mass (chemical ionization using methane and isobutane) spectra and gas chromatographic retention time (5 ft × ⅛ in 10% FFAP column).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.93; H, 10.91.

Acetylation of Dactylenol (1). A mixture of 25 mg of **1**, 1.0 mL of pyridine (dried over molecular sieves), and 1.0 mL of acetic anhydride was heated under nitrogen at 50 °C for 8 h. The solvent was removed in vacuo to yield a semisolid residue that was only partially soluble in hexane. Gas chromatographic analysis of the hexane solubles on a 5 ft × ⅛ in 10% FFAP column showed a peak with a retention time identical with that of **4**, which corresponded to an approximately 10% conversion of alcohol to acetate.

Hydroboration of Dactyloxene-B (5). Dactyloxene-B (200 mg) was added to 3 mL of 9-borabicyclo[3.3.1]nonane–THF solution (0.5 M), and the mixture was stirred at room temperature for 3 h. The solution was cooled in an ice bath, treated with 2.5 mL of 3 N NaOH and then 2.5 mL of 30% hydrogen peroxide, and stirred overnight at room temperature. The solution was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The ether solution was washed with water, dried ($MgSO_4$), and evaporated to give 250 mg of a colorless oil. This oil was chromatographed on 12 g of silica gel (TLC mesh) using chloroform as eluent to give 160 mg of the alcohol **6**: IR (neat) 3450 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.99 and 1.03 (6 H, overlapping d, *J* = 6 Hz, secondary methyls), 1.30 (3 H, s, tertiary methyl), 1.74 (3 H, brd s, vinyl methyl), 3.44–3.96 (2 H, m, –$CH_2C\mathbf{H}_2OH$), 5.34 (1 H, m, olefinic H); MS (70 eV) *m/e* (relative intensity) 182 (M^+ − 56, 8, –C_4H_8), 149 (3), 135 (7), 121 (9), 109 (20), 91 (19), 82 (17), 79 (17), 77 (14), 69 (13), 67 (18), 56 (42), 43 (75), 41 (100).

Acetylation of Alcohol 6. A 64-mg amount of alcohol **6** was acetylated using 0.3 mL of pyridine and 0.3 mL of acetic anhydride at room temperature for 72 h. The reaction mixture was hydrolyzed by adding a 10% $NaHCO_3$ solution and stirring for 3 h. The solution was diluted further with water and extracted with ether (2 × 10 mL). The combined ether layers were washed with a 5% $NaHCO_3$ solution, 1 N HCl, and water and then dried and evaporated to give 60 mg of a colorless oil that was essentially pure as judged by TLC: ^1H NMR (60 MHz, $CDCl_3$) δ 1.00 (6 H, overlapping d, secondary methyls), 1.32 (3 H, s, tertiary methyl), 2.1 (3 H, s, vinyl methyl), 4.22 (2 H, t, –$CH_2C\mathbf{H}_2OH$), 5.38 (1 H, m, vinyl H).

Preparation of the Keto Acetate 7 and Keto Acid 8. According to the procedure of Brown and Garg,[10] the acetate of **6** (60 mg) and lithium borohydride (9.9 mg) in 1 mL of ether were treated with boron trifluoride etherate (20 mg) dissolved in ether (1 mL). The reaction mixture was stirred at room temperature for 2 h, and then water (9.1 mL) and an oxidizing solution (220 mg of $Na_2Cr_2O_7$, 9.16 mL of concentrated H_2SO_4, and 0.9 mL of H_2O) were added and the mixture was heated at 40 °C (reflux condenser) for 2 h. The reaction mixture was cooled to room temperature, the layers were separated, and the water layer was extracted further with ether. The combined ether layers were dried and evaporated to give a colorless oil, 60 mg.

The crude product was chromatographed on 12 g of silica gel. Elution with chloroform–methanol (99:1) yielded 30 mg of the keto acetate **7**. Subsequent elution with chloroform–methanol (95:5) afforded 17 mg of the keto acid **8**: mp 134–145 °C; IR (KBr) 3300–2500 (brd), 1700 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.05, 1.08, and 1.12 (3 H each, d, secondary methyls), 1.27 (3 H, s, tertiary methyl), 2.07 (AB q, –$C\mathbf{H}_2CO_2H$), 6.3 (1 H, brd, exchangeable, –CO_2H); MS (70 eV) *m/e* (relative intensity) 268 (M^+, 11), 223 (2), 212 (25), 197 (77), 170 (19), 149 (30), 109 (41), 83 (43), 67 (68), 60 (44), 55 (62), 44 (55), 43 (93), 41 (100).

Treatment of the Keto Acetate 7 with Base. The keto acetate **7** was dissolved in a few milliliters of methanol in which a small piece of sodium had been dissolved. The mixture was stirred at room temperature overnight and then diluted with water. The product was isolated by extraction with ether and chromatographed on silica gel as described above for the keto acetate/keto acid mixture to give the α,β-unsaturated keto alcohol **9**: IR (film) 3400 (OH), 1660, 1650 cm^{-1}; UV (95% EtOH) λ_{max} 249 nm (ε 16 100); ^1H NMR (100 MHz, $CDCl_3$) δ 1.02 and 1.25 (3 H each, d, secondary methyls), 1.32 (3 H, s, tertiary methyl), 1.78 (3 H, s, vinyl methyl), 3.94 (2 H, t, –$CH_2C\mathbf{H}_2OH$); MS (70 eV) *m/e* (relative intensity) 236 (M^+ −18, 10), 218 (12), 206 (11), 203 (12), 190 (15), 163 (28), 149 (60), 135 (46), 123 (28), 121 (38), 107 (65), 91 (45), 81 (53), 77 (47), 67 (60), 55 (65), 43 (55), 41 (100).

Hydroboration of Dactyloxene-A (12). To 80 mg of **12** in 2 mL of tetrahydrofuran freshly distilled from lithium aluminum hydride was added 16 mg (0.73 mmol) of lithium borohydride. The solution was cooled in an ice bath, and 0.6 mL of a THF solution containing 0.24 mg of boron trifluoride etherate was added over a 25-min period. The ice bath was removed and the mixture stirred overnight. Then 0.1 mL of 3 N NaOH and 0.1 mL of 30% hydrogen peroxide were added, and stirring was continued for 1.25 h at 35–50 °C. Potassium carbonate (0.5 g) was added to cause separation of the water and THF layers, and the water layer was extracted twice more with 10-mL portions of THF. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated, and the product was filtered through a short column of silica gel (0.4 g, 100–200 mesh). Elution with benzene (10 mL) removed a milky oil, and further elution with two 10-mL portions of benzene–methanol (85:15 and then 70:30) yielded 77 mg of the diol **14**: IR ($CHCl_3$) 3600 (w), 3420 (brd s), 1450, 1370, 1090, 1050, 1030 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.90 and 1.03 (overlapping methyl d, *J* = 6 Hz), 1.23 and 1.36 (3 H each, s), 3.2–4.0 (3 H, brd overlapping mult, –$C\mathbf{H}_2OH$ and –C**H**(OH)–).

Dactyloxene-A Diol Monotrityl Ether 15. To 39 mg of the diol **14** dissolved in 2.5 mL of dry pyridine was added 150 mg of trityl chloride. The reaction mixture, protected by a drying tube, was heated on a steam bath for 1.25 h and then cooled to room temperature and diluted with 20 mL of dichloromethane and 15 mL of water. The layers were separated, and the water layer was extracted again with dichloromethane. The combined organic layers were washed with water (3 × 10 mL) and 10% HCl (3 × 10 mL), followed by single washes with water, 10% $NaHCO_3$, and water again. The organic layer was dried (Na_2SO_4) and evaporated. The crude product (89 mg) was chromatographed on 4 g of 100–200 mesh silica gel. The triphenylcarbinol was eluted with benzene–hexane mixtures and pure benzene.

Elution with benzene–methanol (98:2) afforded 23 mg of the monotrityl ether **15**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.83 and 0.90 (overlapping methyl d, J = 6 Hz), 1.13 and 1.20 (3 H each, s), 3.28 (2 H, t, J = 7 Hz, $-CH_2-O-CPh_3$), 3.4–4.0 (1 H, m, $-CH(OH)-$), 7.4 (15 H, m); MS (70 eV) m/e (relative intensity) 498 (M^+, 2), 424 (4), 259 (4), 243 (100, Ph_3C^+), 237 (14), $M^+ - 18$, $-Ph_3C^+$), 211 (25), 193 (10), 165 (46), 135 (10), 121 (7), 105 (21), 91 (6), 77 (13), 69 (10), 55 (17), 43 (31).

Preparation of Keto Trityl Ether 16. The trityl ether **15** dissolved in 3 mL of dichloromethane was added at room temperature to 0.8 mg of a chromium trioxide–pyridine–dichloromethane solution,[11] which was being stirred rapidly. A black precipitate formed immediately. Stirring was continued for 25 min, and then the dichloromethane was decanted off and the insoluble precipitate washed twice with 8-mL portions of ether. The combined organic layers were washed with 5% NaOH (3 × 8 mL), 5% HCl (8 mL), and 5% $NaHCO_3$ and then dried (Na_2SO_4). Evaporation of the solvent gave a quantitative yield of the keto trityl ether **16**: IR (CCl_4) 1712, 1100, 1080, 1058, 1030 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 0.75 and 0.85 (overlapping methyl d), 1.17 and 1.28 (3 H each, s), 3.20 (2 H, t, J = 6 Hz), 7.30 (15 H, m); ^{1}H NMR (C_6D_6) δ 0.63 and 0.98 (methyl d), 0.93 and 1.13 (3 H each, s), 3.41 (2 H, t, J = 7 Hz, $-CH_2-O-CPh_3$), 7.15 and 7.60 (15 H, m, $-CCPh_3$).

Treatment of the Keto Trityl Ether 16 with Base. The crude keto trityl ether **16** (16 mg) in methanol (0.7 mL) was added to 1.5 mL of dry methanol in which a small chip of sodium metal had been dissolved. The reaction mixture was degassed (vacuum), placed under a nitrogen atmosphere, and allowed to stand at room temperature overnight. The reaction mixture was diluted with a few milliliters of water and then extracted with dichloromethane (3 × 8 mL) and benzene (3 × 8 mL). The combined organic layers were washed with water and brine and dried (Na_2SO_4). Evaporation afforded 4 mg of a colorless oil which showed carbonyl absorption (strong) only at 1712 cm^{-1}. The still cloudy basic aqueous methanol layer was acidified with a few drops of 5% HCl and then extracted with dichloromethane (3 × 8 mL). Workup of the organic layer as above yielded an additional 9 mg of product that showed carbonyl absorption (strong) only at 1712 cm^{-1}: ^{1}H NMR (100 MHz, C_6D_6) δ 0.60 and 0.67 (3 H, overlapping d, J = 7 Hz), 0.90 (3 H, s), 0.93 (methyl d), 1.05 and 1.09 (each a singlet, combined area equivalent to 3 H), 3.28 (2 H, t, J = 7 Hz), 7.1 and 7.55 (15 H, m). (The doubling of methyl signals indicates that some epimerization has occurred adjacent to the ketone.)

Hydroboration of Dactyloxene-C (10). Dactyloxene-C (55 mg) was hydroborated using 1.5 mL of 9-borabicyclo[3.3.1]nonane–THF solution (0.5 M) as described above for the hydroboration of **5**. After oxidation, extraction, and chromatography, 40 mg of pure alcohol **11** was obtained: oil; IR (neat) 3400, 1450, 1370, 1100, 1045, 1005 cm^{-1}; ^{1}H NMR (100 MHz, CCl_4) δ 0.98 and 1.00 (overlapping methyl d, J = 6 Hz), 1.36 (3 H, s, $-C(CH_3)-O-$), 1.74 (3 H, m, olefinic methyl), 3.46–4.0 (2 H, complex m, $-CH_2OH$), 5.33 (1 H, m, $-CH=C(CH_3)-$).

Acid Treatment of Dactylenol (1) with Acid. A mixture of 19 mg of **1** in 5 mL of ether containing a few crystals of *p*-toluenesulfonic acid monohydrate was allowed to stand at room temperature for a few hours. The ether solution was then washed with water, dried, and concentrated. The products were analyzed on a 100-ft support coated open tubular (S.C.O.T.) FFAP column. Dactyloxene-A (**12**), a minor component, and dactyloxene-B (**5**), a major component, were identified by peak enhancement. Cyclization catalyzed by BF_3 etherate in ether at 0 °C with warming to room temperature gave similar results.

Acknowledgment. We thank Dr. C. Shew, R. S. Kerr Environmental Research Laboratory, Ada, Okla., and the mass spectrometry facility at Massachusetts Institute of Technology, supported by a grant (Principal Investigator, Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources, for the mass spectra. The ^{13}C NMR spectra were kindly provided by Varian Associates, Palo Alto, Calif. We are grateful for the use of the former Lerner Marine Laboratory, Bimini, Bahamas, for specimen collection, and we acknowledge with thanks grants from the Phillips Petroleum Co., Bartlesville, Okla., and the NSF (GP 38410), which aided in the purchase of NMR spectrometers. We thank Dr. K. H. Hollenbeak for assisting in the reisolation of dactyloxene-A, -B, and -C.

Registry No.—**1**, 58542-82-8; **4**, 58071-43-5; **5**, 54928-03-9; **6**, 54706-65-9; **6** acetate, 67360-86-5; **7**, 67360-87-6; **8**, 54706-68-2; **9**, 67360-88-7; **10**, 54990-55-5; **12**, 54990-54-4; **14**, 67360-89-8; **15**, 67360-90-1; **16**, 67360-91-2; trityl chloride, 76-83-5.

References and Notes

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(17) Melting points are uncorrected. Infrared spectra were taken on Beckman IR-8 or Acculab 3 spectrophotometers. NMR spectra were acquired on Varian T-60 or XL-100 instruments in the solvents specified; signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Mass spectra were obtained on Hitachi RMU-7, Finnegan 3000 D, and CEC (Dupont, Monrovia, Calif.) 110 mass spectrometers. A Perkin-Elmer 141 or Gaertner polarimeter was used for obtaining optical rotations. Microanalyses were obtained from Mr. E. Meier, Department of Chemistry, Stanford University, Stanford, Calif. Chromatographic adsorbents used were Florisil (Fisher, 100–200 mesh) and silicic acid (Mallinckrodt, SilicAR CC-7; Brinkman TLC mesh). The 9-borabicyclo[3.3.1]nonane solution, 0.5 M in tetrahydrofuran, was purchased from Aldrich Chemical Co., Milwaukee, Wis.