analogous to that proposed for an yttrium complex.[85]

The reaction of **2** with toluene also has a parallel in the Sc system.[16] The reaction of **16** with toluene at 80 °C gives $(C_5Me_5)_2ScCH_2C_6H_5$ as the kinetic product which reacts further to form a mixture of tolyl isomers. At room temperature **2** forms the benzyl product exclusively from toluene.

It is more difficult to compare the reactivity of **2** with pyridine and Et_2O to that of **16** and **17** with these substrates. Both the Sc and Lu complexes react with pyridine to form the metalated species $(C_5Me_5)_2M(\eta^2\text{-}C_5H_4N)$ and methane. NMR evidence for a pyridine adduct intermediate, $(C_5Me_5)_2MMe(NC_5H_5)$, is observed.[16,79] In the Sc case, the reaction was run in refluxing benzene. For the samarium complex **2**, pyridine metalation is rapid at room temperature and a mixture of other products is formed which evolves over a several day period.

The reaction of **2** with Et_2O to form the ethoxide complex $(C_5Me_5)_2Sm(OEt)(THF)$ parallels the reaction of $[(C_5Me_5)_2LuH]$[14,15] with Et_2O to form $(C_5Me_5)_2LuOEt$.[79] However, no such reactivity has been reported for $(C_5Me_5)_2MMe(OEt_2)$ complexes (M = Lu, Yb)[55,71] and $(C_5Me_5)_2YbMe(OEt_2)$ was stable enough to allow an X-ray crystal structure determination.[86]

Conclusion

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with Me_3Al has provided two reactive samarium methyl complexes, **1** and **2**. This preliminary survey of the reactivity of **1** and **2** shows that an extensive organometallic chemistry will be available via these species. The initial studies of the C-H activation reactivity of **2** show parallels with unsolvated scandium and lutetium complexes and suggest that this is another complex capable of σ-bond metathesis with a variety of substrates. **2** appears to have some special characteristics in this regard which will form the basis for future investigations. Especially noteworthy is the high reactivity with alkane substrates. With the extension of the C-H metalation reactivity from the small metals Sc, Y, and Lu to the midsized Sm, it appears that this type of reactivity will be general for the lanthanides and similar metals if the proper ligand set and coordination environment are provided.

Acknowledgment. We thank the National Science Foundation for support of this research, the University of California for a Presidential Postdoctoral Fellowship (to L.R.C.), Donald K. Drummond for collecting and partially solving an X-ray data set, Professor Frank J. Feher for helpful discussions, and Dr. Matthew B. Zielinski for arranging the molecular weight distribution measurements. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Registry No. 1a, 115756-72-4; **1b**, 115756-73-5; **2**, 115731-48-1; $AlMe_3$, 75-24-1; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $C_6D_5CD_3$, 2037-26-5; Et_2O, 60-29-7; C_6D_6, 1076-43-3; $(C_5Me_5)_2Sm(OEt)(THF)$, 115731-49-2; $(C_5Me_5)_2Sm(C_6D_5)(THF)$, 115731-50-5; $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$, 115731-51-6; $(C_5Me_5)_2Sm(CD_2C_6D_5)(THF)$, 115731-52-7; C_6D_{12}, 1735-17-7; $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, 84751-30-4; H_2, 1333-74-0; toluene, 108-88-3; pyridine-d_5, 7291-22-7; cyclooctane, 292-64-8; ethylene, 74-85-1; polyethylene, 9002-88-4.

Supplementary Material Available: Tables of complete bond distances and angles and thermal parameters (5 pages); listings of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

(85) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682-683.
(86) Unpublished results cited in ref 55.

Stereochemistry of Vinylallene Cycloadditions

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Abstract: Diels-Alder cycloadditions of three vinylallenes 1,2,4-octatriene (**6**), 2,3,5-nonatriene (**7**), and 2-methyl-2,3,5-nonatriene (**8**) with maleic anhydride and dimethyl fumarate were studied. Product ratios were dominated by the steric and electronic effects between the out-of-plane substituents on the vinylallene terminus and substituents on the dienophile. Excellent control of exocyclic double-bond stereochemistry can be achieved. The cycloaddition of methylmaleic anhydride with **8** gave only a single regio- and stereoisomer, compound **26**, the product formed by approach of vinylallene and dienophile in the least hindered orientation. Configurational assignments to the six isomeric diesters [(*E*)-**16**, (*Z*)-**16**, (*E*)-**17**, (*E*)-**18**, (*Z*)-**18**, (*E*)-**19**] formed by reaction of **7** with maleic anhydride and dimethyl maleate were made on the basis of detailed conformational analysis using MM2 and consideration of proton and carbon NMR spectroscopic data, NOE studies, and 2D proton-carbon correlations. Rate studies of the reaction of a series of vinylallenes with *N*-methylmaleimide also supported the concept that steric interactions with allene substituents play an important role in the transition state. Vinylallenes are slightly more reactive than comparably substituted 1,3-butadienes.

The cycloaddition reactions of vinylallenes have the potential for regio- and stereochemical control resulting from the interaction between the out-of-plane substituents at the terminus of the allene and the dienophile. These effects have not been well defined; in fact, Diels-Alder cycloadditions of vinylallenes and bis(allenes) have in general been little studied.[1a,b,2-4] We report here our work on some aspects of this topic using reactions of several allenes with maleate and fumarate dienophiles.

Previous work on vinylallene Diels-Alder cycloadditions has shown that their reactivity is comparable to similarly substituted

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(4) Intramolecular: Snider, B. B.; Burbaum, B. W. *J. Org. Chem.* **1983**, *48*, 4370. Deutsch, E. A.; Snider, B. B. *J. Org. Chem.* **1982**, *47*, 2682. Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. Chem. Soc., Chem. Commun.* **1974**, 496.

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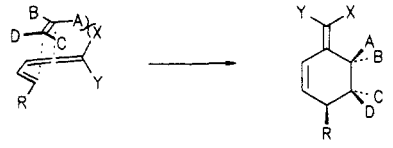
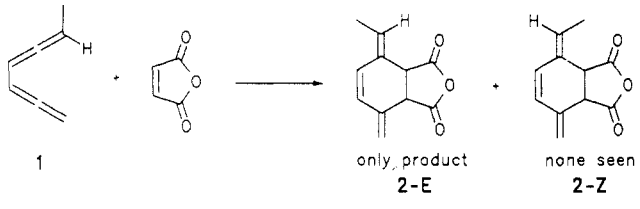
Scheme I



1,3-dienes, the vinylidene "substituent" does not exert any strong regiochemical influence, and normal exo/endo ratios are obtained for reactions with dienophiles.[2a,b] Vinylallenes differ from 1,3-dienes in that cis substituents on the vinyl portion do not reduce the rate of cycloaddition as much as occurs in normal dienes since there is a smaller steric interaction disfavoring the cisoid conformation.[1a,b]

The stereochemical features peculiar to vinyl allenes that are of interest here are illustrated in Scheme I. The crucial interaction is expected to be the one between the substituent(s) at the end of the allene (X, Y), which project above and below the plane of the vinylallene, and the dienophile, which is expected to lie more or less parallel to the plane of the vinylallene and above or below it in the transition state of the cycloaddition. The steric interaction A–X influences the following: (1) exo–endo selectivity when A $\neq$ B; (2) face selectivity when X $\neq$ Y; (3) regioselectivity when C $\neq$ A.

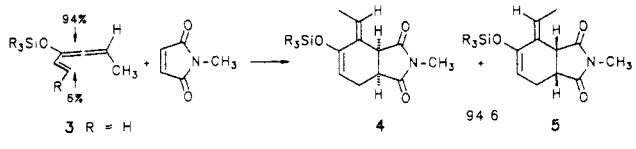
One of the more interesting consequences of these interactions is control of exocyclic stereochemistry, which results from face selectivity. This effect has already been observed by Schoen and Hopf[5] for the case of cycloadditions to bis(allenes) such as **1**.



These authors observed both rate and stereochemical effects (only (*E*)-**2** was formed), which indicated that the interactions of interest were substantial. Although several examples of Diels–Alder reactions involving vinylallenes with a substituent at the allene terminus have been reported, the stereochemistry does not seem to have been accurately assessed.[3]

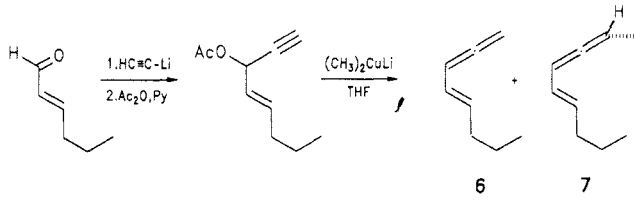
Results

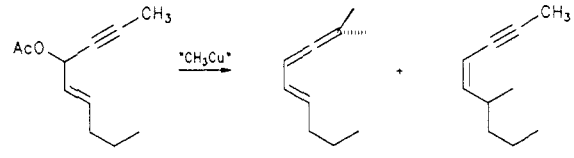
In the course of our studies of silyl ketone chemistry, we developed a facile synthesis of siloxy-substituted vinylallenes such as **3**.[1b,c] The reaction of this compound with *N*-methylmaleimide



gave a greater than 95/5 ratio of the two Diels–Alder adducts (**4**, **5**) differing only in their geometry about the exocyclic double bond. Control of exocyclic double-bond stereochemistry is usually difficult when neither isomer is thermodynamically favored.[6] We therefore thought it worthwhile to examine this question in compounds sufficiently robust to allow more careful product analysis and rate comparison than was possible for siloxydienes such as **3**. The allenes **6**–**8** were chosen for this study.

Preparation of Vinylallenes. The hydrocarbon vinylallenes were prepared by reaction of cuprates with propargyl acetates. Compounds **6** and **7** were serendipitously formed in a single reaction.[7] For the preparation of **8** in good yield proper choice of copper reagent was critical. Lithium dimethyl cuprate gave exclusively

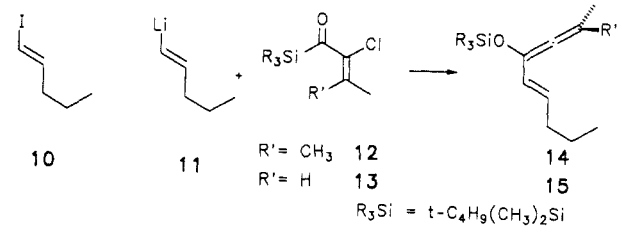




$(CH_3)_2CuLi\cdot LiI$	100/0
CH_3CuCN	40/60
$CH_3Cu\cdot BF_3\cdot Et_2O$	33/66

the desired vinylallene, whereas several other reagents gave predominantly the enyne **9**.

The siloxy-substituted compounds **14** and **15** were readily available from reaction of the vinyllithium reagent **11**, prepared from vinyl iodide **10**, with α-halo silyl enones **12** and **13**.[1b,c]



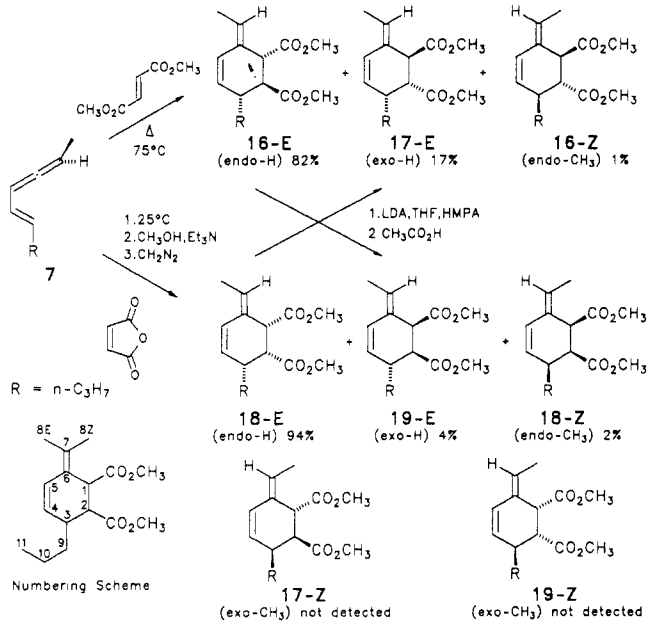
(*E*)-2,3,5-Nonatriene (7). Compound **7** reacted smoothly with maleic anhydride at room temperature and dimethyl fumarate at 75 °C. The maleic anhydride adducts themselves were difficult to characterize stereochemically because of their hydrolytic instability and because such adducts are sometimes in a boat conformation (at least in the case of 1,3-diene adducts[8]) resulting in quite variable coupling constants. They were therefore converted to the corresponding diesters by treatment with methanol and diazomethane. No epimerization occurred during this process: No common products were detected in the maleate and fumarate reactions, all of the products from each reaction had the appropriate stereochemical relationship between the carbomethoxy groups, and the product ratios for the major products of each reaction were identical in the crude anhydride product and the diester. Each set of diesters was then analyzed and separated by HPLC. The results of these experiments are summarized in Scheme II.

Structure determination of the three products obtained in each case was carried out principally by a combination of NMR studies and chemical interconversions. The assignments of exocyclic double-bond stereochemistry were made by using nuclear Overhauser effect studies in which the exocyclic vinyl proton and allylic methyl resonances were irradiated. Enhancements of 10–26% in the area of H-1 were generally observed when the irradiated group was cis to it, −1 to +3% when trans to it. Chemical shift effects in the ^{13}C NMR spectra (Table I), while not compelling, were at least consistent with these assignments. The carbon resonances were assigned on the basis of chemical shift consideration, decoupled INEPT spectra,[9a] selective heteronuclear decoupling experiments, and 2D proton–carbon correlation spectroscopy.[9b]

In this way the two major products from the 82:17:1 mixture of products obtained in the reaction of fumarate with **7** [(*E*)-**16**, (*E*)-**17**] and the two major products from the 94:4:2 mixture of

(5) Schön, G.; Hopf, H. *Liebigs Ann. Chem.* **1981**, 165.
(6) Overman, L. E.; Bell, K. L. *J. Am. Chem. Soc.* **1981**, *103*, 1851.
(7) Crabbé, P.; Carpio, H. *J. Chem. Soc., Chem. Commun.* **1972**, 904.
(8) Hiranuma, H.; Miller, S. I. *J. Org. Chem.* **1983**, *48*, 3096.
(9) (a) Burum, D. P.; Ernst, R. R. *J. Magn. Reson.* **1980**, *39*, 163. (b) Maudsley, A. A.; Müller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.

Scheme II



diesters formed from the maleic anhydride adducts [(*E*)-**18**, (*E*)-**19**] were shown to have the *E*, and the minor products from these two reactions [(*Z*)-**16**, (*Z*)-**18**] the *Z*, stereochemistry. The distinction between (*E*)-**16** and (*E*)-**17**, along with a determination of their respective conformations, was made on the basis of the vicinal coupling constants of (*E*)-**16** (J_{12} = 10.8, J_{23} = 9.6, and J_{34} = 2.1 Hz) compared with (*E*)-**17** (J_{12} = 11.3, J_{23} = 5.3, and J_{34} = 5.3 Hz). These couplings are consistent with structures (*E*)-**16**-eq and (*E*)-**17**-ax. It is interesting to note the $^4J_{35}$ coupling of 2.5 Hz in (*E*)-**16**-eq. the MM2[10] structure of the molecule reveals a dihedral angle (θ_{34} = −82.9°) favorable for a long-range coupling.[11] This coupling was not observed in structure (*E*)-**17** or (*Z*)-**16**, where θ_{34} is 31° and 36°, respectively. Figure 1 summarizes the relevant structural and spectroscopic data. The calculated values for ^3J and ^4J were obtained with the Garbisch[11b] and Bothner-By[12] equations.

We were unable to prepare or detect authenitc (*Z*)-**17**, so the distinction between structures (*Z*)-**16** and (*Z*)-**17** for the minor fumarate product was more difficult, particularly since the substance appeared to have predominantly axial substituents, or to be in boat form as shown by the small vicinal couplings (J_{12} = 3.9 and J_{23} = 3.7 Hz). In order to fit these coupling constants, the compound had to have conformation (*Z*)-**16**-ax if it were (*Z*)-**16**, or if (*Z*)-**17** was the correct structure, conformation (*Z*)-**17**-ax. Examination of molecular models as well as MM2 calculations showed that the J_{34} coupling should be larger for (*Z*)-**16**-ax (dihedral angle 36°) than for (*Z*)-**17**-ax (−86°). The observed coupling of 4.7 Hz is consistent only with (*Z*)-**16**-ax. MM2 calculations also supported the notion that (*Z*)-**16** would have the unusual conformation with all substituents axial (1.8 kcal lower in energy than the all-equatorial isomer). This effect originates in the interaction between a substituent on an exocyclic double bond and an equatorial group in the allylic position (A-strain) as delineated by F. Johnson.[13] In the present system, the steric interactions are exacerbated by buttressing effects between the remaining substituents, some or all of which are equatorial. In contrast, MM2 calculations on (*E*)-**16**, in which the methyl group on the exocyclic double bond is away from the carbomethoxy substituent, indicate no significant energy difference between

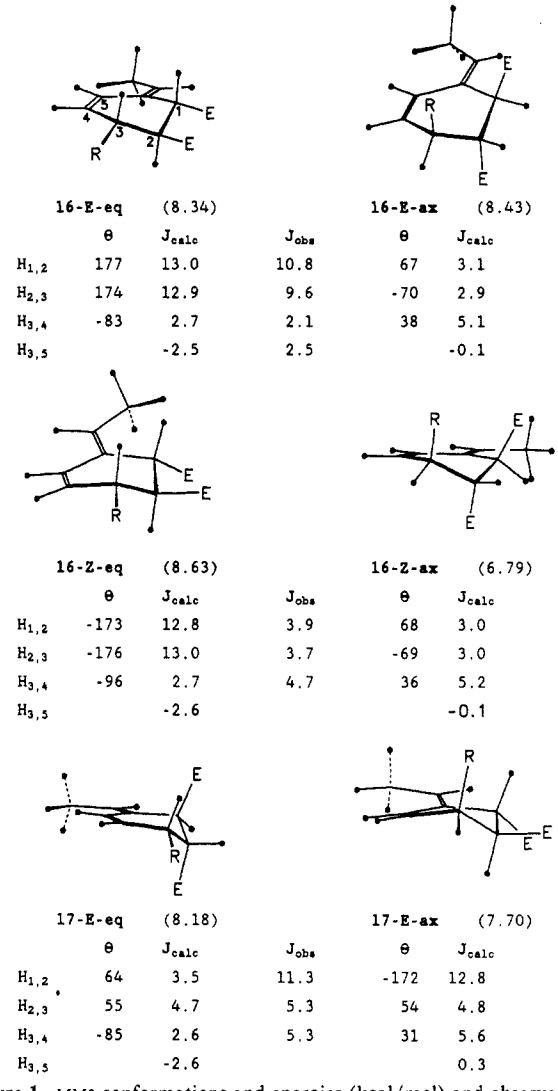


Figure 1. MM2 conformations and energies (kcal/mol) and observed and calculated ^3J and ^4J H–H coupling constants for (*E*)-**16**, (*Z*)-**16**, and (*E*)-**17**.

all-axial and all-equatorial conformers, and the NMR coupling constants (Figure 1) show that substituents are predominantly equatorial.

The 94:4:2 mixture of diesters formed from the adducts of maleic anhydride with **7** were similarly identified as (*E*)-**18**, (*E*)-**19**, and (*Z*)-**18** on the basis of the characteristic NOE effects with the exo-methylene substituents and the J_{12}, J_{23}, and J_{34} values. For identical reasons as described above for (*Z*)-**16**, compound (*Z*)-**18** also proved to be in a conformation with two axial substituents. Compounds **20**–**22**, whose syntheses are described in the next section, contain an exo-isopropylidene group. The NMR parameters showed that the carbomethoxy function at C-1 in each compound was axial. It is clear that the factor determining whether the carbomethoxy function at C-1 will be axial is the presence of a methyl group on the exocyclic double bond in the *Z* position.

The most direct information about conformation was provided by vicinal coupling constants, but the chemical shift of H-1 was also informative. In cases where H-1 was axial, chemical shifts ranged from δ 3.54 to 3.64 (e.g., **28**, **29**, (*E*)-**16**, (*E*)-**17**, (*E*)-**18**, and (*E*)-**19**). However, when H-1 was equatorial, a pronounced downfield shift of ≈0.4 ppm was observed (e.g., (*Z*)-**16**, (*Z*)-**18**, and **20**–**22**; see Table I).

We have also investigated the correlation between structure and conformation using ^{13}C NMR spectroscopy. Figure 2 illustrates the ^{13}C resonances for a set of related compounds. The chemical shifts showed remarkably little change considering the major conformational changes that occur. However, C-1 expe-

(10) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. Burkert, U.; Allinger, N. L. *Molecular Mechanics* ACS Monograph 177; American Chemical Society: Washington, D.C., 1982.
(11) (a) Barfield, M.; Chakrabarti, B. *Chem. Rev.* **1969**, *69*, 757. (b) Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5561.
(12) Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195.
(13) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

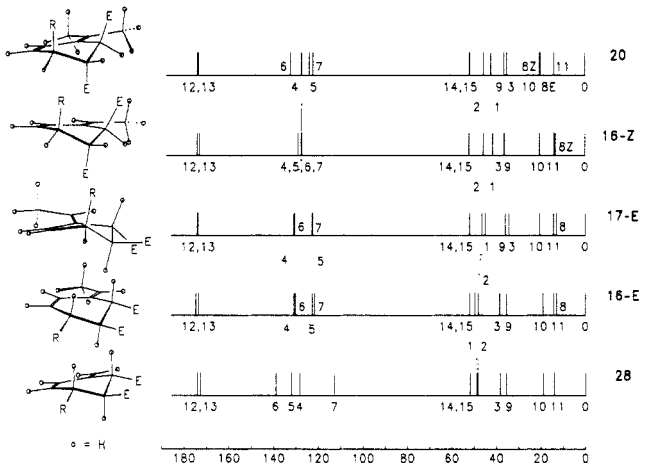
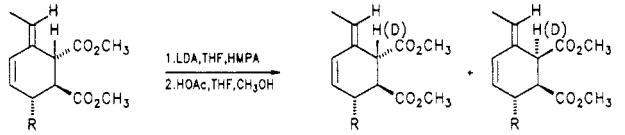


Figure 2. ^{13}C correlation of **28**, (*E*)-**16**, (*E*)-**17**, (*Z*)-**16**, and **20**.

rienced an upfield shift of 4.7 ppm between (*E*)-**16** and (*E*)-**17**, which was due to a γ-effect (steric interaction between R^3 and H-1) as the R^3 group changed from the equatorial to axial position. Carbon-2 also moved upfield 1.6 ppm as a result of a smaller β-interaction incurred when the R group assumed the axial position.[14] As the exo-methylene methyl group changed from the *E* to *Z* position, an additional γ steric shift of 3.3 ppm was seen at C-1. Resonance C-5 also showed the consequences of the γ steric interactions with the *E* exo-methylene methyl group (e.g., **28** to (*E*)-**16** and (*Z*)-**16** to **20**).

Further support for the structure assignments was provided by isomerization of the major fumarate [(*E*)-**16**] and maleate [(*E*)-**18**] products. Under conditions of kinetic control (deprotonation with LDA/THF/HMPA, protonation with acetic acid), (*E*)-**16** was converted to a mixture of (*E*)-**16** and (*E*)-**19**, whereas

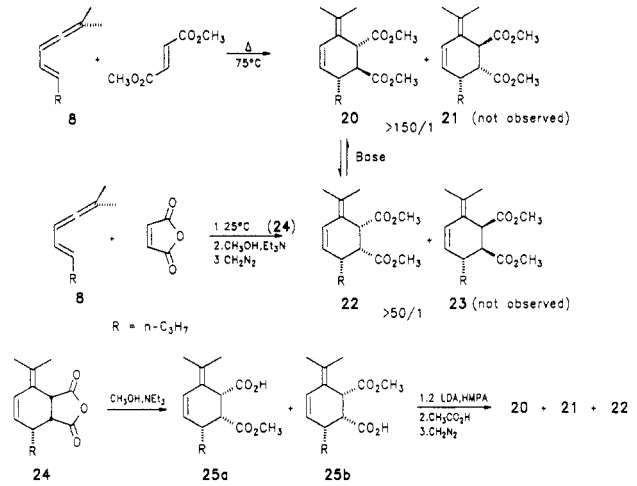


(*E*)-**18** was converted to a mixture of (*E*)-**18** and (*E*)-**17**. Deprotonation and quench with D_2O showed that H-1 was exclusively abstracted. Thus, the two sets of esters are stereochemically related as required by the NMR assignments.

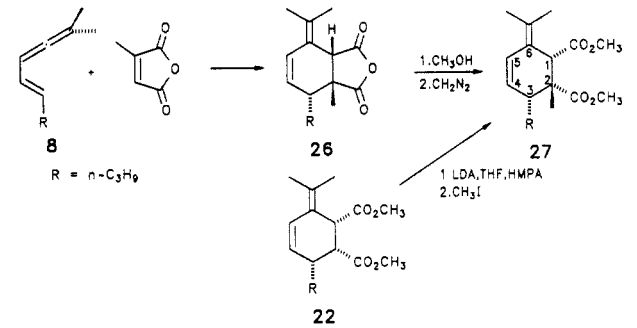
(*E*)-2-Methyl-2,3,5-nonatriene (8). Only a single product could be detected in the reaction of **8** with either maleic anhydride (giving **22**) or dimethyl fumarate (giving **20**). Since one of the aims of this research was to establish the limits of stereochemical control that can be achieved, substantial efforts were made to prepare the other possible isomer (**23**, **21**) in each case (having both isomers also helps to secure the structure assignments). We were unable to prepare **23**, but the trans isomer **21** was successfully prepared by deprotonation–protonation of the half-esters **25** formed by methanolysis of the maleic anhydride adduct **24** (Scheme III). This somewhat roundabout approach to the preparation of **21** was necessary because under conditions of either base-catalyzed exchange or deprotonation–protonation the diester **22** consistently gave **20** as the only new isomer (and vice versa), a consequence of exclusive enolization at H-2. The half-ester strategy works because deprotonation of **25b** α to a lithium carboxylate at the otherwise favored H-2 position is slower than deprotonation at H-1 α to a carbomethoxy group.

Not surprisingly after the results with (*Z*)-**16**, the NMR coupling constants showed **20**–**22** to have predominantly axial substituents (for **20** J_{12} = 3 Hz, J_{23} = 3 Hz, J_{34} = 5 Hz; for **21** J_{12} = 3 Hz, J_{23} = 5 Hz, J_{34} < 1 Hz; for **22** J_{12} = 5 Hz, J_{23} = Hz, J_{34} = 6 Hz). The axial disposition of the carbomethoxy functions also explains why **20** and **22**, in contrast to (*E*)-**16** and (*E*)-**18**, did not deprotonate at the allylic position H-1; the C–H bond is perpendicular to the π-orbital of the exocyclic double bond and hence enolization is not assisted by conjugation.

Scheme III



Scheme IV



Careful gas chromatographic and HPLC examination of the product from reaction of **8** with fumarate showed that the ratio of **20** to **21** was >150:1. A comparison sample of the isomeric cis diester **23** was not available, so for the maleic anhydride cycloaddition we place a limit of >50:1 for the **22**/**23** isomer ratio on the basis of a careful search for another isomer by GC, HPLC, and NMR.

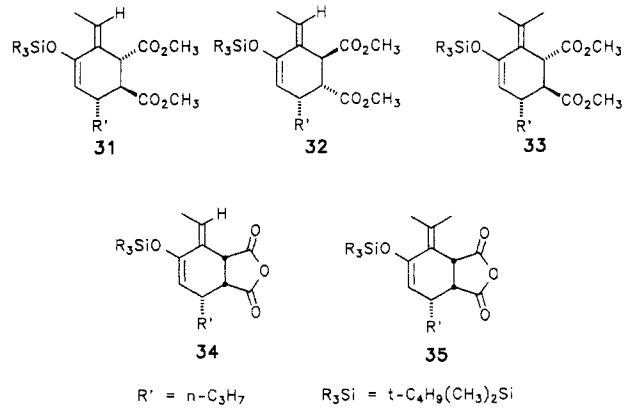
A direct consequence of the large stereochemical control observed for the cycloadditions with the disubstituted dienophiles discussed above is that with trisubstituted dienophiles both regio- and stereochemical control should be observed. Methylmaleic anhydride reacted with **8** at 75 °C to give a single product, whose NMR spectrum had the α-anhydride proton as a singlet at δ 3.60 (Scheme IV). Both the chemical shift and absence of coupling support **26** rather than its regioisomer with methyl at C-1 as the correct structure. To confirm this assignment, anhydride **26** was methanolized and esterified to **27**. Here also the absence of coupling and chemical shift of H-1 (δ 3.77; cf. δ 4.10 for **22**) support the structural assignment. Furthermore, the product was identical with one prepared by deprotonation and methylation of **22**. It was shown that **22** deprotonated exclusively at H-2.

Other Vinylallenes. Reaction products from three other allenes (**6**, **14**, **15**) with maleic anhydride and dimethyl fumarate were also characterized. The results from cycloadditions involving **6** are summarized to Scheme V. We were not able to convert **30** to the corresponding diesters for reliable determination of stereochemistry because double-bond isomerization occurred too easily.

The results of our experiments are summarized in Table II. For the dimethyl fumarate additions we define endo/exo with respect to the carbomethoxy function at C-1 (i.e., closest to the allene group).

Rates of Vinylallene Cycloadditions. In order to determine whether the strong stereochemical control observed for the cy-

(14) Whitesell, J. K.; Minton, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 225.
(15) 1-Methoxybutadiene is 12.3 times as reactive as butadiene toward maleic anhydride: Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16.



cloadditions had a counterpart in the rates, we measured the second-order rate constants for the reaction of **6–8**, **14**, and **15** with *N*-methylmaleimide at 30 °C. We chose this dienophile because it reacted cleanly with all the vinylallenes and because the progress of the cycloadditions could be easily monitored by NMR and, in some cases, by HPLC. The reactions followed good second-order kinetics. In no case was any change in isomer ratio observed as the reaction progressed. The results of the rate study are summarized in Table III. For comparison, we measured the rate of the dienyl analogue 7-phenyl-1,3-heptadiene (**36**). This diene was prepared by regiospecific dehydration of 4-hydroxy-7-phenyl-2-heptene using 2,4-dinitrobenzenesulfonyl chloride.[1d]

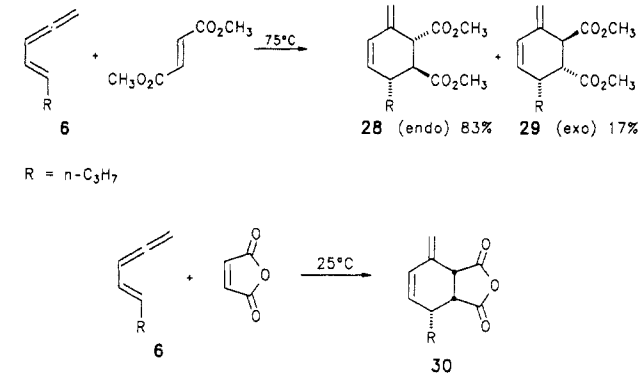
Discussion

From the results presented above, it is clear that A–X interactions as defined in Scheme I dominate the stereochemistry of the cycloadditions discussed here. In all cases, the main product is the one in which the A–X interaction is small (H–H), and products from reactions in which neither A nor X is H were not detected. When A ≠ B, this interaction controls the exo/endo selectivity (Scheme II), and when A ≠ C, it controls regiochemistry (Scheme IV). When X ≠ Y, it results in control of exocyclic double-bond stereochemistry. The latter effect is complicated by inherent reactivity differences in the two faces of the diene resulting from differences in hyperconjugative interaction with the CH and CCH_3 groups at the allene terminus. This factor augments the steric preference for attack on the H face of the vinylallene.

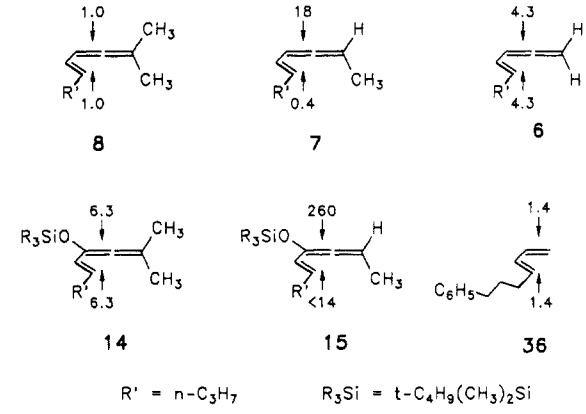
There should be little or no inherent exo/endo preference in the fumarate additions since one carbomethoxy group is always over the diene at the transition state. Hence, the exo/endo ratios observed were expected to be largely the result of interactions between the out-of-plane substituents on the allene and the dienophile. For attack on the H face of the vinylallenes **6**, **7**, and **15** a ratio of ~5:1 was observed, and this therefore represents the difference between an H–H and CO_2CH_3–H interaction. Exact numbers for this interaction when attack occurs on the methyl face of the vinylallene (H–CH_3 vs CO_2CH_3–CH_3) are not available, but may be in excess of 150:1 on the basis of the minimum value established for the ratio **20**:**21** for the reaction-product from **8**.

In addition to the normal preference for endo transition states seen for most Diels–Alder reactions, which has already been determined to be modest in size for vinylallenes by Bertrand, Grimaldi, and Waegell[2a] using methyl vinyl ketone, the A–X interaction as depicted in Scheme I is expected to substantially enhance the stereoselectivity for endo products in appropriately substituted vinylallenes. For the maleic anhydride and *N*-methylmaleimide reactions, and exo/endo ratios are the sum of the normal preference for the endo transition state resulting from secondary orbital overlap and the difference between the H–H and CO–H allene interaction discussed above. Since both effects are in the same direction, substantially larger effects than for fumarate were expected and also observed. For addition of maleic anhydride on the H-face of the allene, the exo/endo preference was ~24:1 for **7**. Again, for attack on the methyl face, too little

Scheme V



Scheme VI



product was formed for us to detect, but the exo/endo ratio was at least 50:1 for **8**. When the dienophile was a trisubstituted olefin with only a single H substituent, as in the case of methylmaleic anhydride, then the only product with vinylallene **8** was the one involving an H–CH_3 interaction (**26**). None of the three other possible isomers could be detected.

Another aspect of the same interactions can be examined by comparing the ratio of attck on the two faces of vinylallenes **7**, **15**, and **3**. For fumarate additions, the ratio is 99:1 for **7**. The ratio is 96:4 for **7** with maleic anhydride and 94:6 for **3** with *N*-methylmaleimide. These can be considered H–H vs H–CH_3 comparisons.

A discussion of the origins of the face selectivity requires a consideration of the kinetic data on the *N*-methylmaleimide reactions, which are summarized in Scheme VI in the form of relative partial rate factors (symmetry corrected). The face selectivity is expected to be the consequence of a combination of steric effects and an electronic component resulting from orbital distortion (e.g., differential σ–π^* interactions of C–H vs C–CH_3 bonds). The magnitude of the electronic effect due to an anti CH_3 group could be as high as the factor of 4.2 in rate by which **6** and **7** differ in H-face reactivity multiplied by the factor of 2.5 by which **7** and **8** differ in their CH_3-face reactivity. These rate effects could, however, be either the consequence of a face-selective orbital distortion or a non-face-selective inductive effect.

Comparison of the siloxy compounds with their unsubstituted analogues revealed rate differences of 6× (for **8**) and 15× (for **7**). This is comparable to rate ratios for alkoxy-substituted 1,3-dienes.[15]

Conclusion. For the cycloaddition of vinylallenes bearing substituents at the allene terminus, the product ratios are invariably controlled by the A–X interaction depicted in Scheme I.

General Experimental Section

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL MH-100, FX-60, IBM WP-200, IBM WP-270, Bruker WH-270, Bruker AM-360 or AM-500 spectrometer, and standard pulse programs were used, which were supplied with the spectrometers. Unless otherwise

stated, all ^1H NMR spectra were measured with reference to $CHCl_3$ (δ 7.24) or TMS (δ 0.0). The $CDCl_3$ triplet (δ 77.0) or C_6H_6 triplet (δ 128.0) was used as reference for ^{13}C NMR. Infrared (IR) spectra were taken of neat liquids, unless otherwise stated, between salt plates and were recorded on a Beckman Acculab 7 spectrophotometer or a Mattson Instruments Polaris FT-IR. An AEI-MS-902 or a Kratos MS-80 spectrometer was used to obtain mass spectra. All elemental analyses were performed by Galbraith Laboratories.

Kugelrohr distillation refers to a bulb-to-bulb distillation apparatus sold by Aldrich Chemical Co. Bath temperatures are reported. The chromatotron refers to a device sold by Harrison Research for preparative, centrifugally accelerated, thin-layer chromatography. High-performance liquid chromatography (HPLC) was done with a Beckman Model 942 gradient elution system on 5 μm reverse-phase octadecylsilane columns (Ultrasphere-ODS, 10 mm × 25 cm). Analytical gas chromatography was carried out with a Varian Model 3700 gas chromatograph on a 12 m × 0.32 mm SE-30 capillary column.

Starting materials were commercially available and used without further purification, except as noted below. The synthesis of 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-butadiene, 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethoxy)-3-methyl-1,2-butadiene, and 2-chloro-3-methyl-1-(*tert*-butyldimethylsilyl)-2-buten-1-one was reported earlier.[1c] Copper iodide was extracted with THF in a soxhlet extractor until the washings were colorless. Dimethyl fumarate was passed through a column of alumina with ether as eluant and then recrystallized from ether. Maleic anhydride was sublimed prior to use. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Triethylamine was dried over CaH_2 and stored over 4-Å molecular sieves. Solutions of lithium diisopropylamide,[1e] methyllithium, and *n*-BuLi were titrated by use of 1-propanol with 1,10-phenanthroline as indicator.[16] All reactions involving organometallics were carried out under an atmosphere of dry nitrogen, in glassware that had been dried at 110 °C for at least 5 h.

(*E*)-4-Octen-1-yn-3-ol. A 250-mL round-bottom flask was charged with 10.2 g (100 mmol) of lithium acetylide–ethylenediamine complex and 50 mL of THF. The mixture was cooled in an ice bath, and 10.0 mL (86.2 mmol) of (*E*)-2-hexenal in 50 mL of THF was added via cannula. The flask was allowed to warm to room temperature and stirred for 2 h. The solution was poured onto ice water and 60 mL of 50% ether/hexane. The organic layer was washed with water (2 × 50 mL) and brine (1 × 30 mL), dried by passage through a cone of Na_2SO_4, and evaporated. The resulting oil was purified by Kugelrohr distillation [bp 40–80 °C (0.4 mm)] to produce 6.045 g (51% yield) of (*E*)-4-octen-1-yn-3-ol: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.87 (t, J = 7.0 Hz, 3 H), 1.39 (hextet, J = 7.0 Hz, 2 H), 2.00 (qm, J = 7 Hz, 2 H), 2.52 (d, J = 2.2 Hz, 1 H), 4.07 (dm, J = 4 Hz, 1 H), 4.77 (dm, J = 5 Hz, 1 H), 5.55 (ddt, J = 15.5, 6, 1.5 Hz, 1 H), 5.86 (dtd, J = 15.5, 7, 1 Hz, 1 H); IR, 3480, 3410, 2960, 2930, 2870, 2120, 1470, 1100, 1070, 1040, 985 cm^{-1}.

(*E*)-3-Acetoxy-4-octen-1-yne. To a 100-mL round-bottom flask were added 6.045 g (44 mmol) of (*E*)-4-octen-1-yn-3-ol, 50 mL of pyridine, and a few crystals of 4-(dimethylamino)pyridine. To the mixture was slowly added 4.5 mL (48 mmol) of acetic anhydride in 25 mL of pyridine. The flask was heated to 60 °C for 5 h. The reaction mixture was partitioned between 150 mL of 2 N HCl and 150 mL of 50% ether/hexane. The aqueous layer was washed with ether/hexane (3 × 30 mL), and the combined organic layers were washed with water (3 × 30 mL) and brine (1 × 40 mL) and dried by passage through a cone of Na_2SO_4.

The solvent was removed in vacuo, yielding (*E*)-3-acetoxy-4-octen-1-yne (6.94 g, 95%), which was used without any additional purification: ^1H NMR ($CDCl_3$, 270 MHz) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.43 (hextet, J = 7.4 Hz, 2 H), 2.06, 2.09 (q, s, J = 7.7 Hz, 5 H), 2.56 (d, J = 2.2 Hz, 1 H), 5.54 (ddt, J = 15.3, 6.5, 1.5 Hz, 1 H), 5.83 (ddd, J = 6.5, 2.1, 1.1 Hz, 1 H), 6.02 (dtd, J = 15.3, 6.8, 1.1 Hz, 1 H); IR, 3100, 2970, 2940, 2880, 2135, 1700, 1475, 1470, 1380, 1240, 1025, 975 cm^{-1}; MS, $(M - 15)^+$ 151.0741, calcd for $C_9H_{11}O_2$ 151.0756; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 13.5, 20.9, 21.8, 33.9, 63.9, 74.4, 79.9, 124.4, 136.3, 169.0.

(*E*)-1,2,4-Octatriene (6) and (*E*)-2,3,5-Nonatriene (7). To a 100-mL round-bottom flask were added 3.4 g (18 mmol) of CuI and 40 mL of THF. The flask was cooled to −30 °C, and 25 mL (36 mmol, 1.45 M in ether) of MeLi was slowly added by syringe to form the cuprate. The solution was allowed to stir at −30 °C for 3 h, and then 2.5 g (15 mmol) of the above acetate in 10 mL of THF was added. This was left at −30 °C for 45 min, placed in an ice bath for 45 min, and then brought to room temperature for 30 min. The mixture was poured onto ice and pentane (50 mL), and the organic layer was washed with saturated NH_4Cl (5 × 25 mL), water (3 × 25 mL), and brine (2 × 30 mL) and dried by passage through a cone of Na_2SO_4. The solvent was distilled off at atmospheric pressure with a fractional distillation apparatus. The remaining liquid was purified by preparative gas chromatography (SE-30 on Chromosorb W, 10 ft × 0.25 in.) to yield 0.23 g (14%) of **6** (retention time 2.5 min) and 0.29 g (16%) of **7** (retention time 5 min), **6**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.89 (t, J = 7.5 Hz, 3 H), 1.40 (hextet, J = 7.5 Hz, 2 H), 2.05 (q, J = 7.5 Hz, 2 H), 4.86 (dm, J = 5.5 Hz, 2 H), 5.52–5.95 (m, 3 H); IR 2970, 2940, 2880, 1948, 1470, 1450, 1392, 980, 860 cm^{-1}; MS, M^+ 108.0939, calcd for C_8H_{12} 108.0936; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 13.8, 22.6, 34.9, 75.8, 93.2, 124.5, 132.4, 210.6. **7**: ^1H NMR ($CDCl_3$, 270 MHz) 0.92 (t, J = 7.5 Hz, 3 H), 1.41 (hextet, J = 7.5 Hz, 2 H), 1.68 (dd, J = 7.5, 3.5 Hz, 3 H), 2.06 (qm, J = 7.3 Hz, 2 H), 5.25 (pentet m, J = 7.5 Hz, 1 H), 5.62 (dtd, J = 15.5, 7.0, 2.0 Hz, 1 H), 5.74 (ddq, J = 10.0, 7.5, 3.5 Hz, 1 H), 5.85 (ddm, J = 15.5, 10.0 Hz, 1 H); IR, 2960, 2930, 2870, 1940, 1460, 1370, 969, 876 cm^{-1}; MS, M^+ 122.1096, calcd for C_9H_{14} 122.1092; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 13.7, 14.4, 22.6, 34.8, 86.6, 93.4, 125.8, 132.0, 206.7. Anal. Calcd for C_9H_{14}: C, 88.5; H, 11.5. Found: C, 88.81; H, 11.37.

Dimethyl (*E*)-(1α,2β,3α)-6-Ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*E*)-16], Dimethyl (*E*)-(1β,2α,3α)-6-Ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*E*)-17], and **Dimethyl (*Z*)-(1α,2β,3α)-6-Ethylidene-3-propyl-4-cyclohexane-1,2-dicarboxylate [(*Z*)-16].** To a test tube were added 0.15 mL (1 mmol) of the vinylallene **7**, 0.13 g (0.9 mmol) of dimethyl fumarate, several mg of methylene blue, and 3 mL of C_6D_6 (passed through dried alumina). After 3 freeze–thaw cycles, the tube was sealed under argon and placed in a 75 °C oil bath for 4 days. The solvent was removed under vacuum. Analysis of the mixture demonstrated the presence of at least two isomers of the product in an overall yield of 77%. The sample was analyzed by HPLC and found to be an 82:17:1 mixture of (*E*)-**16**, (*E*)-**17**, and (*Z*)-**16**, respectively. The reaction mixture was purified by HPLC in 7% ethyl acetate/hexane (flow rate 4 mL/min) to yield two fractions, one containing ester (*Z*)-**16** (retention time 4 min) contaminated by side products and the other a mixture of (*E*)-**16** and (*E*)-**17** (0.165 g, 68%; retention time 5 min). Ester (*Z*)-**16** was purified by HPLC separation with 5% ethyl acetate/hexane (retention time 8 min, flow rate 4 mL/min), whereas (*E*)-**16** (retention time 12 min) and (*E*)-**17** (retention time = 11 min) were separated by HPLC in 3% THF/hexane (flow rate 4 mL/min). (*E*)-**16**: IR, 3040, 2960, 2875, 1750, 1450, 1375, 1360, 1270, 1210, 1170, 1050, 985, 870, 785 cm^{-1}; MS, M^+ 266.1517, calcd for $C_{15}H_{22}O_4$ 266.1518. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.6; H, 8.3. Found: C, 67.95; H, 8.19.

(*E*)-**17**: IR ($CDCl_3$) 2958, 2934, 2874, 1734, 1437, 1261, 1194, 1162, 1030, 906, 898, 811, 769 cm^{-1}; MS, M^+ 266.1533, calcd for $C_{15}H_{22}O_4$ 266.1518.

(*Z*)-**16**: IR ($CDCl_3$) 3029, 2959, 2933, 2875, 1736, 1438, 1262, 1200, 1176, 1097, 1066, 1014, 914, 811, 764 cm^{-1}; MS, M^+ 266.1530, calcd for $C_{15}H_{22}O_4$ 266.1518.

For NMR data on (*E*)-**16**, (*E*)-**17**, and (*Z*)-**16** see Table I.

Dimethyl (*E*)-1α,2α,3α)-6-Ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*E*)-18], Dimethyl (*E*)-1β,2β,3α)-6-Ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*E*)-19], and Dimethyl (*Z*)-(1α,2α,3α)-6-Ethyldiene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*Z*)-18]. To a test tube were added 0.21 mL (1.4 mmol) of the vinylallene **7**, 0.137 g (1.4 mmol) of maleic anhydride, several mg of methylene blue, and 4 mL of C_6D_6 (passed through dried alumina). After 3 freeze–thaw cycles, the tube was sealed under argon. The tube was left at room temperature for 4 days. The contents were then transferred to a round-bottom flask, and the solvent was evaporated. (*E*)-(1α,2α,3α)-6-ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylic anhydride: ^1H NMR (C_6D_6, 500 MHz) δ 0.76 (t, J = 7.5 Hz, 3 H), 1.12 (m, 2 H), 1.39 (dd, J = 7.3, 1.6 Hz, 3 H), 1.45 (dtd, J = 13.5, 9.0, 6.5 Hz, 1 H), 1.64 (tdd, J = 13.5, 9.2, 6.8 Hz, 1 H), 1.90 (m, 1 H), 2.40 (dd, J = 9, 6 Hz, 1 H), 2.96 (dt, J = 9, 1.5 Hz, 1 H), 5.43 (dm, J = 10 Hz, 1 H), 5.68 (qm, J = 7.3 Hz, 1 H), 6.07 (d, J = 10 Hz, 1 H). Also, two minor isomers were detected at δ 3.01 (dt, J = 9, 1.5 Hz) and 3.16 (dm, J = 9 Hz) in a 91.5:3.2:5.3 ratio.

The product was dissolved in 6 mL of methanol, 0.39 mL (2.8 mmol) of triethylamine was added, and the reaction was stirred at room temperature for 4 h. The mixture was then poured into 2 N HCl (30 mL) and 50% ether/hexane (20 mL). The organic phase was washed with brine (1 × 10 mL), dried by passage through a cone of Na_2SO_4, and evaporated.

The light yellow oil in 8 mL of ether was treated with diazomethane (~2 mmole prepared from 0.36 g of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide.[17] The solvent was evaporated. Analysis by ^1H NMR showed a 70% overall yield for all isomers present (calculated from **7**). The sample was analyzed by gas chromatography and was found to be a 91:6:3 mixture of the three isomers (*E*)-**18**, (*E*)-**19**, and (*Z*)-**18**, respectively. Analysis by HPLC utilizing 3% ethyl acetate/hexane (flow

(16) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(17) Moore, J. A.; Reed, D. E. *Org. Synth.* **1961**, *41*, 16.

Table I. ^1H and ^{13}C NMR Chemical Shifts ($CDCl_3$) for 1,2-Dicarbomethoxy-3-propyl-6-methylene-4-cyclohexenes

	δ			δ	
no.	^{13}C	^1H mult; *J*, Hz	no.	^{13}C	^1H mult; *J*, Hz
		(*E*)-**16**			
1	49.6	3.54 dtd; 10.5, 2.0, 0.5	8*Z*		
2	48.1	2.75 dd; 10.8, 9.6	9	35.4	1.38 m
3	38.6	2.49 m	10	19.0	1.20 m
4	131.0	5.64 dt; 10.2, 2.1	11	14.3	0.83 t; 6.9
5	122.7	6.37 dd; 10.2, 2.5	C=O	174.8	
6	130.2		C=O	173.5	
7*E*			CH_3O	51.9	3.65 s
7*Z*	121.6	5.12 qtt; 7.1, 2.2, 1.1	CH_3O	51.9	3.62 s
8*E*	12.9	1.65 ddt; 7.7, 2.0, 0.7			
		(*Z*)-**16**			
1	41.6	4.00 br d; 3.9	8*Z*	13.4	1.64 d; 7.2
2	45.8	3.22 t; 3.7	9	36.6	1.39 m
3	36.2	2.69 m	10	20.4	1.26 m
4	129.0[a]	5.59 br dd; 10.0, 4.7	11	14.1	0.88 t; 7.2
5	127.6[a]	6.06 br d; 10.4	C=O	174.2	
6	127.6[a]		C=O	173.1	
7*E*	127.1[a]	5.65 br q; 7.2	CH_3O	52.2	3.68 s
7*Z*			CH_3O	52.1	3.66 s
8*E*					
		(*E*)-**17**			
1	44.9	3.58 dt; 11.3, 2.1	8*Z*		
2	46.5	3.17 dd; 11.3, 5.3	9	34.2	1.42 m
3	35.9	2.66 br dq; 9.4, 4.7	10	20.4	1.24 m
4	130.8	5.89 ddd; 10.2, 5.3, 1.3	11	14.2	0.87 t; 7.1
5	122.4[a]	6.41 br d; 10.2	C=O	174.1	
6	130.5		C=O	173.7	
7*E*			CH_3O	51.9	3.73 s
7*Z*	122.3[a]	5.28 br q; 7.1	CH_3O	51.7	3.66 s
8*E*	13.0	1.71 dd; 7.0, 2.1			
		(*E*)-**18**[b]			
1	48.5	3.61 m	8*Z*		
2	45.2	2.90 dd; 6, 4.5	9	34.4	1.39 m
3	37.7	2.36 m	10	20.8	1.39 m
4	129.4	5.62 br d; 10	11	14.1	0.86 t; 7
5	122.8[a]	6.47 dd; 10, 2	C=O	172.5	
6	129.8		C=O	171.7	
7*E*			CH_3O	51.7	3.43 s
7*Z*	122.2[a]	5.38 br q; 7	CH_3O	51.1	3.37 s
8*E*	12.9	1.59 d; 7			
		(*Z*)-**18**			
1	40.7	4.08 d; 4.9	8*Z*	13.5	1.71 d; 7.2
2	45.3	2.93 t; 5.1	9	33.9	1.47 m
3	35.8	2.56 m	10	21.5	1.25 m
4	129.5[a]	5.83 dd; 9.9, 5.5	11	14.2	0.88 t; 7.2
5	128.6[a]	6.04 d; 10.1	C=O	172.3	
6	131.9		C=O	173.0	
7*E*	127.0[a]	5.64 q; 7.1	CH_3O	52.0	3.74 s
7*Z*			CH_3O	51.6	3.63 s
8*E*					
		(*E*)-**19**			
1		3.60 ?	8*Z*		
2		2.53 dd; 10.5, 4.5	9		1.49 m
3		2.86 m	10		1.49 m
4		5.77 br d; 10.5	11		0.89 t; 7
5		6.38 dd; 10.5, 2.5	C=O		
6			C=O		
7*E*			CH_3O		3.69 s
7*Z*		5.44 br q; 7.5	CH_3O		3.60 s
8*E*		1.74 d; 7			
		20			
1	42.3	4.07 d; 3	8*Z*	20.5	1.69 s
2	45.6	3.25 t; 3	9	36.4	1.40 m
3	35.2	2.67 m	10	20.3	1.29 m
4	127.4	5.63 dd; 10, 4.5	11	13.9	0.88 t; 7
5	123.9	6.46 d; 10	C=O	174.0	
6	132.3		C=O	173.5	
7*E*	122.3		CH_3O	51.9	3.65 s
7*Z*			CH_3O	51.8	3.64 s
8*E*	20.1	1.84 s			

Table I (Continued)

no.	δ ^{13}C	δ ^{1}H mult; *J*, Hz	no.	δ ^{13}C	δ ^{1}H mult; *J*, Hz
		21			
1		3.96 d; 2.5	8*Z*		1.72 s
2		3.25 ddd; 5, 3, 1	9		1.36 m
3		2.50 m	10		1.36 m
4		5.52 br d; 10	11		0.90 t; 7
5		6.46 dd; 10, 2.9	C=O		
6			C=O		
7*E*			CH_3O		3.68 s
7*Z*			CH_3O		3.60 s
8*E*		1.83 s			
		22			
1	41.8	4.10 d; 4.5	8*Z*	20.9	1.73 s
2	45.8	2.91 t; 5	9	33.7	1.40 m
3	35.5	2.49 m	10	21.6	1.36 m
4	127.2	5.86 dd; 10.5, 5.5	11	14.2	0.86 t; 7
5	123.2	6.40 d; 10.5	C=O	172.6	
6	131.8		C=O	172.2	
7*E*	124.5		CH_3O	51.5	3.72 s
7*Z*			CH_3O	51.4	3.58 s
8*E*	20.2	1.82 s			
		28[c]			
1	48.9[a]	3.64 dt; 12, 2	8*Z*		
2	48.0[a]	2.81 dd; 11.5, 10	9	35.4	2.45 m
3	38.2	2.50 m	10	18.9	2.26 m
4	128.3	5.69 br d; 10	11	14.1	0.88 t; 7
5	132.0	6.15 dd; 10.2, 2.8	C=O	174.2	
6	139.1		C=O	172.8	
7*E*	112.7	5.01 br s	CH_3O	51.8	3.73 s
7*Z*		4.80 br s	CH_3O	51.8	3.68 s
8*E*					
		29[c]			
1	41.1	?	8*Z*		
2	46.2	3.19 dd; 12, 5.5	9	34.1	?
3	35.8	2.66 m	10	20.4	?
4	128.2	5.92 dd; 10.6, 6	11	14.2	0.87 t; 7.5
5	131.9	6.13 d; 10	C=O	173.3	
6	?		C=O	173.1	
7*E*	113.2	5.04 br s	CH_3O	51.9	3.75 s
7*Z*		4.89 br s	CH_3O	51.7	3.67 s
8*E*					

[a] ^{13}C assignments are uncertain. [b] C_6D_6 solvent for ^{1}H NMR. [c] These isomers were not separated.

Table II. Product Ratios for Vinylallene Diels–Alder Reactions

vinylallene				H face				CH_3 face			
no.	R^1	R^2	R^3	endo	(%)	exo	(%)	endo	(%)	exo	(%)
				Dimethyl Fumarate							
6	H	H	H	**28**	(83)	**29**	(17)				
7	H	CH_3	H	(*E*)-**16**	(82)	(*E*)-**17**	(17)	(*Z*)-**16**	(1)	(*Z*)-**17**	(–)
15[a]	OTBS	CH_3	H	**31**	(85)	**32**	(15)		(–)		(–)
8	H	CH_3	CH_3					**20**	(>99)	**21**	(<1)?
14[a]	OTBS	CH_3	CH_3					**33**	(>95)		(<5)[b]
				Maleic Anhydride							
6[a,c]	H	H	H	**30**	(>95)		(<5)				
7[c]	H	CH_3	H	(*E*)-**18**	(92)	(*E*)-**19**	(5)	(*Z*)-**18**	(3)	(*Z*)-**19**	(–)[d]
15[b,c]	OTBS	CH_3	H	**34**	(>95)		(<5)[b]		(–)		(–)
8[c]	H	CH_3	CH_3					**22**	(>98)	**21**	(<2)[b]
14[b,c]	OTBS	CH_3	CH_3					**35**	(>95)		(<5)[b]

[a] Ratio obtained from NMR spectrum. [b] Minor isomer not available for comparison. [c] Analyzed as the diesters after cleavage and esterification. [d] From NMR analysis of the crude Diels–Alder product. *N*-Methylmaleimide gave a 95:3:2 ratio.

rate 2 mL/min) gave a 94:4:2 ratio of (*E*)-**18**, (*E*)-**19**, and (*Z*)-**18** (retention times 4 min [(*E*)-**18**], 5 min [(*E*)-**19**], and 8 min [(*E*)-**18**]. The three isomers were than separated by preparative HPLC with 3% ethyl acetate/hexane (weight of (*E*)-**18**, 0.201 g, 54% yield). (*E*)-**18**: IR, 3025, 2945, 2905, 2860, 1735, 1430, 1380, 1360, 1330, 1245, 1190, 1160, 1030, 780, 730 cm^{-1}; MS, M^+ 266.1517, calcd for $C_{15}H_{22}O_4$ 266.1512. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.6; H, 8.3. Found: C, 66.57; H, 7.94.

(*Z*)-**18**: IR ($CDCl_3$) 3027, 2999, 2956, 2932, 2874, 1737, 1457, 1437, 1317, 1289, 1258, 1203, 1169, 1105, 1033, 1021; MS, M^+ 266.1508, calcd for $C_{15}H_{22}O_4$ 266.1518.

For NMR data on (*E*)-**18**, (*Z*)-**18**, and (*E*)-**19**, see Table I.

Assignment of Exocyclic Stereochemistry of the Diesters (*E*)-16, (*Z*)-16, (*E*)-17, (*E*)-18, (*Z*)-18, and (*E*)-19 by NOE. The diester was dissolved in $CDCl_3$ and placed in an NMR tube, and after 5 freeze–pump–thaw cycles, the tube was sealed under vacuum. The NOE experiment was run under the following set of conditions. The decoupler was turned on for 5 s without acquiring data to build up the NOE, and then the decoupler was gated off while data acquisition occurred. After data acquisition, 20 s elapsed to allow for the decay of any remaining NOE. The whole process was then repeated. A reference spectrum was obtained first, in which the decoupler had been set downfield of chloroform. The exocyclic vinyl methyl group and the exocyclic vinyl proton

Table III. Cycloaddition Rate Constants for Reactions of Vinylallenes with *N*-Methylmaleimide at 30 °C.

diene	k, M^{-1} s^{-1}	diene	k, M^{-1} s^{-1}
6	3.2×10^{-4}	**14**	4.6×10^{-4}
7	6.8×10^{-4}	**15**[a]	$\sim 1.0 \times 10^{-2}$
8	7.3×10^{-5}	**36**	1.1×10^{-4}

[a] Reaction went to completion in 4 min, only one point rate constant was obtained.

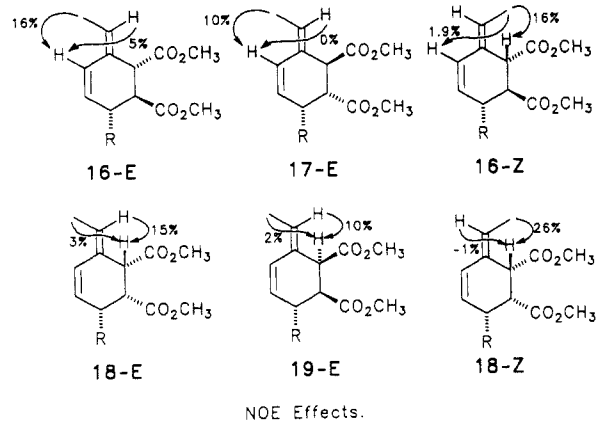


Figure 3. Results from the NOE experiments.

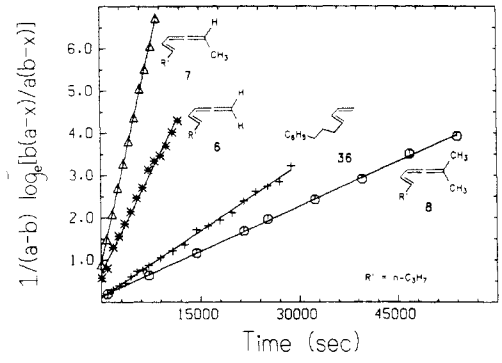


Figure 4. Rate plot of the Diels–Alder reaction of vinylallenes with *N*-methylmaleimide.

were irradiated on each diester. Enhancements are given in Figure 3.

Isomerization of Dimethyl (*E*)-(1α,2α,3α)-6-Ethylidene-3-propyl-4-cyclohexene-1,2-dicarboxylate [(*E*)-18]. To 0.137 g (0.5 mmol) of the dimethyl ester (*E*)-**18** in 4 mL of THF and 0.096 mL (0.55 mmol) of HMPA at −78 °C was added 0.55 mL (0.55 mmol, 1 M in THF/hexane) of LDA. After 10 min, the solution was quenched by addition of acetic acid/THF/methanol (1:49:50). After workup, ^{1}H NMR analysis showed the presence of starting material (*E*)-**18** and diester (*E*)-**17** (66:34).

Dimethyl (1α,2β,3α)-6-Methylene-3-propyl-4-cyclohexene-1,2-dicarboxylate (28) and Dimethyl (1β,2α,3α)-6-Methylene-3-propyl-4-cyclohexene-1,2-dicarboxylate (29). The reaction was carried out as for (*E*)-**16** above, except 0.15 mL (1 mmol) of **6** and 0.13 g (0.9 mmol) of dimethyl fumarate were used. ^{1}H NMR analysis of the mixture showed a 83:17 mixture of **28** and **29**, respectively, in a total yield of 90%. The sample was then purified by HPLC first in 10% ethyl acetate/hexane and then 5% THF/hexane giving 0.207 g (82% yield) of **28** and **29**. Esters **28** and **29** could not be separated under any conditions: IR, 3025, 2970, 2930, 2870, 1740, 1640, 1600, 1440, 1365, 1345, 1285, 1260, 1200, 1160, 1040, 1005, 970, 895, 795, 665 cm^{-1}; MS, M$^+$ 252.1359, calcd for $C_{14}H_{20}O_4$ 252.1356. For NMR data see Table I.

(1α,2α,3α)-6-Methylene-3-propyl-4-cyclohexene-1,2-dicarboxylic Anhydride (30). The reaction was carried out as for (*E*)-**18**, except 0.049 g (0.5 mmol) of maleic anhydride and 0.075 mL (0.5 mmol) of **6** were used. The hydrolysis and esterification steps were not performed. Evaporation of the solvent gave 0.104 g of material. Analysis of the reaction mixture by ^{1}H NMR showed a 95% yield of only one product, anhydride **30**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.92 (t, J = 7 Hz, 3 H), 1.17–1.83 (m, 4 H), 2.57 (m, 1 H), 3.44 (dd, J = 9, 6 Hz, 1 H), 3.92 (d, J = 9 Hz, 1 H), 5.28 (s, 1 H), 5.41 (s, 1 H), 5.86 (dd, J = 10.5, 3 Hz, 1 H), 6.21 (d, J = 11 Hz, 1 H); IR, 2955, 2930, 2870, 1855, 1780, 1635, 1595, 1465, 1380, 1205, 1135, 1065, 1005, 950, 935, 920, 900, 780, 695 cm^{-1}; MS, M$^+$ 206.0943, calcd for $C_{12}H_{14}O_3$ 206.0942; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 14.0, 20.6, 33.4, 34.3, 44.0, 44.7, 117.6, 128.1, 128.2, 131.5, 131.9, 170.4, 170.6.

(*E*)-4-Acetoxy-5-nonen-2-yne. Propyne (8 mL) was condensed into a flask containing 40 mL of THF at −78 °C, and 23 mL (33 mmol, 1.45 M in ether) of MeLi was added slowly. The mixture was left at −78 °C for 20 min and then warmed to 0 °C for 10 min to complete the metalation. A solution of (*E*)-2-hexenal (3.5 mL, 30 mmol) in 10 mL of THF was added. After 20 min at 0 °C, 2.5 mL (35 mmol) of acetyl chloride was added. The reaction was stirred at 0 °C for another 30 min, was warmed to room temperature for 25 min, and was partitioned between saturated $NaHCO_3$ (50 mL) and ether/hexane (1:1; 50 mL). The organic layer was washed with water (2 × 15 mL) and brine (1 × 20 mL), dried by passage through a cone of Na_2SO_4, and evaporated. The oily liquid remaining was purified by Kugelrohr distillation [bp 40–85 °C (0.8 mm)] yielding 4.826 g (89%) of (*E*)-4-acetoxy-5-nonen-2-yne: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85 (t, J = 7 Hz, 3 H), 1.38 (hextet, J = 7.3 Hz, 2 H), 1.83 (d, J = 2.2 Hz, 3 H), 2.0–2.03 (q with s, J = 7 Hz, 5 H), 5.48 (ddt, J = 15.5, 6.5, 1.2 Hz, 1 H), 5.75 (d, J = 5.5 Hz, 1 H), 5.90 (dt, J = 15.5, 7 Hz, 1 H); IR, 2970, 2930, 2880, 2270, 1750, 1470, 1450, 1385, 1245, 1180, 1095, 1030, 980, 965, 930 cm^{-1}; MS, M$^+$ 180.1150, calcd for $C_{11}H_{16}O_2$ 180.1146; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 3.6, 13.6, 21.1, 21.9, 34.0, 64.7, 75.4, 82.8, 125.4, 135.5, 169.2.

(*E*)-2-Methyl-2,3,5-nonatriene (8). A flask containing copper iodide (3.7 g, 19.3 mmol) and 50 mL of THF was placed in a −30 °C cold bath, and 26.6 mL (38.6 mmol, 1.45 M in ether) of MeLi was added. The solution was left at −30 °C for 3 h to complete the formation of the cuprate. A solution of (*E*)-4-acetoxy-5-nonen-2-yne (2.904 g, 16.1 mmol) in 10 mL of THF was added. The mixture was stirred for 20 min at −30 °C, placed in an ice bath for 45 min, and then warmed to room temperature for 30 min. The solution was partitioned between saturated NH_4Cl (75 mL) and pentane (75 mL). The organic layer was washed with water (2 × 20 mL) and brine (1 × 20 mL) and dried by passage through a cone of Na_2SO_4, and the solvent was carefully evaporated. The remaining liquid was purified by Kugelrohr distillation [bp 40–80 °C (15 mm)] producing 1.428 g (65%) of vinylallene **8**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, J = 7 Hz, 3 H), 1.38 (hextet, J = 7.2 Hz, 2 H), 1.69 (d, J = 2.8 Hz, 6 H), 2.03 (q, J = 7.2 Hz, 2 H), 5.47–5.68 (m, 2 H), 5.82 (dd, J = 15, 9.5 Hz, 1 H); IR, 2975, 2945, 2885, 1960, 1470, 1465, 1390, 1375, 1240, 1215, 1200, 980, 975, 850 cm^{-1}; MS, M$^+$ 136.1252, calcd for $C_{10}H_{16}$ 136.1248; ^{13}C NMR ($CDCl_3$, 15 MHz) δ 13.8, 20.6, 22.7, 25.7, 34.8, 92.0, 95.8, 126.6, 131.3, 203.6. Anal. Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.72; H, 11.88.

Dimethyl (1α,2β,3α)-6-(1-Methylethylidene)-3-propyl-4-cyclohexene-1,2-dicarboxylate (20). The reaction was carried out as for (*E*)-**16**, except 0.34 mL (20 mmol) of **8** and 0.144 g (1.0 mmol) of dimethyl fumarate were used. Purification on the chromatotron utilizing 5% ethyl acetate/hexane (collected second band to elute) gave 0.198 g (71%) of **20**. The sample was analyzed by gas chromatography, which shows that **20** was the only isomer formed by a ratio of >170:1. HPLC analysis utilizing 3% ethyl acetate/hexane gave the same results as gas chromatography: IR, 3040, 2960, 2930, 2875, 1740, 1445, 1385, 1250, 1205, 1180, 1120, 1020, 780, 725 cm^{-1}; MS, M$^+$ 280.1675, calcd for $C_{16}H_{24}O_4$ 280.1668. For NMR data see Table I.

Dimethyl (1α,2α,3α)-6-(1-Methylethylidene)-3-propyl-4-cyclohexene-1,2-dicarboxylate (22). The reaction was carried out as for (*E*)-**18**, except 0.67 mL (4.0 mmol) of **8** and 0.39 g (4.0 mmol) of maleic anhydride were used. The solid anhydride was converted to the diester as for (*E*)-**18**.

The sample was purified by preparative TLC on the chromatotron with 5% ethyl acetate/hexane. The most UV intense band was collected. This gave 0.730 g (65% yield from **8**) of diester **22**. Examination of the reaction mixture by HPLC using 3% ethyl acetate/hexane showed ester **22** as the only product in a ratio of >390:1. Gas chromatographic analysis, however, shows possible isomeric products and the best ratio of **22** is 50:1: IR (CCl_4) 2980, 2935, 2880, 1750, 1450, 1270, 1210, 1175, 1120, 1045, 1040 cm^{-1}; MS, M$^+$ 280.1675, calcd for $C_{16}H_{24}O_4$ 280.1668. For NMR data see Table I.

Dimethyl (1β,2α,3α)-6-(1-Methylethylidene)-3-propyl-4-cyclohexene-1,2-dicarboxylate (21). To a solution of the half-ester **25** (0.080 g, 0.3 mmol) in 3 mL of THF was added HMPA (0.10 mL, 0.6 mmol), and the solution was cooled to −78 °C. Upon addition of LDA (0.6 mL, 0.6 mmol, 1 M in THF/hexane), the solution turned dark green. After 10 min, the reaction was quenched by addition of several milliliters of a 90:5:5 THF/methanol/acetic acid mixture. Workup (50% ether/hexane, water, brine) gave crude half-ester, which was converted to diester by treatment with 1 mmol of CH_2N_2 in ether.[17] ^{1}H NMR showed the presence of esters **20** and **22** and at least one new product. HPLC analysis using 3% ethyl acetate/hexane (flow rate 2 mL/min) showed the three components to be present in a 9:69:22 (**20**:**22**:new product) ratio

[retention times 9 min (**20**), 10 min (**22**), and 8 min (new isomer)]. The new isomer was isolated by preparative HPLC with 3% ethyl acetate/hexane and was identified as **21**. For NMR data see Table I.

(1α,2α,3α)-6-(1-Methylethylidene)-2β-methyl-3-propyl-4-cyclohexene-1,2-dicarboxylic Anhydride (26) and Dimethyl (1α,2α,3α)-6-(1-Methylethylidene)-2β-methyl-3-propyl-4-cyclohexene-1,2-dicarboxylate (27). The reaction was carried out as for (*E*)-**18** except 0.090 mL (1.0 mmol) of methylmaleic anhydride and 0.17 mL (1.0 mmol) of **8** were heated to 75 °C for 6 days. ^{1}H NMR analysis showed the presence of only one isomer (regio- or stereoisomer), which was identified as the anhydride **26**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.77 (t, *J* = 7 Hz, 3H), 1.26–1.40 (m with s, 7 H), 1.77 (s, 3 H), 1.83 (s, 3 H), 2.14 (m, 1 H), 3.60 (s, 1 H), 5.68 (dd, *J* = 10.5, 6 Hz, 1 H), 6.37 (d, *J* = 10.5 Hz, 1 H); IR (CCl_4) 2960, 2930, 2870, 1840, 1775, 1450, 1380, 1305, 1245, 1230, 1180, 985, 930, 920, 895 cm^{-1}; MS, M$^+$ 248.1419, calcd for $C_{15}H_{20}O_3$ 248.1407.

Anhydride **26** was converted to diester by methanolysis (MeOH, NEt_3) and esterification (CH_2N_2).[17] ^{1}H NMR showed the presence of only one isomer of the product. The final material was purified by preparative TLC on the chromatotron with 20% ethyl acetate/hexane. The second band gave 0.144 g (49% yield from vinylallene **8**) of the diester **27**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.88 (t, *J* = 7 Hz, 3 H), 1.18 (s, 3 H), 1.22–1.60 (m, 4 H), 1.82 and 1.83 (2 s, 6 H), 2.14 (m, 1 H), 3.60 (s, 3 H), 3.71 (s, 3 H), 3.77 (s, 1 H), 5.76 (dd, *J* = 10.5, 5 Hz, 1 H), 6.35 (d, *J* = 10.5 Hz, 1 H); IR, 2960, 2930, 2880, 1745, 1470, 1445, 1390, 1365, 1270, 1240, 1205, 1175, 1140, 1105 cm^{-1}; MS, M$^+$ 294.1841, calcd for $C_{17}H_{26}O_4$ 294.1824.

Alkylation of Dimethyl (1α,2α,3α)-6-(1-Methylethylidene)-3-propyl-4-cyclohexene-1,2-dicarboxylate. The dimethyl ester **22** (0.204 g, 0.73 mmol), 4 mL of THF, and 0.14 mL (0.80 mmol) of HMPA were cooled to −78 °C and 0.80 mL (0.80 mmol, 1.0 M in THF/hexane) of LDA was added. After 10 min, 0.056 mL (0.90 mmol) of methyl iodide was added. The solution was warmed slightly and poured into a stirred solution of dilute HCl. Workup gave a product shown by ^{1}H NMR analysis to be identical with that of diester **27** reported previously.

7-Phenyl-2-hepten-4-ol. To Mg (6.7 g, 0.28 mol) in ether (200 mL) under a N_2 atmosphere was added 3-phenylbromopropane (24 mL, 0.16 mol). After the addition was complete, crotonaldehyde (11.9 mL, 0.14 mol) was added dropwise. HCl (2 N, ca. 150 mL) was slowly added to the reaction mixture, and the resulting mixture was stirred until the excess Mg was consumed. The ether layer was extracted with 150 mL of 7% $NaHCO_3$ and 150 mL of brine and passed through a cone of Na_2SO_4. Evaporation of the ether gave a yellow liquid, which was purified via Kugelrohr distillation [bp 130–140 °C (4–5 mm)] yielding pure 7-phenyl-2-hepten-4-ol (22 g, 74%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.6 (m, 6 H), 1.68 (d, *J* = 6.3 Hz, 3 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 4.04 (q, *J* = 6.4 Hz, 1 H), 5.45 (dd, *J* = 15.3, 6.8 Hz, 1 H), 5.65 (dq, *J* = 15.3, 6.3 Hz, 1 H), 7.24 (m, 5 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, multiplicity determined by DEPT[18]) δ 17.33 (t), 27.05 (d), 35.52 (d), 36.52 (d), 72.26 (s), 125.29 (s), 125.75 (s), 127.87 (s), 128.01 (s), 134.07 (s), 142.04; IR 3368, 3103, 3080, 3060, 3025, 2928, 2855, 1940, 1868, 1799, 1748, 1666, 1601, 1498, 1450, 1375, 1116, 1067, 1034, 1007, 970, 931, 745, 700 cm^{-1}; MS, M$^+$ 190.1357, calcd for $C_{13}H_{18}O$ 190.1358.

(*E*,*Z*)-7-Phenyl-1,3-heptadiene. To a solution of 2,4-dinitrobenzenesulfenyl chloride (2.40 g, 10.3 mmol) in ethylene dichloride at 0 °C was added a solution of 7-phenyl-2-hepten-4-ol (1.90 g, 10.0 mmol) in Et_3N (3.10 mL, 22.3 mmol). The resulting mixture was refluxed for 1 h. The reaction mixture was cooled and passed along with the pentane washings (30 mL) through a plug of Celite. The solvent was evaporated giving a brown liquid, which was purified on a column of silica gel. The first band to elute (with hexane) was collected, yielding 1.05 g (61%) of a mixture of *E*/*Z* isomers (88:12): ^{1}H NMR ($CDCl_3$, 270 MHz; *E*/*Z*, 88:12) (*E* isomer) δ 1.72 (pentet, *J* = 7.6 Hz, 2 H), 2.12 (q, *J* = 7.3 Hz, 2 H), 2.62 (t, *J* = 7.4 Hz, 2 H), 4.96 (d, 10.1 Hz, 1 H), 5.08 (d, *J* = 16.9 Hz, 1 H), 5.71 (dt, *J* = 15.2, 6.9 Hz, 1 H), 6.06 (dd, *J* = 15.1, 10.3 Hz, 1 H), 6.32 (dt, *J* = 16.9, 10.2 Hz, 1 H), 7.16 (m, 3 H), 7.27 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, multiplicity determined by DEPT[18]) δ 30.81 (d), 31.99 (d), 35.31 (d), 114.77 (d), 125.62 (s), 128.18 (s), 128.33 (s), 131.30 (s), 132.15 (s), 137.15 (s) 142.17; IR (*E*/*Z* mixture) 3085, 3063, 3025, 2928, 2858, 1894, 1820, 1754, 1726, 1694, 1652, 1603, 1497, 1451, 1033, 1001, 971, 953, 900, 748, 699 cm^{-1}.

3-(*tert*-Butyldimethylsiloxy)-1,3,4-hexatriene (3). Excess vinyl bromide (0.740 mL, 10 mmol) was added to *t*-BuLi (7.2 mL, 1.4 M, 10 mmol) and radical inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (1–2 mg) in 20 mL of ether at −78 °C. After 25 min at −78 °C, a solution of 1-(*tert*-butyldimethylsilyl)-2-bromobut-2-en-1-one (1.05 g, 4 mmol) in 5 mL of ether was transferred by cannula to the vinyllithium solution. The reaction mixture was stirred at −78 °C for 20 min, then a few drops of Et_3N were added, and the solution was poured into a separatory funnel containing ether/hexane (1:1) and saturated $NaHCO_3$. The organic phase was washed with H_2O and brine, poured through Na_2SO_4, and dried over K_2CO_3. Kugelrohr distillation [bp 26–60 °C (0.2 mm)] gave 0.610 g (72% yield) of 3-(*tert*-butyldimethylsiloxy)-1,3,4-hexatriene, a pale yellow liquid: ^{1}H NMR (270 MHz) δ 0.10 (s, 6 H), 0.93 (s, 9 H), 1.72 (d, *J* = 7.0 Hz, 3 H), 4.99 (dt, *J* = 10.3, 1.8 Hz, 1 H), 5.41 (dt, *J* = 16.9, 1.8 Hz, 1 H), 5.64 (br q, *J* = 7.0 Hz, 1 H), 6.08 (dd, *J* = 16.9, 10.6 Hz, 1 H); IR, 2967, 2865, 1937, 1620, 1484, 1474, 1255, 1060 cm^{-1}.

(*E*)-4-(*tert*-Butyldimethylsiloxy)-2-methyl-2,3,5-nonatriene (14). To a mixture of 3 mL of ether and *n*-BuLi (0.12 mL, 0.2 mmol, 1.71 M in hexane) at −78 °C was added 0.025 mL (0.2 mmol) of vinyl iodide **10** in 2 mL of ether via cannula. After 20 min, 0.042 mL (0.2 mmol) of silyl ketone **12** was added. The mixture was stirred at −78 °C for 1 h and warmed to room temperature and several milliliters of triethylamine added to prevent hydrolysis during workup. The solution was extracted with $NaHCO_3$. The organic layer was washed with brine (1 × 10 mL) and dried by passage through a cone of Na_2SO_4 and the solvent evaporated. The oil remaining was purified by placing under vacuum to remove any volatile impurities: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.10 (s, 6 H), 0.92 (t, *J* = 7 Hz, 3 H), 0.95 (s, 9 H), 1.42 (hextet, *J* = 7 Hz, 2 H), 1.76 (s, 6 H), 2.06 (q, *J* = 7 Hz, 2 H), 5.72 (d, *J* = 15.5 Hz, 1 H), 5.88 (dt, *J* = 15.5, 6.5 Hz, 1 H); IR, 2960, 2922, 2898, 2860, 1946, 1740, 1640, 1467, 1261, 1240, 1065, 968, 842, 788 cm^{-1}; MS, M$^+$ 266.2065, calcd for $C_{16}H_{30}SiO$ 266.2058.

(*E*)-4-(*tert*-Butyldimethylsiloxy)-2,3,5-nonatriene (15). To a mixture of 3 mL of ether and 0.12 mL of *n*-BuLi (0.2 mmol, 1.71 M in hexane) was added 0.025 mL (0.2 mmol) of vinyl iodide **10** as a solution in 1 mL of ether. After 20 min, 0.040 mL (0.2 mmol) of silyl ketone **13** in 1 mL of ether was added via cannula. The mixture was stirred at −78 °C for 1 h and warmed to room temperature and several milliliters of triethylamine added to prevent hydrolysis during workup. The solution was extracted with saturated $NaHCO_3$. The organic layer was washed with brine (10 mL), dried by passage through a cone of Na_2SO_4, and evaporated. The oil remaining was purified by placing under vacuum to remove any volatile impurities: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.11 (s, 6 H), 0.90 (t, *J* = 7 Hz, 3 H), 0.93 (s, 9 H), 1.41 (hextet, *J* = 7 Hz, 2 H), 1.72 (d, *J* = 7 Hz, 3 H), 2.06 (qm, *J* = 7 Hz, 2 H), 5.62 (qm, *J* = 7 Hz, 1 H), 5.73 (dm, *J* = 15 Hz, 1 H), 5.89 (dtd, *J* = 15, 7, 1 Hz, 1 H); IR, 2960, 2938, 2900, 2860, 1940, 1660, 1642, 1580, 1470, 1250, 990, 970, 845, 788 cm^{-1}; MS, M$^+$ 252.1909, calcd for $C_{15}H_{28}SiO$ 252.1902.

Rate of Reaction of (*E*)-1,2,4-Octatriene (6) with *N*-methylmaleimide. To an NMR tube were added *N*-methylmaleimide (25.5 mg, 0.230 mmol) and *p*-dichlorobenzene (10.4 mg, 0.071 mmol; internal standard). A solution of **6** (9.8 mg, 0.91 mmol) in 0.5 mL of C_6D_6 was added to the NMR tube. The components were mixed, frozen, and degassed. The sample was placed in the NMR probe at 30 °C, and spectra were taken over a 6.5-h period with an automated program. The concentration of the product at various times was determined from each NMR spectrum. The second-order rate constant (3.16×10^{-4} M^{-1} s^{-1}) resulting from the plot of $[1/(a-b)]\ln[b(a-x)/a(b-x)]$ vs time (seconds) was obtained, where *X* was the concentration of product at time *t*, *a* was the initial concentration of the vinylallene (0.137 M), and *b* was the initial concentration of *N*-methylmaleimide (0.45 M).

Other rates were determined similarly and are listed in Table III.

(1α,2α,3α)-*N*-Methyl-3-(3-phenylpropyl)-4-cyclohexene-1,2-dicarboximide. A solution of (*E*,*Z*)-7-phenyl-1,3-heptadiene [*E*/*Z* (88:12); 0.39 g, 2.3 mmol] and *N*-methylmaleimide (0.17 g, 1.5 mmol) in 6 mL of benzene under a N_2 atmosphere was stirred at 22 °C for 66 h. The solvent was evaporated, and the resulting colorless liquid was purified by TLC (1:1 EtOAc/hexane). Workup and characterization of the band at R_f 0.6 produced 0.40 g of the desired imide and *N*-methylmaleimide (89:11). An analytical sample of the desired imide was obtained by TLC (1:1 EtOAc/hexane), collecting the top half of the band at R_f 0.6: ^{1}H NMR ($CDCl_3$, 500.1 MHz) δ 1.79 (m, 3 H), 1.96 (m, 1 H), 2.14 (m, 1 H), 2.27 (m, 1 H) 2.69 (m, 3 H), 2.91 (s, 3 H), 3.09 (m, 2 H), 5.75 (dt, *J* = 9.2, 3.3 Hz, 1 H), 5.86 (ddt, *J* = 9.2, 6.2, 3.2 Hz, 1 H), 7.17 (dm, *J* = 7.5 Hz, 1 H), 7.20 (dm, *J* = 7.5 Hz, 2 H), 7.28 (tm, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, multiplicity determined by DEPT[18]) δ 24.23 (d), 24.68 (t), 30.05 (d), 30.96 (d), 35.95 (d), 36.10 (s), 40.39 (s), 43.06 (s), 125.72 (s), 127.33 (s), 128.28 (s), 128.35 (s), 133.93 (s), 142.37, 177.93, 179.94; IR ($CDCl_3$) 3086, 3064, 3029, 2939, 2858, 1772, 1696, 1492, 1438, 1388, 1288, 1126 cm^{-1}; MS, M$^+$ 283.1572, calcd for $C_{18}H_{21}NO_2$ 283.1572.

(1α,2α,3α)-*N*-Methyl-6-methylidene-3-propyl-4-cyclohexene-1,2-dicarboximide. The adduct obtained from the reaction of **6** with *N*-methylmaleimide was purified by TLC (1:1 Et_2O/pentane). The band

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at R_f 0.25 was the desired product contaminated with *N*-methylmaleimide. An analytical sample was obtained by HPLC (1:9 EtOAc/hexane). The first band to elute was the desired product: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (t, J = 7 Hz, 3 H), 1.30–1.81 (m, 4 H), 2.53 (m, 1 H), 2.93 (s, 3 H), 3.18 (dd, J = 8.5, 6 Hz, 1 H), 3.65 (d, J = 8.5 Hz, 1 H), 5.20 (s, 1 H), 5.45 (s, 1 H), 5.83 (dd, J = 10, 4 Hz, 1 H), 6.20 (dd, J = 10, 2 Hz, 1 H); IR (CCl_4) 2980, 2950, 2890, 1795, 1730, 1455, 1405, 1305, 1130, 1040, 990 cm^{-1}; MS, M$^+$ 219.1259, calcd for $C_{13}H_{17}NO_2$ 219.1255.

***N*-Methyl-6-ethylidene-3-propyl-4-cyclohexene-1,2-dicarboximide**: (*E*)-(1α,2α,3α) isomer: ^{1}H NMR (C_6D_6, 500 MHz) δ 0.87 (t, J = 7.2 Hz, 3 H), 1.28 (m, 2 H), 1.52 (dd, J = 7.2, 1.0 Hz, 3 H) 1.63 (dtd, J = 13, 9, 6 Hz, 1 H), 1.88 (ddt, J = 13, 9.5, 7 Hz, 1 H), 2.09 (tdd, J = 9, 6.5, 3.5 Hz, 1 H), 2.44 (dd, J = 8, 6 Hz, 1 H), 2.61 (s, 3 H), 3.01 (dt, J = 8.5, 1.5 Hz, 1 H), 5.58 (ddd, J = 10, 3.5, 1.5 Hz, 1 H), 5.89 (qqd, J = 7.2, 1.5, 0.8 Hz, 1 H), 6.22 (dm, J = 10 Hz, 1 H); IR (CCl_4) 2950, 2920, 2860, 1770, 1705, 1430, 1380, 1285, 1105, 975 cm^{-1}; MS, M$^+$ 233.1416, calcd $C_{14}H_{19}NO_2$ 233.1411.

Also, two minor isomers were detected δ 3.07 (dt, J = 10, 2.5 Hz) and δ 3.31 (dm, J = 10 Hz) in a 95.1:2.6:2.3 ratio.

(1α,2α,3α)-*N*-Methyl-6-isopropylidene-3-propyl-4-cyclohexene-1,2-dicarboximide: ^{1}*H* NMR ($CDCl_3$, 200 MHz) δ 0.95 (t, J = 7.2 Hz, 3 H), 1.43–1.89 (m, 4 H), 1.91 (s, 3 H), 2.00 (s, 3 H), 2.29 (m, 1 H), 2.79 (s, 3 H), 3.18 (dd, J = 8.5, 6 Hz, 1 H), 4.02 (d, J = 8.2 Hz, 1 H), 5.65 (dd, J = 10, 3.5 Hz, 1 H), 6.35 (dd, J = 10, 2 Hz, 1 H); IR (CCl_4) 2950, 2920, 2965, 1770, 1705, 1430, 1380, 1285, 1260, 1105, 1005, 965 cm^{-1}; MS, M$^+$ 247.1556, calcd for $C_{15}H_{21}NO_2$ 247.1567.

(1α,2α,3α)-*N*-Methyl-5-(*tert*-butyldimethylsiloxy)-6-ethylidene-3-propyl-4-cyclohexene-1,2-dicarboximide: ^{1}H NMR ($CDCl_3$, 200 MHz) δ –0.04, 0.00 (2 s, 6 H), 0.82 (s, 9 H), 0.91 (t, J = 7 Hz, 3 H), 1.30–1.82 (m, 4 H), 1.88 (d, J = 7.2 Hz, 3 H), 2.25 (m, 1 H), 2.87 (s, 3 H), 3.06 (dd, J = 8.5, 5.5 Hz, 1 H), 3.50 (d, J = 8.5 Hz, 1 H), 4.80 (d, J = 3 Hz, 1 H), 5.74 (q, J = 7.2 Hz, 1 H); IR, 2950, 2920, 2850, 1770, 1700, 1610, 1435, 1380, 1285, 1260, 1200, 1170, 1110, 970, 925, 905, 840, 790, 735 cm^{-1}; MS, *m/e* 364, 320, 308, 211.

(1α,2α,3α)-*N*-Methyl-5-(*tert*-butyldimethylsiloxy)-6-isopropylidene-3-propyl-4-cyclohexene-1,2-carboximide: ^{1}H NMR ($CDCl_3$, 200 MHz) δ –0.09, –0.04 (2 s, 6 H), 0.84 (s, 9 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.30–1.86 (m, 4 H), 1.96 (s, 3 H), 2.13 (m, 1 H), 2.86 (s, 3 H), 3.06 (dd, J = 8.2, 5 Hz, 1 H), 4.00 (d, J = 8.2 Hz, 1 H), 4.75 (d, J = 3.4 Hz, 1 H); IR, 2950, 2920, 2850, 1775, 1700, 1610, 1470, 1465, 1430, 1385, 1340, 1285, 1260, 1200, 1110, 980, 930, 905 cm^{-1}; MS, M$^+$ 377.2387, calcd for $C_{21}H_{35}NO_3Si$ 377.2377.

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Solvent and Salt Effects on Binding Constants of Organic Substrates in Macrocyclic Host Compounds. A General Equation Measuring Hydrophobic Binding Contributions[1]

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Abstract: The variation of association constants K_A is investigated with an azoniacyclophane **1**, binding, e.g., negatively charged fluorescence dyes, both by lipophilic and polar interactions, with α-cyclodextrin **2**, showing extremely large lipophilic contributions, and with a macrocyclic tetraphenolate **3**, characterized by almost entirely electrostatic binding mechanisms with ammonium compounds. For a series of aqueous organic solvent mixtures, all log K_A values correlate linearly with solvophobicity parameters S_p of the corresponding medium; the sensitivity a, expressed as the change in K_A between water ($S_p \equiv 1.0$) and hydrocarbon ($S_p \equiv 0.0$) ranges from $10^{1.2}$ (with **3**) to 10^7 (with **2**). The slope a and the ordinate log K_A^0 (for $S_p = 0.0$) from seven very different systems again correlate linearly, showing that both a and K_A^0 can be used as a measure of hydrophobic contributions to binding; both parameters indicate, e.g., for cyclodextrin, an extremely hydrophobic binding mechanism. Salt effects are found to be large only for ion–ion combinations of hosts **1** and **3** with guest compounds bearing opposite charges; they show surprisingly linear correlations as a Debye–Hückel type function of the ionic strength and allow predictable K_A variation by added salts. The decrease of K_A by an organic salt competing with the observed guest, however, can amount to a factor of ~70 with a commonly used glycine buffer. Improved methods for the optimal planning and evaluation of experiments for the K_A determinations are described.

Several aspects make the investigation of solvent and salt effects on organic host–guest equilibria to a timely subject: the use of such systems as synthetic receptor and enzyme analogues[2] requires a sufficient concentration of complexed material; this can be drastically lowered either by organic solvents, which may be necessary for solubility enhancement, or by salts, which are needed as buffer, or as reagents, or as cosubstrates. Furthermore, a predictable change of complexation constants is also useful for investigations of equilibria and rates under varied conditions dictated by the suitable spectroscopic or kinetic method. Besides these practical aspects, which were an incentive for the present study, solvent and salt effects are expected to shed light on the complex binding mechanisms, which are also relevant for the understanding of analogous biological systems.

Detailed studies along these lines have been undertaken largely with crown ethers and cryptands complexing mostly smaller cations.[3a] The full understanding of medium effects on complex

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