Facile Synthesis of Fucoserratene and the (±)-Dictyopterenes B, D, and D′ (= Ectocarpene): Constituents of Marine Brown Algae

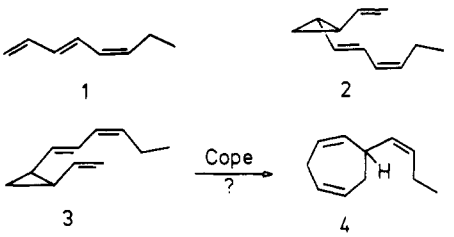
Manfred P. Schneider* and Michael Goldbach

Contribution from the Institut für Chemie, Universität Hohenheim, D-7000 Stuttgart-70, West Germany. *Received January 2, 1980*

Abstract: A low step approach to the title compounds **1-4** has been developed by employing three highly stereo- or regiochemically controlled reactions: (a) a *Z*-stereoselective Wittig reaction; (b) a 1,3-dipolar cycloaddition; (c) a Cope rearrangement. A *Z*-stereoselective Wittig reaction of (*E*)-2,4-pentadienal (**10**) with *n*-propylidenetriphenylphosphorane leads to fucoserratene (**1**) with 97% *Z* configuration at C(5). 1,3-Dipolar cycloaddition of 3-diazo-1-propene (**5**) to **1** yields a mixture of the *cis*- and *trans*-1-pyrazolines (**7**). Thermal or photochemical decomposition of **7** produces only **2** and **4**. Low-temperature photolysis leads to **2** and **3**, the latter being the hypothetical precurser in the biosynthesis of **4**. **3** rearranges readily to **4** under biotic conditions, supporting its role in biosynthesis. The biological activities of **1** and **4** have been established by bioassay.

Introduction

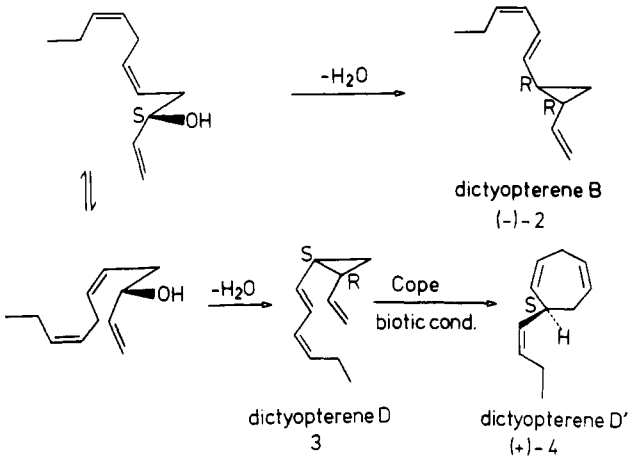
In the last decade a number of constituents of marine brown algae have been isolated,[1] some of which are exhibiting remarkable physiological activities. Fucoserratene (**1**), produced by the mature eggs of *fucus serratus*, has been demonstrated to be a pheromone with enormous chemotactic activity on the mobile spermatozoa of this algae.[2] Similar activity is displayed by ectocarpene (**4**), produced by the female gametes of *ectocarpus siliculosus*.[3] **4** turned out to be identical with dictyopterene D′, which was isolated together with dictyopterene B (**2**) among other compounds from *dictyopteris plagiogramma*, a Pacific brown algae in the waters of Hawaii.[4] Dictyopterene D (**3**) is not known. It was suggested,



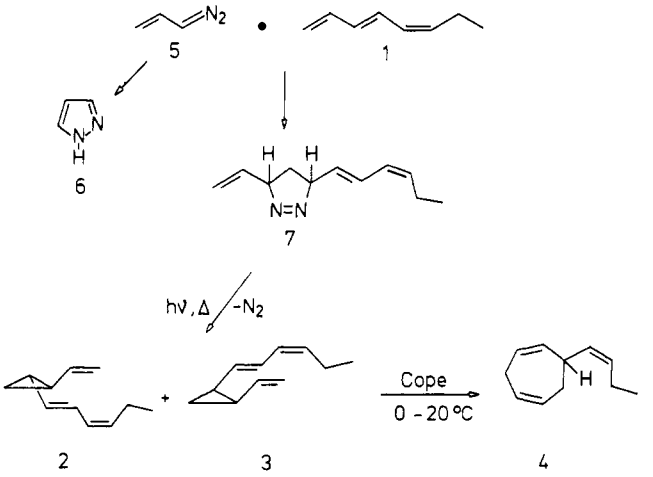
however, as precurser in the biosynthesis of **4**, being in turn produced by concomitant dehydration and ring closure of a metabolic (3*S*)-(*Z*,*Z*)-1,5,8-undecatrien-3-ol (Scheme I).[1]

Previous synthetic approaches to **1-4** were suffering from several disadvantages. No *direct* stereospecific synthesis of **1** has so far become available and known procedures all require the separation of isomers by preparative GC at some stage.[5] Preparation of **2** and **4** not only required multistep procedures[6] (involving construction of the side chain, synthesis of the cyclopropane moiety, connection of the two building blocks by a Wittig reaction, followed by a Cope rearrangement for **4**), but were in fact leading to *E*/*Z* isomers of **2** owing to the lack of stereospecificity at the newly formed carbon–carbon double bond.[7] None of these procedures provided access to **3**.

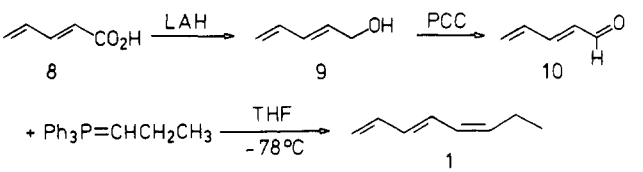
Scheme I



Scheme II



Scheme III



(1) Reviews in connection with the title compounds: Jaenicke, L.; Müller, D. G. *Fortschr. Chem. Org. Naturst.* **1973**, *30*, 61. Moore, R. E. *Acc. Chem. Res.* **1977**, *10*, 40. Moore, R. E. In "Marine Natural Products", Scheuer, P. J., Ed.; Academic Press: New York, 1978; Chapter 2.

(2) Müller, D. G.; Jaenicke, L. *FEBS Lett.* **1973**, *30*, 137.

(3) Müller, D. G. *Planta* **1968**, *81*, 160. Müller, D. G.; Jaenicke, L.; Donike, M.; Akintobi, T. *Science* **1971**, *171*, 815.

(4) Moore, R. E.; Pettus, J. A., Jr.; Mistysin, J. *J. Org. Chem.* **1974**, *39*, 2201.

(5) Jaenicke, L.; Seferiadis, K. *Chem. Ber.* **1975**, *108*, 225. Wiedenmann, B.; Hopf, H. *Z. Naturforsch. B* **1977**, *32*, 119. Both methods lead to isomeric mixtures from which **1** was isolated to preparative GC; no complete spectroscopic data (except MS and UV) were reported.

(6) (a) Ali, A.; Sarantakis, D.; Weinstein, B. *Chem. Commun.* **1971**, *940*. (b) Jaenicke, L.; Akintobi, T.; Müller, D. G. *Angew. Chem.* **1971**, *83*, 537; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 492. (c) Jaenicke, L.; Akintobi, T.; Marner, F.-J. *Justus Liebigs Ann. Chem.* **1973**, 1252.

0002-7863/80/1502-6114$01.00/0

Results

We report here a low-step approach to these compounds based on the strategy outlined in Scheme II and making use of reactions which are known to be highly regio- and stereochemically controlled: (a) a 1,3-dipolar cycloaddition, which should, from our experience[8] and predicted by frontier orbital considerations,[9] proceed in the desired fashion; (b) a Cope rearrangement leading stereospecifically to **4**. This strategy bypasses all previous disadvantages and should even allow an observation of the hypothetical **3**, provided that the following requirements are fulfilled: (a) a simple and highly stereoselective synthesis of **1** can be found; (b) the 1,3-dipolar cycloaddition of 3-diazo-1-propene (**5**) to **1** proceeds indeed in the indication fashion and in reasonable yield; (c) the decomposition of the 1-pyrazolines (**7**) leads to the desired products in high yield and without important side reactions.

Fucoserratene (1). We found that **1** can easily be prepared in a few steps and from readily available materials as outlined in Scheme III. (*E*)-2,4-Pentadienoic acid (**8**)[10] is reduced with lithium aluminum hydride to (*E*)-2,4-pentadienol (**9**),[10b,11] which is then oxidized with pyridinium chlorochromate[12] to (*E*)-2,4-pentadienal (**10**). A *Z*-stereoselective Wittig reaction of **10** with *n*-propylidenetriphenylphosphorane, employing the silazide method,[13] leads to (*E*,*Z*)-1,3,5-octatriene (fucoserratene, **1**) with 97 ± 2% (capillary GC) *Z* configuration at C(5). **1** was identical with the natural product in all respects,[5] including its biological activity.[14]

Dictyopterenes B and D′ (= Ectocarpene). Since **1** has thus become easily available, we were able to use it as a substrate in the synthesis of **2**–**4** (compare Scheme II). Addition of **5**[8] to **1** leads, as expected, to a mixture of the *cis*–*trans*-1-pyrazolines **7** with pyrazole (**6**) as byproduct resulting from the competing intramolecular cyclization of **5**. Since unreacted **1** can be recovered and recycled, it can be almost quantitatively converted into **7** employing in total 2–3-fold excess of **5**. The 1-pyrazolines **7** are rather unstable. They are slowly losing N_2 already at 0 °C and are susceptible to oxidation and tautomerization upon storage. They are therefore difficult to purify and characterize and are best used as crude reaction mixtures.

Thermolysis of **7** (*n*-hexane, reflux, 3 h) or photolysis (*n*-hexane, Pyrex filter, +15 °C) with ultraviolet light produces mixtures of **2** and **4**, **4** being formed by spontaneous Cope rearrangement of the primary product **3** under these conditions. It is worthwhile to note that this method, in contrast to earlier attempts,[6] yields only one (the desired) isomer of **2**, since the stereochemistry of the C(3) and C(5) double bonds in **1** is fully retained throughout the synthesis. **2** and **4**, which can be separated easily by GC, were identical with the natural products in all respects.[4]

2 is thermally stable up to ~80 °C and rearranges rapidly above 100 °C into **4** ($t_{1/2}$ = 7 min at 125 °C).[15] If, therefore, the above mixtures of **2** and **4**, produced in the thermolysis or photolysis of **7**, are heated to ~125 °C for 1.5 h (~13 half-lives), **4** is obtained as sole product. Thus, starting from **1** and **5**, bypassing isolation of either **7** or **2**, the method in fact provides a stereospecific "one-pot" and "one-step" synthesis of racemic ectocarpene (**4**).

4 was identical with the natural pheromone on three different columns in the GC (high performance capillary GC, 50-m columns of OV 101 and 225 and Ucon-75-H-90000) and by comparison with all available spectroscopic data. The biological activity of **4** was determined by bioassay.[14] Using the dilution technique, the threshold concentration for a reaction of our synthetic material with the male gametes of *ectocarpus siliculosus* was determined to be 3×10^{-6} M in FC-78 (a fluorinated hydrocarbon used for application), a value which was exactly identical with earlier measurements of synthetic materials.[6b,c,16]

Dictyopterene D (3) by Low Temperature Photolysis of 7. A sufficiently pure sample of **7** can be obtained by low-temperature workup of the crude reaction mixture of the 1,3-dipolar cycloaddition of **1** and **5** (see above) and removal of all volatile reaction products (formed during manipulation) on a high vacuum line at −10 °C. Irradiation of such a sample with ultraviolet light (λ >310 nm) at −40 °C in a mixture of $CDCl_3$ + CD_2Cl_2 (2:5) (the reaction can be carried out in the probe of an NMR spectrometer, allowing a direct observation of all processes[8]) leads to a mixture of **2** and **3**, which displays no allylic protons in the ^1H NMR below δ 2.25 ppm. The rearrangement **3** → **4** can be observed between 0 and 20 °C (estimated half-life ~50 min at +15 °C) by the appearance of the allylic protons of **4** at δ 2.22 (2 H), 2.85 (2 H), and 3.45 (1 H) ppm.[17] Photolysis of **7** therefore provides, as expected, a route to **3**, whose Cope rearrangement occurs readily under biotic conditions. This observation supports the suggestion that **3** could well serve as a precurser in the biosynthesis of **4**.

In summary, the here introduced method provides a low-step synthesis of the natural products **1**–**4**, avoiding multistep procedures (even bypassing the synthesis of the cyclopropane moiety) by the use of a simple stereo- and regiochemically controlled reaction sequence.

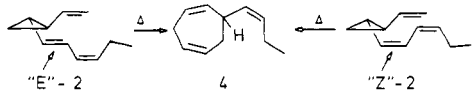
Experimental Section

^1H NMR spectra were measured at 90 MHz on a Bruker HX90R instrument and at 60 MHz on a Varian EM 360 instrument. Chemical shifts are reported in δ units relative to internal Me_4Si. ^{13}C NMR spectra were measured at 22.625 MHz on the Bruker HX90R. Carbon resonances are reported in δ_C units relative to Me_4Si. Infrared spectra were measured on a Zeiss IMR 25 instrument and were calibrated with the 1601-cm^{-1} absorption of polystyrene. UV spectra were measured on a Zeiss DMR 10 spectrophotometer. Mass spectra were determined using a Varian 311A instrument with GC–MS system 44S. VPC analysis were performed on a Carlo Erba Fractovap 2150 employing 2 m × 5 mm columns: (1) 5% Apiezon L; (2) 5% 1,2,3-tris(2-cyanoethoxy)propane; (3) 5% Carbowax 1500 all on Chromosorb W-AW-DMCS; (4) 25 m Apiezon L capillary column (capillary GC work was carried out on a Carlo Erba 2900 instrument with this column). Elemental analyses were performed in the microanalytical laboratory of the Universität Stuttgart. Melting points and boiling points are uncorrected.

(*E*)-2,4-Pentadienoic Acid (8). The compound was synthesized employing a modification of a published procedure.[10] To a solution of 500 g (4.8 mol) of malonic acid in 700 mL of pyridine, heated to 75–80 °C, was added under vigorous stirring 340 g (6 mol) of acrolein. Stirring was continued until the evolution of CO_2 ceased. The cooled solution was poured onto a mixture of 3 kg of ice and 400 mL of 98% sulfuric acid. After 15 min the precipitated **8** was collected by filtration and recrystallized from hot (75 °C) water (ratio 1:10). Drying over $CaCl_2$ and sublimation (65–70 °C, 0.2 Torr) yielded 270 g (57%) of pure **8**, mp 73.5 °C (lit.[10] 72–75 °C).

(*E*)-2,4-Pentadienol (9). The compound was synthesized analogously to a procedure published for the reduction of sorbic acid.[10b,11] To a suspension of 25 g (0.66 mol) of $LiAlH_4$ in 500 mL of absolute ether at room temperature was added under vigorous stirring and as rapidly as

(7) In contrast to the published procedure[6a] only *E*/*Z* mixtures of **2** were



obtained this way. Thermal rearrangment of both isomers leads then indeed to the identical product **4**.

(8) Schneider, M. P.; Rau, A. *J. Am. Chem. Soc.* **1979**, *101*, 4426.

(9) Houk, K. N.; Sim, J.; Duke, R. E.; Strozier, R. W.; Georgie, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* **1973**, *95*, 7301.

(10) (a) Glushkov, R. G.; Magidson, O. Yu. *Med. Prom. SSSR* **1962**, *16*, 27; *Chem. Abstr.* **1963**, *58*, 442b. (b) Mori, K. *Tetrahedron* **1974**, *30*, 3807.

(11) Nystron, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 2548.

(12) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(13) Bestmann, H. J.; Stransky, W.; Vostrowsky, O. *Chem. Ber.* **1976**, *109*, 1694. We are greatly indebted to Professor Bestmann for kindly assisting us in the application of his method to our problem.

(14) We are greatful to Dr. D. G. Müller, Universität Konstanz, for kindly testing the biological activities of our synthetic products **1** and **4**.

(15) Pettus, J. A., Jr.; Moore, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3087.

(16) A quantitative determination of the threshold concentration of the natural pheromone has so far not been carried out owing to lack of material (private communication from Dr. D. G. Müller, Universität Konstanz).

(17) The complicated nature, with overlapping signals, of the high-field region of the mixture so far precluded a recording of the ^1H NMR spectrum of **3**, as well as an accurate determination of the half-life for the rearrangement **3** → **4**. This is quite in contrast to simpler cases.[8] Within a series of *cis*-1,2-divinylcyclopropanes we are presently trying to solve these problems with the aid of proton noise decoupled ^{13}C NMR.

possible (to maintain good reflux) 52 g (0.53 mol) of **8** dissolved in 250 mL of absolute ether. Excess $LiAlH_4$ was carefully destroyed with water and a 10% aqueous solution of sulfuric acid was added until the ether layer became clear. After the mixture was washed with sodium bicarbonate and brine, the ether phase was dried over Na_2SO_4. Removal of solvent and distillation yielded 32.2 g (72%) of **9**, bp_{70} 88–89 °C.

(*E*)-2,4-Pentadienal (10). To a suspension of 43 g (0.2 mol) of pyridinium chlorochromate[12] and 6 g of sodium acetate in 200 mL of absolute methylene chloride was added rapidly and under stirring a solution of 9 g (0.1 mol) of **9** dissolved in 20 mL of CH_2Cl_2. After the mixture was stirred for 90 min, 150 mL of absolute ether was added. The suspension was filtered and the solids were washed three times with 150-mL portions of absolute ether. The combined solutions were passed through a short column of Florisil and a trace of hydroquinone was added. Removal of solvent followed by distillation yielded 6.1 g (70%) of **10**, bp_{35} 59 °C. **10** was stored under argon at −78 °C to avoid polymerization and should be used for the next step as rapidly as possible: ^1H NMR (CCl_4) δ 5.50–7.70 (m, 5 H), 9.50 (d, 1 H); IR (neat) 1685, 1638, 1175, 1110, 1020 cm^{-1}; mass spectrum *m/e* 82 (parent ion, 100%), 53 (93%); UV (95% EtOH) nm (log ϵ_{max}), 257 (4.35). Anal. Calcd for C_5H_6O: C, 73.13; H, 7.38. Found: C, 72.53; H, 7.76.

(*E,Z*)-1,3,5-Octatriene (Fucoserratene, 1). A stirred mixture of 9.2 g (0.05 mol) of sodium bis(trimethylsily)amide and 19.2 g (0.05 mol) of *n*-propyltriphenylphosphonium bromide in 150 mL of *n*-hexane was refluxed under argon for 3 h. The resulting suspension was cooled to −20 °C and centrifuged in airtight plastic containers. The supernatant liquid (containing hexamethyldisilazane) was discarded. The precipitate (consisting of the ylide and sodium bromide) was stirred with absolute THF at room temperature and centrifuged again to precipitate the sodium bromide. The clear supernatant solution (now only containing the pure and salt free ylide in THF) was added slowly and with stirring to a solution of 4.5 g (0.055 mol) of **10** in 100 mL of THF at −78 °C. The mixture was kept at −78 °C for 1.5 h, warmed slowly to ambient temperature, and centrifuged. The solids were washed three times with THF, all solutions were combined, and the THF was removed at reduced pressure (bp_{400} ~45 °C). The residue was diluted with ether, washed with $NaHSO_3$ solution (to remove excess **10**), dried over Na_2SO_4, and distilled to give 4.2 g (78%) of **1**: bp_{40} 54 °C; capillary GC (column **4**) revealed that **1** has 97 ± 2% *Z* configuration at C(5); ^1H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.5 Hz, 3 H), 2.14 (dq, *J* = 7.6, 1.3 Hz, 2 H), 5.01–5.62 (m, 3 H), 5.86–6.56 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ_C 14.2, 21.2, 116.8, 127.9, 128.6, 133.0, 135.0, 137.3 (characteristically C(7) appears 4.6 ppm upfield compared with C(7) in (*E,E*)-1,3,5-octatriene (25.8 ppm) and compares well with other naturally occurring trienes);[4] IR (neat) 3090, 3010, 2970, 2940, 2880, 1008, 940, 900 cm^{-1}; mass spectrum *m/e* 108 (parent ion, 45%), 79 (base peak, 100%); UV (*n*-hexane) nm (log ϵ_{max}), 254 (4.45), 263 (4.58), 274 (4.48). Exact mass calcd for C_8H_{12}: 108.0939. Found: 108.0939.

***trans*-1-[(*E,Z*)-1,3-Hexadienyl]-2-vinylcyclopropane (Dictyopterene B, 2) and 6-[(*Z*)-1-Butenyl]-1,4-cycloheptadiene (Dictyopterene D′ = Ectocarpene, 4). ("One pot"): Method A.** **1** (5 g, 0.045 mol) and 3.6 g (0.053 mol) of 3-diazo-1-propene (**5**)[8] were mixed at −20 °C and kept under argon at +4 °C until the deep red color of the diazo compound had faded (~3 days). All volatile materials, consisting of unreacted **1** (2.15 g, 42%) and the already formed reaction products **2** and **4** (the 1-pyrazolines **7** slowly lose N_2 already at 0 °C) (1.0 g, 14%), were condensed off the reaction mixture at 0 °C (0.05 torr). Unreacted **1** was separated from **2** + **4** by distillation and recycled. The residue was taken up in cold *n*-hexane, washed three times with ice–water (to remove **6**), and directly thermolized (reflux, 3 h) or photolized (Pyrex filter, +15 °C, Hanau TQ 150 lamp, 6 h). Removal of solvent and trap to trap distillation yielded a mixture of **2** and **4** in the ratio 1:1.4 (photolysis) and 1:1.2 (thermolysis), respectively. The isolated yields of **2** + **4**, based on **1** and for 58% conversion (42% **1** recovered; see above), were 1.63 (42%, photolysis) and 1.73 g (45%, thermolysis), respectively. Together with the already recovered material from the crude reaction mixture (~1.0 g; see above), the total yields were 2.63 (68%, photolysis) and 2.73 g (71%, thermolysis), respectively.

Method B. The reaction was carried out as described in method A. After all volatile materials were condensed off as before, the residue was taken up in ice-cold *n*-pentane, washed three times with ice–water (to remove **6**), and dried over Na_2SO_4. All these manipulations should be carried out as rapidly as possible. Removal of *n*-pentane at −10 °C on a high vacuum line (10^{-4} torr) yielded a mixture (~1:1) of *cis*- and *trans*-3-[(*E,Z*)-1,3-hexadienyl]-5-vinyl-1-pyrazolines **7** as slightly yellow oil. The yield based on **1** and ~60% conversion was 2.6 g (55%). The 1-pyrazolines **7** are extremely sensitive. They slowly lose N_2 already at 0 °C and are susceptible to oxidation and tautomerization. They should always be stored under argon at −78 °C. They cannot be purified by distillation or chromatography. The rather complicated ^1H NMR spectrum[17] of the crude mixture of **7** displays absorptions at δ 0.5–1.0, 1.0–1.1, 1.5–1.8, 2.15, 4.5, and 4.8–6.8 (ratio 1:8:1:4:2:8).

Thermolysis of 7. **7** (1.75 g, 0.01 mol) was stirred under vacuum (0.05 Torr) at room temperature for 12 h. The produced mixture of **2** + **4** codistilled into a cold trap at −196 °C. The yield was 1.1 g (74%) (ratio 1:1.2).

Photolysis of 7. **7** (0.5 g, 0.028 mol), dissolved in 350 mL of *n*-pentane, was irradiated with ultraviolet light (Pyrex filter, +15 °C, Hanau TQ 150 lamp) for 6 h. Removal of solvent and workup by trap to trap distillation yielded 0.28 g (70%) of a mixture of **2** + **4** (ratio 1:1.4).

Separation and Analytical Data for 2 and 4. **2** and **4** can be separated conveniently by preparative GC with the following retention times: **2**, 3.7 min and **4**, 2.03 min (column 2, *T* = 85 °C, 50 mL of N_2/min flow); **2**, 7.83 min and **4**, 4.92 min (column 3, *T* = 90 °C, 50 mL of N_2/min flow). ^1H NMR spectra were recorded both in $CDCl_3$ and C_6D_6, the latter for direct comparison with published data on the natural products.[4] **2**: ^1H NMR (C_6D_6) δ 0.65 (m, 1 H), 0.72 (m, 1 H), 0.92 (t, *J* = 7 Hz, 3 H), 1.33 (m, 2 H), 2.10 (d of quintets, *J* = 7.3, 1.2 Hz, 2 H), 4.85 (dd, *J* = 9.5, 2.5 Hz, 1 H), 4.96 (dd, *J* = 15 Hz, 1 H), 5.2 (m, 1 H), 5.3 (m, 1 H), 5.99 (tt, *J* = 10.5, 1.3 Hz, 1 H), 6.35 (dd, *J* = 15, 10.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ_C 14.3, 15.5, 21.1, 24.3, 25.1, 112.4, 124.1, 127.7, 131.6, 135.9, 140.3; IR (neat) 3080, 3020, 3000, 2960, 2930, 2870, 1645, 1635, 1460, 975, 940, 895, 850 cm^{-1}; UV (*n*-hexane) nm (log ϵ_{max}) 246 (4.42). Exact mass calcd for $C_{11}H_{16}$: 148.1252. Found: 148.1251. **4**: ^1H NMR (C_6D_6) δ 0.87 (t, *J* = 7.2 Hz, 3 H), 1.97 (quintet, 2 H), 2.22 (m, 2 H), 2.70 (m, 2 H), 3.5 (m, 1 H), 5.30 (m, 1 H), 5.40 (m, 1 H), 5.56–5.82 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ_C 14.4, 20.7, 28.5, 33.7, 36.2, 127.2, 128.9, 129.7, 130.8, 133.2, 135.5; IR (neat) 3010, 2970, 2940, 2910, 2890, 1660, 1655, 1470 cm^{-1}; UV end absorption. Exact mass calcd. for $C_{11}H_{16}$: 148.1252; found: 148.1251.

Dictyopterene D′ (= Ectocarpene, 4) by Thermal Rearrangement of 2. Solutions of **2** (3% in *n*-hexane) were sealed under vacuum into several ampules and heated in a constant-temperature oil bath at 125 °C. Samples were removed after 5, 10, 20, 30, and 60 min. Ratios of **2**:**4** were determined by GC leading to the rate constant $k = 1.665 \times 10^{-3}$ s^{-1} for the rearrangement **2** → **4** at that temperture, corresponding to a half-life of $t_{1/2}$ = 7 min. For a practical synthesis of **4**, the mixtures of **2** + **4**, obtained from photolysis or thermolysis of **7** by either method A or B, were sealed in ampules under vacuum and heated at 125 °C for 1.5 h (~13 half-lives). Trap to trap distillation yielded pure **4**, bp_{15} 78–80 °C, in practically quantitative yield.

***cis*-1-[(*E,Z*)-1,3-hexadienyl]-2-vinylcyclopropane (dictyopterene D, 3) by Low Temperature Photolysis of 7.** Irradiations were carried out in an apparatus already described.[8] **7** (50 mg), obtained by method B (see above), dissolved in 0.5 mL of a mixture of $CDCl_3$ and CD_2Cl_2 (ratio 2:5) was irradiated at −40 °C with ultraviolet light (Pyrex filter) until the N_2 evolution had ceased completely (~30 min). The ^1H NMR spectrum of the so-obtained mixture of **2** + **3** showed no absorptions below δ 2.22 ppm, a clear indication that no **4** was present at that stage. The signals of the allylic protons of **4** at δ 2.22 (2 H), 2.85 (2 H), 3.45 (1 H) did appear upon an increase of the probe temperature to +15 °C with an estimated half-life of ~50 min. Because of the complicated nature of the high-field region, the observation remains qualitative and no ^1H NMR spectrum of **3** could be obtained. Similiarly, determinations of the half-life for the rearrangement **3** → **4** can only be estimated. We are presently trying to solve these remaining problems by the use of proton noise decoupled ^{13}C NMR, where the situation should be much more simple.

Acknowledgments. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this research.