failed to show the presence of $C_6H_5C{\equiv}CCH_2D$. On the other hand, when compared to mass spectra for authentic undeuterated *cis*- and *trans*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 119 (7), 118 (71), 117 (100), 115 (40), and 91 (27)], the observed mass spectral data for the minor electrolysis products, *cis*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 120 (78), 119 (100), 118 (69), 117 (54), 116 (56), and 115 (52)] and *trans*-1-phenyl-1-propene [*m/e* (70 eV) (relative intensity) 120 (40), 119 (83), 118 (100), 117 (70), 116 (57), and 115 (76)], suggest that these olefins possessed at least one if not two deuterium atoms per molecule. In fact, the *cis*-1-phenyl-1-propene, a product which is formed early in an electrolysis of 1-phenyl-1-deuteriopropadiene (Table II), did appear, on the basis of its mass spectrum, to contain two deuterium atoms per molecule; however, the *trans*-1-phenyl-1-propene, formed later during an electrolysis, seems to be a mixture of monodeuterated and dideuterated species.

Ostensibly, the preceding results show that unreduced phenylpropadiene acts as a proton donor for the anionic precursors of *cis*- and *trans*-1-phenyl-1-propene, although our findings do not exclude the possibility that another source of protons is involved as well; evidence exists that certain carbon acids (fluorene and 9-methylfluorene)[19,20] function well as proton donors for their own or related conjugate bases in dimethyl sulfoxide and, presumably, other similar solvents. If radical-anion **2** is protonated by unreduced starting material (**1**) to yield allyl radical **3** and the conjugate base, $C_6H_5\bar{C}{=}C{=}CH_2$ (**5**), of phenylpropadiene, the latter anion (**5**) could simply be protonated to regenerate **1**. However, **5** could rearrange and then accept a proton (conceivably from another molecule of phenylpropadiene) to give 1-phenyl-1-propyne via what becomes essentially a self-propagating *intermolecular* allene-to-alkyne isomerization. An alternative process is that once **5** is formed it could act catalytically to promote the *intramolecular* "conducted tour" rearrangement of phenylpropadiene to 1-phenyl-1-propyne. More investigations are underway in our laboratory to characterize further the electrolytically induced, base-catalyzed alkyne–allene transformations that 1-phenyl-1-hexyne and phenylpropadiene both undergo in dimethylformamide.

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(20) Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 1730.

Thermal and Catalyzed Intramolecular Diels–Alder Cyclizations of 2,8,10-Undecatrienals

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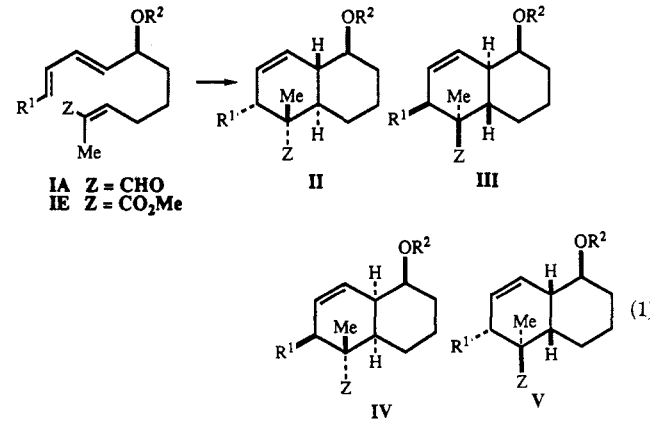
A comparative study of thermal and Lewis acid catalyzed intramolecular Diels–Alder cyclizations of substituted 2,8,10-undecatrienals was undertaken to determine the effect of substituents on the stereochemistry of the reaction. Substituents examined included 11-methyl, 4-methyl, 9-Me_3Si, 7-OMOM, 7-OTBS, and anti-4,6-dimethyl in various combinations. In all cases, the catalyzed reactions were highly endo selective (90:10 or greater). In thermal cyclizations the 9-Me_3Si, the 4-methyl, and the anti-4,6-dimethyl derivatives showed complete endo selectivity and the 11-methyl derivative was moderately endo selective.

We have previously shown that 2,8,10-undecatrienals IA undergo facile intramolecular Diels–Alder cyclizations upon treatment with alkylaluminum halides at −78 to −10 °C.[1] These reactions proceed with high endo selectivity affording the trans-fused diastereoisomers IIA and IIIA as major products. The corresponding esters, IE, on the other hand, give no reaction when treated similarly and decompose when warmed to 0 °C or above in the presence of Lewis acids.[2] Thermal cyclizations of IE lead to a mixture of all four stereoisomeric hydronaphthalenes with the exo products IVE and VE predominating.[2] The endo product II is of special interest as a substructural unit of the macrocyclic antibiotic chlorothricolide.[3]

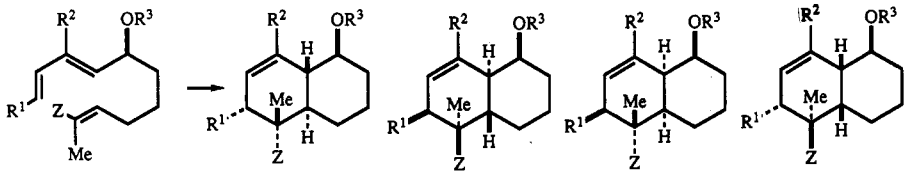


In view of the enhanced reactivity shown by the conjugated aldehyde dienophile we thought it worthwhile to extend our studies to thermal Diels–Alder cyclizations of various 2,8,10-undecatrienals. Conjugated aldehydes have only rarely been employed for intramolecular Diels–Alder reactions so the results of such a study would provide useful semiquantitative information on the directing ability of this dienophile.[4] In addition, we were interested in the

(1) (a) Marshall, J. A.; Audia, J. E.; Grote, J. *J. Org. Chem.* **1984**, *49*, 5277. (b) Marshall, J. A.; Audia, J. E.; Grote, J. *J. Org. Chem.* **1986**, *51*, 1155. (c) Marshall, J. A.; Grote, J.; Shearer, B. G. *J. Org. Chem.* **1986**, *51*, 1633. (d) Marshall, J. A.; Audia, J. E.; Shearer, B. G. *J. Org. Chem.* **1986**, *51*, 1730. (e) Marshall, J. A.; Audia, J. E.; Grote, J.; Shearer, B. G. *Tetrahedron* **1986**, *42*, 2893.
(2) Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, *103*, 5200.
(3) Keller-Schierlein, P. W.; Muntwyler, R.; Pache, W.; Zähner, H. *Helv. Chim. Acta* **1969**, *52*, 127. Muntwyler, R.; Widmer, J.; Keller-Schierlein, W. *Helv. Chim. Acta* **1970**, *53*, 1544. Muntwyler, R.; Keller-Schierlein, W. *Helv. Chim. Acta* **1972**, *55*, 2071. Brufani, M.; Cerrini, S.; Fedeli, W.; Mazza, F.; Muntwyler, R. *Helv. Chim. Acta* **1972**, *55*, 2094.

0022-3263/87/1952-1236$01.50/0

Table I. Intramolecular Diels–Alder Cyclizations of 7-Alkoxy-2,8,10-undecatrienals



1a-e 2a-e 3a-e 4a-e 5a-e

entry	compd	R^1	R^2	R^3	Z	conditions[a]	yield,[b] %	ratios[c] 2/3/4/5	ratios[c] endo/exo	ratios[c] e/a[e]
1	1a	H	H	MOM	CHO	A	92	41:49:7:3	90:10	48:52
2						B	88	37:23:25:15	60:40	62:38
3	1b	H	Me_3Si	MOM	CHO	A	72	70:30:0:0	100:0	70:30
4						B	74	89:11:0:0	100:0	89:11
5	1c	Me	H	MOM	CHO	A	88	56:40:4:0	96:4	60:40
6						B	98	63:21:16:0	84:16	79:21
7	1d	Me	H	TBS	CHO	A	84	15:75:0:10	90:10	15:85
8						B	94	27:27:13:33	54:46	40:60
9	1e	Me	H	TBS	CO_2Me	B	72	16:9:24:51	25:75	33:67
10						B	90	15:13:23:49[d]	28:72[d]	38:62[d]

[a] (A) Me_2AlCl, CH_2Cl_2, −78 to −15 °C, ~0.08 M; (B) 150–160 °C, toluene, ~0.008 M, BHT. [b] Chromatographed product mixture. [c] Determined by glass capillary GC. [d] The results of Roush and Hall.[2] [e] Equatorial/axial.

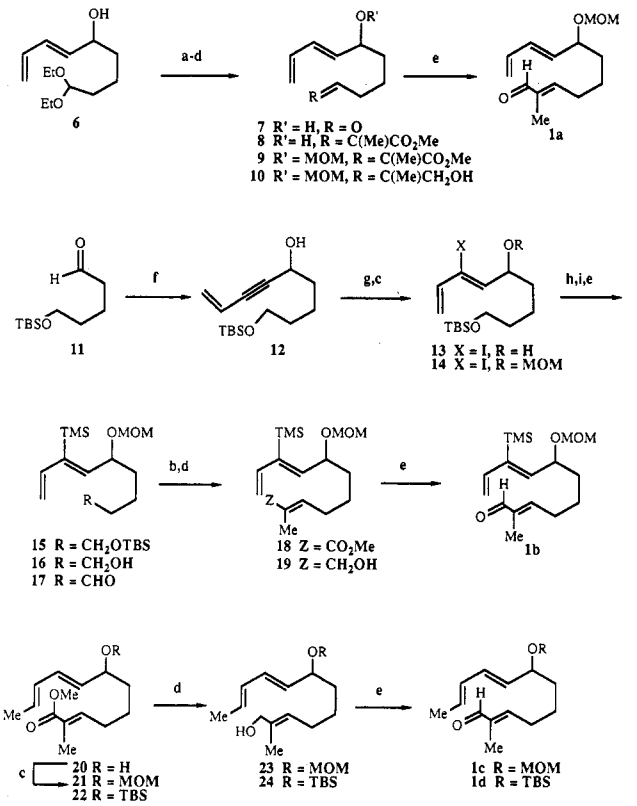
effect of chain substitution on the diastereoselectivity of such cyclizations. These matters are directly relevant to the synthesis of prototype hydronaphthalene subunits of several macrocyclic natural products with antitumor and antibiotic activity.[3,5]

Initial investigations were carried out on the trienals **1a–d**, prepared as outlined in Scheme I. Cyclizations were effected with dimethylaluminum chloride in methylene chloride at −78 to −15 °C or thermally at 150–160 °C in toluene containing BHT as a free radical inhibitor. The crude product mixtures were filtered through silica gel without separation of diastereoisomers, and the purified mixtures were analyzed by capillary gas chromatography. The results are summarized in Table I.

Structural assignments were made by analysis of high-field ^1H NMR spectra of purified or enriched samples of the aldehyde products **2–5**. The **2a–5a and 2d–5d** mixtures were not readily separated by chromatography on silica gel. However, the corresponding mixtures of alcohols (Z = CH_2OH) could be partially separated and then oxidized to enriched samples of the corresponding aldehydes for ^1H NMR analysis. A direct correlation of aldehydes **2d–5d** with the known esters (**2e–5e**), whose structures have been rigorously determined by Roush and Hall,[2] provided additional support for the assignments.

Certain trends are evident from inspection of Table I. Most striking is the complete endo selectivity engendered by the C9-Me_3Si grouping (R^2) of trienal **1b** in both catalyzed and thermal cyclizations (entries 3 and 4). This effect, first reported for a C9-CH_3 substituent by Wilson[6] and more recently for Me_3Si by Boeckmann[7] and Br by Roush in analogous trienoate cyclizations,[8] can be attributed to unfavorable steric interactions in the transition

Scheme I[a]



[a] (a) $(CO_2H)_2$, H_2O, THF; (b) $Ph_3P{=}C(Me)CO_2Me$, CH_2Cl_2; (c) MOMCl, $(i\text{-}Pr)_2NEt$, CH_2Cl_2; (d) $i\text{-}Bu_2AlH$, Et_2O, −78 °C; (e) $(COCl)_2$, Me_2SO, Et_3N, −78 °C; (f) $CH_2{=}CHC{\equiv}CLi$, THF, −78 °C; (g) Red-Al, Et_2O, 0 °C; I_2, THF, −78 °C; (h) 2 equiv of t-BuLi, Et_2O; Me_3SiCl, −78 °C; (i) $(n\text{-}Bu)_4NF$, THF.

states C → **4** and D → **5** (Figure 1) between the substituent R^2 and the developing cyclohexane ring. In essence, both C and D afford cyclization products with axial vinyl substituents. Steric effects may additionally favor the A → **2** over the B → **3** pathway.

Catalyzed cyclizations generally show a strong tendency for endo dienophile/diene orientation. This preference tends to be lost at elevated temperatures in the thermal reactions (barring large steric directing effects as in **1b**). Even then, the aldehyde substituent is a stronger endo

(4) Roush, W. R.; Peseckis, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 6696. Taber, D. F.; Campell, C.; Gunn, B. P.; Chiu, I.-C. *Tetrahedron Lett.* **1981**, *22*, 5141.

(5) Mallams, A. K.; Puar, M. S.; Rossman, R. R.; McPhail, A. T.; McFarlane, R. D.; Stephens, R. L. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1497. Mallams, A. K.; Puar, M. S.; Rossman, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3938. Hirayama, N.; Kasai, M.; Shirahata, K.; Ohasahi, Y.; Sasada, Y. *Tetrahedron Lett.* **1980**, *21*, 2559.

(6) Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 6289.

(7) Boeckmann, R. K.; Barta, T. E. *J. Org. Chem.* **1985**, *50*, 3421.

(8) Roush, W. R.; Kageyama, M. *Tetrahedron Lett.* **1985**, *26*, 4327. A 55:45 mixture of endo/exo products was obtained. This represents an improvement over the R^2 = H system, but the effect is more modest than that observed for R^2 = Me or R^2 = Me_3Si.[6,7]

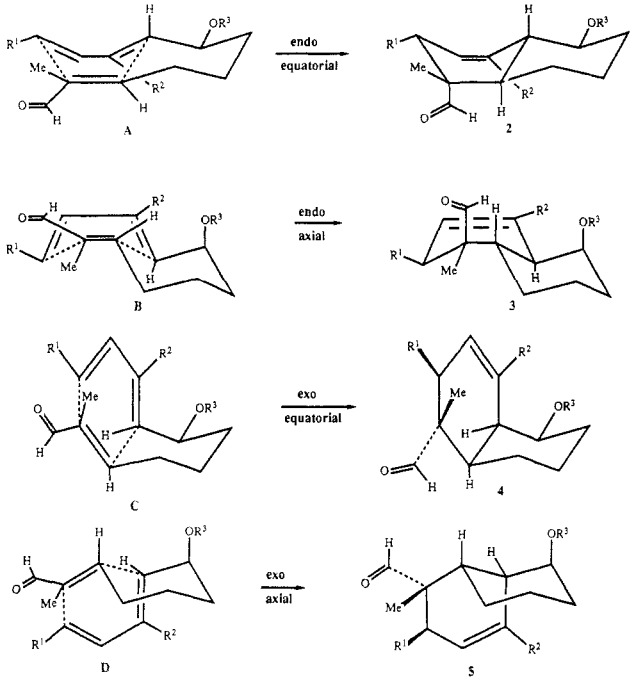


Figure 1. Diels–Alder cyclization pathways for 7-alkoxy-2,8,10-undecatrienals.

director than an ester (entries 8 vs. 9 and 10).

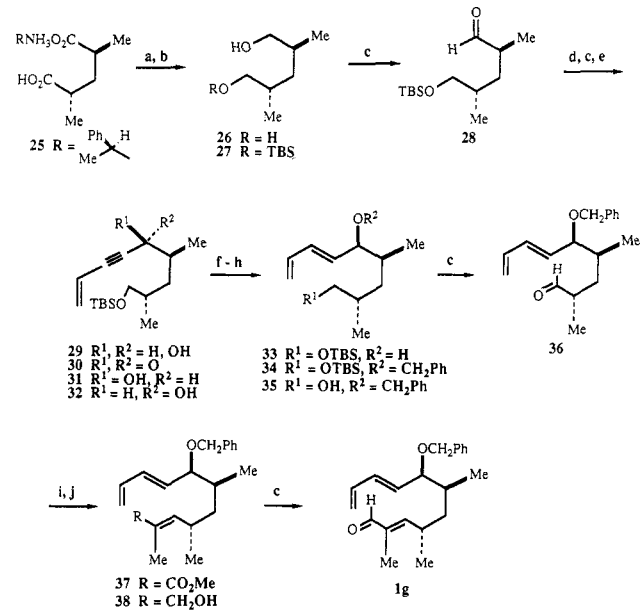
A C11 (R^1) substituent also seems to favor the formation of endo products in thermal (entries 2 vs. 6) as well as catalyzed cyclizations (entries 1 vs. 5), although the effect is less pronounced than that of a C9 (R^2) substituent. Steric interactions between R^1 and the C2-methyl grouping as in C → **4** and D → **5** (Figure 1) vs. the smaller R^1/CHO interactions in A → **2** and B → **3** could account for this observation. Larger R^1 groups should enhance this effect.

"Equatorial/axial" diastereoselectivity is also sensitive to chain substitution. These terms refer to the orientation of the alkoxy groups OR^3 in the diastereomeric products **2–5** (Figure 1) and the secondary Me groups in **2–5** of Figure 3. In the former set a TBS ether shows a marked preference for the axial orientation, especially in the catalyzed reaction (entry 7). Thermal cyclizations tend to give higher equatorial/axial ratios than the corresponding catalyzed reactions for all systems examined.

We previously found that ratios of diastereomeric endo products from Lewis acid catalyzed Diels–Alder cyclizations of 2,8,10-undecatrienals could be correlated with stabilities of the boat–chair conformers (compare **2** with **3**, Figure 1) as calculated by molecular mechanics.[1,9] These findings are consistent with a product-like transition-state geometry. Applying the same calculations to the exo products (compare **4** with **5**), we found less than 0.3 kcal/mol energy differences between **4c** and **5c** and **4d** and **5d**.[10] Accordingly, nearly 1:1 mixtures of equatorial and axial products **4** and **5** would be expected for a product-like transition state. In fact, **4c** greatly predominated over **5c** and **5d** was favored over **4d**. Therefore, product-like transition states seem unlikely for these exo cyclizations. The high equatorial/axial ratios observed in the thermal cyclization of the 9-Me_3Si derivative **1b** (entry 3, **2b**/**3b** = 70:30) may reflect crowding in conformation B (Figure 1) for R^2 substituents larger than hydrogen, suggestive of a reactant-like transition state. Indeed, Roush noted that when R^2 = Br (R^1 = CH=$CHCH_2OH$, R^3 = benzyl) the endo product of thermal cyclization is exclusively equatorial (**2**).[8]

We now turn to the C4-methyl-substituted undecatrienals **1f** and **1g**, possible acyclic precursors of kijanolide and tetronolide substructure prototypes.[5] The Lewis acid catalyzed Diels–Alder cyclization of these trienals (eq 2 and 3) was previously surmised to afford only the endo products **2f** and **2g**.[1b] However, analysis of the **1g** cyclization was complicated by the presence of an equal amount of C7 benzyloxy epimer, a consequence of the synthetic route employed for its preparation. For the present study we modified our previous route and were able to produce nonracemic **1g** of >90% enantiomeric excess and ~90% diastereomeric excess at C7 (Scheme II). This was achieved through resolution of (±)-2,4-dimethylglutaric acid with (−)-α-methylbenzylamine, as described by Stanton and co-workers,[11] followed by reduction and monoprotection as previously reported by us.[1b] The al-

Scheme II[a]



[a] (a) $LiAlH_4$, THF; (b) TBSCl, Et_3N, CH_2Cl_2, DMF; (c) $(COCl)_2$, Me_2SO, CH_2Cl_2, Et_3N, −78 °C; (d) LiC≡CCH=CH_2, THF, −78 °C; (e) L-Selectride, THF, −78 °C; (f) Red-Al, Et_2O, 0 °C; (g) $PhCH_2Br$, *n*-BuLi, THF, HMPA, −78 to 25 °C; (h) *n*-Bu_4NF, THF; (i) Ph_3P=C(Me)CO_2Me, CH_2Cl_2; (j) *i*-Bu_2AlH, Et_2O, −78 °C.

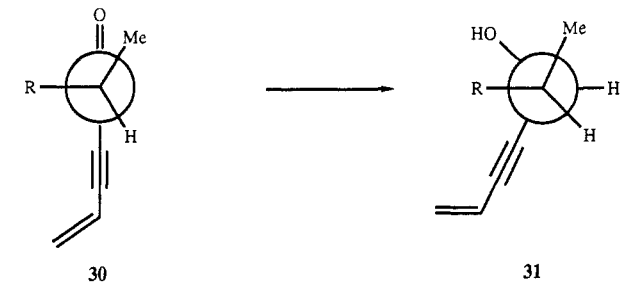


Figure 2. Diastereoselective reduction of ketone **30**.

(9) Calculations were performed with the program Macromodel on a VAX 11/780 computer. We are indebted to Professor W. Clark Still and Dr. Wayne Guida for a prototype copy of the program.

(10) The related methyl and *tert*-butyl ethers (e.g., Figure 1, **4c**, **5c** with Me or *t*-Bu in place of MOM) differed by less than 0.2 kcal/mol. Calculations could not be completed for the pairs **4a**, **5a** and **4b**, **5b** because the A ring reverted to the more stable half-chair conformation during minimization. A non-H R^1 group in the boat–chair conformers **2–5** (Figure 1) prevents conversion of the A ring to a half-chair conformation by imposing a large energy barrier to rotation of the C3/C4 bond.[1b]

(11) Gruenfeld, N.; Stanton, J. L.; Yuan, A. M.; Ebetino, F. H.; Browne, L. J.; Gude, C.; Huebner, C. F. *J. Med. Chem.* **1983**, *26*, 1277.

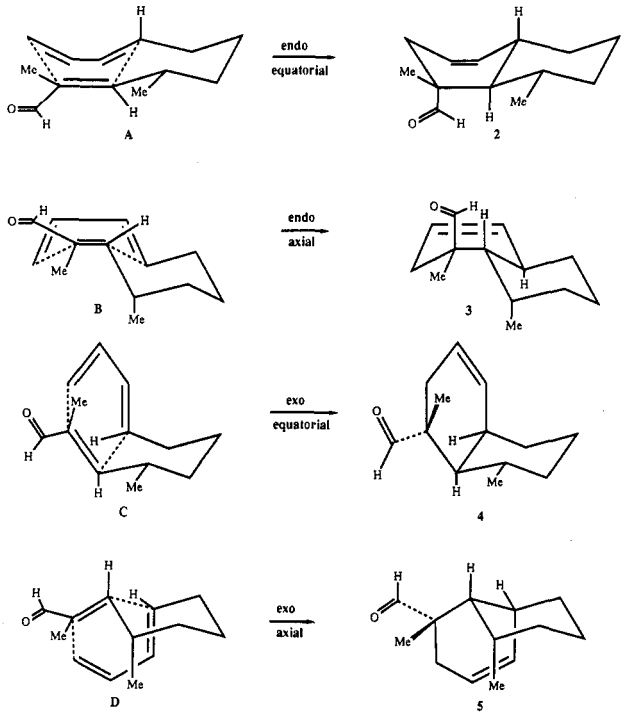
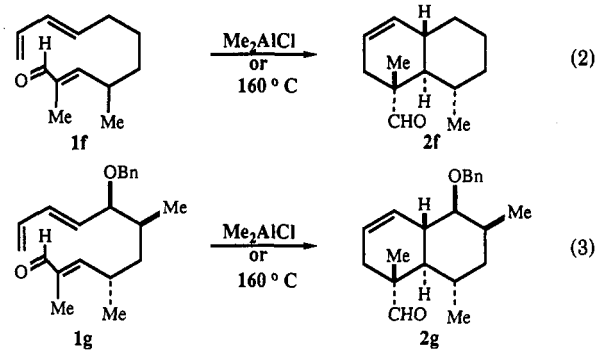


Figure 3. Diels–Alder cyclization pathways for 4-methyl-2,8,10-undecatrienals.

dehyde **28**, obtained via Swern oxidation,[12] afforded the 1:1 mixture of diastereomeric alcohols **29** previously obtained in racemic form upon addition of lithium vinylacetylide. Swern oxidation[12] of this mixture yielded ketone **30** whose reduction with L-Selectride (Aldrich) at −78 °C led to a 90:10 mixture of diastereomeric alcohols **31** and **32**.[13] The predominance of **31** was expected from consideration of the Felkin transition state (Figure 2). Benzylation followed by silyl ether cleavage and homologation, as previously described for the racemic diastereomeric mixture **29**,[1b] afforded trienal **1g** as a nonracemic 90:10 mixture of C7 epimers.

Both **1f** and **1g** underwent smooth thermal cyclization, the former at an appreciably slower rate. Enal **1f** yielded a single racemic product **2f** and **1g** gave a 90:10 mixture of nonracemic **2g** and the benzyloxy epimer derived from alcohol **32**. Neither **2f** nor **2g** showed significant (>1%)



contamination by diastereoisomers corresponding to **3–5** (Figure 3) according to capillary GC analysis. The structures were readily confirmed through comparison of high-field ^{1}H NMR spectra and GC retention times with material secured via Lewis acid catalyzed cyclization. In addition, **2g** was subjected to 2D *J*-resolved ^{1}H NMR and NOE analysis revealing H4a as a triplet (J = 10.3 Hz) at 1.49 ppm and enhancement of the CHO signal upon irradiation of the C5-CH_3, in accord with the assigned structure.

The 4-methyl group imposes a strong endo-directing effect on both thermal and catalyzed Diels–Alder cyclizations of 2,8,10-undecatrienals.[14] If these cyclizations proceeded via a reactant-like transition state we might expect a mixture of endo equatorial and exo equatorial products **2** and **4** to be formed owing to the energetic similarity of A and C. A product-like transition state, on the other hand, would strongly favor the endo equatorial product **2** according to molecular mechanics calculations.[9] The observed exclusive formation of **2f** and **2g** thus supports a late transition state, in accord with both molecular mechanics and ab initio calculations.[15]

The results of these studies support previous findings that endo or exo transition state preferences of intramolecular Diels–Alder reactions can be markedly influenced by substituents.[6-8] We also find that the dienophilic moiety can play an important role in such preferences. Ratios of diastereomeric products from reactions proceeding via endo transition states appear to correlate with product stabilities, in accord with a late transition state. No such correlation is found for reactions occurring via exo transition states, however. An early transition state may better reconcile these latter processes.

Experimental Section

The apparatus and methods described by G. W. Kramer, M. M. Midland, and A. B. Levy[16] were used to maintain an argon or nitrogen atmosphere in the reaction flask. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (diethyl ether, tetrahydrofuran), P_2O_5 (dichloromethane), or sodium (benzene). Infrared absorption maxima are reported in wavenumbers (cm^{-1}). Proton magnetic resonance samples were prepared as dilute solutions in deuteriochloroform ($CDCl_3$). Chemical shifts (δ) are reported downfield from tetramethylsilane (Me_4Si), in parts per million (ppm) of the applied field. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; pentuplet, p; envelope, e; multiplet, m. Coupling constants (J) are reported in hertz (Hz). Glass capillary gas chromatography was performed on a Superox 4 25M column. Combustion microanalyses were performed by Atlantic Laboratories, Atlanta, GA. Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with E. Merck Silica Gel 60 F254 of 0.25-mm thickness, supplied by Brinkmann Instruments, were used. E. Merck Silica Gel 60 (230–400 ASTM mesh) was employed for column chromatography according to the procedure of Still.[17]

(*E*,*E*)-2-Methyl-7-(methoxymethoxy)undeca-2,8,10-trienal (1a). To a stirred, cooled (−78 °C) solution of 145 mg (1.15 mmol) of oxalyl chloride in 2.0 mL of CH_2Cl_2 was added 176 mg (2.25 mmol) of Me_2SO. The mixture was stirred for 5 min, and 148 mg (0.61 mmol) of alcohol **10** in 1.0 mL of CH_2Cl_2 was added dropwise. After 10 min, 363 mg (3.59 mmol) of triethylamine was added. The mixture was warmed to room temperature, poured into water, and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 10% EtOAc in hexanes to afford 135 mg (93%) of trienal **1a**: IR (film) ν 2925, 1690, 1460, 1160, 1110, 1040 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.60 (4 H, m, H5 and H6), 1.74 (3 H, s, vinyl CH_3), 2.37 (2 H, m, H4), 3.37 (3 H, s, OCH_2OCH_3), 4.05 (1 H, m, H7), 4.59 (AB q, J_{AB} = 9.1 Hz, $\Delta\nu$ = 5.9 Hz, OCH_2OCH_3), 5.10 (1 H, d, J = 9.4 Hz, H11 cis), 5.22

(12) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(13) Cf.: Midland, M. M.; Kwon, Y. C. *Tetrahedron Lett.* **1984**, *25*, 5981.
(14) For a recent example of this effect in the thermal cyclization of a trienone analogue of **1f**, see: Ichihara, A.; Kawagishi, H.; Tokugawa, N.; Sakamura, S. *Tetrahedron Lett.* **1986**, *27*, 1347.
(15) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609.
(16) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975; pp 191–202.
(17) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(1 H, d, J = 16.3 Hz, H11 trans), 5.52 (1 H, dd, J = 9.4, 16.3 Hz, H8), 6.19 (1 H, dd, J = 9.4, 16.3 Hz, H9), 6.32 (1 H, ddd, J = 9.4, 9.4, 16.3 Hz, H10), 6.47 (1 H, t, J = 7.7 Hz, H3), 9.40 (1 H, s, CHO). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.63; H, 9.32.

Cyclizations of Trienal 1a. A. Lewis Acid Cyclization. To a stirred, cooled (−78 °C) solution of 59 mg (0.25 mmol) of trienal **1a** (azeotropically dried with benzene) in 3 mL of CH_2Cl_2 was added 0.25 mL (0.25 mmol) of 1.0 M Me_2AlCl in hexane. The mixture was stirred for 1 h at −78 °C, then warmed to −18 °C, and stirred for 18 h. After quenching with saturated aqueous $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and solvent was removed at reduced pressure. The residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 54 mg (92%) of a pale yellow oil determined to be a 41:49:7:3 mixture of diastereomers **2a/3a/4a/5a** by glass capillary GC analysis. Reduction with $LiAlH_4$ followed by careful chromatography and Swern oxidation[12] provided samples of **2a**, **3a**, and **4a**: IR (film) ν 2925, 1725, 1455, 1160, 1065 cm^{-1}.

2a: ^1H NMR (300 MHz) δ 1.03 (3 H, s, C4-CH_3), 2.15, 2.03, 1.80 (10 H, m), 3.25 (1 H, m, H8), 3.44 (3 H, s, OCH_2OCH_3), 4.71 (AB q, J_{AB} = 7.1 Hz, $\Delta\nu$ = 39.8 Hz, OCH_2OCH_3), 5.56 (1 H, m, H2), 5.88 (1 H, d, J = 11.1 Hz, H1), 9.59 (1 H, s, CHO).

3a: ^1H NMR (300 MHz) δ 0.93 (3 H, s, C4-CH_3), 1.19–1.86 (6 H, m), 1.94 (1 H, br d, J = 15.1 Hz, H8a), 2.10 (1 H, dt, J = 15.1, 6.1 Hz, H4a), 2.40 (2 H, br d, J = 15.0 Hz, H3), 3.37 (3 H, s, OCH_2OCH_3), 3.94 (1 H, br s, H8), 4.64 (AB q, J_{AB} = 7.1 Hz, $\Delta\nu$ = 34.7 Hz, OCH_2OCH_3), 5.52 (1 H, br d, J = 11.1 Hz, H1), 5.67 (1 H, m, H2), 9.44 (1 H, s, CHO).

4a: ^1H NMR (300 MHz) δ 1.03 (3 H, s, C4-CH_3), 1.20–1.94 (9 H, m), 2.45 (1 H, br s), 3.30 (3 H, s, OCH_2OCH_3), 3.45 (1 H, m, H8), 4.51 (AB q, J_{AB} = 7.1 Hz, $\Delta\nu$ = 13.4 Hz, OCH_2OCH_3), 5.44 (1 H, m, H2), 5.93 (1 H, d, J = 11.1 Hz, H1), 9.56 (1 H, s, CHO).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found; C, 70.45; H, 9.33.

B. Thermal Cyclization. A solution of 20 mg (0.08 mmol) of trienal **1a** in 10 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 155 °C in an oil bath for 24 h. The tube was cooled to room temperature and opened, solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 17.5 mg (88%) of a pale yellow oil determined to be a 37:23:25:15 mixture of diastereomers **2a/3a/4a/5a** by glass capillary GC analysis.

(*E*,*Z*)-2-Methyl-7-(methoxymethoxy)-9-(trimethylsilyl)-undeca-2,8,10-trienal (1b). The procedure described above for **1a** was employed with 199 mg (0.63 mmol) of alcohol **19**. Following workup, the crude product was chromatographed on silica gel by eluting with 5% EtOAc in hexane to afford 179 mg (92%) of aldehyde **1b** as a pale yellow oil: IR (film) ν 2950, 1690, 1260, 1160, 1110, 1045 cm^{-1}; ^1H NMR (300 MHz) δ 0.18 (9 H, s, $Si(CH_3)_3$), 1.70–1.40 (4 H, m, H5 and H6), 1.73 (3 H, s, vinyl CH_3), 2.37 (2 H, br q, J = 6.9 Hz, H4), 3.34 (3 H, s, OCH_2OCH_3), 4.32 (1 H, m, H7), 4.57 (AB q, J_{AB} = 6.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 4.91 (1 H, d, J = 9.3 Hz, H11 cis), 5.12 (1 H, d, J = 17.1 Hz, H11 trans), 5.98 (1 H, d, J = 9.7 Hz, H8), 6.35 (1 H, dd, J = 9.3, 17.1 Hz, H10), 6.47 (1 H, t, J = 7.3 Hz, H3), 9.37 (1 H, s, CHO). Anal. Calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.89; H, 9.80.

Cyclizations of Trienal 1b. A. Lewis Acid Cyclization. To a stirred, cooled (−78 °C) solution of 46 mg (0.15 mmol) of trienal **1b** (azeotropically dried with benzene) in 2 mL of CH_2Cl_2 was added 0.15 mL (0.15 mmol) of 1 M Me_2AlCl in hexanes. After being stirred for 1 h at −78 °C, the mixture was warmed to −15 °C, stirred for 24 h, and quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. Solvent was removed at reduced pressure and the residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 33 mg (72%) of a pale yellow oil determined to be a 70:30 mixture of diastereomers **2b/3b** by glass capillary GC analysis. Reduction with $LiAlH_4$ followed by extremely careful chromatography and Swern oxidation provided samples of each diastereomer: IR (film) ν 2925, 1725, 1455, 1255, 1120, 1050 cm^{-1}.

2b: ^1H NMR (400 MHz) δ 0.07 (9 H, s, $SiC(CH_3)_3$), 0.95 (3 H, s, C4-CH_3), 1.03–1.80 (7 H, m), 2.06 (1 H, t, J = 13.3 Hz, H8a), 2.40 (2 H, m, H3), 3.25 (1 H, m, H8), 3.37 (3 H, s, OCH_2OCH_3), 4.68 (2 H, s, OCH_2OCH_3), 6.12 (1 H, d, J = 7.0 Hz, H2), 9.39 (1 H, s, CHO).

3b: ^1H NMR (400 MHz) δ 0.08 (9 H, s, $SiC(CH_3)_3$), 0.98 (3 H, s, C4-CH_3), 1.05–1.89 (7 H, m), 2.18 (1 H, br d, J = 14.0 Hz, H8a), 2.37 (2 H, d, J = 11.2 Hz, H3), 3.39 (3 H, s, OCH_2OCH_3), 4.13 (1 H, br s, H8), 4.68 (AB q, J_{AB} = 7.0 Hz, $\Delta\nu$ = 19.9 Hz, OCH_2OCH_3), 6.04 (1 H, m, H2), 9.38 (1 H, s, CHO).

B. Thermal Cyclization. A solution of 27 mg (0.087 mmol) of trienal **1b** in 10 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 155 °C in an oil bath for 24 h. The tube was cooled to room temperature and opened, and solvent was removed at reduced pressure. The residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 20 mg (74%) of a pale yellow oil determined to be a 89:11 mixture of diastereomers **2b/3b** by glass capillary GC analysis.

(*E*,*E*,*E*)-2-Methyl-7-(methoxymethoxy)dodeca-2,8,10-trienal (1c). The procedure described above for **1a** was employed with 878 mg (3.45 mmol) of alcohol **23**. Following workup, the crude product was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 703 mg (81%) of trienal **1c**: IR (film) ν 2900, 1680, 1450, 1160, 1030 cm^{-1}; ^1H NMR (300 MHz) δ 1.57 (4 H, m), 1.72 (3 H, s, vinyl CH_3), 1.77 (3 H, s, vinyl CH_3), 2.34 (2 H, m, H4), 3.29 (3 H, s, OCH_2OCH_3), 4.00 (1 H, m, H7), 4.59 (AB q, J_{AB} = 9.1 Hz, $\Delta\nu$ = 63.7 Hz, OCH_2OCH_3), 5.31 (1 H, dd, J = 9.4, 16.3 Hz), 5.76–5.64 (1 H, m, H9), 6.19–5.96 (2 H, m, H10 and H11), 6.46 (1 H, t, J = 7.7 Hz, H3), 9.37 (1 H, s, CHO). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.40; H, 9.58. Found: C, 71.45; H, 9.62.

Cyclizations of Trienal 1c. A. Thermal Cyclization. A solution of 160 mg (0.63 mmol) of trienal **1c** in 10 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated to 155 °C in an oil bath for 24 h. The tube was cooled to room temperature and opened, solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 10% EtOAc in hexanes to afford 157 mg (98%) of a colorless oil determined to be a 63:21:16 mixture of diastereomers **2c/3c/4c** by glass capillary GC analysis. Reduction with $LiAlH_4$ followed by careful, repeated chromatography and Swern oxidation provided samples of each diastereomer: IR (film) ν 2900, 1720, 1460, 1380, 1160, 1050 cm^{-1}.

2c: ^1H NMR (300 MHz) δ 0.98 (3 H, s, C4-CH_3), 1.24 (3 H, d, J = 6.3 Hz, C3-CH_3), 1.47–2.35 (9 H, m), 3.27 (1 H, m, H8), 3.39 (3 H, s, OCH_2OCH_3), 4.71 (AB q, J_{AB} = 6.8 Hz, $\Delta\nu$ = 39.2 Hz, OCH_2OCH_3), 5.59 (1 H, m, H2), 5.88 (1 H, d, J = 10.1 Hz, H1), 9.59 (1 H, s, CHO).

3c: ^1H NMR (300 MHz) δ 1.00 (3 H, s, C4-CH_3), 1.08 (3 H, d, J = 7.1 Hz, C3-CH_3), 1.20–2.08 (8 H, m), 2.37 (1 H, d, J = 11.1 Hz, H3), 3.37 (3 H, s, OCH_2OCH_3), 3.93 (1 H, br s, H8), 4.67 (AB q, J_{AB} = 6.8 Hz, $\Delta\nu$ = 26.8 Hz, OCH_2OCH_3), 5.49 (1 H, d, J = 10.6 Hz, H1), 5.59 (1 H, m, H3), 9.64 (1 H, s, CHO).

4c: ^1H NMR (300 MHz) δ 1.01 (3 H, s, C4-CH_3), 1.03 (3 H, d, J = 7.9 Hz, C3-CH_3), 1.12–1.64, 1.76 (7 H, m), 2.44 (1 H, m, H4a), 2.67 (1 H, d, J = 7.7 Hz, H3), 3.31 (3 H, s, OCH_2OCH_3), 3.74 (1 H, m, H8), 4.62 (2 H, s, OCH_2OCH_3), 5.68 (2 H, s, H2 and H1), 9.36 (1 H, s, CHO).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.40; H, 9.58. Found: C, 71.50; H, 9.62.

B. Lewis Acid Cyclization. To a stirred, cooled (−78 °C) solution of 26 mg (0.10 mmol) of trienal **1c** (azeotropically dried with benzene) in 1.2 mL of CH_2Cl_2 was added 0.10 mL (0.10 mmol) of 1.0 M Me_2AlCl in hexane. The mixture was stirred for 1 h at −78 °C and then warmed to −15 °C while being stirred for 5 h. After quenching with saturated aqueous $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and solvent was removed at reduced pressure. The resulting residue was chromatographed on silica gel by eluting with 10% EtOAc in hexanes to afford 23 mg (88%) of a colorless oil determined to be a 56:40:4 mixture of diastereomers **2c/3c/4c** by glass capillary GC analysis.

Cyclizations of Trienal 1d. A. Lewis Acid Cyclization. Trienal **1d** was cyclized as previously described affording a 15:75:10 mixture of diastereomers **2d/3d/5d** as determined by glass capillary GC analysis.[1e] Reduction with $LiAlH_4$ followed by ex-

tremely careful chromatography and Swern oxidation provided pure samples of each diastereomer: IR (film) ν 3000, 2910, 2840, 2670, 1720, 1460, 1375, 1260 cm^{-1}.

2d: ^1H NMR (400 MHz) δ 0.08, 0.11 (6 H, 2 s, $Si(CH_3)_2$), 0.91 (3 H, s, C4-CH_3), 0.94 (9 H, s, $SiC(CH_3)_3$), 1.06 (3 H, d, J = 7.1 Hz, C3-CH_3), 1.40, 1.79, 2.04 (9 H, m), 3.35 (1 H, m, H8), 5.58 (1 H, ddd, J = 10.2, 4.9, 2.8 Hz, H1), 5.90 (1 H, d, J = 10.2 Hz, H2), 9.60 (1 H, s, CHO).

3d: ^1H NMR (400 MHz) δ 0.03, 0.05 (6 H, 2 s, $Si(CH_3)_2$), 0.89 (9 H, s, $SiC(CH_3)_3$), 0.99 (3 H, s, C4-CH_3), 1.04 (3 H, d, J = 7.1 Hz, C3-CH_3), 2.45 (1 H, dt, J = 2, 11.4 Hz, H4a), 4.06 (1 H, br s, H8), 5.36 (1 H, br d, J = 10.2 Hz, H2), 5.53 (1 H, ddd, J = 10.2, 4.9, 2.8 Hz, H1), 9.65 (1 H, s, CHO).

5d: ^1H NMR (400 MHz) δ 0.03, 0.05 (6 H, 2 s, $Si(CH_3)_2$), 0.89 (9 H, s, $SiC(CH_3)_3$), 0.98 (3 H, s, C4-CH_3), 1.01 (3 H, d, J = 8.5 Hz, C3-CH_3), 2.03 (1 H, br s, H8a), 2.16 (1 H, dt, J = 11.5, 4.5 Hz, H4a), 2.65 (1 H, m), 3.79 (1 H, br s, H8), 5.31 (1 H, br d, J = 10.1 Hz, H1), 5.56 (1 H, ddd, J = 10.1, 6.6, 3.3 Hz, H2), 9.29 (1 H, s, CHO).

Anal. Calcd for $C_{19}H_{34}O_3Si$: C, 70.75; H, 10.67. Found: C, 70.82; H, 10.63.

B. Thermal Cyclization. A solution of 17 mg (0.052 mmol) of trienal **1d** in 6 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 155 °C in an oil bath for 24 h. The tube was cooled at room temperature and opened, solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 2% EtOAc in hexanes followed by 10% EtOAc in hexanes which afforded 16 mg (94%) of a colorless oil determined to be a 27:27:13:33 mixture of diastereomers **2d**/**3d**/**4d**/**5d** by glass capillary GC analysis.

Cyclization of Trienoate 1e. A solution of 64 mg (0.18 mmol) of trienoate **1e** in 5 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated at 150 °C in an oil bath for 16 h. The tube was cooled and opened, and solvent was removed at reduced pressure. The resulting residue was chromatographed on silica gel by eluting with 1% EtOAc in hexanes to afford 46 mg (72%) of a colorless oil determined to be a 16:9:24:51 mixture of diastereomers **2e**, **3e**, **4e**, and **5e** by glass capillary GC analysis. The major component of this mixture was identified through comparison of the ^1H NMR spectrum with the spectrum of pure **5e** provided by Prof. Roush. Further elution afforded 18 mg (28% of starting trienoate. Reduction of the bicyclic ester mixture with $LiAlH_4$ followed by Swern oxidation and chromatography afforded a 16:9:24:51 mixture of diastereomers **2d**, **3d**, **4d**, and **5d** as determined by glass capillary GC analysis.

Cyclizations of Trienal 1f. A. Lewis Acid Cyclization. To a stirred, cooled (−78 °C) solution of 29 mg (0.15 mmol) of trienal **1f** (azeotropically dried with benzene) in 2 mL of CH_2Cl_2 was added 0.15 mL (0.15 mmol) of 1 M Me_2AlCl in hexanes. After being stirred for 1 h at −78 °C, the mixture was warmed to −15 °C for 18 h and quenched with aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 2% EtOAc in hexanes to afford 17.5 mg (61%) of cyclized product **2f** determined to be a single isomer by glass capillary GC analysis: IR (film) ν 3000, 2900, 2840, 2670, 1720, 1440, 1380 cm^{-1}; ^1H NMR (300 MHz) δ 0.74 (3 H, d, J = 6.2 Hz, C5-CH_3), 1.05 (3 H, s, C4-CH_3), 1.90–1.10 (9 H, m), 2.17 (2 H, br d, J = 18.5 Hz, H3α, H8a), 5.45 (1 H, br d, J = 9.9 Hz, H1), 5.60–5.50 (1 H, m, H2), 9.45 (1 H, s, CHO). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.96; H, 10.57. Further elution afforded 2 mg (7%) of starting trienal.

B. Thermal Cyclization. A solution of 22 mg (0.11 mmol) of trienal **1f** in 10 mL of toluene containing a single crystal of BHT was placed in a thick-wall tube and degassed. The tube was sealed and heated in an oil bath at 170 °C for 72 h. The tube was cooled to room temperature and opened, solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 2% EtOAc in hexanes to afford 7 mg (32%) of cyclized product determined to be a single isomer by glass capillary GC analysis. Further elution afforded 2 mg (9%) of starting trienal.

Cyclizations of Trienal 1g. A. Lewis Acid Cyclization. To a stirred, cooled (−78 °C) solution of 32 mg (0.10 mmol) of trienal **1g** (azeotropically dried with benzene) in 1.5 mL of CH_2Cl_2 was added 0.10 mL (0.10 mmol) of 1.0 M Me_2AlCl in hexanes. The mixture was stirred for 1 h at −78 °C, warmed to −15 °C, and stirred an additional 9 h. The mixture was quenched by the rapid addition of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and solvent was removed at reduced pressure. The resulting residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 30 mg (91%) of a pale yellow oil, which was determined to be a 9:1 mixture of 8*S*/8*R* epimers (**2g** and 8-*epi*-**2g**) by glass capillary GC: IR (film) ν 3025, 2900, 1725, 1465, 1290, 1080 cm^{-1}; ^1H NMR (400 MHz) δ 0.73 (3 H, d, J = 6.6 Hz, $CHCH_3$), 1.01 (3 H, d, J = 6.1 Hz, $CHCH_3$), 1.06 (3 H, s, C4-CH_3), 1.24–1.80 and 2.16–2.47 (8 H, m), 3.23 (1 H, dd, J = 10.7, 5.7 Hz, H8), 4.51 (AB q, J_{AB} = 11.4 Hz, $\Delta\nu$ = 79.5 Hz, OCH_2Ph), 5.63 (1 H, br d, J = 10.1 Hz, H2), 6.01 (1 H, ddd, J = 10.1, 3.0, 1.2 Hz, H1), 7.22–7.38 (5 H, m, aryl H), 9.46 (1 H, s, CHO); $[\alpha]_D$ +88.8° (c 1.69, CH_2Cl_2). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.63; H, 9.11.

B. Thermal Cyclization. A solution of 15 mg (0.048 mmol) of trienal **1g** in 5 mL of toluene containing a single BHT crystal was placed in a thick-wall tube and degassed. The tube was sealed and placed in a 155 °C oil bath for 24 h. The cooled tube was opened, and solvent was removed at reduced pressure. The resulting residue was chromatographed on silica gel by eluting with 3% EtOAc in hexanes to afford 14 mg (93%) of **2g** as a pale yellow oil.

Methyl (*E*,*E*)-2-Methyl-7-hydroxyundeca-2,8,10-trienoate (8). To a stirred, cooled (0 °C) solution of 30 mL of 5% aqueous oxalic acid in 30 mL of THF was added slowly a solution of 3.86 g (16.9 mmol) of (*E*)-5-hydroxy-6,8-nonadienal diethyl acetal (**6**)[1d] in 15 mL of THF. The solution was stirred for 24 h at room temperature under argon, poured into 1:1 CH_2Cl_2–saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over anhydrous Na_2CO_3–Na_2SO_4. Solvent was removed at reduced pressure. The crude lactol product was dissolved in 40 mL of CH_2Cl_2 and cooled to 0 °C, and 5.90 g (16.9 mmol) of methyl α-(triphenylphosphoranylidene)propionate was added. The mixture was warmed slowly to room temperature while being stirred for 12 h. Solvent was removed at reduced pressure and the resulting residue was chromatographed on triethylamine-deactivated silica gel eluting with 15% EtOAc in hexanes to afford 3.10 g (81%) of trienoate **8**: IR (film) ν 3400, 2925, 1710, 1440, 1270, 1010 cm^{-1}; ^1H NMR (300 MHz) δ 1.54 (4 H, m, H5 and H6), 1.80 (3 H, s, vinyl CH_3), 2.17 (2 H, m, H4), 3.71 (3 H, s, CO_2CH_3), 4.13 (1 H, br s, H7), 5.09 (1 H, d, J = 9.4 Hz, H11 cis), 5.20 (1 H, d, J = 16.3 Hz, H11 trans), 5.67 (1 H, dd, J = 7.7, 16.3 Hz, H8), 6.19 (1 H, dd, J = 9.4, 16.3 Hz, H9), 6.30 (1 H, ddd, J = 9.4, 9.4, 16.3 Hz, H10), 6.71 (1 H, t, J = 7.7 Hz, H3). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.64; H, 9.02.

Methyl (*E*,*E*)-2-Methyl-7-(methoxymethoxy)undeca-2,8,10-trienoate (9). To a stirred, cooled (0 °C) solution of 1.68 g (7.5 mmol) of alcohol **8** in 25 mL of CH_2Cl_2 was added 848 mg (10.5 mmol) of chloromethyl methyl ether followed by 1.41 g (10.9 mmol) of *N*,*N*-diisopropylethylamine. The mixture was warmed slowly to room temperature while being stirred for 36 h, and then it was washed with 3% aqueous HCl. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 1.31 g (65%) of methoxymethyl ether **9**: IR (film) ν 2925, 1710, 1440, 1265, 1100, 1050 cm^{-1}; ^1H NMR (300 MHz) δ 1.56 (4 H, m, H5 and H6), 1.80 (3 H, s, vinyl CH_3), 2.17 (2 H, m, H4), 3.34 (3 H, s, OCH_2OCH_3), 3.71 (3 H, s, CO_2CH_3), 4.03 (1 H, m, H7), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 5.08 (1 H, d, J = 9.4 Hz, H11 cis), 5.20 (1 H, d, J = 16.3 Hz, H11 trans), 5.49 (1 H, dd, J = 9.4, 16.3 Hz, H8), 6.16 (1 H, dd, J = 9.4, 16.3 Hz, H9), 6.31 (1 H, ddd, J = 9.4, 9.4, 16.3 Hz, H10), 6.87 (1 H, t, J = 7.7 Hz, H3). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.47; H, 8.97.

(*E*,*E*)-2-Methyl-7-(methoxymethoxy)undeca-2,8,10-trien-1-ol (10). To a stirred, cooled (−78 °C) solution of 460 mg (1.7

mmol) of ester **9** in 17 mL of Et_2O was added 3.8 mL (3.8 mmol) of 1.0 M DIBAH in CH_2Cl_2 dropwise. The mixture was stirred for 15 min, quenched with methanol, and warmed to 0 °C, and 10 mL of saturated aqueous potassium sodium tartrate was added. The mixture was warmed to room temperature, stirred for 1 h, and extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure to afford 405 mg (99%) of alcohol **10**: IR (film) ν 3400, 2925, 1445, 1150, 1030 cm^{-1}; ^1H NMR (300 MHz) δ 1.46 (4 H, m, H5 and H6), 1.63 (3 H, s, vinyl CH_3), 2.03 (2 H, m, H4), 3.43 (3 H, s, OCH_2OCH_3), 4.00 (3 H, m, H7 and H1), 4.59 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 5.07 (1 H, d, J = 9.4 Hz, H11 cis), 5.19 (1 H, d, J = 16.3 Hz, H11 trans), 5.36 (1 H, t, J = 7.7 Hz, H3), 5.49 (1 H, dd, J = 9.4, 16.3 Hz, H8), 6.14 (1 H, dd, J = 9.4, 16.3 Hz, H9), 6.30 (1 H, ddd, J = 9.4, 9.4, 16.3 Hz, H10). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.88; H, 10.11.

5-[(*tert*-Butyldimethylsilyl)oxy]pentanal (11). To a stirred, cooled (0 °C) solution of 12.0 g (115.2 mmol) of 1,5-pentanediol in 60 mL of 7:1 CH_2Cl_2–DMF was added a catalytic amount of DMAP followed by 5.8 g (57.4 mmol) of triethylamine. After 5 min, 4.3 g (28.7 mmol) of *tert*-butyldimethylchlorosilane in 10 mL of CH_2Cl_2 was added over 1.5 h. The mixture was warmed to room temperature, stirred for 1 h, and poured into 1:1 Et_2O–hexane. The organic layer was washed with water (2×) and brine and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with hexane followed by 50% Et_2O in hexanes to afford 5.5 g (87%) of monoprotected alcohol as a colorless oil: IR (film) ν 3350, 2950, 1475, 1270, 1110 cm^{-1}; ^1H NMR (90 MHz) δ 3.58 (4 H, m, H1 and H5), 1.70–1.10 (6 H, m, H2, H3 and H4), 0.85 (9 H, s, $SiC(CH_3)_3$), 0.03 (6 H, s, $Si(CH_3)_2$). Anal. Calcd for $C_{11}H_{26}O_2Si$: C, 60.49; H, 12.00. Found: C, 60.57; H, 12.03.

To a stirred, cooled (−78 °C) solution of 2.33 g (18.3 mmol) of oxalyl chloride in 30 mL of CH_2Cl_2 was added 2.86 g (36.6 mmol) of Me_2SO in 5 mL of CH_2Cl_2 dropwise. The mixture was stirred for 5 min, and 2.65 g (12.1 mmol) of the above described alcohol in 10 mL of CH_2Cl_2 was added over a 5-min period. After 30 min, 6.1 g (60.3 mmol) of triethylamine was added. The mixture was warmed to room temperature and washed twice with water. The combined aqueous layers were extracted with CH_2Cl_2, and the combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel eluting with 20% Et_2O in hexanes to afford 2.44 g (93%) of aldehyde **11** as a pale yellow oil: IR (film) ν 2950, 1730, 1470, 1270, 1015 cm^{-1}; ^1H NMR (90 MHz) δ 0.05 (6 H, s, $Si(CH_3)_2$), 0.92 (9 H, s, $SiC(CH_3)_3$), 1.35–1.92 (4 H, m, H3 and H4), 2.48 (2 H, t, J = 6.0 Hz, H2), 3.62 (2 H, t, J = 6.0 Hz, H5), 9.78 (1 H, s, CHO). Anal. Calcd for $C_{11}H_{24}O_2$: C, 61.06; H, 11.18. Found: C, 61.15; H, 11.21.

1-[(*tert*-Butyldimethylsilyl)oxy]non-8-en-6-yn-5-ol (12). To a stirred, cooled (−78 °C) solution of 1.2 mL (9.0 mmol) of a 50% xylene solution of vinylacetylene in 20 mL of THF was added 6.0 mL (9.0 mmol) of 1.5 M butyllithium in hexanes. The mixture was stirred for 15 min and 1.17 g (5.4 mmol) of aldehyde **11** was added dropwise. After being stirred for 1 h, the mixture was poured into saturated aqueous sodium bicarbonate and extracted with Et_2O. The combined organic layers were dried over anhydrous K_2CO_3–Na_2SO_4. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes followed by 15% EtOAc in hexanes to afford 1.26 g (87%) of alcohol **12** as a pale yellow oil: IR (film) ν 3350, 2925, 1465, 1260, 1110 cm^{-1}; ^1H NMR (90 MHz) δ 0.05 (6 H, s, $Si(CH_3)_2$), 0.90 (9 H, s, $SiC(CH_3)_3$), 1.95–1.40 (6 H, m, H2, H3, and H4), 3.66 (2 H, t, J = 6.0 Hz, H1), 4.53 (1 H, t, J = 6.0 Hz, H5), 6.03–5.38 (3 H, m, H8 and H9). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.52. Found: C, 66.92; H, 10.59.

(*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-7-iodo-6,8-nonadien-5-ol (13). To a stirred, cooled (0 °C) solution of 1.6 mL (5.44 mmol) of 3.4 M Red-Al in toluene diluted with 3 mL of Et_2O was added 845 mg (3.14 mmol) of propargylic alcohol **12** in 3 mL of Et_2O dropwise. After 1 h, excess Red-Al was quenched with 1 mL of anhydrous ethyl acetate. The mixture was cooled to −78 °C, and 997 mg (3.93 mmol) of iodine in 4 mL of THF was added dropwise. The mixture was warmed to room temperature while being stirred for 1 h, poured into saturated aqueous potassium sodium tartrate, and extracted with Et_2O. The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ and brine and dried over anhydrous K_2CO_3–Na_2SO_4. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 20% Et_2O in hexanes to afford 1.10 g (88%) of vinyl iodide **13** as a pale yellow liquid: IR (film) ν 3350, 2925, 1465, 1260, 1110 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (6 H, s, $Si(CH_3)_2$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.73–1.31 (6 H, m, H2, H3, and H4), 1.92 (1 H, br s, OH), 3.59 (2 H, t, J = 6.1 Hz, H1), 4.54 (1 H, m, H5), 5.26 (1 H, d, J = 9.4 Hz, H9 cis), 5.49 (1 H, d, J = 16.3 Hz, H9 trans), 6.00–5.91 (2 H, m, H6 and H8). Anal. Calcd for $C_{15}H_{29}IO_2Si$: C, 45.45; H, 7.38. Found: C, 45.52; H, 7.39.

(*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5-(methoxymethoxy)-7-iodo-6,8-nonadiene (14). To a stirred, cooled (0 °C) solution of 350 mg (0.91 mmol) of dienol **13** in 1 mL of CH_2Cl_2 was added 191 mg (2.37 mmol) of chloromethyl methyl ether followed by 593 mg (4.59 mmol) of *N,N*-diisopropylethylamine. The mixture was warmed slowly to room temperature while stirring for 18 h, and then it was poured into 3% aqueous HCl and extracted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 10% Et_2O in hexanes to afford 353 mg (91%) of diene **14** as a pale yellow liquid: IR (film) ν 2925, 1470, 1260, 1160, 1110, 1040 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (6 H, s, $Si(CH_3)_2$), 0.87 (9 H, s, $SiC(CH_3)_3$), 1.73–1.33 (6 H, m, H2, H3 and H4), 3.37 (3 H, s, OCH_2OCH_3), 3.59 (3 H, t, J = 6.1 Hz, H1 and H5), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 33.4 Hz, OCH_2OCH_3), 5.26 (1 H, d, J = 9.4 Hz, H9 cis), 5.47 (1 H, d, J = 16.3 Hz, H9 trans), 5.86 (1 H, d, J = 10.2 Hz, H6), 5.97 (1 H, dd, J = 9.4, 16.3 Hz, H8). Anal. Calcd for $C_{17}H_{33}IO_3Si$: C, 46.36; H, 7.55. Found: C, 46.42; H, 7.58.

(*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-5-(methoxymethoxy)-7-(trimethylsilyl)-6,8-nonadiene (15). To a stirred, cooled (−78 °C) solution of 252 mg (0.57 mmol) of vinyl iodide **14** in 5 mL of Et_2O was added 0.7 mL (1.19 mmol) of 1.7 M *tert*-butyllithium in pentane. The mixture was stirred for 15 min, and 1.5 mL (1.5 mmol) of 1.0 M chlorotrimethylsilane in THF was added dropwise. The mixture was stirred for 1 h, poured into brine, and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 2% EtOAc in hexanes to afford 163 mg (74%) of vinyl silane **15** as a pale yellow liquid: IR (film) ν 2940, 1470, 1260, 1160, 1110, 1050 cm^{-1}; ^1H NMR (300 MHz) δ 0.02 (6 H, s, $Si(CH_3)_2$), 0.18 (9 H, s, $Si(CH_3)_3$), 0.87 (9 H, s, $SiC(CH_3)_3$), 1.69–1.29 (6 H, m, H2, H3 and H4), 3.34 (3 H, s, OCH_2OCH_3), 3.60 (2 H, t, J = 6.2 Hz, H1), 4.29 (1 H, m, H5), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 4.92 (1 H, d, J = 10.6 Hz, H9 cis), 5.13 (1 H, d, J = 17.2 Hz, H9 trans), 5.97 (1 H, d, J = 9.8 Hz, H6), 6.36 (1 H, dd, J = 10.6, 17.2 Hz, H8). Anal. Calcd for $C_{20}H_{42}O_3Si_2$: C, 62.12; H, 10.95. Found: C, 62.27; H, 11.00.

(*Z*)-5-(Methoxymethoxy)-7-(trimethylsilyl)-6,8-nonadien-1-ol (16). To a stirred, cooled (0 °C) solution of 688 mg (1.78 mmol) of silyl ether **15** in 2 mL of THF was added 5.3 mL (5.3 mmol) of 1.0 M tetrabutylammonium fluoride in THF. The mixture was allowed to warm slowly while being stirred for 1.5 h, poured into water, and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, and solvent was removed at reduced pressure. The resulting residue was chromatographed on silica gel by eluting with 10% EtOAc in hexanes to afford 451 mg (93%) of alcohol **16** as a colorless oil: IR (film) ν 3350, 2925, 1440, 1260, 1160, 1045 cm^{-1}; ^1H NMR (300 MHz) δ 0.16 (9 H, s, $Si(CH_3)_3$), 1.72–1.16 (6 H, m, H2, H3 and H4), 3.34 (3 H, s, OCH_2OCH_3), 3.64 (2 H, t, J = 7.1 Hz, H1), 4.30 (1 H, m, H5), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 4.90 (1 H, d, J = 9.4 Hz, H9 cis), 5.10 (1 H, d, J = 16.3 Hz, H9 trans), 5.97 (1 H, d, J = 9.7 Hz, H6), 6.34 (1 H, dd, J = 9.4, 16.3 Hz, H8). Anal. Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.81; H, 10.42.

(*Z*)-5-(Methoxymethoxy)-7-(trimethylsilyl)-6,8-nonadienal (17). To a stirred, cooled (−78 °C) solution of 291 mg (2.29 mmol) of oxalyl chloride in 4 mL of CH_2Cl_2 was added 363 mg (4.64 mmol) of Me_2SO. The mixture was stirred for 5 min, and 434 mg (1.59 mmol) of alcohol **16** in 2 mL of CH_2Cl_2 was added dropwise. After 10 min, 798 mg (7.89 mmol) of triethylamine was

added. The mixture was warmed to room temperature, poured into water, and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 5% EtOAc in hexanes to afford 365 mg (85%) of aldehyde **17** as a pale yellow oil: IR (film) ν 2940, 1725, 1460, 1415, 1260, 1160, 1100, 1040 cm^{-1}; ^1H NMR (300 MHz) δ 0.17 (9 H, s, $Si(CH_3)_3$), 1.91–1.37 (4 H, m, H3 and H4), 2.47 (2 H, t, J = 7.2 Hz, H2), 3.34 (3 H, s, OCH_2OCH_3), 4.30 (1 H, m, H5), 4.56 (AB q, J_{AB} = 7.1 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 4.91 (1 H, d, J = 9.1 Hz, H9 cis), 5.10 (1 H, d, J = 17.2 Hz, H9 trans), 5.96 (1 H, d, J = 9.1 Hz, H6), 6.30 (1 H, dd, J = 9.1, 17.2 Hz, H8), 9.66 (1 H, s, CHO). Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 62.12; H, 9.69.

Methyl (*E*,*Z*)-2-Methyl-7-(methoxymethoxy)-9-(trimethylsilyl)-2,8,10-undecatrienoate (18). To a stirred, cooled (0 °C) solution of 344 mg (1.27 mmol) of aldehyde **17** in 4 mL of CH_2Cl_2 was added 598 mg (1.72 mmol) of methyl α-(triphenylphosphoranylidene)propionate. The mixture was warmed to room temperature while stirring for 40 h. Solvent was removed at reduced pressure, and the residue was dissolved in a minimal amount of benzene and chromatographed on silica gel by eluting with 3% EtOAc in hexanes to afford 420 mg (97%) of trienoate **18** as a colorless oil: IR (film) ν 2940, 1620, 1440, 1260, 1160, 1100, 1040 cm^{-1}; ^1H NMR (300 MHz) δ 0.18 (9 H, s, $Si(CH_3)_3$), 1.72–1.37 (4 H, m, H5 and H6), 1.81 (3 H, s, vinyl CH_3), 2.19 (2 H, br q, J = 6.7 Hz, H4), 3.33 (3 H, s, OCH_2OCH_3), 3.71 (3 H, s, CO_2CH_3), 4.30 (1 H, m, H7), 4.56 (AB q, J_{AB} = 6.8 Hz, $\Delta\nu$ = 55.7 Hz, OCH_2OCH_3), 4.92 (1 H, d, J = 10.6 Hz, H11 cis), 5.11 (1 H, d, J = 17.1 Hz, H11 trans), 5.97 (1 H, d, J = 10.3 Hz, H8), 6.37 (1 H, dd, J = 10.6, 17.1 Hz, H10), 6.73 (1 H, t, J = 6.0 Hz, H3). Anal. Calcd for $C_{18}H_{32}O_4Si$: C, 63.49; H, 9.47. Found: C, 63.61; H, 9.53.

(*E*,*Z*)-2-Methyl-7-(methoxymethoxy)-9-(trimethylsilyl)-2,8,10-undecatrien-1-ol (19). To a stirred, cooled (−78 °C) solution of 410 mg (1.2 mmol) of ester **18** in 12 mL of Et_2O was added 2.5 mL (2.5 mmol) of 1.0 M DIBAH in hexanes dropwise. The mixture was stirred for 15 min, quenched with methanol, and warmed to 0 °C, and saturated aqueous potassium sodium tartrate was added. The mixture was stirred for 30 min at room temperature and extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure to afford 366 mg (98%) of alcohol **19** as a colorless oil: IR (film) ν 3375, 2940, 1450, 1260, 1135, 1100, 1040 cm^{-1}; ^1H NMR (300 MHz) δ 0.19 (9 H, s, $Si(CH_3)_3$), 1.60–1.20 (4 H, m, H5 and H6), 1.66 (3 H, s, vinyl CH_3), 2.06 (2 H, br q, J = 7.1 Hz, H4), 3.34 (3 H, s, OCH_2OCH_3), 3.99 (2 H, d, J = 7.7 Hz, H1), 4.30 (1 H, m, H7), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 55.2 Hz, OCH_2OCH_3), 4.92 (1 H, d, J = 9.4 Hz, H11 cis), 5.11 (1 H, d, J = 16.3 Hz, H11 trans), 5.40 (1 H, t, J = 7.7 Hz, H3), 5.97 (1 H, d, J = 9.4 Hz, H8), 6.37 (1 H, dd, J = 9.4, 16.3 Hz, H10). Anal. Calcd for $C_{17}H_{32}O_3Si$: C, 65.33; H, 10.32. Found: C, 65.26; H, 10.33.

Methyl (*E*,*E*,*E*)-2-Methyl-7-(methoxymethoxy)dodeca-2,8,10-trienoate (21). To a stirred, cooled (0 °C) solution of 44 mg (0.18 mmol) of alcohol **20** in 0.5 mL of CH_2Cl_2 was added 42 mg (0.52 mmol) of chloromethyl methyl ether followed by 111 mg (0.86 mmol) of *N*,*N*-diisopropylethylamine. The mixture was warmed slowly to room temperature while being stirred for 18 h, diluted with CH_2Cl_2, and washed with 3% aqueous HCl. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 2% EtOAc in hexanes to afford 43 mg (85%) of methoxymethyl ether **21**: IR (film) ν 2925, 1710, 1430, 1260, 1150, 1100, 1030 cm^{-1}; ^1H NMR (300 MHz) δ 1.57 (4 H, m, H5 and H6), 1.74 (3 H, d, J = 6.9 Hz, vinyl CH_3), 1.80 (3 H, s, vinyl CH_3), 2.20 (2 H, m, H4), 3.34 (3 H, s, OCH_2OCH_3), 3.72 (3 H, s, CO_2CH_3), 3.97 (1 H, m, H7), 4.57 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 63.9 Hz, OCH_2OCH_3), 5.31 (1 H, dd, J = 9.4, 16.3 Hz, H8), 5.74–5.63 (1 H, m, H9), 6.17–5.97 (2 H, m, H10 and H11), 6.72 (1 H, t, J = 7.7 Hz, H3). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.15; H, 9.28.

(*E*,*E*,*E*)-2-Methyl-7-(methoxymethoxy)dodeca-2,8,10-trien-1-ol (23). To a stirred, cooled (−78 °C) solution of 1.13 g (4.0 mmol) of trienoate **21** in 40 mL of Et_2O was added 8.2 mL (8.2 mmol) of 1.0 M DIBAH in hexanes dropwise. The mixture was stirred for 15 min, quenched with methanol, and warmed to 0 °C, and 20 mL of saturated aqueous potassium sodium tartrate was carefully added. The mixture was stirred for 1 h at room temperature and extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure to afford 997 mg (98%) of alcohol **23**: IR (film) ν 3375, 2900, 1450, 1210, 1150, 1050 cm^{-1}; ^1H NMR (300 MHz) δ 1.43 (4 H, m, H5 and H6), 1.66 (3 H, s, vinyl CH_3), 1.74 (3 H, d, J = 6.9 Hz, vinyl CH_3), 2.04 (2 H, m, H4), 3.34 (3 H, s, OCH_2OCH_3), 3.97 (3 H, br s, H1 and H7), 4.59 (AB q, J_{AB} = 7.7 Hz, $\Delta\nu$ = 63.9 Hz, OCH_2OCH_3), 5.43–5.27 (2 H, m, H8 and H3), 5.74–5.61 (1 H, m, H9), 6.17–5.97 (2 H, m, H10 and H11). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.72; H, 10.34.

(2*S*,4*S*)-2,4-Dimethylpentane-1,5-diol (26). The (*S*)-1-phenylethylamine salt of (2*S*,4*S*)-2,4-dimethylglutaric acid[11] (5.44 g, 19.4 mmol) was added portionwise under nitrogen to a suspension of lithium aluminum hydride (2.9 g, 77 mmol) in 50 mL of THF at 0 °C. After the mixture was stirred at room temperature for 24 h, it was quenched with H_2O (2.9 mL), 15% NaOH (2.9 mL), and H_2O (8.7 mL). The white salts were filtered and washed with EtOAc (50 mL). The combined filtrates were concentrated under reduced pressure, and the oily residue (5.01 g) was taken up in EtOAc (100 mL), washed with 10% HCl (2 × 10 mL), and dried over $MgSO_4$. Removal of solvent left 2.48 g (97%) of the crude diol. Flash chromatography on a 2.5 × 20 cm column of silica gel, eluting with 10% EtOAc–hexane and then 40% EtOAc–hexane, gave 2.10 g (82%) of the diol **26**: $[\alpha]_D$ −34.3° (*c* 2.36, MeOH); IR (film) ν 3310, 2950, 2915, 2860, 1470, 1390 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 (6 H, d, J = 6.7 Hz, $CHCH_3$), 1.19 (2 H, t, J = 6.9 Hz, CH_2), 1.73 (2 H, 6 lines, CH_3CH), 2.08 (2 H, br s, OH), 3.43 (4 H, d, J = 6.3 Hz, CH_2OH). Satisfactory analytical values could not be obtained (3 trials).

(2*S*,4*S*)-5-[(*tert*-Butyldimethylsilyl)oxy]-2,4-dimethylpentan-1-ol (27). A solution of 1.86 g (14.1 mmol) of (2*S*,4*S*)-2,4-dimethylpentane-1,5-diol (**26**), 3.9 mL (28 mmol) of triethylamine, and 0.05 g (0.4 mmol) of DMAP in 12 mL of CH_2Cl_2 and 3 mL of DMF at 0 °C was treated dropwise with 2.34 g (15.5 mmol) of *tert*-butyldimethylsilyl chloride in 6 mL of CH_2Cl_2. The mixture was stirred at room temperature for 10 h, then was diluted with 100 mL of ether, washed with H_2O (3 × 5 mL), and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography on a 2.5 × 20 cm column of silica gel, eluting with 15% EtOAc–hexane, provided 1.70 g (49%) of the silyl ether **27**: $[\alpha]_D$ −19.2° (*c* 4.68, MeOH): IR (film) ν 3325, 2950, 2850, 1470 cm^{-1}; ^1H NMR (300 MHz) δ 0.02 (6 H, s, $Si(CH_3)_2$), 0.84 (3 H, d, J = 6.7 Hz, $CHCH_3$), 0.87 (3 H, d, J = 6.7 Hz, $CHCH_3$), 0.88 (9 H, s, $SiC(CH_3)_3$), 1.15 (2 H, 13 lines, CH_2), 1.58 (1 H, br s, OH), 1.72 (2 H, m, $CHCH_3$), 3.37–3.49 (4 H, m, OCH_2). Anal. Calcd for $C_{13}H_{30}O_2Si$: C, 63.35; H, 12.27. Found: C, 63.28; H, 12.31.

(2*S*,4*S*)-5-[(*tert*-Butyldimethylsilyl)oxy]-2,4-dimethylpentanal (28). The procedure of Swern[12] was followed. A solution of 0.36 mL (4.1 mmol) of oxalyl chloride in 5 mL of CH_2Cl_2 was cooled to −78 °C, and 0.59 mL (8.3 mmol) of Me_2SO in 0.5 mL of CH_2Cl_2 was added dropwise. Alcohol **27** (0.51 g, 2.1 mmol) in 2.5 mL of CH_2Cl_2 was then added dropwise. The mixture was stirred at −78 °C for 30 min, and then 2.6 mL (18 mmol) of Et_3N was added. After 15 min, the cold bath was removed, and when the suspension reached ca. 10 °C, H_2O (5 mL) was added. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were washed with brine and then dried over anhydrous $MgSO_4$. Removal of solvent under reduced pressure followed by chromatography on a 1.5 × 20 cm column with hexane and then 5% ether–hexane as eluant afforded 0.46 g (91%) of the aldehyde **28**: $[\alpha]_D$ +3.40° (*c* 3.65, CH_2Cl_2); IR (film) ν 2950, 2850, 2690, 1725, 1465 cm^{-1}; ^1H NMR (300 MHz) δ 0.01 (6 H, s, $Si(CH_3)_2$), 0.85 (3 H, d, J = 6.5 Hz, $CHCH_3$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.05 (3 H, d, J = 6.9 Hz, $CHCH_3$), 1.43 (2 H, 14 lines, CH_2), 1.68 (1 H, m, $CHCH_3$), 2.40 (1 H, m, $OHCCHCH_3$), 3.39, 3.43 (2 H, AB of ABX, J_{AX} = 5.8 Hz, J_{BX} = 5.9 Hz, J_{AB} = 9.8 Hz, CH_2OTBS), 9.59 (1 H, d, J = 2.0 Hz, CHO). Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55. Found: C, 63.79; H, 11.44.

(5*R*,6*S*,8*S*)- and (5*S*,6*S*,8*S*)-9-[(*tert*-Butyldimethylsilyl)oxy]-6,8-dimethylnon-1-en-3-yn-5-ol (29). To a solution of 2.6 mL (20 mmol) of a 50% solution of 1-buten-3-yne in xylenes in 2 mL of THF at −78 °C was added 3.2 mL (8.4 mmol) of 2.6

M *n*-BuLi in hexanes. After 25 min, aldehyde **28** (818 mg, 3.35 mmol) in 1.5 mL of THF was added dropwise, and the yellow solution was stirred at −78 °C for 1.5 h. The mixture was poured into saturated $NaHCO_3$ and extracted into ether (2 × 25 mL), and the combined organic phases were dried over $MgSO_4$. Removal of solvent and then chromatography on a 1.5 × 20 cm column of silica gel, eluting with hexane, 5% ether–hexane, and then 15% ether–hexane, provided 887 mg (90%) of the diastereomeric alcohols **29** as a roughly 1:1 mixture by glass capillary GC: $[\alpha]_D$ −11.6° (*c* 1.68, CH_2Cl_2); IR (film) ν 3350, 2945, 2875, 2850, 1610, 1470 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (6 H, s, $Si(CH_3)_2$), 0.84 (3 H, d, J = 6.6 Hz, $CHCH_3$), 0.88 (9 H, s, $SiC(CH_3)_3$), 0.95 and 0.97 (3 H, d and d, J = 5.1 and 5.1 Hz, $CHOHCHCH_3$), 1.24 and 1.31 (2 H, m and m, CH_2), 1.58 (1 H, br s, OH), 1.69–2.02 (2 H, m, $CHCH_3$), 3.40 (2 H, d and d, J = 3.1 and 6.4 Hz, CH_2OTBS), 4.35 (1 H, m, $CHOH$), 5.45 (1 H, dd, J = 2.3, 10.9 Hz, cis H of $C{=}CH_2$), 5.61 (1 H, dd, J = 2.3, 17.5 Hz, trans H of $C{=}CH_2$), 5.75–5.85 (1 H, m, C=CH). Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 69.19; H, 11.06.

(6*S*,8*S*)-9-[(*tert*-Butyldimethylsilyl)oxy]-6,8-dimethylnon-1-en-3-yn-5-one (30). Swern's procedure[12] was followed, with diastereomeric alcohols **29** (639 mg, 2.17 mmol) being added at −78 °C to 0.38 mL (4.4 mmol) of oxalyl chloride and 0.622 mL (8.7 mmol) of Me_2SO in a total of 10 mL of CH_2Cl_2. The mixture was stirred for 30 min at −78 °C and Et_3N (2.7 mL, 20 mmol) was added. Extractive isolation and then chromatography on a 1.5 × 20 cm column of silica gel, eluting with hexane, 1.5% ether–hexane, and 5% ether–hexane, gave 577 mg (91%) of the ketone **30**: $[\alpha]_D$ −7.03° (*c* 2.36, CH_2Cl_2); IR (film) ν 2950, 2915, 2845, 2185, 1670, 1465 cm^{-1}; ^1H NMR (300 MHz) δ 0.01 (6 H, s, $Si(CH_3)_2$), 0.86 (3 H, d, J = 6.4 Hz, $CHCH_3$), 0.86 (9 H, s, $SiC(CH_3)_3$), 1.14 (3 H, d, J = 6.9 Hz, $CHCH_3$), 1.42–1.68 (3 H, 17 lines, $TBSOCH_2CHCH_2$), 2.62–2.69 (1 H, m, $C(O)CHCH_3$), 3.41 (2 H, d, J = 5.9 Hz, CH_2OTBS), 5.75–5.84 (1 H, m, C=CH), 5.90–5.93 (2 H, m, $C{=}CH_2$). Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.27; H, 10.27.

(5*S*,6*S*,8*S*)-9-[(*tert*-Butyldimethylsilyl)oxy]-6,8-dimethylnon-1-en-3-yn-5-ol (31). To a stirred, cooled (−78 °C) solution of 244 mg (0.83 mmol) of propargylic ketone **30** in 8 mL of THF was added 1.65 mL (1.65 mmol) of 1.0 M L-Selectride in THF dropwise. The mixture was stirred for 1 h and warmed to 0 °C, and 0.5 mL of water was added followed by 0.55 mL (1.65 mmol) of 3 M NaOH and 0.55 mL of 30% H_2O_2. After being stirred 10 h at room temperature, the mixture was poured into water and extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. Solvent was removed at reduced pressure, and the residue was chromatographed on silica gel by eluting with 3% EtOAc in hexanes to afford 197 mg (80%) of alcohol **31** as a pale yellow oil, which was determined to be a 91:9 mixture of 5*S*/5*R* alcohols by glass capillary gas chromatography: IR (film) ν 3350, 2950, 1465, 1390, 1260, 1100 cm^{-1}; ^1H NMR (300 MHz) δ 0.20 (6 H, s, $Si(CH_3)_2$), 0.84 (3 H, d, J = 6.6 Hz, $CHOHCHCH_3$), 0.88 (9 H, s, $SiC(CH_3)_3$), 0.97 (3 H, d, J = 6.6 Hz, CH_3CHCH_2OTBS), 1.20 and 1.32 (2 H, m and m, H7), 1.70 and 1.89 (2 H, m and m, CH_3CH), 3.39 (2 H, d, J = 6.4 Hz, H9), 4.36 (1 H, br s, H5), 5.47 (1 H, d, J = 11.0 Hz, H1 cis), 5.61 (1 H, d, J = 17.6 Hz, H1 trans), 5.80 (1 H, dd, J = 11.0, 17.6 Hz, H2); $[\alpha]_D$ −6.0° (*c* 1.33, CH_2Cl_2). Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.94; H, 10.94.

(3*E*)-(5*S*,6*S*,8*S*)-9-[(*tert*-Butyldimethylsilyl)oxy]-6,8-dimethyl-1,3-nonadien-5-ol (33). The propargylic alcohol **31** (449 mg, 1.53 mmol) in 5 mL of ether was cooled to 0 °C and 0.90 mL (3.1 mmol) of 3.4 M Red-Al in toluene was injected dropwise over 20 min. Stirring was continued for 1 h at room temperature. The mixture was quenched at 0 °C by dropwise addition of 2 mL of saturated Rochelle's salt solution and was then extracted into Et_2O. The combined extracts were dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography on a 1 × 15 cm column of silica gel with 10% ether–hexane as eluant afforded 357 mg (79%) of the alcohol **33**: $[\alpha]_D$ −6.11° (*c* 3.52, CH_2Cl_2); IR (film) ν 3350, 2950, 2910, 2850, 1610, 1465 cm^{-1}; ^1H NMR (300 MHz) δ 0.00 (6 H, s, $Si(CH_3)_2$), 0.80 (3 H, d, J = 5.1 Hz, $CHCH_3$), 0.82 (3 H, d, J = 5.2 Hz, $CHCH_3$), 0.85 (9 H, s, $SiC(CH_3)_3$), 1.15 (2 H, m, CH_2), 1.60–1.76 (2 H, m, CH_2OTBS), 3.92 (1 H, br m, $CHOH$), 5.04 (1 H, dd, J = 1.8, 9.2 Hz, cis H of $C{=}CH_2$), 5.16 (1 H, dd, J = 1.9, 16 Hz, trans H of $C{=}CH_2$), 5.67 (1 H, dd, J = 7.0, 15.1 Hz, C=CH), 6.14–6.37 (3 H, 11 lines, C=CH). Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.32; H, 11.51.

(3*E*)-(5*S*,6*S*,8*S*)-9-[(*tert*-Butyldimethylsilyl)oxy]-6,8-dimethyl-5-(benzyloxy)-1,3-nonadiene (34). Alcohol **33** (363 mg, 1.23 mmol) was dissolved in 1.2 mL of THF and a crystal of 1,10-phenanthroline was added. The solution was cooled to −78 °C, and 0.47 mL (1.2 mmol) of 2.6 M *n*-BuLi in hexanes was added, giving a dark brown solution at the endpoint. Benzyl bromide (0.19 mL, 1.6 mmol) and HMPA (0.43 mL, 2.5 mmol) were added within 5 min. The thick suspension was stirred at −78 °C for 5 min, then the cold bath was removed, and stirring was continued for 1 h. The clear yellow solution was poured into saturated $NaHCO_3$ and was extracted into ether. The organic phase was dried over $MgSO_4$, solvent was removed under reduced pressure, and the residue was chromatographed on a 1.5 × 20 cm column of silica gel, eluting with 1.5% ether–hexane to afford 387 mg (81%) of the benzyl ether **34**: $[\alpha]_D$ −13.0° (*c* 3.65, CH_2Cl_2); IR (film) ν 3075, 3025, 2950, 2850, 1610, 1470 cm^{-1}; ^1H NMR (300 MHz) δ 0.02 (6 H, s, $Si(CH_3)_2$), 0.82 and 0.86 (6 H, d and d, J = 6.4 and 6.0 Hz, $CHCH_3$), 0.87 (9 H, s, $SiC(CH_3)_3$), 1.10–1.25 (2 H, m, CH_2), 1.60–1.83 (2 H, m, $CHCH_3$), 3.37 (2 H, m, CH_2OTBS), 3.56 (1 H, m, CHOBn), 4.32 and 4.57 (2 H, AB q, J_{AB} = 12.0 Hz, OCH_2Ph), 5.09 (1 H, d, J = 10.1 Hz, cis H of $C{=}CH_2$), 5.20 (1 H, d, J = 15.3 Hz, trans H of $C{=}CH_2$), 5.56–5.64 (1 H, m, C=CH), 6.12–6.20 (1 H, m, C=CH), 6.31–6.43 (1 H, m, C=CH), 7.23–7.32 (5 H, m, aryl H). Anal. Calcd for $C_{24}H_{40}O_2Si$: C, 74.17; H, 10.37. Found: C, 74.28; H, 10.39.

(3*E*)-(2*S*,4*S*,5*S*)-2,4-Dimethyl-5-(benzyloxy)-6,8-nonadien-1-ol (35). To a solution of silyl ether **34** (307 mg, 0.799 mmol) in 0.8 mL of THF at 0 °C was added 1.6 mL (1.6 mmol) of 1 M tetrabutylammonium fluoride in THF. After 6 h at room temperature, the solution was partitioned between H_2O and ether. The organic phase was dried over $MgSO_4$, solvent was removed, and the residue was chromatographed on a 1.5 × 19 cm column of silica gel by eluting with 35% ether–hexane to afford 214 mg (99%) of the alcohol **35**: $[\alpha]_D$ −14.8° (*c* 2.10, CH_2Cl_2); IR (film) ν 3355, 3075, 3025, 2955, 2910, 2855, 1605, 1465 cm^{-1}; ^1H NMR (300 MHz) δ 0.85 (3 H, d, J = 6.8 Hz, $CHCH_3$), 0.86 (3 H, d, J = 6.7 Hz, $CHCH_3$), 1.10–1.35 (2 H, m, CH_2), 1.55 (1 H, br s, OH), 1.71 and 1.80 (2 H, m and m, $CHCH_3$), 3.42 (2 H, m, CH_2OH), 3.54 (1 H, m, CHOBn), 4.31 and 4.57 (2 H, AB q, J_{AB} = 12.0 Hz, OCH_2Ph), 5.10 (1 H, d, J = 10.0 Hz, cis H of $C{=}CH_2$), 5.21 (1 H, dd, J = 2.0 and 17.0 Hz, trans H of $C{=}CH_2$), 5.56–5.64 (1 H, m, C=CH), 6.13–6.21 (1 H, m, C=CH), 6.31–6.43 (1 H, m, C=CH), 7.23–7.35 (5 H, m, aryl H). Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.89; H, 9.61.

(3*E*)-(2*S*,4*S*,5*S*)-2,4-Dimethyl-5-(benzyloxy)-6,8-nonadienal (36). The alcohol **35** (204 mg, 0.745 mmol) was oxidized with 0.13 mL (1.5 mmol) of oxalyl chloride, 0.21 mL (3.0 mmol) of Me_2SO, and 0.93 mL (6.7 mmol) of triethylamine in a total of 5 mL of CH_2Cl_2 as described above.[12] Chromatography on a 1 × 15 cm column of silica gel with hexane and then 5% ether–hexane as eluant gave 165 mg (82%) of aldehyde **36**: $[\alpha]^{22}_D$ +7.87° (*c* 3.15, CH_2Cl_2); IR (film) ν 2950, 2900, 2850, 2700, 1720, 1605, 1460, 1075 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 (3 H, d, J = 6.9 Hz, CH_3CHCHO), 1.53 (2 H, m, CH_2), 1.81 (1 H, m, $CH_3CHCHOBn$), 2.39 (1 H, m, $CHCHO$), 3.56 (1 H, dd, J = 6.5 and 8.2 Hz, CHOBn), 4.29 and 4.56 (2 H, AB q, J_{AB} = 12.0 Hz, CH_2OBn), 5.11 (1 H, d, J = 9 Hz, cis H of $C{=}CH_2$), 5.22 (1 H, d, J = 17 Hz, trans H of $C{=}CH_2$), 5.58 (1 H, dd, J = 8.2, 15.3 Hz, C=CH), 6.19 (1 H, dd, J = 10.5, 15.2 Hz, C=CH), 6.31–6.43 (1 H, m, C=CH), 7.22–7.35 (5 H, m, aryl H), 9.57 (1 H, d, J = 2 Hz, CHO). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.16; H, 8.93.

(2*E*,8*E*)-(4*S*,6*S*,7*S*)-Methyl 2,4,6-Trimethyl-7-(benzyloxy)-2,8,10-undecatrienoate (37). To aldehyde **36** (90.2 mg, 0.332 mmol) in 1 mL of CH_2Cl_2 was added 231 mg (0.664 mmol) of methyl α-(triphenylphosphoranylidene)propionate in several portions at 0 °C. The mixture was stirred at room temperature for 3 days. Purification by chromatography on a 1 × 15 cm column of silica gel with 5% ether–hexane as eluant gave 110 mg (97%) of the ester **37**: $[\alpha]_D$ +24.1° (*c* 2.18, CH_2Cl_2); IR (film) ν 2950, 2910, 2860, 1715, 1650, 1605, 1460, 1440 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 (3 H, d, J = 6.8 Hz, $CHCH_3$), 0.94 (3 H, d, J = 6.6 Hz, $CHCH_3$), 1.07–1.20 (2 H, m), 1.47–1.63 (2 H, m), 1.77 (3 H, d, J = 1.4 Hz, vinyl CH_3), 2.56 (1 H, m), 3.55 (1 H, dd, J = 5.7, 8.3

Hz, CHOBn), 3.71 (3 H, s, CH_3CCO), 4.29 and 4.55 (2 H, AB q, J_{AB} = 12.0 Hz, CH_2OBn), 5.10 (1 H, d, J = 11.4 Hz, cis H of C=CH_2), 5.21 (1 H, d, J = 16.8 Hz, trans H of C=CH_2), 5.58 (1 H, dd, J = 8.3, 15.3 Hz, C=CH), 6.17 (1 H, dd, J = 10.5, 15.2 Hz, C=CH), 6.31–6.43 (1 H, m, C=CH), 6.50–6.58 (1 H, m, C=CH), 7.25–7.34 (5 H, m, aryl H). Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83. Found: C, 77.23; H, 8.84.

(2*E*,8*E*)-(4*S*,6*S*,7*S*)-2,4,6-Trimethyl-7-(benzyloxy)-2,8,10-undecatrien-1-ol (38). To a solution of 108 mg (0.316 mmol) of ester **37** in 5 mL of ether at −78 °C was added 0.83 mL (0.83 mmol) of 1 M DIBAH in hexanes dropwise over 5 min. Stirring was continued for 35 min at −78 °C, and the mixture was quenched with 1 mL of saturated Rochelle's salt solution, extracted into ether, and dried over $MgSO_4$. Chromatography on a 1 × 15 cm column of silica gel with 50% ether–hexane afforded the allylic alcohol **38** in quantitative yield: $[\alpha]^{22}_D$ −3.1° (*c* 2.67, CH_2Cl_2); IR (film) ν 3340, 2950, 2845, 2840, 1600, 1450, 1375 cm^{-1}; ^1H NMR (300 MHz) δ 0.87 and 0.88 (6 H, d and d, J = 6.9 and 6.6 Hz, $CHCH_3$), 1.01 and 1.41 (2 H, m), 1.29 (1 H, br s, OH), 1.59 (3 H, d, J = 1.4 Hz, vinyl CH_3), 1.79 (1 H, m), 2.45 (1 H, m), 3.59 (1 H, dd, J = 5.6, 8.2 Hz, CHOBn), 3.94 (2 H, br s, CH_2OH), 4.30 and 4.56 (2 H, AB q, J_{AB} = 12.1 Hz, OCH_2Ph), 5.08–5.24 (3 H, m, C=CH_2 and $HOCH_2C(CH_3)$=C*H*), 5.60 (1 H, dd, J = 8.3, 15.3 Hz, C=CH), 6.17 (1 H, dd, J = 10.5, 15.3 Hz, C=CH), 6.31–6.44 (1 H, m, C=CH), 7.23–7.34 (5 H, m, aryl H). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.34; H, 9.64.

(2*E*,8*E*)-(4*S*,6*S*,7*S*)-2,4,6-Trimethyl-7-(benzyloxy)-2,8,10-undecatrienal (1g). Trienol **38** (59 mg, 0.19 mmol) was oxidized by the method of Swern[12] with 40 μL (0.46 mmol) of oxalyl chloride, 50 μL (0.71 mmol) of Me_2SO, and 240 μL (1.7 mmol) of triethylamine in 2 mL of CH_2Cl_2 as described above. Purification by chromatography on a 1 × 10 cm column of silica gel with 10% ether–hexane as eluant gave 53 mg (89%) of the aldehyde **1g**: $[\alpha]_D$ −3.79° (*c* 2.72, CH_2Cl_2); IR (film) ν 2950, 2910, 2850, 2700, 1690, 1640, 1605, 1460 cm^{-1}; ^1H NMR (300 MHz) δ 0.88 (3 H, d, J = 6.8 Hz, $CHCH_3$), 0.99 (3 H, d, J = 6.6 Hz, $CHCH_3$), 1.10–1.24 (1 H, m), 1.55–1.72 (2 H, m), 1.67 (3 H, d, J = 1.3 Hz, vinyl CH_3), 2.77 (1 H, m), 3.54 (1 H, dd, J = 6.1, 8.2 Hz, CHOBn), 4.28 and 4.56 (2 H, AB q, J_{AB} = 12.1 Hz, OCH_2Ph), 5.11 (1 H, d, J = 11.5 Hz, cis H of C=CH_2), 5.22 (1 H, d, J = 16.7 Hz, trans H of C=CH_2), 5.58 (1 H, dd, J = 8.4, 15.3 Hz, C=CH), 6.12–6.40 (3 H, m), 7.24–7.31 (5 H, m, aryl H). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.65; H, 9.09.

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Inter- and Intramolecular Reactions of Nitrenes and Their Cyclic Isomers in the Photodecomposition of Some Substituted 2-Azidophenazines

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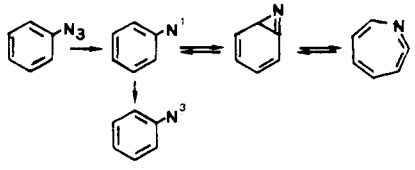
The photodecomposition of 2-azido-1-(3,5-dimethylpyrazolyl)phenazine (**1a**) and 2-azido-1-methoxyphenazine (**1b**) is investigated in benzene and ethanol and in the presence of acids or bases. This is a suitable model for the chemical characterization of nitrenes and their cyclic isomers (benzoazirines and dehydroazepines) formed under these conditions. In an unreactive medium, singlet nitrene from **1a** is trapped intramolecularly to yield the heteropentalene **2**, but in ethanol substitution of the azido group via excited azide and addition to the azirine to give the aziridine **6** (yielding the oxidation product **5** during workup) are observed. In the presence of acids phenazine imines **10** and **11** (undergoing hydrolysis to **8** and **9**) are obtained through the nitrenium cation. In bases, addition to the dehydroazepine takes place to give the ethoxyazepine **13**. In the case of **1b**, the dehydroazepine is trapped via an unprecedented cycloaddition with the azide (yielding **18**) or reacts with bases to yield the dimeric product **28**. Triplet nitrene reactions (inter- or intramolecular hydrogen abstraction, reaction with oxygen to yield the rearranged nitroso derivative **22**) are more important from **1b**. Substituent and solvent effects are discussed in connection with recent hypotheses on the equilibrium between different reactive species from the decomposition of azides.

Introduction

Photochemical decomposition of aromatic azides is a subject of active research in organic chemistry[1] as well as in applicative areas such as cross-linking of polymers[2] and photochemical labeling in biochemistry.[3]

Scheme I



The synthetic outcome of the photodecomposition of azides depends widely on the structure of the starting material and the conditions of the experiments, untractable "tars" accounting in several cases for a large portion of the

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