Structural Effects Affecting the Thermal Electrocyclic Ring Closure of Vinylallenes to Alkylidenecyclobutenes

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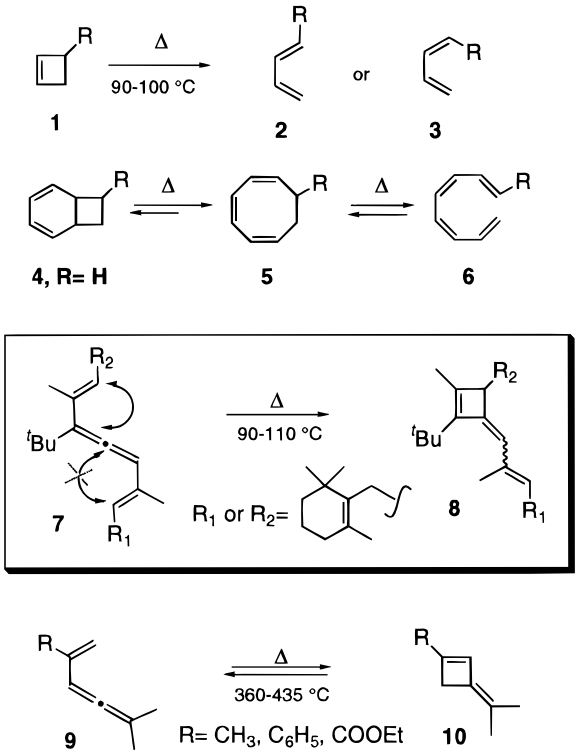
Abstract: The thermal electrocyclic ring closure of (2*E*,7*E*)-3,4,7-trialkylnona-2,4,5,7-tetraenes (divinyl-4,5-allenes) is regioselective, occurring at the most sterically congested vinylallene subunit to afford the trisubstituted alkylidenecyclobutene. Ring closure of both divinylallenes and vinylallenes displays high torquoselectivity (exclusive formation of the (*E*)-alkylidenecyclobutenes) when the substituent at C_4 is a sterically demanding alkyl group and the substituent at C_2 is a formyl group. *Ab initio* calculations clearly demonstrate the dominant steric influence of the bulky C_4 substituent in these selectivities. However, torquoselectivity appears to be enhanced if cyclization involves loss of conjugation by a π system encompassing the C_2 substituent.

The symmetry-based selection rules for electrocyclic reactions (*i.e.* for the formation of a σ bond between the termini of a fully conjugated π system or the reverse process) distinguish only between disrotatory and conrotatory modes.[1] They do not allow prediction of *torquoselectivity*, *i.e.* they do not distinguish between the two possible disrotatory modes or the two possible conrotatory modes for substituted polyenes.[2−4] Early attempts at torquoselectivity prediction were based on the steric effects of the substituents.[1c] More recently, *ab initio* calculations of the transition structures corresponding to the two alternative directions of twist have been carried out.[4] It is found that 3-substituted cyclobutenes **1** (four-electron systems[5]) with different 3-substituents differ by as much as 20 kcal/mol in the difference between the energies of the two transition structures and that these large differences are best rationalized in terms of the electronic nature of the substituents: for electron donors, *outward* rotation (**1** to **2** in Scheme 1) is favored because it minimizes repulsive cyclic four-electron interactions and maximizes stabilizing cyclic two-electron interactions, while the opposite electronic effects of electron acceptors favor *inward* rotation to **3**.[4b] However, analogous calculations for the six-electron[6] ring opening of bicyclo[4.2.0]octa-2,4-diene (**4**) to cycloocta-1,3,5-triene (**5**, R = H) and the eight-electron[6,7] ring opening of compounds **5** to 1-substituted octa-1,3,5,7-tetraenes (**6**) have found transition structures in which the relationships between the substituents at the interacting termini and the breaking or forming C−C bond are essentially independent of the direction of twist; the consequent theoretical prediction of just a small preference for the *outward* twist mode (due to the steric effect of the substituent) in the ring opening of 7-substituted cycloocta-1,3,5-trienes **5** is in keeping with experimental findings.[7]

Scheme 1



As part of our research on structural influences on the activities of retinoids as cell differentiation promoters, we

† Departamento de Química Física.

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(1) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. (b) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (c) Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980. (d) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.

(2) Houk, K. N. Stereoselective Electrocyclizations and Sigmatropic Shifts of Strained Rings: Torquoelectronics, in *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, 1989; pp 25−37.

(3) The alternative term *rotoselectivity* is also used; see, for example: Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 12491.

(4) (a) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (c) Houk, K. N.; Spellmeyer, D. C.; Jefford, C. W.; Rimbault, C. G.; Wang, Y.; Miller, R. D. *J. Org. Chem.* **1988**, *53*, 2125. (d) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412. (e) Kallel, E. A.; Wang, Y.; Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 6759. (f) Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A. B.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157. (g) Nakamura, K.; Houk, K. N. *J. Org. Chem.* **1995**, *60*, 686.

(5) For a review, see: Durst, T.; Breau, L. Cyclobutene Ring Opening Reactions, in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Volume 5, Chapter 6.1, pp 675−697.

(6) Thomas, B. E.; Evanseck, J. D.; Houk, K. N. *Isr. J. Chem.* **1993**, *33*, 287.

(7) Thomas, B. E.; Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 4165.

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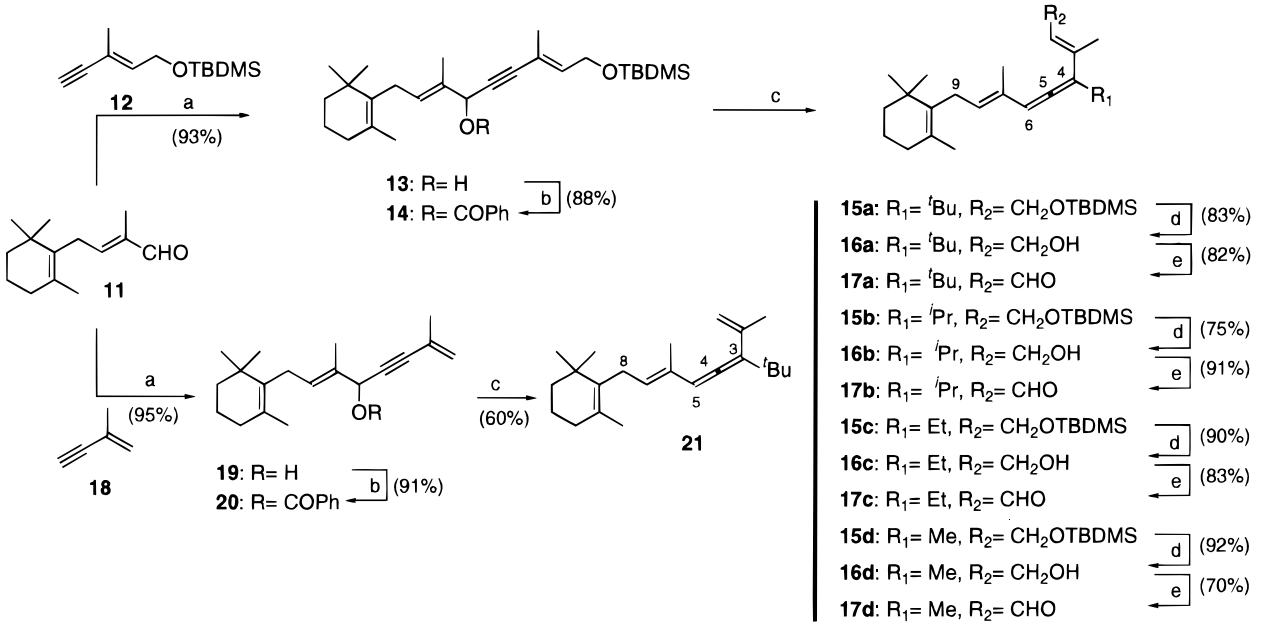
Scheme 2[a]



[a] (a) *n*-BuLi, −78 °C to room temperature; (b) *n*-BuLi, PhCOCl, −78 °C to room temperature; (c) for **15a**, *t*-BuLi, CuCN, −78 °C to room temperature, 71%; for **15b**, *i*-PrMgCl, CuBr·SMe_2, THF, −60 °C, 1 h, then 12 h at room temperature, 70%; for **15c**, EtMgBr, CuBr·SMe_2, THF, −60 °C, 1 h, then 12 h at room temperature, 60%; for **15d**, MeMgBr, CuI·LiBr, THF, 0 °C, 5 h, 70%; (d) TBAF, THF, room temperature; (e) MnO_2, CH_2Cl_2, room temperature. See supporting information for experimental procedures and spectroscopic characterization of these compounds.

introduced an allene group in the retinoid side chain.[8,9] On studying the thermal behaviour of these divinylallenes (**7**), we discovered that, under relatively mild conditions, a four-electron electrocyclic ring closure took place[10a] (*cf.*,[11] **9**−**10**). Since in some cases the reaction exhibited remarkable regioselectivity (exclusive cyclization to alkylidenecyclobutenes **8**) and torquoselectivity[10b] (exclusive cyclization to the *E*-alkylidenecyclobutenal **8** when R_2 = CHO), we were prompted to a fuller investigation of its dependence on steric and electronic effects.

We describe here the results of this investigation, which included kinetic studies and comprehensive analysis of model systems by means of *ab initio* calculations. We evaluated both steric effects (by varying the bulk of the alkyl substituent on the allene: *t*-Bu, *i*-Pr, Et, or Me), and the electronic effect of the terminal R_2 group (H, alkyl, CHO). Experimental results and theoretical analysis indicate that in these systems torquoselectivity is mainly of steric origin but is further enhanced by electronic effects if R_2 is a formyl group.

Results and Discussion

Preparation of the Divinylallenes. The preparation of substituted divinylallenes was based on the regioselective S_N2' displacement of propargylic benzoates by organocopper reagents.[8,9,12] Incorporation of the *tert*-butyl group requires the mixed heterocuprate dilithium di-*tert*-butyl cyanocuprate,[12b,c] but the less bulky alkyl derivatives are best synthesized with the Grignard reagent in the presence of stoichiometric amounts of copper salts.[12a,d]

The lithium salt of TBDMS-protected (*E*)-3-methylpent-2-en-4-yn-1-ol (**12**)[13a] was reacted with aldehyde **11**[13b] to afford propargylic alcohol **13** in 93% yield. Benzoylation of **13** afforded **14** in 88% yield. Addition of the benzoate **14** to (*t*-Bu)$_2$Cu(CN)Li_2 in ether at −78 °C gave a 71% yield of the TBDMS-protected 4,5-allenic alcohol **15a**, in which the bulky *tert*-butyl group is borne at position C_4 (C_{12} of the retinoid side chain[9]). Deprotection of **15a** by treatment with TBAF[14] gave an 83% yield of the 4-*tert*-butyl-substituted divinylallenol **16a**, which was oxidized with MnO_2[15] to divinylallenal **17a** in 82% yield (Scheme 2).

Addition of the benzoate **14** to a solution of the cuprate obtained by reaction of *i*-PrMgCl or EtMgBr with CuBr·SMe_2 cooled to −60 °C afforded allenes **15b** and **15c**, respectively. For the incorporation of the methyl group at C_4 in **15d**, benzoate **14** was added to a solution of the cuprate obtained by treating

(8) For leading references on the chemistry of vinylallenes, see: (a) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81. (b) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (c) Okamura, W. H.; Curtin, M. L. *Synlett* **1990**, 1. For monographs, see: (d) *The Chemistry of Ketenes, Allenes and Related Compounds, Part I and Part II*; Patai, S., Ed.; John Wiley and Sons: New York, 1980. (e) Landor, S. R. *The Chemistry of the Allenes*; Academic Press: New York, 1982. (f) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Chemistry*; Wiley: New York, 1984.

(9) For a review on allenic retinoids, see: de Lera, A. R.; Chandraratna, R. A. S.; Okamura, W. H. Synthesis and Studies of 12-s-*cis* Conformationally Locked Retinoids. In *Chemistry and Biology of Synthetic Retinoids*; Dawson, M. I., Okamura, W. H., Eds.; CRC Press: Boca Raton, FL, 1990; Chapter 9, pp 201−227.

(10) (a) García Rey, J.; Rodríguez, J.; de Lera, A. R. *Tetrahedron Lett.* **1993**, *34*, 6293. (b) López, S.; García Rey, J.; Rodríguez, J.; de Lera, A. R. *Tetrahedron Lett.* **1995**, *36*, 4669. Note that these communications used the retinoid nomenclature and numbering system (IUPAC−IUB Joint Commission on Biochemical Nomenclature, *Eur. J. Biochem.* **1982**, *129*, 1). Due to the non-retinoid nature of some of the compounds involved in the work now reported, systematic nomenclature has been used throughout this article.

(11) (a) Upon heating to 170 °C, the parent penta-1,2,4-triene gives, among other dimeric products, the parent methylenecyclobutene. See: Schneider, R.; Siegel, H.; Hopf, H. *Liebigs Ann. Chem.* **1981**, 1812. We thank Prof. Hopf for calling our attention to some of his early ideas on periselectivity in vinylallenes: Hopf, H. *Nachr. Chem. Techn.* **1975**, *23*, 235. For thermal 4π electrocyclic ring closure of substituted vinylallenes, see: (b) Gil-Av, E.; Herling, J. *Tetrahedron Lett.* **1967**, 1. (c) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1989**, *54*, 4028. (d) Murakami, M.; Amii, H.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1476.

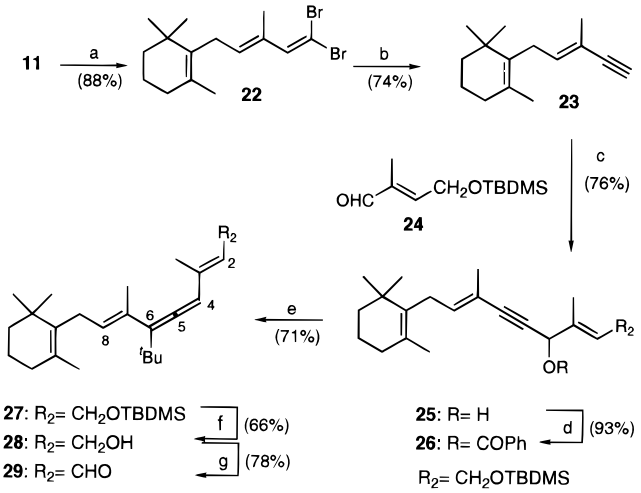
(12) (a) Erdik, E. *Tetrahedron* **1984**, *40*, 641. (b) Lipshutz, B. H. *Synthesis* **1987**, 325. (c) Lipshutz, B. H.; Sengupta, S. *Org. React. N.Y.* **1992**, *41*, 135. (d) Westmijze, H.; Meijer, J.; Bos, H. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 299.

(13) (a) Marshall, J. A.; Tang, Y. *J. Org. Chem.* **1994**, *59*, 1457. (b) Isler, O.; Huber, W.; Ronco, A.; Kofler, M. *Helv. Chim. Acta* **1947**, *30*, 1911.

(14) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(15) Fatiady, A. J. *Synthesis* **1976**, 65.

Scheme 3[a]



[a] (a) Ph_3P, CBr_4, CH_2Cl_2, 0 °C; (b) *n*-BuLi, THF, −78 °C to room temperature; (c) *n*-BuLi, THF, −78 °C to room temperature; (d) *n*-BuLi, PhCOCl, THF, −78 °C to room temperature; (e) *t*-BuLi, CuCN, ether, −78 °C to room temperature; (f) TBAF, THF, room temperature; (g) MnO_2, CH_2Cl_2, room temperature. See supporting information for experimental procedures and spectroscopic characterization of these compounds.

a solution of CuI/LiBr in THF with MeMgBr at 0 °C. Functional group manipulations[14,15] provided, uneventfully, the alcohols **16b**−**d** and aldehydes **17b**−**d** in the yields shown in Scheme 2. Finally, the unfunctionalized C_3-*tert*-butyl-substituted allene **21** (Scheme 2) was prepared following the same strategy, starting from 2-methylbut-1-en-3-yne (**18**).

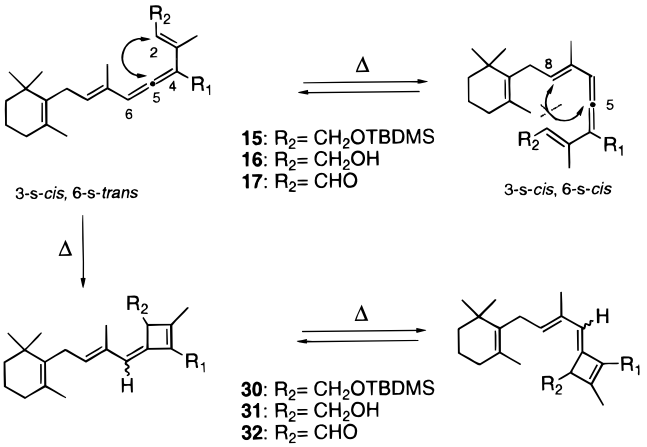
The same general synthetic strategy afforded the 6-*tert*-butyl-4,5-allenes (10-*tert*-butyl-11,7-*retro*retinoids[9]) **27**−**29** (Scheme 3). The propargylic benzoate precursor **26** was derived in 93% yield from alcohol **25**, which was itself obtained by condensation of the protected aldehyde **24**[16] with the conjugated enyne **23**. The one-carbon homologation of aldehyde **11** to alkyne **23** was carried out in 65% overall yield by the Corey−Fuchs procedure,[17] with dibromide **22** as intermediate.

Regioselectivity and Kinetics of the Thermal Rearrangement. The thermal rearrangement products of the divinylallenes were identified by analysis of the ^{1}H NMR spectra of the reaction mixtures (the appearance of mutually coupled signals between δ ∼3.0 ppm and δ 4.5 ppm, together with the vinyl hydrogen singlet indicated a four-electron electrocyclization), and for the *tert*-butyl-substituted divinylallenes these identifications were supported by the fact that, for stereochemical and structural reasons, these *t*-Bu compounds, unlike other series of vinylallenes,[8] cannot undergo the alternative facile sigmatropic shifts ([1,3]-H, [1,5]-H, [1,7]-H) or six-electron electrocyclization.

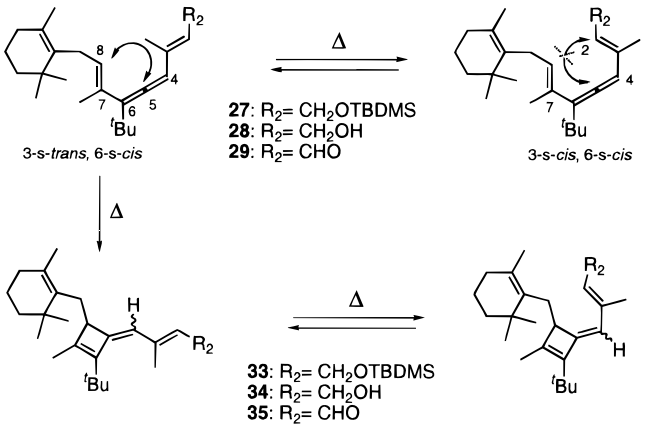
The regioselectivity of the process was remarkable. Only products arising from four-electron electrocyclizations at the more congested trisubstituted vinylallene subunit were detected (originating from the 3-*s*-*cis* conformer shown in Scheme 4 for **15**−**17** and from the 6-*s*-*cis* conformation shown in Scheme 5 for the positional isomers **27**−**29**), regardless of the steric bulk of the R_1 substituent, the nature of the polar group R_2, or the location of R_2 relative to the cyclization termini.

For kinetic analysis of the reactions, dilute solutions of the divinylallenes in benzene-d_6 were heated in sealed NMR tubes at appropriate temperatures (range 90−120 °C), and their ^{1}H NMR spectra were recorded periodically. Particularly helpful for quantitative analysis was the disappearance of the allenyl proton singlet and its replacement by the equivalent vinyl singlet(s). The integration of these signals allowed calculation of the mole fractions of starting material and product(s) at successive times (see supporting information).

Scheme 4



Scheme 5



Analysis of the kinetic data for the C_4-alkyl-substituted divinylallenes (supporting information),[18] showed a first-order behavior, except where indicated in Table 1, which lists rate constants and half-lives. For a given R_1, the half-lives of the protected and unprotected alcohols **15** and **16** were similar and much shorter than those of the corresponding aldehydes (**17**) (Table 1).[19] The long half-lives (high activation energies) of compounds **17** are probably due to the formation of compounds **32** involving loss of conjugation in the transition state. For comparison with other pericyclic reactions, the activation parameters of the reaction of **15a** were calculated from the rate constants determined (Figure 1 shows the dissappearance of **15a** at 90 °C) in the range 90−110 °C: plotting ln k against $1/T$ (Figure 2) gave values of $\Delta H^{\ddagger} = 26.6 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger} = +7.4 \pm 0.4$ cal/mol K ($E_a = 27.3$ kcal/mol at 98.9 °C).[18]

The kinetics for the C_6-*tert*-butyl series were more complex, due to reversibility (*vide infra*). Moreover, whereas the reactions of **27** and **28** required heating at 100 °C, **29** rearranged at 80 °C, which may be explained by reversing the argument

(16) Torrado, A.; Iglesias, B.; López, S.; de Lera, A. R. *Tetrahedron* **1995**, *51*, 2435.

(17) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

(18) We thank Prof. Okamura for generously providing a copy of the kinetic analysis computer program.

(19) Our *ab initio* calculations (not shown) confirm previous findings that the ionic canonical structures, thought to diminish electron density at the diene terminus in **17a**−**d**, do not contribute significantly to the ground state structures of enals. For an in-depth treatment, see: Wiberg, K. B.; Schreiber, S. L. *J. Org. Chem.* **1988**, *53*, 783.

Table 1. Kinetic and Stereochemical Characteristics the Thermal Rearrangement of Divinylallenes to Alkylidenecyclobutenes (Scheme 6)

divinylallene	R_1	R_2	T (°C)	$k \times 10^{-2}$ (h^{-1})	$\tau_{1/2}$ (h)	product	*E*/*Z* ratio	yield (%)
15a	*t*-Bu	$CH_2OTBDMS$	100	9.6	7.2	**30a**	83:17	85
16a	*t*-Bu	CH_2OH	100	10.0	6.9	**31a**	86:14	89
17a	*t*-Bu	CHO	100	2.9	24.1	**32a**	>99:1	92
15b	*i*-Pr	$CH_2OTBDMS$	120	6.9	10.0	**30b**	80:20	81
16b	*i*-Pr	CH_2OH	120	7.2	9.6	**31b**	82:18	84
17b	*i*-Pr	CHO	120	0.77	90.0	**32b**	>99:1	79[a,b]
15c	Et	$CH_2OTBDMS$	120	4.7	14.7	**30c**	66:34	75
16c	Et	CH_2OH	120	4.4	15.5	**31c**	60:40	79
17c	Et	CHO	120	*c*		**32c**	*d*	5[a,e]
15d	Me	$CH_2OTBDMS$	120	4.7	14.6	**30d**	50:50	53[a]
16d	Me	CH_2OH	120	5.0	13.7	**31d**	58:42	67[a]
17d	Me	CHO	120	*c*		**32d**	*d*	5[a,e]
21	*t*-Bu	H	120	5.2	13.3	**36**	91:9	80

[a] Unstable.[21] [b] Yield for the total mass balance, after 40 h of reaction, with ~72% of starting material still present; after longer reaction times, signals for additional products were observed in the ^{1}H NMR spectrum. [c] Complex kinetic behavior. [d] Not determined, due to the low yield of alkylidenecyclobutene. [e] The yield of isolated (*E*)-alkylidenecyclobutene; the major product was an aldehyde of complex, still undetermined, structure.

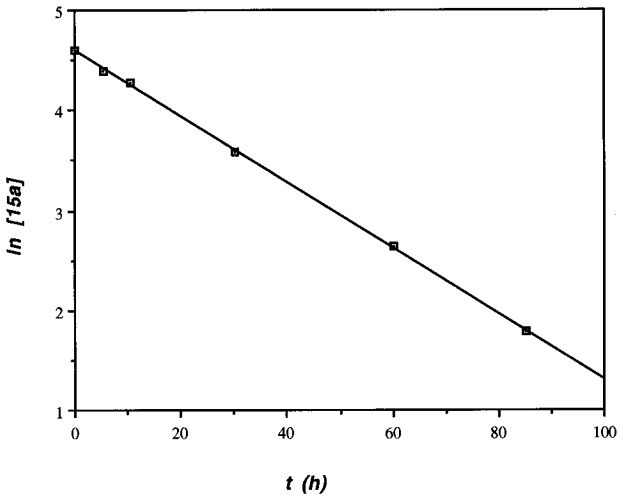


Figure 1. Plot of ln [**15a**] versus time for the rearrangement of **15a** to **30a** in C_6D_6 at 90 °C ([**15a**] measured by monitoring the ^{1}H NMR signals attributed to H_6 of the reactant and $H_{1'}$ of the product). Assuming irreversible first-order kinetics, this plot implies a half-life of 21.16 h and a rate constant $k = 3.27 \times 10^{-2}$ h^{-1}.

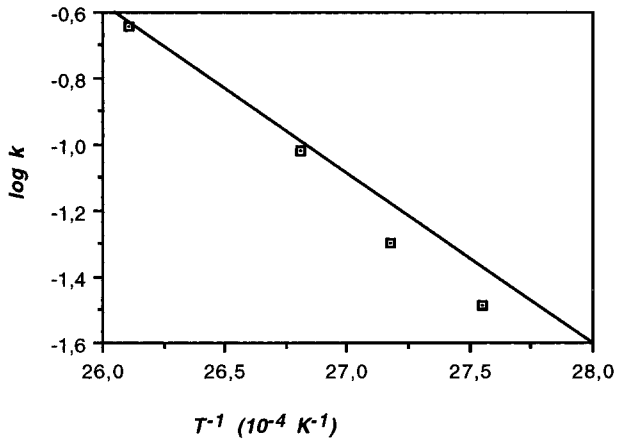
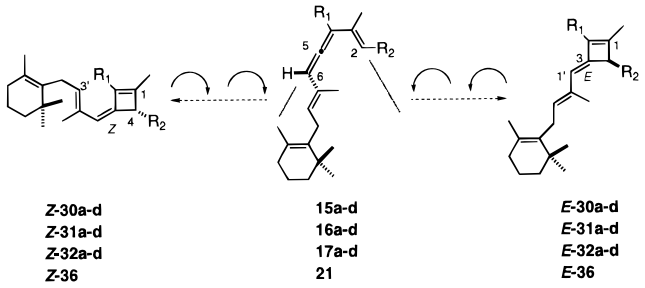


Figure 2. Arrhenius plot for the electrocyclization of **15a** to **30a** in the range 90 to 110 °C.

applied to the C_4-*tert*-butyl series: milder reaction conditions are possible for **29** because of an increase in conjugation in the transition state leading to trienal **35**.

Stereo/Torquoselectivity. The *E*/*Z* ratios estimated from the ^{1}H NMR spectra of the crude final reaction mixtures were confirmed by HPLC whenever possible. The results for the C_4-alkyl series are listed in Table 1.

Scheme 6



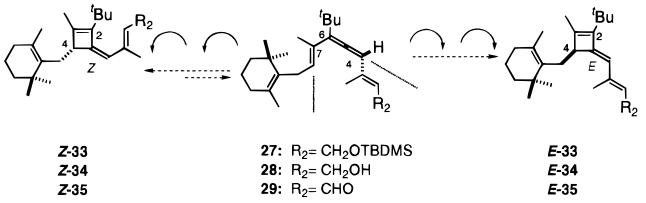
Starting from **15a**, two isomers, ***E*-30a** and ***Z*-30a** (Scheme 6), were isolated in an 83:17 ratio. A strong NOE on $H_{1'}$ after saturation of the C_2-*tert*-butyl group established that ***E*-30a** was *E* with respect to the exocyclic double bond, while *Z* stereochemistry and a predominant 1′-*s*-*cis* conformation for isomer ***Z*-30a** were mainly supported by an NOE cross peak between the C_2-*tert*-butyl group and $H_{3'}$. The high degree of stereoselectivity was attributed to the bulky C_4-*tert*-butyl group favoring the conrotatory motion in which the substituent at the allene terminus (C_6) rotates *inward*, as depicted in Scheme 6.[20] This explanation is supported by the *E*/*Z* ratios of **30b** (80:20), **30c** (66:34), and **30d**[21] (50:50), which show that the predominance of the "C_6-*inward*" conrotatory mode decreases with decreasing steric bulk of the C_4 substituent. *E*/*Z* ratios similar to those of the silyl ethers were observed upon reaction of the corresponding alcohols **16a**−**d** (Table 1). Isomer identification is based on the fact that ^{1}H NMR signals for H_1 in (*E*)-alkylidenecyclobutenes resonate downfield (up to 0.4 ppm) from the corresponding (*Z*)-alkylidenecyclobutene signals.

The ^{1}H NMR spectra of the crude final reaction mixtures obtained from the C_4-*tert*-butyl and C_4-*iso*-propyl 4,5-allenals **17a** and **17b** each showed only the corresponding (*E*)-alkylidenecyclobutenal (***E*-32a** or ***E*-32b**). The *E* geometry was confirmed by NOE experiments. However, prolonged heating (120 °C, 66 h) of the C_4-ethyl and C_4-methyl divinylallenals **17c** and **17d** produced only small quantities (~5%) of the alkylidenecyclobutenals ***E*-32c** and ***E*-32d** together with major

(20) Note that an *inward* movement of the C_6 substituent in the enantiomer shown in Scheme 6 could also be described as a combined *outward* movement of the C_5 sp center and *inward* movement of the C_2 sp^2 center (*outward*−*inward*) for the conrotatory mode leading to the (*E*)-alkylidenecyclobutenes.

(21) After HPLC separation, the evaporation of solvent followed by rapid acquisition of ^{1}H NMR data in C_6D_6 and evaporation of deuterated solvent resulted in complete loss of product. Characterization was therefore based on the comparison of available NMR data with relevant data for ***E*-30a** and ***Z*-30a**.

Scheme 7



components whose structure have not been completely determined but are unlikely to have arisen from the missing ***Z*-32c** and ***Z*-32d**.

In the reactions of the C_6-*tert*-butyl series **27**−**29** the electron-acceptor group played no discriminant role. After short reaction times, the alkylidenecyclobutenes **33**−**35** were all obtained in *E/Z* ratios of ∼70:30. After longer reaction times, only the (*E*)-alkylidenecyclobutenes ***E*-34** and ***E*-35** were isolated from the reaction mixtures of **28** and **29**, and although the mixture derived from **27** could not be separated by HPLC, its qualitative behavior was similar to that of **29** (described below). These results can be explained, in keeping with the kinetic results, in terms of reversible electrocyclization (Scheme 7). To prove reversibility, pure ***Z*-35**, isolated from the short-time reaction mixture of **29**, was resubjected to the same reaction conditions (heating to 80 °C); ^{1}H NMR monitoring clearly showed the development of a mixture of **29**, ***E*-35**, and ***Z*-35** (in a 30:14:56 ratio after 5 h and 33:49:18 ratio after 45 h; after 71 h, no ***Z*-35** was detected, and the **29**/***E*-35** ratio was 33:67). Steric interactions between the substituents of the cyclobutene in ***Z*-33**, ***Z*-34**, and ***Z*-35** may be responsible for the observed thermodynamic equilibration to the more stable (*E*)-alkylidenecyclobutenes.

To determine whether the difference in torquoselectivity between the reactions of **17** (**a** and **b**) and those of the corresponding alcohols and silyl ethers was due to an electronic effect of the formyl group[22] or merely to its not impairing the steric dominance of the C_4-*tert*-butyl or C_4-*iso*-propyl groups, we studied the behavior of pentaene **21** (Scheme 2) which has no polar end group. Heating **21** at 120 °C provided, after HPLC purification, a 91:9 mixture of the highly unstable[21] alkylidenecyclobutenes ***E*-36** and ***Z*-36** (Scheme 6, Table 1). Had the steric effect been the only factor involved in the torquoselectivity of the electrocyclic ring closure, ***E*-36** should have been the only product obtained from **21**. The especially high torquoselectivity of the reactions of **17a** and **17b** may therefore be attributed in part to an electronic effect of the formyl group. Consequently, the uniform behavior of **27**−**29** is attributable to the electronic effect of R_2 being extinguished by the greater distance between R_2 and the cyclization site in these compounds.

***Ab Initio* Studies: (A) Regioselectivity.** To investigate further the regioselectivity of ring closure in divinylallenes, we performed *ab initio* calculations[23] on the substituted vinylallenes **38** and **39** (comprised in the model divinylallene **37**) and **44** (Chart 1).

Conformational analysis of **38** and **39** using a 6-31G* basis set and complete optimization[24] provided potential energy curves for rotation about the C_3−C_4 bond (Figure 3). For **39**, the most stable conformation is 3-*s*-*trans* (**39′**: $C_2C_3C_4C_5 = 180.0°$), in agreement with the results of calculations on similar systems.[25]

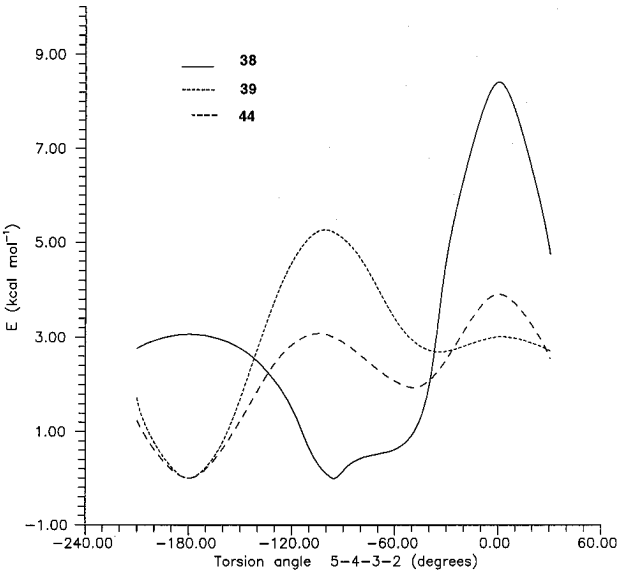
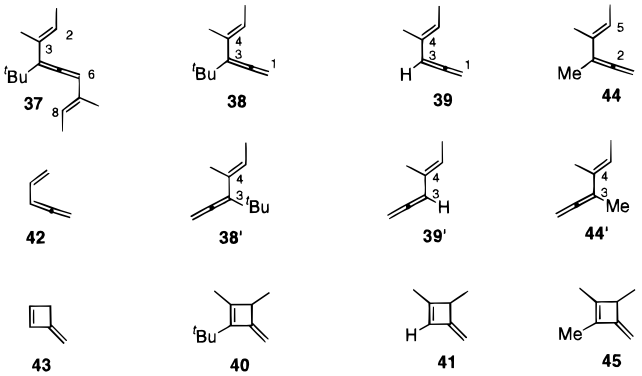


Figure 3. Computed energies of the vinylallenes **38**, **39**, and **44** as functions of the torsion angle $C_2C_3C_4C_5$.

Chart 1



There is, however, another stable conformation with a dihedral angle of 34.5°, closer to the 3-*s*-*cis* form required for cyclization. In contrast, only a single stable conformer, with a dihedral angle of 96.7°, was obtained for **38**.

The electrocyclic conversion of the vinylallenes **38**, **39**, and **44** to the corresponding cyclobutenes was investigated at the 6-31G* level with complete optimization and, for reactants, transition structures and products,[23] single-point calculations including electron correlation by second-order Møller−Plesset perturbation theory (MP2).[24] The main geometric parameters are listed in Table 2, and the cartesian coordinates are available in the supporting material. The transition structures are shown in Figure 4, and the absolute and relative energies of the electrocyclization processes are listed in Table 3.

In keeping with the regioselectivity observed in our experiments with divinylallenes, the calculated barrier to cyclization of 3-*tert*-butyl-4-methylhexa-1,2,4-triene (**38**) is lower than the barriers to cyclization of either conformer of 4-methylhexa-1,2,4-triene (**39** and **39′**) (Table 3). This difference is attributed to repulsive interactions between the C_3-*tert*-butyl and C_4-methyl groups in **38**, facilitating the proximity of the cyclization termini C_2 and C_5 in the transition state (Figure 4), in which the atoms

(22) The *A* values for formyl, methyl, and hydroxymethyl substituents are 0.56−0.73, 1.70, and 1.76, respectively. See: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; pp 696−697.

(23) For reviews on transition-structure modeling discussing the use of RHF wave functions, see: (a) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Eksterowicz, J. E.; Houk, K. N. *Chem. Rev.* **1993**, *93*, 2439.

(24) Gaussian 92/DFT, Revision G.4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1993.

(25) Bond, D. *J. Org. Chem.* **1990**, *55*, 661.

Table 2. Main Geometric Parameters (Bond Lengths in Angstroms, Bond Angles in Degrees) of Substrates, Products, and Transition Structures in the Electrocyclization of Vinylallenes to Methylenecyclobutenes (Chart 1)[a]

atoms[b]	**38**	TS	**40**	**39**	**39′**	TS	**41**	**44**	**44′**	TS	**45**
2−5	3.260	2.102	1.528	3.009	3.636	2.114	1.537	2.993	3.630	2.111	1.534
4−5	1.325	1.403	1.524	1.326	1.329	1.406	1.529	1.326	1.330	1.404	1.527
2−3	1.300	1.369	1.486	1.300	1.302	1.368	1.472	1.301	1.305	1.369	1.476
3−4	1.515	1.405	1.340	1.491	1.481	1.392	1.332	1.501	1.494	1.396	1.335
1−2	1.298	1.311	1.319	1.296	1.296	1.309	1.317	1.297	1.296	1.311	1.318
4−5−2	40.10	71.54	83.97	54.62	*c*	71.93	83.80	53.23	*c*	71.58	83.64
3−2−5	42.40	76.90	88.91	52.82	*c*	75.90	88.42	53.35	*c*	76.46	88.79
3−4−5	119.97	105.36	94.75	120.94	118.18	105.08	94.11	119.97	120.09	105.64	94.53
2−3−4	117.00	100.03	92.37	126.00	125.73	102.03	93.66	121.13	121.05	100.99	93.03
1−2−3	179.62	154.77	138.50	179.61	180.00	154.49	137.16	179.69	180.00	153.53	136.56
2−3−4−5	96.68	25.54	0.19	34.47	180.00	23.30	0.23	49.94	180.05	23.88	0.21

[a] At the MP2/6-31G*//RHF/6-31G* level. [b] See Chart 1. [c] Irrelevant for the 3-*s*-*trans* conformation.

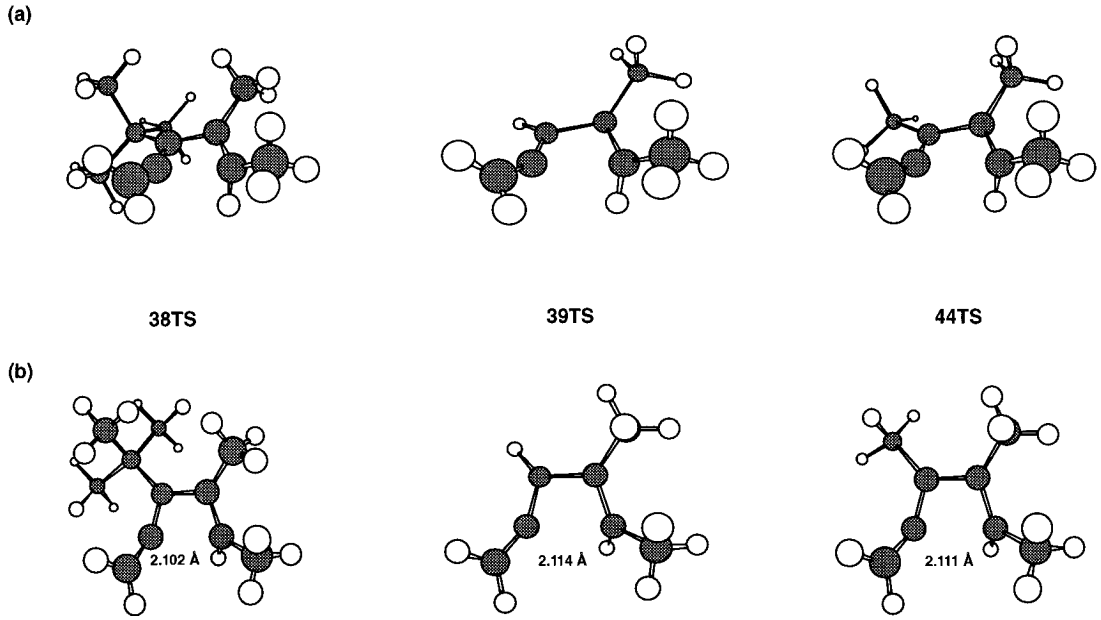


Figure 4. Front (a) and top (b) views of the transition structures calculated at the RHF/6-31G* level for cyclization of vinylallenes **38**, **39**, and **44** to methylenecyclobutenes **40**, **41**, and **45**, respectively.

Table 3. Total and Relative Energies of Reactants, Transition Structures, and Products (Chart 1) in the Electrocyclization of Vinylallenes to Methylenecyclobutenes[a]

structure[b]	total energy[c]	relative energy[d]
38	−428.376 87	0.0
($t_{2-3-4-5}$ = 96.7°)		
TS	−428.334 71	26.4
40	−428.400 58	−14.9
39′	−271.709 23	0.0
($t_{2-3-4-5}$ = 180.0°)		
39	−271.704 96	2.7
($t_{2-3-4-5}$ = 34.5°)		
TS	−271.657 51	32.5
41	−271.722 47	−8.3
44′	−310.878 41	0.0
($t_{2-3-4-5}$ = 180.0°)		
44	−310.874 80	2.3
($t_{2-3-4-5}$ = 49.9°)		
TS	−310.830 31	30.2
45	−310.897 69	−12.1

[a] At the MP2/6-31G*//RHF/6-31G* level. [b] Dihedral angles in parentheses. [c] In hartrees. [d] In kcal/mol.

forming the 4-membered ring are almost coplanar. Consistent with this steric argument are the distances between the cyclization termini in the transition state, 2.102 and 2.114 Å for **38** and **39**, respectively. Furthermore, although the energy values in Table 3 clearly show that cyclization is thermodynamically favored for both **38** and **39**, the methylenecyclobutenes being more stable than the corresponding vinylallenes, stabilization is substantially greater for the C_3-*tert*-butyl-substituted vinylallene **38** (14.9 kcal/mol) than for vinylallenes **39** (11.0 kcal/mol) or **39′** (8.3 kcal/mol). This result contrasts with the equilibrium observed in the parent system, in which the vinylallene (**42**) and the methylenecyclobutene (**43**) are of similar stability.[11]

The parameters determined for 3,4-dimethylhexa-1,2,4-triene (**44**), a vinylallene with methyl substituents at both C_3 and C_4, are intermediate between those found for the equivalent conformers of **38** and **39**. The consequent prediction that cyclization of **15d**, **16d**, and **17d** should take place with total regioselectivity is, as we have seen, borne out experimentally.

(B) Torquoselectivity. The observed torquoselectivity of the electrocyclic ring closure of divinylallene **15a** and analogues was studied further by performing MP2/6-31G*//RHF/6-31G* calculations[24] for the electrocyclic ring closure of the tetraenes and triene depicted in Scheme 8.

The chief geometric parameters of the transition structures for the conrotatory processes leading to the (*E*)- and (*Z*)-alkylidenecyclobutenes are listed in Table 4; cartesian coordinates can be found in the supporting information.

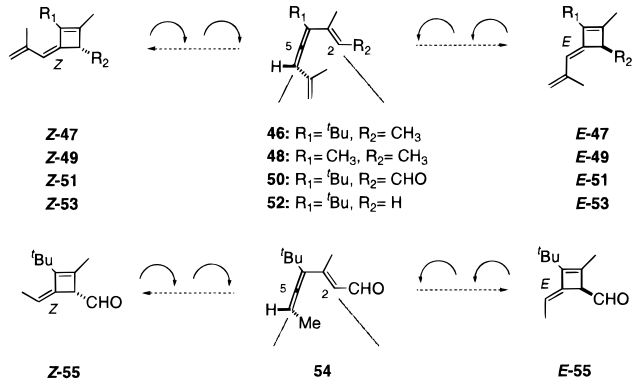
The geometries of the transition structures[26] (Figure 5) are roughly similar and are comparable to those computed for the ring closure of vinylallene **38** (Figure 4). The substantial bending of the allene group ($C_4C_5C_6$ ranges from 18.7° for **50**

Table 4. Main Geometric Parameters (Bond Lengths in Angstroms, Bond Angles in Degrees) of the Transition Structures Corresponding to the Alternative Conrotatory Modes of the Electrocyclization of Vinylallenes to Alkylidenecyclobutenes (Scheme 8)[a]

	46		**48**		**50**		**52**		**54**	
atoms[b]	TS-*Z*	TS-*E*	TS-*Z*	TS-*E*	TS-*Z*	TS-*E*	TS-*Z*	TS-*E*	TS-*Z*	TS-*E*
2−5	2.064	2.111	2.095	2.129	2.061	2.103	2.052	2.102	2.094	2.107
2−3	1.404	1.406	1.404	1.406	1.413	1.415	1.400	1.399	1.413	1.414
4−5	1.371	1.372	1.369	1.372	1.380	1.379	1.374	1.372	1.380	1.379
3−4	1.407	1.401	1.398	1.393	1.399	1.395	1.406	1.403	1.397	1.396
5−6	1.320	1.320	1.318	1.319	1.315	1.314	1.320	1.319	1.306	1.306
3−2−5	72.47	71.50	71.94	71.40	72.94	72.04	72.89	71.77	72.34	72.00
4−5−2	77.74	76.59	76.83	75.87	77.40	76.41	77.80	76.55	76.62	76.31
2−3−4	104.47	105.53	105.23	105.94	103.99	104.86	104.28	105.31	104.72	104.97
3−4−5	99.33	100.55	100.67	101.81	100.08	101.10	99.17	100.25	100.92	101.15
4−5−6	159.91	149.20	156.04	148.09	161.34	151.54	159.42	150.12	158.19	156.41
2−3−4−5	24.78	24.92	23.72	23.25	23.89	24.28	24.45	25.45	23.76	24.27

[a] At the MP2/6-31G*//RHF/6-31G* level; *E* and *Z* refer to the geometry of the exocyclic double bond formed in the process. [b] The same numbering system (see Scheme 8) was adopted for all the vinylallenes, irrespective of their substitution pattern.

Scheme 8



to 31.9° for **48**) is not surprising, having previously been observed in cumulenes.[27c,28] What is of note is that steric interactions between the substituent at C_4 and the substituent at the ensuing exocyclic double bond, which are negligible for **38**, seem likely to play a predominant role in determining the preferred direction of twist: when R_1 is bulky (*t*-Bu or, presumably, *i*-Pr), steric crowding appears to be greater in the transition structure leading to the (*Z*)-alkylidenecyclobutene (TS-*Z*) than in TS-*E*, the transition structure leading to the (*E*)-alkylidenecyclobutene; this would seem to explain why, for R_1 = *t*-Bu (**46** in Scheme 8), the difference between the energies of TS-*E* and TS-*Z* is 1.18 kcal/mol in favor of the former (Table 5). This value is in reasonable agreement with the *E*/*Z* isomer ratio of 83:17 obtained on the thermal rearrangement of divinylallene **15a** to **30a** in solution (Scheme 6, Table 1). For the C_4-methyl tetraene **48**, the energy difference between TS-*Z* and TS-*E* is negligible (0.08 kcal/mol). This again is in keeping with the *E*/*Z* isomer ratio of 50:50 obtained upon heating the corresponding divinylallene, **15d** (Table 1). These calculations thus support the conclusions drawn above from the experimental results: that the preference for electrocyclization to the (*E*)-alkylidenecyclobutene that is shown by divinylallenes with bulky C_4 substituents is due mainly to steric interaction between the C_4 substituent and the substituent on the ensuing exocyclic double bond; this interaction causes the energy of the TS-*Z* transition state to be higher than that of the TS-*E* transition state.

Table 5. Total and Relative Energies, and C_2-C_5 Distances, of the Alternative Transition Structures for the Electrocyclization of Vinylallenes to (*Z*)- and (*E*)-Alkylidenecyclobutenes (Scheme 8)[a]

structure	E[b]	ΔE_a[c]	r_{C-C}[d]	Δr_{C-C}[e]
46				
TS-*Z*	−544.644 08	1.18	2.064	0.047
TS-*E*	−544.645 96		2.111	
48				
TS-*Z*	−427.141 44	−0.08	2.095	0.035
TS-*E*	−427.141 57		2.130	
50				
TS-*Z*	−618.497 32	2.43	2.061	0.042
TS-*E*	−618.501 20		2.103	
52				
TS-*Z*	−505.471 11	1.51	2.052	0.050
TS-*E*	−505.473 52		2.102	
54				
TS-*Z*	−541.358 99	0.79	2.094	0.013
TS-*E*	−541.360 25		2.107	

[a] At the MP2/6-31G*//RHF/6-31G* level. [b] In hartrees. [c] $\Delta E_a = E_{TS-Z} - E_{TS-E}$ in kcal/mol. [d] C_2-C_5 distance in Å. [e] $\Delta r_{C-C} = r_{C-C}$(TS-*E*) − r_{C-C}(TS-*Z*) in Å.

The experimental results had also suggested that the electronic properties of a formyl group at the other cyclization terminus also contributed to torquoselectivity (see above). Computational investigations of this effect began with calculations of the energy difference between TS-*E* and TS-*Z* for **50** and **52**. As expected, both differences were in favor of TS-*E*, by 2.43 and 1.51 kcal/mol for **50** and **52**, respectively (Table 5). The order **46** < **52** < **50** defined by these values and the value already obtained for **46** confirms that the torquoselective effect of the C_2 substituent is not primarily steric. However, the hypothesized electronic effect does not seem to be due, as might be expected, to the mixing of frontier orbitals to which torquoselectivity in 3-substituted cyclobutenes is attributed,[4b] even though the geometries of the relevant parts of **46**, **50**, and **52** in the transition states are similar to those calculated for **1**.[4] Firstly, the energy differences between TS-*E* and TS-*Z* for **46**, **50**, and **52** differ by no more than 1.25 kcal/mol, whereas orbital mixing is thought to be responsible for observed differences of up to 20 kcal/mol for **1**.[4b] Secondly, the fact that in the ring closure of vinylallenes the sp center at C_5 is transformed into an sp^2 center means that the C_2 substituent has very much the same relationship to the breaking or forming σ bond, regardless of whether it rotates *inwards* or *outwards*, so that the "intended correlation" of the orbitals involved in the breaking and forming bonds cannot explain the stereoselectivity. Nor does interaction

(26) The process described here might qualify as a *pseudopericyclic reaction*[27] according to the definition of Lemal *et al.*:[27a] "a concerted transformation whose primary changes in bonding encompass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbitals interchange roles...". For a detailed discussion and *ab initio* theoretical analysis of pseudopericyclic reactions, see ref 27c.

(27) (a) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325. (b) Henriksen, U.; Snyder, J. P.; Halgren T. A. *J. Org. Chem.* **1981**, *46*, 3767. (c) Birney, D. M.; Wagenseller, P. E. *J. Am. Chem. Soc.* **1994**, *116*, 6262.

(28) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303 and references cited therein.

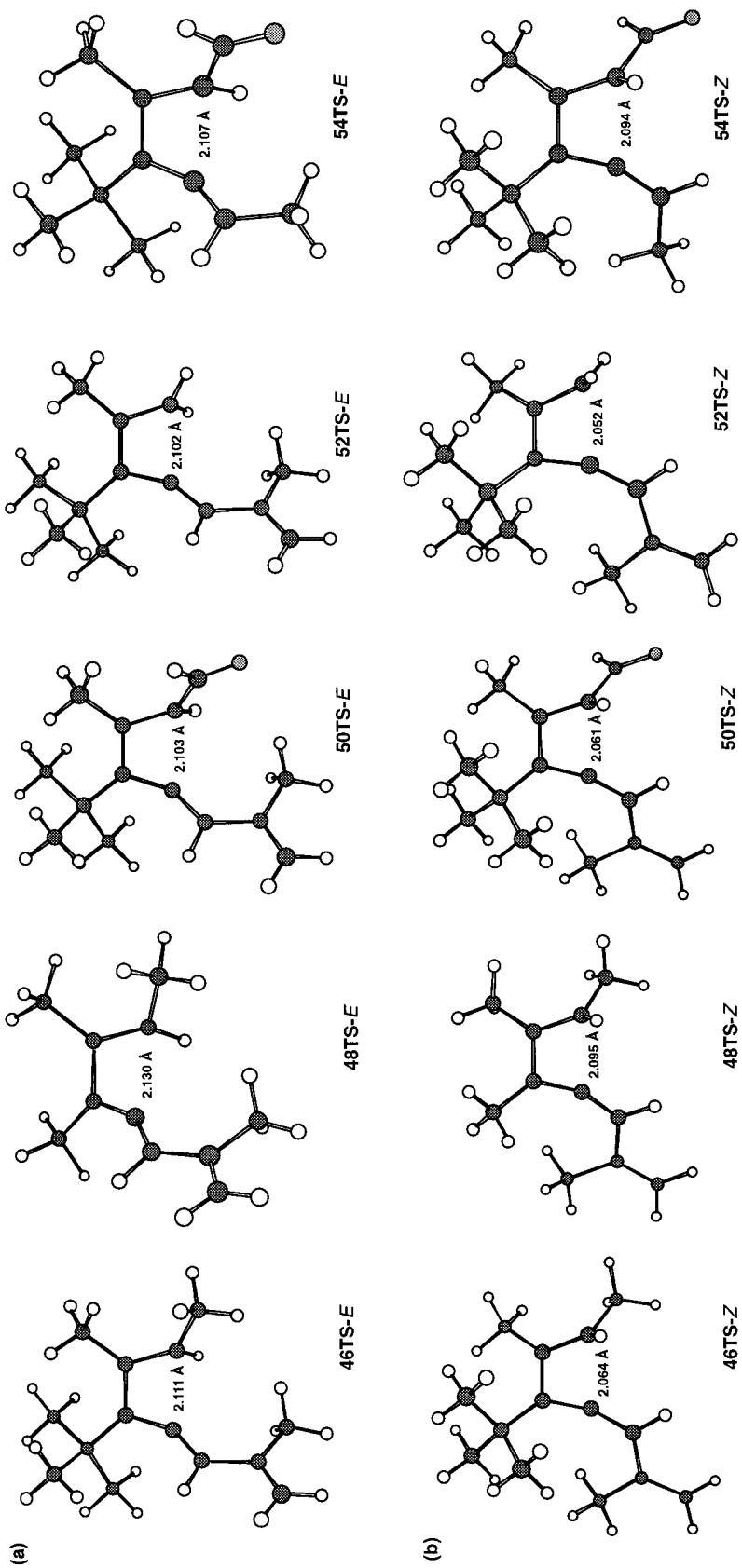


Figure 5. Top views of the transition structures calculated at the MP2/6-31G*//RHF/6-31G* level for the alternative conrotatory modes of the cyclization of vinylallenes **46**, **48**, **50**, **52**, and **54** to (a) the (*E*)- and (b) the (*Z*)-alkylidenecyclobutenes (**TS-*E*** and **TS-*Z***, respectively). Front views are too crowded to be informative.

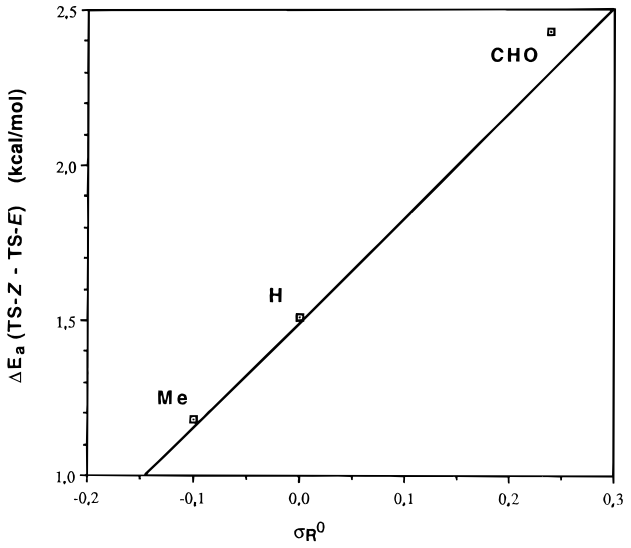


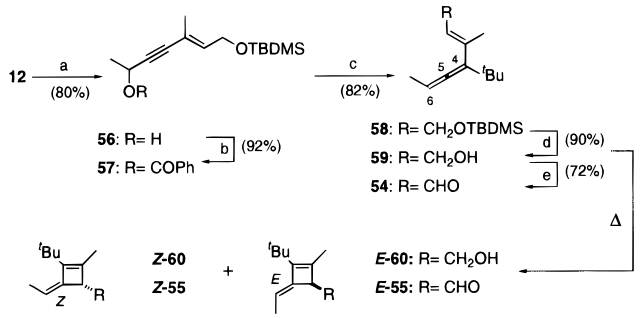
Figure 6. Plot of ΔE_a versus σ_R° for the electrocyclic ring closures of substituted divinylallenes to alkylidenecyclobutenes.

between the exocyclic diene and the formyl group in **50** seem possible, since the diene is *s-trans* in the most stable conformations of both the (*E*)- and the (*Z*)-alkylidenecyclobutenes and the formyl group is also *s-trans* throughout the reaction.

Interaction of the −CHO group with substituents or with the forming σ bond having thus been ruled out, we surmised that the extra torquoselectivity imparted by −CHO might have the same origin as the long reaction times associated with the presence of this group in **17a** and **17b** (Table 1): its conjugation with the vinylallene polyene system. This hypothesis is supported by the good correlation between TS-*Z* − TS-*E* energy differences of **46**, **50**, and **52** and the values of the empirical resonance parameter σ_R° for the corresponding R_2 groups[29] (Figure 6); similar correlation has been reported for the ring opening of 3-substituted cyclobutenes (**1**) and 7-substituted cycloocta-1,3,5-trienes (**5**).[7] The cause of the relationship would appear to be that, to judge from the Δr_{C-C} values listed in Table 5, the transition state is reached earlier during cyclization to the (*E*)-alkylidenecyclobutene than during cyclization to the (*Z*)-alkylidenecyclobutene; this must mean that conjugation between the formyl group and the polyene system is maintained to a greater extent in TS-*E* than in TS-*Z*, which must further lower the energy of TS-*E* with respect to TS-*Z*. It may further be noted that this mechanism appears to be modulated by the steric effect of the substituent at C_4, since Δr_{C-C} is greater for **46**, **50**, and **52** than for **48**.

Experimental verification of the torquoselective effect of −CHO in the absence of steric interaction between the C_6 substituent and a bulky C_4 substituent was frustrated by the complexity of the reaction mixture obtained upon heating the divinylallenal **17d**. Computational verification was sought by calculating transition structures for the ring closure of 4-*tert*-butyl-3-methylhepta-2,4,5-trienal (**54**), in which the steric effect of the C_4-*tert*-butyl is reduced, relative to **50**, by reducing the size of the C_6 substituent. The energy difference between TS-*E* and TS-*Z* for **54** is 0.79 kcal/mol in favor of TS-*E* (Table 5). We interpret this small difference as being the resultant of two effects: (a) elimination of most of the "direct" steric effect of the C_4 substituent; and (b) the presence of a small effect due to the formyl group. The smallness of this latter effect is attributable to the absence of C_4-C_6 steric interaction having resulted in TS-*E* occurring only very little earlier than TS-*Z* ($\Delta r_{C-C} = 0.013$ Å, as against ~0.040 Å in the series **46**, **48**, **50**, **52**; see Table 5)[30] so that the effect of −CHO itself is diminished. Experimental proof of the effect was nevertheless obtained following synthesis of **54** from **59**, itself obtained following the general sequence used for **15a** (Scheme 9): side-by-side thermolysis of vinylallenol **59** and vinylallenal **54** at 90 °C led to a mixture containing a 66:34 ratio of the alcohols ***E*-60** and ***Z*-60** as against an 83:17 ratio of the aldehydes ***E*-55** and ***Z*-55**, in sound quantitative agreement with expectations based on the computations.

Scheme 9[a]



[a] Same reagents and reaction conditions as described in Scheme 2 for **15a**, with the yields indicated in parentheses. See supporting information for experimental procedures and spectroscopic characterization of these compounds.

Summary and Conclusions

The thermal rearrangement of (2*E*,7*E*)-4-alkyl-3,7-dimethylocta-2,4,5,7-tetraenes (related to 11,7-*retro*retinoids[9]) to trisubstituted alkylidenecyclobutenes is peri-, regio-, and torquoselective if the alkyl substituent at C_4 is large. A formyl group at C_2 has an additional torquoselective influence: in particular, the single alkylidenecyclobutenal ***E*-32** is obtained from divinylallenals **17a** and **17b**. The effect of the formyl group is ascribed to the reluctance of the starting vinylallenal to relinquish extended π conjugation: because of this reluctance, the energy of the transition structure leading to the (*E*)-alkylidenecyclobutenes, which *ab initio* calculations on **50** show to occur earlier than the alternative leading to the (*Z*)-alkylidenecyclobutenes, is lower than that of the latter transition structure.

Experimental Section[31]

General Procedures:[32] **Computational Methods.** Structures were fully optimized at the Hartree−Fock level using the program GAUSSIAN 92 with the standard 6-31G* basis set. The correlated energies of all optimized structures were then calculated at the MP2/6-31G*

(29) (a) Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* **1977**, *77*, 639. (b) Ruff, F.; Csizmadia, I. G. *Organic Reactions. Equilibria, Kinetics and Mechanism. Studies in Organic Chemistry 50*; Elsevier: Amsterdam, 1994; Chapter 7, pp 161−209.

(30) The value of the reaction progress[4b] at the transition state has been calculated for two of the representative divinylallenes, **46** and **48**. It is greater for the latter and for the transition structures leading to the *Z* isomers: **46** → ***E*-47**, 54%; **46** → ***Z*-47**, 56%; **48** → ***E*-49**, 56%; **48** → ***Z*-49**, 59%. The geometric parameters of the vinylallenes **46** and **48** and the alkylidenecyclobutenes ***E*-47**, ***Z*-47**, ***E*-49**, and ***Z*-49** can be found in the supporting information.

(31) Experimental procedures for the preparation of the vinylallenes, and complete spectroscopic characterization of all compounds described in the text, are provided in the supporting information. For alkylidenecyclobutenes, selected ^1H and complete ^{13}C NMR spectral data are presented in abbreviated form, in the Experimental Section. General experimental procedures are also presented in the supporting information. The purities of all compounds were evaluated by a combination of HPLC and ^1H and ^{13}C NMR analysis before mass spectral determinations. As evidence of purity, NMR spectra are included in the supporting information.

(32) Description of general procedures: de Lera, A. R.; Iglesias, B.; Rodríguez, J.; Alvarez, R.; López, S.; Villanueva, X.; Padrós, E. *J. Am. Chem. Soc.* **1995**, *117*, 8220.

level. In each case, a set of possible rotamers was explored. Transition structures were located and are characterized by a single negative eigenvalue. Complete structural details in the form of Cartesian coordinates for the RHF/6-31G*-optimized structures and transition structures can be found in the supporting information.

General Procedure for the Thermal Electrocyclic Reactions. A solution of the vinylallene ($\sim 10^{-4}$ M) in C_6D_6 (1.1 mL) was introduced into a thick-walled NMR tube (rinsed with base, water, and acetone and dried in an oven at 140 °C), and the tube was then flame-sealed under argon, submerged in a thermostated oil bath for a measured time, and rapidly cooled in a dry ice bath. The relative molar fractions of starting material and product were determined by integration of the ^{1}H NMR signals attributed to the allenic and exocyclic vinyl protons, respectively. The NMR tube was then broken open, contents were transferred to a round-bottomed flask containing ether, and the solvents were removed. The resulting residue was purified by flash chromatography (to isolate the mixture of isomers for which the yield is given) and/or HPLC (using the same eluant); isomer ratios obtained by ^{1}H NMR integration were confirmed by weight when the isomers were stable. In order to rule out the possibility of acid-induced rearrangements, selected divinylallenes (**15a**, **16a**, **17a**) were treated with Cl_3-Fe·SiO_2 or *p*-TsOH in C_6D_6 solution for 24 h at room temperature; *p*-TsOH deprotected silyl ether **15a**, and the remaining experiments led to unaffected starting material.

Reaction of Vinylallene 15a (Table 1). Purification by flash chromatography (hexane) afforded compound **30a** (85% yield) as a mixture of isomers (***E*-30a**/***Z*-30a**, 83:17 ratio) which were separated by HPLC. **Major isomer (*E*-30a):** ^{1}H NMR ($CDCl_3$) δ 5.64 (1H, s), 5.21 (1H, t, J = 6.4 Hz), 4.07 (1H, dd, J = 10.0, 3.8 Hz), 3.51 (1H, dd, J = 10.0, 8.5 Hz), 3.26 (1H, dd, J = 8.5, 3.8 Hz), 2.79 (2H, d, J = 6.4 Hz), 2.02 (3H, s), 1.85 (3H, s), 1.19 (9H, s); ^{13}C NMR ($CDCl_3$) δ 150.7, 145.7, 137.8, 136.8, 131.5, 130.7, 127.7, 116.0, 66.2, 51.2, 39.8, 34.9, 33.9, 32.9, 29.2 (^{t}Bu), 28.3 (2×), 27.7, 25.9 (^{t}Bu), 19.8, 19.6, 18.2, 15.3, 15.0, −5.4 (2×). **Minor isomer (Z-30a):** ^{1}H NMR ($CDCl_3$) δ 5.21 (1H, t, J = 6.3 Hz), 5.14 (1H, s), 3.72 (1H, dd, J = 10.1, 5.8 Hz), 3.60 (1H, dd, J = 10.1, 6.7 Hz), 2.81 (1H, dd, J = 6.7, 5.8 Hz), 2.73 (2H, d, J = 6.3 Hz), 1.95 (3H, s), 1.71 (3H, s), 1.12 (9H, s); ^{13}C NMR ($CDCl_3$) δ 151.0, 146.0, 137.4, 136.1, 132.0, 129.0, 127.7, 115.9, 65.3, 50.7, 39.8, 34.9, 33.2, 32.9, 29.3 (^{t}Bu), 28.4 (2×), 27.5, 25.9 (^{t}Bu), 19.9, 19.5, 18.2, 17.4, 15.0, −5.4 (2×).

Reaction of Vinylallenol 16a (Table 1). Purification by flash chromatography (83:17 hexane/ethyl acetate) afforded compound **31a** (89% yield) as a mixture of isomers (***E*-31a**/***Z*-31a**, 86:14 ratio) which were separated by HPLC. **Major isomer (*E*-31a):** ^{1}H NMR ($CDCl_3$) δ 5.70 (1H, s), 5.28 (1H, t, J = 6.2 Hz), 3.8−3.7 (2H, m), 3.35 (1H, br), 2.77 (2H, d, J = 6.2 Hz), 1.95 (3H, s), 1.82 (3H, d, J = 0.9 Hz), 1.20 (9H, s); ^{13}C NMR ($CDCl_3$) δ 152.4, 142.5, 136.6, 136.5, 131.3, 131.1, 127.9, 116.8, 61.9, 51.2, 39.8, 34.9, 34.1, 32.9, 29.2 (^{t}Bu), 28.3 (2×), 27.7, 19.7, 19.5, 15.6, 13.8. **Minor isomer (*Z*-31a):** ^{1}H NMR ($CDCl_3$) δ 5.3−5.2 (2H, m), 3.79 (1H, dd, J = 10.8, 4.2 Hz), 3.7−3.6 (1H, m), 2.9−2.8 (1H, m), 2.8−2.7 (2H, m), 1.95 (3H, s), 1.73 (3H, s), 1.15 (9H, s); ^{13}C NMR ($CDCl_3$) δ 152.4, 144.5, 136.3, 136.0, 131.6, 129.5, 127.9, 116.3, 62.1, 50.8, 39.8, 34.9, 33.4, 32.9, 29.3 (^{t}Bu), 28.4 (2×), 27.5, 19.9, 19.5, 17.4, 14.3.

Reaction of Vinylallenal 17a (Table 1). Purification by HPLC (98:2 hexane/ethyl acetate) afforded compound ***E*-32a** as a single isomer (> 99:1 ratio) in 92% yield: ^{1}H NMR ($CDCl_3$) δ 9.12 (1H, d, J = 6.1 Hz), 6.00 (1H, s), 5.30 (1H, t, J = 6.6 Hz), 3.76 (1H, d, J = 6.1 Hz), 2.77 (2H, d, J = 6.6 Hz), 1.92 (3H, s), 1.68 (3H, d, J = 1.0 Hz), 1.24 (9H, s); ^{13}C NMR ($CDCl_3$) δ 202.2, 157.6, 136.5, 136.3, 134.5, 131.3, 130.1, 128.1, 121.1, 62.6, 39.7, 34.9, 34.3, 32.8, 29.1 (^{t}Bu), 28.2 (2×), 27.5, 19.7, 19.5, 14.8, 14.4.

Reaction of Vinylallene 15b (Table 1). Purification by flash chromatography (hexane) afforded compound **30b** (81% yield) as a mixture of isomers (***E*-30b**/***Z*-30b**, 80:20 ratio) which were separated by HPLC. **Major isomer (*E*-30b):** ^{1}H NMR ($CDCl_3$) δ 5.52 (1H, s), 5.21 (1H, t, J = 6.2 Hz), 4.09 (1H, dd, J = 10.0, 3.9 Hz), 3.53 (1H, dd, J = 10.0, 8.4 Hz), 3.34 (1H, dd, J = 8.4, 3.9 Hz), 2.77 (2H, d, J = 6.2 Hz), 2.5−2.4 (1H, m), 1.94 (3H, s), 1.84 (3H, s), 1.12 (3H, d, J = 7.0 Hz), 1.11 (3H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 149.4, 145.9, 138.4, 136.8, 131.4, 130.8, 127.7, 114.6, 66.2, 52.1, 39.9, 34.9, 32.9, 30.7 (2×), 28.3, 27.6, 26.1, 25.9 (^{t}Bu), 20.9, 19.7, 19.6, 18.2, 15.0, 14.1, −5.0 (2×). **Minor isomer (*Z*-30b):** ^{1}H NMR ($CDCl_3$) δ 5.21 (1H, t, J = 6.6 Hz), 5.17 (1H, s), 3.72 (1H, dd, J = 10.0, 6.1 Hz), 3.59 (1H, dd, J = 10.0, 7.1 Hz), 2.89 (1H, dd, J = 7.1, 6.1 Hz), 2.75 (2H, d, J = 6.6 Hz), 2.7−2.6 (1H, m), 1.94 (3H, s), 1.77 (3H, s), 1.06 (6H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 148.9, 147.2, 138.4, 136.4, 130.6, 128.8, 127.7, 116.2, 65.4, 51.2, 39.9, 34.9, 32.9, 28.2 (2×), 27.9, 27.6, 25.8 (^{t}Bu), 21.4, 21.1, 19.7, 19.6, 18.1, 16.9, 14.7, −5.4 (2×).

Reaction of Vinylallenol 16b (Table 1). Purification by flash chromatography (83:17 hexane/ethyl acetate) afforded compound **31b** (84% yield) as a mixture of isomers (***E*-31b**/***Z*-31b**, 82:18 ratio) which were separated by HPLC. **Major isomer (*E*-31b):** ^{1}H NMR ($CDCl_3$) δ 5.59 (1H, s), 5.26 (1H, t, J = 6.3 Hz), 3.84 (2H, br), 3.44 (1H, br), 2.77 (2H, d, J = 6.3 Hz), 2.6−2.5 (1H, m), 1.90 (3H, s), 1.84 (3H, s), 1.14 (6H, d, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 150.9, 142.8, 136.6 (2×), 131.3, 131.0, 127.8, 115.5, 62.1, 52.1, 39.8, 34.9, 32.8, 28.2 (2×), 27.6, 26.2, 21.1, 21.0, 19.6, 19.5, 15.2, 13.0. **Minor isomer (*Z*-31b):** ^{1}H NMR (C_6D_6) δ 5.57 (1H, t, J = 7.0 Hz), 5.45 (1H, s), 3.7−3.6 (2H, m), 3.0−2.8 (3H, m), 1.87 (3H, s), 1.84 (3H, s), 1.10 (6H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 150.1, 143.4, 136.6 (2×), 130.1, 127.9, 121.0, 110.5, 62.6, 52.5, 39.9, 34.9, 32.9, 31.5, 28.3 (2×), 27.7, 22.5, 20.9, 19.6, 19.5, 14.1, 13.9.

Reaction of Vinylallenal 17b (Table 1). Purification by HPLC (98:2 hexane/ethyl acetate) afforded the very unstable compound ***E*-32b** as a single isomer (>99:1 ratio) in 79% yield: ^{1}H NMR ($CDCl_3$) δ 9.16 (1H, d, J = 6.1 Hz), 5.88 (1H, s), 5.32 (1H, t, J = 6.4 Hz), 3.84 (1H, d, J = 6.1 Hz), 2.79 (2H, d, J = 6.4 Hz), 2.7−2.5 (1H, m), 1.88 (3H, s), 1.69 (3H, s), 1.19 (6H, d, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 202.0, 155.9, 137.4, 136.4, 134.2, 131.2, 130.8, 128.2, 119.8, 63.1, 39.9, 34.9, 32.9, 28.3 (2×), 27.6, 26.7, 21.1, 20.9, 19.7, 19.6, 14.3, 14.0.

Reaction of Vinylallene 15c (Table 1). Purification by flash chromatography (hexane) afforded compound **30c** (75% yield) as a mixture of isomers (***E*-30c**/***Z*-30c**, 66:34 ratio) which were separated by HPLC. **Major isomer (*E*-30c):** ^{1}H NMR ($CDCl_3$) δ 5.48 (1H, s), 5.22 (1H, t, J = 6.4 Hz), 4.11 (1H, dd, J = 9.8, 3.9 Hz), 3.54 (1H, dd, J = 9.8, 9.0 Hz), 3.39 (1H, dd, J = 9.0, 3.9 Hz), 2.78 (2H, d, J = 6.4 Hz), 2.07 (2H, q, J = 7.6 Hz), 1.91 (3H, s), 1.84 (3H, s), 1.06 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 147.2, 145.9, 139.3, 136.8, 131.4, 130.9, 127.8, 114.2, 66.3, 52.6, 39.9, 35.0, 32.9, 28.3 (2×), 27.7, 25.9 (^{t}Bu), 19.7, 19.6, 18.2, 17.8, 15.0, 13.5, 12.2, −5.4 (2×). **Minor isomer (*Z*-30c):** ^{1}H NMR ($CDCl_3$) δ 5.24 (1H, t, J = 6.8 Hz), 5.24 (1H, s), 3.77 (1H, dd, J = 10.0, 6.0 Hz), 3.60 (1H, dd, J = 10.0, 7.5 Hz), 2.98 (1H, dd, J = 7.5, 6.0 Hz), 2.77 (2H, d, J = 6.8 Hz), 2.2−2.1 (2H, m), 1.88 (3H, s), 1.81 (3H, s), 1.01 (3H, t, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 149.0, 145.0, 138.8, 136.6, 131.0, 129.6, 127.9, 116.8, 65.7, 51.6, 39.9, 35.1, 32.9, 28.4 (2×), 27.7, 25.9 (^{t}Bu), 20.7, 19.8, 19.6, 18.3, 16.4, 13.3, 13.0, −5.4 (2×).

Reaction of Vinylallenol 16c (Table 1). Purification by flash chromatography (83:17 hexane/ethyl acetate) afforded compound **31c** (79% yield) as a mixture of isomers (***E*-31c**/***Z*-31c**, 60:40 ratio) which were separated by HPLC. **Major isomer (*E*-31c):** ^{1}H NMR ($CDCl_3$) δ 5.56 (1H, s), 5.27 (1H, t, J = 6.4 Hz), 3.9−3.8 (2H, m), 3.49 (1H, br), 2.78 (2H, d, J = 6.4 Hz), 2.12 (2H, q, J = 7.4 Hz), 1.88 (3H, s), 1.84 (3H, d, J = 1.0 Hz), 1.09 (3H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 147.3, 144.1, 137.9, 136.7, 131.5, 131.0, 127.9, 115.1, 62.2, 52.6, 39.9, 34.9, 32.9, 28.3 (2×), 27.6, 19.7, 19.6, 17.9, 15.2, 12.5, 12.3. **Minor isomer (*Z*-31c):** ^{1}H NMR ($CDCl_3$) δ 5.30 (1H, s), 5.27 (1H, t, J = 6.2 Hz), 3.79 (1H, dd, J = 11.0, 4.7 Hz), 3.7−3.6 (1H, m), 3.05 (1H, br), 2.78 (2H, d, J = 6.2 Hz), 2.21 (2H, q, J = 7.7 Hz), 1.87 (3H, s), 1.83 (3H, s), 1.02 (3H, t, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 147.2, 146.2, 137.4, 136.4, 130.6, 131.2, 127.9, 117.5, 62.4, 51.7, 39.9, 34.2, 32.9, 28.3 (2×), 27.7, 20.7, 19.8, 19.6, 16.4, 13.0, 12.6.

Reaction of Vinylallenal 17c (Table 1). Purification by HPLC (98:2 hexane/ethyl acetate) afforded, among other products, the highly unstable compound ***E*-32c** in 5% yield: ^{1}H NMR (C_6D_6) δ 9.32 (1H, d, J = 6.0 Hz), 5.95 (1H, s), 5.55 (1H, t, J = 6.5 Hz), 3.90 (1H, d, J = 6.0 Hz), 2.87 (2H, d, J = 6.5 Hz), 2.0−1.8 (4H, m), 1.86 (3H, d, J = 1.0 Hz), 0.96 (3H, t, J = 7.1 Hz).

Reaction of Vinylallene 15d (Table 1). Purification by HPLC (hexane) afforded the unstable compound **30d** (53% yield) as a mixture of isomers (***E*-30d**/***Z*-30d**, 50:50 ratio). ***E*-30d**: ^{1}H NMR (C_6D_6) δ 5.74 (1H, s), 5.54 (1H, t, J = 6.4 Hz), 4.28 (1H, dd, J = 10.0, 4.1 Hz),

3.78 (1H, dd, J = 10.0, 8.5 Hz), 3.59 (1H, dd, J = 8.5, 4.1 Hz), 2.97 (2H, d, J = 6.4 Hz), 2.00 (3H, d, J = 0.9 Hz), 1.94 (3H, s), 1.67 (3H, s), 1.60 (3H, d, J = 1.2 Hz). ***Z*-30d:** ^{1}H NMR (C_6D_6) δ 5.66 (1H, s), 5.60 (1H, t, J = 6.3 Hz), 3.93 (1H, dd, J = 9.8, 5.8 Hz), 3.78 (1H, dd, J = 9.8, 7.5 Hz), 3.27 (1H, br), 2.96 (2H, d, J = 6.3 Hz), 1.98 (3H, s), 1.85 (3H, s), 1.79 (3H, s), 1.67 (3H, s).

Reaction of Vinylallenol 16d (Table 1). Purification by HPLC (83:17 hexane/ethyl acetate) afforded the unstable compound **31d** (67% yield) as a mixture of isomers (***E*-31d/*Z*-31d**, 58:42 ratio). **Major isomer (*E*-31d):** ^{1}H NMR (C_6D_6) δ 5.73 (1H, s), 5.55 (1H, t, J = 6.4 Hz), 3.91 (1H, dd, J = 10.8, 3.6 Hz), 3.80 (1H, dd, J = 10.8, 5.9 Hz), 3.40 (1H, br), 2.96 (2H, d, J = 6.4 Hz), 1.94 (3H, d, J = 1.0 Hz), 1.74 (3H, s), 1.68 (3H, s). **Minor isomer (*Z*-31d):** ^{1}H NMR (C_6D_6) δ 5.61 (1H, s), 5.57 (1H, t, J = 6.6 Hz), 3.68 (2H, d, J = 5.5 Hz), 3.06 (1H, br), 2.96 (2H, d, J = 6.6 Hz), 1.95 (3H, d, J = 1.2 Hz), 1.75 (3H, d, J = 1.0 Hz), 1.71 (3H, s).

Reaction of Vinylallenal 17d (Table 1). Purification by HPLC (96:4 hexane/ethyl acetate) afforded, together with a major component of complex, still undetermined structure, the highly unstable compound ***E*-32d** in 5% yield: ^{1}H NMR (C_6D_6) δ 9.38 (1H, d, J = 5.0 Hz), 5.93 (1H, s), 5.59 (1H, t, J = 6.2 Hz), 3.97 (1H, d, J = 5.0 Hz), 2.93 (2H, d, J = 6.2 Hz), 1.91 (3H, s), 1.67 (3H, s), 1.65 (3H, s).

Reaction of Vinylallene 21 (Table 1). Purification by HPLC (83:17 hexane/ethyl acetate) afforded the unstable compound **36** (80% yield) as a mixture of isomers (***E*-36/*Z*-36**, 91:9 ratio) which were separated by HPLC. **Major isomer (*E*-36):** ^{1}H NMR ($CDCl_3$) δ 5.75 (1H, s), 5.20 (1H, t, J = 6.4 Hz), 2.89 (2H, s), 2.80 (2H, d, J = 6.4 Hz), 1.96 (3H, s), 1.82 (3H, s), 1.24 (9H, s); ^{13}C NMR (C_6D_6) δ 151.1, 140.7, 137.1, 136.9, 133.6, 131.0, 128.0, 116.8, 40.2, 39.5, 35.2, 34.1, 33.1, 29.3 (^{t}Bu), 28.5 (2×), 27.8, 19.9, 19.8, 15.6, 14.2. **Minor isomer (*Z*-36):** ^{1}H NMR ($CDCl_3$) δ 5.24 (1H, t, J = 6.5 Hz), 5.06 (1H, s), 2.74 (2H, d, J = 6.5 Hz), 2.51 (2H, br), 1.97 (3H, s), 1.73 (3H, s); ^{13}C NMR (C_6D_6) δ 150.9, 142.9, 136.5, 135.1, 132.6, 129.6, 128.0, 117.5, 40.2, 39.1, 35.1, 33.2, 30.3, 29.5 (^{t}Bu), 28.6 (2×), 27.9, 20.1, 19.9, 17.6, 16.2.

Reaction of Vinylallenol 28. The sample was maintained at 100 ± 0.1 °C during the entire experiment. This reaction exhibited non-first-order kinetics; the isomer ratio is given for a reaction time of 19 h. The solvent was removed, and the residue was purified by flash chromatography (hexane) to afford starting **28** and compound **34** in 70% joint yield. Purification by HPLC afforded a mixture of compounds ***E*-34** and ***Z*-34** in 67:33 ratio. **Major isomer (*E*-34):** ^{1}H NMR ($CDCl_3$) δ 5.58 (1H, t, J = 7.1 Hz), 5.58 (1H, s), 4.24 (2H, d, J = 7.1 Hz), 3.43 (1H, dd, J = 10.6, 6.0 Hz), 2.51 (1H, dd, J = 14.2, 6.0 Hz), 2.24 (1H, dd, J = 14.2, 10.6 Hz), 1.90 (3H, s), 1.89 (3H, s), 1.17 (9H, s); ^{13}C NMR ($CDCl_3$) δ 150.2, 148.6, 146.0, 136.9, 135.6, 128.4, 126.3, 113.1, 59.6, 48.4, 40.0, 34.8, 33.9, 32.9, 32.1, 29.9, 29.1 (^{t}Bu), 28.3, 20.8, 19.4, 15.7, 15.1. **Minor isomer (*Z*-34):** ^{1}H NMR ($CDCl_3$) δ 5.58 (1H, t, J = 7.1 Hz), 5.12 (1H, s), 4.20 (2H, br), 2.96 (1H, t, J = 7.1 Hz), 2.3−2.2 (2H, m), 1.90 (3H, s), 1.72 (3H, s), 1.12 (9H, s); ^{13}C NMR ($CDCl_3$) δ 149.4, 149.1, 142.2, 138.4, 135.9, 128.1, 126.7, 114.3, 59.7, 48.1, 40.4, 34.9, 33.0, 33.0, 31.1, 29.4 (^{t}Bu), 29.4, 21.3, 19.5, 17.6, 14.1, 14.0.

Reaction of Vinylallenal 29. The sample was maintained at 80 ± 0.1 °C during the entire experiment. This reaction exhibited non-first-order kinetics; the isomer ratio is given for a reaction time of 17 h. The solvent was evaporated under vacuum, and the residue was purified by HPLC (96:4 hexane/ethyl acetate) to afford, in 63% yield, starting **29** and compound **35** in 69:31 ratio. **Major isomer (*E*-35):** ^{1}H NMR ($CDCl_3$) δ 10.01 (1H, d, J = 8.2 Hz), 5.93 (1H, d, J = 8.2 Hz), 5.70 (1H, s), 3.50 (1H, dd, J = 10.3, 8.5 Hz), 2.52 (1H, dd, J = 14.2, 6.6 Hz), 2.34 (3H, s), 2.25 (1H, dd, J = 14.2, 10.3 Hz), 1.95 (3H, s), 1.18 (9H, s); ^{13}C NMR ($CDCl_3$) δ 190.8, 156.5, 154.2, 151.3, 135.0, 129.0, 127.2, 116.5, 112.9, 48.9, 39.9, 34.9, 33.8, 32.8, 31.7, 29.8, 29.0 (^{t}Bu), 28.3, 20.9, 19.4, 16.7, 15.6. **Minor isomer (*Z*-35):** ^{1}H NMR ($CDCl_3$) δ 9.98 (1H, d, J = 8.4 Hz), 6.05 (1H, d, J = 8.4 Hz), 5.23 (1H, s), 3.01 (1H, dd, J = 8.3, 7.6 Hz), 2.3−2.2 (2H, m), 2.20 (3H, s), 1.95 (3H, s), 1.11 (9H, s); ^{13}C NMR ($CDCl_3$) δ 190.9, 159.8, 154.7, 152.9, 145.6, 143.5, 129.2, 120.8, 113.6, 48.2, 40.2, 34.9, 33.8, 32.9, 30.9, 29.4 (^{t}Bu), 21.3, 19.4, 19.4, 18.5, 15.0 (2×).

Reaction of Vinylallenol 59. The sample was maintained at 90 ± 0.1 °C during the entire experiment ($k = 1.15 \times 10^{-1}$ h^{-1}; $\tau_{1/2}$ = 6.0 h). The reaction mixture was evaporated, and the residue was purified by flash chromatography (85:15 hexane/ethyl acetate) to afford compound **60** (91% yield) as a mixture of isomers (***E*-60/*Z*-60**, 66:34 ratio), which were separated by HPLC. **Major isomer (*E*-60):** ^{1}H NMR ($CDCl_3$): δ 5.12 (1H, q, J = 6.8 Hz), 3.81 (2H, d, J = 3.8 Hz), 3.13 (1H, br), 1.92 (3H, s), 1.64 (3H, d, J = 6.8 Hz), 1.16 (9H, s); ^{13}C NMR ($CDCl_3$) δ 151.8, 140.3, 138.8, 106.1, 62.3, 50.2, 34.1, 29.3 (^{t}Bu), 13.7. **Minor isomer (*Z*-60):** ^{1}H NMR ($CDCl_3$) δ 4.77 (1H, q, J = 7.2 Hz), 3.78 (1H, dd, J = 10.9, 4.3 Hz), 3.66 (1H, dd, J = 10.9, 4.3 Hz), 2.87 (1H, t, J = 4.3 Hz), 1.94 (3H, s), 1.83 (3H, d, J = 7.2 Hz), 1.22 (9H, s); ^{13}C NMR ($CDCl_3$) δ 152.0, 143.1, 138.5, 104.9, 62.2, 50.8, 33.2, 29.6 (^{t}Bu), 15.5, 14.0.

Reaction of Vinylallenal 54. The sample was maintained at 90 ± 0.1 °C during the entire experiment ($k = 3.7 \times 10^{-2}$ h^{-1}; $\tau_{1/2}$ = 18.5 h). The solvent was evaporated, and the residue was purified by column chromatography (98:2 hexane/ethyl acetate) to afford compound **55** (90% yield) as a mixture of isomers (***E*-55/*Z*-55**, 83:17 ratio), which were separated by HPLC. **Major isomer (*E*-55):** ^{1}H NMR ($CDCl_3$) δ 9.15 (1H, d, J = 5.8 Hz), 5.36 (1H, q, J = 6.6 Hz), 3.58 (1H, d, J = 5.8 Hz), 1.93 (3H, s), 1.55 (3H, d, J = 6.6 Hz), 1.20 (9H, s); ^{13}C NMR ($CDCl_3$) δ 202.5, 156.0, 134.9, 133.0, 110.5, 60.6, 34.1, 28.9 (^{t}Bu), 14.8, 12.9. **Minor isomer (*Z*-55):** ^{1}H NMR ($CDCl_3$) δ 9.04 (1H, d, J = 5.8 Hz), 4.72 (1H, q, J = 7.2 Hz), 3.37 (1H, d, J = 5.8 Hz), 1.98 (3H, s), 1.87 (3H, d, J= 7.2 Hz), 1.21 (9H, s); ^{13}C NMR ($CDCl_3$) δ 202.2, 161.7, 129.6, 128.0, 111.4, 62.0, 29.6, 29.4 (^{t}Bu), 22.6, 14.0.

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Supporting Information Available: General experimental procedures, preparation of substrates, complete spectroscopic characterizations, kinetic analyses, ^{1}H NMR or ^{13}C NMR spectra for the compounds described in the text, and RHF/6-31G* geometries of transition structures and products in the form of cartesian coordinates (116 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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