6π-Electrocyclization of 1-Azatrienes to 1,2-Dihydropyridines

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Received November 7, 1994[⊗]

A series of α,β-*cis*-dienals were synthesized by oxidation and then in situ isomerization of easily available β-allenic alcohols. Subsequent reaction between the α,β-*cis*-dienals and primary amines represents a simple and useful method for the direct preparation of 1,2-dihydropyridines. Reactivity profiles and activation parameters for the cyclization of α,β-*cis*-dienimines are similar to those of the carbocyclic counterparts except the reaction is much faster. Despite the lack of a clear stereochemical label, the disrotatory nature of the ring closure is illustrated by the greater cyclization rates of **8′c** and **8′d** as compared to **7′c** and **7′d**, respectively. The observation that sterically more hindered systems (**8′c** and **8′d**) cyclize faster than less hindered ones (**7′c** and **7′d**) is a feature of 6π-electrocyclizations that is unprecedented.

Introduction

Reaction of 13-*tert*-butyl-13-*cis*-retinal (**1**) with n-butylamine afforded not the expected Schiff base **2**, but rather the stable 6π-electron electrocyclized 1,2-dihydropyridine (DHP) **3**.[1] While the transformation of **1** to **3** was shown under milder conditions to involve initial formation of Schiff base **2**, it was surprising to find that no **2** was observed even though it is a conjugated imine (Scheme 1). Moreover, 13-*cis*-retinal, the corresponding oxa system, exhibited no propensity to exist as a dihydropyran. This ring closure is, of course, analogous to the well-known thermal ring closure of 1,3,5-hexatrienes to 1,3-cyclohexadienes.[2] What is noteworthy about the cyclization of the Schiff base **2** (also referred to as a 1-azatriene or dienimine), however, is the extremely mild reaction conditions under which ring closure occurs. Cyclization of **2** to **3** occurred at 23 °C with a half-life of only 11 min.[1] By contrast, the electrocyclization of all-carbon triene analogues requires elevated temperatures, typically >130 °C (or about ~10^5 to 10^6 slower than the nitrogen substituted system[1]).[3,4]

Since the direct formation of 1,2-dihydropyridines by simply mixing dienals and primary amines under ambient conditions is uncommon, and because the factors affecting the rate of cyclization of dienimines are not well understood, it was deemed of interest to evaluate the steric, electronic, and conformational effects of this cyclization through appropriate structure–reactivity studies. It is the purpose of this paper to report not only the results of the latter study, but also to highlight the synthesis of a variety of 1,2-dihydropyridines.[5]

Results and Discussion

The dienals **4**–**8** shown in Chart 1 were utilized in the preparation of selected dienimines **4′**–**8′** via reaction with a series of primary amines. The cyclization of these dienimines to afford 1,2-dihydropyridines **4″**–**7″** were then studied both preparatively and in terms of reactivity. The cyclizations of **4′**–**8′** were monitored quantitatively using ^{1}H-NMR analyses (and by UV spectroscopy in selected cases). A reasonably complete evaluation of pertinent steric and electronic factors was achievable by study of a selection of 12 of the 30 possible dienimines shown in Chart 1, namely **4′a**–**f**, **5′c**, **6′c**, **7′c,d**, and **8′c,d**. In addition, a study of the electrocyclization of dienimines **8′c,d** in comparison to the parent aldehyde **8** was also carried out.

The starting aldehydes **4**–**8** were prepared according to Scheme 2. The lithium salt of *tert*-butyldimethylsilyl ether of 3-butyn-1-ol[6a] was coupled to the appropriate aldehyde to produce propargylic alcohols **10** (80–86%). The latter **10** were transformed into the benzoates (or mesylate) **11** and S_N2' displacement of the propargylic ester using the higher order cyanocuprate,[6b,7] dilithium di-*tert*-butylcyanocuprate, afforded the allenes **12** in 68–90% yields. The silyl ethers **12** were then cleanly converted to alcohols **13** in 75–90% yields using TBAF[6c] in THF. Allenols **13** were oxidized with rearrangement via **14** to the corresponding dienals **4**-**7** using the Swern procedure,[8] whereas the Dess–Martin periodinane oxidation method[9] was used to convert **13d** to the unrearranged, β-allenic aldehyde **14d**. Regarding the expected allenal intermediates **14a**–**c** leading to **4**–**6** (82, 94, and 91% yields, respectively), it was not determined whether the isomerization occurred either during the reaction or during chromatographic purification. The allenal **14d** obtained in 90% yield was surprisingly stable and its isomerization was effected by a base-induced isomerization with triethylamine. The resulting dienal **7** was observed to deteriorate upon chromatography.

For the rearrangement of β-allenals **14** to the corresponding dienals (Scheme 2), it was anticipated that the

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1995.

(1) de Lera, A. R.; Reischl, W.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 4051.

(2) (a) Okamura, W. H.; de Lera, A. R. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Paquette, L. A., Volume Ed.; Pergamon Press: London, 1991; Vol. 5, Chapter 6.2, pp 699–750. (b) Marvel, E. N. *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980.

(3) (a) Marvell, E. N.; Caple, G.; Schatz, B.; Pippin, W. *Tetrahedron* **1973**, *29*, 3781. (b) Marvell, E. N.; Caple, G.; Delphey, C.; Platt, J.; Polston, N.; Tashiro, J. *Tetrahedron* **1973**, *29*, 3797.

(4) Spangler, C. W.; Jondahl, T. P.; Spangler, B. *J. Org. Chem.* **1973**, *38*, 2478.

(5) (a) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, 72, 1. (b) Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223. (c) Gilchrist, T. L. *Heterocyclic Chemistry*; Wiley: New York, 1985.

(6) (a) Posner, G. H.; Weitzberg, M.; Hamill, T. G.; Asirvatham, E.; Cun-Heng, H.; Clardy, J. *Tetrahedron Lett.* **1986**, *42*, 2919. (b) Shen, G.-Y.; de Lera, A. R.; Norman, T. C.; Haces, A.; Okamura, W. H. *Tetrahedron Lett.* **1987**, *28*, 2917. (c) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(7) (a) Lipshutz, B. H. *Synthesis* **1987**, 325. (b) Wu, K.-M.; Midland, M. M.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 4381.

(8) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(9) (a) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. (b) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156.

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Scheme 1

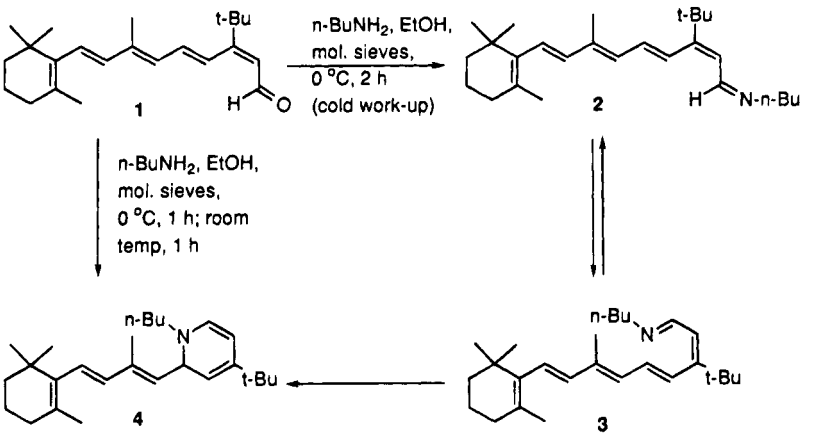
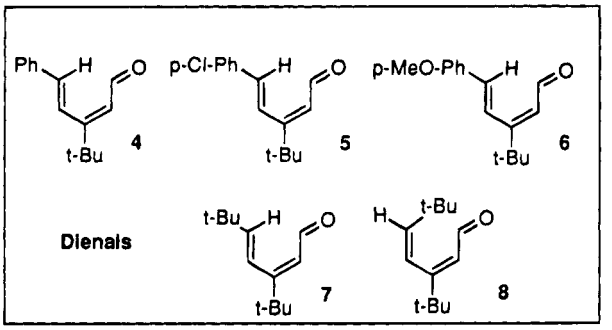
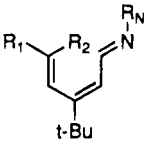


Chart 1.[a] Summary of the Dienals, Dienimines and 1,2-Dihydropyridines



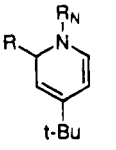
Dienimines



4', R_1 = Ph; R_2 = H
5', R_1 = *p*-Cl-Ph; R_2 = H
6', R_1 = *p*-MeO-Ph; R_2 = H
7', R_1 = *t*-Bu; R_2 = H
8', R_1 = H; R_2 = *t*-Bu

a, R_N = *n*-Bu
b, R_N = *s*-Bu
c, R_N = *t*-Bu
d, R_N = Ph
e, R_N = *p*-Cl-Ph
f, R_N = *p*-MeO-Ph

1,2-Dihydropyridines



4'', R = Ph
5'', R = *p*-Cl-Ph
6'', R = *p*-MeO-Ph
7'', R = *t*-Bu

[a] For convenience, the dienimines and dihydropyridines are numbered analogously to the aldehydes from which they are derived [unprimed for the aldehydes; primed (') for the dienimines (Schiff bases or 1-azatrienes) and double primed ('') for the dihydropyridines (DHPs)]. Of the thirty dienimine derivatives possible for the five aldehydes (**4**-**8**) and the six primary amines ($R_N = NH_2$; see **a**-**f**), twelve dienimines (see text) were selected for study.

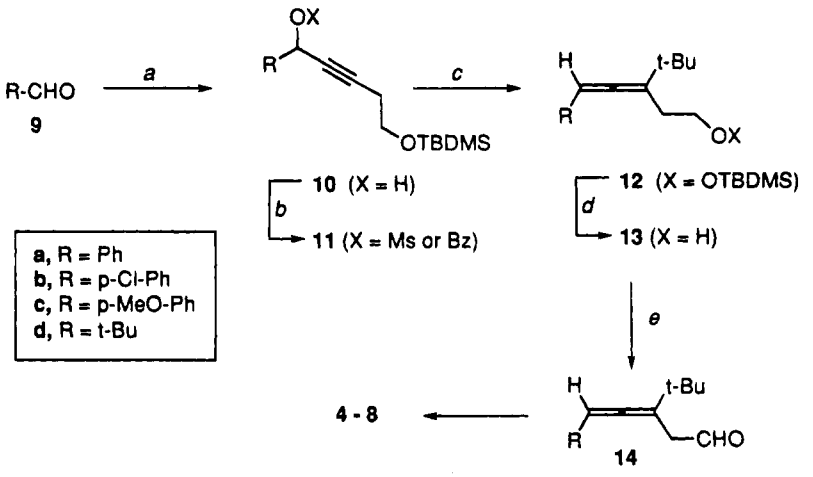
γ-double bond of the 2,4-dienal would be formed in the *Z*-configuration, not *E* as in **4**–**7**. For example (Scheme 3), the first step in the isomerization of **14d** was expected to involve enolization to the *Z*-enol tautomer **15** (considered to be in equilibrium with the *E*-enol). Intramolecular [1,5]-hydrogen shift could occur (an intermolecular hydrogen transfer occurring via either the *Z*- or *E*-enol form is also possible) from the less hindered side of the allene, resulting in protonation from the side opposite the bulky t-Bu group (as shown by the arrow in **15** of Scheme 3).[10] The resulting di-*cis*-dienal **8** could then undergo thermal 6π-electron electrocyclic ring closure to produce 1,2-dihydropyran (α-pyran) **16**. Retro 6π-electron electrocyclic ring opening may then occur to yield *trans*-dienal **7**.[11]

The *Z*-dienal **8** synthesized in an independent manner could be shown to isomerize to **7** via the intermediacy of α-pyran **16** (Scheme 4). The *Z*-dienal **8** was obtained by first reducing the (2*E*,4*E*)-dienal **7** with DIBAL-H[12] in

(10) (a) Amos, R. A.; Katzenellenbogen, J. A. *J. Org. Chem.* **1978**, *43*, 555. (b) Bartlett, P. A.; Hahne, W. F. *J. Org. Chem.* **1979**, *44*, 882.

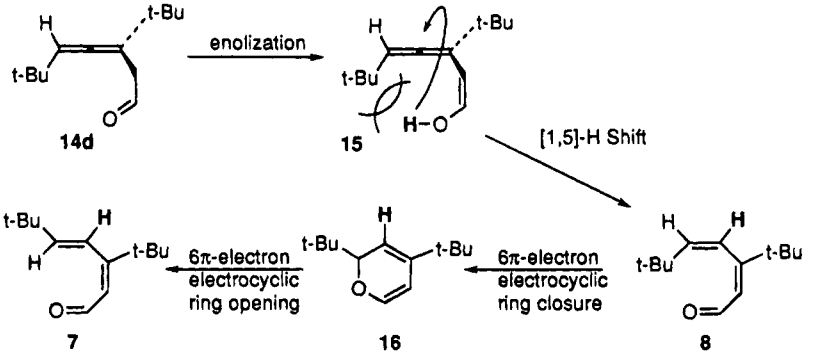
(11) (a) Kluge, A. F.; Lillya, C. P *J. Am. Chem. Soc.* **1971**, *93*, 4458. (b) Kluge, A. F.; Lillya, C. P. *J. Org. Chem.* **1971**, *36*, 1988. (c) Kluge, A. F.; Lillya, C. P. *J. Org. Chem.* **1971**, *36*, 1977. (d) Chandraratna, R. A. S.; Okamura, W. H. *Tetrahedron Lett.* **1984**, *25*, 1003. (e) Knudsen, C. G.; Chandraratna, R. A. S.; Walkeapää, L. P.; Chauhan, Y. S.; Carey, S. C.; Cooper, T. M.; Birge, R. R.; Okamura, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 1626. (f) Büchi, G.; Yang, N. C. *J. Am. Chem. Soc.* **1957**, *79*, 2318. (g) Marvell, E. N.; Chadwick, T.; Caple, G.; Gosink, T.; Zimmer, G. *J. Org. Chem.* **1972**, *37*, 2992. (h) Marvell, E. N.; Gosink, T.; Churchley, P.; Li, T. H. *J. Org. Chem.* **1972**, *37*, 2989. (i) Schiess, P.; Chia, H. L. *Helvetica Chim. Acta* **1970**, *53*, 485. (j) Schiess, P.; Seeger, R.; Suter, C. *Helvetica Chim. Acta* **1970**, *53*, 1713. (k) Tsuda, T.; Kiyoi, T.; Miyane, T.; Saegusa, T. *J. Am. Chem. Soc.* **1988**, *110*, 8570. (l) Trehan, A.; Mirzadegan, T.; Liu, R. S. H. *Tetrahedron* **1990**, *46*, 3769. (m) Zhu, Y.; Ganapathy, S.; Liu, R. S. H. *J. Org. Chem.* **1992**, *57*, 1110. (n) Kini, A.; Matsumoto, H.; Lui, R. S. H. *J. Am. Chem. Soc.* **1979**, *101*, 5078.

Scheme 2

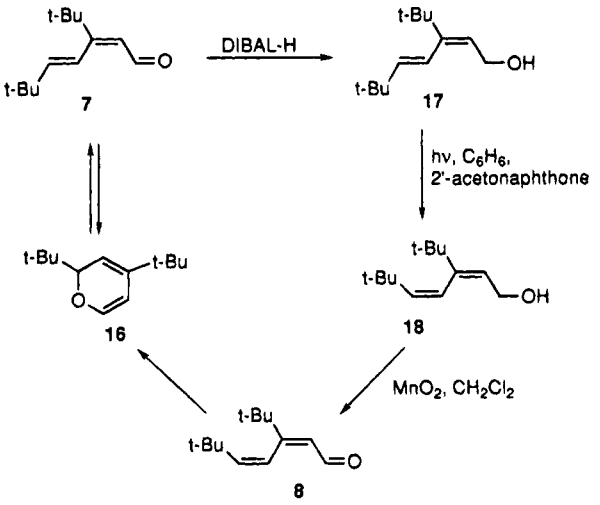


Reagents: (*a*) $LiC_2CH_2CH_2OTBDMS$, THF; (*b*) BzCl or MsCl, DMAP, Pyr; (*c*) $Li_2CuCN(t\text{-}Bu)_2$, THF; (*d*) TBAF, THF; (*e*) Swern oxidation (Dess-Martin oxidation of **13d** allowed the isolation of **14d**).

Scheme 3



Scheme 4



hexanes to produce (2*E*,4*E*)-dienol **17**. Photochemical isomerization[13] of the latter to the more hindered (2*E*,4*Z*)-isomer **18** was achieved using 2′-acetonaphthone as a triplet sensitizer in benzene (Pyrex). A chromatographically separable, ~95:5 photostationary state mixture of **18** and **17** was obtained after 2 days of irradiation. The (2*E*,4*Z*)-allylic alcohol **18** was then oxidized to the (2*E*,4*Z*)-dienal **8** using MnO_2 in CH_2Cl_2.[14] The availability of (2*E*,4*Z*)-dienal **8** nicely allowed a study of its reaction with primary amines to afford the (2*E*,4*Z*)-dienimine of type **8′** and also allowed a study of the cyclization of dienal **8** itself to 1,2-dihydropyran **16** (the observed product is **7**, but the formation of **16** is considered to be rate limiting).[11]

Schiff Base Formation and Cyclization to Dihydropyridines (DHPs). The general preparative procedure for Schiff base formation and cyclization to DHP involved reacting the α,β-dienal with excess primary amine in absolute ethanol containing 4 Å molecular sieves at 0 °C for 1 h. The solution was then filtered through a short column of $MgSO_4$, concentrated, and redissolved in ether. The dienimine was then allowed to cyclize at room temperature. Upon complete cyclization as monitored by TLC, the solution was concentrated, and, depending on the stability of the DHP, purified via flash chromatography and HPLC.

The cyclization of dienimines to DHPs occurred cleanly with little or no observable side products. Although cyclization was complete in most cases (as determined by ^{1}H-NMR), DHPs **5″c** and **6″c** were found to be in equilibrium with their corresponding uncyclized dienimine isomers **5′c** and **6′c**, respectively (The ratios of **5″c:**

(12) Wilson, K. E.; Seidner, R. T.; Masamune, S. *Chem. Commun.* **1970**, 213.

(13) (a) Ramamurthy, V.; Tustin, G.; Yau, C. C.; Liu, R. S. H. *Tetrahedron* **1975**, *31*, 193. (b) Ramamurthy V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *J. Org. Chem.* **1973**, *38*, 1247.

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

5′c and **6″c:6′c** were determined to be 94:6 and 91:9, respectively). In general, all DHPs were stable for several days if kept dilute in ether and stored at −78 °C. However, storing the DHPs neat, even at −78 °C resulted in their decomposition to several unidentified components. Yields of isolated DHPs ranged between 68 and 87%.

Kinetic Studies. To study the rate of cyclization, two methods for the formation of Schiff bases (dienimines) were employed.[15] In method A, used for cyclizations involving the low boiling amines, *n*-butyl-, *sec*-butyl-, and *tert*-butylamine, the dienal (~20 mg) in EtOH containing 4 Å molecular sieves was mixed with a 5-fold excess of amine, which after 10 min was filtered through a short column of $MgSO_4$. The filtrate was concentrated (at water aspirator pressure on a rotary evaporator and then at higher vacuum on an oil pump) over a 5−10 min period, and then the Schiff base was redissolved in an appropriate solvent to allow cyclization to the DHP. In method B, used for the higher boiling or crystalline amines, aniline, *p*-chloroaniline, and *p*-methoxyaniline, the dienal in EtOH containing 4 Å molecular sieves was cooled to 0 °C and 1.1 equiv of amine added. Monitoring the reaction by UV spectroscopy indicated that Schiff base formation was complete within 10 min at 0 °C. All operations were conducted below room temperature with ice bath cooling whenever feasible. Workup was identical to that in method A. For ^{1}H-NMR kinetic runs,[16] rates were followed at four temperatures over a range of 30 °C, or in several cases only at 0 °C. Selected UV kinetic runs[17] were conducted at 25 °C, and the results agreed well with those monitored by ^{1}H-NMR analysis.

Table 1 summarizes the kinetic data and/or activation parameters of the cyclization of twelve dienimines and one dienal as determined by ^{1}H-NMR monitoring.[16] The cyclization of dienimines **4′e** and **4′f** was monitored only at 0 °C, while that of **8′c** was monitored at 25 °C (half-life of ~13 h). Attempts to obtain additional kinetic data for the latter at higher temperatures in $CDCl_3$ resulted in the decomposition of the dienimine. Cyclization generally occurred more cleanly in C_6D_6; e.g., **8′c** isomerized analogously with a half-life of ~9 h at 25 °C, but most of the dienimines had to be studied in $CDCl_3$ to access the lower end of the temperature range examined. The tri-*tert*-butyl dienimine **7′c** did not cyclize, even upon thermolysis at 55 °C for 48 h in C_6D_6.

Some generalizations can be noted here. Log *A* values for the dienimines range from 12.4 for **6′c** to 10.7 for **4′d** and 12.9 for the only aldehyde (**8**) studied. These values fall well within the range of other 6π-electron electrocyclizations.[18] The enthaphies of activation ($\Delta H^{\ddagger}$) for these cyclizations range from 17.5 to 22.5 kcal/mol, which are 5 to 10 kcal/mol less than those reported for the all carbon hexatriene analogues.[2-4] As noted earlier, these 1-azahexatrienes cyclize ~10^5 to 10^6 times faster than all carbon hexatriene derivatives.[1]

Table 1. Kinetic Data and Activation Parameters for the Cyclization of Dienimines and Dienal[a]

dienimine	Log *A*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$k \times 10^{6}$ [b]
4′a	10.8(1.0)	18.0(1.7)	−11.5(1.0)	21.0 (1.6)	95.9
4′b	11.5(0.2)	20.0(0.3)	−7.61(0.1)	22.0(0.3)	13.9
4′c	12.6(0.3)	22.5(0.5)	−2.8(0.1)	23.3(0.5)	1.45
4′d	10.7(0.6)	17.5(1.0)	−10.8(0.7)	20.6(1.1)	190
4′e	nd	nd	nd	nd	222
4′f	nd	nd	nd	nd	271
5′c	12.2(0.2)	21.6(0.4)	−4.7(0.1)	22.9(0.4)	2.10
6′c	12.4(1.0)	21.6(1.3)	−3.7(0.3)	22.6(1.4)	4.51
7′c	this compound does not cyclize[c]				
7′d	11.4(0.2)	20.8(0.4)	−8.1(0.2)	23.0(0.4)	2.10
8′c	nd	nd	nd	nd	0.14
8′d	12.3(0.4)	21.4(0.8)	−4.2(0.1)	22.6(0.8)	4.46
8	12.9(0.1)	21.7(0.7)	−1.5(0.1)	22.2(0.1)	10.6

[a] $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ in kcal/mol; $\Delta S^{\ddagger}$ in cal/mol K; *A* and *k* in s^{-1}, standard deviation in parenthesis (nd, not determined). [b] *k* is calculated from activation parameters extrapolated to 0 °C, except for **4′e** and **4′f**, which is the average of three runs at 0 ± 0.2 °C and **8′c**, which is the average of three runs at 25.0 ± 0.2 °C. [c] This substance did not cyclize even after heating at 55 °C for 48 h in C_6D_6.

The entropy of activation ($\Delta S^{\ddagger}$) for this cyclization ranged from −11.5 to −3.7 eu for the eight dienimines and −1.5 eu for dienal **8**. The experimental values for $\Delta S^{\ddagger}$ are similar to those obtained for other 6π-electron electrocyclization reactions, reflecting loss of rotational freedom characteristic of the cyclic transition state.[2-4]

One aspect of steric effects in this series is illustrated by the results obtained for **4′a−c**, wherein the substituent on nitrogen is systematically varied. As the steric bulk of the nitrogen substituent decreases (*tert*-butyl < *sec*-butyl < *n*-butyl), the relative rate of cyclization increases (1.0, 9.6, and 66 for **4′c**, **4′b** and **4′a**, respectively). Another aspect of steric effects can be seen in the comparison of **4′c** with **7′d** in which the t-Bu and Ph groups on opposite ends of the dienimine system have been reversed. It was found that dienimine **7′d** cyclized only moderately faster (~1.5) than **4′c**. Thus, there is an absence of a large difference in reactivity whether substituents are attached to carbon or nitrogen.

A most interesting aspect of steric considerations, namely the effect of geometry[19] on the rate of cyclization of *N*-phenyl-substituted dienimines **7′d** and **8′d**, proved counterintuitive. The more hindered terminal *Z*-dienimine **8′d** cyclized over twice as fast as its *E*-isomer **7′d**. A more emphatic example of this phenomenon is seen in the comparison of the corresponding di-*tert*-butyl capped azatrienes **7′c** and **8′c** (Scheme 5). Although the seemingly very sterically congested **8′c** (2*E*,4*Z*) easily cyclized (half life ~13 h at 25 °C), dienimine **7′c** with the (2*E*,4*E*) geometry failed to cyclize even upon thermolysis at 55 °C for 48 h. This difference in reactivity can be explained by considering the anticipated disrotatory nature of the thermal electrocyclization (Scheme 5). The cyclization

(15) Ghirlando, R.; Berman, E.; Baasov, T.; Sheves, M. *Magn. Reson.* **1987**, *25*, 21.

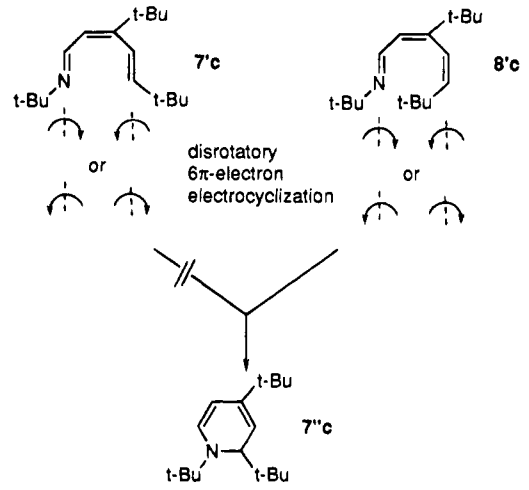
(16) ^{1}H-NMR analyses were carried out using procedures outlined previously (ref 1). The kinetic data were analyzed as previously described: Shen, G.-Y.; Ph.D. Dissertation, University of California, Riverside, California: August, 1986.

(17) As a cross check on the ^{1}H-NMR method of kinetic analysis, the rates of cyclization of dienimines in a few selected cases (**4′a−d**) were followed by both UV and ^{1}H-NMR spectroscopy. The dienimines investigated show UV ($CHCl_3$) absorption maxima at ~290 nm while the corresponding 1,2-dihydropyridines show maxima at ~280 and 350−380 nm. Kinetic results at 25.0 ± 0.2 °C for **4′a−d** in $CHCl_3$ (UV) [**4′a**, 1.63 (0.13) × 10^{-3}; **4′b**, 3.25 (0.06) × 10^{-4}; **4′c**, 5.40 (0.28) × 10^{-5}; **4′d**, 3.23 (0.17) × 10^{-3}] and $CDCl_3$ (^{1}H-NMR) (**4′a**, 1.69 (0.13) × 10^{-3}; **4′b**, 3.20 (0.04) × 10^{-4}; **4′c**, 5.06 (0.11) × 10^{-5}; **4′d**, 3.07 (0.18) × 10^{-3}] exhibit excellent agreement (standard deviations of rate constants are given in parentheses) since two different techniques covering a concentration range of greater than 3 orders of magnitude afforded similar results.

(18) Burnier, J. S.; Jorgensen, W. L. *J. Org. Chem.* **1984**, *49*, 3001.

(19) The geometric configuration of the imine moiety is assumed to be *E* for steric reasons. Professor K. N. Houk (UCLA) has kindly informed us that for the parent 1-azahexatrienes, after optimizing the *Z,Z*- and *E,Z*-structures, and then finding the transition state for cyclization for both, there is a large preference (~16 kcal/mol) for the transition state structure with the hydrogen outside and lone pair inside (*E*-imine).

Scheme 5



of the sterically less hindered **7'c** should result in a sterically congested syn disposition of the di-t-Bu groups in the transition state leading to DHP **7'c**. Thus, **7'c** fails to cyclize to **7"c**. In contrast, the disrotatory cyclization of **8'c** should result in a sterically less congested anti-disposition of the terminal t-Bu substituents in the transition state, allowing for cyclization to DHP **7"c**.

Next, a comparison of cyclization rates of dienimine **8'd** and dienal **8,** the latter with no substituent on the heteroatom, cyclized faster than the dienimine, but only by a factor of 2.4. Both dienal and dienimine lack inside terminal substituents on the heteroatom that could hinder the formation of the cyclic *s-cis,s-cis* conformation required for cyclization. The observed difference in cyclization rates can probably be attributed to an inherent difference in reactivity of the imine versus the carbonyl moiety. As indicated above, the isomerization of **8** affords **7** via **16**. It is believed that **7** is in equilibrium with **16**, strongly favoring the former. The preference for DHP in the nitrogen case can be attributed to at least two factors.[1] First, the longer C–N bond (1.48 Å) versus the shorter C–O bond (1.43 Å) results in a less strained six-membered ring. Secondly, the less electronegative nitrogen should afford greater resonance stabilization in the dienamine moiety versus the more electronegative oxygen in the corresponding dienol ether.

Finally, to examine how electronic factors[20] affect rates of electrocyclization, a few *para*-substituted aryl moieties were studied (Table 1). The relative order of reactivity for the cyclization of *para*-substituted dienimines substituted at the carbon terminus was determined to be **4'c** < **5'c** < **6'c** (relative rates: 1.0, 1.4, and 3.1, respectively). The relative order of cyclization of *para*-substituted dienimines substituted at the nitrogen terminus was established to be **4'd** < **4'e** < **4'f** (relative rates: 1.0, 1.2, and 1.4, respectively). It can be seen that the placement of either a donor or an acceptor group resulted in a modest increase in the rate of cyclization over the parent system. Similar trends have been observed for the reactivity order in the Diels–Alder cycloaddition reaction, wherein both donor and acceptor groups have been observed to accelerate reaction rates,[21] but only moderately so. Attempts to study the rate of cyclization of the dienimines derived from the condensation of *p*-(trifluoromethyl)aniline and *p*-(dimethylamino)aniline with dienal **4** were unsuccessful, however.

Summary

The cyclization of 1-azatrienes, formed in situ by simply mixing the *tert*-butyl-substituted α,β-cis dienal with primary amine, represents a useful method for the preparation of 1,2-dihydropyridines. The reactivity profile and the activation parameters for the cyclization have been determined and they generally correlate mechanistically with carbocyclic 6π-electron electrocyclization reactions. However, 1-azatriene electrocyclizations are much faster. The mechanism of these thermal cyclizations can be considered to involve the classical concerted, disrotatory mode of electrocyclizations. Despite the lack of a clear stereochemical label, the disrotatory nature of the ring closing is best illustrated by the greater cyclization rates of **8'c** and **8'd** as compared to **7'c** and **7'd,** respectively. That sterically more hindered systems (**8'c** and **8'd**) cyclize faster than less hindered ones (**7'c** and **7'd**) is a feature of 6π-electrocyclizations not previously observed.

Experimental Section[22]

(2*E*,4*E*)-3-*tert*-Butyl-5-phenyl-2,4-pentadienal (4). To a stirred, cooled (−78 °C) solution of oxalyl chloride (0.175 mL, 2.01 mmol) in CH_2Cl_2 (distilled over CaH_2, 4.6 mL) was added dropwise by syringe DMSO (0.311 mL, 4.53 mmol). After stirring for 10 min, a solution of **13a** (0.393 g, 1.82 mmol) in CH_2Cl_2 (2 mL plus 2 × 1 mL rinsings) was added to the Swern reagent by cannula. After 15 min, Et_3N (1.3 mL) was added dropwise, and the mixture was allowed to warm to room temperature. The reaction was quenched with H_2O (9 mL), and the resulting mixture extracted with CH_2Cl_2 (3 × 10 mL) and dried ($MgSO_4$). After solvent removal, the crude product was purified by flash chromatography (5% EtOAc/hexanes) to afford the dienal **4** (0.365 g, 94%) as a pale yellow oil. For characterization, a sample was further purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 20% EtOAc/hexanes) to afford the spectroscopically homogeneous sample. ^{1}H-NMR: δ 1.21 (9H, t-Bu, s), 6.16 (1H, H_2, d, J = 7.4 Hz), 6.64 (1H, H_4, d, J = 15.6 Hz), 6.87 (1H, H_5, d, J = 15.6 Hz), 7.3–7.8 (5H, Ar, m), 9.79 (1H, CHO, d, J = 7.4 Hz).

(2*E*,4*E*)-3-*tert*-Butyl-5-(4'-chlorophenyl)-2,4-pentadienal (5). Using the above Swern protocol for preparing **4**, allenol **13b** (0.553 g, 2.21 mmol) was oxidized to dienal **5** (0.489 g, 89%, yellow solid, mp 46–47 °C). ^{1}H-NMR: δ 1.20 (9H, t-Bu, s), 6.16 (1H, H_2, d, J = 7.4 Hz), 6.58 (1H, H_4, d, J = 15.6 Hz), 6.83 (1H, H_5, d, J = 15.6 Hz), 7.34 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.5 Hz), 7.40 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.5 Hz), 9.76 (1H, CHO, d, J = 7.4 Hz).

(2*E*,4*E*)-3-*tert*-Butyl-5-(4'-methoxyphenyl)-2,4-pentadienal (6). Using the above Swern protocol for preparing **4**, allenol **13c** (0.763 g, 3.09 mmol) was oxidized to dienal **6** (0.613 g, 82%), obtained as a pale yellow oil. ^{1}H-NMR: δ 1.20 (9H, t-Bu, s), 3.84 (3H, OMe, s), 6.14 (1H, H_2, d, J = 7.4 Hz), 6.59 (1H, H_4, d, J = 15.5 Hz), 6.73 (1H, H_5, d, J = 15.5 Hz), 6.91 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.7 Hz), 7.42 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.7 Hz), 9.76 (1H, CHO, d, J = 7.4 Hz).

(2*E*,4*E*)-3-*tert*-Butyl-6,6-dimethyl-2,4-heptadienal (7). Using the above Swern protocol for preparing **4**, allenol **13d**

(20) (a) Marvell, E. N.; Hilton, C.; Cleary, M. *J. Org. Chem.* **1983**, *48*, 4272. (b) Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114* , 1157. (c) Epiotis, N. C. *J. Am. Chem. Soc.* **1973**, 95, 1200.

(21) (a) Sustmann, R.; Schubert, R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1987; pp 112–113.

(22) Spectral and other analytical data are given in the supplementary material. Essential ^{1}H-NMR spectral data are presented in the Experimental Section as well. General experimental procedures are also presented in the supplementary material section and the purity of all new compounds were estimated by a combination of HPLC and NMR analysis. Satisfactory combustion analyses were obtained for selected compounds. The level of purity is indicated by the inclusion of copies of ^{1}H-NMR spectra and selected ^{13}C-NMR spectra in the supplementary material.

(0.211 g, 1.07 mmol) was oxidized to dienal **7**. Due to its chromatographic instability, no further purification of **7** was possible. The ^{1}H-NMR spectrum of the **7** exhibited: δ 1.08 (9H, t-Bu, s), 1.09 (9H, t-Bu, s), 5.76 (1H, H_5, d, J = 15.6 Hz), 5.99 (1H, H_2, d, J = 8.36 Hz), 6.00 (1H, H_4, d, J = 15.0 Hz), 9.65 (1H, CHO, d, J = 7.7 Hz). Superimposed on the spectrum of the aldehyde (see supplementary material) were signals attributed to the dihydropyran tautomer **16**: δ 0.95 (9H, t-Bu, s), 1.05 (9H, t-Bu, s), 4.23 (1H, H_2, d, J = 3.1 Hz), 5.0 (1H, H_3, m), 5.18 (1H, H_5, dd, J = 5.8 Hz, 1.9 Hz), 6.48 (1H, H_6, d, J = 5.8 Hz).

(2*E*,4*Z*)-3-*tert*-Butyl-6,6-dimethyl-2,4-heptadienal (8). A solution of dienol **18** (30 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (1 mL) was cooled to 0 °C. To this solution was added MnO_2 (65 mg, 0.75 mmol) in one portion and the resulting solution vigorously stirred for 30 min. The reaction mixture was filtered through a short column of $MgSO_4$ and concentrated to afford 26 mg (87%) of dienal **8**. Due to the difficulties in purifying this material, including its ease of electrocyclic ring closure-ring opening reaction (to dihydropyran **16** and then to the (2*E*,4*E*)-isomer **7**), only a ^{1}H-NMR spectrum was obtained.

In a separate experiment, by analyzing the sample immediately after workup and vacuum drying (the initial sample typically consisted of 90% (2*E*,4*Z*)- and 10% (2*E*,4*E*)-dienal), little if any dihydropyran could be detected by ^{1}H-NMR analysis. For the kinetic investigations the crude dienal was dissolved in $CDCl_3$ (freshly passed through activated neutral aluminum oxide to remove any acid) such that its final concentration was approximately 10 mg/mL $CDCl_3$. The sample was divided among a series of NMR tubes which were immediately cooled to −78 °C. For a kinetic run, a sample was removed and placed in the ^{1}H-NMR probe which was calibrated and preset to a specific temperature. When the sample had reached thermal equilibrium with the probe, ^{1}H-NMR spectra (300 MHz) were recorded at regular time intervals. The rate of the isomerization was monitored by following the disappearance of the aldehyde hydrogen signal (δ 9.85) of the (2*E*,4*Z*)-dienal wherein ^{1}H-NMR peaks due to dihydropyran **16** and (2*E*,4*E*)-isomer **7** grew simultaneously. The rate limiting step is considered to be the irreversible ring closure to dihydropyran. ^{1}H-NMR: δ 1.02 (9H, t-Bu, s), 1.17 (9H, t-Bu, s), 5.69 (1H, H_5, d, J = 13.4 Hz), 5.84 (1H, H_4, d, J = 13.4 Hz), 6.01 (1H, H_2, d, J = 7.9 Hz), 9.85 (1H, CHO, d, J = 7.9 Hz).

***tert*-Butyl-[(2*E*,4*E*)-3-*tert*-butyl-6,6-dimethyl-2,4-heptadienylidene]amine (7′c).** A solution of (2*E*,4*E*)-dienal **7** (20 mg, 0.11 mmol) in anhydrous ethanol (1 mL) containing 4 Å molecular sieves was cooled to 0 °C. *t*-Butylamine (41 mg, 0.55 mmol) was added dropwise and the reaction mixture stirred for 1 h at 0 °C. The molecular sieves were removed by filtration through a short column of $MgSO_4$, and the filtrate was concentrated by vacuum drying to afford an essentially quantitative yield of dienimine **7′c**. Although the dienimine was stable at room temperature, this material could not be further purified by chromatographic methods.

In a separate experiment, the crude dienimine (15 mg, 0.060 mmol) was dissolved in benzene-d_6 (1 mL) and heated for 48 h at 55 °C. Analysis of this sample during the heating period by ^{1}H-NMR spectroscopy showed no formation of cyclized 1,2-dihydropyridine (only uncyclized dienimine was present along with some indication of sample deterioration). ^{1}H-NMR: ($CDCl_3$ δ 1.09 (18H, t-Bu, s), 1.20 (9H, t-Bu, s), 5.59 (1H, H_5, d, J = 15.9 Hz), 5.89 (1H, H_4, d, J = 15.9 Hz), 6.17 (1H, H_2, d, J = 8.6 Hz), 8.15 (1H, H_1, d, J = 8.6 Hz). (C_6D_6) δ 0.97 (9H, t-Bu, s), 1.02 (9H, t-Bu, s), 1.27 (9H, t-Bu, s), 5.50 (1H, H_1, d, J = 15.8 Hz), 5.80 (1H, H_4, d, J = 15.8 Hz), 6.48 (1H, H_2, d, J = 8.6 Hz), 8.26 (1H, H_1, d, J = 8.6 Hz).

(2*E*,4*Z*)-3-*tert*-Butyl-6,6-dimethyl-2,4-heptadienylidene(phenyl)amine (8′d). A solution of dienol **17** (45 mg, 0.23 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was cooled to 0 °C. To this solution was added MnO_2 (98 mg, 1.1 mmol) in one portion. The resulting solution was vigorously stirred for 30 min and then filtered through a short column of $MgSO_4$. The colorless filtrate was concentrated to afford 41 mg (91%) of crude dienal **8**. Great care was taken to keep the (2*E*,4*Z*)-dienal **8** cool (0 °C) due to the ease with which it isomerizes to the (2*E*,4*E*)-dienal **7**.

Immediately after oxidation, **8** (41 mg, 0.21 mmol) was dissolved in anhydrous EtOH (2.0 mL) containing 4 Å molecular sieves, and the mixture was cooled to 0 °C. Aniline (98 mg, 1.1 mmol) was added and the resulting mixture stirred for 15 min. The molecular sieves were then removed by filtration through a short column of $MgSO_4$. The filtrate was concentrated, the residue was dissolved in 5 mL of $CDCl_3$ (freshly passed through activated neutral aluminum oxide to remove acid), and then the solution was evenly divided among six NMR tubes. Each sample was then cooled to −78 °C (dry ice/acetone bath) to retard the formation of cyclization product.

Analyzing the sample immediately after workup revealed that the sample typically consisted of a 9:1 ratio of (2*E*,4*Z*)-dienimine **8′d** to its (2*E*,4*E*)-dienimine isomer **7′d**, along with the excess aniline. For a kinetic run, the rate of the reaction was monitored by following the disappearance of the hydrogen signal at δ 5.61 (assigned to H_5 of the imine **8′d**). This signal was the only peak which did not overlap with a hydrogen signal of the (2*E*,4*E*)-dienimine isomer or cyclized DHP. ^{1}H-NMR (300 MHz): ($CDCl_3$) δ 1.04 (9H, t-Bu, s), 1.21 (9H, t-Bu, s), 5.61 (1H, H_5, d, J = 13.3 Hz), 5.83 (1H, H_4, dd, J = 13.3 Hz, 1.3 Hz), 6.44 (1H, H_2, dd, J = 9.2 Hz, 1.3 Hz), 8.42 (1H, H_1, d, J = 9.2 Hz).

1-n-Butyl-4-*tert*-butyl-2-phenyl-1,2-dihydropyridine (4″a). A solution of dienal **4** (29.4 mg, 0.137 mmol) in anhydrous EtOH (1 mL) containing 4 Å molecular sieves was cooled to 0 °C. n-Butylamine (51.3 mg, 0.687 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at 0 °C. The molecular sieves were removed by filtration through a short column of $MgSO_4$, and the filtrate was concentrated (rotary evaporator and oil pump). The 1-azatriene **4′a** (^{1}H-NMR: δ 0.91 (3H, $C_{4'}$-CH_3, t), 1.16 (9H, t-Bu, s), 3.40 (2H, $C_{1'}$-CH_2, t, J = 6.8 Hz), 6.28 (1H, H_2, d, J = 8.8 Hz), 6.50 (1H, H_4, d, J = 16.0 Hz), 6.78 (1H, H_5, d, J = 16.0 Hz), 8.16 (1H, H_1, d, J = 8.8 Hz)) was redissolved in dry ether to allow cyclization to the 1,2-dihydropyridine **4″a** to be completed at room temperature. After 3 h, the ether was removed by rotary evaporation to afford the 1,2-dihydropyridine (**4″a**) in 73% yield (26.9 mg). After cyclization to DHP, further purification was not possible due to the instability of the DHP. ^{1}H-NMR: δ 0.85 (3H, $H_{4'}$, t, J = 7.3 Hz), 1.05 (9H, t-Bu, s), 1.1−1.5 (4H, $H_{3'}$ and $H_{2'}$), 2.6−2.8 (1H, $H_{1'}$, m), 2.8−3.0 (1H, $H_{1'}$, m), 4.63 (1H, H_5, dd, J = 7.5 Hz, 1.8 Hz), 4.83 (1H, H_3, dd, J = 4.5 Hz, 1.8 Hz), 5.12 (1H, H_2, d, J = 4.5 Hz), 6.08 (1H, H_6, d, J = 7.5 Hz), 7.5−7.2 (5H, ArH, m).

1-*sec*-Butyl-4-*tert*-butyl-2-phenyl-1,2-dihydropyridine (4″b). Using the above procedure for the formation of Schiff base **4″a**, dienal **4** (20.1 mg, 0.094 mmol) in anhydrous EtOH (1 mL) was reacted with *sec*-butylamine (34.2 mg, 0.468 mmol) to afford 1-azatriene **4′b** (^{1}H-NMR: δ 0.83 (3H, $C_{3'}$-CH_3, t, J = 7.5 Hz), 1.04 (3H, $C_{1''}$-CH_3, d, J = 2.7 Hz), 1.17 (9H, t-Bu, s), 2.0−2.1 (2H, $2H_{2'}$, m), 2.9−3.1 (1H, $H_{1'}$, m), 6.31 (1H, H_2, d, J = 8.8 Hz), 6.50 (1H, H_4, d, J = 15.9 Hz), 6.78 (1H, H_5, d, J = 15.9 Hz), 8.17 (1H, H_1, d, J = 8.8 Hz)), which after cyclization and HPLC afforded DHP **4″b** (17.2 mg) in 68% yield. ^{1}H-NMR: δ 0.65 (1.5H, $H_{3'}$, t, J = 7.4 Hz), 0.88 (1.5H, $H_{3'}$, t, J = 7.4 Hz), 0.93 (1.5H, $H_{1''}$, d, J = 6.8 Hz), 1.03 (4.5H, t-Bu, s), 1.04 (4.5H, t-Bu, s), 1.05 (1.5H, $H_{1''}$, d, J = 6.8 Hz), 1.1−1.6 (2H, m), 2.7−2.9 (1H, $H_{1'}$, m), 4.6−4.7 (1H, H_5, m), 4.7−4.8 (1H, H_3, m), 5.2−5.1 (1H, H_2, m), 6.2−6.1 (1H, H_6, m), 7.5−7.2 (5H, ArH, m).

1,4-Di-*tert*-butyl-2-phenyl-1,2-dihydropyridine (4″c). Using the above procedure for the formation of Schiff base **4″a**, dienal **4** (30.0 mg, 0.140 mmol) in EtOH (1 mL) containing 4 Å molecular sieves at 0 °C was reacted with *tert*-butylamine (51.3 mg, 0.687 mmol) to form 1-azatriene **4′c** (^{1}H-NMR: δ 1.18 (9H, t-Bu, s), 1.19 (9H, t-Bu, s), 6.32 (1H, H_2, d, J = 8.6 Hz), 6.48 (1H, H_4, d, J = 16.0 Hz), 6.79 (1H, H_5, d, J = 16.0 Hz), 7.2−7.6 (5H, Ar, m), 8.25 (1H, H_1, d, J = 8.6 Hz)), which was allowed to cyclize to DHP **4″c**. Following standard workup procedures, purification was not possible due to the instability of this DHP. ^{1}H-NMR spectra revealed the presence of small amounts of open chain Schiff base (1-azatriene). ^{1}H-NMR: δ 1.02 (9H, t-Bu, s), 1.21 (9H, t-Bu, s), 4.88 (1H, H_5,

dd, J = 7.7 Hz, 2.0 Hz), 4.97 (1H, H_3, dd, J = 6.3 Hz, 2.0 Hz), 5.17 (1H, H_2, d, J = 6.3 Hz), 6.50 (1H, H_6, d, J = 7.7 Hz), 7.2 (3H, ArH, m), 7.4 (2H, ArH, m).

4-*tert*-Butyl-1,2-diphenyl-1,2-dihydropyridine (4″d). Following the procedure for the formation of Schiff base **4″a**, dienal **4** (39 mg, 0.14 mmol) in ethanol (1 mL) containing 4 Å molecular sieves was reacted with aniline (41 mg, 0.43 mmol) to form 1-azatriene **4″d** (^{1}H-NMR: δ 1.23 (9H, t-Bu, s), 6.53 (1H, H_2, d, J = 9.0 Hz), 8.44 (1H, H_1, d, J = 9.0 Hz)), which was allowed to cyclize to afford after workup and purification DHP **4″d** (39 mg) in 87% yield. ^{1}H-NMR: δ 1.05 (9H, t-Bu, s), 5.32 (1H, H_5, dd, J = 7.6 Hz, 1.9 Hz), 5.39 (1H, d, J = 6.2 Hz), 5.48 (1H, d, J = 6.2 Hz), 6.78 (1H, H_6, d, J = 7.6 Hz), 6.92 (2H, ArH, m), 7.4–7.2 (8H, ArH, m).

4-*tert*-Butyl-1-(4′-chlorophenyl)-2-phenyl-1,2-dihydropyridine (4″e). Following the procedure for the formation of Schiff base **4″a**, dienal **4** (30 mg, 0.14 mmol) in EtOH (1 mL) containing 4 Å molecular sieves was reacted with *p*-chloroaniline (53 mg, 0.42 mmol) to form 1-azatriene **4′c** (^{1}H-NMR: δ 1.22 (9H, t-Bu, s), 6.50 (1H, H_2, d, J = 9.0 Hz), 8.39 (1H, H_1, d, J = 9.0 Hz)), which was allowed to cyclize to afford after workup and purification, DHP **4″e** (31 mg) as a colorless oil in 81% yield. ^{1}H-NMR: δ 1.05 (9H, t-Bu, s), 5.34 (1H, H_5, dd, J = 7.9 Hz, 0.6 Hz), 5.40 (1H, H_2, d, J = 6.6 Hz), 5.44 (1H, H_3, d, J = 6.6 Hz), 6.71 (1H, H_6, d, J = 7.9 Hz), 6.83 (2H, ArH, d, J = 8.9 Hz), 7.17 (2H, ArH, d, J = 8.8 Hz), 7.3 (5H, ArH, m).

4-*tert*-Butyl-1-(4′-methoxyphenyl)-2-phenyl-1,2-dihydropyridine (4″f). Following the procedure for the formation of Schiff base **4″a**, dienal **4** (24 mg, 0.12 mmol) in EtOH (0.5 mL) containing 4 Å molecular sieves was reacted with *p*-methoxyaniline (28 mg, 0.23 mmol) to form 1-azatriene **4″f** (^{1}H-NMR: δ 1.21 (9H, t-Bu, s), 3.78 (3H, MeO, s), 8.44 (1H, H_1, d, J = 9.0 Hz)), which was allowed to cyclize to afford after workup and purification 1,2-DHP **4″f** (DHP, 32 mg) in 87% yield. ^{1}H-NMR: δ 1.06 (9H, t-Bu, s), 3.74 (3H, OMe, s), 5.23 (1H, H_5, dd, J = 7.6 Hz, 0.9 Hz), 5.31 (1H, H_3, dd, J = 6.3 Hz, 1.6 Hz), 5.44 (1H, H_2, d, J = 6.3 Hz), 6.70 (1H, H_6, d, J = 7.6 Hz), 6.79 (2H, $H_{2'}$, $H_{6'}$, d, J = 9.1 Hz), 6.87 (2H, $H_{3'}$, $H_{5'}$, d, J = 9.1 Hz), 7.4–7.2 (5H, ArH, m).

1,4-Di-*tert*-butyl-2-(4′-chlorophenyl)-1,2-dihydropyridine (5″c). Following the procedure for the formation of Schiff base **4″a**, dienal **5** (30.2 mg, 0.122 mmol) in EtOH (1 mL) containing 4 Å molecular sieves was reacted with *tert*-butylamine (44 mg, 0.61 mmol) to form 1-azatriene **5′c** (^{1}H-NMR: δ 1.18 (9H, t-Bu, s), 1.19 (9H, t-Bu, s), 6.34 (1H, H_2, d, J = 8.6 Hz), 6.44 (1H, H_4, d, J = 15.9 Hz), 6.76 (1H, H_5, d, J = 15.9 Hz), 7.34 (4H, Ar, m), 8.21 (1H, H_1, d, J = 8.6 Hz)). Purification of the cyclized product was not possible due to the instability of the DHP, which was observed to be in equilibrium with the open chain 1-azatriene (94/6, DHP/azatriene, as determined by ^{1}H-NMR analysis). ^{1}H-NMR: δ 1.91 (9H, t-Bu, s), 1.21 (9H, t-Bu, s), 4.90 (1H, H_5, dd, J = 7.5 Hz, 1.9 Hz), 4.96 (1H, H_2, dd, J = 6.4 Hz, 1.9 Hz), 5.14 (1H, H_3, dd, J = 6.4 Hz, 1.2 Hz), 6.51 (1H, H_6, d, J = 7.5 Hz), 7.21 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.4 Hz), 7.35 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.4 Hz).

1,4-Di-*tert*-butyl-2-(4′-methoxyphenyl)-1,2-dihydropyridine (6″c). Following the procedure for the formation of Schiff base **4″a**, dienal **6** (40.0 mg, 0.164 mmol) in EtOH (3 mL) containing 4 Å molecular sieves was reacted with *tert*-butylamine (59.8 mg, 0.82 mmol) to form 1-azatriene **6′c** (^{1}H-NMR: δ 1.18 (9H, t-Bu, s), 1.19 (9H, t-Bu, s), 3.83 (3H, MeO, s), 6.30 (1H, H_2, d, J = 8.6 Hz), 6.43 (1H, H_4, d, J = 15.9 Hz), 6.65 (1H, H_5, d, J = 15.9 Hz), 6.99 (2H, $H_{2'}$, $H_{6'}$, d, J = 5.9 Hz), 7.37 (2H, $H_{3'}$, $H_{5'}$, d, J = 5.9 Hz), 8.25 (1H, H_1, d, J = 8.6 Hz)), which was allowed to cyclize. Purification of the cyclized DHP was not possible due the instability of the DHP, which was observed to be in equilibrium with the open chain 1-azatriene (91/9, DHP/1-azatriene, as determined by ^{1}H-NMR analysis). ^{1}H-NMR: δ 1.03 (9H, t-Bu, s), 1.19 (9H, t-Bu, s), 3.78 (3H, O-CH_3, s), 4.87 (1H, H_5, dd, J = 7.7 Hz, 2.0 Hz), 4.96 (1H, H_3, dd, J = 6.2 Hz, 2.0 Hz), 5.13 (1H, H_2, d, J = 6.2 Hz), 6.46 (1H, H_6, d, J = 7.7 Hz), 6.79 (2H, $H_{2'}$, $H_{6'}$, d, J = 7.1 Hz), 7.36 (2H, $H_{3'}$, $H_{5'}$, d, J = 7.1 Hz).

1,2,4-Tri-*tert*-butyl-1,2-dihydropyridine (7″c). A solution of dienal **8** (40 mg, 0.21 mmol) in EtOH (1 mL) containing 4 Å molecular sieves was reacted with *tert*-butylamine (75 mg, 1.0 mmol) to form 1-azatriene **8′c** (^{1}H-NMR: (C_6D_6) δ 0.97 (18H, t-Bu, s), 1.01 (9H, t-Bu, s), 5.33 (1H, H_5, d, J = 13.1 Hz), 5.61 (1H, H_4, d, J = 13.1 Hz), 6.38 (1H, H_2, d, J = 8.6 Hz), 8.26 (1H, H_1, d, J = 8.6 Hz)), which was allowed to cyclize to afford after purification DHP **7″c** (43 mg) as a colorless oil in 81% yield. ^{1}H-NMR: δ 0.80 (9H, t-Bu, s), 1.06 (9H, t-Bu, s), 1.13 (9H, t-Bu, s), 3.53 (1H, H_2, dd, J = 6.7 Hz, 1.7 Hz), 4.86 (1H, H_3, br d, J = 6.7 Hz), 5.29 (1H, H_5, dd, J = 7.3 Hz, 1.8 Hz), 6.20 (1H, H_6, d, J = 7.3 Hz). (C_6D_6) δ 0.96 (9H, t-Bu, s), 1.04 (9H, t-Bu, s), 1.15 (9H, t-Bu, s), 3.47 (1H, H_2, dd, J = 6.4 Hz, 1.7 Hz), 4.91 (1H, H_3, d with fine structure, J = 6.4 Hz), 5.40 (1H, H_5, dd, J = 7.4 Hz, 1.8 Hz), 6.21 (1H, H_6, br d, J = 7.4 Hz).

2,4-Di-*tert*-butyl-1-phenyl-1,2-dihydropyridine (7″d). Following the procedure for the formation of Schiff base **4″a**, dienal **7** (50.1 mg, 0.232 mmol) in EtOH (1 mL) containing 4 Å molecular sieves was reacted with aniline (32.4 mg, 0.347 mmol) to form 1-azatriene **7′d** (^{1}H-NMR: δ 1.12 (9H, t-Bu, s), 1.16 (9H, t-Bu, s), 5.75 (1H, H_5, d, J = 15.8 Hz), 6.00 (1H, H_4, d, J = 15.8 Hz), 6.41 (1H, H_2, d, J = 9.0 Hz), 6.6–7.5 (5H, Ar, m), 8.4 (1H, H_1, d, J = 9.0 Hz) which was allowed to cyclize to afford, after workup and purification, DHP **7″d** (57.4 mg) as a colorless oil in 86% yield. ^{1}H-NMR: δ 0.92 (9H, t-Bu, s), 1.10 (9H, t-Bu, s), 4.33 (1H, H_2, d, J = 6.1 Hz), 5.11 (1H, H_3, d, J = 6.1 Hz), 5.39 (1H, H_5, dd, J = 7.4 Hz, 1.4 Hz), 6.60 (1H, H_6, d, J = 7.4 Hz), 6.89 (1H, ArH, t, J = 7.2 Hz), 7.10 (2H, ArH, d, J = 8.2 Hz), 7.3-7.2 (2H, ArH, m).

5-[(*tert*-Butyldimethylsilyl)oxy]-1-hydroxy-1-phenyl-2-pentyne (10a). A dried 500 mL flask equipped with a magnetic stir bar, septum, and gas inlet was flushed with argon. A solution of 4-[(*tert*-butyldimethylsilyl)oxy]-1-butyne (3.82 g, 20.7 mmol) in dry THF (100 mL) was cooled to −78 °C, and *n*-butyllithium (15.1 mL, 1.50 M in hexanes, 22.6 mmol) was added dropwise to the reaction flask. The solution was stirred for 5 min at −78 °C and 20 min at rt and then recooled to −78 °C. A solution of benzaldehyde (2.00 g, 18.8 mmol) in THF (15 mL) was cooled to −78 °C and added dropwise via cannula to the cold acetylide solution. The reaction mixture was stirred for 1 h at −78 °C, warmed to rt, and quenched with 50 mL of ice cooled saturated NaCl solution. After separation from the organic layer, the aqueous phase was extracted with ether (3 × 10 mL). The combined organic layers were washed with NaCl (1 × 20 mL) and dried ($MgSO_4$). The solvent was removed under vacuum and the residue distilled (bp 200–210 °C, 0.5 mm) to afford 5.18 g (86%) of the propargyl alcohol (**10a**) as a clear oil. ^{1}H-NMR: δ 0.08 (6H, Si-Me, s), 0.91 (9H, Si-t-Bu, s), 2.50 (2H, H_4, dt, J = 7.1 Hz, 1.8 Hz), 3.76 (2H, H_5, t, J = 7.0 Hz), 5.40 (1H, H_1, br s), 7.3–7.6 (5H, ArH, m).

5-[(*tert*-Butyldimethylsilyl)oxy]-1-hydroxy-1-(4′-chlorophenyl)-2-pentyne (10b). As for preparing **10a**, a solution of 4-[(*tert*-butyldimethylsilyl)oxy]-1-butyne (6.56 g, 35.6 mmol) in dry THF (100 mL) was cooled to −78 °C and n-BuLi (25.0 mL, 1.50 M in hexanes, 39.1 mmol) added dropwise. 4-Chlorobenzaldehyde (5 g, 35.6 mmol) in 50 mL of THF was then added via cannula to the cold acetylide solution. The mixture was stirred for 1 h at −78 °C and then warmed to rt. Following workup, the crude residue was purified (Kugelrohr distillation, bp 200–210 °C, 0.5 mm) to afford 9.47 g (82%) of the propargyl alcohol **10b** as a clear oil. ^{1}H-NMR: δ 0.06 (6H, Si-Me, s), 0.89 (9H, Si-t-Bu, s), 2.49 (2H, H_4, dt, J = 6.9 Hz, 1.6 Hz), 3.74 (2H, H_5, t, J = 6.9 Hz), 5.42 (1H, H_1, br s), 7.33 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.4 Hz), 7.48 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.4 Hz).

5-[(*tert*-Butyldimethylsilyl)oxy]-1-hydroxy-1-(4′-methoxyphenyl)-2-pentyne (10c). As in the preparation of **10a**, 4-[(*tert*-butyldimethylsilyl)oxy]-1-butyne (6.30 g, 34.2 mmol) in dry THF (300 mL) was cooled to −78 °C and n-BuLi (24.0 mL, 1.50 M in hexanes, 37.5 mmol) was added. A solution of 4-methoxybenzaldehyde (4.66 g, 34.1 mmol) in 50 mL of THF was then added via cannula to the cold acetylide solution. Following standard workup procedures, the crude residue was then purified (Kugelrohr distillation, bp 210–220 °C, 0.5 mm) to afford 9.24 g (85%) of the propargyl alcohol **10c** as a clear oil. ^{1}H-NMR: δ 0.07 (6H, Si-Me, s), 0.90 (9H, Si-t-Bu, s), 2.50 (2H, H_2, dt, J = 7.0 Hz, 1.6 Hz), 3.75 (2H, H_1, t, J = 7.0 Hz),

3.81 (3H, OMe, s), 5.39 (1H, H_1, br s), 6.89 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.6 Hz), 7.46 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.6 Hz).

1-[(*tert*-Butyldimethylsilyl)oxy]-6,6-dimethyl-5-hydroxy-3-heptyne (10d). As in the preparation of **10a**, 4-[(*tert*-butyldimethylsilyl)oxy]-1-butyne (9.74 g, 52.0 mmol) in THF (200 mL) was cooled to −78 °C and n-BuLi (98.0 mL, 1.50 M in hexanes, 58.0 mmol) was added. A solution of trimethylacetaldehyde (5.00 g, 5.80 mmol) in 100 mL of THF was then added via cannula to the cold acetylide solution. Following standard workup procedures, the crude residue was purified (Kugelrohr distillation, 165−170 °C, 1 mm) to afford 11.4 g of the propargyl alcohol **10d** (80% yield) as a clear oil. ^{1}H-NMR: δ 0.05 (6H, Si-Me, s), 0.88 (9H, Si-t-Bu, s), 0.96 (9H, C-t-Bu, s), 2.42 (2H, H_2, dt, J = 1.8 Hz, 7.1 Hz), 3.70 (2H, H_1, t, J = 7.1 Hz), 3.97 (1H, H_5, dt, J = 1.8 Hz, 5.9 Hz).

1-(Benzoyloxy)-5-[(*tert*-butyldimethylsilyl)oxy]-1-phenyl-2-pentyne (11a). A solution of propargyl alcohol **10a** (2.00 g, 6.89 mmol) in pyridine (10 mL) and DMAP (0.084 g, 0.69 mmol) was cooled (0 °C) and benzoyl chloride (1.06 g, 7.59 mmol) added. The pyridinium chloride precipitated as a white solid. The reaction mixture was stirred for 12 h to ensure completion of the reaction. The mixture was brought to rt and then diluted with 25 mL of ether. After washing with saturated NH_4Cl (3 × 20 mL) and saturated NaCl (1 × 20 mL), the organic layer was dried over $MgSO_4$. The solvent was removed and the crude residue purified by flash chromatography (silica gel, 90:10:2, hexane:ether:pyridine) to give 2.65 g (97%) of the benzoate as a clear oil which was sufficiently pure for the next step. For characterization, a sample was purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 10% EtOAc/hexanes) to afford the spectroscopically homogeneous sample. ^{1}H-NMR: δ 0.09 (6H, $SiCH_3$, s), 0.92 (9H, Si-t-Bu, s), 2.54 (2H, H_4, td, J = 6.8 Hz, 1.8 Hz), 3.79 (2H, H_5, t, J = 6.8 Hz), 6.78 (1H, H_1), 7.3−7.6 (5H, aryl-H, m), 7.66 (2H, aryl-H, d, J = 6.4 Hz), 8.12 (2H, aryl, d, J = 7.4 Hz).

1-(Benzoyloxy)-5-[(*tert*-butyldimethylsilyl)oxy]-1-(4′-chlorophenyl)-2-pentyne (11b). Via the procedure for the preparation of **11a**, propargyl alcohol **10b** (3.30 g, 10.2 mmol) in pyridine (45 mL) and DMAP (0.12 g, 1.0 mmol) was reacted with benzoyl chloride (2.85 g, 20.3 mmol) to afford, after workup and purification, benzoate **11b** (89% yield, 3.87 g). ^{1}H-NMR: δ 0.06 (6H, Si-Me, s), 0.88 (9H, Si-t-Bu, s), 2.51 (2H, H_4, t, J = 6.6 Hz), 3.75 (2H, H_5, t, J = 6.7 Hz), 6.69 (1H, H_1, s), 7.3−7.4 (5H, aryl-H, m), 7.56 (2H, aryl-H, d, J = 7.8 Hz), 8.07 (2H, aryl-H, d, J = 7.8 Hz).

1-(Benzoyloxy)-5-[(*tert*-butyldimethylsilyl)oxy]-1-[4′-(methyloxy)phenyl]-2-pentyne (11c). Via the procedure for the preparation of **11a**, propargyl alcohol **10c** (5.00 g, 15.6 mmol) in pyridine (60 mL) and DMAP (0.19 g, 1.56 mmol) was reacted with benzoyl chloride (2.41 g, 17.2 mmol) to afford after workup, benzoate **11c** (5.89 g, 89% yield). ^{1}H-NMR: δ 0.05 (6H, Si-Me, s), 0.88 (9H, Si-t-Bu, s), 2.50 (2H, H_4, td, J = 7.0 Hz, 1.8 Hz), 3.75 (2H, H_5, t, J = 7.0 Hz), 3.82 (3H, OMe, s), 6.67 (1H, H_1, s), 6.90 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.6 Hz), 7.42 (2H, $2H_m$ of benzoyl, t, J = 7.7 Hz), 7.54 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.6 Hz), 7.5 (1H, H_p of benzoyl, m), 8.06 (2H, $2H_o$ of benzoyl, d, J = 7.4 Hz).

1-[(*tert*-Butyldimethylsilyl)oxy]-6,6-dimethyl-5-(methanesulfonoxy)-3-heptyne (11d). Propargyl alcohol **10d** (2.00 g, 7.39 mmol) in pyridine (40 mL) and DMAP (0.09 g, 0.74 mmol) was cooled (0 °C) and mesyl chloride (0.93 g, 8.1 mmol) added dropwise. After stirring for 1 h, the mixture was diluted with 50 mL of ether, quenched with saturated NH_4Cl (50 mL), and repeatedly washed with a saturated solution of $CuSO_4$ to remove the pyridine. The organic layer was then washed with saturated $NaHCO_3$ (20 mL) and dried ($MgSO_4$). The solvent was removed, and the crude mesylate **11d** (2.1 g, 80% yield) was used without further purification in the next step. For characterization, a sample was purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 20% EtOAc/hexanes) to afford the spectroscopically homogeneous sample. ^{1}H-NMR: δ 0.04 (6H, Si-Me, s), 0.87 (9H, Si-t-Bu, s), 1.03 (9H, t-Bu, s), 2.45 (2H, H_2, td, J = 6.6 Hz, 1.6 Hz), 3.09 (3H, SO_3-Me, s), 3.71 (2H, H_1, t, J = 6.6 Hz), 4.80 (1H, H_5, s).

3-*tert*-Butyl-1-[(*tert*-butyldimethylsilyl)oxy]-5-phenyl-3,4-pentadiene (12a). A solution of *tert*-butyllithium (25.5 mL, 1.70 M in pentanes, 43.7 mmol) was cooled to −78 °C and added dropwise via cannula to a suspension of CuCN (1.94 g, 21.7 mmol) in dry Et_2O (50.0 mL) at −78 °C under argon. The mixture was stirred for 2 min, warmed to 0 °C for 15 min, and recooled to −78 °C. The propargylic benzoate **11a** (4.28 g, 10.8 mmol) in ether (10 mL) at −78 °C was added dropwise via cannula and the resulting clear tan mixture was allowed to stir for 1 h at −78 °C. The reaction mixture was warmed to 0 °C for 10 min and then quenched with saturated NH_4Cl. The organic layer was decanted and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The crude material was purified by flash chromatography (silica gel, 5% EtOAc/hexanes) to afford the allene **12a** (2.68 g, 75% yield) as a clear oil. The sample for spectroscopic analysis was purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 5% EtOAc/hexanes). ^{1}H-NMR: δ 0.04 (6H, SiMe, s), 0.06 (3H, SiMe, s), 0.91 (9H, Si-t-Bu, s), 1.16 (9H, t-Bu, s), 2.3−2.5 (2H, H_2, m), 3.74 (2H, H_1, t, J = 7.7 Hz), 6.18 (1H, H_5, t, J = 3.0 Hz), 7.1−7.3 (5H, H-aryl, m).

3-*tert*-Butyl-1-[(*tert*-butyldimethylsilyl)oxy]-5-(4′-chlorophenyl)-3,4-pentadiene (12b). As in the preparation of **12a**, *tert*-butyllithium (27.2 mL, 1.70 M in pentanes, 46.2 mmol) was added dropwise to a suspension of CuCN (2.07 g, 23.1 mmol) in dry ether (100 mL) at −78 °C. To this solution was added propargylic benzoate **11b** (4.71 g, 11.0 mmol) in Et_2O (50 mL) at −78 °C to yield after workup allene **12b** (3.61 g, 90% yield) as a colorless oil. ^{1}H-NMR: δ 0.01 (3H, $SiCH_3$, s), 0.03 (3H, $SiCH_3$, s), 0.88 (9H, Si-t-Bu, s), 1.12 (9H, t-Bu, s), 2.2−2.5 (2H, H_2, m), 3.6−3.8 (2H, H_1, m), 6.11 (1H, H_5, t, J = 2.9 Hz), 7.18 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.5 Hz), 7.25 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.5 Hz).

3-*tert*-Butyl-1-[(*tert*-butyldimethylsilyl)oxy]-5-(4′-methoxyphenyl)-3,4-pentadiene (12c). As in the preparation of **12a**, *tert*-butyllithium (33.0 mL, 1.70 M in pentanes, 55.5 mmol) was added dropwise to a suspension of CuCN (2.48 g, 27.7 mmol) in ether (100 mL) at −78 °C. The propargylic benzoate **11c** (5.89 g, 13.9 mmol) in ether (50 mL) was then added to yield after workup allene **12c** (3.42 g, 68% yield) as a colorless oil. ^{1}H-NMR: δ 0.01 (3H, $SiCH_3$, s), 0.02 (3H, $SiCH_3$, s), 0.87 (9H, Si-t-Bu, s), 1.11 (9H, t-Bu, s), 2.2−2.4 (2H, H_2, m), 3.69 (2H, H_1, t, J = 7.3 Hz), 3.80 (3H, CH_3O, s), 6.10 (1H, H_5, t, J = 3.0 Hz), 6.82 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.6 Hz), 7.18 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.6 Hz).

3-*tert*-Butyl-1-[(*tert*-butyldimethylsilyl)oxy]-6,6-dimethyl-3,4-heptadiene (12d). As in the preparation of **12a**, *tert*-butyllithium (47.9 mL, 1.70 M in pentanes, 81.5 mmol) was added to a suspension of CuCN (3.65 g, 40.7 mmol) in ether (200 mL). The propargylic mesylate **11d** (7.01 g, 20.4 mmol) in dry ether (50 mL) was added to yield after workup and purification allene **12d** (5.69 g, 90% yield) as a colorless oil. ^{1}H-NMR: (δ 0.06 (3H, Si-Me, s), 0.90 (9H, Si-t-Bu, s), 1.00 (9H, t-Bu, s), 1.03 (9H, t-Bu, s), 2.20 (2H, H_2, dt, J = 8.5 Hz, 3.1 Hz), 3.64 (2H, H_1, t, J = 8.5 Hz), 5.09 (1H, H_5, t, J = 3.1 Hz).

3-*tert*-Butyl-5-phenyl-3,4-pentadien-1-ol (13a). Allene **12a** (0.567 g, 1.72 mmol) was cooled (0 °C) and reacted with a solution of TBAF (5.18 mL, 1 M in THF, 5.18 mmol). The mixture was warmed to rt and stirred for 3 h. After quenching the reaction with saturated NaCl (10 mL), the aqueous phase was extracted with ether (3 × 10 mL). The organic layer was washed with saturated $NaHCO_3$ and dried over $MgSO_4$. After the solvent was removed, the residue was purified by flash chromatography (50:50 hexanes/ether) to afford 336 mg (90%) of the alcohol **13a** as a colorless oil. Further purification by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 50:50 EtOAc/hexanes) afforded the spectroscopically homogeneous sample. ^{1}H-NMR: δ 1.26 (9H, t-Bu, s), 2.4−2.6 (2H, H_2, m), 3.85 (2H, H_1, t, J = 6.3 Hz), 6.34 (1H, H_5, t, J = 3.3 Hz), 7.2−7.5 (5H, aryl-H, m).

3-*tert*-Butyl-5-(4′-chlorophenyl)-3,4-pentadien-1-ol (13b). Following the procedure for **13a**, TBAF (18.8 mL, 1 M in THF, 18.8 mmol) was added to the TBDMS-protected allenol **12b** (3.43 g, 9.40 mmol) which afforded, after workup and purification, 2.00 g (85%) of the alcohol **13b** as a white solid (mp 62.5−63.5 °C). ^{1}H-NMR: δ 1.13 (9H, t-Bu, s), 2.3−2.5 (2H, H_2, m),

3.73 (2H, H_1, t, J = 6.4 Hz), 6.19 (1H, H_5, t, J = 3.2 Hz), 7.18 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.5 Hz), 7.26 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.5 Hz).

3-*tert*-Butyl-5-(4′-methoxyphenyl)-3,4-pentadien-1-ol (13c). Following the procedure for **13a**, TBAF (17.8 mL, 1 M in THF, 17.8 mmol) was added to the TBDMS-protected allenol **12c** (3.21 g, 8.92 mmol) which afforded, after workup and purification, 1.82 g (83%) of the alcohol **13c** as a clear, colorless oil. ^{1}H-NMR: δ 1.14 (9H, t-Bu, s), 2.3–2.5 (2H, H_2, m), 3.74 (2H, H_1, t, J = 6.1 Hz), 3.79 (3H, OCH_3, s), 6.21 (1H, H_5, t, J = 3.3 Hz), 6.86 (2H, $H_{3'}$, $H_{5'}$, d, J = 8.6 Hz), 7.20 (2H, $H_{2'}$, $H_{6'}$, d, J = 8.6 Hz).

3-*tert*-Butyl-6,6-dimethyl-3,4-heptadien-1-ol (13d). Following the procedure for **13a**, TBAF (4.69 mL, 1 M in THF, 4.69 mmol) was added to the TBDMS-protected allenol **12d** (1.01 g, 23.2 mmol) which afforded, after workup and purification, 0.475 g (75%) of the alcohol **13d** as a clear, colorless oil. ^{1}H-NMR: δ 1.02 (9H, t-Bu, s), 1.04 (9H, t-Bu, s), 2.2–2.3 (2H, H_2, m), 2.72 (2H, H_1, t, J = 6.1 Hz), 5.20 (1H, H_5, t, J = 3.3 Hz).

3-*tert*-Butyl-6,6-dimethyl-3,4-heptadienal (14d). A solution of allenol **13d** (387 mg, 2.10 mmol) in CH_2Cl_2 (1 mL) was added to Dess–Martin periodinane (1.25 g, 2.95 mmol) in CH_2Cl_2 (3 mL) with stirring. After 20 min the reaction mixture was diluted with ether (10 mL), and then the resulting suspension was added to a solution of saturated $NaHCO_3$ with a 7-fold excess of sodium thiosulfate (3.46 g, 13.9 mmol). After the mixture was stirred for 30 min, the ether layer was removed and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was dried over $MgSO_4$, concentrated, and purified by flash chromatography (silica gel, 5% EtOAc/hexanes) to afford the allenal **14d** (0.360 g, 93% yield) as a colorless oil. For characterization, a sample was further purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 20% EtOAc/hexanes) to afford the spectroscopically homogeneous sample. It was observed that allenal **14d** could be isomerized to dienal **7** with base. Allenal **14d** (50 mg, 0.27 mmol) was placed in ethanol (1 mL) and triethylamine (10 μL) and stirred for 3 h. The solvent was then removed to afford a quantitative yield of dienal **7**. ^{1}H-NMR: δ 1.02 (9H, t-Bu, s), 1.06 (9H, t-Bu, s), 2.96 (2H, H_2, dd, J = 2.6 Hz, 2.8 Hz). 5.24 (1H, H_5, t, J = 2.4 Hz), 9.62 (1H, CHO, t, J = 2.8 Hz).

(2*E*,4*E*)-3-*tert*-Butyl-6,6-dimethylhepta-2,4-dien-1-ol (17). A solution of dienal **7** (210 mg, 1.1 mmol) dissolved in hexanes (13 mL) was cooled to −60 °C and DIBAL-H (1.0 M in hexanes, 1.6 mL, 1.6 mmol) was added dropwise. The reaction mixture was stirred for 3 h before warming to 0 °C. After mixing for 1 h at 0 °C, the reaction was quenched with saturated NaCl (15 mL). Stirring was continued for an additional 1 h at room temperature. The reaction mixture was extracted with ether (3 × 10 mL) and then the organic layer was dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (10% EtOAc/hexanes) afforded 153 mg (70%) of dienol **17** as a clear oil. For characterization, a sample was purified by HPLC (Rainin Dynamax 60A silica column, 25 × 1 cm, 10% EtOAc/hexanes) to afford the spectroscopically homogeneous sample. ^{1}H-NMR: δ 1.04 (9H, t-Bu, s), 1.05 (9H, t-Bu, s), 4.21 (2H, H_1, d, J = 6.4 Hz), 5.39 (1H, H_4, d, J = 16.0 Hz), 5.48 (1H, H_2, t, J = 6.4 Hz), 5.78 (1H, H_5, d, J = 16.0 Hz).

(2*E*,4*Z*)-3-*tert*-Butyl-6,6-dimethylhepta-2,4-dien-1-ol (18). A solution of dienol **17** (473 mg, 2.40 mmol) and 2′-acetonaphthone (40 mg, 0.24 mmol) in benzene-d_6 (2 mL) was placed in an NMR tube taped to a standard photochemical reaction well (Pyrex). After argon was bubbled through the solution for 5 min, a small magnetic stir bar was introduced and the sample was irradiated with mixing for 48 h with a 450-W Hanovia medium pressure lamp. The progress of the reaction was followed by ^{1}H-NMR analysis (after removal of the stir bar). The crude product was concentrated and purified by flash chromatography (silica gel, 20% EtOAc/hexanes). The product (246 mg, 52%, 95/5:*Z*/*E* mixture) was obtained as a clear oil. For characterization, a sample was purified by HPLC (Rainin Dynamax 60A silica column, 25 x 1 cm, 10% EtOAc/hexanes) to afford 227 mg (48%) of **18** as a spectroscopically homogeneous sample. ^{1}H-NMR: δ 1.01 (9H, t-Bu, s), 1.10 (9H, t-Bu, s), 4.05–4.18 (1H, H_1, m), and 4.3–4.2 (1H, $H_{1'}$, m), [this molecule exhibits atropisomerism rendering H_1 and $H_{1'}$ nonequivalent], 5.42 (1H, H_5, d, J = 13.1 Hz), 5.46 (1H, H_2, d with additional coupling, J = 7.3 Hz), 5.63 (1H, H_4, d, J = 13.1 Hz).

Acknowledgment. This study was generously supported by a grant from the National Science Foundation (NSF-CHE-8903581) and the Graduate Division (Graduate Council Fellowship) and the Committee on Research (Intramural Research Grant) of the University of California, Riverside.

Supplementary Material Available: Spectral and analytical data (49 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO941882L