Palladium-Catalyzed Oxidative Cyclization of 1,5-Dienes. Influence of Different Substitution Patterns on the Regio- and Stereochemistry of the Reaction

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Oxidative cyclization of 1,5-dienes in acetic acid and in the presence of the Pd(II) regenerating catalyst system $Pd(OAc)_2/MnO_2/p$-benzoquinone has been shown to yield, depending on the structure of the 1,5-diene, acetoxyexomethylenecyclopentanes or acetoxyvinylcyclopentanes. 1,5-Dienes with substitutents in the 1- and/or 3-position show a high preference for formation of regioisomers obtained by acetate attack at the sterically least hindered double bond, but the products are usually mixtures of diastereomeric cis and trans cyclopentanes. *trans*-1-Phenyl-1,5-hexadienes react with complete stereoselectivity to yield exomethylenecyclopentanes with a single configuration of the exocyclic double bond. The oxidative cyclization method is synthetically useful, affording a large variety of cyclopentane systems.

Introduction

Mono- and bicyclic compounds are important substrates in organic and natural product chemistry. Due to their widespread occurrence in nature, cyclopentane derivatives have attracted much attention, and major efforts have been devoted to their synthesis.[1,2] Particularly useful methods for the construction of five-membered carbocycles are based on cycloaddition[3] and metal-catalyzed cyclization[4] strategies. A powerful example combining these methods is the trimethylene methane (TMM) cycloaddition reaction.[5]

Another approach to cyclic systems consists of submitting suitable, nonconjugated dienes to palladium(II)-catalyzed oxidation reactions.[6] One reaction which has been extensively studied is the palladium-mediated nucleophilic addition to norbornadiene[7] to yield organopalladium intramolecular coordination compounds.[8] The desired organic products can be liberated via carbonylation[9] and reductive[10] or oxidative[11] cleavage of the carbon–palladium bond. Although stoichiometric[12,13] with respect to palladium, these transformations have recently been applied to the synthesis of prostaglandine endoperoxide analogues.[14]

The first observation of cyclopentane formation by palladium-catalyzed oxidative cyclization was described by Brewis and Hughes in 1965.[15] In the presence of palladium(II) phosphine complexes, carbon monoxide, and high-pressure conditions, various substituted cyclopentanes could be obtained from dienes such as 1,5-hexadiene. Extreme conditions and/or fairly low yields are characteristics of these early transformations.[16,17] 1,5-Cyclooctadiene shows a particular behavior, and palladium(II)-mediated cyclization takes place with lead tetraacetate as a reoxidant,[18] under photochemical conditions,[19] or with carbon monoxide and phosphine ligands.[20] Examples involving palladium-promoted formation of cyclopentane derivatives from noncyclic dienes include cyclization of 1,6-dienes,[21] intramolecular coupling of vinylic halides,[22,23]

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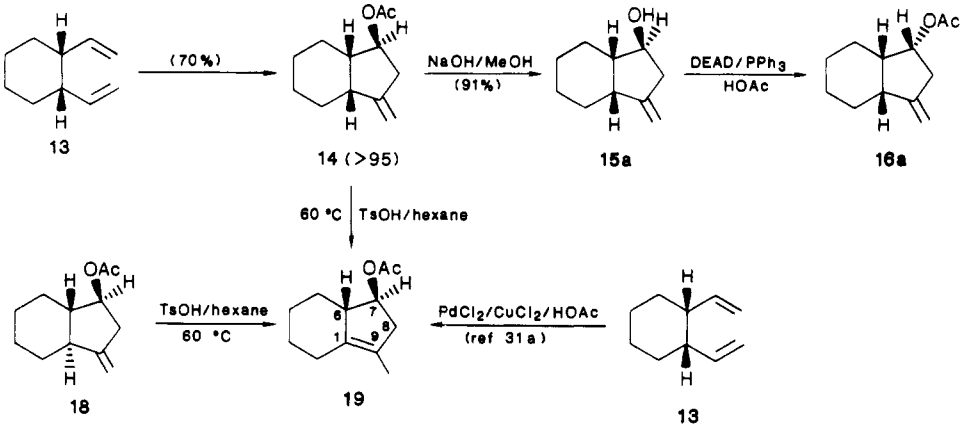
Scheme I



cyclization of enol ethers,[24] and oxidative cyclization of 1,5-dienes.[25,26] The synthesis of a number of mono-, bi-, and tricyclic systems has been realized in this way. However, most of these reactions are stoichiometric with respect to palladium. In those which are catalytic, the choice of the reoxidation system is important. The classical "Wacker"[27] catalyst $PdCl_2$–$CuCl_2$ gives quite selective but not general results.[28] Using the three-component system Pd(II)/*p*-benzoquinone/MnO_2, we obtained conditions for both selective and general cyclization of 1,5-dienes.[29,30] We report in this paper full experimental details for the selective formation of substituted exomethylenecyclopentanes in oxidative cyclization reactions.

Results and Discussion

Reactions. A great variety of "1,5-hexadienes" have been cyclized by means of $Pd(OAc)_2$. In the presence of the palladium(0) reoxidation system benzoquinone/MnO_2 (in some cases benzoquinone alone), the reaction is catalytic with respect to the noble metal catalyst (1–5 mol %). An important feature concerns the substitution pattern on the diene; modification on both the saturated and unsaturated parts of the diene strongly influence the regio- and diastereoselectivities of the cyclization reactions.

Cyclization ($Pd(OAc)_2$/*p*-benzoquinone/MnO_2 1/4/20, 5 mol % Pd) of 1,5-hexadiene (**1**) in acetic acid resulted in the formation of a 65/25/10 mixture of the unsaturated acetates **2**, **3**, and **4** in a total yield of 72% (Table I). Dienes with two chemically different olefinic groups underwent attack of acetate preferentially at the sterically less hindered site. From *d,l*-3-methyl-1,5-hexadiene (**5**), five isomers (ratio 39/30/12/12/7) were obtained in a total yield of 49%. The three major isomers (81% of the mixture) were exomethylenecyclopentanes **6a** and **6b** and the rearranged compound **7**, all obtained by acetate attack at C5 of the diene. The trans/cis (**6b**/**6a**) ratio was 57/43. The two resulting isomers were thought to be the regioisomers **8a** and **8b**, the ratio of acetate attack of the two double bonds thus being ca. 81/19. The ratio of the two isomers of **8** could be estimated to 63/37, showing a larger discrimination between formation of these two diastereomers than of those of **6**. It was not, however, possible to assign the stereochemistry of the individual isomers.

The ratio of attack at the two double bonds of *d,l*-3-phenyl-1,5-hexadiene (**9**) turned out to be considerably higher (97/3), affording **10** and **11** as major isomers and only a minor amount of the regioisomer **12** (total yield 62%). The diastereoselectivity of the reaction was similar to that found for **5**, as shown by the formation of a 48/52 mixture of the trans and cis isomers of compound **10**. The two diastereomers could, however, be separated by crystallization of the trans isomer or by preparative HPLC.

In contrast to the reactions above, remarkably high diastereoselectivity was observed upon cyclization of *cis*-1,2-divinylcyclohexane (**13**), which yielded (1*R**,6*S**,7*S**)-7-acetoxy-9-methylenebicyclo[4.3.0]nonane (**14**) as the sole product (70%, Table I). The stereoselectivity of the reaction was verified by allowing the product to undergo base-catalyzed hydrolysis to afford **15a**, followed by the Mitsunobu[31a] reaction to yield the endo isomer **16a**, which could be shown to be absent in the cyclization reaction mixture (Scheme I). Likewise, in the cyclization of *d,l*-1,2-divinylcyclohexane (**17**) only the (1*S**,6*S**,7*S**) diastereoisomer (**18**) was formed, along with the isomerized compound **19** (total yield 54%, ratio 87/13) and two unidentified acetates (10%, Table I). Both the *cis*- and *trans*-acetoxyindan derivatives **14** and **18** could easily be isomerized (TsOH, hexane, 60 °C) to the same

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(28) (a) Heumann, A.; Reglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 866 and 867. (b) Heumann, A.; Reglier, M.; Waegell, B. *Tetrahedron Lett.* **1983**, *24*, 1971.

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(31) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Another procedure could also be used for the inversion: Kaulen, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 773.

Table I. Cyclization of 1,5-Dienes

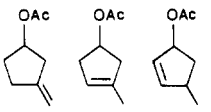
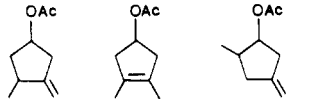
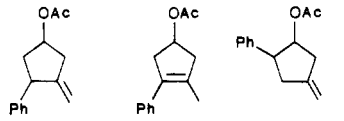
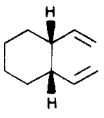
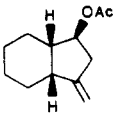
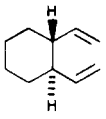
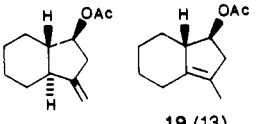
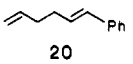
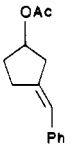
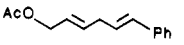
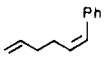
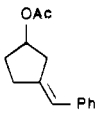
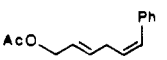
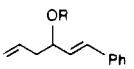
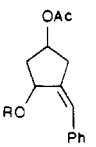
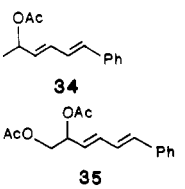
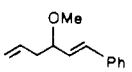
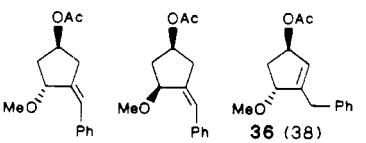
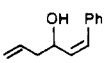
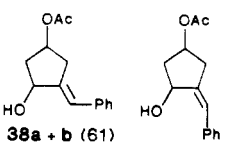
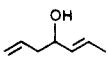
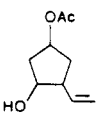
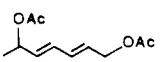
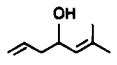
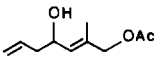
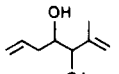
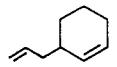
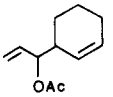
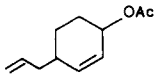
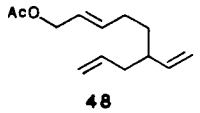
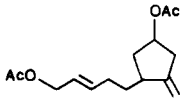
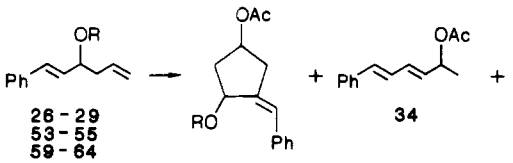
1,5-diene	yields of cyclized products,[a] %	cyclized products (normalized yields, %)	regioisomer ratio	diastereomer ratio	other acetates (yields, %)
 1	72	 **2** (65) **3** (25) **4** (10)			
 5	49	 **6a** (cis, 30) **6b** (trans, 39) **7** (12) **8** (cis and trans, 7 and 12)	81/19	**6**: 57/43 **8**: 63/37	
 9	62	 **10a** (cis, 45) **10b** (trans, 42) **11** (10) **12** (3)	97/3	48/52	
 13	70	 **14** (>95)		>99/1	
 17	54	 **18** (87) **19** (13)		84/16	two other acetates (10)
 20	33	 **21**		>99/1	 **22** (4) + two other acetates (11)
 23	17	 **24** (79) **21** (21)		79/21	 **25** (4)
 **26-29** **53-55** **59-64**		 **30-33** **65-73** } cf. Table II	>99/1		 **34** **35**
 27	34[b]	 **31a** (12) **31b** (50) **36** (38)	>99/1	50/50	
 37	36	 **38a + b** (61) **30a + b** (39)	>99/1	**38**: 74/26 **30**: 85/15	
 39	41	 **40**	>99/1	not determined	 **41** (10)

Table I (Continued)

1,5-diene	yields of cyclized products,[a] %	cyclized products (normalized yields, %)	regioisomer ratio	diastereomer ratio	other acetates (yields, %)
 **42**				 **43** (23)	 **44** (16)
 **45**				 **46** (23)	 **47** (6)
 **48**	54	 **49a** (cis, 33) **49b** (trans, 67)	>75/25	67/33	18

[a] Catalytic conditions, cf. Experimental Section. [b] $Pd(OAc)_2$ 1 equiv.

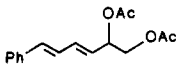
Table II. Cyclization of 1,3-Disubstituted 1,5-Hexadienes



26-29
53-55
59-64

30-33
65-73
a = trans
b = cis

34



35

compd no.	product no.	yields,[a] % cyclic compd	34	35	trans/cis ratio
26, R = H	**30**	43	8	15	55/45
26, R = H	**30**	38			44/56[c]
27, R = Me	**31**	42[b]	7[b]	15[b]	54/46
28, R = CH_2Ph	**32**	43[b]	7[b]	24[b]	57/43
29, R = Ac	**33**	41[b]	1[b]	19[b]	52/48
53, R = $(CH_2)_2OH$	**65**	46	8	20	60/40
54, R = $(CH_2)_3OH$	**66**	46	5	18	55/45
55, R = $(CH_2)_4OH$	**67**	42	9	20	55/45
59, R = $(CH_2)_2CN$	**68**	50	3	15	60/40
60, R = $(CH_2)_3CN$	**69**	44[b]	5[b]	12[b]	58/42
61, R = $(CH_2)_4CN$	**70**	46	8	15	59/41
62, R = CH_2COOH	**71**	40	8	17	70/30
63, R = $(CH_2)_2COOH$	**72**	43	7	16	63/37
64, R = $(CH_2)_3COOH$	**73**	46	7	20	60/40

[a] Catalytic conditions, cf. Experimental Section. [b] Yields calculated on consumed starting material. [c] Benzoquinone, 1 equiv, without MnO_2.

bridgehead olefin **19** (Scheme I). The latter compound can also be obtained directly by the $PdCl_2/CuCl_2$-catalyzed cyclization of diene **13**.[28a]

Palladium-catalyzed cyclization of the 1-substituted compound 1-phenyl-1,5-hexadiene (**20**), which was obtained as the trans isomer by Cope-rearrangement of **9**,[32] turned out to be highly stereo- and regioselective. This reaction yielded compound **21** with pure *E* configuration of the double bond as the main product (33%) along with the noncyclic acetate **22** (4%) (formed by allylic oxidation of **20**[33]) and two unidentified noncyclic acetates (11%, Table I). However, cyclization of the cis isomer **23**, prepared via condensation of benzaldehyde and 1-(4-pentenyl)diphenylphosphine oxide, proceeded with considerably lower stereoselectivity, affording a 79/21 mixture of the expected *Z* isomer **24** and the *E* isomer **21**, along with the noncyclic acetate **25**.

Methods for the preparation of cyclopentane rings with oxygen functionalities are of great interest for the synthesis of various natural products. Therefore, cyclizations of the 1,3-disbustituted 1,5-dienes **26–29** carrying oxygen functionalities in the 3-position were attempted (Table II). These dienes were conveniently prepared from cinnamic aldehyde and allyl bromide in the presence of tin and aluminum.[34] They cyclized smoothly when subjected to the reaction conditions to yield the acetoxycyclopentanes **30–33** (41–43%), all with pure *Z* configuration of the double bonds. As expected, the products consisted of mixtures of the trans and cis isomers, in each case with a slight excess (ca. 55/45) of the former.

All cyclizations of 3-*O*-substituted 1,5-dienes were accompanied by the formation of high quantities of the conjugated acetates **34** and **35** (1–8 and 15–24%, respectively, see Table II). The noncyclic acetates were shown to be formed via palladium-catalyzed processes,[33] since only starting material was recovered in blank experiments without the noble metal catalyst.

(*Z*)-3-Hydroxy-1-phenyl-1,5-hexadiene (**37**) (prepared by $LiBH_4$ reduction of *cis*-methyl cinnamate[35] in methanol[36] followed by oxidation[37] to *cis*-cinnamic aldehyde and coupling with allyl magnesium bromide) afforded, in addition to the expected cyclic products **38a** and **38b** (22%) and some unidentified noncyclic products, the *Z* isomers **30a,b** (14%, Table I). Cyclization of the *Z* isomer proceeded, however, with considerably higher stereoselectivity with respect to the substituents on the ring than cyclization of the *E* isomer, the ratios of **38a/b** and **30a/b** being 74/26 and 85/15, respectively.

1,5-Dienes with substituents in the 1-position carrying α-hydrogens did not afford exomethylenecyclopentanes,

(32) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417.

(33) For allylic oxidation reactions with a similar catalyst, cf.: Heumann, A.; Åkermark, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 453. Heumann, A.; Åkermark, B.; Hansson, S.; Rein, T. *Org. Synth.*, in press.

(34) Nonami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191.

(35) Engler, T.; Falter, W. *Tetrahedron Lett.* **1986**, *27*, 4119.

(36) Soai, K.; Oookawa, A. *J. Org. Chem.* **1986**, *51*, 4000.

(37) Fatiadi, A. J. *Synthesis* **1976**, 65.

but rather yielded the corresponding vinyl compounds. For example, 4-hydroxy-1,5-heptadiene (**39**) gave the hydroxyacetate **40** (41%) as a mixture of all four possible diastereomers, along with the conjugated noncyclic diacetate **41** (10%, Table I). The four diastereomers **40a–d** could be separated by HPLC and characterized by ^{1}H NMR spectroscopy, but the stereochemistry of the individual products could not be assigned. Attempted cyclization of the alcohol **42**, containing one trisubstituted double bond, resulted in allylic oxidation[33,38] affording the hydroxyacetates **43** (23%) and **44** (16%), the latter as a 40/60 mixture of two diastereomers. Likewise, no cyclized products were obtained from 2-allylcyclohexene (**45**). Instead, allylic oxidation took place to afford on 80/20 ratio of 3-(1-acetoxy-2-propenyl)cyclohexene (**46**) and 3-acetoxy-6-(2-propenyl)cyclohexene (**47**) in 29% yield, together with some unidentified products.

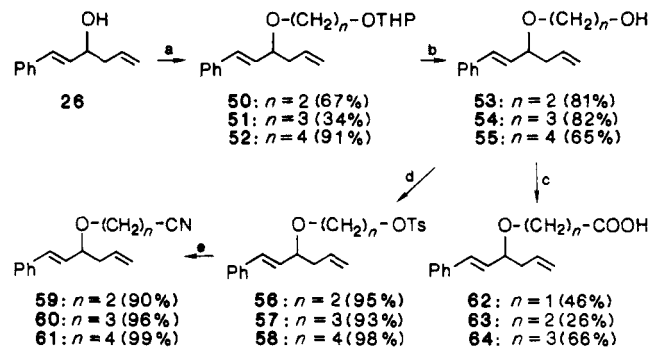
Some experiments were performed using modified oxidation systems, resulting in significant effects on product patterns. When a stoichiometric amount of *p*-benzoquinone and no MnO_2 was used for the reoxidation of Pd(0) in the cyclization of the alcohol **26** (Table II), the trans and cis isomers (**30a,b**) were obtained (38%) in a reverse ratio (44/56, compared to 55/45 for the reaction using a catalytic amount of *p*-benzoquinone). The use of a stoichiometric amount of palladium acetate and no reoxidant in the cyclization of the methyl ether **27** resulted in a 12/50/38 ratio of the acetoxyexomethylenecyclopentanes **31a** and **31b** and the allylic acetate **36** (Table I). Since the substituents in the latter compound assume a trans configuration,[39] the formation of **36** is thought to occur via isomerization of the trans isomer **31a**, implying a diastereomeric ratio of 50/50 of the primary products. Since no higher diastereoselectivity was observed, the effects of further modifications were not investigated.

In order to investigate whether steric crowding of the benzoquinone would affect the diastereoselectivity, *p*-benzoquinone supported on polystyrene–divinylbenzene was used as oxidant in the cyclization of 3-phenyl-1,5-hexadiene (**9**). The polymeric reagent proved to be useful for the cyclization, but the cis/trans ratio of the product (**10a/10b**) was similar to that obtained using monomeric benzoquinone (about 50/50).

We have previously observed that cyclization of the allylic acetate **48** yields acetoxycyclopentanes **49** with a trans/cis ratio of 67/33.[29] It does not seem plausible that the reason for this rather high preference for the trans isomer is a favored pseudoequatorial substitution of the palladium–diene complex originating from the bulkiness of the substitutent, since no such preference was observed for 3-phenyl-1,5-hexadiene (**9**). Since square-planar palladium(II) complexes have a tendency to become five coordinate,[40] weak coordination of the acetate group to palladium may be considered as the reason favoring a pseudoequatorial palladium–diene complex.

In order to investigate whether increased stereoselectivity may result from the presence of a functional group capable of coordination to palladium, a series of 3-*O*-substituted 1,5-hexadienes carrying alcohol, nitrile, and carboxylic acid groups at various distances from the diene center were prepared. For this purpose, the alcohol **26** was reacted with tetrahydropyranyl ethers of α,ω-chloro alcohols containing 2, 3, and 4 carbon atoms (Scheme II). After deprotection, the alcohols **53–55** were obtained. These alcohols were tosylated to give compounds **56–58**, which were converted to the desired nitriles **59–61**. The carboxylic acids **62–64** were finally obtained by oxidation of the alcohols **53–55**.

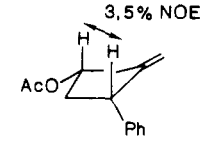
Scheme II[a]



[a] (a) Cl-$(CH_2)_n$-OTHP, KOH, DMSO, 40 °C; (b) *p*-TsOH, MeOH, room temperature; (c) pyridinium dichromate, DMF, (d) TsCl, pyridine, 0 °C; (e) NaCN, DMSO, room temperature.

The results of the cyclizations of the above compounds are shown in Table II. In the absence of coordinating ability of the substituents, trans/cis ratios comparable to those observed upon cyclization of the dienes **26–29**, i.e. approximately 50/50, are expected. For several of these compounds somewhat higher ratios were observed, which may indicate a weak chelation effect in the cyclization.

Structure Elucidation. The stereochemistry of the cyclized products was determined by NMR methods. A cis stereochemistry was assigned to compound **10a** due to a 3.5% NOE effect of the ring proton adjacent to the phenyl group (C5-H) upon irradiation of the proton next to the acetoxy group (C3-H) and the lack of an NOE effect of the other isomer. Due to the characteristic coupling



10a (cis)

pattern for the proton next to the acetoxy group (a triplet of triplets for the trans isomer and a quintet for the cis isomer) in acetoxymethylenecyclopentanes with substituents in 2-position, the stereochemistry of these compounds could be deduced from that of **10**.

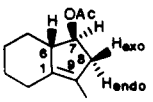
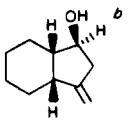
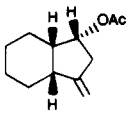
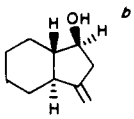
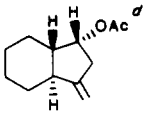
The structures of the indan derivatives **15**, **16**, and **19** were determined by high resolution NMR spectroscopy (Table III). In acetate **19**, a tetrasubstituted olefinic group was indicated by the presence of two signals from sp^2 carbons in the ^{13}C NMR spectrum (δ 135.3, C1, and 125.1, C9), and by the absence of signals from vinylic protons in the ^{1}H NMR spectrum. Furthermore, a resonance from a vinylic methyl group lacking ^2J and ^3J couplings was identified at δ 1.6. The stereochemistry (endo or exo) was determined from the coupling constants. Inspection of molecular models suggests that the dihedral angles between the hydrogen adjacent to the functional group (C7-H) and the neighbouring hydrogens at C6 and C8 are quite different in the two stereoisomers. According to the Karplus equation,[41] the proton resonance pattern should be different in compounds whose stereochemistry differ

(38) Heumann, A.; Reglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 366; *Angew. Chem. Suppl.* **1982**, 922.

(39) This result can be explained by the initial formation of a ca. 50/50 mixture of the expected trans and cis isomers **31a** and **31b**, i.e. a similar ratio to that observed under catalytic conditions, followed by rearrangement of the trans isomer to yield **36**. Since the zero-valent palladium formed during the cyclization is not reoxidized under these conditions, it seems reasonable to assume that the rearrangement is catalyzed by Pd(0).

(40) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 6, p 233.

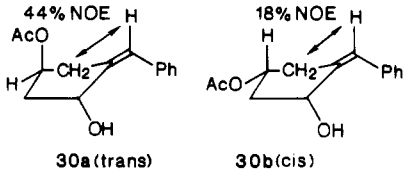
Table III. ^{1}H NMR Resonances of Indan Derivatives[a]

indan derivative	H_1 (δ)	H_6	H_7 (J, Hz)	H_{8endo} (J, Hz)	H_{8exo} (J, Hz)
 19		2.38	4.84 (8 + 4 + 4)	2.69 (16 + 8)	2.23 (16)[c]
 15a	2.72	1.91	3.99 (6 + 3 + 3)	2.81 (18 + 6)[c]	2.30 (18)[c]
 16a	2.55	2.28	5.05 (8 + 8 + 6)	2.44 (17.5 + 8)[c]	2.82 (17.5 + 8)
 15b	2.0 – 2.11		3.85 (8 + 8 + 4)	2.86 (17 + 8)	2.16 (17 + 8)[c]
 16b	2.0 – 2.18		5.21 (6 + 3)	2.41 (19)	2.69 (19 + 6)

[a] 400 MHz, we thank H. Kolshorn, University of Mainz, for very valuable help with the NMR spectra. [b] In the corresponding acetates **14** and **18** the H_7 signals (δ = 4.82 and 4.72 ppm, respectively) are partially or totally hidden by the patterns of the vinylic protons. [c] Additionally there is a number of small (2–2.5 Hz) couplings. [d] Prepared from **15b** according to ref 31.

at C7. In compound **19**, the dihedral angles between C7-H and C6-H, and between C7-H and C8-H_{exo}, are both estimated to approximately 130°, whereas the dihedral angle between C7-H and C8-H_{endo} is approximately 10°. The signal observed (δ 4.84, dt, J_1 = 8, J_2 = J_3 = 4 Hz, Table III) corresponds nicely to this arrangement. In the case of cyclopentanes, caution is required when the relative stereochemistry of two (or more) groups is to be determined by the Karplus equation.[42] In our molecule, however, annulation of the six-membered ring decreases the conformational mobility of the five-membered ring, rendering the above analysis plausible. The stereochemistry of compound **14** (and the derived alcohol **15a**) was verified by isomerization of **14** to **19**, a process which does not affect the stereochemistry at C7 (Scheme I). Additional support for our stereochemical assignments is provided by the ^{1}H NMR spectrum of alcohol **15a**, as well as that of the *endo*-acetate **16a**. Although the coupling constants are more difficult to predict in these more mobile systems, the differences in chemical shifts between the C8-H_{endo} protons of **14** and **16a** (δ 2.83 and 2.44, respectively) and of the C7-H_{exo} protons of the two epimers (δ 2.35 and 2.82, respectively, Table III) are consistent with our interpretation. The same arguments can be used to verify stereochemical assignments for compounds **15b**, **16b**, and **18**.

The stereochemical assignments of acetoxymethylenecyclopentanes **30–33** were made by results from NOE experiments. The stereochemistry of the exocyclic double bond was deduced from irradiation of the olefinic proton next to the phenyl group. Compounds **30a** and **30b** gave a total enhancement of 44% and 18%, respectively, of the methylene protons (C5-H_2), indicating *Z* configuration of the olefins. Irradiation of the proton adjacent to the



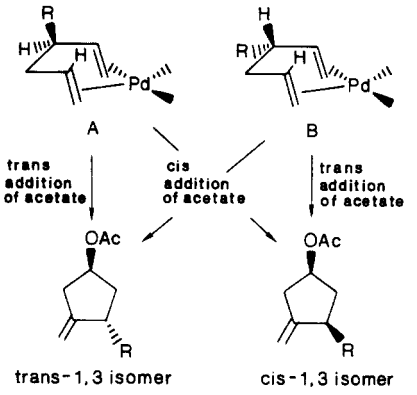
30a (trans) 30b (cis)

acetoxy group (C4-H) in compound **30a** resulted in a 9% enhancement of the resonance for the hydroxyl proton. This effect was absent in compound **30b**, and, therefore, **30a** was assigned a trans stereochemistry. The stereochemistry of compounds **31–33** as well as of **65–73** was assigned by comparison of the ^{1}H NMR and ^{13}C NMR spectra of these compounds with those of **30a** and **30b**.

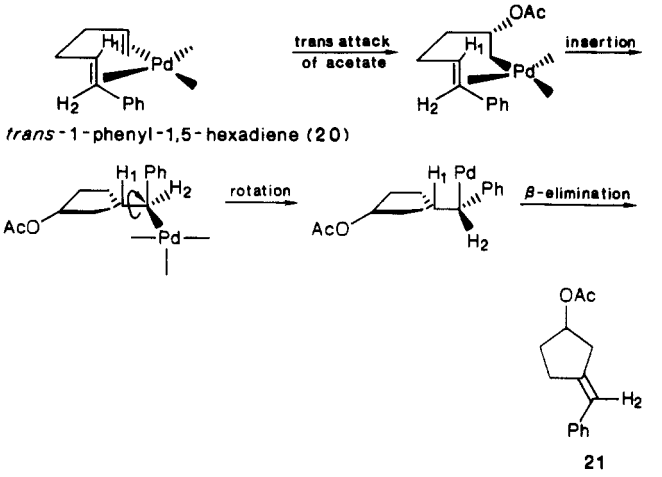
Mechanistic Aspects. 1,5-Dienes are known to readily complex to palladium(II), and such complexes have been the subject of extensive experimental[43] as well as theoretical[44] studies. Although they are thermodynamically quite stable, they react with nucleophiles[45] to form new

(41) Günther, H. *NMR Spektroskopie*, 2nd ed.; G. Thieme: 1983; p 105.
(42) *Stereochemistry, Vol 1: Determination of Configurations by Spectrometric Methods*; Kagan, H. D., Ed.; G. Thieme: Leipzig, 1977; p 89.
(43) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, 53. Zakharava, I. A.; Leites, L. A.; Aleksanyan, V. T. *J. Organomet. Chem.* **1974**, *72*, 283.
(44) Albright, T. A.; Hoffmann, R.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3802. Ziegler, T.; Rank, A. *Inorg. Chem.* **1979**, *18*, 1558.
(45) Bäckvall, J. E. In *Reaction of Coordinated Ligands*; Praterman, P. S., Ed.; Plenum Press: New York, 1986.

Scheme III

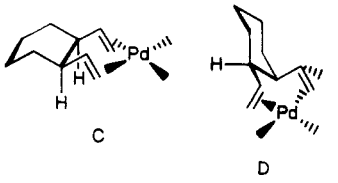


Scheme IV



carbon–heteroatom bonds. With conformationally nonrestricted olefins, these complexes adopt a pseudo-square-planar coordination with two double bonds aligned perpendicular to the coordination plane. It seems highly likely that the first step in the palladium-catalyzed cyclization of 1,5-dienes is the formation of a di-π-palladium–diene complex and also that the different selectivities observed during the reactions are closely related to the structure of this (these) complex(es). The unreactivity of diene **45** (with respect to cyclization) supports this hypothesis since, for steric reasons, this olefin is unlikely to form such a palladium–diene complex. However, similar dienyl cyclohexene derivatives, with an oxygen-substituted double bond in the ring, have been cyclized with stoichiometric amounts of palladium(II).[24] Furthermore, the allylic oxidation products from **45**, as well as those from dienes such as 4-vinylcyclohexene,[38] are formed via Pd catalysis, and consequently, via a coordination step.

The second important selectivity-controlling step is the acetate attack at one of the coordinated double bonds. Markovnikov type addition occurs, rendering the reaction completely chemoselective. At the same time, the diastereochemistry of the cyclization of 3- and 3,4-substituted dienes is determined. The formation of two diastereomers may be due either to nucleophilic attack on two isomeric palladium complexes A and B (Scheme III), or to competing cis and trans attack of the nucleophile (relative to palladium, Scheme III). It has been demonstrated that, in chloride-free acetic medium, the acetate attack on olefins coordinated to palladium occurs in a stereospecific trans fashion.[46] In addition, considering the high diastereoselectivity observed upon cyclization of *cis*-1,2-divinylcyclohexane (**13**), competing cis and trans attack of acetate seems highly improbable. Instead, inspection of molecular models suggests that one isomer of the palladium complex of **13**, with the cyclohexane ring either in a boat conformation (C, with efficient coordination of both



double bonds to palladium), or in a chair form (D, with a more stable conformation of the ligand) should be considerably more stable than other possible isomers, which suffer from severe hydrogen–hydrogen interactions or have unfavorable diaxial substitution patterns. Trans attack of acetate on either of these preferred isomers (C or D) would, indeed, lead to the observed stereoisomer.[47] For the noncyclic 3-substituted dienes, the two different isomers A and B are expected to be about equally stable, leading to the observed mixtures of diastereomers (their ratios ranging from 50/50 to 57/43 for products obtained by acetate attack at C5). The addition of a phenyl substituent at C1 in a trans configuration does not alter this picture. For 1-cis-substituted 1,5-dienes, however, complexes with pseudoequatorial substituents should be more stable, and, therefore, higher amounts of cyclic trans compounds are expected. This is in accordance with our findings. Our experimental results are, thus, nicely explained by initial formation of, depending on the structure of the diene, either one palladium–diene complex and the observation of high diastereoselectivity, or two isomeric such complexes and less selective reaction.

The cyclization step can be explained by the insertion of the second olefin of the σ-π-palladium complex (formed after the addition of the nucleophile to the di-π-olefin complex) into the Pd–carbon σ bond. The elimination of palladium hydride liberates the cyclic organic product (Scheme IV). Both of these processes are known to be cis-stereospecific.[48] This feature is well demonstrated by the stereospecific formation of *E* exocyclic olefins (with respect to the acetate) from *trans*-1-phenyl-substituted 1,5-dienes **20**, **26**–**29** (Table I). The reaction of *cis*-1-phenyl 1,5-dienes **23** and **37**, however, seems to be much less straightforward: in both cases, the major products are the expected *Z* stereoisomers, but, in addition, considerable amounts of the unexpected *E* isomers are formed. This observation may be explained by an isomerization process. An isomerized starting olefin should also give, as a side product, some isomerized allylic acetate. However, we could not detect any acetate **22** from **23**! On the other hand, we have never observed any isomerization of the exocyclic double bond with the oxidizing system used for the cyclization reactions. Thus, at the present time, it seems difficult to rationalize the isomerization process.

Conclusions

We have shown that the catalytic system palladium acetate/benzoquinone/manganese dioxide promotes cyclization of a great number of acyclic and cyclic 1,5-dienes.

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In acetic acid[49] a Wacker type catalytic reaction takes place to yield cyclopentanes with acetate and exomethylene groups in a 1,3 configurational relationship. Substituents in the 1,3- and/or 4-positions of the 1,5-diene are tolerated, but not in the 2- and 5-positions. As a consequence, this oxidation constitutes a general, synthetically useful[50] method for the preparation of 1,3- or 1,3,5-substituted five-membered carbocycles. The preparation of the starting olefins is performed by general routes, e.g. the allylic coupling reaction. One drawback to these reactions is the undesirable allylic rearrangement, affording mixtures of isomers. This has been overcome by several highly selective, primarily metal-catalyzed reactions.[51] Furthermore, it has been shown that the cyclization reaction is compatible with the presence of different functional groups: alcohols, acetates (including allylic acetates), ethers, nitriles, and carboxylic acids. In general, no isomerized products have been found. The diastereoselectivities depend strongly upon the structure of the starting olefin; fairly good to very good diastereoselectivity ratios have been observed.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WP 200 FT spectrometer (200 and 50.3 MHz) or on a Bruker AM 400 FT spectrometer (400 and 100.6 MHz, respectively). ^1H NMR spectra were recorded in $CDCl_3$ with Me_4Si as internal standard. ^{13}C NMR were recorded in $CDCl_3$ ($CDCl_3$ δ 77.0 as internal standard unless otherwise stated) or in CD_3CO (CD_3CO δ 29.8 as internal standard). DEPT (distortionless enhancement by polarization transfer) spectra were determined to assign carbon multiplicities (s, C; d, CH; t, CH_2; q, CH_3). Nuclear Overhauser Enhancement (NOE) experiments were performed in degassed $CDCl_3$. Analytical GLC was performed on a Pye Unicam Serie 207 instrument using a 30 m × 0.237 mm DBWAX column or a 25 m × 0.2 mm Carbowax 20 M column, a Varian Model 3700 instrument using a 25 m × 0.2 mm cross-linked methylsilicone capillary column or on a Pye GCD chromatograph using a 1.2 m × 2 mm glass column of 5% SE-30 on Chromosorb W. Infrared spectra were run on a Perkin-Elmer 257 spectrometer. High-pressure liquid chromatography (HPLC) was performed on a Waters M-45 instrument with a microporasil column (silica, 10 μm packing, 0.4 cm × 30 cm). Melting points were measured on a Büchi 510 apparatus and are uncorrected. Mass spectra were run on a LKB 9000 and on a Finnigan 4021 GLC–MS instrument at 70 eV. For slow additions a Sage Instruments Model 355 syringe pump was used. Flash chromatography was done according to the method described by Still, Kahn, and Mitra[52] using silica gel 60 (230–400 mesh) obtained from Merck. By "in vacuo" a rotary evaporator operating at water aspirator pressure is meant. Microanalyses were performed by Analytical Laboratories, Engelskirchen, Germany, and by the "Service de Microanalyse de la Faculté de St. Jérôme", Marseille, France.

Materials. Palladium(II) acetate obtained from Engelhardt, 3-methyl-1,5-hexadiene from Aldrich, 1,5-hexadiene, *cis*- and *trans*-1,2-divinylcyclohexane from Fluka, and *p*-benzoquinone and MnO_2 from Merck were used as received. *n*-BuLi (Aldrich) was titrated with benzyl alcohol using 1,10-phenanthroline as indicator. Polymer-supported *p*-benzoquinone was prepared by a literature procedure from chloromethylated polystyrene–2% divinylbenzene.[53] 3-Methylbutenal was a generous gift from BASF. Hexane, petroleum ether (bp 30–50 °C), pentane, and ethyl acetate were distilled before use. Dry Et_2O and THF were obtained by distillation from benzophenone ketyl. Dimethyl sulfoxide (DMSO) was dried with activated molecular sieves (4Å). Acetic acid (puriss) was used as received.

Cyclization of 1,5-Hexadiene (1). 1,5-Hexadiene (164 mg, 2 mmol) was added to a well-stirred mixture of $Pd(OAc)_2$ (22 mg, 0.1 mmol), MnO_2 (174 mg, 2 mmol), and benzoquinone (54 mg, 0.5 mmol) in 10 mL of acetic acid. After the mixture was stirred at ambient temperature for 42 h, 5 mL of brine was added and the reaction mixture was filtered. The filter cake was washed with 20 mL of pentane/Et_2O (7/3), and the mother liquor was extracted with 5 × 20 mL pentane/Et_2O (7/3). The combined organic phase was then washed with 5 mL of H_2O and 3 × 5 mL of saturated aqueous Na_2CO_3 and dried ($MgSO_4$). Removal of the solvent at atmospheric pressure gave 245 mg of a dark oil. Purification of the crude product by flash chromatography (9/1 pentane/Et_2O) gave 202 mg (72%) of a 65/25/10 mixture of **2**, **3**, and **4**. Spectroscopic data for compound **2** were in agreement with earlier data.[26,29] **3**: ^1H NMR (200 MHz) δ 5.35 (tt, J = 7 Hz and 2.7 Hz, 1 H, methine proton), 5.30 (br s, 1 H, olefinic), 2.83–2.58 (m, 2 H, allylic), 2.43–2.12 (m, 2 H, allylic), 2.03 (s, 3 H, OAc), 1.74 (br s, 3 H, Me).

Cyclization of 3-Methyl-1,5-hexadiene (5). The cyclization of **5** was performed on a 1-mmol scale following the procedure described for the cyclization of compound **1**, except that merely 0.75 mmol of MnO_2 was used. After the mixture was stirred at ambient temperature for 27 h, brine (10 mL) was added, the aqueous phase was extracted with petroleum ether/Et_2O (3 × 20 mL 8/2, 10 mL 7/3), and the organic phase was washed with saturated $NaHCO_3$ (4 × 10 mL) and dried ($MgSO_4$). The solvent was evaporated in vacuo using a bulb-to-bulb apparatus. Flash chromatography (using a stepwise gradient of petroleum ether/Et_2O, 8/2, 7/3, 6/4, 5/5, 4/6, 50 mL of each) yielded a mixture of compounds **6–8** (49%) along with trace amounts of some unidentified acetates. Selected peaks from the ^1H NMR spectrum of the isomeric mixture: 5.18 (tt, J = 5.5 and 2 Hz, 1 H, CH(OAc) in **6b**), 5.09 (quintet, J = 6 Hz, 1 H, CH(OAc) in **6a**), 4.84–4.87 and 4.89–4.93 (m, CH_2= in **6a** and **6b**), 2.26–2.34 (m, 1 H, allylic in **6a**), 2.01–2.09 (3 s, OAc), 1.63 (t, J = 1 Hz, 3 H, CH_3 in **7**), 1.45–1.53 (ddd, J = 13.5, 11 and 5 Hz, 1 H, CH_2CHCH_3 in **6b**), 1.39–1.44 (m, 1 H, CH_2CHCH_3 in **6a**), 1.15 (d, J = 6.8 Hz, 3 H, CH_3 in **6a**), 1.11 (d, J = 6.7 Hz, 3 H, CH_3 in **6b**), 1.03 (d, J = 7.1 Hz, 3 H, CH_3 in **8a** or **8b**), 0.98 (d, J = 6.9 Hz, 3 H, CH_3 in **8a** or **8b**).

3-Phenyl-1,5-hexadiene (9). *n*-BuLi (1.45 M in hexane, 31 mL, 45 mmol) was added during 10 min to a stirred slurry of triphenylmethylphosphonium bromide (16.1 g, 45 mmol) in 70 mL of anhydrous Et_2O under a nitrogen atmosphere. After the mixture was stirred for 2 h at ambient temperature, 2-phenyl-4-pentenal (4.8 g, 30 mmol)[54] dissolved in 17 mL of anhydrous Et_2O was added during 80 min, and the mixture was stirred for an additional 22 h. Et_2O was added to the reaction mixture, and the precipitate formed was removed by filtration. The organic phase was washed with water until the aqueous phase became neutral and dried ($MgSO_4$). The solvent was removed in vacuo to afford 3.86 g of a slurry. Following flash chromatography (silica gel, Et_2O/pentane, 1/9) 1.2 g (7.6 mmol, 25%) of **9**[55] was obtained.

Cyclization of Compound 9. The procedure described for compound **5** was used for the cyclization of **9** (1 mmol). After the mixture was stirred at ambient temperature for 29 h, 10 mL of brine was added and the aqueous phase was extracted with 3 × 20 mL and 10 mL of pentane/Et_2O (4/1). The combined organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (2 × 5 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo afforded 196 mg of a brown oil. The crude product was flash chromatographed (Et_2O/hexane, 1/4) to give a mixture (130 mg, 60%) of **10a**, **10b**, **11**, and **12** in a ratio of 45/42/10/3, as determined by capillary GLC (carbowax 20 M). Compound **10b** was obtained in a pure form from the mixture by crystallization with hexane at −20 °C. The other isomers were separated by HPLC (hexane/EtOAc 98/2) for structural deter-

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mination. **10a**: ^{1}H NMR (200 MHz) δ 7.15–7.4 (m, 5 H, Ph), 5.2 (quintet, J = 7 Hz, 1 H, C*H*OAc), 4.98–5.05 (m, 1 H, CH_2=C), 4.53–4.60 (m, 1 H, CH_2=C), 3.65 (br t, J = 10 Hz, 1 H, C*H*(Ph)), 2.83–3.02 (m, J_{gem} = 17 Hz, 1 H, =CCH_2), 2.45–2.67 (m, 2 H, CH_2CH(OAc)CH_2), 2.04 (s, 3 H, OAc), 1.86–2.05 (ddd, J = 13, 10, and 7 Hz, 1 H, CH_2CHPh); ^{13}C NMR (100.6 MHz) δ 170.86, 152.04, 143.47, 128.37, 128.32, 126.36, 109.30, 73.62, 48.35, 41.01, 39.68, 21.18. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.73; H, 7.46. Found: C, 77.48; H, 7.49. **10b**: ^{1}H NMR (200 MHz) δ 7.15–7.4 (m, 5 H, Ph), 5.33 (br t, J = 5 Hz, 1 H, C*H*OAc), 4.98–5.06 (m, 1 H, CH_2=C), 4.58–4.65 (m, 1 H, CH_2=C), 3.78–3.94 (m, 1 H, C*H*Ph), 2.81–2.98 (m, 1 H, =CCH_2), 2.55–2.7 (m, 1 H, =CCH_2), 2.24–2.39 (m, 1 H, CH_2CHPh), 2.07 (s, 3 H, OAc), 1.95–2.13 (m, 1 H, CH_2CHPh); ^{13}C NMR (100.6 MHz) δ 170.81, 152.93, 143.35, 128.45, 128.24, 126.41, 109.13, 74.59, 48.40, 41.85, 40.05, 21.37. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.73; H, 7.46. Found: C, 77.65; H, 7.37. **11**: ^{1}H NMR (200 MHz) δ 7.15–7.45 (m, 5 H, Ph), 6.6–6.75 (m, 2 H, C=C*H*C*H*(OAc)), 3.5–3.65 (m, 1 H, C*H*(Ph)), 2.8–3.0 (m, 1 H, CH_2), 2.07 (s, 3 H, OAc), 1.75–1.9 (m, 1 H, CH_2), 1.55 (br s, 3 H, Me). **12**: ^{1}H NMR (200 MHz) δ 7.15–7.4 (m, 5 H, Ph), 5.15 (q, J = 7 Hz, 1 H, C*H*OAc), 4.92–5.06 (m, 2 H, CH_2=C), 3.32 (q, J = 7 H, 1 H, C*H*Ph), 2.78–3.04 (m, 2 H, CH_2(CH_2=C)CH_2), 2.45–2.67 (m, 1 H, CH_2CHPh), 2.27–2.45 (m, 1 H, CH_2CHOAc), 2.01 (s, 3 H, OAc).

Cyclization of *cis*-1,2-Divinylcyclohexane (13). To a well-stirred mixture of $Pd(OAc)_2$ (112 mg, 0.5 mmol), MnO_2 (870 mg, 10 mmol), and benzoquinone (216 mg, 2 mmol) in 50 mL of acetic acid was added **13** (1.36 g, 10 mmol), and the mixture was stirred at ambient temperature for 42 h; 10 mL water was added, and the aqueous phase was extracted with petroleum ether. The organic phase was washed with 2 M NaOH and water and dried ($MgSO_4$). Removal of the solvent in vacuo and flash chromatography (petroleum ether/Et_2O, 97/3) afforded 1.35 g (7 mmol, 70%) of **14**: ^{1}H NMR (400 MHz) δ 4.90 (br, $w_{1/2}$ = 6 Hz, 1 H, C*H*(OAc)), 4.82 (br, $w_{1/2}$ = 9.5 Hz, 2 H, CH_2=C), 2.83 (m, part of AB, J = 18, 7.5, 2.5, and 2.5 Hz, 1 H, CH_2CH(OAc)), 2.67 (br, $w_{1/2}$ = 15 Hz, 1 H), 2.35 (d, part of AB, J = 18 Hz, 1 H, CH_2CH(OAc)), 1.98 (s, 3 H, OAc), 1.93–2.08 (m, 1 H), 1.75 (br, $w_{1/2}$ = 21 Hz, 1 H), 1.57–1.7 (m, 3 H), 1.27–1.36 (m, 2 H), 1.13–1.27 (m, 1 H), 0.85–0.96 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 170.7, 150.5, 105.8, 76.7, 44.8, 41.2, 37.5, 25.5, 25.2, 24.1, 21.6, 21.2. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.30.

Cyclization of *trans*-1,2-Divinylcyclohexane (17). Compound **17** (272 mg, 2 mmol) was cyclized under the same conditions as **13** (72 h reaction time). Workup according to the procedure described for **13** gave 250 mg (1.29 mmol, 64%) of a mixture of **18**, **19** (87/13, 54%), and two other unidentified monoacetates in a ratio of 64/36 (10%). **18**: ^{1}H NMR (400 MHz) δ 4.67–4.75 (m, 3 H), 2.93 (m, 1 H), 2.01 (s, 3 H), 1.88–2.14 (m, 3 H), 1.63–1.80 (m, 3 H), 1.00–1.37 (m, 5 H); ^{13}C NMR (100.6 MHz) δ 171.2, 150.7, 103.4, 76.7, 50.3, 46.7, 37.5, 29.5, 28.4, 25.6, 25.4, 20.99. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.33; H, 9.32.

Hydrolysis of Acetate 14. To a solution of **14** (1.098 g, 5.68 mmol) in 20 mL of MeOH was added 3.4 mL of 2 M NaOH (6.8 mmol), and the mixture was heated to reflux for 5 min. MeOH was removed in vacuo, 10 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (30 mL, 8/2, 30 mL, 1/1). The organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo to give 829 mg of a yellow oil. Bulb-to-bulb distillation (170 °C, ca. 0.5 Torr) afforded 785 mg (5.16 mmol, 91%) of **15a** as a colorless oil. **15a**: R_f = 0.28 (petroleum ether/Et_2O, 7/3); ^{1}H NMR (400 MHz) δ 4.92 (m, 1 H, CH_2=C), 4.84 (m, 1 H, CH_2=C), 3.99 (dt, J = 6.2 and 3.0 Hz, 1 H, C*H*OH), 2.81 (dd, J = 18 and 6 Hz, 1 H), 2.72 (m, 1 H), 2.3 (br d, J = 18 Hz, 1 H), 2.04–2.14 (m, 1 H), 1.91 (m, 1 H), 1.68–1.78 (m, 1 H), 1.46–1.63 (m, 3 H), 1.31–1.39 (m, 2 H), 1.2–1.32 (m, 1 H), 0.96–1.06 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 151.37 (s), 105.62 (t), 74.24 (d), 47.63 (d), 40.84 (d), 40.36 (d), 26.11 (t), 25.44 (t), 23.99 (t), 22.07 (t).

Cyclization of *trans*-1-Phenyl-1,5-hexadiene (20). The diene **20** was prepared by Cope rearrangement of **9** (230 °C, 3 h; the ^{1}H NMR spectrum of **20** was in accordance with literature data[55]) and cyclized (1 mmol scale) according to the procedure described for compound **9**. After 43 h at ambient temperature 5 mL of brine was added, and the solution was extracted with petroleum ether/Et_2O (3 × 20 mL, 8/2, 10 mL, 7/3). The combined organic phase was washed with saturated aqueous $NaHCO_3$ (3 × 5 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to yield 143 mg (66%) of a crude mixture, which was purified by flash chromatography with petroleum ether/Et_2O (8/2) to give a mixture of **21** (33%), **22** (40%), and two unidentified acetates (11%). The cyclic product **21** was separated from **22** by HPLC (hexane/EtOAc, 95/5). **21**: ^{1}H NMR (200 MHz) δ 7.06–7.31 (m, 5 H), 6.38 (quintet, J = 4 Hz, 1 H, =CH), 5.18–5.28 (m, 1 H, C*H*OAc), 2.5–3.0 (m, 4 H), 1.9–2.1 (m, 2 H), 2.03 (s, 3 H). **22**: ^{1}H NMR (200 MHz) δ 7.08–7.45 (m, 5 H), 6.42 (A part of ABX_2, J_{AB} = 16 and J_{AX} = 0 Hz, 1 H, PhC*H*=), 6.21 (B part of ABX_2, J_{AB} = 16 and J_{BX} = 6.5 Hz, 1 H, PhCH=C*H*), 5.87 (A part of ABX_2, J_{AB} = 15, J_{AX} = 6 Hz, 1 H, C*H*=CHCH_2OAc), 5.68 (B part of ABX_2, J_{AB} = 15, J_{BX} = 6 Hz, 1 H, C*H*CH_2OAc), 4.52 (dd, J = 6.1 and 0.9 Hz, 2 H, CH_2OAc), 2.98 (br t, J = 6 Hz, 2 H), 2.07 (s, 3 H).

***cis*-1-Phenyl-1,5-hexadiene (23).** Diphenyl-1-(4-pentenyl)-phosphine oxide was treated with 1 equiv of LDA, and the resulting anion reacted with benzaldehyde to yield *erythro*-2-(diphenylphosphinoyl)-1-phenyl-5-hexen-1-ol, which in turn was treated with 1 equiv of NaH in dry DMSO[56] to afford **23** and **20** in a ratio of 85/15. Chromatography on a silica gel column impregnated with $AgNO_3$ (a stepwise gradient of petroleum ether/Et_2O, 99.5/0.5, 99/1, 98.5/1.5, etc. was used) yielded **23** (99% pure by GLC). The phosphine oxide: ^{1}H NMR (200 Hz) δ 7.3–7.8 (m, 10 H), 5.60–5.85 (m, 1 H), 4.90–6.05 (m, 2 H), 2.05–2.35 (m, 4 H), 1.58–1.85 (m, 2 H); IR 1176 cm^{-1} (P=O). The betaine: ^{1}H NMR (200 MHz) δ 7.4–8.1 (m, 10 H), 7.1–7.4 (m, 5 H), 5.26 (br d, J_{PH} = 9.5 Hz, 1 H, C*H*OH), 5.10 (ddt, J = 17, 10, and 6.5 Hz, 1 H), 4.80 (s, 1 H), 4.63–4.78 (m, 1 H), 4.43–4.59 (m, 1 H), 2.50 (br q, J_{PH} = J_{HH} = 5.5 Hz, 1 H), 1.78–2.13 (m, 1 H), 1.40–1.78 (m, 1 H), 1.31 (br q, J = 7 Hz, 2 H). **23**: ^{1}H NMR (200 MHz) δ 7.1–7.5 (m, 5 H), 6.42 (br d, J = 11.5 Hz, 1 H, PhC*H*=CH), 5.87 (ddt, J = 17, 10.5, and 6.5 Hz, 1 H, C*H*=CH_2), 5.69 (dt, J = 11.5 and 7 Hz, 1 H, PhCH=C*H*), 4.90–5.12 (m, 2 H), 2.44–2.55 (m, 2 H), 2.05–2.55 (m, 2 H).

Cyclization of 23. The cyclization of **23** was performed on a 0.2-mmol scale following the procedure described for the cyclization of compound **1**. The same workup procedure as that described for **5** afforded 39 mg of an oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 99/1, 98/2, 97/3, 96/4, 95/5 was used) gave 9 mg (21%) of a mixture of cyclic (**21** and **24**) noncyclic (**25**) products, by capillary GLC in a ratio of 79/21. The ratio **24**/**21** was 79/21 by NMR. **24**: ^{1}H NMR (400 MHz, in mixture with **21** and **25**) δ 7.25–7.40 (m, 5 H), 6.41 (quintet, 1 H, =CH), 5.28–5.33 (m, 1 H, C*H*OAc), 2.5–3.0 (m, 4 H), 1.8–2.0 (m, 2 H), 2.02 (s, 3 H); ^{13}C NMR (100.6 MHz, Me_4Si as internal standard) δ 170.90, 142.18, 138.11, 128.29, 127.96, 126.09, 122.71, 76.52, 37.72, 32.69, 31.19, 21.19. **25**: ^{1}H NMR (400 MHz, in mixture with **21** and **24**) δ 7.15–7.40 (m, 5 H), 6.53 (br d, J = 11.5 Hz, 1 H, PhC*H*=), 5.8–5.9 (m, 1 H), 5.69 (dt, J = 11.5 and 7 Hz, 1 H, PhCH=C*H*), 5.65–5.71 (m, 1 H), 4.55 (dq, J = 6.5 and 1 Hz, 2 H, CH_2OAc), 3.08 (t of quintets, J = 7 and 1.5 Hz, 2 H), 2.06 (s, 3 H).

Cyclization of *trans*-3-Hydroxy-1-phenyl-1,5-hexadiene (26).[36] This reaction was run on a 5-mmol scale using the procedure described for **9**. After the mixture was stirred at ambient temperature for 45 h, 25 mL of brine was added and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 40 mL, 7/3, 25 mL, 1/1). The organic phase was washed with water (10 mL) and saturated aqueous Na_2CO_3 (15 and 10 mL). The combined aqueous phase was extracted with petroleum ether/Et_2O (25 mL 1/1), and the organic phase was washed with saturated aqueous Na_2CO_3 and dried ($MgSO_4$). The solvent was removed in vacuo to yield 1.023 g of an oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 3/2, 1/1, and 2/3 was used) gave **34** (86 mg, 0.397 mmol), **35** (202 mg, 0.738 mmol), and a mixture of **30a** and **30b** (500 mg, 2.15 mmol, 43%) in a ratio of 55/45. The two diastereomers **30a,b** were separated on HPLC (hexane/EtOAc, 9/1) for structural determination. **34**: R_f = 0.56 (petroleum ether/Et_2O, 2/3); MS m/e 216 (M^+); ^{1}H NMR (200 MHz) δ 7.1–7.45 (m, 5 H, Ph), 6.72 (dd, J = 15 and 10 Hz, 1 H,

(56) Buss, A. D.; Cruse, W. B.; Kennard, O.; Warren, S. *J. Chem. Soc. Perkin Trans. 1* **1984**, 243.

PhCH=C*H*) 6.55 (d, J = 15 Hz, 1 H, PhC*H*=CH), 6.40 (dd, J = 15 and 10 Hz, 1 H, PhCH=CHC*H*), 5.79 (dd, J = 15 and 6.5 Hz, 1 H, =C*H*CHOAc), 5.44 (apparent quintet, 1 H, C*H*OAc), 2.06 (s, 3 H, OAc), 1.37 (d, J = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (100.6 MHz) δ 170.30, 137.03, 133.52, 132.72, 131.88, 128.60, 127.92, 127.69, 126.41, 70.69, 21.36, 20.24. **35**: R_f = 0.4 (petroleum ether/Et_2O, 2/3); MS m/e 274 (M^+); ^1H NMR (200 MHz) δ 7.15–7.45 (m, 5 H, Ph), 6.78 (dd, J = 15 and 10 Hz, 1 H, PhCH=C*H*), 6.60 (d, J = 15 Hz, 1 H, PhC*H*=CH), 6.50 (dd, J = 15 and 10 Hz, 1 H, PhCH=CHC*H*), 5.71 (dd, J = 15 and 7 Hz, 1 H, =C*H*CHOAc), 5.58 (dt, J = 4 and 7 Hz, 1 H, C*H*OAc), 4.27 (A part of ABX, J_{AB} = 12, J_{AX} = 4 Hz, 1 H, CH_2OAc), 4.14 (B part of ABX, J_{AB} = 12, and J_{BX} = 7 Hz, 1 H, CH_2OAc), 2.10 (s, 3 H, OAc), 2.07 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 170.65, 170.07, 136.72, 134.70, 134.55, 128.63, 127.94, 127.38, 126.58, 126.52, 71.82, 64.87, 21.11, 20.77. **30a**: R_f = 0.22 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.5 (m, 5 H, Ph), 6.50 (br s, $w_{1/2}$ = 5 Hz, 1 H, C=C*H*Ph), 5.36 (apparent quintet, 1 H, C*H*OAc), 5.02 (br s, $w_{1/2}$ = 12 Hz, 1 H, C*H*OH), 3.11 (br dd, J = 17 and 6.5 Hz, 1 H, =CCH_2), 2.53 (br dd, J = 17 and 4.5 Hz, 1 H, =CCH_2), 2.24 and 2.14 (AB part of ABMX, J_{AB} = 13.7, J_{AM} = 4, J_{AX} = 5.8, J_{BM} = 5.5, and J_{BX} = 5.5 Hz, 2 H, CH_2CH(OH)), 2.03 (s, 3 H, OAc), 1.74 (br s, 1 H, OH); ^{13}C NMR (100.6 MHz) δ 170.85, 142.96, 136.57, 128.66, 128.29, 127.22, 127.01, 73.13, 70.18, 42.53, 39.54, 21.20; IR (film) 3600–3200, 3060, 3020, 2970, 1730, 1600, 1500, 1250, 1045, 750, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; O, 20.67. Found: C, 72.13; H, 6.85; O, 20.54. **30b**: R_f = 0.26 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.55 (d, J = 7 Hz, 2 H, Ph), 7.2–7.4 (m, 3 H, Ph), 6.54 (br s, $w_{1/2}$ = 6 Hz, 1 H, C=C*H*Ph), 5.33 (br quintet, J = 4 Hz, 1 H, C*H*OAc), 4.80 (br s, $w_{1/2}$ = 17 Hz, 1 H, C*H*OH), 2.84 (br s, $w_{1/2}$ = 8 Hz, 2 H, C=CCH_2), 2.1–2.27 (m, 3 H, CH(O*H*)CH_2), 2.06 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 170.34, 143.15, 136.74, 128.53(2C), 128.05, 127.21, 74.88, 70.96, 42.41, 40.29, 21.39; IR (film) 3600–3200, 2970, 1730, 1600, 1500, 1250, 1040, 760, 705 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; O, 20.67. Found: C, 72.17; H, 6.95; O, 20.51.

***trans*-3-Methoxy-1-phenyl-1,5-hexadiene (27).** 3-Hydroxy-1-phenyl-1,5-hexadiene (**26**) (1.74 g, 10 mmol), dissolved in 5 mL of dry THF, was added to a well-stirred slurry of NaH (400 mg as an 80% suspension in oil 15 mmol) in 10 mL of dry THF under a nitrogen atmosphere. After stirring for 45 min, MeI (7.1 g, 50 mmol) dissolved in 10 mL dry THF was added, and the mixture was left for 1 h at ambient temperature and then heated to 40 °C overnight. The excess NaH was destroyed with 1 mL of MeOH, the mixture was concentrated in vacuo, and 100 mL of Et_2O was added to the concentrate. The organic phase was washed with water (2 × 20 mL) and brine (20 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to yield 1.84 g of an oil. Following flash column chromatography (petroleum ether/Et_2O, 7/3), 1.81 g (9.6 mmol, 96%) of **27** was obtained as a colorless oil. **27**: R_f = 0.6 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.45 (m, 5 H, Ph), 6.45 (A part of ABX, J_{AB} = 16, J_{AX} = 0 Hz, 1 H, PhC*H*=CH), 6.08 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.5 Hz, 1 H, PhCH=C*H*), 5.85 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.02–5.18 (m, 2 H, CH_2=CH), 3.78 (m, 1 H, C*H*(OMe)), 3.33 (s, 3 H, OMe), 2.27–2.55 (m, 2 H, CH_2); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 136.74, 134.46, 132.41, 129.86, 128.57, 127.69, 126.53, 116.98, 82.01, 56.27, 40.24; IR (film) 3080, 3030, 2980, 2930, 1640, 1450, 1100, 970, 915, 750, 695 cm^{-1}.

Cyclization of Compound 27. To a well-stirred solution of **27** (564 mg, 3 mmol) in 15 mL of acetic acid was added $Pd(OAc)_2$ (33.7 mg, 0.15 mmol), MnO_2 (196.8 mg, 2.26 mmol), and benzoquinone (82 mg, 0.76 mmol). The mixture was stirred for 48 h, and additional amounts of MnO_2 (39.2 mg, 0.45 mmol) and benzoquinone (16.2 mg, 0.15 mmol) were added. After stirring for an additional 24 h and 30 min, brine (15 mL) was added, and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 30 mL 8/2 and 10 mL 1/1). The combined organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (2 × 10 mL). The combined aqueous phase was then extracted with petroleum ether/Et_2O (15 mL, 1/1), and the organic phase was washed with Na_2CO_3 (saturated). The combined organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo to afford 691 mg of an oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O 19/1, 9/1, 4/1, and 7/3 was used) gave **27** (39 mg, 0.207 mmol), **34** (45 mg, 0.208 mmol), one fraction containing a mixture of **31a** and **31b** (234 mg, 0.951 mmol), and one fraction containing a mixture of **31** (57 mg, 0.232 mmol) and **35** (116 mg, 0.423 mmol). Yield of **31a/31b**, 40%; ratio, 54/46. The two diastereomers were partially separated on HPLC (petroleum ether/EtOAc, 9/1) for structural determination. **31a**: R_f = 0.22 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.18–7.44 (m, 5 H, Ph), 6.58 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.31 (m, 1 H, C*H*OAc), 3.42 (br s, $w_{1/2}$ = 12 Hz, 1 H, C*H*OMe), 3.31 (s, 3 H, OMe), 3.05 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.49 (br dd, J = 17 and 4 Hz, partially overlapping with one of CH(OMe)CH_2, 1 H, C=CCH_2)), 2.39 and 1.97 (AB part of ABMX, J_{AB} = 14.5, J_{AM} = 6, J_{AX} = 3, J_{BM} = 6, and J_{BX} = 6 Hz, 2 H, CH(OMe)CH_2), 2.01 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 170.84, 140.74, 137.04, 128.54, 128.28, 128.16, 126.97, 78.30, 73.37, 54.99, 39.71, 38.22, 21.21. **31b**: R_f = 0.22 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.18–7.45 (m, 5 H, Ph), 6.58 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.13 (apparent quintet, 1 H, C*H*OAc), 4.30 (br t, J = 4 Hz, 1 H, C*H*OMe), 3.34 (s, 3 H, OMe), 2.87 and 2.79 (AB part of ABX, broadened by allylic coupling to PhC*H*=C, J_{AB} = 17, J_{AX} = 6.5 Hz and J_{BX} = 5.5 Hz, 2 H, C=CCH_2), 2.1–2.25 (m, 2 H, CH(OMe)CH_2), 2.07 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 171.07, 140.08, 136.92, 128.54, 128.34, 128.28, 127.03, 78.23, 72.89, 54.99, 40.05, 37.23, 21.26.

Cyclization of Compound 27 Using a Stoichiometric Amount of $Pd(OAc)_2$. After a mixture of **27** (188.3 mg, 1 mmol) and $Pd(OAc)_2$ (224.5 mg, 1 mmol) in 5 mL of acetic acid was stirred at ambient temperature for 72 h, 5 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 15 mL 7/3, 10 mL 1/1). The combined organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (2 × 5 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to give 209.2 mg of a dark oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 9/1, 4/1, 7/3, 3/2, 1/1, and 2/3 was used) gave a mixture of **31a** (9.8 mg, 4%), **31b** (41.8 mg, 17%), and **36** (32 mg, 13%). **36**: R_f = 0.3 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.40 (m, 5 H, Ph), 5.53 (br s, $w_{1/2}$ = 5 Hz, 1 H, CH=C), 5.44 (br s, $w_{1/2}$ = 16 Hz, 1 H, C*H*OAc), 4.1 (dd, J = 7.5 and 4 Hz, 1 H, C*H*OMe), 3.58 (A part of AB, J_{AB} = 16 Hz, 1 H, PhCH_2), 3.41 (B part of AB, J = 16 Hz, 1 H, PhCH_2), 3.33 (s, 3 H, OMe), 2.7 (dt, J = 15 and 7.5 Hz, 1 H, CH_2CHOMe), 2.01 (s, 3 H, OAc), 1.74 (dt, J = 15 and 4 Hz, 1 H, CH_2CHOMe); ^{13}C NMR (100.6 MHz) δ 170.94, 150.22, 138.57, 129.06, 128.44, 127.24, 126.27, 83.11, 76.12, 56.20, 36.70, 34.90, 21.19.

***trans*-3-(Benzyloxy)-1-phenyl-1,5-hexadiene (28).** This compound was prepared according to the procedure described for **27** using $PhCH_2Cl$ instead of MeI: ^1H NMR (200 MHz) δ 7.19–7.45 (m, 10 H, 2 Ph), 6.55 (A part of ABX, J_{AB} = 16, J_{AX} = 0 Hz, 1 H, PhC*H*=CH) 6.14 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.86 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.0–5.17 (m, 2 H, CH_2=CH), 4.63 (A part of AB, J_{AB} = 12 Hz, 1 H, CH_2Ph), 4.43 (B part of AB, J_{AB} = 12 Hz, 1 H, CH_2Ph), 3.98 (apparent q, 1 H, CHO), 2.31–2.61 (m, 2 H, CH_2CH=); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 138.80, 136.70, 134.51, 132.45, 130.07, 128.56, 128.28, 127.65, 127.39, 126.55, 116.98, 79.71, 70.21, 40.39 (2 C overlapping in the aromatic region); IR (film) 3060, 3030, 2980, 1640, 1450, 1090, 1070, 970, 915, 750, 695 cm^{-1}.

Cyclization of Compound 28. Compound **28** (792.5 mg, 3 mmol) was cyclized via the procedure described for **9**. After the mixture was stirred at ambient temperature for 66 h, 15 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 40 mL 4/1 and 10 mL 1/1). The organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (2 × 5 mL). The aqueous phase was then extracted with petroleum ether/Et_2O (15 mL 1/1), and the organic phase was washed with saturated aqueous Na_2CO_3 (5 mL). The combined organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo to afford a dark oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 1/0, 19/1, 9/1, 4/1, and 7/3 was used) gave **28** (34 mg, 0.129 mmol), **34** (43 mg, 0.2 mmol), **32a/32b** (354 mg, 1.1 mmol), and one fraction containing a mixture of **32a/32b** (39 mg, 0.121 mmol) together with **35** (184 mg, 0.675 mmol). Yield of **32a/32b**: 41% in a ratio of 57/43. The two diastereomers were partially separated on HPLC (petroleum

ether/Et_2O, 9:1) for structural determination. **32a**: R_f = 0.3 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.42 (m, 10 H, 2 Ph), 6.57 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.36 (m, 1 H, C*H*OAc), 4.7 (br s, $w_{1/2}$ = 12 Hz, 1 H, C*H*OCH_2Ph), 4.47 (A part of AB, J_{AB} = 11 Hz, 1 H, OCH_2Ph), 4.43 (B part of AB, J_{AB} = 11 Hz, 1 H, OCH_2Ph), 3.11 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.4–2.58 (m, 2 H, C=CCH_2 and $CH_2CH(OCH_2Ph)$), 1.95–2.12 (m, 1 H, $CH_2CH(OCH_2Ph)$), 2.02 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 170.79, 142.26, 139.26, 138.17, 129.46, 129.07, 129.04, 128.90, 128.36, 128.29, 127.67, 77.52, 73.85, 70.25, 40.51, 39.47, 21.02. **32b**: R_f = 0.3 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.42 (m, 10 H, 2 Ph), 6.57 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhCH=C), 5.16 (apparent quintet, J = 6 Hz, 1 H, C*H*OAc), 4.56 (m, 1 H, C*H*(OCH_2Ph)), 4.52 (A part of AB, J_{AB} = 11 Hz, 1 H, OCH_2Ph), 4.47 (B part of AB, J_{AB} = 11 Hz, 1 H, OCH_2Ph), 2.76–2.99 (m, 2 H, C=CCH_2), 2.13–2.37 (m, 2 H, $CH_2CH(OCH_2Ph)$), 2.05 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 170.87, 142.45, 139.58, 138.10, 129.46, 129.07, 129.04, 128.90, 128.31, 128.25, 127.71, 77.37, 73.41, 70.13, 41.05, 38.59, 21.09. Anal. Calcd for (mixture of **32a/32b**) $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.10; H, 6.90.

***trans*-3-Acetoxy-1-phenyl-1,5-hexadiene (29).** 3-Hydroxy-1-phenyl-1,5-hexadiene (**26**) (1.74 g, 10 mmol) was dissolved in 12 mL of Et_3N, and 3.1 mL of acetic acid anhydride was added. After addition of 4-(*N*,*N*-dimethylamino)pyridine (305 mg, 2.5 mmol) during 5 min and stirring for an additional 18 h at ambient temperature, 35 mL of methanol was added, and the mixture was stirred for another 2 h and 15 min. After the mixture was concentrated in vacuo, 100 mL of ether was added, and the organic phase was washed with water (20 mL) and saturated aqueous $NaHCO_3$ (2 × 30 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo afforded 1.935 g of a dark oil. Following flash chromatography (petroleum ether/Et_2O, 4/1), 1.336 g (6.2 mmol, 62%) of **29** was obtained as a colorless oil. **29**: R_f = 0.44 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.2–7.45 (m, 5 H, Ph), 6.62 (A part of ABX, J_{AB} = 16 and J_{AX} = 0 Hz, 1 H, PhC*H*=CH), 6.15 (B part of ABX, J_{AB} = 16 and J_{BX} = 7 Hz, 1 H, PhCH=C*H*), 5.79 (ddt, J = 17, 10, and 7 Hz, 1 H, C*H*=CH_2), 5.48 (q, J = 7 Hz, 1 H, C*H*OAc), 5.02–5.2 (m, 2 H, CH=C*H*$_2$), 2.48 (br t, J = 7 Hz, 2 H, CH_2), 2.08 (s, 3 H, OAc); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 170.03, 136.43, 133.17, 132.66, 128.57, 127.93, 127.26, 126.62, 118.0, 73.72, 39.14, 21.16; IR (film) 3080, 3060, 3030, 2980, 1740, 1645, 1375, 1240, 1020, 970, 920, 750, 695 cm^{-1}.

Cyclization of Compound 29. The procedure described for **28** was used for the cyclization **29** (3 mmol). After the mixture was stirred for 49 h at ambient temperature and 20 h at 50 °C, 15 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 30 mL 7/3 and 10 mL 1/1). The organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (2 × 10 mL). The aqueous phase was extracted with petroleum ether/Et_2O (15 mL 1/1), and the organic phase was washed with saturated aqueous Na_2CO_3 (5 mL). The combined organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo to afford 702 mg of a brownish oil. Flash chromatography (petroleum ether/Et_2O, 7/3) gave one fraction consisting of a mixture of **29** (80 mg, 0.37 mmol) and **34** (4 mg, 0.019 mmol) and another fraction containing a mixture of **33a/33b** (297 mg, 1.08 mmol) and **35** (139 mg, 0.507 mmol). Compounds **33a/33b** were formed in a total yield of 36% in a ratio of 52/48. The isomers were separated on HPLC (petroleum ether/EtOAc, 9/1) for structural determination. **33a**: R_f = 0.14 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.4 (m, 5 H, Ph), 6.59 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.91 (m, 1 H, PhCH=CC*H*OAc), 5.3 (apparent quintet, 1 H, $CH_2CH(OAc)CH_2$), 3.08 (br dd, J = 17 and 6.5 Hz, 1 H, C=CCH_2), 2.58 (br d, J = 17 Hz, 1 H, C=CCH_2), 2.32 and 2.15 (AB part of ABMX, J_{AB} = 15, J_{AM} = 6.5, J_{AX} = 5, J_{BM} = 4, and J_{BX} = 5.5 Hz, 2 H, $CH_2CH(OAc)$-C=C), 2.04 (s, 3 H, OAc), 1.91 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 170.75, 170.50, 138.32, 136.40, 128.46, 128.36, 128.14, 127.20, 72.72, 72.63, 40.51, 40.00, 21.20, 20.93. Anal. Calcd (mixture of **33a** and **35**) for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.99; H, 6.58. **33b**: R_f = 0.14 (petroleum ether/Et_2O, 7/3); ^1H NMR (200 MHz) δ 7.15–7.38 (m, 5 H, Ph), 6.60 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.77 (br d, J = 6.5 Hz, 1 H, PhCH=CC*H*OAc), 5.16 (m, 1 H, $CH_2CH(OAc)CH_2$), 2.93 (ddd, A part of AB, J = 17, 6 and 2 Hz, 1 H, C=CCH_2), 2.82 (br d, B part of AB, J = 17, 1 H, C=CCH_2), 2.41 (dt, J = 15.5 and 6.5 Hz, 1 H, C=CCH(OAc)CH_2), 2.1 (m, 1 H, C=CCH(OAc)CH_2), 2.05 (s, 3 H, OAc), 1.98 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz) δ 170.79, 170.60, 138.59, 136.33, 128.86, 128.41, 128.20, 127.33, 72.63 (2 C), 40.54, 40.27, 21.27, 21.09. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.95; H, 6.50.

***cis*-3-Hydroxy-1-phenyl-1,5-hexadiene (37).** Allyl bromide (641 mg, 5.3 mmol) dissolved in 3 mL of dry Et_2O was added during 10 min to magnesium turnings (386 mg, 15.9 mmol) in 3 mL of dry Et_2O under a nitrogen atmosphere. After the mixture was stirred at ambient temperature for 30 min, *cis*-3-phenyl-2-propenal[35-37] (350 mg, 2.65 mmol) in 7 mL of dry Et_2O was added. The reaction mixture was stirred for another 3.5 h and then poured into ice/water. The aqueous phase was acidified by the addition of 2 M HCl and extracted with Et_2O (15 + 10 mL). The combined organic phase was dried ($MgSO_4$), and the solvent was removed in vacuo to give 422 mg of an oil. Flash chromatography (petroleum ether/Et_2O, 1/1) gave 406 mg (2.33 mmol, 88%) of **37**: R_f = 0.32 (petroleum ether/Et_2O, 1/1); ^1H NMR (200 MHz) δ 7.2–7.4 (m, 5 H, Ph), 6.58 (d, J = 12 Hz, 1 H, PhC*H*=CH), 5.85 (m, 1 H, CH_2=C*H*), 5.69 (dd, J = 12 and 9 Hz, 1 H, PhCH=C*H*), 5.11–5.23 (m, 2 H, CH_2=CH), 4.62 (m, 1 H, C*H*OH), 2.4 (m, 2 H, =CHCH_2), 1.7 (d, J = 4 Hz, 1 H, OH); ^{13}C NMR (100.6 MHz) δ 136.50, 133.95, 133.54, 131.38, 129.74, 128.27, 127.27, 118.37, 66.83, 42.06.

Cyclization of Compound 37. The reaction was performed on a 1-mmol scale according to the procedure described for **9**. Workup was done according to the procedure described for **26**. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 7/3, 3/2, 1/1, 2/3, and 3/7 was used) gave 31 mg (0.14 mmol, 14%) of **30a/30b** (ratio 85/15) and 50.1 mg (0.22 mmol, 22%) of **38a/38b** (ratio 74/26). **38a**: R_f = 0.1 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.4 (m, 5 H, Ph), 6.63 (q, J = 2.6 Hz, 1 H, PhC*H*=C), 5.40 (m, 1 H, C*H*OAc), 4.83 (m, 1 H, C*H*OH), 3.20 (br dd, J = 18 and 7 Hz, 1 H, C=CCH_2), 2.68 (br d, J = 18 Hz, 1 H, C=CCH_2), 2.1–2.2 (m, 1 H, CH(OAc)-CH_2CHOH), 2.02 (s, 3 H, OAc), 1.88–2.02 (m, 1 H, CH(OAc)-CH_2CHOH), 1.69 (d, J = 5.5 Hz, 1 H, OH); ^{13}C NMR (100.6 MHz) δ 170.74, 143.55, 137.01, 128.43 (2 C), 127.00, 124.95, 76.10, 73.60, 40.57, 36.37, 21.19. **38b**: R_f = 0.1 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz, in mixture with **38a**) δ 7.2–7.4 (m, 5 H, Ph), 6.73 (m, 1 H, PhC*H*=C), 5.27–5.4 (m, 1 H, C*H*OAc), 4.65 (m, 1 H, C*H*OH), 2.99 (ddd, part of AB, J = 18.6 and 3 Hz, 1 H, C=CCH_2), 2.88 (br d, part of AB, J = 18.6 Hz, 1 H, C=CCH_2), 2.05 (s, 3 H, OAc), 1.9–2.35 (m, 3 H, CH_2 and OH).

Cyclization of *trans*-4-Hydroxy-1,5-heptadiene (39).[34] The procedure described for **9** was used for the cyclization of the alcohol **39** (561 mg; 5 mmol). After 48 h at ambient temperature, 25 mL of brine was added, and the solution was extracted with petroleum ether/Et_2O (2 × 125 mL 7/3, 2 × 125 mL 1/1). The combined organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 125 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to yield 634 mg (75%) of a black liquid. The crude mixture was purified by flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 4/1 and 3/2, was used) to afford 0.46 g of a mixture the alcohols **40a–d** (41%) and **41** (10%). The cyclic products **40a–d** and the diacetate **41** were formed in a ratio of 80/20. The diastereomers **40a–d** were formed in unequal amounts (two major diastereomers **40a** and **40b** two minor diastereomers **40c** and **40d**) and were separated on HPLC (eluting with a 7/3 mixture of hexane/EtOAc). **40a**: ^1H NMR (200 MHz) δ 5.92 (ddd, J = 17, 10.5 and 6.5 Hz, 1 H), 5.09–5.39 (m, 3 H, CH=CH_2, C*H*OAc), 4.21–4.35 (m, 1 H, C*H*OH), 2.68–2.90 (m, 1 H), 2.02 (s, 3 H), 1.66–2.36 (m, 5 H). **40b**: ^1H NMR (200 MHz) δ 5.79 (ddd, J = 17, 10.5, and 6.5 Hz, 1 H), 5.0–5.28 (m, 3 H), 3.96–4.12 (m, 1 H), 2.22–2.51 (m, 1 H), 2.04 (s, 3 H), 1.72–2.22 (m, 5 H). **40c**: ^1H NMR (200 MHz) δ 5.98 (ddd, J = 17, 10.5 and 6 Hz, 1 H), 5.04–5.30 (m, 3 H), 4.09–4.21 (m, 1 H), 2.39–2.62 (m, 1 H); 2.04 (s, 3 H), 1.70–2.42 (m, 5 H). **40d**: ^1H NMR (200 MHz) δ 5.75 (ddd, J = 17, 10 and 7.5 Hz, 1 H), 5.0–5.28 (m, 3 H), 3.89 (q, J = 7 Hz, 1 H), 2.40–2.74 (m, 1 H), 2.02 (s, 3 H), 1.45–2.19 (m, 5 H). **41**: ^1H NMR (200 MHz) δ 6.13–6.35 (m, 2 H), 5.60–5.92 (m, 2 H), 5.39 (quintet, J = 6.5 Hz, 1 H, C*H*OAc), 4.60 (d, J = 6 Hz, 2 H, CH_2), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.32 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (100.6 MHz) δ 170.71, 170.24, 133.80, 133.11, 130.28, 127.70, 70.34, 64.43, 21.29, 20.90, 20.11.

2-Methyl-2,6-heptadien-4-ol (42). Allyl bromide (4.3 mL, 50 mmol) was converted into its corresponding Grignard reagent according to a previously described procedure[57] except that the bromide was added over only 1 h. The Grignard solution was heated to reflux for 1 h and then transferred to another flask. Freshly distilled 3-methylbutenal (1.9 mL, 20 mmol) in dry Et_2O was added dropwise to the Grignard reagent over 10 min. After stirring overnight, the reaction mixture was poured onto 25 mL of ice, the white precipitate was removed by careful addition of 2 M hydrochloric acid, the two phases were separated, and the aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic phase was dried ($MgSO_4$), concentrated in vacuo, and purified by Kugelrohr distillation (0.15 Torr, 100 °C) to give 1.3 g (52%) of **42** as a colorless liquid: ^1H NMR (200 MHz) δ 5.66–5.91 (m, 1 H), 5.0–5.22 (m, 3 H), 4.41 (dt, J = 9 and 6.5 Hz, 1 H), 2.28 (t, J = 6.5 Hz, 2 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.65 (s, 1 H).

Oxidation of Compound 42. The alcohol **42** (630 mg; 5.0 mmol) was treated in the same way as **39**, except that a higher temperature was used (50 °C for 8 h). Brine (25 mL) was added, and the solution was extracted with petroleum ether/Et_2O (2 × 125 mL 7/3, 2 × 125 mL, 1/1). The combined organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 25 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to yield 0.78 g (85%) of a black liquid. The crude mixture was purified by flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 9/1 and 2/3, was used) to afford 0.36 g (39%) of a mixture of the alcohols **43** and **44** in a ratio of 60/40. The ratio **44a/b** was 40/60 by ^1H NMR. The diastereomers were separated on HPLC (eluting with a 4/1 mixture of hexane/EtOAc). **43**: ^1H NMR (200 MHz) δ 5.81 (ddt, J = 17, 10 and 7 Hz, 1 H), 5.49 (dd, J = 8.5 and 1 Hz, 1 H), 5.05–5.24 (m, 2 H), 4.46 (br s, 3 H, CH_2OAc, $CHOH$), 2.30 (t, J = 7 Hz, 2 H, CH_2), 2.05 (s, 3 H, OAc), 1.73 (s, 3 H, CH_3), 1.65 (s, 1 H, OH); ^{13}C NMR (100.6 MHz) δ 170.74, 133.92, 132.58, 130.21, 118.15, 68.91, 67.19, 41.76, 20.81, 14.25. **44a**: ^1H NMR (400 MHz) δ 5.78 (ddt, J = 17, 10, and 7 Hz, 1 H), 4.94–5.08 (m, 5 H, 2 $=CH_2$, $CHOAc$), 4.20 (br t, J = 4 Hz, 1 H), 2.36–2.42 (m, 2 H, CH_2), 2.06 (s, 3 H, CH_3COO), 1.92 (d, J = 4 Hz, 1 H, OH), 1.55 (s, 3 H, CH_3). **44b**: ^1H NMR (400 MHz) δ 5.85 (ddt, J = 17, 10, and 7 Hz, 1 H), 5.12–5.17 (m, 2 H), 5.09 (d, J = 5.3 Hz, 1 H, $CHOAc$), 5.02–5.04 (m, 2 H), 3.82 (ddt, J = 4.5, 5.3, and 7 Hz, 1 H), 2.17–2.32 (m, 2 H), 2.13 (s, 3 H), 1.90 (d, J = 4.5 Hz, 1 H), 1.78 (s, 3 H); ^{13}C NMR (100.6 MHz) δ 170.18, 140.92, 133.87, 118.33, 114.45, 79.11, 70.35, 37.52, 21.03, 19.23.

Oxidation of Compound 45.[58] The diene **45** (611 mg, 5 mmol) was treated in the same way as **42**. After the addition of brine the solution was extracted with petroleum ether/Et_2O (3 × 125 mL 4/1, 2 × 125 mL 7/3). The combined organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (4 × 125 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to yield 1.0 g of a black liquid. The crude mixture was dissolved in 25 mL of Et_2O, washed with saturated $NaHCO_3$ (3 × 10 mL), and dried ($MgSO_4$), and the solvent was removed in vacuo to yield 0.43 g (47%) of a mixture of **46** and **47**. The crude mixture was purified by flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 9/1 and 1/1, was used) to afford 0.26 g (29%) of a mixture of the acetates **46** and **47**, by GLC in a ratio of 80/20, together with minor amounts of unidentified products. The products were separated by HPLC (eluting with a 99/1 mixture of hexane/EtOAc). **46**: ^1H NMR (200 MHz) δ 5.56–5.92 (m, 3 H), 5.20–5.36 (m, 1 H), 4.92–5.10 (m, 2 H), 2.14–2.32 (m, 2 H), 2.05 (s, 3 H), 1.80–1.96 (m, 2 H), 1.48–1.69 (m, 1 H), 1.20–1.45 (m, 2 H); ^{13}C NMR (100.6 MHz) δ 170.84, 136.32, 135.64, 126.44, 116.45, 69.53, 39.83, 34.85, 27.48, 26.15, 21.37. **47**: ^1H NMR (200 MHz) δ 5.62–5.95 (m, 3 H), 5.20 (br q, J = 4 Hz, 1 H, $CHOAc$), 4.92–5.14 (m, 2 H), 2.05 (s, 3 H), 1.92–2.18 (m, 3 H), 1.59–1.92 (m, 3 H), 1.32–1.59 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 170.77, 136.62, 133.08, 125.0, 116.23, 68.64, 37.34, 35.72, 25.32, 23.85, 21.16.

Cyclization of 6-(2-Ethenyl)-2,8-nonadienyl Acetate (48).[59] This reaction was run on a 2.52-mmol scale according to the procedure described for **9**. After the mixture was stirred for 40 h at 20 °C, 13 mL of brine was added, and the aqueous phase was extracted with 4 × 15 mL of pentane/ether. The combined organic phase was washed with water (1 × 5 mL) and saturated aqueous Na_2CO_3 (2 × 5 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to afford 604 mg of an oil. Following flash chromatography (using a stepwise gradient of pentane/Et_2O, 3/1 and 7/3), a mixture of **49a** and **49b** (54%) together with some unidentified acetates (18%) was obtained (ratio of **49a/49b** = 33/67). The two diastereomers were separated by HPLC (hexane/EtOAc, 19/1) for structural determination. **49a**: R_f = 0.35 (pentane/Et_2O, 7/3); ^1H NMR (200 MHz) δ 5.78 (dt, part of AB, J = 16 and 6.5 Hz, 1 H, CH=$CHCH_2OAc$), 5.60 (dt, part of AB, J = 16 and 6.5 Hz, 1 H, CH=$CHCH_2OAc$), 5.07 (quintet, J = 6.5 Hz, 1 H, $CHOAc$), 4.83–4.94 (m, 2 H, CH_2=C), 4.51 (d, J = 6.5 Hz, 2 H, CH_2OAc), 2.72–2.80 (m, 1 H, CH_2=CHH_2), 2.36–2.44 (m, 1 H, CH_2=CCH_2), 2.25–2.34 (m, 1 H, $CH(OAc)CH_2CH$), 2.07 (s, 3 H, CH_2OAc), 2.03 (s, 3 H, $CHOAc$), 2–2.2 (m, 3 H, $CHCH_2CH_2CH$=), 1.72–1.81 (m, 1 H, CH_2CH_2CH=), 1.39–1.48 (m, 2 H, CH_2CH_2CH= and $CH(OAc)CH_2CH$); ^{13}C NMR (100.6 MHz) δ 170.7 (2 C) 152.00, 135.59, 124.32, 106.55, 73.99, 65.10, 41.17, 39.51, 37.88, 33.93, 30.29, 21.16, 20.93. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.62; H, 8.33. Found: C, 67.51; H, 8.26. **49b**: R_f = 0.35 (pentane/Et_2O, 7/3); ^1H NMR (200 MHz) δ 5.80 (dt, part of AB, J = 15.5 and 6.5 Hz, 1 H, CH=$CHCH_2OAc$), 5.60 (dt, part of AB, J = 15.5 and 6.5 Hz, 1 H, CH=$CHCH_2OAc$), 5.19 (tt, J = 5 and 2.5 Hz, 1 H, $CHOAc$), 4.85–4.98 (m, 2 H, CH_2=C), 4.52 (dd, J = 6.3 and 0.84 Hz, 2 H, CH_2OAc), 2.67 (m, part of AB, J_{AB} = 17 Hz, 1 H, CH_2=CHH_2), 2.6 (m, 1 H, CH_2=CCH), 2.46 (m, part of AB, J_{AB} = 17 Hz, 1 H, CH_2=CCH_2), 2.07 (s, 3 H, CH_2OAc), 2.02 (s, 3 H, $CHOAc$), 2–2.2 (m, 3 H, one of $CH(OAc)CH_2CH$ and CH_2CH=$CHCH_2OAc$), 1.67–1.87 (m, 1 H, CH_2CH_2CH=CH), 1.54 (ddd, J = 14, 10 and 5 Hz, 1 H, $CH(OAc)CH_2CH$), 1.35 (m, 1 H, CH_2CH_2CH=CH); ^{13}C NMR (100.6 MHz) δ 170.76, 170.72, 152.67, 135.85, 124.25, 106.32, 74.50, 65.10, 40.87, 39.82, 38.64, 33.44, 30.24, 21.26, 20.93. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.62; H, 8.33. Found: C, 67.47; H, 8.20.

***trans*-3-(ω-Hydroxyalkoxy)-1-phenyl-1,5-hexadienes (53–55).** To a slurry of finely powdered KOH (4.48 g, 80 mmol) in 34 mL of dry DMSO was added *trans*-3-hydroxy-1-phenyl-1,5-hexadiene (**26**) (3.48 g, 20 mmol) dissolved in 6 mL of dry DMSO and the appropriate ω-chloro alcohol tetrahydropyranyl ether (40 mmol). After the mixture was stirred at 40 °C for 20 h, water (100 mL) was added, and the aqueous phase was extracted with Et_2O (100 mL and 2 × 50 mL). The combined organic phase was washed with water (2 × 25 mL) and brine (25 mL) and dried ($MgSO_4$). Removal of the solvent and the excess tetrahydropyranyl ether in vacuo (bulb-to-bulb apparatus, 100 °C ca. 0.5 Torr) afforded an oil. Following flash chromatography (using a stepwise gradient of petroleum ether/Et_2O, 9/1, 4/1, 7/3, 3/2, and 1/1) **50** (67%), **51** (34%), and **52** (91%), respectively, were obtained. **50**: R_f = 0.58 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.45 (m, 5 H, Ph), 6.55 (A part of ABX, J_{AB} = 16 and J_{AX} = 0 Hz, 1 H, PhCH=CH), 6.10 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=CH), 5.86 (m, 1 H, CH_2=CH), 5.0–5.16 (m, 2 H, CH_2=CH), 4.61 (br t, J = 3 Hz, 1 H, $OCHO$), 3.42–4.02 (m, 7 H, $CHOCH_2CH_2OCHOCH_2$), 2.26–2.58 (m, 2 H, CH_2=$CHCH_2$), 1.4–1.9 (m, 6 H, $OCH_2CH_2CH_2CH_2$). **51**: R_f = 0.58 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.17–7.42 (m, 5 H, Ph), 6.52 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhCH=CH), 6.08 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=CH), 5.85 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=CH), 5.0–5.16 (m, 2 H, CH_2=CH), 4.57 (m, 1 H, OCHO), 3.36–3.93 (m, 7 H, $CHOCH_2CH_2CH_2OCHOCH_2$), 2.39 (m, 2 H, C=CCH_2), 1.87 (quintet, J = 6 Hz, 2 H, $OCH_2CH_2CH_2O$), 1.4–1.9 (m, 6 H, $CH_2CH_2CH_2CH_2O$). **52**: R_f = 0.58 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.19–7.44 (m, 5 H, Ph), 6.52 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhCH=CH), 6.09 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.8 Hz, 1 H, PhCH=CH), 5.86 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=CH), 5.01–5.16 (m, 2 H, CH_2=CH), 4.57 (m, 1 H, OCHO), 3.86 (apparent q, 1 H, $CHOCH_2CH_2CH_2OCHO$),

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3.4–3.9 (m, 6 H, $OCH_2CH_2CH_2CH_2OCHOCH_2$), 2.26–2.55 (m, 2 H, $C{=}CCH_2$), 1.4–1.9 (m, 10 H, pyranyl and $OCH_2CH_2CH_2CH_2O$).

To a solution of the appropriate tetrahydroparanyl ether (**50–52**) in MeOH (8 mL per mmol substrate) was added *p*-TsOH (0.05 equiv), and the mixture was stirred at ambient temperature for 1 h. After removal of MeOH in vacuo, Et_2O (150 mL) was added, and the organic phase was washed with saturated aqueous Na_2CO_3 and dried ($MgSO_4$). Removal of the solvent in vacuo afforded an oil. Following flash chromatography (petroleum ether/Et_2O, 1/1, for **53** and **55** and a stepwise gradient of petroleum ether/Et_2O, 2/3 and 1/4, for **54**) **53** (81%), **54** (82%), and **55** (65%) were obtained as colorless oils. **53**: R_f = 0.26 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.45 (m, 5 H, Ph), 6.54 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$, 1 H, PhC*H*=CH), 6.09 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.85 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.03–5.19 (m, 2 H, CH_2=CH), 3.93 (apparent q, 1 H, CHO), 3.61–3.79 (m, 3 H, OCH_2CH_2OH), 3.40–3.55 (m, 1 H, OCH_2CH_2OH), 2.29–2.56 (m, 2 H, CH_2=CHCH_2), 2.0 (t, J = 6 Hz, 1 H, OH); ^{13}C NMR (50.3 MHz) δ 136.54, 134.38, 132.33, 129.79, 128.56, 127.76, 126.52, 117.23, 80.77, 69.73, 61.92, 40.25; IR (film) 3600–3160, 3080, 3030, 2980, 2940, 2860, 1640, 1150, 1065, 970, 915, 750, and 695 cm^{-1}. **54**: R_f = 0.26 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.43 (m, 5 H, Ph), 6.53 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.08 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.84 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 5.04–5.18 (m, 2 H, CH_2=CH), 3.90 (apparent q, 1 H, CHO), 3.71–3.83 (m, 3 H, $OCH_2CH_2CH_2OH$), 3.45–3.56 (m, 1 H, $OCH_2CH_2CH_2OH$), 2.45 (t, J = 5.5 Hz, 1 H, OH), 2.28–2.53 (m, 2 H, $C{=}CCH_2$), 1.83 (quintet, J = 5.5 Hz, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (50.3 MHz) δ 135.94, 133.76, 131.79, 129.26, 128.07, 127.25, 126.02, 116.87, 80.52, 67.44, 61.57, 40.40, 32.32; IR (film) 3600–3200, 3070, 3060, 3030, 2930, 2860, 1640, 1190–1170, 970, 915, 750, 695 cm^{-1}. **55**: R_f = 0.24 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.2–7.43 (m, 5 H, Ph), 6.53 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PHC*H*=CH, 6.09 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.9 Hz, 1 H, PhCH=C*H*), 5.84 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.02–5.17 (m, 2 H, CH_2=CH), 3.89 (apparent q, 1 H, CHO), 3.65 (m, 2 H, CH_2OH), 3.59 (A part of ABX_2, J_{AB} = 9.5 and J_{AX} = 6 Hz, 1 H, $ROCH_2$), 3.48 (B part of ABX_2, J_{AB} = 9.5 and J_{BX} = 6 Hz, 1 H, $ROCH_2$), 2.27–2.56 (m, 3 H, $C{=}CCH_2$ and OH), 1.62–1.73 (m, 4 H, $OCH_2CH_2CH_2CH_2O$); ^{13}C NMR (100.6 MHz) δ 136.45, 134.25, 132.24, 129.86, 128.54, 127.70, 126.46, 117.17, 80.68, 68.47, 62.64, 40.23, 30.21, 26.77.

***trans*-3-(ω-Cyanoalkoxy)-1-phenyl-1,5-hexadienes 59–61.** *p*-Toluenesulfonyl chloride (1.1 equiv) was added during 10 min to a well-stirred solution of the appropriate alcohol (**53–55**) in dry pyridine (0.3 mL per mmol) at 0 °C. After the mixture had been stirred for an additional 4 h at 0 °C, 2 M HCl (3 mL/mmol substrate) was added, and the aqueous phase was extracted with Et_2O. The combined organic phase was washed with saturated aqueous Na_2CO_3 and dried ($MgSO_4$). Removal of the solvent in vacuo gave **56** (95%), **57** (93%), and **58** (98%), respectively. **56**: ^1H NMR (200 MHz) δ 7.79 (d, J = 8.5 Hz, 2 H, *p*-tolSO_3) 7.2–7.4 (m, 7 H, *p*-tolSO_3 and Ph), 6.48 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 5.98 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.76 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 4.98–5.12 (m, 2 H, CH_2=CH), 4.16 (apparent t, 2 H, $CH_2CH_2OSO_2R$), 3.85 (apparent q, 1 H, CHO), 3.49–3.75 (m, 2 H, $OCH_2CH_2OSO_2R$), 2.42 (s, 3 H, Me), 2.33 (m, 2 H, $C{=}CCH_2$). **57**: ^1H NMR (200 MHz) δ 7.77 (d, J = 8.5 Hz, 2 H, *p*-tolSO_3), 7.2–7.4 (m, 7 H, *p*-tolSO_3 and Ph), 6.48 (A part of ABX, J_{AB} = 16 Hz and J_{AX} = 0 Hz, 1 H, PhC*H*=CH), 6.0 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.8 Hz, 1 H, PhCH=C*H*), 5.75 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 4.87–5.11 (m, 2 H, CH_2=CH), 4.07–4.24 (m, 2 H, *p*-tolSO_2OCH_2), 3.97 (apparent q, 1 H, CHO), 3.55 (A part of ABX_2, J_{AB} = 9.7 and J_{AX} = 6 Hz, 1 H, $CHOCH_2CH_2$), 3.35 (B part of ABX_2, J_{AB} = 9.7 and J_{BX} = 6 Hz, 1 H, $CHOCH_2CH_2$), 2.18–2.45 (m, 2 H, $C{=}CCH_2$), 2.42 (s, 3 H, Me), 1.90 (quintet, J = 6 Hz, 2 H, $CH_2CH_2CH_2$). **58**: ^1H NMR (200 MHz) δ 7.78 (d, J = 8.4 Hz, 2 H, *p*-tolSO_3), 7.2–7.42 (m, 7 H, *p*-tolSO_3 and Ph), 6.49 (A part of ABX, J_{AB} = 16.2 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.04 (B part of ABX, J_{AB} = 16.2 and J_{BX} = 7.7 Hz, 1 H, PhCH=C*H*), 5.80 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 5.0–5.14 (m, 2 H, CH_2=CH), 4.06 (t, J = 6.3 Hz, 2 H, CH_2OSO_2-*p*-tol), 3.8 (m, 1 H, CHO), 3.49 (A part of ABX_2, J_{AB} = 9.5 and J_{AX} = 6 Hz, 1 H, $CHOCH_2$) 3.28 (B part of ABX_2, J_{AB} = 9.5 and J_{BX} = 6 Hz, 1 H, $CHOCH_2$), 2.43 (s, 3 H, Me), 2.1–2.49 (m, 2 H, $C{=}CCH_2$), 1.5–1.84 (m, 4 H, $OCH_2CH_2CH_2CH_2CN$).

To a solution of the appropriate tosylate (**56–58**) in dry DMSO (3 mL/mmol substrate) was added NaCN (1 equiv), and the mixture was stirred for 19 h at ambient temperature. After addition of water and brine the aqueous phase was extracted with Et_2O. The combined organic phase was washed with water and brine and dried ($MgSO_4$). The solvent was removed in vacuo to give an oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 4/1 and 3/2, was used) gave **59** (90%), **60** (96%), and **61** (99%), respectively. **59**: R_f = 0.48 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz), δ 7.2–7.43 (m, 5 H, Ph), 6.56 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.07 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.85 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 5.03–5.18 (m, 2 H, CH_2=CH), 3.94 (apparent q, 1 H, CHO), 3.76 (A part of ABX_2, J_{AB} = 9.5 Hz, J_{AX} = 6.4 Hz, 1 H, OCH_2CH_2CN), 3.58 (B part of ABX_2, J_{AB} = 9.5 Hz and J_{BX} = 6.4 Hz, 1 H, OCH_2CH_2CN), 2.59 (t, J = 6.4 Hz, 2 H, CH_2CN), 2.28–2.54 (m, 2 H, $C{=}CCH_2$); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 135.45, 133.20, 132.18, 128.25, 127.89, 127.23, 125.85, 117.17, 116.72, 80.78, 62.71, 39.97, 18.93; IR (film) 3080, 3060, 3030, 2980, 2250, 1640, 1100, 975, 920, 755, 695 cm^{-1}. **60**: R_f = 0.52 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.17–7.43 (m, 5 H, Ph), 6.53 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.06 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.8 Hz, 1 H, PhCH=C*H*), 5.83 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.01–5.17 (m, 2 H, CH_2=CH), 3.87 (apparent q, 1 H, CHO), 3.65 (A part of ABX_2, J_{AB} = 9.7 and J_{AX} = 6 Hz, 1 H, $CHOCH_2CH_2$), 3.42 (B part of ABX_2, J_{AB} = 9.7 and J_{BX} = 6 Hz, 1 H, $CHOCH_2CH_2$), 2.26–2.53 (m, 4 H, $C{=}CCH_2$ and CH_2CN), 1.9 (quintet, J = 6 Hz, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 136.49, 134.28, 132.31, 129.71, 128.56, 127.76, 126.51, 119.41, 117.11, 80.67, 65.83, 40.21, 26.00, 14.6; IR (film) 3080, 3060, 3030, 2940, 2250, 1640, 1100, 970, 920, 750, 695 cm^{-1}. **61**: ^1H NMR (200 MHz) δ 7.2–7.43 (m, 5 H, Ph), 6.52 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.07 (B part of ABX, J_{AB} = 16.0 and J_{BX} = 7.8 Hz, 1 H, PHCH=C*H*), 5.84 (ddt, J = 17, 10 and 7 Hz, 1 H, CH_2=C*H*), 5.08–5.17 (m, 2 H, CH_2=CH), 3.85 (apparent q, 1 H, *CH*O), 3.58 (A part of ABX_2, J_{AB} = 9.6 and J_{AX} = 5.7 Hz, 1 H, $CHOCH_2$), 3.36 (B part of ABX_2, J_{AB} = 9.6 and J_{BX} = 5.9 Hz, 1 H, $CHOCH_2$), 2.25–2.53 (m, 2 H, $C{=}CCH_2$), 2.38 (t, J = 7 Hz, 2 H, CH_2CN), 2.64–2.85 (m, 4 H, $CH_2CH_2CH_2CH_2CN$); ^{13}C NMR (100.6 MHz) δ 136.44, 134.41, 132.16, 129.92, 128.58, 127.74, 126.46, 119.69, 117.06, 80.57, 67.22, 40.28, 28.68, 22.67, 16.96.

***trans*-3-(Carboxyalkoxy)-1-phenyl-1,5-hexadienes 62–64.**[60] To a solution of pyridinium dichromate (3 equiv) in dry DMF (0.6 mL per mmol substrate) was added the appropriate alcohol (**53–55**) dissolved in 2 mL of dry DMF. After the mixture was stirred at ambient temperature for 18 h and water was added, the aqueous phase was extracted with Et_2O. The organic phase was washed with water and extracted with aqueous saturated Na_2CO_3. The basic aqueous phase was acidified by addition of 2 M HCl and then extracted with Et_2O. After drying ($MgSO_4$) and removal of the solvent in vacuo **62** (46%), **63** (26%), and **64** (66%) were obtained as colorless oils. **62**: ^1H NMR (200 MHz) δ 7.21–7.43 (m, 5 H, Ph), 6.57 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.05 (B part of ABX, J_{AB} = 16 and J_{BX} = 8 Hz, 1 H, PhCH=C*H*), 5.86 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 5.08–5.23 (m, 2 H, CH_2=CH), 4.18 (A part of AB, J_{AB} = 16.5 Hz, 1 H, CH_2COOH), 4.05 (B part of AB, J_{AB} = 16.5 Hz, 1 H, CH_2COOH), superimposed on 3.97–4.1 (m, 1 H, CHO), 2.36–2.64 (m, 2 H, $C{=}CCH_2$); ^{13}C NMR (50.3 MHz, Me_4Si as internal standard) δ 173.81, 135.19, 133.26, 132.98, 127.87, 127.38, 127.20, 125.90, 117.04, 81.11, 64.75, 39.81. **63**: ^1H NMR (200 MHz) δ 7.2–7.43 (m, 5 H, Ph), 6.55 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx 0$ Hz, 1 H, PhC*H*=CH), 6.08 (B part of ABX, J_{AB} = 16 and J_{BX} = 7.5 Hz, 1 H, PhCH=C*H*), 5.83 (ddt, J = 17, 10, and 7.5 Hz, 1 H, CH_2=C*H*), 5.02–5.16 (m, 2 H, CH_2=CH), 3.92 (apparent

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q, 1 H, CHO), 3.83 (A part of ABX_2, J_{AB} = 9.5 and J_{AX} = 6 Hz, 1 H, OCH_2CH_2COOH), 3.64 (B part of ABX_2, J_{AB} = 9.5 and J_{BX} = 6 Hz, 1 H, OCH_2CH_2COOH), 2.64 (t, J = 6 Hz, 2 H, CH_2COOH), 2.26–2.54 (m, 2 H, C=CCH_2); ^{13}C NMR (100.6 MHz) δ 176.96, 136.39, 134.19, 132.47, 129.44, 128.57, 127.79, 126.53, 117.23, 81.01, 63.57, 40.19, 34.97. **64**: ^1H NMR (200 MHz) δ 7.18–7.42 (m, 5 H, Ph), 6.51 (A part of ABX, J_{AB} = 16 and $J_{AX} \approx$ 0 Hz, 1 H, PhC*H*=CH), 6.06 (B part of ABX, J_{AB} = 16.0 and J_{BX} = 7.8 Hz, 1 H, PhCH=C*H*), 5.83 (ddt, J = 17, 10, and 7 Hz, 1 H, CH_2=C*H*), 5.0–5.15 (m, 2 H, CH_2=CH), 3.85 (m, 1 H, CHO), 3.58 (A part of ABX_2, J_{AB} = 9.5 and J_{AX} = 6.0 Hz, 1 H, $CHOCH_2$), 3.37 (B part of ABX_2, J_{AB} = 9.5 and J_{BX} = 6.0 Hz, 1 H, $CHOCH_2$), 2.46 (t, J = 7.3 Hz, 2 H, CH_2COOH), 2.25–2.52 (m, 2 H, C=CCH_2), 1.89 (m, 2 H, CH_2CH_2COOH); ^{13}C NMR (100.6 MHz), δ 179.27, 136.51, 134.38, 132.19, 129.92, 128.57, 127.71, 121.50, 117.09, 80.56, 67.20, 40.25, 31.09, 24.88.

Cyclization of *trans*-3-(2-Hydroxyethoxy)-1-phenyl-1,5-hexadiene (53). This compound (2 mmol) was reacted according to the procedure described for **9**. After the mixture was stirred for 67 h at ambient temperature, 10 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (3 × 20 mL 2/3). The combined organic phase was washed with water (5 mL) and saturated aqueous Na_2CO_3 (4 × 5 mL). The combined aqueous phase from the wash was then extracted with petroleum ether/Et_2O (25 mL 2/3), and the organic phase was washed with saturated aqueous Na_2CO_3 (2 × 5 mL). After drying ($MgSO_4$) and removal of the solvent in vacuo, 535 mg of an oil was obtained. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 2/3, 1/9, was used) gave **34** (33.9 mg, 0.157 mmol), **35** (112.3 mg, 0.41 mmol), and **65a/65b** (256 mg, 0.926 mmol). Yield of **65a/65b**: 46%, ratio 60/40. The two diastereomers were separated by HPLC (petroleum ether/EtOAc, 3/2) for structural determination. **65a**: R_f = 0.12 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.17–7.5 (m, 5 H, Ph), 6.58 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.31 (m, 1 H, C*H*OAc), 4.67 (m, 1 H, $CHOCH_2$), 3.4–3.8 (m, 4 H, OCH_2CH_2OH), 3.05 (br dd, J = 17 and 6.5 Hz, 1 H, C=CCH_2), 2.51 (br d, J = 17 Hz, 1 H, C=CCH_2), 2.41–2.26 (ddd, part of AB, J = 14.6, 6, and 3.5 Hz, 1 H, CH(OAc) CH_2CHO), 1.97–2.15 (m, 1 H, CH(OAc)CH_2CHO), 2.02 (s, 3 H, OAc), 1.73 (t, J = 6.2 Hz, 1 H, OH); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 170.80, 142.29, 138.18, 129.55, 129.06, 128.32, 127.66, 77.98, 73.84, 70.12, 61.94, 40.47, 39.40, 21.01. **65b**: R_f = 0.12 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.18–7.43 (m, 5 H, Ph), 6.58 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.22 (m, 1 H, C*H*(OAc)), 4.53 (br d, J = 5 Hz, 1 H, $CHOCH_2$), 3.5–3.85 (m, 4 H, OCH_2CH_2OH), 2.92 (ddd, part of AB, J = 17.5, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.82 (br d, part of AB, J = 17.5 Hz, 1 H, C=CCH_2), 2–2.33 (m, 3 H, OH and CH(OAc)CH_2CHO), 2.07 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, acetone-d_6) δ 170.88, 142.40, 138.08, 129.57, 129.06, 128.36, 127.72, 77.81, 73.46, 69.82, 61.9, 40.98, 38.48, 21.05.

Cyclization of *trans*-3-(Hydroxypropoxy)-1-phenyl-1,5-hexadiene (54). The diene **54** (2 mmol) was cyclized according to the procedure described for **9**. After the mixture was stirred at ambient temperature for 42 h, 10 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (3 × 40 mL 1/1). The organic phase was washed with water (20 mL) and saturated aqueous Na_2CO_3 (2 × 20 mL). The combined aqueous phase from the wash was extracted with petroleum ether/Et_2O (50 mL 1/1), and the organic phase was washed with saturated aqueous Na_2CO_3 (2 × 5 mL). After drying of the combined organic phase ($MgSO_4$) and removal of the solvent in vacuo, 537.6 mg of a dark oil was obtained. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 2/3 and 1/4, was used) gave **34** (23.5 mg, 0.11 mmol), **35** (100 mg, 0.365 mmol), and a mixture of **66a/66b** (263 mg, 0.91 mmol). Yield of **66a/66b**, 46%; ratio, 55/45. The two diastereomers were separated by HPLC (petroleum ether/EtOAc, 3/2) for structural determination. **66a**: R_f = 0.1 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.18–7.42 (m, 5 H, Ph) 6.57 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.30 (m, 1 H, C*H*OAc), 4.58 (br s, $w_{1/2}$ = 12 Hz, 1 H, CHO), 3.47–3.74 (m, 4 H, $OCH_2CH_2CH_2OH$), 3.04 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.50 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.30–2.44 (ddd, part of AB, J = 14.5, 6, and 3 Hz, 1 H, CH(OAc)CH_2CHO), 1.93–2.09 (m, 1 H, CH(OAc)CH_2CHO), 2.02 (s, 3 H, OAc), 1.72–1.90 (m, 3 H, $CH_2CH_2CH_2$ and OH); ^{13}C NMR (100.6 MHz) δ 170.86, 140.60, 137.07, 128.47, 128.30, 128.14, 127.03, 77.21, 73.33, 66.00, 61.26, 39.66, 38.74, 32.35, 21.22. **66b**: R_f = 0.1 (petroleum ether/Et_2O, 2/3); ^1H NMR (200 MHz) δ 7.17–7.38 (m, 5 H, Ph), 6.55 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.18 (m, 1 H, C*H*(OAc)), 4.41 (br d, J = 5 Hz, 1 H, CHO), 3.73 (q, J = 5.5 Hz, 2 H, CH_2OH), 3.60 (t, J = 5.5 Hz, 2 H, $OCH_2CH_2CH_2OH$), 2.88 (ddd, part of AB, J = 17.5, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.79 (br d, part of AB, J = 17.5 Hz, 1 H, C=CCH_2), 2.39 (t, 1 H, OH), 2.0–2.28 (m, 2 H, CH(OAc)CH_2CHO), 2.07 (s, 3 H, OAc), 1.72–1.93 (m, 2 H, $OCH_2CH_2CH_2O$); ^{13}C NMR (100.6 MHz) δ 171.12, 141.08, 137.10, 128.46, 128.29 (2 C), 127.09, 77.48, 73.18, 67.09, 62.14, 40.07, 38.03, 32.19, 21.21.

Cyclization of *trans*-3-(4-Hydroxybutoxy)-1-phenyl-1,5-hexadiene (55). Compound **55** (2 mmol) was cyclized according to the procedure described for **9**. After the mixture was stirred for 52 h at ambient temperature, the reaction mixture was worked up in the same way as described for **54** to give 625.2 mg of a dark oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 3/2, 1/1, 2/3, 1/9, was used) gave 38.9 mg (0.18 mmol) of **34**, 109.6 mg (0.4 mmol) of **35**, and 255 mg (0.84 mmol, 42%) of **67a/67b** in a ratio of 55/45. **67a**: R_f = 0.08 (petroleum ether/Et_2O, 2/3); ^1H NMR (400 MHz, peaks assigned from a mixture of **67a/67b**) δ 7.2–7.4 (m, 5 H, Ph), 6.56 (br s, 1 H, PhC*H*=C), 5.31 (m, 1 H, C*H*(OAc)), 4.54 (m, 1 H, CHO), 3.38–3.67 (m, 4 H, $OCH_2CH_2CH_2CH_2OH$), 3.06 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.49 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.36 (ddd, J = 14.5, 6 and 3 Hz, 1 H, CH(OAc)CH_2CHO), ca. 2.15 (1 H, OH), 2.01 (s, 3 H, OAc), 1.99 (dt, J = 14.5 and 6 Hz, 1 H, CH(OAc)-CH_2CHO), 1.56–1.74 (m, 4 H, OCH_2, $CH_2CH_2CH_2OH$); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **67a/67b**) δ 171.07 (s, 1 C), 140.65 (s, 1 C), 136.94 (s, 1 C), 128.1–128.5 (d, 2 C, overlapping peaks), 127.99 (d, 1 C), 126.86 (d, 1 C), 77.05 (d, 1 C), 73.33 (d, 1 C), 67.40 (t, 1 C), 62.47 (t, 1 C), 39.60 (t, 1 C), 38.71 (t, 1 C), 29.83 (t, 1 C), 26.56 (t, 1 C), 21.13 (q, 1 C). **67b**: R_f = 0.08 (petroleum ether/Et_2O, 2/3); ^1H NMR (400 MHz, peaks assigned from a mixture of **67a/67b**) δ 7.2–7.4 (m, 5 H, Ph), 6.56 (br s, 1 H, PhC*H*=C), 5.13 (m, 1 H, C*H*(OAc)), 4.42 (m, 1 H, CHO), 3.38–3.67 (m, 4 H, $OCH_2CH_2CH_2OH$), 2.86 (ddd, part of AB, J = 17, 6.5 and 2 Hz, 1 H, C=CCH_2), 2.80 (br d, part of AB, J = 17 Hz, 1 H, C=CCH_2), 2.1–2.2 (m, 3 H, CH(OAc)CH_2CHO and OH), 2.06 (s, 3 H, OAc), 1.56–1.74 (m, 4 H, $OCH_2CH_2CH_2CH_2OH$); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **67a/67b**) δ 170.80 (s, 1 C) 140.82 (s, 1 C), 137.03 (s, 1 C), 128.24 (d, 1 C), 128.2–128.5 (d, 2 C, overlapping peaks), 126.94 (d, 1 C), 77.09 (d, 1 C), 72.91 (d, 1 C), 67.49 (t, 1 C), 62.41 (t, 1 C), 40.07 (t, 1 C), 37.78 (t, 1 C), 30.00 (t, 1 C), 26.68 (t, 1 C), 21.18 (q, 1 C).

Cyclization of *trans*-3-(2-Cyanoethoxy)-1-phenyl-1,5-hexadiene (59). Compound **59** (2 mmol) was treated in the same way as **9**. After the mixture was stirred at ambient temperature for 30.5 h, 5 mL of brine was added and the aqueous phase was extracted with petroleum ether/Et_2O (3 × 40 mL 1/1). The combined organic phase was washed with water (20 mL) and saturated aqueous Na_2CO_3 (2 × 20 mL). The aqueous phase from the wash was then extracted with petroleum ether/Et_2O (30 mL 1/1), and the organic phase was washed with aqueous saturated Na_2CO_3 (5 mL). After drying ($MgSO_4$) of the combined organic phase and removal of the solvent in vacuo, 532 mg of an oil was obtained. Following flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 3/2, 2/3, and 1/4, was used), **34** (13 mg, 0.06 mmol), **35** (84 mg, 0.306 mmol), and one fraction containing a mixture of **68a** and **68b** (287 mg, 1.0 mmol) and one other isomer (43 mg, 0.151 mmol) were obtained. Yield of **68a/68b**, 50%; ratio, 60/40. **68a**: R_f = 0.22 (petroleum ether/Et_2O, 2/3); ^1H NMR (400 MHz, peaks assigned from a mixture of **68a/68b**) δ 7.2–7.4 (m, 5 H, Ph), 6.61 (br s, 1 H, PhC*H*=C), 5.32 (m, 1 H, C*H*OAc), 4.63 (m, 1 H, CHO), 3.5–3.6 (m, 2 H, OCH_2CH_2CN), 3.06 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.49 (t, J = 6.3 Hz, 2 H, CH_2CN), 2.45–2.53 (m, 1 H, C=CCH_2), 2.36 (ddd, J = 14.5, 6, and 3 Hz, 1 H, CH(OAc)CH_2CHO), 2.02 (s, 3 H, OAc), 1.95–2.05 (m, 1 H, CH(OAc)CH_2CHO); ^{13}C NMR (100.6 MHz; peaks assigned from a mixture of **68a/68b**) δ 170.69 (s, 1 C), 139.76 (s, 1 C), 136.75 (s, 1 C), 128.2–128.4 (d, 3 C, overlapping peaks), 127.09 (d, 1 C), 117.78 (s, 1 C), 77.3 (d, 1 C), 73.02 (d, 1 C), 62.12 (t, 1 C), 39.25 (t, 1 C), 38.57 (t, 1 C), 21.05 (q, 1 C), 18.81 (t, 1 C). **68b**: R_f = 0.22 (petroleum ether/Et_2O, 2/3); ^1H NMR (400 MHz, peaks

assigned from a mixture of **68a/68b**) δ 7.2–7.4 (m, 5 H, Ph), 6.61 (br s, 1 H, PhC*H*=C), 5.15 (m, 1 H, C*H*(OAc)), 4.50 (m, 1 H, C*H*O), 3.55–3.65 (m, 2 H, OCH_2CH_2CN), 2.88 (ddd, part of AB, J = 17, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.79 (br d, part of AB, J = 17 Hz, 1 H, C=CCH_2), 2.55 (t, J = 6.2 Hz, 2 H, CH_2CN), 2.1–2.24 (m, 2 H, CH(OAc)CH_2CHO), 2.07 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **68a/68b**) δ 170.98 (s, 1 C), 139.96 (s, 1 C), 136.65 (s, 1 C), 128.2–128.4 (d, 3 C, overlapping peaks), 127.16 (d, 1 C), 117.70 (s, 1 C), 77.3 (d, 1 C), 72.57 (d, 1 C), 62.08 (t, 1 C), 39.83 (t, 1 C), 37.69 (t, 1 C), 21.14 (q, 1 C), 18.92 (t, 1 C).

Cyclization of *trans*-3-(3-Cyanopropoxy)-1-phenyl-1,5-hexadiene (60). Compound **60** was cyclized using the procedure described for **9** and worked up in the same way as **59** to yield 564.9 mg of an oil. Following flash chromatography (same gradient as for **59**) one fraction containing a mixture of **60** (63.5 mg, 0.263 mmol), **34** (19.7 mg, 0.09 mmol), and **35** (55.8 mg, 0.203 mmol) and another fraction containing a mixture of **69a,b** (260 mg, 0.87 mmol) together with another isomer (33 mg, 0.11 mmol) were afforded. Yield of **69a/69b**, 44%; ratio, 58/42. The two diastereomers were partially separated on HPLC (petroleum ether/EtOAc, 7/3). **69a**: R_f = 0.26 (petroleum ether/Et_2O, 2/3); ^{1}H NMR (200 MHz) δ 7.2–7.42 (m, 5 H, Ph), 6.57 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.3 (m, 1 H, C*H*(OAc)), 4.64 (m, 1 H, CHO), 3.38–3.6 (m, 2 H, OCH_2CH_2), 3.04 (br dd, J = 17 and 6.5 Hz, 1 H, C=CCH_2), 2.50 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.25–2.4 (m, 1 H, CH(OAc)CH_2CHO), 2.32 (t, J = 7 Hz, 2 H, CH_2CN), 2.03 (s, 3 H, OAc), 1.95–2.1 (m, 1 H, CH(OAc)CH_2CHO), 1.87–1.93 (m, 2 H, CH_2CH_2CH_2CN); ^{13}C NMR (100.6 MHz) δ 170.81, 140.44, 137.03, 128.42, 128.34, 128.17, 127.13, 119.42, 77.14, 73.19, 64.73, 39.66, 38.68, 25.94, 21.21, 14.11. **69b**: R_f = 0.26 (petroleum ether/Et_2O, 2/3); ^{1}H NMR (200 MHz) δ 7.17–7.42 (m, 5 H, Ph), 6.57 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.16 (apparent quintet, 1 H, C*H*OAc), 4.49 (m, 1 H, CHO), 3.44–3.64 (m, 2 H, OCH_2CH_2), 2.89 (ddd, part of AB, J = 17, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.78 (br d, part of AB, J = 17 Hz, 1 H, C=CC*H*), 2.42 (t, J = 6.5 Hz, 2 H, CH_2CN), 2.14–2.22 (m, 2 H, CH(OAc)-CH_2CHO), 2.07 (s, 3 H, OAc), 1.84–2.0 (m, 2 H, CH_2CH_2CH_2CN); ^{13}C NMR (100.6 MHz) δ 170.92, 140.62, 136.92, 128.37 (2 C), 127.22, 126.59, 119.45, 77.15, 72.83, 64.49, 40.19, 37.78, 26.03, 21.28, 14.12. Anal. Calcd for (mixture of **69a/69b**) $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.16; H, 7.08; N, 4.59.

Cyclization of *trans*-3-(4-Cyanobutoxy)-1-phenyl-1,5-hexadiene (61). Compound **61** (2.75 mmol) was treated in the same way as **60**. Workup yielded 815.3 mg of a dark oil. Flash chromatography (a stepwise gradient of petroleum ether/Et_2O, 7/3, 3/2, 1/1, and 2/3, was used) gave 47 mg (0.22 mmol) of **34**, 112 mg (0.41 mmol) of **35**, and 397 mg (1.27 mmol, 46%) of **70a/70b** in a ratio of 59/41. **70a**: R_f = 0.16 (petroleum ether/Et_2O, 1/1); ^{1}H NMR (400 MHz, peaks assigned from a mixture of **70a/70b**) δ 7.2–7.4 (m, 5 H, Ph), 6.57 (br s, 1 H, PhC*H*=C), 5.30 (m, 1 H, C*H*OAc), 4.58 (m, 1 H, C*H*O), 3.34–3.51 (m, 2 H, OCH_2, 3.05 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.50 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.25–2.35 (m, 1 H, hidden by CH_2CN in the two diastereomers, CH(OAc)CH_2CHO), 2.25–2.3 (m, 2 H, CH_2CN), 2.02 (s, 3 H, OAc), 1.97–2.05 (m, 1 H, CH-(OAc)CH_2CHO), 1.63–1.7 (m, 4 H, $OCH_2CH_2CH_2$); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **70a/70b**) δ 170.77 (s, 1 C), 140.65 (s, 1 C), 137.05 (s, 1 C), 128.1–128.4 (d, 2 C, overlapping peaks), 127.93 (d, 1 C), 126.95 (d, 1 C), 119.51 (s, 1 C), 76.96 (d, 1 C), 73.23 (d, 1 C), 66.31 (t, 1 C), 39.58 (t, 1 C), 38.64 (t, 1 C), 28.77 (t, 1 C), 22.47 (t, 1 C), 21.13 (q, 1 C), 16.86 (t, 1 C). **70b**: R_f = 0.16 (petroleum ether/Et_2O, 1/1); ^{1}H NMR (400 MHz, peaks assigned from a mixture of **70a/70b**) δ 7.2–7.4 (m, 5 H, Ph), 6.57 (br s, 1 H, PhC*H*=C), 5.14 (m, 1 H, C*H*OAc), 4.43 (m, 1 H, CHO), 3.34–3.51 (m, 2 H, OCH_2), 2.87 (ddd, part of AB, J = 17, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.78 (br d, part of AB, J = 17 Hz, 1 H, C=CCH_2), 2.3–2.35 (m, 2 H, CH_2CN), 1.99–2.22 (m, 2 H, CH(OAc)CH_2CHO), 2.06 (s, 3 H, OAc), 1.7–1.75 (m, 4 H, $OCH_2CH_2CH_2$); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **70a/70b** δ 170.92 (s, 1 C), 140.79 (s, 1 C), 136.93 (s, 1 C), 128.1–128.4 (d, 2 C, overlapping peaks), 128.15 (d, 1 C), 127.03 (d, 1 C), 119.51 (s, 1 C), 76.92 (d, 1 C), 72.83 (d, 1 C), 66.24 (t, 1 C), 40.10 (t, 1 C), 37.75 (t, 1 C), 28.82 (t, 1 C), 22.67 (t, 1 C), 21.21 (q, 1 C), 16.88 (t, 1 C).

Cyclization of *trans*-3-(Carboxymethoxy)-1-phenyl-1,5-hexadiene (62). The diene **62** (2 mmol) was cyclized using the procedure described for **9**. After the mixture was stirred for 70 h at ambient temperature, 10 mL of brine was added, and the aqueous phase was extracted with petroleum ether/Et_2O (2 × 30 mL 7/3, and 20 mL 1/1). The organic phase was washed with 7 × 5 mL of H_2O and extracted with saturated Na_2CO_3 (2 × 20 mL). The carbonate phase was acidified by the addition of 2 M HCl (50 mL) and extracted with Et_2O (3 × 30 mL). After drying ($MgSO_4$) of the combined organic phase and removal of the solvent in vacuo, 230.3 mg (0.79 mmol, 40%) of **71a/71b** in a ratio of 70/30 was obtained. The organic phase obtained after the extraction with Na_2CO_3 was dried ($MgSO_4$), and the solvent was removed. Flash chromatography (petroleum ether/Et_2O, 7/3) yielded 34.2 mg (0.158 mmol) of **34** and 92.3 mg (0.337 mmol) of **35**. **71a**: ^{1}H NMR (400 MHz, peaks assigned from a mixture of **71a/71b**) δ 7.2–7.45 (m, 5 H, Ph), 6.66 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.3–5.37 (m, 1 H, C*H*OAc), 4.87 (m, 1 H, CHO), 3.99 (s, 2 H, CH_2COOH), 3.09 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.51 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.38 (ddd, J = 15, 6 and 3 Hz, 1 H, CH(OAc)CH_2CHO), 2.04 (s, 3 H, OAc), 2.21 (m, 1 H, CH(OAc)CH_2CHO); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **71a/71b**) δ 174.50 (s, 1 C), 170.97 (s, 1 C), 139.33 (s, 1 C), 136.61 (s, 1 C), 128.3–128.5 (d, 3 C, overlapping peaks), 127.18 (d, 1 C), 77.46 (d, 1 C), 73.13 (d, 1 C), 64.38 (t, 1 C), 39.21 (t, 1 C), 38.71 (t, 1 C), 21.07 (q, 1 C). **71b**: ^{1}H NMR (400 MHz, peaks assigned from a mixture of **71a/71b** δ 7.2–7.45 (m, 5 H, Ph), 6.66 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.28–5.35 (m, 1 H, C*H*OAc), 4.77 (br d, J = 5 Hz, 1 H, C*H*O), 4.15 (A part of AB, J_{AB} = 16.3 Hz, 1 H, CH_2COOH), 4.01 (B part of AB, J_{AB} = 16.3 Hz, 1 H, CH_2COOH), 2.95 (ddd, part of AB, J = 17.5, 7, and 2 Hz, 1 H, C=CCH_2), 2.82 (br d, part of AB, J = 17.5, 1 H, C=CCH_2), 2.2–2.26 (m, 1 H, CH(OAc)CH_2CHO), 2.1–2.16 (m, 1 H, CH(OAc)CH_2CHO), 2.08 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **71a/71b**) δ 173.70 (s, 1 C), 170.97 (s, 1 C), 139.3 (s, 1 C), 136.44 (s, 1 C), 128.3–128.5 (d, 3 C, overlapping peaks), 127.35 (d, 1 C), 77.76 (d, 1 C), 72.99 (d, 1 C), 64.41 (t, 1 C), 39.75 (t, 1 C), 37.94 (t, 1 C), 21.07 (q, 1 C).

Cyclization of *trans*-3-(2-Carboxyethoxy)-1-phenyl-1,5-hexadiene (63). Cyclization of **63** (1 mmol) and workup according to the procedure described for **62** afforded 10.8 mg (0.05 mmol) of **34**, 43.2 mg (0.158 mmol) of **35**, and 130.5 (0.43 mmol, 43%) of **72a/72b** in a ratio of 63/37. **72a**: ^{1}H NMR (400 MHz, peaks assigned for a mixture of **72a/72b**) δ 7.2–7.45 (m, 5 H, Ph), 6.58 (br s, 1 H, PhC*H*=C), 5.31 (m, 1 H, C*H*OAc), 4.57 (m, 1 H, CHO), 3.68 (t, J = 6.1 Hz, 2 H, OCH_2CH_2COOH), 3.06 (br dd, J = 17 and 7 Hz, 1 H, C=CCH_2), 2.60 (t, J = 6.1 Hz, 2 H, CH_2COOH), 2.48 (br dd, J = 17 and 4 Hz, 1 H, C=CCH_2), 2.41 (ddd, J = 14.5, 6, and 3 Hz, 1 H, CH(OAc)CH_2CHO), 2.02 (s, 3 H, OAc), 1.95–2.04 (m, 1 H, CH(OAc)CH_2CHO); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **72a/72b**) δ 177.22 (s, 1 C), 171.01 (s, 1 C), 140.26 (s, 1 C), 136.87 (s, 1 C), 128.2–128.5 (d, 3 C, overlapping peaks), 126.97 (d, 1 C), 77.17 (d, 1 C), 73.36 (d, 1 C), 62.26 (t, 1 C), 39.59 (t, 1 C), 38.45 (t, 1 C), 34.81 (t, 1 C), 21.13 (q, 1 C). **72b**: ^{1}H NMR (400 MHz, peaks assigned from a mixture of **72a/72b**) δ 7.2–7.45 (m, 5 H, Ph), 6.60 (br s, 1 H, PhC*H*=C), 5.17 (m, 1 H, C*H*OAc), 4.49 (m, 1 H, CHO), 3.71 (t, J = 6.0 Hz, 2 H, OCH_2CH_2COOH), 2.88 (ddd, part of AB, J = 17.6 and 2 Hz, 1 H, C=CCH_2), 2.80 (br d, part of AB, J = 17 Hz, 1 H, C=CCH_2), 2.65 (t, J = 6.0, 2 H, CH_2COOH), 2.11–2.26 (m, 2 H, CH(OAc)-CH_2CHO), 2.06 (s, 3 H, OAc); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **72a/72b**) δ 177.05 (s, 1 C), 171.28 (s, 1 C), 140.29 (s, 1 C), 136.76 (s, 1 C), 128.2–128.5 (d, 3 C, overlapping peaks), 127.07 (d, 1 C), 77.24 (d, 1 C), 72.94 (d, 1 C), 62.26 (t, 1 C), 40.00 (t, 1 C), 37.58 (t, 1 C), 34.87 (t, 1 C), 21.13 (q, 1 C).

Cyclization of *trans*-3-(3-Carboxypropoxy)-1-phenyl-1,5-hexadiene (64). Cyclization of **64** (1.9 mmol) and workup according to the procedure described for **62** afforded 28.7 mg (0.133 mmol) of **34**, 104.2 mg (0.38 mmol) of **35**, and 281 mg (0.87 mmol, 46%) of **73a/73b** in a ratio of 60/40. **73a**: ^{1}H NMR (400 MHz, peaks assigned from a mixture of **73a/73b**) δ 7.2–7.4 (m, 5 H, Ph), 6.55 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.30 (m, 1 H, C*H*OAc), 4.54 (m, 1 H, CHO), 3.45–3.51 (m, 2 H, OCH_2), 3.06 (br dd, J = 17 and 6.5 Hz, 1 H, C=CCH_2), 2.45–2.53 (m, 1 H, C=CCH_2), 2.33 (ddd, J = 14.6 and 3 Hz, 1 H, CH(OAc)CH_2CHO), 2.39 (m, 2 H, CH_2CHO), 2.01 (s, 3 H, OAc), 1.95–2.0 (m, 1 H, CH(OAc)-

CH_2CHO), 1.86 (m, 2 H, OCH_2CH_2); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **73a/73b**) δ 179.17 (s, 1 C), 170.89 (s, 1 C), 140.57 (s, 1 C), 136.92 (s, 1 C), 127.9–128.4 (d, 3 C, overlapping peaks), 126.86 (d, 1 C), 76.89 (d, 1 C), 73.33 (d, 1 C), 66.08 (t, 1 C), 39.56 (t, 1 C), 38.62 (t, 1 C), 30.64 (t, 1 C), 24.82 (t, 1 C), 21.05 (q, 1 C). **73b**: ^1H NMR (400 MHz, peaks assigned from a mixture of **73a/73b**) δ 7.2–7.4 (m, 5 H, Ph), 6.55 (br s, $w_{1/2}$ = 6 Hz, 1 H, PhC*H*=C), 5.14 (m, 1 H, C*H*(OAc)), 4.40 (m, 1 H, CHO), 3.37–3.43 (m, 2 H, OCH_2), 2.88 (ddd, part of AB, J = 17, 6.5, and 2 Hz, 1 H, C=CCH_2), 2.81 (br d, part of AB, J = 17 Hz, 1 H, C=CCH_2), 2.45–2.51 (m, 2 H, CH_2COOH), 2.1–2.2 (m, 2 H, CH(OAc)-CH_2CHO), 2.06 (s, 3 H, OAc), 1.92 (m, 2 H, OCH_2CH_2); ^{13}C NMR (100.6 MHz, peaks assigned from a mixture of **73a/73b**) δ 179.17 (s, 1 C), 171.16 (s, 1 C), 140.74 (s, 1 C), 136.84 (s, 1 C), 127.9–128.4 (d, 3 C, overlapping peaks), 126.96 (d, 1 C), 76.95 (d, 1 C), 72.97 (d, 1 C), 65.93 (t, 1 C), 39.99 (t, 1 C), 37.62 (t, 1 C), 30.69 (t, 1 C), 24.82 (t, 1 C), 21.10 (q, 1 C).

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Supplementary Material Available: ^1H NMR spectra of compounds for which elemental analyses are lacking (74 pages). Ordering information is given on any current masthead page.

Photoreactions of *N*-Methylphenanthrene-9,10-dicarboximide with Alkenes and Dienes. Heavy-Atom Effect of Halides

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Photoreaction (>400 nm) of *N*-methylphenanthrene-9,10-dicarboximide (**1**) in benzene gave the dimer *syn*-**2**. Photoreaction (>400 nm) of **1** with alkenes and dienes **3** in benzene gave **2**, products **4** of insertion of the double bond of **3** into the C–N bond of **1**, and cyclobutanes **5** and **7**. Irradiation of **2**, **4a**, **4m,n**, and **5a** at a shorter wavelength (>320 nm) gave, respectively, **1**, decarbonylation product **6**, intramolecular cycloadducts **8m,n**, and **1** + **3a**. In the photoreaction of **1** with **3b**, addition of methyl iodide to benzene (1:1 v/v) suppressed the dimerization and insertion reactions, and only cyclobutanes **5b** and **7b** were formed. Methyl iodide and iodobenzene were equally effective in increasing the ratio (**5b** + **7b**)/**4b** with increasing halide concentration; butyl bromide and bromobenzene were less effective. The ratio **5**:**7** was independent of the concentration of methyl iodide. Dilution plots of insertion and cyclobutane formation in the photoreaction of **1** with **3b** showed that methyl iodide quenched the excited state of **1** which led to insertion. The results indicate that the syn dimerization and the insertion occurred from the singlet excited state of **1**, and the cyclobutane arose mainly from the triplet excited state. The activity of the halides in these photoreactions is attributed to the heavy-atom effect.

Introduction

Photochemistry of phthalimides in the presence of alkenes has been the subject of many investigations.[1] Several types of reactions have been observed, including alcohol addition (electron-transfer reaction),[2] insertion of the alkene into the imide moiety,[3] oxetane formation,[4] and photoreduction.[5] The effect of arene structure on the photochemistry of arenedicarboximides has been investigated.[6,7] We have studied the effect of an extended π-conjugation system and have reported photoreactions in which the arene structure plays a crucial role in determining the reaction pathway.[7] Thus the predominant reactions of *N*-methylnaphthalene-1,8-, -2,3-, and -1,2-dicarboximides with alkenes are cyclobutane formation,[7c] oxetane formation,[7d] and insertion of the alkene into the imide bond,[7b] respectively.

Here we report on the photoreactions of *N*-methylphenanthrene-9,10-dicarboximide (**1**) with alkenes dienes and on the heavy-atom effect on these reactions. Internal

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