to surmount. Moreover, our calculations without the full optimization overestimate the barrier height. The primary hydroxy groups on the glucopyranose unit turn inward to fill the empty space formerly occupied by one DOTC molecule, and this yields a strain in the CD ring higher than in the fully optimized monomer inclusion compound. The calculation on the $(DODC)_2$-β-CD system also gives two potential barriers. The height of the second, higher, barrier is rather large (42 kcal mol^{-1}) in this case. This is due to the shorter methine chain in DODC compared to DOTC which forces the CD ring to deform more severely than in the DOTC case. However, the actual barrier height must be much smaller than calculated, because the inclusion of the DODC dimer as well as the DOTC dimer in a β-CD cavity occurs experimentally.[11,12] The dye molecule remaining in the CD cavity must make some displacement in the y and/or z direction which would reduce the barrier height. A full optimization with such displacements should result in a smaller barrier height.

Conclusions

Molecular mechanics calculations are applied to inclusion compounds formed by cyanine dye monomers or dimers and β- or γ-CD. These calculations account for the stabilization of the total system by the inclusion process and explain why the $(DOC)_2$-β-CD system is much less stable than other systems. This result is in accordance with the experimental studies which find that the DODC and DOTC dimers are included in both β- and γ-CD cavities, whereas the DOC dimer is included only in a γ-CD cavity. The calculations show that the dimer dye–CD (D_2–CD) system is more stable than the corresponding monomer dye–CD (D–CD) system, except for the case of DOC and β-CD. This feature is rationalized by noting that the van der Waals stabilization energy is larger in the D_2–CD system where the atomic pair distances between the guest and host are smaller than in the D–CD case. Among many factors which influence the energetics of inclusion, the van der Waals interaction dominates in the stabilization. Electrostatic guest–host interactions and dimerization of the dye play additional roles.

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Supplementary Material Available: Procedure for the determination of MM force-field parameters of cyanine dyes; a table on the comparison of bond lengths and bond angles of the MMP2-optimized and MNDO-optimized structures of DOC, DODC, and DOTC; figures on the structure of α-CD dihydrate ($(H_2O)_2$ inclusion compound) optimized by the MMP2 calculation (with and without the charge option) and the experimental structure (data from ref 15) of α-CD hexahydrate for comparison; tables on the comparison of bond lengths, bond angles, and dihedral angles of the MMP2-optimized (with and without the charge option) and experimental (from ref 15) structures of α-CD; tables of net atomic charges of DOC and DODC; figures of optimized geometry of β-CD and γ-CD with several different symmetries; figures of the optimized geometry of $(DOC)_2$-, $(DODC)_2$-, $(DOTC)_2$-γ-CD, DOC-, DOTC-β-CD, DOC-, DODC-, and DOTC-γ-CD inclusion compounds (29 pages). Ordering information is given on any current masthead page.

Thermal Rearrangements of Allenes. Synthesis and Mechanism of Cycloaromatization of π and Heteroatom Bridged Diallenes[1]

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Abstract: The synthesis and thermal rearrangement of several π and heteroatom bridged diallenes has been investigated. *o*-Diallenylbenzenes **5**, **14**, **24** and bis(γ,γ-dimethylallenyl) ether **8** were prepared by addition of dibromocarbene to the corresponding divinyl precursor, followed by treatment of the resulting dibromocyclopropane derivative with methyllithium. Bis(γ,γ-dimethylallenyl) sulfide **10** was generated by reaction of (γ,γ-dimethylallenyl)lithium with sulfur dichloride, while the corresponding selenides **12** and **16** were synthesized by an S_N2' reaction of sodium selenide with α,α-dimethylpropargyl bromide. All diallenes prepared display a remarkable thermal reactivity and undergo a facile cycloaromatization. Gentle heating of diallenes **5**, **14**, **12**, and **16** gave the naphthalene derivatives **6** and **15** and selenophene derivatives **13** and **17**, respectively, in practically quantitative yields. Diallenes **8**, **10**, and **24** underwent spontaneous cyclization during preparation yielding furan **9**, thiophene **11**, and naphtho[*b*]cyclobutane **25**, respectively. A kinetic study of the rearrangement and measurement of the kinetic isotope effect using diallenes **5**, **14**, **12**, and **16**, revealed that the cyclization is a two-step process. The first and rate-determining step is an electrocyclic reaction yielding as intermediates ω-xylylenes **20** and **21**, while the second and more rapid step entails a [1,5]hydrogen transfer.

Allenes, the simplest and best studied of all cumulenes, have reached their 100th anniversary.[2,3] One of the best studied and most useful reactions of allenes is their thermal dimerization to 1,2-dimethylenecyclobutanes.[4] The central mechanistic question

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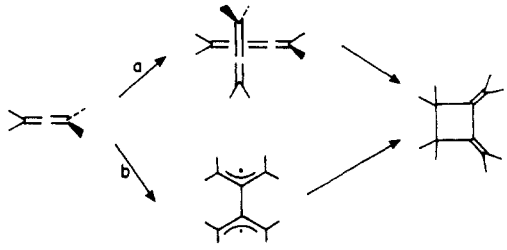
of this reaction has been whether the process is concerted or free radical in nature (eq 1).

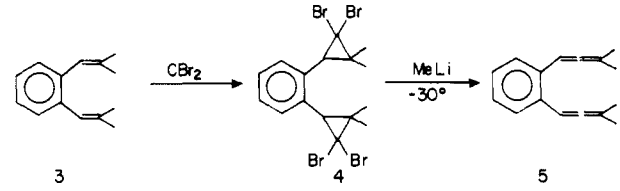


(1)

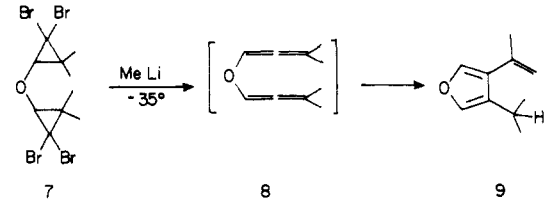
The concerted electrocyclic $[\pi_s^2 + \pi_a^2]$ mechanism requires a perpendicular approach of the two allenic partners and is an allowed process[5] but is unable to explain the complete absence of the 1,3-dialkylidenecyclobutane isomers in the cyclodimerization of substituted allenes.[3b,4,6] The formation of 1,3-dimethylenecyclobutane as a minor product has only been reported for the reaction of allene itself, at elevated temperatures.[4,7a] On the other hand, assuming that dimerization takes place by a free-radical mechanism,[3a] one may suggest a two-step process, involving formation of an orthogonal 2,2'-bisallyl (tetramethyleneethane) diradical in the first step, followed by formation of a σ bond between the two allylic carbons and ring closure. The actual configuration of the intermediate, planar or orthogonal, as well as the mode of its cyclization are influenced by the nature of the substituents.[6-13]

From this brief review one may conclude that the question of the mechanism of allene dimerization has not been settled, as yet. The general tendency is to explain the reaction by a two-step mechanism involving the intermediacy of a 2,2'-bisallyl diradical. However, the concerted $[\pi_s^2 + \pi_a^2]$ mechanism cannot be ruled out, since occasionally it offers a simpler and more convenient interpretation.

Scheme I



Scheme II



In view of the great amount of interesting work performed so far on the intermolecular dimerization of monoallenic systems, it is surprising that the study of the corresponding intramolecular process of diallenic systems has received relatively little attention in the past. 2,7-Dimethyl-2,3,5,6-octatetraene, 1,2,6,7-octatetraene, and 1,2,6,7-cyclodecatetraene undergo intramolecular reactions to various products.[14] In the reaction of the second diallene, a triplet diradical intermediate has been detected by the use of the CIDNP technique.[14a] Examination of the thermal intramolecular dimerization of both meso and racemic 2,3,7,8-decatetraenes has shown that the lifetime of the postulated diradicals is long enough for bond rotation and loss of stereochemistry before ring closure.[15] Conjugated diallenes undergo thermal cyclization to derivatives of 3,4-dimethylenecyclobutenes[14a,16] and have been suggested as intermediates in the rearrangement of 1,5-hexadiynes to the same type of products.[17]

Bridging of two allenic units by a double bond gives rise to an exceptionally active diallenic system which upon intra-intermolecular reaction may produce a number of products. For example, 1,2,4,6,7-octapentaene and 1,2-diallenylbenzene undergo rapid intramolecular cyclization with subsequent intermolecular coupling of the reaction intermediates to produce dibenzo- and dinaphthocyclooctadienes, respectively, together with other dimeric products. These intermediates can also be trapped by means of $^3O_2$ and active dienophiles and have been suggested to have a 1,2-quinodimethane structure.[18] Bridging of the two allenyl groups by heteroatoms possessing unshared electron pairs may also cause rapid intramolecular dimerization.[19] Thus, diallenyl sulfide, ether, bis(γ-phenylallenyl)-*N*-methylamine, and diallenyl-*N*-ethylamine and bis(γ-*tert*-butylallenyl) sulfide, ether, and *N*-methylamine have been reported to undergo cyclization to heteroaromatic systems.[19]

All the bridged diallenic systems mentioned so far are either lacking an allylic hydrogen or are unsubstituted at the γ-carbon. Previously, we have shown that bis(γ,γ-dimethylallenyl) sulfone (**1**) undergoes a facile cyclization on heating at 75 °C to 3-iso-

(1) Taken in part from the Ph.D. Thesis of Y. Duar, Bar-Ilan University Ramat-Gan, 1982. Presented in part at a plenary lecture at the Eleventh International Symposium on the Organic Chemistry of Sulfur, Lindau, FRG, September 10–14th, 1984. See: Braverman, S. *Phosphorus Sulfur* **1985**, *23*, 297.

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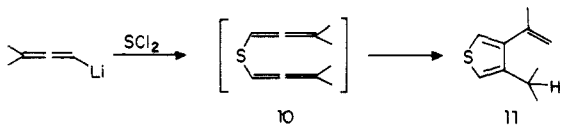
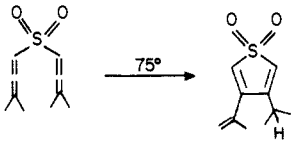
Scheme III



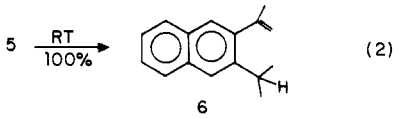
propenyl-4-isopropylthiophene 1,1-dioxide (**2**) in quantitative yield.[20] A mechanistic study of this reaction suggested a two-step



process involving intramolecular formation of a 2,2'-bisallyl-type diradical intermediate in the first, rate-determining step, followed by a fast intramolecular hydrogen abstraction and formation of the new double bond. Prompted by these results we decided to investigate the cyclization of other bridged bis(γ,γ-dimethylallenes), especially those in which the bridge contributes an aromatic character, and consequently an extra driving force for cyclization. In this paper, we describe results of a detailed study of the preparation of various π and heteroatom bridged bis(γ,γ-dimethylallenes), their facile and practically quantitative cycloaromatization, as well as a more quantitative study of the reaction mechanism.[21]

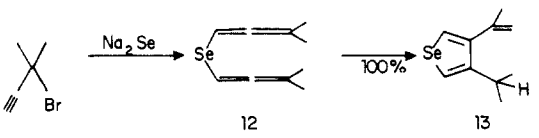
Results and Discussion

Synthesis and Cycloaromatization of Bridged Diallenes. Unlike the convenient preparation of diallenic sulfones involving a double [2,3]sigmatropic rearrangement of propargylic sulfoxylates,[20,22] the preparation of the bridged diallenes described below was based on general methods of allene synthesis[23] and usually involved several steps of a varying degree of efficiency. For example, *o*-bis(γ,γ-dimethylallenyl)benzene (**5**) was prepared by the sequence shown in Scheme I. *o*-Diisobutenylbenzene (**3**)[24] was obtained by a Wittig reaction between isopropyltriphenylphosphonium bromide[25] and phthaldialdehyde. Addition of dibromocarbene to **3** proceeds in low yield by using either phase-transfer catalysis[26] or more conventional methodology. On the other hand, the conversion of the addition product **4** to the desired diallene **5**, using the well-known methyllithium procedure[23,27] proceeded in high yield. The latter, a liquid, could be stored in the cold for several days only, due to its facile rearrangement. The product, 2-isopropenyl-3-isopropylnaphthalene (**6**), a white crystalline solid, is obtained in quantitative yield on standing in ether solution at room temperature overnight.



(2)

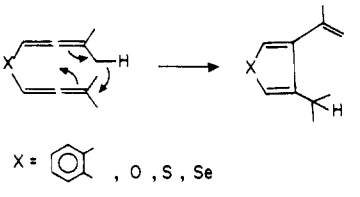
Scheme IV



Attempted preparation of bis(γ,γ-dimethylallenyl) ether (**8**) by a similar procedure (Scheme II) has shown that the product cannot be isolated under the reaction conditions due to its spontaneous cyclization to 3-isopropenyl-4-isopropylfuran (**9**). The reaction of ether **7** with methyllithium at −35 °C afforded cycloaromatization product **9** directly in high yield. Similar results were also obtained in the preparation of bis(γ,γ-dimethylallenyl) sulfide (**10**). Although diisobutenyl sulfide was easily prepared by base-catalyzed isomerization of dimethallyl sulfide,[28] the compound failed to undergo dibromocarbene addition under a variety of conditions[26,29] apparently due to competing addition to the sulfur atom.[30] The S_N2' reaction of sodium sulfide on α,α-dimethylpropargyl bromide under various conditions was also unsuccessful in spite of the facile S_N2' reaction of this substrate with sodium selenide (vide infra) or sodium thiocyanate.[31] However, reaction between sulfur dichloride and (γ,γ-dimethylallenyl)lithium, prepared by treatment of the corresponding bromide with butyllithium, afforded 3-isopropenyl-4-isopropylthiophene (**11**) directly but in only very low yield (Scheme III).

Bis(γ,γ-dimethylallenyl) selenide (**12**) was conveniently prepared by the S_N2' reaction of sodium selenide with α,α-dimethylpropargyl bromide.[32] The new selenide **12** readily undergoes cyclization to 3-isopropenyl-4-isopropylselenophene (**13**) on mild heating and in quantitative yield. Bis(γ,γ-dimethylallenyl) telluride can be prepared in an analogous manner, by reaction of sodium telluride with α,α-dimethylpropargyl bromide. However, this compound is very unstable and decomposes even during its isolation. Nevertheless, both its formation and its cyclization at room temperature to the tellurium analogue of **13** could be observed by NMR and IR spectroscopy.

One-Step Process. Unlike the γ-unsubstituted and γ-*tert*-butyl- or phenyl-substituted diallenes,[19] the γ-methyl-substituted diallenes **5**, **8**, **10**, and **12** are well suited for the occrrence of a facile one-step intramolecular ene reaction (eq 3).[33] This reaction is allowed



(3)

by the rules of orbital symmetry conservation and can also be regarded as a variant of the symmetry-allowed 1,5-hydrogen shift.[5,34] Furthermore, it can be shown that energetically alkylallenes are better suited for ene reactions than the corresponding alkylolefins. It is therefore not surprising that this reaction is well-documented for both inter-[35] as well as intramolecular[36]

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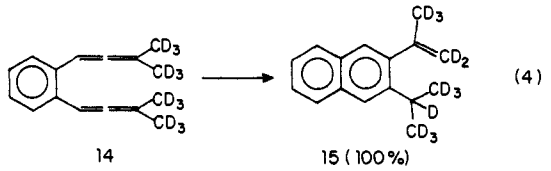
reactions of alkylallenes with various enophiles. Recalling that the cyclization of the bridged diallenes described above is also favored energetically by the accompanying aromatization, one may assume that these reactions indeed occur by such a one-step process. This possibility has been tested by the use of the kinetic isotope effect, and for this purpose deuterated substrates **14** and **16** were prepared.

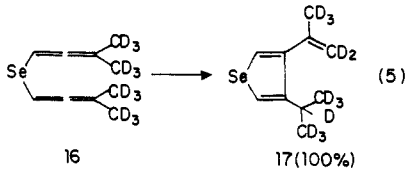
In order to prepare *o*-bis(γ,γ-dimethyl-d_6-allenyl)benzene (**14**) by using the procedure shown in Scheme I, *o*-bis(β,β-dimethyl-d_6-vinyl)benzene was required. We first attempted to prepare this compound by a Wittig condensation of the double ylide resulting from *o*-xylylenebis(triphenylphosphonium bromide)[37] with acetone-d_6, by using sodium hydride in DMSO to improve the low reactivity of acetone.[38] However, since part of the deuterium atoms in the product were replaced by hydrogen, this relatively short route was abandoned. Therefore, the original procedure has been used, involving LAH reduction of acetone-d_6, followed by bromination with HBr and Wittig reaction as described for the preparation of **3**. Deuterated diallene **14** was then prepared by the dibromocarbene method as shown in Scheme I and was positively identified by its molecular peak of 222 in the mass spectrum and complete absence of allylic hydrogens in the NMR spectrum. Diallene **14** rearranged to 2-pentadeuterioisopropenyl-3-heptadeuterioisopropylnaphthalene (**15**) under identical conditions to the undeuterated compound **5** and in practically quantitative yield.



(4)

14 15 (100%)

Bis(γ,γ-dimethyl-d_6-allenyl) selenide (**16**) was prepared as described above for the undeuterated compound (**12**), by the action of sodium selenide on α,α-dimethyl-d_6-propargyl bromide, which in turn was prepared by condensation of lithium monoacetylide[39] with acetone-d_6, followed by reaction with PBr_3. Deuterated diallene **16** underwent cycloaromatization to 3-pentadeuterioisopropenyl-4-heptadeuterioisopropylselenophene (**17**) under exactly the same conditions as the undeuterated analogue and in practically quantitative yield.



(5)

16 17 (100%)

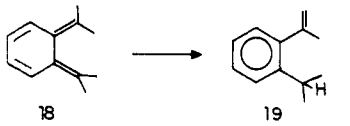
Kinetic Measurements and Isotope Effects. In order to gain information with regard to the mechanism of cycloaromatization of the bridged diallenes **5** and **12** to **6** and **13**, respectively, a kinetic study of the reaction was undertaken with special attention to the effect of solvent polarity and deuterium substitution on the rate of cyclization. The first-order rate constants for disappearance of diallenylbenzene **5** and selenide **12** as well as for their corresponding deuterated analogues **14** and **16** are presented in Tables I and II.

[1,5]Sigmatropic hydrogen migrations have been studied extensively in both cyclic and acyclic systems.[34] Because of the pericyclic nature of these rearrangements, the values of the kinetic isotope effects observed are usually high. For example, in the [1,5]hydrogen migration of 1-methylcyclopentadiene k_H/k_D = 5.75 (27 °C),[40a] while a comparison of the rate of rearrangement of 1,1-dideuterio-1,3-pentadiene with that of 5,5,5-trideuterio-1,3-pentadiene gave k_H/k_D = 12.2 (25 °C).[40b] Similarly, for the [1,5]hydrogen migration of the transient 7,7,8,8-tetramethyl-*o*-xylylene (**18**) to styrene derivative **19** a kinetic isotope effect (k_H/k_D) of 5.4 (38.5 °C) was observed.[41]

Table I. Rate Constants[a] for the Rearrangement of Diallenylbenzene **5** to Naphthalene **6** (k_H) and Diallenylbenzene **14** to Naphthalene **15** (k_D)

solvent	temp, °C	$10^5 k_H$, s^{-1} [b]	$10^5 k_D$, s^{-1} [b]	k_H/k_D
carbon tetrachloride[c]	30	7.625 ± 0.188	7.753 ± 0.289	0.98
	50	27.65 ± 0.98		
chloroform-d_1[d]	30	9.430 ± 0.244	9.389 ± 0.179	1.00
	50	47.77 ± 1.96		
acetone-d_6	30	8.707 ± 0.205		

[a] Determined by NMR. [b] [Diallene] = 0.45–0.8 M. [c] In this solvent $\Delta H^{\ddagger}$ = 11.79 ± 0.58 kcal/mol, $\Delta S^{\ddagger}$ = −38.47 ± 1.97 eu, and E_a = 20 kcal/mol. [d] In this solvent $\Delta H^{\ddagger}$ = 14.39 ± 0.77 kcal/mol, $\Delta S^{\ddagger}$ = −29.49 ± 2.62 eu, and E_a = 19.9 kcal/mol.



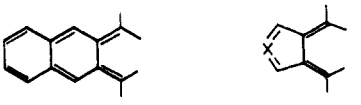
(6)

18 19

Examination of the data of Tables I and II indicates the practically complete absence of a kinetic isotope effect for both the cyclization of bisallenylbenzene **5** and selenide **12**. Consequently, one may conclude that these reactions do not proceed by the one-step ene mechanism.

The sensitivity of rates of reactions involving polar or ionic transition states to the change in polarity of the solvent is well-known.[20a,22,42-45] Inspection of the kinetic data for the rearrangement of *o*-bis(γ,γ-dimethylallenyl)benzene (**5**), bis(γ,γ-dimethylallenyl) selenide (**12**), and their deuterated derivatives (Tables I and II) indicates that the rates of rearrangement of these diallenes is practically insensitive to the change in the polarity of the solvent. This result may be taken as evidence for the absence of significant change in charge separation between the ground state and transition state. Consequently, the operation of an ionic mechanism for these cyclizations may also be ruled out.

Two-Step Mechanism. As previously mentioned, the absence of a kinetic isotope effect rules out any mechanism in which the hydrogen transfer takes place in the rate-determining step. The reverse possibility of a slow step first and a fast hydrogen transfer next may well suit the observed data. However, the question of the exact structure of the intermediate formed in the first step is not a simple one. A six-electron electrocyclic closure of the conjugated π-system in a disrotatory mode leads to 2,3-naphthoquinodimethane **20** or to the analogous structure **21** (X^- = Se, Te, S).



20 21

Sondheimer,[18] Garratt,[19] and their co-workers have shown that the reaction intermediates formed during the cyclization and dimerization of unsubstituted or γ-*tert*-butyl-substituted bridged diallenes can be trapped. For example, when the reactions of these systems were conducted in the presence of $^3O_2$, cyclic peroxides

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Table II. Rate Constants[a] for the Rearrangement of Selenide 12 to Selenophene 13 (k_H) and Selenide 16 to Selenophene 17 (k_D)

solvent	temp, °C	$10^5 k_H$, s^{-1} [b]	$10^5 k_D$, s^{-1} [b]	k_H/k_D
carbon tetrachloride	30	1.229 ± 0.090	1.134 ± 0.013	1.08
chloroform-d_1	30	1.446 ± 0.009	1.410 ± 0.026	1.02
acetone-d_6	30	1.359 ± 0.030		

[a] Determined by NMR. [b] [Diallene] = 0.45–0.9 M.

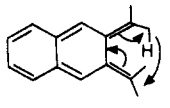
were formed, and in the presence of dienophiles, the formation of [4 + 2] adducts was observed.

Attempts to trap reaction intermediates in the rearrangement of *o*-bisallenylbenzene **5** and bisallenyl selenide **12** were unsuccessful. Trapping agents included triplet oxygen,[18,19,46] sulfur dioxide,[47] and reactive dienophiles like tetracyanoethylene, maleic anhydride, dimethyl maleate and fumarate, and acetylene dimethyl carboxylate. In all these cases only the normal cycloaromatization products were observed. The ability of the *o*-xylylene intermediates to react with both triplet states ($^3O_2$) as well as with singlet states (closure to cyclobutane and even Diels–Alder addition) is explained by the assumption that the energy levels of the singlet and triplet states are sufficiently close to each other to enable reaction from either one.[19,48] This assumption is also supported by calculations of biradicaloid species which by their definition require energy difference between the HOMO and LUMO.[48] Both experiment and calculations have shown that the ground state of *o*-xylylenes is a singlet with planar geometry.[48-51] The energy gap between the singlet S_0 and triplet T_1 for *o*-xylylene itself (**22**) is assumed to be 5000–8000 cm^{-1}. No ESR signals could be detected for this triplet.[48]

The failure to observe reaction with either triplet trapping agents and various dienophiles in the cycloaromatization of diallenes **5** and **12** does not necessarily prove the absence of *o*-xylylenic structures as reaction intermediates. It is possible that the intramolecular reaction of hydrogen transfer is fast and does not allow competition of intermolecular reactions. McCullough and co-workers have reported that 7,8-dimethylxylylene, 7,7,8,8-tetramethylxylylene (**18**), and tetramethylnaphthylene (**20**), all of which could be detected spectroscopically, could not be trapped by various dienophiles.[41a] Since the lifetime of **20** (5 μs) is much shorter than that of **18** (177 s),[41a] it is reasonable to assume that the intramolecular reaction is much faster than the bimolecular reaction.

The total lack of a kinetic isotope effect in the ring closure reactions of **14** and **16** is interesting and may provide further mechanistic information. In going from **14** and **16** to the product the dimethyl-substituted termini of the two allene units must undergo a 90° rotation. If this occurs during the rate-determining step, indicated to be the formation of the intermediates **20** and **21**, then there must be a considerably secondary isotope effect (a rotational isotope effect with a theoretical maximum of 1.44 if both termini are rotating). The lack of an isotope effect suggests that little or no rotation has occurred in the transition state for intermediate formation. This in turn would suggest a very early transition state in a highly exothermic reaction.

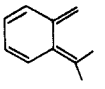
Finally, the high negative values for the entropy of activation observed for the cyclization of bisallenylbenzene **5** ($\Delta S^{\ddagger} = -38.47$ and −29.49 eu for CCl_4 and $CDCl_3$, respectively, Table I) are consistent with a highly ordered transition state, as required from the transition state leading to a 1,2-quinodimethane intermediate.



→ 6 (7)

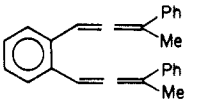
The second stage of the cyclization reaction, the [1,5]hydrogen shift (eq 7), is thermally allowed if it occurs suprafacially. In principle, however, this rearrangement can take place either suprafacially or antarafacially without special steric strain in either one of the corresponding transition states: aromatic (supra) or antiaromatic (antara). Calculations performed by Dewar[52] on *cis*-piperylene show that the transition state of the forbidden antarafacial [1,5]H shift is higher than the allowed rearrangement by only 8.7 kcal/mol. As a result of this low-energy difference between the two transition states, the occurrence of the antarafacial [1,5]H migration is expected by this author for those systems whose spatial geometry require that.

22

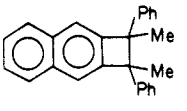


23

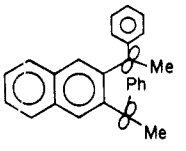
In the work of McCullough and co-workers, the methyl-substituted *o*-xylylenes **18**, **23**, and **20** were generated by decarbonylation of the corresponding indanones.[41,49] On the basis of considerable kinetic isotope effect (5.4 at 38.5°) and negative entropy of activation for the rearrangement of **18** to **19** as well as the negative $\Delta S^{\ddagger}$ for the cyclization of **23** an antarafacial [1,5]sigmatropic rearrangement has been suggested by the authors for the reaction of **18**, **23**, and **20**. This also explains the relative slowness of the thermal process and the sensitivity of the intermediates to photochemical processes.[41,49] The rearrangement of *o*-bisallenylbenzene **24** to a distinct product (**25**) may also be explained by a different mechanism. One possible explanation of the different reaction in this case is by assuming an intermediate different from 2,3-naphthoquinodimethane.



24



25



26

Such an intermediate can be the orthogonal diradical **26** which is free from the steric interactions present in the *o*-xylylenes and enjoys the aromatic stabilization of the naphthalene moiety. The transition state which leads to this intermediate should also be more stable since it not only does not lose the aromatic stabilization of the benzene ring (as happens in the case of *o*-xylylene) but also gains stabilization of the naphthalene system.

This reaction can be understood also in terms of the effect of phenyl substituents on butadiene–cyclobutene equilibria. Since the phenyl substituents lower the E_a of the route to cyclobutene substantially, the competition in this case favors the electrocyclic ring closure over sigmatropic [1,5]H migration.

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(55) We are grateful to one of the referees for calling our attention to this point.

Experimental Section

General Methods. ^1H NMR spectra were recorded on Varian HA 100 NMR or Varian EM-360A spectrometers in either $CDCl_3$ or CCl_4 as solvents with TMS as internal standard. Chemical shifts are reported in δ ppm units, and coupling constants are in Hz units. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer in $CDCl_3$ as a solvent with TMS as internal standard. Chemical shifts are reported in δ ppm units and coupling constants in Hz units. Infrared spectra were recorded on a Perkin-Elmer grating infrared spectrometer Model 457. Mass spectra were obtained on Hitachi Perkin-Elmer RMU6 mass spectrometer or on a Finnigan-4000 GC/MS instrument, by using either electronic ionization (EI) or chemical ionization (CI). Microanalyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Engelskirchen, West Germany and at the Hebrew University, Jerusalem. Solvents and reagents were purified by standard methods.

Phosphonium Salts. Isopropyltriphenylphosphonium bromide was obtained by heating a mixture of 2-bromopropane (21.7 g, 176 mmol) and triphenylphosphine (46.2 g, 176 mmol) in a sealed ampoule at 150 °C for 12 h. The salt thus obtained (42 g) was crystallized from a small amount of ethanol and a little ether and dried in a vacuum oven at 100 °C (15 Torr) for 4 h: yield 38 g (55.9%); mp 238–239 °C (lit.[25] mp 238–239 °C). 1-Phenylethyltriphenylphosphonium bromide was obtained by heating a mixture of 1-bromo-1-phenylethane (82.5 g, 445 mmol) and triphenylphosphine (116.5 g, 445 mmol) in a sealed ampoule at 100 °C for 24 h. After crystallization from ethanol the expected salt was obtained (100 g, 50.2%), mp 228–229 °C.

1,2-Bis(2-methyl-1-propenyl)benzene (3). In a three-necked flask equipped with a mechanical stirrer, dry ice–acetone condenser, and rubber septum were placed isopropyltriphenylphosphonium bromide (102 g, 264 mmol) and 200 mL of dry ether. A 15% solution of *n*-butyllithium in hexane (164 mL, 270 mmol) was added by means of a syringe at 0 °C with stirring under a blanket of nitrogen, followed by heating under reflux for 4 h. The reaction mixture, which turned orange-red, was cooled to ambient temperature and a solution of phthaldialdehyde (18.3 g, 136 mmol) in dry ether (150 mL) was slowly added. After heating under reflux for 3 h and stirring overnight, the reaction was quenched with a little water, and the organic phase was washed in succession with 5% aqueous $NaHCO_3$ (150 mL), water (3 × 150 mL), and saturated NaCl solution (150 mL). The organic layer was separated, dried ($MgSO_4$), and concentrated under vacuum to afford an oil. On addition of a little pentane, triphenylphosphine oxide precipitated. Filtration and evaporation of the solvent, followed by distillation at 105–110 °C (14 Torr) afforded the expected product (10.2 g, 40%) as a clear and colorless oil: ^1H NMR ($CDCl_3$) δ 7.12 (s, 4 H), 6.16 (m, 2 H), 1.86 and 1.68 (d, J = 1 Hz, 6 H each); IR (neat) 3090 (w), 3060 (w), 3030 (w), 1651 (m), 1595 (w), 1475 (m), 745 (s) cm^{-1}; UV, λ_{max} (ethanol) 230 nm (ϵ 14 500) and 252 (9500).

1,2-Bis(2,2-dibromo-3,3-dimethylcyclopropyl)benzene (4). A solution of 50% aqueous NaOH (13.5 mL) was added dropwise with stirring and heating at 40–45 °C to a mixture of bromoform (13.6 g, 53.8 mmol), **3** (2.5 g, 13.4 mmol), triethylbenzylammonium chloride (80 mg), and a drop of ethanol. The mixture darkened and became viscous. After addition of 3 mL of CH_2Cl_2 stirring was continued for 5 h at the same temperature. On cooling, CH_2Cl_2 (150 mL) was added, and the organic phase was washed with 5% aqueous HCl (3 × 150 mL), followed by extraction of the acid washings with CH_2Cl_2 (50 mL). The combined organic layers were washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated under vacuum affording a black viscous residue which was extracted with boiling hexane and treated with a little active charcoal. On concentration of this solution, the expected product precipitated as white crystals (1.35 g, 20%) mp 132–132.5 °C: ^1H NMR ($CDCl_3$) δ 7.13 (m, 4 H), 2.94 (s, 2 H), 1.67 (s, 6 H), 1.46 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 137.0, 129.2, 126.6 (aromatic), 47.3 (CBr_2), 42.2 (CPh), 30.9 (CMe_2), 28.8, 22.2 (CH_3); IR ($CHCl_3$) 3010, 1595, 1475, 1450, 1375, 1005 cm^{-1}; MS, *m/e* (%) (EI) 453, 451, 449, 447 (M – Br, 1:3:3:1, 13), 371, 369, 367 (M – Br – HBr, 1:2:1, 10), 290, 288 (M – 2Br – HBr, 1:1, 11), 289, 287 (M – Br – 2HBr, 1:1, 10), 229, 227, 225 ($C_5H_7Br_2$, 1:2:1, 18), 210 (M – 4Br, 25), 209 (M – 3Br – HBr, 100), 208 (M – 2Br – 2HBr, 41), 207 (M – Br – 3HBr, 16), 195 (M – 4Br – CH_3, 18), 194 (M – 3Br – HBr – CH_3, 37), 193 (M – 2Br – 2HBr – CH_3, 50), 192 (M – Br – 3HBr – CH_3, 10), 180 (M – 4Br – $2CH_3$, 17), 179 (M – 3Br – HBr – $2CH_3$, 48), 178 (M – 2Br – 2HBr – $2CH_3$, 41), 165 (M – 4Br – $3CH_3$, 51), 65 (C_5H_5, 30); (CI) 453, 451, 449, 447 (1:3:3:1, 33), 371, 369, 367 (1:2:1, 39), 291, 289 (1:1, 21), 290, 288 (1:1, 30), 289, 287 (1:1, 28), 229, 227, 225 (1:2:1, 13), 210 (17), 209 (100), 208 (40), 207 (23), 165 (18). Anal. Calcd for $C_{16}H_{18}Br_4$: C, 36.22; H, 3.41; Br, 60.37. Found: C, 36.31; H, 3.48; Br, 60.24.

1,2-Bis(3-methyl-1,2-butadienyl)benzene (5). To a cooled (−30 to −40 °C) solution of **4** (380 mg, 0.71 mmol) in 30 mL of dry ether was added under stirring a 5% solution of MeLi in ether (5 mL) by means of a syringe under a blanket of nitrogen. Stirring was continued for 1.5 h at the same temperature, and after addition of 100 mL of ether the solution was washed with water (2 × 50 mL). After drying ($MgSO_4$) and removal of the solvent, 146 mg (98%) of the expected product were obtained as a colorless liquid: ^1H NMR ($CDCl_3$) δ 7.28 (m, 2 H), 7.07 (m, 2 H), 6.3 (sep, J = 3 Hz, 2 H), 1.76 (d, J = 3 Hz, 12 H); IR (neat) 3060 (w), 1950 (m), 1595 (w), 1490 (m), 1440 (s) cm^{-1}; UV λ_{max} (MeOH) 227, 267 nm; MS, *m/e* (%) (EI) 210 (M^+, 51), 195 (100), 180 (30), 165 (81), 67 (98), 65 (75), 55 (85). The mass spectrum also contains fragments resulting from cyclization to **6**.

2-Isopropenyl-3-isopropylnaphthalene (6). Solutions of **5** in various solvents (pentane, $CHCl_3$, acetone, ether, CCl_4) were kept under various conditions (−15 to 50 °C and 3–24 h). Removal of the solvent afforded a white solid in 100% yield. The product was purified by sublimation, mp 65–66 °C: ^1H NMR ($CDCl_3$) δ 7.1–7.7 (m, 6 H), 5.24 (m, 1 H), 4.94 (m, 1 H), 3.27 (sep, J = 6 Hz, 1 H), 2.12 (br s, 3 H), 1.33 (d, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 146.1 (C-3), 144.8 (C-2), 133.0, 131.8 (C-9, C-10), 127.3, 126.4, 125.4, 125.2, 123.8 (C-1, C-4, C-5, C-6, C-7, C-8), 142.5 (=C(CH_3)), 115.1 (=CH_2), 29.8 (CH), 25.8 (CH_3—C=), 24.8 (CH_3—C); IR ($CHCl_3$) 3050, 3000, 1630, 1590, 1485, 885 cm^{-1}; UV λ_{max} (MeOH) 319 nm (ϵ 600); MS, *m/e* (%) (EI) 210 (M^+, 53), 195 (100), 180 (34), 179 (26), 167 (22), 166 (30), 165 (79), 153 (32), 152 (23), 141 (14), 128 (10), 115 (14); (CI) 211 (M^+ + 1, 100), 210 (26), 169 (58). Anal. Calcd for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.26; H, 8.75.

1,1,1,3,3,3-Hexadeuterio-2-propanol. To a stirred and cooled (0 °C) suspension of $LiAlH_4$ (9.05 g, 238 mmol) in dry ether (200 mL) was added very slowly a solution of acetone-d_6 (30.47 g, 476 mmol) in dry ether (100 mL). The mixture was stirred overnight at room temperature, followed by careful addition of ice (8.6 g, 477 mmol), ether (200 mL), and anhydrous $MgSO_4$ to assist granulation of the gel. After filtration of the solid, washing with ether, and drying of the ether solution with anhydrous $MgSO_4$, the solvent was removed by slow distillation to afford the expected alcohol (13.5 g, 43%): ^1H NMR ($CDCl_3$) δ 3.97 (s, 1 H), 2.28 (s, 1 H, exchanged by D_2O). A control reduction of acetone, using the same method, gave 2-propanol: ^1H NMR ($CDCl_3$) δ 3.92 (sep, J = 6 Hz, 1 H), 3.3 (br s, 1 H, exchanged by D_2O), 1.17 (d, J = 6 Hz, 6 H).

1,1,1,3,3,3-Hexadeuterio-2-bromopropane. Hydrobromic acid (47%, 100 mL) was added to 1,1,1,3,3,3-hexadeuterio-2-propanol (13.5 g, 205 mmol), followed by slow distillation between 58 °C (bp of bromide) and 125 °C, until the volume of the liquid was reduced to one half. The product was separated from the aqueous layer and dried over anhydrous $MgSO_4$ (23 g, 87%): ^1H NMR ($CDCl_3$) δ 4.23 (s). A control preparation of 2-bromopropane was also performed: ^1H NMR ($CDCl_3$) δ 4.15 (sep, J = 6 Hz, 1 H), 1.80 (d, J = 6 Hz, 6 H).

1,2-Bis(2-methyl-1-propenyl)benzene-d_{12} (3a). 1,1,1,3,3,3-Hexadeuterio-2-propyltriphenylphosphonium bromide, prepared by the method described above mp 236–237 °C (34.4 g, 88 mmol), a 15% solution of *n*-BuLi in hexane (55 mL, 90 mmol), and phthaldialdehyde (6.1 g, 45 mmol) were reacted as described for **3**. Distillation at 105–115 °C (14 Torr) afforded 3.7 g (42%) of the expected product: ^1H NMR ($CDCl_3$) δ 7.3 (s, 4 H), 6.18 (s, 2 H); IR (neat) 3060 (m), 3030 (m), 2230 (m), 2200 (m), 2120 (w), 2050 (w), 1590 (w), 760 (s) cm^{-1}; MS, *m/e* (%) (EI) 198 (M^+, 62), 180 (M – CD_3, 65), 162 (M – $2CD_3$, 35), 150 (M – C_3D_6, 73), 144 (M – $3CD_3$, 35), 132 (M – CD_3 – C_3D_6, 100); (CI) 199 (M + 1, 100), 180 (35), 150 (81), 144 (58).

1,2-Bis(2,2-dibromo-3,3-dihexadeuteriomethylcyclopropyl)benzene (4a). Compound **3a** (2.62 g, 13.4 mmol), bromoform (13.6 g, 53.8 mmol), 50% aqueous NaOH (13.5 mL), triethylbenzylammonium chloride (80 mg), and a drop of ethanol were reacted as described for the undeuteriated material (**4**). After crystallization from hexane, 2.2 g (30%) of the expected product were obtained, mp 134–135 °C: ^1H NMR ($CDCl_3$) δ 7.22 (m, 4 H), 2.93 (s, 2 H); IR ($CHCl_3$) 3025 (w), 2240 (w), 2205 (m), 2120 (w), 2060 (w), 1595 (m), 1480 (m), 1450 (m), 1050 (s) cm^{-1}; MS, *m/e* (%) (EI) 465, 463, 461, 459 (M – Br, 1:3:3:1, 3), 302, 300 (M – 2Br – HBr, 1:1, 7), 301, 299 (M – 2Br, – DBr, 1:1, 7), 235, 233, 231 ($C_5HD_6Br_2$, 1:2:1, 23), 222 (M – 4Br, 23), 221 (M – 3Br – HBr, 100), 220 (M – 3Br, – DBr, 63), 219 (M – 2Br – DBr – HBr, 23), 218 (M – 2Br – 2DBr, 19), 217 (M – Br – 2DBr – HBr, 11), 204 (M – 4Br – CD_3, 19), 203 (M – 3Br – HBr – CD_3, 24), 202 (M – 3Br – DBr – CD_3, 33), 201 (M – 2Br – DBr – HBr – CD_3, 40), 200 (M – 2Br – 2DBr – CD_3, 22), 186 (M – 3Br – HBr – $2CD_3$, 43), 184 (M – 3Br – DBr – $2CD_3$, 49), 183 (M – 2Br – DBr – HBr – $2CD_3$, 34), 182 (M – 2Br – 2DBr – $2CD_3$, 20), 168 (M – 4Br – $3CD_3$, 34), 167 (M – 3Br – HBr – $3CD_3$, 10), 65 (C_5H_5, 17); (CI) 465, 463, 461, 459 (1:3:3:1, 37), 383, 381, 379 (1:2:1, 30), 382, 380, 378 (1:2:1, 43), 303, 301 (1:1, 20), 302, 300 (1:1, 31), 301, 299 (1:1, 53), 235, 233, 231 (1:2:1, 11), 222 (12), 221 (91), 220 (100), 219 (59), 218 (46), 217 (26).

1,2-Bis(3-methyl-1,2-butadienyl)benzene-d_{12} (14). Compound **4a** (260 mg, 0.48 mmol) was treated with a 5% solution of MeLi in ether (3.35

mL) as described for the preparation of **5**. The expected product (103 mg, 97%) was obtained as a clear and colorless liquid: ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 2 H), 7.12 (m, 2 H), 6.34 (s, 2 H); IR (neat) 3050 (w), 2220 (m), 2205 (m), 2120 (w), 2055 (w), 1950 (m), 1595 (w), 1495 (m), 1445 (m) cm^{-1}; MS, *m/e* (%) (EI) 222 (M, 48), 204 (M - CD_3, 100), 186 (M - $2CD_3$, 35), 168 (M - $3CD_3$, 42) 73 (C_5HD_6, 85). The mass spectrum also shows peaks resulting from cyclization to the naphthalene derivative.

2-Pentadeuterioisopropenyl-3-heptadeuterioisopropylnaphthalene (15). This material was obtained from *o*-bis(γ,γ-hexadeuteriomethylallenyl)-benzene by the same method as described for the corresponding undeuteriated material (**5**). In each case the cyclization was quantitative. The product is a white solid, which can be purified by sublimation, mp 64–65 °C: ^{1}H NMR ($CDCl_3$) δ 7.80–7.05 (m); IR ($CHCl_3$) 3050 (m), 3000 (m), 2235 (w), 2200 (m), 2160 (w), 2125 (w), 2055 (w), 1635 (m), 1590 (m) cm^{-1}; MS, *m/e* (%) (EI) 222 (M^+, 62), 204 (M - CD_3, 100), 186 (M - $2CD_3$, 28), 184 (M - $2CD_3$ - D, 20), 166 (M - $3CD_3$ - D, 70), 172 (M - C_3D_7, 25); (CI) 223 (M + 1, 100), 222 (M, 15).

2,2-Dibromo-3,3-dimethylcyclopropyl Ether (7). Method A. To a stirred suspension of potassium *tert*-butoxide (3.59 g, 32 mmol) in dry pentane (50 mL) was added a solution of diisobutenyl ether (2.0 g, 16 mmol)[53] in dry pentane (40 mL) at 0 °C under nitrogen. After slow dropwise addition of bromoform (8.1 g, 32 mmol) at the same temperature, stirring was continued for 2 days at room temperature. Most of the pentane was evaporated, and methylene chloride (250 mL) was added. The solution was washed successively with water (3 × 150 mL), 1% aqueous HCl solution (100 mL), and water (100 mL) again. The organic layer was dried ($MgSO_4$), and the solvents were evaporated. The residue (5.4 g), a brown solid, was washed with pentane and crystallized from acetone. The white crystalline material (2.1 g, 28% yield) decomposes on standing at room temperature for a short time. **Method B.** A solution of diisobutenyl ether (1.28 g, 10 mmol) in bromoform (10.12 g, 40 mmol) containing a drop of ethanol and 5 mg of benzyltriethylammonium chloride was treated with a solution of 50% aqueous NaOH, as described for the preparation of **4**. Crystallization from CH_2Cl_2 gave white crystals (520 mg, 11%), mp 126–129 °C (d): ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 2 H), 1.24 (s, 3 H), 1.36 (s, 3 H); IR ($CHCl_3$) δ 1080 (m), 1030 (m) cm^{-1}; MS, *m/e* (%) (EI) 393, 391, 389, 387 (M - Br, 1:3:3:1, 3), 312, 310, 308 (M - 2Br, 1:2:1, 6), 229, 227, 225 ($C_5H_7Br_2$, 1:2:1, 4), 201, 199, 197 ($C_5H_7Br_2$ - C_2H_4, 1:2:1, 11), 164, 162 ($C_5H_7Br_2O$ - Br, 1:1, 6), 165, 163 ($C_5H_7Br_2OH$ - Br, 1:1, 11), 148, 146 ($C_5H_7Br_2$ - Br, 1:1, 11), 147, 145 ($C_5H_7Br_2$ - HBr, 1:1, 17), 67 ($C_5H_7Br_2$ - 2Br, 40), 66 ($C_5H_7Br_2$ - HBr - Br, 63), 65 ($C_5H_7Br_2$ - 2HBr, 100).

3-Isopropenyl-4-isopropylfuran (9). 2,2-Dibromo-3,3-dimethylcyclopropyl ether (350 mg, 0.74 mmol) was reacted with a 5% solution of MeLi in ether (4 mL) as described for the preparation of **5**. The expected product (105 mg, 95%) was obtained as a clear colorless liquid: ^{1}H NMR ($CDCl_3$) δ 7.28 (d, J = 1 Hz, 1 H), 7.12 (d, J = 1 Hz, 1 H), 5.80 (br s, 1 H), 4.98 (m, 1 H), 2.95 (sep, J = 7 Hz, 1 H), 1.99 (s, 3 H), 1.18 (d, J = 7 Hz, 6 H); IR (neat) 3050 (w), 1715 (w), 1660 (m), 955 (s), 770 (s) cm^{-1}; MS, *m/e* (%) (EI) 150 (M^+, 64), 135 (M - CH_3, 100), 121 (M - CHO, 22), 107 (M - C_3H_7, 6), 65 (C_5H_5, 12), 29 (HCO, 10). These data are in accord with those of its isomer 3-propenyl-4-propylfuran.[54]

3-Isopropenyl-4-isopropylthiophene (11). A 20% solution of *n*-butyllithium in hexane (9.3 mL, 20 mmol) was added dropwise to a cooled (-78 °C) and stirred solution of 3,3-dimethyl-1-bromoallene (3 g, 20 mmol) in dry ether (20 mL) under a nitrogen atmosphere. Stirring was continued at -78 °C (30 min), and then a solution of freshly distilled SCl_2 (1.03 g, 10 mmol) in dry THF (30 mL) was added slowly at the same temperature. The solution became yellow-brown and darkened before addition was over. Stirring was continued at -78 °C (1 h) followed by addition of ether (150 mL) and washing with water (4 × 100 mL). After the organic layer was dried ($MgSO_4$) and the solvent was evaporated, a viscous orange material (1.7 g) was obtained, which on vacuum distillation (bp 36 °C (1 Torr)) afforded the expected product (120 mg, 8%) as a clear colorless liquid which decomposes on standing at room temperature for short times: ^{1}H NMR ($CDCl_3$) δ 6.99, 6.90 (dd, J = 3 Hz, 2 H), 5.10 (m, 1 H), 4.94 (br s, 1 H), 3.08 (sep, J = 7 Hz, 1 H), 2.04 (s, 3 H), 1.20 (d, J = 7 Hz, 6 H); IR (neat) 3080 (w), 1640 (m), 1450 (s), 1380 (m), 1365 (m), 900 (m), 870 (m), 790 (s) cm^{-1}; MS, *m/e* (%) (EI) 166 (M^+, 54), 165 (M - CH_3, 100), 125 (M - C_3H_5, 8), 121 (M - HCS, 15), 106 (M - HCS - CH_3, 10), 100 (M - C_3H_5CCH, 12), 45 (HCS, 21).

3-Isopropenyl-4-isopropylthiophene 1,1-Dioxide (2). To a cooled (0 °C) solution of 3-isopropenyl-4-isopropylthiophene (50 mg, 0.3 mmol) in dry methylene chloride (15 mL) was added *m*-CPBA (130 mg, 0.6 mmol). After 5 h of stirring at 0 °C, the mixture was heated to room temperature, and stirring was continued for another 15 h. A white precipitate was observed. After addition of ether (150 mL), the solution was washed in succession with 10% aqueous potassium iodide solution (4 × 50 mL), saturated sodium thiosulfate (2 × 10 mL), 10% aqueous sodium bicarbonate (4 × 50 mL), and water (2 × 50 mL). The organic layer was separated, dried ($MgSO_4$), and concentrated under vacuum to afford a brown viscous oil (40 mg). Purification with active charcoal and crystallization from ether–pentane afforded a white solid (12 mg, 20%) of the expected product, mp 68–69 °C (lit.[20] 68–69 °C): ^{1}H NMR ($CDCl_3$) δ 6.28 (m, 2 H), 5.30 (m, 1 H), 5.12 (m, 1 H), 2.70 (sep, J = 7 Hz, 1 H), 2.02 (br s, 3 H), 1.16 (d, J = 7 Hz, 6 H); IR ($CHCl_3$) 1300 (s), 1138 (s); MS, *m/e* (%) (EI) 198 (M^+, 10), 183 (M - CH_3, 8), 181 (M - OH, 30), 91 (100).

Bis(3-methyl-1,2-butadienyl) Selenide (12). To a three-necked, round-bottomed flask equipped with a magnetic stirrer and drying tube (KOH pellets) and containing 100 mL of liquid ammonia at -78 °C under nitrogen was added 730 mg (31.7 mmol) of sodium metal. After all the sodium reacted, selenium powder (1.12 g, 14.1 mmol) was added to the deep blue solution, and stirring was continued for 2 h at -78 °C. Removal of the cooling bath and an excess of ammonia with a stream of nitrogen afforded sodium selenide as a white solid. Next, dry THF (30 mL) was added, followed by the dropwise addition during 1 h with stirring at room temperature of a solution of α,α-dimethylpropargyl bromide[32] (4.4 g, 29.9 mmol) in dry THF (40 mL). Stirring was continued for another hour, followed by addition of ether (150 mL), washing with water (4 × 100 mL), and drying of the organic layer ($MgSO_4$). Removal of the solvent afforded a yellowish liquid purified with active charcoal (1.4 g, 47%). The product decomposes on standing at room temperature after a short time: ^{1}H NMR ($CDCl_3$) δ 5.73 (sep, J = 2 Hz, 2 H), 1.76 (d, J = 2 Hz, 12 H); IR (neat) 1950 (m), 1450 (s), 1365 (m), 1155 (s), 1010 (m), 740 (s); MS, *m/e* (%) (EI) 216, 214, 212, 211, 210 (M^+, 1:6:3:1:1, 44), 201, 199, 197, 196, 195 (M - CH_3, 1:6:3:1:1, 100), 67 (C_5H_7, 26).

3-Isopropenyl-4-isopropylselenophene (13). Various quantities of bis(3-methyl-1,2-butadienyl) selenide dissolved in different solvents (pentane, $CHCl_3$, ether, CCl_4, acetone) were maintained at temperatures ranging from 15 °C to refluxing $CHCl_3$, for various time intervals (2–48 h). After removal of the solvent the cyclization product was obtained as a colorless liquid in quantitative yield. The compound decomposes after short times at room temperature: ^{1}H NMR ($CDCl_3$) δ 7.54 (m, 2 H), 5.1 (m, 1 H), 4.88 (m, 1 H), 2.98 (sep, J = 7 Hz, 1 H), 2.02 (s, 3 H), 1.18 (d, J = 7 Hz, 6 H); IR (neat) 3080 (w), 1630 (m), 1450 (m), 1375 (m), 900 (s), 790 (s) cm^{-1}; MS, *m/e* (%) (EI) 216, 214, 212, 211, 210 (M, 1:6:3:1:1, 48), 201, 199, 197, 196, 195 (M - 15, 1:6:3:1:1, 100), 173, 171, 169, 167 (M - C_3H_7, 1:6:3:1:1, 8), 119 (M - Se - CH_3, 56), 118 (M - HSe - CH_3, 84), 117 (M - H_2Se - CH_3, 44), 107, 105, 103, 102, 101 (C_2HSe, 1:6:3:1:1, 28), 95, 93, 91, 90, 89 (HCSe, 1:6:3:1:1, 52).

2-Methyl-3-butyn-2-ol-d_6. A solution of monolithium acetylide, obtained by treatment of a solution of acetylene (3 g, 115 mmol) in dry THF (200 mL) with a 15% solution of *n*-butyllithium in hexane (67 mL, 110 mmol), was reacted with acetone-d_6 (6.4 g, 100 mmol) by the same procedure as described by Midland[39] for the preparation of the corresponding undeuteriated material. The alcohol was separated from the solvent by slow distillation at atmospheric pressure using a long fractionating column (bp 100–105 °C, 5.75 g, 62%): ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 1 H), 2.80 (s, 1 H, exchanges with D_2O); IR (neat) 3300 (s), 3270 (s), 2200 (m) cm^{-1}.

3-Methyl-3-bromo-1-butyne-d_6 was prepared by reaction of 2-methyl-3-butyn-2-ol-d_6 (11.2 g, 123 mmol) with PBr_3 (10.8 g, 40 mmol), as described by Shiner and Humphrey[32] for the corresponding undeuteriated material (bp 36–38 °C (90 Torr), 4 g, 22%): ^{1}H NMR ($CDCl_3$) δ 2.60 (s).

Bis(3-methyl-1,2-butadienyl-d_6) selenide (16) was obtained as described for the preparation of **12** by reaction of liquid ammonia (70 mL), sodium metal (665 mg, 29 mmol), selenium powder (1.02 g, 12.9 mmol), and 3-methyl-3-bromo-1-butyne-d_6 (4 g, 26.2 mmol). The expected product (700 mg, 24%) was obtained as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 5.68 (s); IR (neat) 2240 (m), 2200 (m), 2100 (m), 2060 (m), 1950 (m), 1150 (m), 1045 (s), 780 (m); MS, *m/e* (%) (EI) 228, 226, 224, 223, 222 (M^+, 1:6:3:1:1, 43), 210, 208, 206, 205, 204 (M - CD_3, 1:6:3:1:1, 100), 73 (C_5HD_6, 39).

3-Pentadeuterioisopropenyl-4-heptadeuterioisopropylselenophene (17) was obtained quantitatively from bis(3-methyl-1,2-butadienyl-d_6) selenide, as described for the undeuteriated compound: ^{1}H NMR ($CDCl_3$) δ 7.52 (br s); IR (neat) 3080 (w), 2240 (w), 2205 (w), 2155 (w), 2120 (m), 2050 (w), 1635 (m) cm^{-1}; MS, *m/e* (%) (EI) 228, 226, 224, 223, 222 (M^+, 1:6:3:1:1, 41), 210, 208, 206, 205, 204 (M - CD_3, 1:6:3:1:1, 100), 178, 176, 174, 173, 172 (M - C_3D_7, 1:6:3:1:1, 5), 95, 93, 91, 90, 89 (HCSe, 1:6:3:1:1, 61).

1,2-Bis(2-phenyl-1-propenyl)benzene (27). 1-Phenylethyltriphenylphosphonium bromide (44.7 g, 100 mmol), 15% hexane solution of *n*-butyllithium (67 mL, 110 mmol), and phthaldialdehyde (6.7 g, 50 mmol)

were reacted as described for the preparation of **3**, except that the reflux after addition of the base was continued for 9 h. The product (12.5 g, 81%) was first distilled at 160 °C (0.015 Torr) as a viscous yellowish oil and next crystallized from pentane to a white crystalline mixture of isomers, mp 45–56 °C: ^{1}H NMR (CCl_4) δ 7.36–7.02 (m, 14 H), 6.8 (br s, 2 H), 2.06 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.44, 141.7, 138.76, 137.73, 137.54, 137.38, 129.87, 129.73, 129.48, 129.33, 128.74, 128.28, 128.12, 127.96, 127.0, 126.9, 126.35, 126.4, 125.87 (aromatic carbons) 132.3, 131.8 (=C(CH_3)C_6H_5), 125.58 (HC=), 26.0, 17.2, 17.0 (CH_3); IR ($CHCl_3$) 3040 (m), 1680 (m), 1590 (m), 1480 (m), 1430 (s) cm^{-1}; MS, *m/e* (%) (EI) 310 (M, 30), 295 (M - CH_3, 8), 218 (M - $C_6H_5CH_3$, 11), 217 (M - C_6H_6 - CH_3, 13), 205 (M - C_6H_5 - C_2H_4, 59), 203 (M - C_2H_6 - C_6H_5, 20), 105 ($C_6H_5CHCH_3$, 100), 91 (C_7H_7, 44), 77 (C_6H_5, 24), 65 (C_5H_5, 8) (Cl) 311 (M + 1, 29), 310 (M, 100), 105 (56). Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.59; H, 6.86.

1,2-Bis(2,2-dibromo-3-methyl-3-phenylcyclopropyl)benzene (28). To a suspension of potassium *tert*-butoxide (2.89 g, 25.8 mmol) in dry pentane (150 mL) cooled to 0 °C under nitrogen was added **27** (2 g, 6.5 mmol). The mixture was cooled to −75 °C, and bromoform (6.53 g, 25.8 mmol) was added slowly with stirring. Stirring was continued for 24 h at ambient temperature, and after addition of ether–methylene chloride, the solution was washed with 100 mL of 1% HCl solution and water (4 × 100 mL). The organic phase was dried ($MgSO_4$) and treated with active charcoal. Evaporation of the solvent afforded 3.3 g of a brown and very viscous liquid. On addition of a little ether white crystals separated, which were recrystallized from ether (100 mg), mp 155–156 °C: ^{1}H NMR ($CDCl_3$) δ 7.54 (m, 14 H), 3.68 (s, 2 H), 1.75 (s, 6 H); IR ($CHCl_3$) 3030 (m), 1595 (s), 1490 (s), 1440 (s), 1375 (m), 1025 (m) cm^{-1}; MS, *m/e* (%) (EI) 495, 493, 491 (M - HBr - Br, 1:2:1, 2), 414, 412 (M - HBr - 2Br, 1:1, 15) 413, 411 (M - 2HBr - Br, 1:1, 82), 333 (M - HBr - 3Br, 31), 332 (M - 2Br - 2HBr, 100), 331 (M - 3HBr - Br, 86), 318 (M - 3Br - HBr - CH_3, 9), 317 (M - 2Br - 2HBr - CH_3, 35), 316 (M - Br - 3HBr - CH_3, 29), 255 (M - 2Br - 2HBr - C_6H_5, 11), 254 (M - Br - 3HBr - C_6H_5, 19), 253 (M - 4HBr - C_6H_5, 33), 239 (M - 3HBr - Br - CH_3 - C_6H_5, 23), 129 ($HCCCCH_3C_6H_5$, 8); (Cl) 577, 575, 573, 571 (M - Br, 1:3:3:1, 1), 495, 493, 491 (1:2:1, 12), 414, 412 (1:1, 18), 413, 411 (1:1, 48), 334 (M - 4Br, 13), 333 (48), 332 (100), 331 (81), 105 ($C_6H_5CHCH_3$, 53).

1,2-Dimethyl-1,2-diphenylnaphtho[*b*]cyclobutane (25). To a stirred and cooled (−30 °C) solution of **28** (100 mg, 0.15 mmol) in dry ether (60 mL, N_2) was added 1 mL of a 5% solution of MeLi in ether. After 1.5 h at −30 °C and quenching with water, the organic layer was washed with water (2 × 60 mL), dried ($MgSO_4$), concentrated to afford a yellowish viscous oil (48 mg, 96%), recrystallized from ether–methanol, and identified as the title compound, mp 125–26 °C: ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 2 H), 7.65 (s, 2 H), 7.35 (m, 2 H), 6.85 (s, 10 H), 1.90 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 148.9 (C-10), 144.59 (C-13), 134.64 (C-11), 128.41, 127.44, 127.21, 125.48, 125.04, 121.21 (C-9, C-8, C-7, C-14, C-15, C-16), 61.19 (C-1), 23.90 (CH_3); IR (CCl_4) 3040 (m), 3005 (m), 2940 (s), 2870 (m), 1595 (w), 1485 (m), 1415 (m), 1290 (s), 1195 (s), 1015 (m), 905 (s) cm^{-1}; UV (cyclohexane) λ_{max}, nm, 232 (ϵ_{max} = 109 166), 262 (20 000), 271 (21 250, 281 (20 000), 294 (15 000), 307 (9160), 321 (7080); MS, *m/e* (%) (EI) 334 (M, 100), 319 (M - CH_3, 89), 304 (M - 2CH_3, 40), 257 (M - C_6H_5, 25), 256 (M - C_6H_6, 56), 242 (M - C_6H_5 - CH_3, 19), 241 (M - C_6H_6 - CH_3, 26), 229 (M - C_6H_6 - C_2H_3, 11), 228 (M - C_6H_6 - C_2H_4, 18), 153 ($C_{12}H_9$, 17); (Cl) 335 (M + 1, 100), 257 (65) 207 (40). Anal. Calcd for $C_{26}H_{22}$: C, 93.15; H, 6.61. Found: C, 93.36, H, 6.63.

Kinetic Measurements. Kinetic measurements were performed by the use of ^{1}H NMR, by following the rate of decrease in substrate concentration with respect to a constant concentration of an inert reference. A weighed quantity of diallenes **5**, **12**, **14**, and **16** was dissolved in 1 mL of the appropriate solvent (CCl_4, $CDCl_3$, or CD_3CN) containing *p*-dimethoxybenzene as reference. About 0.5 mL of this solution was transferred to an NMR tube and immersed in a constant temperature bath after sealing. At appropriate time intervals the change in integration of the allenic protons around δ 6.34 and 5.58 for **14** and **16**, respectively, and of the γ-methyl protons at δ 1.76 for both **5** and **12**, with respect to the integration of the methoxy protons at δ 3.76, was recorded. In each case, control runs using *p*-dimethoxybenzene in a separate tube and immersed in the NMR tube, as an external reference, were also performed. The rate constants were calculated from the first-order kinetic expression $k = (2.303/t) \log (a/(a - x))$, where a represents the ratio of the allenic proton area and the methoxy proton area at $t = 0$, while $(a - x)$ is the same ratio after t. Plots of log $(a - x)$ vs time gave good straight lines for each run. Errors were calculated by means of an IBM 360/50 computer, using the APL language.

Registry No. **3**, 2223-64-5; **3a**, 67560-59-2; **4**, 61838-62-8; **4a**, 127229-20-3; **5**, 61838-63-9; **6**, 61838-59-3; **7**, 61838-61-7; **9**, 61838-58-2; **11**, 61838-57-1; **12**, 67560-52-5; **13**, 127208-21-3; **14**, 67560-57-0; **15**, 67560-58-1; **16**, 67560-54-7; **17**, 67560-56-9; **25**, 127208-22-4; **27**, 127208-23-5; **28**, 127208-24-6; isopropyltriphenylphosphonium bromide, 1530-33-2; 2-bromopropane, 75-26-3; 1-phenylethyltriphenylphosphonium bromide, 53213-26-6; 1-bromo-1-phenylethane, 585-71-7; phthaldialdehyde, 643-79-8; cetone-d_6, 666-52-4; 1,1,1,3,3,3-hexadeuterio-2-propanol, 3976-29-2; 1,1,1,3,3,3-hexadeuterio-2-bromopropane, 52809-76-4; 1,1,1,3,3,3-hexadeuterio-2-propyltriphenylphosphonium bromide, 127208-25-7; diisobutenyl ether, 764-51-2; 3,3-dimethyl-1-bromoallene, 6214-32-0; α,α-dimethylpropargyl bromide, 6214-31-9; 2-methyl-3-butyn-2-ol-d_6, 57444-27-6; acetylene, 74-86-2; 3-methyl-3-bromo-1-butyne-d_6, 67560-55-8.

Spherands Containing Cyclic Urea Units[1a,b]

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Abstract: Three new spherands (**1**–**3**) and one new hemispherand (**4**) are reported, all having in common two $(CH_2)_3N_2C{=}O$ cyclic urea units, three anisyl units, and one CH_2ACH_2 unit. In **1**, **2**, and **3** A = O, S, and $C(CO_2Et)_2$, respectively, and these together with the other units provide 18-membered macrorings whose enforced cavities are lined by (roughly) octahedrally arranged heteroatoms. In **4** A = 1,2-$C_6H_4O_2$ (catechol), and the macroring is 21-membered and is partially preorganized. Crystal structures are reported for **1**,**1**·Na picrate, **2**·$NaSbF_6$, **4**, and **10**·H_2O. The association constants (K_a, M^{-1}) and free energies of binding ($-\Delta G°$, kcal mol^{-1}) were determined at 25 °C for Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and $(CH_3)_3CNH_3^+$ picrates in $CDCl_3$ saturated with D_2O. Peak binding was observed for **1** and **2** with Na^+ (19.5 and 19.1 kcal mol^{-1}, respectively), for **3** with Li^+ (16.1 kcal mol^{-1}), and for **4** with K^+ (12.4 kcal mol^{-1}). The results further illustrate the utility of the principles of complementarity and preorganization. The rates of complexation–decomplexation during $CHCl_3$–water extractions were rapid on the human time scale. The greatest specificity was shown by **2** toward the physiologically important Li^+, Na^+, and K^+ ions: $K_a^{Na^+}/K_a^{Li^+}$ = 250; $K_a^{Na^+}/K_a^{K^+}$ = 10 000.

Cyclic trimethylene ureas ($(CH_2)_3N_2C{=}O$) have proven to be strongly binding ligands[2] for alkali metal, ammonium, and alkylammonium ions when incorporated along with anisyl units into 20-membered macroring systems, as in **5**–**8**.[2b] Hosts **5**–**8** bind

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