Zorbax SIL column (21.2 × 250 mm) eluted at 9.9 mL/min with 25% Et_2O in hexane (rotations in THF): 43 mg, less polar diastereomer, $k' = 2.52$, $[\alpha]_D$ −553°; 41 mg, more polar diastereomer, $k' = 3.11$, $[\alpha]_D$ +581°. The NMR spectrum (300 MHz, $CDCl_3$) of the less polar (−) diastereomer had H_9 δ 7.11 and H_{10} δ 5.50 with $J_{9,10} = 2.8$ Hz, and the more polar (+) diastereomer had H_9 δ 7.02 and H_{10} δ 5.68 with the same coupling constant. Treatment of either bromo MTPA ester (33 mg) with dry NaOMe (75 mg) in stirred THF (4 mL) overnight at room temperature provided the 9,10-oxide in 80% yield. The less polar (−) diastereomer gave **24** with $[\alpha]_D$ +418° (2 mg/mL, THF) whereas the more polar (+) diastereomer gave **24** with $[\alpha]_D$ −430° (2 mg/mL, THF). When racemic oxide was chromatographed on a covalently bonded dinitrobenzoyl-(*R*)-phenylglycine column (0.41 × 25 cm, Regis Chemical Co.) eluted at 3.0 mL/min with 0.33% EtOH and 0.17% CH_3CN in hexane, the enantiomers emerged at 15.0 and 16.9 min. (+)-Oxide from the less polar (−) diastereomer corresponds to the earlier (15.0 min) of these peaks.

Reaction of Benzo[*g*]chrysene 9,10-Oxide with Methoxide. Benzo[*g*]chrysene 9,10-oxide is quantitatively converted to a pair of methanol adducts (with UV spectra identical with that of the 9,10-dihydrodiol) on storage in 1 M NaOMe at 40 °C for 5 h. After standard workup, the adducts were separated by HPLC on a Du Pont Zorbax SIL column (0.95 × 25 cm) eluted with 1% methanol and 10% EtOAc in hexane: $k' = 2.50$, 60%, and $k' = 3.59$, 40%. Both adducts gave mass spectra (CI, NH_3) with *m/e* 344 corresponding to $(M + NH_4^+)$. NMR spectra (300 MHz, acetone-d_6) for each had $J_{9,10} \sim 2.3$ Hz consistent with axial, trans substituents. These adducts must be trans since in acidic methanol an additional pair of cis adducts are formed. The major, early-eluting adduct (CH_3O at δ 3.30) has H_{10} at δ 4.52 shifted 0.36 upfield relative to the 9,10-dihydrodiol due to the methyl group and H_9 δ 5.54 (OH coupled) shifted 0.09 downfield and thus corresponds to the product from methoxide attack at C_{10} on the oxide. The minor, late-eluting adduct (CH_3O at δ 3.48) has H_9 at δ 5.19 shifted 0.26 upfield due to the methyl group and H_{10} δ 5.14 (OH coupled) and thus corresponds to methoxide attack at C_9 on the oxide. Rotations of the methanol adducts were measured at 1.2 mg/mL in THF. From (+)-oxide: major (less polar), 10-*O*-methyl, $[\alpha]_D$ −912°; minor (more polar), 9-*O*-methyl, $[\alpha]_D$ +850°. From (−)-oxide: major (less polar), 10-*O*-methyl, $[\alpha]_D$ +975°; minor (more polar), 9-*O*-methyl, $[\alpha]_D$ −870°.

A Study of the Stereochemistry of the Electrocyclic Ring Closure of Substituted Bisallenes to Substituted 3,4-Bisalkylidenecyclobutenes

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The stereochemistry of the quantitative electrocyclic ring closure of the bisallenes **5**, **8**, **11**, and *erythro*- and *threo*-**14** to the substituted 3,4-bisalkylidenecyclobutenes in solution at 65 °C in the presence of cuprous chloride (believed to be a radical-anion, chain process) and in the gas phase at 300–350 °C has been determined. With **5**, **8**, and **11** there is only modest stereoselectivity favoring the least sterically strained product. With *erythro*- and *threo*-**14** the electrocyclic ring closure occurs in a strictly conrotatory manner under both sets of conditions, again showing only modest selectivity for formation of the least sterically strained product. In view of the fact that neither the conrotatory nor the disrotatory motions between the ground states in the radical-anion process are allowed by orbital symmetry, the observed conrotatory motion is attributed to less of a steric interaction in the conrotatory process than in the disrotatory process. With **8**, **11**, and **14** the electrocyclic ring closure reactions are considerably less stereoselective in the solution-phase reactions in the presence of cuprous chloride. The extensive formation of **10**, **12**, and **15** and **17** in the ring-closure reactions of **8**, **11**, and **14e** and **14t** suggest that the reactions occur via rather early transition states in which very little of the final steric strain energy has been developed. The results of theoretical and thermodynamic calculations indicate that the 3,4-bisalkylidenecyclobutenes are highly enthalpically favored; thus, their formation is expected to occur via rather early transition states in these electrocyclic ring-closure reactions, with the transition states for the ring closure of the radical anions occurring earlier than those for the ring closure of the neutrals. A comparison is made with the butadiene–cyclobutene system in which butadiene is the enthalpically favored product. The electronic properties of the 3,4-bisalkylidenecyclobutenes are briefly discussed.

Introduction

The electrocyclic ring-opening reactions of substituted cyclobutenes to form substituted 1,3-butadienes have been extensively studied.[1] In general, the substituted 1,3-butadienes are highly thermodynamically favored except when the diene is highly strained,[2a,b] halogen substituted,[2c] or when the ring closure results in the formation of an aromatic system.[2d] These reactions occur in an exclusively conrotatory manner,[3] which is controlled by orbital symmetry.[4] Recent interest in the author's laboratories has

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[1] For recent monographs, see: (a) Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.

[2] Shumate, K. N.; Neuman, P. N.; Fonken, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3996. (b) Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 3582. (c) Brune, H. A.; Schwab, W. *Tetrahedron* **1969**, *25*, 4375. (d) Steiner, R. P.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6415.

[3] Vogel, E. *Angew. Chem.* **1954**, *66*, 640. Vogel, E. *Justus Liebigs Ann. Chem.* **1958**, *615*, 14. Criegee, R.; Noll, K. *Justus Liebigs Ann. Chem.* **1959**, *627*, 1. Adam, W. *Chem. Ber.* **1964**, *97*, 1811. Criegee, R.; Seeback, D.; Winter, R. E.; Borretzen, B.; Brune, H.-A. *Chem. Ber.* **1965**, *98*, 2339. Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207. Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131. Freedman, H. M.; Doorakian, G. A.; Sandel, R. F. *J. Am. Chem. Soc.* **1965**, *87*, 3019. Walsh, R.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 650. Branton, G. R.; Frey, H. M.; Skinner, R. F. *Trans. Faraday Soc.* **1966**, *62*, 1546. Srinivasan, R. *J. Am. Chem. Soc.* **1969**, *91*, 7557. Maier, G.; Wiessler, M. *Tetrahedron Lett.* **1969**, 4987. Brauman, J. I.; Archie, W. C., Jr. *Tetrahedron* **1971**, *27*, 1275. Winter, R. E. K.; Honig, M. L. *J Am. Chem. Soc.* **1971**, *93*, 4616. Brauman, J. I.; Archie, W. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4262. Dalrymple, D. L.; Russo, W. B. *J. Org. Chem.* **1975**, *40*, 492.

0022-3263/89/1954-3544$01.50/0

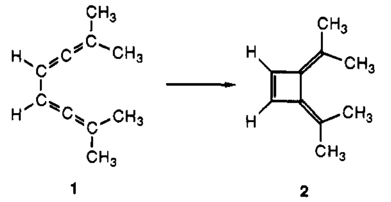
focused on the electrocyclic ring closure of bisallenes to 3,4-bisalkylidenecyclobutenes as a possible step in the formation of 3,4-bisalkylidenecyclobutenes from the reactions of substituted propargyl chlorides with tris(triphenylphosphine)nickel(0).[5] The results of initial studies showed that the reaction of the bisallene **1** with various nickel(0) complexes resulted in the formation of a cyclic dimer and trimer, with very little formation of **2**.[6] The ring closure of **1** to **2** was weakly catalyzed by bis(triphenylphosphine)nickel dibromide.[6]

The observed quantitative ring closure of **1** to **2**[6] initially was rather surprising. The reaction represents the reverse of the cyclobutene-to-butadiene process and appeared to be very unfavorable in view of the formation of the highly strained 3,4-bisalkylidenecyclobutene system. The results of more recent studies have indicated that the ring closure of **1** to **2** occurs quantitatively in solution by what is thought to be a chain process involving a radical-anion intermediate when initiated by cuprous salts or dimethylcuprate (and is inhibited by the presence of 1,4-dinitrobenzene) or by a chain process involving a radical-cation intermediate when initiated by tris(4-bromophenyl)aminium cation.[7,8] A purely thermal-induced ring closure of **1** to **2** in solution up to 200 °C could not be accomplished. Because of the very unusual nature of the ring closure of **1** to **2**, we have carried out a study of the stereoselectivity of the ring-closure reaction in solution initiated by cuprous chloride at 65 °C and in the gas phase at low pressure (a pure thermally induced process) at 300–350 °C with the bisallenes **5**, **11**, and *erythro*- and *threo*-**14**. The only previous reports of electrocyclic ring closures of bisallenes appears to be that of the parent 1,2,4,5-hexatriene[9a] and *meso*-**3** in the presence of cuprous chloride, which gives only **4** in a conrotatory process.[9b,10] In no case has the stereochemistry of the electrocyclic ring closure of both diatereoisomers of a substituted bisallene been determined.

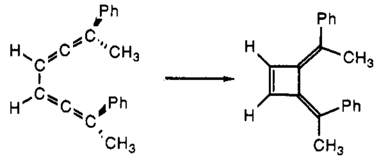
Attempts to separate and isolate pure bisalkylidenecyclobutenes by chromatographic techniques have failed. These compounds are extremely reactive, undergoing polymerization when in concentrated form or on exposure to air or possible sources of radicals. Structural assignments have been made on the basis of NMR spectral comparisons, and in some cases by iodine-induced isomerization reactions.

Results

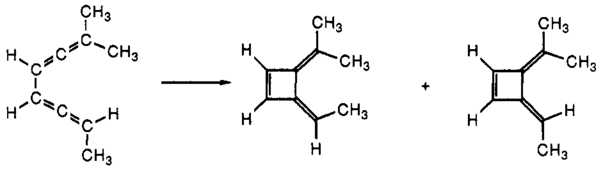
The electrocyclic ring closure of **5** in deuteriochloroform in the presence of cuprous chloride at 65 °C quantitatively produces a mixture of **6** and **7**. The stereochemistry of **6** and **7** is assigned on the basis of the relative chemical shifts of the methyl groups and the vinyl hydrogen on the exocyclic double bond (long-range couplings could not be resolved). In **7** there are two high-field methyl resonances at δ 1.73 and 1.75 and one low-field methyl resonance at δ 1.83. The lower field resonance is consistent with an inner-oriented methyl group, which is long-range deshielded by the proximate exocyclic double bond. In the NMR spectrum of **6** there are two low-field methyl resonances at δ 1.89 and 1.94 and one high-field methyl resonance consistent with two inner-oriented methyl groups. The vinyl hydrogens in **6** and **7** show similar differences in chemical shift, in **7** the inner-oriented vinyl hydrogen suffering long-range deshielding by the adjacent double bond and appearing at δ 5.30, while the outward-oriented vinyl hydrogen of **6** appears at δ 5.08. The ratio of **6** to **7** formed in the solution-phase reaction is 34.4:65.6, while in the gas phase at 322 °C the ratio is 41.1:58.9.



1 **2**

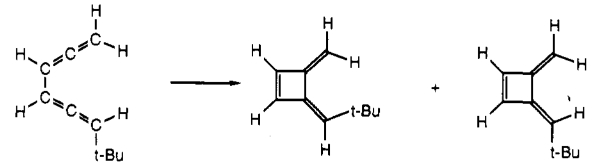


3 **4**



5 **6** **7**

The ring closure of **8** in solution at 65 °C in the presence of cuprous chloride produces **9** and **10** in a ratio of 34.0:66.0. The assignment of stereochemistry is made on the basis of the relative chemical shifts of the *tert*-butyl groups and the vinyl hydrogens in **9** and **10**. In **9** the *tert*-butyl resonance appears at lower field (δ 1.17) than in **10** (δ 1.12), while the vinyl hydrogen shows an opposite trend appearing at lower field in **10** (δ 5.15) than in **9** (δ 5.13). There is also a considerable long-range deshielding effect by the *tert*-butyl group on the adjacent methylene hydrogens in **9**. Similar long-range deshielding effects by the *tert*-butyl group are apparent in the 3,4-bisalkylidenecyclobutenes, which have an inward-oriented *tert*-butyl group.



8 **9** **10**

The electrocyclic ring closure of **11** produces a mixture of **12** and **13**. The *tert*-butyl and methyl resonances in **12** (δ 1.23, 1.80 and 2.00) appear at lower field than in **13** (δ 1.15, 1.73, and 1.86), while the vinyl hydrogen resonance appears at lower field in **13** (δ 5.34) than in **12** (δ 5.21). Heating the reaction mixture with a catalytic quantity of iodine resulted in the quantitative isomerization of **12** to **13**, providing additional support for the stereochemical

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(4) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. Longuet-Higgens, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045. Fukui, K. *Tetrahedron Lett.* **1965**, 2009.

(5) Pasto, D. J.; Mitra, D. K. *J. Org. Chem.* **1982**, *47*, 1381.

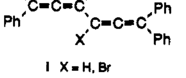
(6) Pasto, D. J.; Huang, N.-Z. *J. Org. Chem.* **1985**, *50*, 4465.

(7) Pasto, D. J.; Yang, S.-H. *J. Org. Chem.*, submitted for publication.

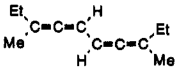
(8) Only **1** has been shown to undergo ring closure in the presence of the aminium cation. Lesser alkyl-substituted bisallenes do not undergo ring closure; apparently the ionization potential of the lesser alkyl-substituted bisallenes being too high for abstraction of an electron by the aminium cation.

(9) (a) Hopf, H. *Angew. Chem.* **1970**, *82*, 703. Hopf, H.; Lenich, F. T. *Chem. Ber.* **1973**, *106*, 3461. (b) Kleveland, K.; Skattebol. L. *J. Chem. Soc., Chem. Commun.* **1973**, 432.

(10) The substituted allenes **i** and **ii** also undergo ring closure at room temperature in the presence of cuprous chloride (private communication from Prof. L. Skattebol).

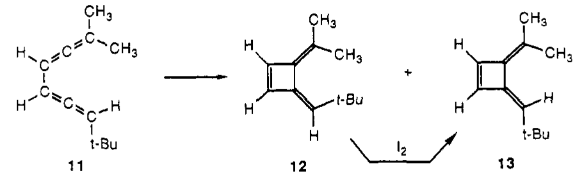


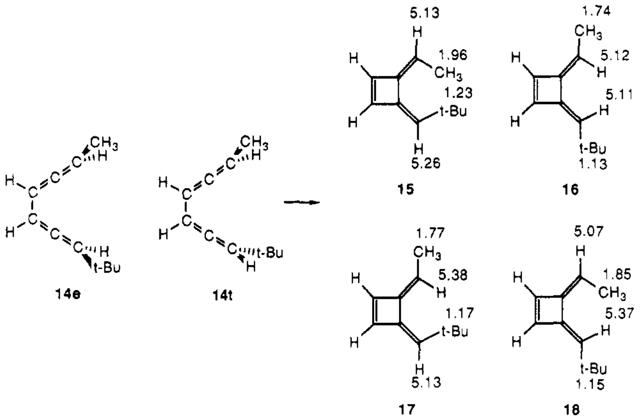
i X = H, Br



ii (mixture of stereoisomers)

assignments. The ratio of **12** to **13** formed at 65 °C in solution in the presence of cuprous chloride is 20.6:79.4, while in the gas phase at 350 °C the ratio is 5.5:94.5.





The electrocyclic ring closure of a mixture of *erythro*-**14** (**14e**) and *threo*-**14** (**14t**) produces a mixture of the four bisalkylidenecyclobutenes, **15–18**. The resonances of the four products are well resolved, providing for easy assignment and integration (see Figure 1). The assignment of the stereochemistry in the four products is again based on relative chemical shifts of the *tert*-butyl and methyl groups and the exocyclic methylene vinyl hydrogens as described above (see the chemical shifts indicated in the structures). Further support for the stereochemical assignments is derived from the observation that on treatment with a catalytic quantity of iodine at 65 °C, **15** is rapidly isomerized to **18**, **17** is isomerized at an intermediate rate to **16**, while **18** is rather slowly isomerized to **16**. This kinetic trend is consistent with the degree of internal strain energy expected to be present in **15–18**.

$$\begin{tikzcd}
15 \arrow[r, "I_2", "\text{fast}"'] & 18 \arrow[d, "I_2", "\text{slow}"'] \\
17 \arrow[r, "I_2", "\text{intermediate}"'] & 16
\end{tikzcd}$$

The electrocyclic ring closure of pure **14t**[11] at 300 °C results in approximately 50% ring closure to form only **15** and **16** in a ratio of 10.4:89.6 The unreacted **14** is pure **14t**, indicating that no isomerization of **14t** to **14e**, or vice versa, occurs under the reaction conditions. In solution at 65 °C in the presence of cuprous chloride again only **15** and **16** are formed from **14t**, in this case in a ratio of 24.0:76.0. The progress of the reaction was followed by NMR, giving a plot for the rate of formation of **15** and **16** similar to that observed for the formation of **2** and **1**,[7] which resembles a chain process and not a typical first-order plot. The "rate" of ring closure of **14t** occurs considerably more slowly than does **1**. No isomerization of **14t** to **14e** was observed during the monitoring of the ring closure of **14t** in solution in the presence of cuprous chloride.

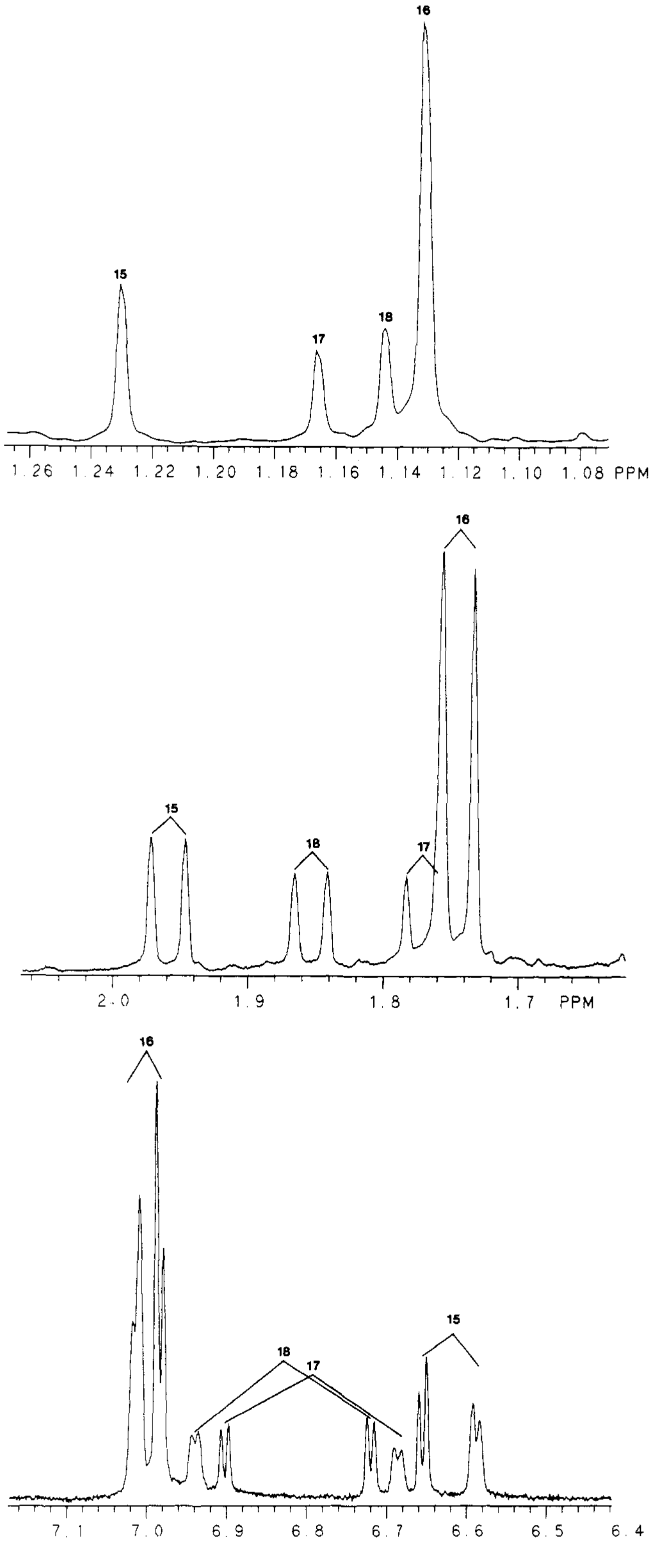


Figure 1. The *tert*-butyl, methyl, and ring vinyl hydrogen resonance regions in the NMR spectrum of a mixture of **15–18**.

The results of the ring closure reactions of different mixtures of **14e** and **14t** in the gas phase and in solution in the presence of cuprous chloride are given in Table I. The ring closure at 350 °C was essentially complete (95%), while at 300 °C the ring closure had proceeded to approximately 50%.

Discussion

Although two different types of processes are involved in the electrocyclic ring-closure reactions described in this

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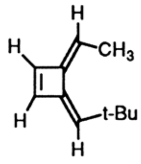
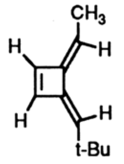
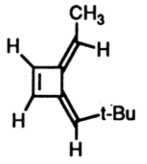
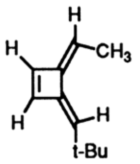
[11] Pure **14t** can be isolated from a mixture of **14e** and **14t** after reaction with *N*-phenylmaleimide at room temperature, which reacts much more rapidly with **14e** (Pasto, D. J.; Yang, S.-H. *J. Org. Chem.*, submitted for publication).

Table I. Relative Yields of Ring-Closure Products Derived from 14 in the Gas Phase and in Solution

	threo–erythro ratios	 **15**	 **16**	 **17**	 **18**
		Gas Phase			
350 °C	49.7:50.3 (before) 55.6:44.4 (after)	3.5	44.3	15.2	37.0
300 °C	39.1:60.9 (before) 41.7:58.3 (after)	4.1	32.2	19.2	44.5
300 °C	100:0 (before) 100:0 (after)	10.4	89.6	–	–
		Solution ($CuCl/CDCl_3$)			
65 °C	40.6:59.4 (before) 49.4:50.6 (after)	11.5	28.4	27.0	33.1
65 °C	100:0 (before) 100:0 (after)	24.0	76.0	–	–

article, it is more expedient to discuss them together and make comparisons. The ring-closure reactions in solution in the presence of cuprous chloride are believed to occur via radical-anion intermediate, chain processes,[7] while the gas-phase reactions are believed to occur via purely thermal electrocyclic reactions of the neutrals. The implications of these differences will be addressed later.

The ring-closure reactions of **5**, **8**, **11**, and **14** exhibit only modest stereoselectivities. This is especially noteworthy with **8**, **11**, and **14** in which considerable amounts of product are formed (**9**, **12**, and **15** and **17**, respectively) in which the *tert*-butyl group is in a very sterically congested position. This very modest selectivity for the formation of the much more thermodynamically stable product suggests that the transition states for the formation of these products occur very early along the reaction coordinate before much of the strain energy of the product is generated.

The ring-closure reactions of **5**, **8**, and **11** do not provide any information as to whether the ring-closure reactions occur in a conrotatory or a disrotatory manner. The stereochemical results obtained with the stereoisomers of **14** provide that answer. The ring closure of **14t** occurs with exclusive conrotatory motion, both in solution in the presence of cuprous chloride and in the gas phase. No isomerization of **14t** to **14e** is observed in either case. When the reaction is carried out in the gas phase at 300 °C, approximately 50% ring closure occurs; no **14e** can be detected. Similarly, when monitoring the ring closure of **14t** in solution in the presence of cuprous chloride, no **14e** can be detected during the reaction. In the case of the ring closure of **14t** only **15** and **16** are formed, both of which are formed by a conrotatory process. The ring-closure reactions of mixtures of **14e** and **14t** produce mixtures of **15** and **16** in ratios that are within experimental error (by NMR analysis) of those formed from pure **14t**. This also indicates that no isomerization of **14e** to **14t**, or vice versa, occurs during these reactions. Thus, one must conclude that both stereoisomers of **14** undergo ring closure with complete stereospecificity in a *conrotatory* manner under *both* sets of conditions.

Why is exclusive conrotatory motion observed in both of these types of ring-closure reactions? In the pure thermal processes in the gas-phase conrotatory motion is expected according to the conservation of orbital symmetry,[12] the termini of the two allene units undergoing rotation in the same direction as the 2p AO's at the termini of the central butadiene chromophore (see Figure 2). But what about the radical-anion process? The principle of conservation of orbital symmetry has been applied to the butadiene–cyclobutene radical-cation system with the conclusion that neither disrotatory nor conrotatory opening is associated with a ground-state to ground-state interconversion corresponding to a favorable thermal reaction.[13] The same is true for the radical-anion process, the correlations involving orbitals of same symmetry and occupancy relate the electronic ground state of the reactant (or product) with an electronic excited state of the product (or reactant). It is very doubtful that excited states are involved in these reactions, in that the reactions were run in glass NMR tubes and were not subjected to any source of radiation, and that the results of theoretical calculations (discussed later) do not indicate that such a process would be feasible under the reaction conditions.

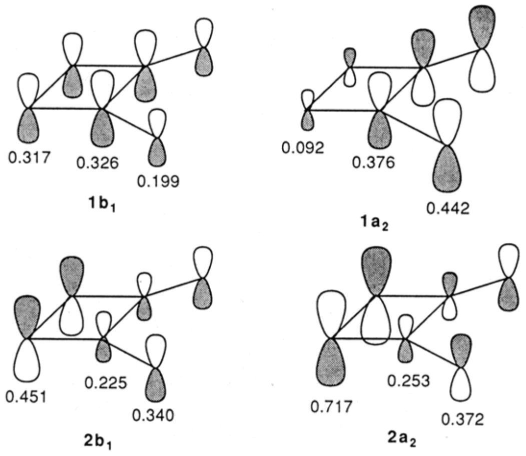


Figure 2. The π wave functions of **20**. The numbers are the coefficients of the 2p AO's.

At the present time, we attribute the observed direction of rotation as arising purely from steric interactions between the groups attached to the termini of the allene units; the conrotatory motion involves no adverse steric interaction between the groups while the disrotatory motion requires that either the top or the bottom groups rotate toward each other (see illustration in Figure 2).

A comparison of the ratios of **14e** to **14t** before and after partial ring closure and the ratios of (**15** + **16**) to (**17** + **18**) formed in the gas phase (see Table I) indicates that **14t**

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[12] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press, Inc.: New York, 1970.

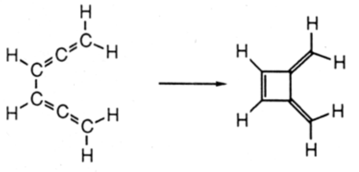
[13] Dunkin, I. R.; Andrews, L. *Tetrahedron* **1985**, *41*, 145.

undergoes ring closure slightly slower than does **14e**. This would appear to be due to the fact that one of the modes of ring closure of **14t** produces the most highly sterically congested product (**15**). This mode of reaction is expected to be retarded relative to the other modes of ring closure of **14e** and **14t**, resulting in an overall reduction in the reactivity of **14t** relative to **14e**.

It is interesting to compare the ratios of the products formed from **8**, **11**, and **14** in the gas phase with the ratios formed in solution at 65 °C in the presence of cuprous chloride. In all three cases, considerably more of the more sterically congested product is formed in the solution reactions at 65 °C. This is not what one would have expected if the transitions states occurred at the same positions along the reaction coordinate (i.e. identical transition-state structures) in the two processes, in which case less of the more sterically congested product should be formed in the lower temperature solution-phase reactions at 65 °C. This suggests that in the solution-phase reactions occurring via radical-anion intermediates the transition states for ring closure occur earlier along the reaction coordinates in which less steric strain has been generated.

Theoretical Analysis. The results discussed above suggest that the electrocyclic ring-closure reactions of substituted bisallenes occur via rather early transition states, with the transition state for ring closure of the radical-anion occurring earlier than those for the ring closure of the neutral bisallenes. According to the Hammond postulate,[14] this implies that the reactions must be substantially exothermic. The results of theoretical and thermodynamic calculations support this view.

Ab initio MO calculations have been carried out on the neutral and radical-anion parent systems **19** and **20** at the HF and UHF 4-31G level with full geometry optimization using the GAUSSIAN82 package of programs.[15] The total energies are given in Table II. The change in total energy for the conversion of neutral **19** to neutral **20** is −7.6 kcal/mol, while at the MP2/6-31G* level on the 4-31G geometry the difference in total energy is −19.4 kcal/mol. This is in contrast to the butadiene–cyclobutene system in which butadiene is calculated to be lower in total energy than cyclobutene by 7.6 kcal/mol at the MP2/6-31G* level.[16] The changes in ΔH_f, $T\Delta S_f$, and ΔG_f at 298 K have been calculated by the method of Benson,[17] giving values of −29.1, +10.8, and −18.3 kcal/mol. (The comparable values for the butadiene–cyclobutene system are +10.7, +1.0, and +11.7 kcal/mol, consistent with the experimental observations that butadiene is thermodynamically favored.) Thus, both types of calculations indicate that **20** is considerably lower in energy than **19** and should be formed from **19** via an early transition state.



19 20

Ab initio calculations on the radical anions of **19** and **20** give a difference in total energy of −10.6 kcal/mol at the UHF 4-31G level. This value is *greater* than that for the neutrals of −7.6 kcal/mol, indicating that the ring closure of the radical anion of **19** is more exothermic than the ring closure of neutral **19**, and, because the two electrocyclic ring-closure reactions are identical structurely, the transition state for the ring closure of the radical anion should occur earlier, and with a lower energy barrier, than that for the ring closure of neutral **19**. This is fully consistent with the conclusions drawn from the stereoselectivity results.

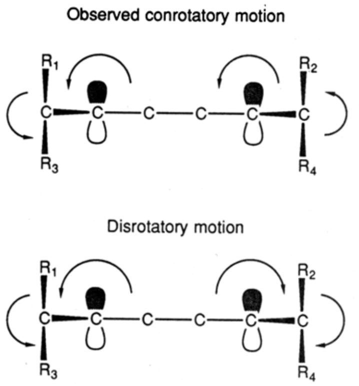


Figure 3. Illustration of the steric interactions generated on conrotatory and disrotatory ring-closure processes.

Table II. Calculated Total Energies for the Neutral and Radical Anions of 19 and 20

structure	energy, au
19	−230.244 50
$\mathbf{19}^-$	−230.168 99
20	−230.256 62
$\mathbf{20}^-$	−230.185 93

Why is **20** heavily thermodynamically favored over **19**, whereas in the butadiene–cyclobutene system butadiene is heavily thermodynamically favored? An answer is derived from an analysis of the calculations of the ΔH_f's using the method of Benson.[17] The calculated ΔH_f for **19** is very positive (+94.48 kcal/mol at 298 °C), primarily due to the very positive group value for the heat of formation of the allenic carbon atom (+34.20 kcal/mol per allenic carbon atom), which more than offsets the positive heat of formation of the cyclobutene ring (+29.8 kcal/mol). Olefinic carbon atoms have ΔH_f group values in the range of +6 to +10 kcal/mol, considerably less than that for an allenic carbon atom, thus explaining why the two equilibria lie far to opposite sides. Current studies are focusing on the electrocyclic reactions of the intermediate class of compounds, the substituted vinylallenes.

Molecular Orbital Properties of 20. As a class of compounds, the 3,4-bisalkylidenecyclobutenes are exceptionally reactive, thus far precluding their isolation as pure substances. These compounds possess a very unusual π-system. The calculated 4-31G wave functions are illustrated in Figure 3. The $1b_1$, $1a_2$ and $2b_1$ MO's are doubly occupied, with the $2b_1$ MO being the HOMO with an energy of −8.629 eV. The 2a2 MO is the LUMO (+3.511 eV). It should be noted that the largest coefficients in both the HOMO and LUMO appear at C1 and C2 of the ring, suggesting that these compounds should be very reactive with nucleophilic, radical, and electrophilic reagents. In addition, the bonding interaction between C3 and C4 in the $1b_1$ and $2b_1$ MO's is greater than the antibonding interaction between these carbon atoms in the $1a_2$ MO resulting in a net π Mulliken population between C3 and C4 of 0.0023. This should impart some cyclobutadienoid character to these systems. The chemistry of this interesting class of compounds is being explored.

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Experimental Section

Preparation of Substituted Bisallenes. 2-Methyl-2,3,5,6-octatetraene (**5**), 7,7-dimethyl-1,2,4,5-octatetraene (**8**), 2,8,8-trimethyl-2,3,5,6-nonatetraene (**11**), and 8,8-dimethyl-2,3,5,6-nonatetraene (**14**) were prepared by the Pd(0)-catalyzed coupling of an allenylzinc chloride with a propargyl chloride as described by Ruitenberg et al.[18]

5: ^{1}H NMR δ (300 MHz, CDCl$_3$) 1.68 (dd, J = 7.02, 2.99 Hz, 3 H), 1.708 (d, J = 2.73 Hz, 3 H), 1.714 (d, J = 2.73 Hz, 3 H), 5.27 (ddq, J = 7.02, 5.95, 0.68 Hz, 1 H), 5.46 (ddhept, J = 10.26, 2.72, 0.68 Hz, 1 H), 5.54 (ddq, J = 10.26, 5.94, 2.99 Hz, 1 H); ^{13}C NMR δ 14.33, 20.45, 20.52, 87.30, 88.14, 90.38, 96.96, 203.77, 206.40.

8: NMR δ (300 MHz, CDCl$_3$) 1.02 (s, 9 H), 4.88 (d, J = 5.59 Hz, 1 H), 4.89 (d, J = 5.59 Hz, 1 H), 5.31 (d, J = 5.75 Hz, 1 H), 5.58 (dd, J = 10.28, 5.75, 1 H), 5.64 (dt, J = 10.28, 5.69 Hz, 1 H).

11: ^{1}H NMR δ (300 MHz, CDCl$_3$) 1.05 (s, 9 H), 1.71 (d, J = 2.76 Hz, 3 H), 1.72 (d, J = 2.76 Hz, 3 H), 5.29 (dd, J = 6.16, 0.92 Hz, 1 H), 5.43 (ddhept, J = 10.05, 0.92, 2.76 Hz, 1 H), 5.61 (dd, J = 10.05, 6.16 Hz, 1 H); ^{13}C NMR δ 20.52, 20.63, 30.17, 88.47, 92.54, 96.93, 104.68, 203.09, 203.78.[19]

14 (erythro): NMR δ (300 MHz, CDCl$_3$) 1.045 (s, 9 H), 1.680 (dd, J = 6.92, 3.14 Hz, 3 H), 5.280 (ddq, J = 5.25, 0.62, 6.92 Hz, 1 H), 5.304 (dd, J = 5.84, 0.52 Hz, 1 H), 5.54 (dddq, J = 10.26, 5.25, 0.52, 3.14 Hz, 1 H), 5.64 (ddd, J = 10.26, 5.84, 0.62 Hz, 1 H); (threo) 1.050 (s, 9 H), 1.687 (dd, J = 6.90, 2.92 Hz, 3 H), 5.287 (br dq, J = 6.90, 5.41 Hz, 1 H), 5.310 (br d, J = 5.30 Hz, 1 H), 5.545 (ddq, J = 10.16, 5.41, 2.92 Hz, 1 H), 5.641 (br dd, J = 10.16, 5.30 Hz, 1 H).

Gas-Phase Electrocyclic Ring-Closure Reactions. A solution of 0.1 g of the bisallene in 1.0 mL of CDCl$_3$ (except as noted) was placed in a small round-bottomed flask. The flask was connected to a vertically oriented quartz tube (20 × 2 cm) wrapped with a heated tape. The bottom of the quartz tube was connected to a small trap equipped with a vacuum takeoff sidearm, which was immersed in liquid nitrogen. The quartz tube was heated to 350 °C, and the bisallene was evaporatively distilled through the heated quartz column under full vacuum line pressure (5–10 mTorr). In general, only a single pass through the column was required for complete ring closure to occur. (For the more volatile bisallenes, the round-bottomed flask was immersed in ice water during the process to slow the evaporation process.) The trap was removed from the apparatus and allowed to warm to room temperature, the contents were removed and placed in an NMR tube, and the 300-MHz NMR spectrum was recorded. The structures of the ring-closed products were determined directly from the NMR spectra of the product mixture from the relative integrals and coupling constant relationships. Stereochemical assignments were made on the basis of NOE and iodine isomerization experiments.

Solution-Phase Electrocyclic Ring-Closure Reactions. A solution of 0.1 g of the bisallene in 1.0 mL of CDCl$_3$ (except as noted) was placed in an NMR tube, and 5 mg of cuprous chloride was added. The contents of the tube were triply freezed–degassed, and the tube was sealed under vacuum. The tube was heated in an oil bath at 65 °C. Periodically the tube was removed from the sand bath, and the 300-MHz NMR spectrum was recorded.

Electrocyclic Ring Closure of 5. The electrocyclic ring closure of **5** produced a mixture of **6** and **7** in a ratio of 34.4:65.6 in solution and 41.1:58.9 in the gas phase. Heating the reaction mixture at 65 °C with a catalytic quantity of iodine failed to result in the isomerization of **6** to **7**.

6: NMR δ (300 MHz, CDCl$_3$) 1.78 (s, 3 H), 1.89 (dd, J = 7.37, 0.57 Hz, 3 H), 1.94 (s, 3 H), 5.08 (br q, J = 7.37 Hz, 1 H), 6.59 (br d, J = 2.88 Hz, 1 H), 6.84 (d, J = 2.88 Hz, 1 H). Irradiation of the δ 1.89 resonance of **6** resulted in an 11% increase in the intensity of the δ 1.94 methyl resonance.

7: NMR δ (300 MHz, CDCl$_3$) 1.73 (s, 3 H), 1.75 (d, J = 6.96 Hz, 3 H), 1.83 (s, 3 H), 5.30 (br q, J = 6.97 Hz, 1 H), 6.83 (br d, J = 2.76 Hz, 1 H), 6.89 (d, J = 2.76 Hz, 1 H). Irradiation of the δ 1.83 resonance resulted in a 16% increase in the intensity of the δ 5.30 vinyl-hydrogen resonance.

Electrocyclic Ring Closure of 8. The electrocyclic ring closure of **8** produced **9** and **10** in a ratio of 34.0:66.0 in solution.

9: NMR δ (300 MHz, CD$_3$COCD$_3$) 1.12 (s, 9 H), 4.57 (d, J = 0.64 Hz, 1 H), 4.69 (br s, 1 H), 5.13 (s, 1 H), 6.89 (dd, J = 2.55, 0.64 Hz, 1 H), 7.23 (d, J = 2.55 Hz, 1 H).

10: NMR δ (300 MHz, CD$_3$COCD$_3$) 1.17 (s, 9 H), 4.74 (s, 1 H), 4.91 (s, 1 H), 5.15 (s, 1 H), 6.78 (br d, J = 2.75 Hz, 1 H), 6.88 (d, J = 2.75 Hz, 1 H).

Electrocyclic Ring Closure of 11. The electrocyclic ring closure of **11** produced **12** and **13** in a ratio of 20.6:79.4 in solution and 5.5:94.5 in the gas phase. Heating the reaction mixture with a catalytic quantity of iodine at 65 °C resulted in the isomerization of **12** to **13**.

12: NMR δ (300 MHz, CDCl$_3$) 1.232 (s, 9 H), 1.795 (s, 3 H), 1.997 (s, 3 H), 5.21 (s, 1 H), 6.54 (d, J = 2.90 Hz, 1 H), 6.89 (d, J = 2.90 Hz, 1 H); ^{13}C NMR δ 21.85, 21.94, 31.98, 34.68, 117.25, 127.15, 137.30, 139.84, 141.31, 142.32.

13: NMR δ (300 MHz, CDCl$_3$) 1.149 (s, 9 H), 1.73 (s, 3 H), 1.86 (s, 3 H), 5.34 (br s, 1 H), 6.88 (br d, J = 2.85 Hz, 1 H), 6.91 (dd, J = 2.85, 0.49 Hz, 1 H); ^{13}C NMR δ 19.19, 20.91, 30.92, 34.23, 117.02, 124.65, 137.72, 139.37, 141.26, 142.71.

Electrocyclic Ring Closure of *threo*-14. The electrocyclic ring closure of **14t** resulted in the formation of a mixture of **15** and **16** in a ratio of 24.4:75.6 in solution and 10.4:89.6 in the gas phase at 300 °C.

15: NMR δ (300 MHz, CDCl$_3$) 1.23 (s, 9 H), 1.96 (d, J = 7.57 Hz, 3 H), 5.12 (br q, J = 7.57 Hz, 1 H), 5.26 (d, J = 0.92 Hz, 1 H), 6.59 (br d, J = 2.70 Hz, 1 H), 6.66 (d, J = 2.70 Hz, 1 H). Irradiation of the δ 1.96 methyl resonance resulted in a 12% increase in the intensity of the δ 1.23 *tert*-butyl resonance.

16: NMR δ (300 MHz, CDCl$_3$) 1.13 (s, 9 H), 1.74 (dd, J = 7.02, 0.55 Hz, 3 H), 5.10 (br s, 1 H), 5.14 (br q, J = 7.02 Hz, 1 H), 6.98 (d, J = 2.57 Hz, 1 H), 7.00 (br d, J = 2.57 Hz, 1 H).

Electrocyclic Ring Closure of a Mixture of 14e and 14t. The electrocyclic ring closure of a 59.4:40.6 ratio of **14e**:**14t** in solution at 65 °C for 2.5 h resulted in the formation of a mixture of **15**, **16**, **17**, and **18** in a ratio of 11.5:28.4:27.0:33.1, along with 29.3% of unreacted **14** in a ratio of 50.6:49.4 **14e**:**14t**. Rearrangement in the gas phase at 300 °C resulted in the formation of a mixture of **15**, **16**, **17**, and **18** in a ratio of 4.1:32.2:19.2:44.5, along with 50% unreacted **14e** and **14t** in a ratio of 58.3:41.7. At 350 °C, the product ratio was 3.5:44.3:15.2:37.0, along with 13.7% unreacted **14e** and **14t** in a ratio of 47.8:52.2. The NMR spectra of **17** and **18** were obtained by subtracting the NMR spectra of **15** and **16** formed from **14t** from the reaction mixture derived from the mixture of **14e** and **14t**.

17: NMR δ (300 MHz, CDCl$_3$) 1.17 (s, 9 H), 1.77 (dd, J = 7.01, 0.57 Hz, 3 H), 5.13 (s, 1 H), 5.38 (br d, J = 7.01 Hz, 1 H), 6.69 (br d, J = 2.82 Hz, 1 H), 6.90 (d, J = 2.82 Hz, 1 H). Irradiation of the δ 5.38 vinyl-hydrogen resonance resulted in an 11% increase in the intensity of the *tert*-butyl resonance.

18: NMR δ (300 MHz, CDCl$_3$) 1.14 (s, 9 H), 1.85 (dd, J = 7.20, 0.72 Hz, 3 H), 5.07 (br q, J = 7.20 Hz, 1 H), 5.37 (s, 1 H), 6.72 (d, J = 2.54 Hz, 1 H), 6.94 (br d, J = 2.54 Hz, 1 H). Irradiation of the δ 5.37 vinyl-hydrogen resonance resulted in a 13% increase in the intensity of the methyl resonance.

Iodine-Catalyzed Isomerization of the Reaction Mixture Derived from a Mixture of 14e and 14t. A mixture of **15**, **16**, **17**, and **18** in CDCl$_3$ in a NMR tube was heated with a catalytic quantity of iodine at 65 °C. The NMR spectrum was periodically recorded and the integral determined. A comparison of the integrals indicated the rapid disappearance of **15** with an increase in **18**, followed by the slower disappearance of **17**, and finally, the very slow disappearance of **18** with the exclusive formation of **16**.

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