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Pericyclic Reactions in Nature: Evidence for a Spontaneous [1.7]-Hydrogen Shift and an 8πe Electrocyclic Ring Closure in the Biosynthesis of Olefinic Hydrocarbons from Marine Brown Algae (Phaeophyceae).

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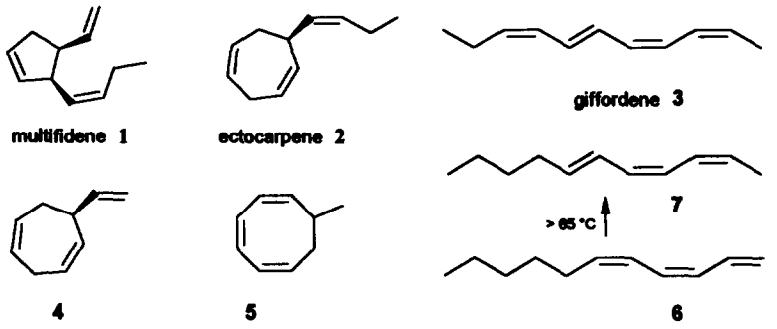
Abstract: The stereochemistry of the algal $C_{11}H_{16}$ hydrocarbon giffordene **3** results from a spontaneous [1.7]-sigmatropic hydrogen shift of the thermolabile (1,3*Z*,5*Z*,8*Z*)-undecatetraene **8**. An 8πe electrocyclisation of (1,3*Z*,5*Z*,-7*E*)-nonatetraene **9** is substantiated for the biosynthesis of 7-methylcyclooctatriene **5**, a product of the Mediterranean brown alga *Cutleria multifida*. Low temperature syntheses (-30 °C) of the thermolabile precursors **8** and **9** are described. The activation energies of the [1.7]-sigmatropic hydrogen shift **8** → **3** (E_a = 67.4 kJ·mol^{-1}) and of the 8πe electrocyclisation **9** → **5** (E_a = 59.4 kJ mol^{-1}) are the lowest values currently known for natural pericyclic reactions.

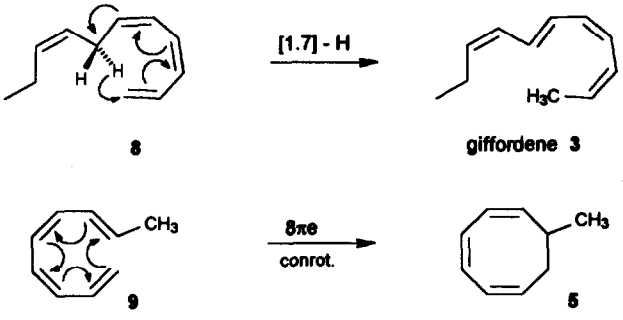
The sexual reproduction of marine brown algae (Phaeophyceae) is assisted by chemical signals which are released from the female gamete to attract their conspecific males.[1,2,3,4] Most of these plant pheromones are simple acyclic or cyclic hydrocarbons with the molecular formulas $C_{11}H_{14}$, $C_{11}H_{14}O$, $C_{11}H_{16}$ and $C_{11}H_{18}$. In general the pheromone blends are composed of one major product and a few by-products in the range of 1 → 15%. This is different in the case of the Mediterranean phaeophyte *Cutleria multifida* which releases a rather complex pattern of C_9- and C_{11} hydrocarbons into the environment.[5,6] The major products are the biologically active multifidene **1**, ectocarpene **2** and an inactive cyclohexene derivative called aucantene.[5] Besides of these major compounds there are minor- and trace constituents among which the structures of **3**, **4** and **5** are particularly noteworthy.[6] Giffordene **3** was first identified as the major compound among the hydrocarbons produced from the brown alga *Giffordia mitchellae*.[7,8,9]



The co-occurrence of the two olefins **2** and **4** within the same blend is important and may be considered as a strong argument for a common biosynthesis of the C_{11}- and the C_9 hydrocarbons as well. According to previous studies, the whole family of the C_{11} hydrocarbons is derived from highly unsaturated C_{20} fatty acids like 20:4, 20:5 and 20:6 by an oxidative degradation.[10,11] In contrast, higher plants utilise dodeca-3,6,9-trienoic acid for the synthesis of **2**.[12]

Besides of the still unsolved mode(s) of the activation and degradation of the icosanoids to the C_{11} fragment, the current biosynthetic concept assumes several pericyclic isomerisations of thermolabile intermediates to account for the ring size or stereochemistry of some of the pheromones.[10,11] Evidence for the involvement of an [1.7]-hydrogen shift as an essential step in the biosynthesis of giffordene **3** stems from the fact that gametophytes of *G. mitchellae* produce **3** together with a small amount of the (1,3*Z*,5*Z*)-undecatriene **6**. At elevated temperatures (> 65 °C) this hydrocarbon suffers a thermally allowed, antarafacial [1.7]-hydrogen shift and yields (2*Z*,4*Z*,6*E*)-undecatriene **7** possessing the same *Z,Z,E*-segment than giffordene **3**.[13] This analogy strongly suggests that **3** is formed *via* the terminally unsaturated (1,3*Z*,5*Z*,8*Z*)-tetraene **8** (*vide infra*) which either may rearrange spontaneously or demands for enzyme catalysis(?) to achieve this transformation at biotope conditions (18 °C, Scheme 1). Owing to the formation of a conjugated tetraene, the rearrangement of **8** → **3** should proceed much more readily than the rearrangement of **6** → **7**, but without experimental kinetic data and reactivity parameters no final conclusions concerning these questions can be drawn.

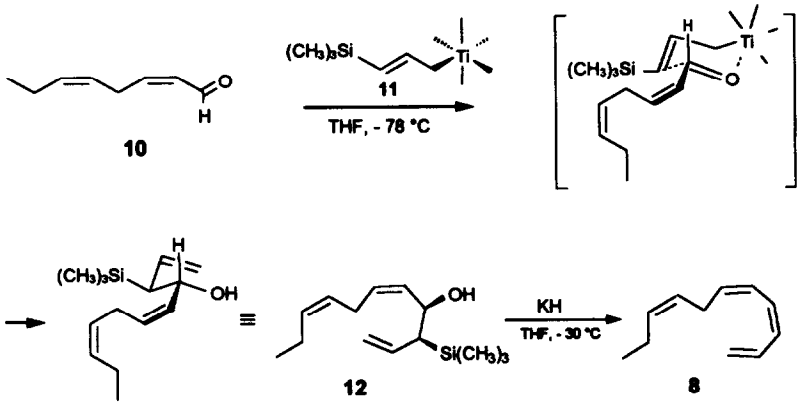
Scheme 1



To account for 7-methylcycloocta-1,3,5-triene **5** as a natural product, the assumption of a second pericyclic reaction, namely an 8π*e* electrocyclic ring closure of a hypothetical (1,3*Z*,5*Z*,7*E*)-nonatetraene **9** appears to be an attractive hypothesis (Scheme 1). The required acyclic precursor **9** can be generated from unsaturated fatty acids along the same routes that have been evidenced for the C_{11} hydrocarbons from marine brown algae.[10,11] A similar 8π*e* ring closure has been previously substantiated as the key step of the biosynthesis of the endiandric acids A-D in the Australian plant *Endiandra introsa* (Lauraceae).[14,15] The current work describes an efficient and highly stereoselective low-temperature approach to the thermally unstable precursors **8** and **9**. The activation parameters for the [1.7]-hydrogen shift **8** → **3** and the electrocyclic ring closure **9** → **5** are determined.

Low temperature synthesis of 8 and 9. In order to determine the kinetics of the two pericyclic reactions **8** → **3** and **9** → **5** and to evaluate the biological properties of the two unknown olefins **8** and **9**, we planned to generate these compounds at about -30 °C to prevent their thermal isomerisation. Such an approach towards thermolabile, but stereo-defined olefins would have a more general importance, since there is a lack of activation parameters for the electrocyclic ring closure reactions of the type **9** → **5** leading to 7-alkylcycloocta-1,3,-5-trienes.[16] As the key step of the synthesis of **8** and **9** we utilised a modified version[17] of the *Peterson*-reaction,[18] which is depicted in Scheme 2 and 3. The ß-hydroxysilanes **12** and **17** are stable at r.t., can be prepared with high configurational purity and can be selectively transformed into (*Z*)- and (*E*)-olefins.

Scheme 2



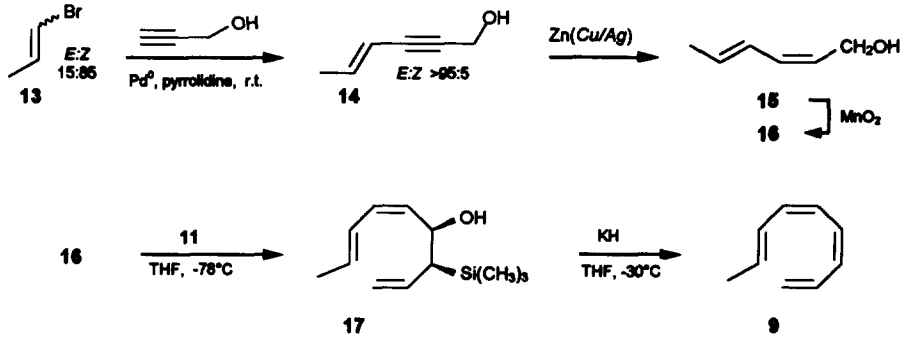
Thus, alkylation of freshly prepared (2*Z*,5*Z*)-octadienal **10** (see experimental) with the allyltitanium reagent[17] **11** proceeds with high diastereoselectivity and provides the ß-hydroxysilane **12** (*threo/erythro* >95:5). Final purification of **12** is achieved on deactivated SiO_2. Non-deactivated SiO_2 induces the decomposition of **12** to give configurationally pure 1,3*E*,5*Z*,8*Z*-undecatriene (= finavarrene),[19] the product of an acid catalysed *anti*-elimination.[18] Since finavarrene is not thermolabile, this olefin can be analyzed by GLC, and its high configurational purity corroborates the homogeneity of the ß-hydroxysilane **12**.

As expected, the base induced (KH) elimination of **12** can be achieved at temperatures as low as -30 °C and prevents the thermal isomerisation of **8**. Owing to the *syn*-fashion of this reaction[18] the (3*Z*)-double bond is introduced with complete configurational purity.

The synthesis of the tetraene **9** follows the same concept and is outlined in Scheme 3. The aldehyde **16** is obtained in three steps from commercial 1-bromo-1-propene **13** (*Z*:*E*, 85:15) starting with a Pd^0 catalysed coupling of **13** with propynol.[20] Irrespective of the very unfavorite isomer composition, at r.t. and at low catalyst concentration (*E*)-**13** reacts preferentially and allows a kinetically controlled synthesis of (4*E*)-**14** (*E*:*Z* > 95:5). The reduction of the conjugated triple bond in **14** using Zn(*Cu/Ag*)[8] is stereospecific and provides (2*Z*,4*E*)-**15**. Brief oxidation (ca. 15 min) with activated MnO_2 yields the aldehyde **16** (>95% 2*Z*,4*E*;

GLC) which is converted into the ß-hydroxysilane **17** as described for **12**. Treatment of **17** with KH at -30 °C affords the very thermolabile tetraene **9**.

Scheme 3



Kinetics. Both pericyclic reactions were studied at different temperatures by UV spectroscopy. Owing to the irreversible formation of a conjugated tetraene, the [1.7]-hydrogen shift **8** → **3** is easily followed by the emergence of a new absorption at 318 nm (THF). In the case of the 8πe electrocyclic ring closure **9** → **5**, the disappearance of the absorption at 304.9 nm (methanol) can be used to monitor the reaction. According to GLC- and NMR data the sigmatropic rearrangement **8** → **3** yields (2*Z*,4*Z*,6*E*,8*Z*)-undecatetraene **3** (= giffordene) as the only product. (2*Z*,4*Z*,6*Z*,8*Z*)-Undecatetraene, the product of a fully helical transition state geometry of the isomerisation is not observed.[21] The kinetic measurements were performed in THF or methanol as solvents. Each reaction was followed over 2 to 3 half life times, and each run was typically repeated in triplicate. The data were analysed according to a first-order kinetic following the method of Swinbourne[22] which allows the calculation of the rate constants without the need for exact concentrations of the unstable hydrocarbons at the beginning or the end of the reaction. Figure 1 shows the Arrhenius plot for the [1.7]-hydrogen shift **8** → **3** between 15 °C and 35 °C. The Arrhenius plot for the 8πe electrocyclisation **9** → **5** in the range of -14 °C to 5 °C is shown in Figure 2. The kinetic constants of the two reactions **8** → **3**, **9** → **5** and the data of some related or naturally occurring isomerisations are compiled in Table 1.

Figure 1 Arrhenius plot for the [1.7]-H shift **8** → **3** in the range of 15 °C to 35 °C.

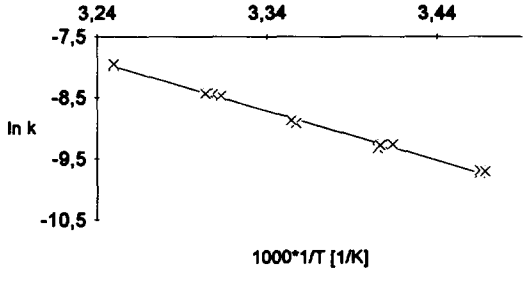


Figure 2 Arrhenius plot of the 8πe electrocyclisation **9** → **5** in the range of -14 °C to 10 °C

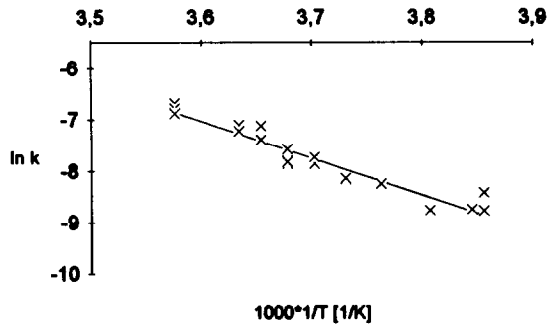


Table 1 First order rate constants and activation parameters of selected [1.7]-hydrogen shifts and 8πe electrocyclic ring closures.

reaction	E_a [kJ mol^{-1}]	$\Delta H^{\#}_{298}$ [kJ mol^{-1}]	$\Delta S^{\#}_{298}$ [J mol^{-1}K^{-1}]	$\tau_{1/2}$ [min]	ref.
8 → **3**	67.4	64.9	-91.9	148 (18 °C)	
previtamin D_3 → vitamin D_3	80.3	77.8	-82	344 (50 °C)	23
1,3*Z*,5*Z*-octatriene → 2*Z*,4*Z*,6*E*-octatriene	84.5	81.6	-79.5	19 (85 °C)	21
9 → **5**	59.4	57.1	-89.7	33 (-5 °C) 3.4 (18 °C)	
1,3*Z*,5*Z*,7-octatetraene → 1,3,5-cyclooctatriene	71.1	68.6	-	0.45 (25 °C)	26
2*E*,4*Z*,6*Z*,8*E*-decatetraene → trans-1,8-dimethylcycloocta-2,4,6-triene	65.4	63.16	-79.5	27 (0°C)	24

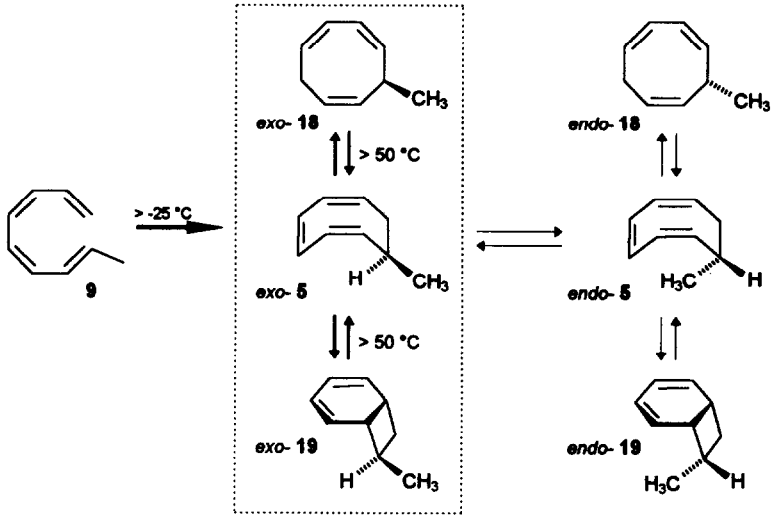
Compared to the activation parameters of the previously studied [1.7]-hydrogen shift from 1,3*Z*,5*Z*-octatriene to 2*Z*,4*Z*,6*E*-octatriene[21] or those of the isomerisation[23] of previtamin D_3 to vitamin D_3, the current reaction **8** → **3** has the lowest energy of activation (cf. Table 1). This pronounced effect is due to the formation of the extended π-system of the tetraene **3** and is also observed, if the C(8)=C(9) double bond of **8** is replaced by a C(8)≡C(9) triple bond (E_a = 65.7 kJ mol^{-1}, $\tau_{1/2}$ = 118 min at 20 °C). Owing to the short half life time of **8** at biotope conditions (2.5 h; 18 °C), the [1.7]-hydrogen shift of **8** *en route* to giffordene **3** needs not to be catalysed by an enzyme.

The nonatetraene **9** is even less stable. At biotope conditions (18 °C) the half life time of this hydrocarbon is only 3.5 min. According to Table 1, the activation energy of this isomerisation is significantly lower than that of the well studied electrocyclisation of (2*E*,4*Z*,6*Z*,8*E*)-decatetraene to *trans*-1,8-dimethylcycloocta-

2,4,6-triene.[24,25] Since at ambient temperature *exo*-**5** is observed as the only conformer (^{1}H NMR: δ = 0.98 ppm; Table 2), this difference of 6 kJ mol^{-1} in the activation energies must be attributed to the steric repulsion between a single *endo*-methyl group and the distal ring segment of the *trans*-dimethylcyclooctatriene. The observed difference is also in agreement with calculated values of Houk et al.[16] and suggests that the rather high activation parameters of the cyclisation of 1,3*Z*,5*Z*,7-octatetraene[26] (Table 1) need to be verified.

At elevated temperatures (> 50 °C) two new methyl signals at δ = 1.05 and 1.08 ppm emerge. On the basis of literature data[27] they can be attributed to *exo*-**19** and 8-methylcycloocta-1,3,6-triene *exo*-**18** which is the product of a thermally allowed, suprafacial [1.5]-hydrogen shift. Within the limits of error (^{1}H NMR) *endo*-**5**, *endo*-**18** or *endo*-**19** do not contribute to the equilibrium. Since the equilibration of the isomers is frozen below ca. 50 °C, a reliable determination of the isomer distribution around ambient temperature[27] can be done only starting from **9** or pure *exo*-**5**.

Scheme 4



The composition of the equilibrium mixtures at different temperatures is compiled in Table 2. Above 104 °C (determined up to 132 °C) no further shift in the composition of the isomers is observed.

Table 2

T [°C]	*exo*-**5** (%)	*exo*-**19** (%)	*exo*-**18** (%)
50	100	-	-
83	74	14	12
104	62	24	14

Bioassays. The sexual reproduction of the brown alga *Giffordia mitchellae* is accompanied by a vigorous chemotactic response of male gametes towards a chemical released from the female.[28] Since none of the pre-

viously isolated and characterised C_{11} hydrocarbons triggers the chemotactic response, the assumption of a thermolabile precursor with a limited life span, much shorter than that required for the isolation,[28] appeared to be an attractive explanation for this failure. However, when a suspension of male gametes of *G. mitchellae* in seawater was exposed to dilutions of **8** in the biologically inert fluorocarbon FC 72 (3M Company, Düsseldorf, Germany) no attraction[7] could be seen. Thus, the chemical nature of this chemotactic signal still remains unsolved.

Experimental

General remarks. Reactions were performed under Ar. Solvents and reagents were purified and dried prior to use. Anh. $MgSO_4$ was used for drying. Boiling points are not corrected. ^1H- and ^{13}C NMR: Bruker Cryospec WM 250 and Bruker WM 400; $CDCl_3$, as solvent and internal standard. IR: Perkin-Elmer-882 IR spectrophotometer. UV: Perkin-Elmer Lambda 2. MS: Finnigan MAT 90 GLC/MS system and Finnigan ITD 800 combined with a Carlo-Erba gas chromatograph, model Vega, equipped with a fused-silica capillary SE 30, (10m x 0.32 mm); carrier gas, He at 30cm/s; scan range: 35-249 Dalton/s. Analytical GLC: Carlo-Erba gas chromatograph, HRGC 5300, Mega series, equipped with fused silica capillaries, SE 30 (10m x 0.32mm) and carbowax (40m x 0.32 mm); H2 at 30 cm/s as carrier. Silica gel, Si 60 (0.040-0.063 mm, E. Merck, Darmstadt, Germany) was used for liquid chromatography.

(5*Z*,8*Z*)-3-Trimethylsilylundeca-1,5,8-trien-4-ol (12). *a)* (2*Z*,5*Z*)-Octadienal (**10**): Argon is bubbled for 10 min through a rapidly stirred suspension of active MnO_2 in dichloromethane (25 ml). (2*Z*,5*Z*)-Octadienol[29] (0.5 g, 3.97 mmol) is added, and stirring is continued for ca. 30 min at r.t. Extended reaction times result in a rapid decrease of the configurational purity of the (2*Z*)-double bond of the aldehyde. The solids are removed by suction and are carefully extracted with ether (4 x 30 ml). Removal of solvents affords the unstable aldehyde **10** along with some starting material (ca. 30%). The crude mixture is used for the next step. b) alkylation of **10**: *t*-butyllithium (2.6 ml of 1.7M solution in *n*-hexane, 4.4 mmol) is injected into a cold (-78 °C) and well stirred solution of allyltrimethylsilane (560 mg, 4.9 mmol) and *N,N,N',N'*-tetramethylethylenediamine (520 mg, 4.4 mmol) in dry THF (20 ml). Stirring is continued for 2 h at -30 °C, and, after recooling to -78 °C, Ti(O-*i*-Pr)$_4$ (1.39 g, 4.9 mmol) is added. After 1 h at -78 °C, the above aldehyde **10** is added. The reaction is complete after 2 h at -78 °C, and the mixture is poured into a chilled, saturated solution of NH_4Cl. Extractive work-up with ether and removal of solvents affords crude **12** which is further purified on deactivated SiO_2 (10% water) using pentane/ether (90:10) for elution. Removal of solvents yields **12** as a colorless liquid (0.51 g, 54% with respect to octadienol). ^1H-NMR (250 MHz, $CDCl_3$): δ 0.02 (s, 9H), 1.0 (t, 3H), 1.68 (s, 1H), 1.78 (dd, 1 H), 2.08 (quint., 2H), 2.88 (m, 2H), 4.64 (t, 1H), 4.98 (d, 1H), 5.17 (d, 1H), 5.3 (m, 1H), 5.30-5.55 (m, 3H), 5.8 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ -1.9 (3C), 14.2, 20.6,

25.9, 44, 67, 115.5, 126.4, 130.4, 132.3, 132.5, 136.2; IR (KBr, cm^{-1}) 3448, 3074, 3012, 2961, 2933, 1721, 1415, 1247, 1097, 1037, 1004, 749. MS (%) 238($M^{+\bullet}$,0.02), 182(20), 167(7), 124(7), 119(17), 107(14), 105 (23), 91(37), 80(30), 79(65), 75(68), 73(100), 67(15) 55(12); HR-MS: *m/z* calcd. for $C_{14}H_{26}OSi$: 238.1753, found: 238.1742.

(3*Z*,5*Z*,8*Z*)-Undeca-1,3,5,8-tetraene (8). A slurry of potassium hydride in mineral oil (200 mg of a 35% slurry in oil, ~1.75 mmol) is briefly stirred with pentane (5 ml). Then, the supernatant liquid is removed and replaced by dry THF (10 ml). The suspension is cooled to -78 °C , and a solution of **12** (0.20 g, 0.84 mmol) in dry THF (2 ml) is added. The mixture is allowed to come slowly to -35°C and, after stirring for 15 min at this temperature, the solution is poured into a cold, sat. aq. solution of NH_4Cl. Extractive work-up (cold! ether), removal of solvents at -10 °C, followed by chromatography on SiO_2 at the same temperature (pentane for elution) afforded **8** as a colorless liquid (0.10 g, 80%) ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.92 (t, 3H), 2.01 (quint., 2H), 2.88 (t, 2H), 5.18 (d, 1H), 5.26 (d(br.), 1H), 5.35 (m, 1H), 5.42 (m, 1H), 5.52 (m, 1H), 6.04 (t, 1H), 6.32 (t, 1H), 6.47 (t, 1H), 6.82 (td, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 14.3, 20.6, 25.8, 118.3, 123.4, 124.6, 126.4, 129.9 , 131.7, 132, 132.5; UV (methanol, nm): 255.5sh, 264.3, 273.8sh.

(2*Z*,4*Z*,6*E*,8*Z*)-Undeca-2,4,6,8-tetraene (= Giffordene) (3). The hydrocarbon **8** is unstable at r.t. and rearranges quantitatively to giffordene (**3**). The spectroscopic data have been described previously.[8]

(4*E*)-Hex-4-en-2-yn-1-ol (14). Tetrakis(triphenylphosphane)palladium (0.34 g, 0.3 mmol) is added to a well stirred solution of 1-bromo-1-propene (**13**) (28 g, 0.23 mol, *E*:*Z* = 15:85) in pyrrolidine (80 ml). After 5 min. propynol (22.8 g, 0.4 mol) is added, and the progress of the reaction (configurational purity) is monitored by GLC. After stirring for about 30 h at r.t., the stereoselectivity of the reaction decreases, and the mixture is poured into a chilled solution of sat. NH_4Cl. Extractive work-up with ether, removal of solvents and distillation affords **14** as a colourless liquid (1.6 g, 28% with respect to (*E*)-**13**, *E*:*Z* > 96:4). Bp. 66 °C/8 Torr. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.73 (d, 3H), 4.3 (d(br), 1H); 5.45 (dt, 1H), 6.11 (m, 1H). IR (KBr, cm^{-1}): 3352, 3030, 2969, 2916, 2869, 2249, 2217, 1444, 1294, 1108, 1017, 734; MS (%): 95($M^{+\bullet}$-1(0.25)), 81(69), 79 (26), 77(30), 67(22), 66(42), 65(38), 55(11), 53(27), 51(27), 41(36), 40(40), 39(100).

(2*Z*,4*E*)-Hexa-2,4-dien-1-ol (15). (4*E*)-Hex-4-en-2-yn-1-ol (**14**) (0.53 g, 5.6 mmol) in methanol/water (15 ml, 1:1, v/v) is stirred at 40 °C with activated Zn(*Cu/Ag*)[8] (6.0 g). The progress of the reduction is followed by GLC. After complete conversion (ca. 2 h), the metal is removed by filtration and the solids are carefully washed with methanol (2 x 20 ml) and ether (2 x 20 ml). Most of the solvents are removed (ca. 2/3), and the remaining aq. suspension is extracted with ether (2 x 50 ml). Removal of solvents and chromatography on SiO_2 (pentane/ether, 70:30) yield **15** as a colourless liquid (0.37 g, 67%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.71 (d, 3H), 1.71 (s(br.), 1H), 4.2 (d, 2H), 5.39 (m, 1H), 5.7 (m, 1H), 5.98 (t, 1H), 6.28 (t, 1H). IR (KBr,

cm^{-1}): 3330, 3024, 2961, 2915, 2882, 2853, 1655, 1450, 1029. MS (%): 98($M^{+\bullet}$,9), 83(27), 81(47), 80(34), 79(27), 73(21), 69(24), 59(31), 55(51), 53(26), 45(39), 44(37), 43(63), 42(24), 41(100), 40 (55), 39 (91).

(2*Z*,4*E*)-2,4-Hexadienal (16). A solution of the alcohol **15** (250 mg, 2.6 mmol) in dichloromethane (10 ml) is rapidly stirred with activated MnO_2 (5.2 g). After complete conversion (GLC, 15 min) the MnO_2 is immediately filtered off and extracted with ether (4 x 25 ml). The combined organic layers are evaporated, and the crude product is used without purification for the alkylation. Yield: 0.213 g (85%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.86 (d, 3H), 5.7 (t, 1H), 6.15 (m, 1H), 6.78-7.08 (m, 2H), 10.1 (d, 1H). IR (KBr, cm^{-1}): 2963, 2917, 2850, 1671, 1638, 1262, 1227, 1157, 1092, 952; MS (%): 97 ($M^{+\bullet}$+1(0.28)), 81(100), 67(23), 65(23), 53(36), 41(39), 39(73).

(5*Z*,7*E*)-3-(Trimethylsilyl)-1,5,7-nonatrien-4-ol (17). The alkylation of **16** (0.18 g, 1.80 mmol) is achieved as described for **12**. Yield: 0.29 g (76%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.0 (s, 9H), 1.8 (d, 3H), 1.70-1.82 (m, 2H), 4.69 (t, 1H), 4.96 (d, 1H), 5.07 (d, 1H), 5.29 (t, 1H), 5.69-5.88 (m, 2H), 6.0 (t, 1H), 6.28-6.44 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ -1.9(3C), 18.3, 44, 67.2, 115.5, 126.5, 130.3, 130.5, 132, 136.3; IR (KBr, cm^{-1}): 3439, 3075, 3023, 2956, 2899, 1693, 1625, 1248, 1045, 841, 790, 697. MS (%): 210 ($M^{+\bullet}$,2), 169 (11), 120(36), 105(55), 97(100), 91(19), 75(54), 73(70), 59(6), 55(9); HR-MS *m/z* (M^+) calcd. for $C_{12}H_{22}OSi$: 210.1440, found: 210.1421.

(3*Z*,5*Z*,7*E*)-1,3,5,7-Nonatetraene (9). The ß-hydroxysilane **17** (0.09 g, 0.43 mmol) is treated with KH in THF at -35 °C as described for the synthesis of **8**. UV (methanol, nm): 267.7(sh); 279,3; 291,4; 304,9.

7-Methyl-1,3,5-cyclooctatriene (5). At r.t. the tetraene **9** rearranges quantitatively to **5**. Yield: 46.8 mg (93% overall from **17**). ^{1}H-NMR (400 MHz, DMSO-D_6): δ 0.98 (d, 3H), 2.24 (m, 2H), 2.79 (m, 1H), 5.6-5.96 (m, 6H); ^{13}C-NMR (100 Mhz, $CDCl_3$): δ 22.7, 33.3, 35.5, 124.3, 126.1, 126.5, 126.9, 134.2, 141; IR (KBr cm^{-1}) 3005, 2960, 2928, 2869, 1456, 1261, 1122, 649. MS (%): 120($M^{+\bullet}$,2), 119(24), 104(27), 90(20), 77(100), 73(35), 58(39), 44(24), 42(19); HR-MS: calcd. for C_9H_{12}: 120.0939, found: 120.0925. UV (methanol, nm) 274(3500).

Kinetic Measurements. Dilute solutions of **8** (ca. 0.01% in THF) or **9** (ca. 0.01% in methanol) in quartz cuvettes were placed into a water thermostated cell-holder of the spectrophotometer, connected to a Haake D8 cryostat (± 0.1 °C). The temperature was continuously recorded as function of time using a NiCr-Ni thermocouple, type K, and a precision digital voltmeter. A typical run was followed over 2 to 3 half life times and repeated in triplicate. The isomerisation **8** → **3** was followed by the increase of the tetraene absorption at the highest wavelength (318 nm, in THF). The progress of the electrocyclisation **9** → **5** was monitored by

the disappearance of the tetraene absorption at 304.9 nm in methanol. From the raw data, recorded as a function of time, the rate constants were calculated according to the method of Swinbourne.[22] The activation parameters were then taken from the two Arrhenius plots shown in Figure 1 and Figure 2. [1.7]-Hydrogen shift **8** → **3**: E_a = 67.4 kJ mol^{-1} ± 1.2 kJ mol^{-1}, $\Delta H^{\#}_{298}$ = 64.9 kJ mol^{-1} ± 1.2 kJ mol^{-1}, $\Delta S^{\#}_{298}$ = -91.9 J mol^{-1} K^{-1} ± 4.1 J mol^{-1} K^{-1}. 8πe Electrocyclisation **9** → **5**: E_a = 59.4 kJ mol^{-1} ± 2.5 kJ mol^{-1}, $\Delta H^{\#}_{298}$ = 57.1 kJ mol^{-1}, ± 2.5 kJ mol^{-1}, $\Delta S^{\#}_{273}$ = -89.7 J mol^{-1} K^{-1} ± 6 J mol^{-1} K^{-1}.

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