C, 52.78; H, 4.89. The two epimers were separated by column chromatography (CH_2Cl_2, silica gel) **9b(endo)** was first eluted ($R_f \simeq 0.6$, by TLC) as a colorless solid: mp 47.4 °C; IR (CCl_4) 1740 (COOR), 1340, 1310, 1190. ^1H NMR ($CDCl_3$, 250 MHz) 1.26 (t, 3 H, CH_3), 3.42 (dt, 1 H, $J_{2,F_e} = 20.7$ Hz, $J_{2,F_a} = 4.4$ Hz, $J_{2,1} = 4.4$ Hz, $(C_2)H$), 4.16 (m, 2 H, CH_2), 4.83 ($\simeq$dtd, $J_{4,F_e} = 6.0$ Hz, $J_{4,F_a} \simeq 2.2$ Hz, $J_{4,5} \simeq 2.2$ Hz, $J = 1.1$ Hz, $(C_4)H$), 5.13 (mbr, 1 H, $(C_1)H$), 6.42 ($\simeq$ddt, 1 H, $J_{5,6} = 5.8$ Hz, $J = 1.8$ and 1.5 Hz, $(C_5)H$), 6.91 (dt, 1 H, $J_{6,5} = 5.8$ Hz, $J_{6,1} = 1.6$ Hz, $J_{6,F_a} = 1.6$ Hz, $(C_6)H$) [H_1 and H_4, H_4 and H_5 are coupled as determined by COSY experiments at 500 MHz]; ^{19}F NMR ($CDCl_3$, 84.7 MHz) -98.4 (dddd, $J_{F_a,F_e} = 222$ Hz, $J_{F_e,2} = 20.7$ Hz, $J_{F_e,4} = 6.0$ Hz, $J = 0.7$ Hz, F_e), -107.0 (dm, $J_{F_e,F_e} = 222$ Hz, $w_{1/2} = 9.6$ Hz, F_a). Then **9b(exo)** ($R_f \simeq 0.4$, by TLC) as a colorless oil: ^1H NMR ($CDCl_3$, 250 MHz) 1.31 (t, 3 H, CH_3), 2.80 (dd, 1 H, $J_{2,F_a} = 11.4$ Hz, $J_{2,F_e} = 6.2$ Hz, $(C_2)H$), 4.27 (m, 2 H, CH_2), 4.78 (d(mbr), 1 H, $J_{4,F_e} \simeq 6.0$ Hz, $(C_4)H$), 5.35 (sext br, 1 H, $(C_1)H$), 6.54 (d($\simeq$qbr), 1 H, $J_{5,6} = 5.8$ Hz, $(C_5)H$), 6.69 (dm, 1 H, $J_{6,5} = 5.8$ Hz, $(C_6)H$); ^{19}F NMR ($CDCl_3$, 84.7 MHz) -101.4 (dd quint, $J_{F_a,F_e} = 225$ Hz, $J_{F_a,2} = 11.4$ Hz, $J = 1.1$ Hz, F_a), -110.0 (dt, $J_{F_e,F_a} = 225$ Hz, $J_{F_e,2} = 6.2$ Hz, $J_{F_e,4} = 6.2$ Hz, F_e).

Ethyl 2-Fluoro-3-hydroxybenzoate (14). Tetrabutylammonium fluoride trihydrate (2 g, 6.3 mmol) was heated for 48 h in a round-bottomed flask with magnetic stirring at 45 °C under vacuum (0.05 mmHg). The melted adduct **9b** (0.4 g, 1.9 mmol) was added at this temperature under an inert atmosphere. The paste liquefied and the mixture was heated for 2 h with stirring. After cooling, the reaction was quenched with water and extracted with ether. Drying ($MgSO_4$) and concentration gave a viscous brown oil which was purified by preparative TLC (20% AcOEt/C_6H_6, silica gel) giving pure **14** (0.1 g, 0.54 mmol) as a solid: ^1H NMR ($CDCl_3$) 1.39 (t, 3 H, CH_3), 4.39 (q, 4 H, CH_2), 6.44 (s br, 1 H, OH), $\simeq$ 6.90-7.50 (m, 3 H, H Ar); ^{19}F NMR ($CDCl_3$) -137 (t, $J = 6.3$ Hz); mass spectrum, m/e (relative intensity) 184 (M^+), 156, 139 (100), 111, 83.

Registry No. **2**, 109-92-2; **3**, 1993-81-3; **4**, 1645-58-5; **5**, 105836-29-1; **6**, 35245-99-9; *endo*-**9b**, 105836-30-4; *exo*-**9b**, 105836-31-5; **14**, 105836-28-0; CF_2Br_2, 75-61-6; furan, 110-00-9.

A Stereospecific Synthesis of All Four Isomers of 9,11-Tetradecadienyl Acetate Using a General Method Applicable to 1,3-Dienes

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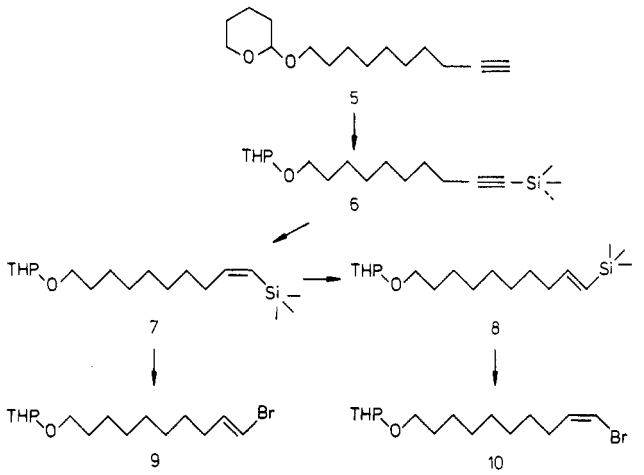
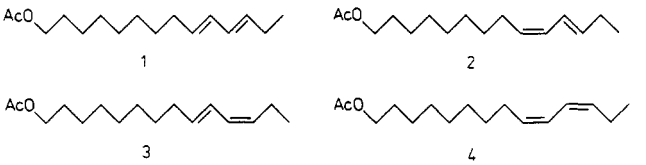
An important structural feature of many insect pheromones and other biologically active compounds is a conjugated diene system. The need for regio- and stereochemically pure compounds for biological tests is well-recognized,[1] and a large number of methods for the stereoselective synthesis of conjugated dienes have been developed.[2-4] Among the more recent and promising methods is the direct coupling of two alkenyl moieties in the presence of a catalyst.[5-8] This strategy is also used in the present study where we now report a convergent and general synthesis of all four isomers of 9,11-tetradecadienyl acetate (**1**-**4**). The 9*Z*,11*E*-isomer **2** is the main pheromone component of the Egyptian cotton leafworm *Spodoptera littoralis*[9] and the cone pyralid *Dioryctria abietella*.[10] In order to perform biological tests, all four isomers are needed.

Scheme I

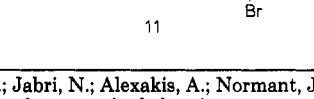




Preparation of the isomerically pure *E* and *Z* vinyl bromides **9** and **10** from the acetylene **5** via the corresponding vinylsilanes[11] **7** and **8** and the cross-coupling of these bromides with alkenylboranes using a palladium catalyst[5,6,12] is shown to be an attractive method for the synthesis of these diene systems.

Silylation of 1-(2-tetrahydropyranyloxy)-9-decyne[13] (**5**) with trimethylsilyl chloride gave the alkynylsilane **6** in a 90-95% yield (Scheme I). Hydroalumination of the triple bond with diisobutylaluminum hydride followed by protonation gave the *Z* vinylsilane **7** in a 79% yield of >97% isomeric purity. Isomerization of **7** (NBS, pyridine, $h\nu$)[14] yielded the corresponding *E* vinylsilane **8** in a 70% yield of >98% isomeric purity. The two *Z* and *E* vinylsilanes **7** and **8** were obtained isomerically pure (>99.9%) by chromatography on $AgNO_3$-impregnated silica gel.[15]

Bromination of the *Z* vinylsilane **7** followed by desilicohalogenation with sodium methoxide according to a method previously described[11] gave the vinyl bromide **9** together with 10-15% of the product **11** formed by undesired hydrogen bromide elimination. However, bro-



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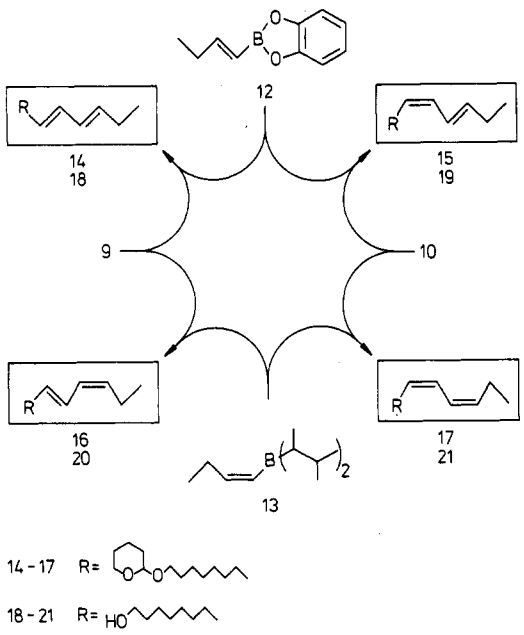
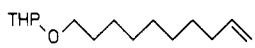
0022-3263/87/1952-0292$01.50/0

Scheme II



mination and subsequent desilicohalogenation with tetra-*n*-butylammonium fluoride in THF was found to give the isomerically pure *E* and *Z* vinyl bromides **9** and **10** in 58% and 60% yields, respectively, without hydrogen bromide elimination.

Cross-coupling of the alkenyl bromides **9** or **10** with (*E*)-1-butenyl-1,3,2-benzodioxaborole (**12**), prepared from 1-butyne and catecholborane,[16] in the presence of Pd(PPh_3)$_4$ and sodium ethoxide gave *E,E* diene **14** or *Z,E* diene **15** in 87% and 85% isolated yields, respectively (cf. Scheme II). Complete retention of the configuration was observed in the coupling reactions. Coupling of **9** or **10** with (*Z*)-1-butenyldisiamylborane (**13**), prepared from 1-bromo-1-butyne[17] and disiamylborane,[18] under similar conditions gave isomerically pure *E,Z* diene **16** or *Z,Z* diene **17**, respectively, both in 63% yields. The latter coupling also gave 10% debromination of the starting alkenyl bromides **9** and **10** to form the corresponding terminal ene **22**.[12]



22

After deprotection (pyridinium tosylate in ethanol),[19] this byproduct could be removed from the diene alcohols **18–21** by distillation or low-temperature crystallization. Acetylation of **18–21** (Ac_2O, pyridine) yielded the isomerically pure tetradecadienyl acetates **1–4** in quantitative yields.

We believe that this method (Scheme II) for the stereospecific formation of diene systems is useful and general for the syntheses of all isomers of long-chain dienic pheromones.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker WP 200 spectrometer. A PYE Unicam 4000 instrument was used to record IR spectra. Analytical GC was performed on a PYE 204 instrument with a flame ionization detector using fused silica capillary columns (Carbowax 20 M, 25 m or SE-54, 50 m). Liquid chromatography was performed with Merck silica gel (0.040–0.063 mm) or the same gel impregnated with $AgNO_3$ with use of gradient elution with hexane and increasing amounts of ethyl acetate.[20] All reactions of air- and water-sensitive materials were performed under inert conditions (N_2 or Ar).

1-(2-Tetrahydropyranyloxy)-10-(trimethylsilyl)-9-decyne (6). Methyllithium (1.2 equiv, 1.6 M in hexane) was added to 1-(2-tetrahydropyranyloxy)-9-decyne (**5**) (12.9 g, 54 mmol) in 100 mL of Et_2O at −78 °C while the temperature was kept below −60 °C. The mixture was stirred for 2 h at −78 °C and warmed to −20 °C for 15 min and then recooled. Trimethylsilyl chloride (7.3 g, 1.25 equiv) in 15 mL of Et_2O was slowly added. After 0.5 h at −78 °C and 2 h at 25 °C, ice-cold $NaHCO_3$ (10% aqueous) was added and the product extracted with Et_2O, washed (H_2O, brine), dried ($MgSO_4$), and concentrated under reduced pressure. Distillation or chromatography yielded **6** in >90% yield: ^1H NMR δ 4.58 (brs, 1 H), 3.95–3.30 (m, 4 H), 2.21 (t, 2 H), 1.80–1.20 (unresolved m, 18 H), 0.14 (s, 9 H); ^{13}C NMR δ 107.6, 98.7, 84.2, 67.5, 62.2, 30.8, 29.7, 29.3, 29.0, 28.7, 28.6, 26.2, 25.5, 19.8, 19.6, 0.13.

1-(2-Tetrahydropyranyloxy)-10-(trimethylsilyl)-(*Z*)-9-decene (7). Diisobutylaluminum hydride (1.2 equiv, 5.4 M) was added to 1-(2-tetrahydropyranyloxy)-10-(trimethylsilyl)-9-decyne (**6**) (3.74 g, 12.1 mmol) in 40 mL of Et_2O at 0 °C. The mixture was then stirred at 25 °C for 20 min and at 40 °C for 3 h. Cold NaOH (1 M) was carefully added at 0 °C, and then the aqueous layer was extracted (Et_2O). The combined organic phases were washed (H_2O, brine), dried ($MgSO_4$), and concentrated under reduced pressure (yield 2.95 g, 79%, with isomeric purity >97%). Further purification to remove the *E* isomer was done by chromatography on $AgNO_3$-impregnated silica gel and gave pure (>99.9%) **7**: ^1H NMR δ 6.30 (dt, J_{BA} = 14 Hz, J_{BC} = 7.3 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 5.46 (d, J_{AB} = 14 Hz, 1 H), 4.60 (brs, 1 H), 3.95–3.30 (m, 4 H), 2.16 (dt, 2 H), 1.80–1.20 (unresolved m, 18 H), 0.14 (s, 9 H); ^{13}C NMR δ 149.1, 128.7, 98.7, 67.5, 62.1, 33.4, 30.7, 29.7 (2 C), 29.4, 29.3, 29.2, 26.2, 25.5, 19.6, 0.16.

1-(2-Tetrahydropyranyloxy)-10-(trimethylsilyl)-(*E*)-9-decene (8). To a solution of crude 1-(2-tetrahydropyranyloxy)-10-(trimethylsilyl)-(*Z*)-9-decene (**7**) (5 g, 16 mmol) and pyridine (1.3 g) in 100 mL of Et_2O was added *N*-bromosuccinimide (5 × 150 mg) at intervals of 15 min while the reaction mixture was irradiated with a UV sunlamp (275 W). The temperature was maintained at 25–30 °C throughout the reaction (ice-bath). The reaction mixture was decanted and washed with aqueous HCl (10%), brine, and H_2O and then dried ($MgSO_4$). Evaporation of the solvents followed by chromatography yielded the product **8**: 3.4 g (70%), >98% isomerically pure. Chromatography on $AgNO_3$-impregnated silica gel gave pure (>99.9%) **8**: ^1H NMR δ 6.02 (dt, J_{BA} = 18.5 Hz, J_{BC} = 3.1 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 5.61 (dt, J_{AB} = 18.5 Hz, J_{AC} = 1.4 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 4.60 (brs, 1 H), 3.95–3.30 (m, 4 H), 2.1 (dt, 2 H) 1.80–1.20 (unresolved m, 18 H), 0.14 (s, 9 H); ^{13}C NMR δ 147.2, 129.4, 98.6, 67.5, 62.0, 36.6, 30.7, 29.7, 29.6, 29.3, 29.1, 28.6, 26.2, 25.5, 19.6, −1.24.

10-Bromo-1-(2-tetrahydropyranyloxy)-(*E*)-9-decene (9). Bromine (1 M in CH_2Cl_2) was added dropwise to 1-(2-tetrahydropyranyloxy)-10-(trimethylsilyl)-(*Z*)-9-decene (**7**) (5 g, 0.02 mmol) in CH_2Cl_2 (50 mL) at −78 °C until the first persistence of halogen color. The solution was then shaken with aqueous Na_2SO_3 (10% aqueous). The organic layer was separated and the aqueous phase extracted (3 × 30 mL of CH_2Cl_2). The combined organic layers were washed with brine and water and then dried ($MgSO_4$). Tetrabutylammonium fluoride trihydrate (1.1 equiv, 1 M in THF) was then added to the crude intermediate in CH_2Cl_2 at −20 °C. Silica gel was added and the solvent evaporated followed by chromatography giving 58% of isomerically pure product: ^1H NMR δ 6.18 (dt, J_{AB} = 13.5 Hz, J_{BC} = 6.9 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 6.00 (dt, J_{AB} = 13.5 Hz, J_{AC} = 1.05 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.03 (dt, 2 H), 1.8–1.2 (unresolved m, 18 H); ^{13}C NMR δ 138.7, 104.0, 98.7, 67.5, 62.1, 32.8, 30.7, 29.7, 29.2 (2 C), 28.8, 28.5, 26.1, 25.5, 19.6.

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Compound **11**: ^{1}H NMR δ 6.22 (t, 1 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.25 (dt, 2 H), 1.8–1.2 (unresolved m, 18 H), 0.14 (s, 9 H); ^{13}C NMR δ 142.1, 131.3, 98.9, 67.7, 62.3, 32.5, 30.9, 29.8, 29.4, 29.4, 29.2, 28.1, 26.2, 25.6, 19.7, -1.9.

10-Bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (10) was prepared in the same way as the *E* isomer **9** from 1-(2-tetrahydropyranyloxy)-10-(trimethylsilyl)-(*E*)-9-decene (**8**) in a 60% yield. No *E* isomer could be detected: ^{1}H NMR δ 6.15 (d, J_{AB} = 7.0 Hz, $CH_{2C}CH_B{=}CH_A$, 1 H), 6.10 (dt, J_{AB} = 7.0 Hz, J_{BC} = 6.8 Hz, 1 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.19 (dt, 2 H), 1.8–1.2 (unresolved m, 18 H); ^{13}C NMR δ 134.7, 107.4, 98.6, 67.4, 62.0, 30.7, 29.6, 29.5, 29.2 (2 C), 28.9, 28.0, 26.1, 25.4, 19.5.

(*E*)-Butenyl-1,3,2-benzodioxaborole (12) was prepared from 1-butyne and catecholborane according to literature procedure[16] and was distilled before use.

(*Z*)-1-Butenyldisiamylborane (13) was prepared from 1-bromobutyne[17] and disiamylborane according to literature procedure.[18]

1-(2-Tetrahydropyranyloxy)-(9*E*,11*E*)-9,11-tetradecadiene (14). A mixture of (*E*)-1-butenyl-1,3,2-benzodioxaborole (**12**) (0.5 mL, 1 M in toluene), sodium ethoxide (0.5 mL, 2 M in ethanol), and 3-*tert*-butyl-4-hydroxyanisol (BHA) (5 mol %) was added to 10-bromo-1-(2-tetrahydropyranyloxy)-(*E*)-9-decene (**9**) (112 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (3 mol %) in 1 mL of toluene at 25 °C.[12] The mixture was then warmed to 65 °C, and after about 45 min, the reaction was found to be complete by GC. Aqueous H_2O_2 (1 mL, 30% aqueous) and NaOH (1 mL, 2 M aqueous) were then added at 25 °C to destroy excess borane. The product was then taken up in Et_2O, which was washed (brine, H_2O) and dried ($MgSO_4$). Chromatography gave an 87% yield of **14** with no detectable isomers: ^{1}H NMR δ 6.05–5.90 (m, 2 H), 5.64–5.47 (m, 2 H), 4.58 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.02 (m, 4 H), 1.8–1.2 (unresolved m, 18 H), 0.96 (t, 3 H).

1-(2-Tetrahydropyranyloxy)-(9*Z*,11*E*)-9,11-tetradecadiene (15) was prepared as described above from the corresponding 10-bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (**10**) and (*E*)-1-butenyl-1,3,2-benzodioxaborole (**12**) in an 85% yield: ^{1}H NMR δ 6.30 (m, 1 H), 5.91 (dd, J_{AB} = 10.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.66 (dt, J_{CD} = 15.1 Hz, $J_{D,CH2}$ = 6.5 Hz, 1 H), 5.26 (dt, J_{AB} = 10.5 Hz, $J_{A,CH2}$ = 7.1 Hz, 1 H), 4.55 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.1 (m, 4 H), 1.8–1.2 (unresolved m, 18 H), 1.01 (t, 3 H).

1-(2-Tetrahydropyranyloxy)-(9*E*,11*Z*)-9,11-tetradecadiene (16) was similarly prepared from 10-bromo-1-(2-tetrahydropyranyloxy)-(*E*)-9-decene (**9**) and (*Z*)-1-butenyldisiamylborane in 73% yield (63% of pure diene contaminated with 10% of the terminal ene **22**) and was used as such in the next step. Compound **22**: ^{1}H NMR δ 5.89–5.69 (m, 1 H), 5.02–4.86 (dd, 2 H), 4.56 (brs, 1 H), 3.95–3.3 (m, 4 H), 2.0 (m, 2 H), 1.8–1.2 (unresolved m, 12 H).

1-(2-Tetrahydropyranyloxy)-(9*Z*,11*Z*)-9,11-tetradecadiene (17) was similarly prepared from 10-bromo-1-(2-tetrahydropyranyloxy)-(*Z*)-9-decene (**10**) and (*Z*)-1-butenyldisiamylborane in a 73% yield (63% of pure diene contaminated with 10% of the terminal ene **22**) and was used as such in the next step.

Deprotection of the 1-(2-Tetrahydropyranyloxy)-9,11-tetradecadienes (14–17). A typical procedure was as follows. 1-(2-Tetrahydropyranyloxy)-(9*E*,11*Z*)-9,11-tetradecadiene (**16**) (100 mg, 0.34 mmol) was added to pyridinium tosylate (8.5 mg, 0.1 equiv) in ethanol (3 mL). 3-*tert*-Butyl-4-hydroxyanisol (BHA, 0.1 mol %) was then added to the mixture, which was warmed to 45 °C for 3 h. Sodium bicarbonate (100 mg) was added and the solvent evaporated. Chromatography yielded 85% of the isomerically pure product. The elution order of the alcohols on capillary GC on Carbowax 20 M, 25 m, at 160 °C was *Z,E*, *E,Z*, *Z,Z*, and *E,E*.

(9*E*,11*E*)-9,11-Tetradecadienol (18): ^{1}H NMR δ 6.05–5.98 (m, 2 H), 5.7–5.5 (m, 2 H), 3.65 (m, 2 H), 2.08 (m, 4 H), 1.37–1.27 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 133.8, 132.3, 130.4, 129.5, 63.1, 32.9, 32.6, 29.4, 29.4, 29.1, 29.1, 25.7, 25.6, 13.7.

(9*Z*,11*E*)-9,11-Tetradecadienol (19): ^{1}H NMR δ 6.28 (dd, 1 H), 5.93 (dd, 1 H), 5.67 (dt, J_{CD} = 15.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{AB} = 10.2 Hz, 1 H), 3.62 (m, 2 H), 2.1 (m, 4 H), 1.35–1.25 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 136.1, 130.0, 128.7, 124.8, 63.1, 32.8, 29.7, 29.4, 29.4, 29.2, 27.6, 25.8, 25.7, 13.6.

(9*E*,11*Z*)-9,11-Tetradecadienol (20): ^{1}H NMR δ 6.28 (dd, 1 H), 5.89 (dd, 1 H), 5.63 (dt, J_{AB} = 15.1 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{CD} = 10.4 Hz, 1 H), 3.62 (m, 2 H), 2.1 (m, 4 H), 1.35–1.25 (unresolved m, 12 H), 0.97 (t, 3 H); ^{13}C NMR δ 134.3, 131.3, 127.8, 125.3, 63.2, 33.1, 33.1, 29.8, 29.7, 29.7, 29.5, 26.1, 21.4, 14.7.

(9*Z*,11*Z*)-9,11-Tetradecadienol (21): ^{1}H NMR δ 6.27–6.12 (m, 2 H), 5.50–5.33 (m, 2 H), 3.65 (q, 2 H), 2.18 (m, 4 H), 1.36–1.24 (unresolved m, 12 H), 1.0 (t, 3 H); ^{13}C NMR δ 133.6, 132.0, 123.6, 123.1, 63.1, 32.9, 29.6, 29.5, 29.4, 29.2, 27.5, 25.8, 20.8, 14.2.

Acetylation of the 9,11-Tetradecadienols (18–21). A typical procedure was as follows. (9*E*,11*E*)-9,11-Tetradecadienol (**18**) (35 mg, 0.17 mmol) was added to acetic anhydride (0.8 mL) and pyridine (4 mL) at -10 °C and left in the refrigerator overnight. The mixture was then poured into ice–water, extracted (Et_2O), and chromatographed to give an almost quantitative yield of >99% pure product. No loss in isomeric purity was observed. The elution order of the acetates on capillary GC on Carbowax 20 M, 25m was *Z,E*, *E,Z*, *Z,Z*, and *E,E*.

(9*E*,11*E*)-9,11-Tetradecadienyl acetate (1): ^{1}H NMR δ 6.05–5.90 (m, 2 H), 5.65–5.5 (m, 2 H), 4.03 (t, 2 H), 2.05 (m, 4 H), 2.02 (s, 3 H), 1.37–1.22 (unresolved m, 12 H), 0.97 (t, 3 H).

(9*Z*,11*E*)-9,11-Tetradecadienyl acetate (2): ^{1}H NMR δ 6.28 (dd, 1 H), 5.93 (dd, 1 H), 5.69 (dt, J_{CD} = 15.5 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{AB} = 10.2 Hz, 1 H), 4.03 (t, 2 H), 2.1 (m, 4 H), 2.02 (s, 3 H), 1.33–1.23 (unresolved m, 12 H), 1.0 (t, 3 H).

(9*E*,11*Z*)-9,11-Tetradecadienyl acetate (3): ^{1}H NMR δ 6.2 (dd, 1 H), 5.9 (dd, 1 H), 5.6 (dt, J_{AB} = 15.1 Hz, $CH_A{=}CH_BCH_C{=}CH_D$, 1 H), 5.28 (dt, J_{CD} = 10.4 Hz, 1 H), 4.03 (t, 2 H), 2.17 (m, 4 H), 2.02 (s, 3 H), 1.37–1.21 (unresolved m, 12 H), 0.98 (t, 3 H).

(9*Z*,11*Z*)-9,11-Tetradecadienyl acetate (4): ^{1}H NMR δ 6.30–6.12 (m, 2 H), 5.48–5.36 (m, 2 H), 4.03 (t, 2 H), 2.15 (m, 4 H), 2.02 (s, 3 H), 1.35–1.23 (unresolved m, 12 H), 0.97 (t, 3 H).

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Reactions of Singlet Oxygen with Alkoxy-Substituted Dienes. Formation of Dioxetanes in the Singlet Oxygenations of *s*-Cis Fixed Dienes (*Z,Z*)- and (*E,Z*)-4,5-Diethylidene-2,2-dimethyl-1,3-dioxolanes

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Extensive investigations over the past several years have established that singlet oxygen has a proclivity to undergo 2 + 2^2 4 + 2,[3] and ene[4] reactions with organic substrates. In addition, physical quenching of singlet oxygen by substrates with low ionization potentials[5] or low triplet energies[6] also occurs.

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