Articles

Study of the Substituted Vinylallene–Methylenecyclobutene Electrocyclic Equilibria. Comparison with the Butadiene–Cyclobutene and Bisallene–Bismethylenecyclobutene Electrocyclic Equilibria

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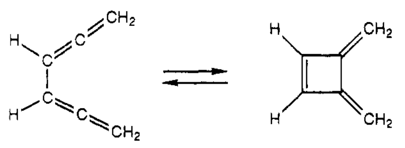
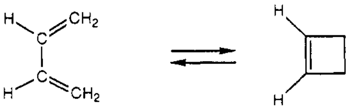
A number of substituted vinylallenes and 3-alkylidenecyclobutenes have been prepared and their electrocylic reactions studied. The electrocyclic ring-closure equilibria of the parent vinylallene, 1,2,4-pentatriene (**5**), has been determined at a number of temperatures in the gas phase, and the thermodynamic parameters have been calculated. Theoretical calculations have been carried out on **5a**, **5s**, and **6** at the fully geometry optimized 6-31G* level with further single-point calculations being carried out at the MP2/6-31G* level and with zero-point energy corrections. Thermodynamic calculations on the **5**–**6** system have also been carried out using Benson's method. The correlation between the experimental and calculated thermodynamic parameters is excellent, indicating that **6** is enthalpically favored, while **5** is entropically favored. These results are compared with similar calculations on the butadiene–cyclobutadiene and bisallene–3,4-bisalkylidenecyclobutene systems in which in the former the butadiene is heavily enthalpically favored and in the latter the bisalkylidenecyclobutene is heavily enthalpically favored. The observed trends in the electrocyclic equilibria are discussed in terms of the relative heats of formation of the open-chain compounds which differ substantially. With the 2-substituted 1,3,4-hexatrienes **9**, **11**, and **13**, equilibrium constants were obtained in the gas phase at 360 and 435 °C, allowing for the calculation of the equilibrium thermodynamic parameters. However, with the 1-substituted systems **15** and **19** the corresponding ring-closed products **16** and **20** could not be detected. Heating **15c** or **15t** produces **18**. The transformation of **15t** to **18** involves isomerization of **15t** to **15c**, presumably via **16**, which undergoes electrocyclic ring closure to **17** followed by a [1,5]-hydrogen sigmatropic rearrangement. Heating a mixture of **19c** and **19t** at 360 °C produces a mixture of **21** and **22**, and a third compound tentatively assigned structure **23**. The transformation of **19t** to **19c** is believed to proceed via **20**, which then undergoes a [1,5]-sigmatropic rearrangement to **21** followed by ring closure to **22**. Substituents in the 4-position of the 3-isopropylidenecyclobutene apparently destabilize the cyclic structures, which shifts the equilibria in favor of the acyclic trienes, which when having a group at the 1-position are able to undergo other types of reactions.

Introduction

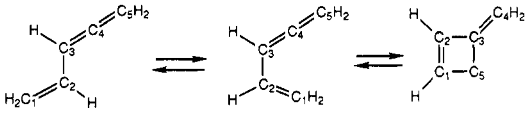
One of our recent research interests has focused on the electrocyclic ring-closure reactions of substituted bisallenes which occur essentially quantitatively to produce 3,4-bisalkylidenecyclobutenes as exemplified by the ring closure of the parent system **1** to produce **2**.[1,2] Ab initio MO calculations and thermodynamic calculations using Benson's method indicate that **2** is heavily favored enthalpically.[2] The position of the electrocyclic equilibrium between **1** and **2** is in distinct contrast to that of the electrocyclic equilibrium between butadiene (**3**) and cyclobutene (**4**) in which the former is heavily favored enthalpically.[2] This interesting contrast in the position of the two equilibria led us to inquire as to where the equilibria might lie with the intermediate substituted vinylallene–alkylidenecyclobutene systems represented by the parent system **5** and **6**. There appears to be only one previous report on such an electrocyclic system, that being with **7** and **8** in which an equilibrium constant of nearly unity has been observed.[3]



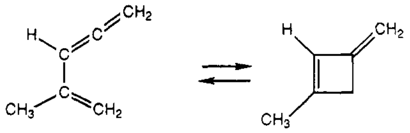
1 **2**



3 **4**



5a **5s** **6**



7 **8**

In this paper we report the results of studies on the electrocyclic reactions of a number of substituted vinylallenes and alkylidenecyclobutenes which have been prepared either by the coupling of a vinyl Grignard reagent with 3-chloro-3-methyl-1-butyne (CMB) in the presence of Pd(0) or by the cycloaddition of an alkyne with 1,1-dimethylallene (DMA).[4]

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[1] Pasto, D. J.; Yang, S.-H. *J. Org. Chem.*, submitted for publication.

[2] Pasto, D. J.; Yang, S.-H. *J. Org. Chem.*, submitted for publication.

[3] Gil-Av, E.; Herling, R. *Tetrahedron Lett.* **1967**, 1.

0022-3263/89/1954-4028$01.50/0

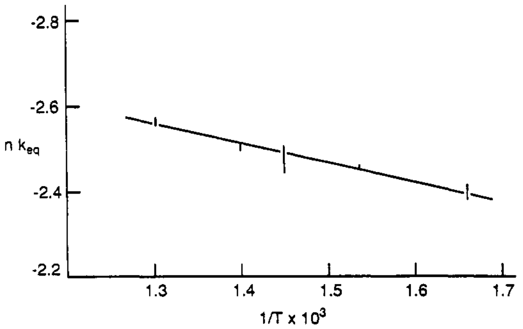

Figure 1. Plot of ln K_{eq} versus $1/T$ for the equilibrium between **5** and **6**.

Table I. Equilibrium Constants for the 5 ⇄ 6 System at Various Temperatures

temp, °C	K_{eq}	temp, °C	K_{eq}
327	0.091 ± 0.002	441	0.082 ± 0.007
374	0.087 ± 0.001	493	0.077 ± 0.001
416	0.085 ± 0.040		

Results

The electrocyclic reactions of the vinylallenes and isopropylidenecyclobutenes were carried out in the gas phase by repeatedly passing the vinylallene or the isopropylidenecyclobutene through a heated quartz tube at 360 and 435 °C (except for **5** which was carried out at a greater number of temperatures) at pressures of 0.05–0.10 mTorr until a constant ratio of the products was obtained as determined by integration of the 300-MHz NMR spectra.[5]

1,2,4-Pentatriene (5). Compound **5** was passed through the heated tube at a number of temperatures in the 327–493 °C range producing mixtures of **5** and **6**. The ratios of **5**:**6** were determined by integration of the NMR spectra of the thermolysis mixtures.

The equilibrium constants are given in Table I. A plot of ln K_{eq} versus $1/T$ is nicely linear (Figure 1) and gives values of ΔH of –0.87 kcal/mol and ΔS of –6.20 eu.

Ab initio MO calculations have been carried out on the anti and syn conformations of **5** (**5a** and **5s**) and **6** at the 6-31G* level with full-geometry optimization using the GAUSSIAN86 program.[6] The calculated structural parameters are given in Table II. There is excellent correspondence between the calculated structural parameters of **5a** and those determined experimentally by electron diffraction[7] (see Table II). Compound **5a** exists as a completely planar structure. The calculations on **5s** indicate that it exists in a rather flat potential energy minimum in a planar, or very nearly so, conformation.

The total energies calculated for **5a**, **5s**, and **6** at the 6-31G* level with full geometry optimization, at the MP2/6-31G* level at the 6-31G* optimized structures, and at the 6-31G* level with zero-point energy point corrections are given in Table III. Compound **5a** is calculated to be lower in energy than **5s** by 2.79 kcal per mole which is consistent with the results derived from the earlier electron diffraction[6] and NMR studies.[8] The total energy of **6** is calculated to lower than that of **5a** by 0.60 kcal/mol at the fully geometry optimized 6-31G* level compared to the experimentally observed change in enthalpy of 0.87 kcal/mol. At the MP2/6-31G* level **6** is calculated to be 4.69 kcal/mol lower in energy; however, at the MP2/6-31G* the structures were not geometry optimized. The entropies of **5a**, **5s**, and **6** were calculated at the 6-31G* level using the FREQ procedure of the GAUSSIAN86 program, and are also given in Table III. The conversion of **5a** to **6** is calculated to be associated with a change in entropy of –4.49 eu compared to the experimental value of –6.20 eu.

Table II. Calculated Structural Parameters for 5a, 5s, and 6

parameter	5a	5a[a]	5s	6
C1–C2	1.322	1.338	1.321	1.330
C2–C3	1.470	1.462	1.480	1.477
C3–C4	1.302	1.310	1.302	1.317
C4–C5	1.295	1.310	1.295	–
C1–C5	–	–	–	1.522
C1–H1	1.076	1.093[b]	1.076	1.074
C1–H2	1.075	1.093	1.075	–
C2–H2	–	–	–	1.074
C2–H3	1.077	1.093	1.077	–
C3–H4	1.078	1.093	1.078	–
C4–H3	–	–	–	1.076
C4–H4	–	–	–	1.076
C5–H5(H6)	1.076	1.093	1.077	1.085
C1–C2–C3	123.88	124.1	126.44	93.28
C2–C3–C4	123.81	124.3	125.89	136.89
C2–C1–C5	–	–	–	94.60
H1–C1–C2	121.92	121.0	122.10	133.43
H2–C1–C2	121.43	121.0	121.03	–
H2–C2–C1	–	–	–	133.95
H3–C2–C1	120.00	116.8	118.96	–
H4–C3–C2	117.50	119.1[c]	116.59	–
H3–C4–C3	–	–	–	121.52
H4–C4–C3	–	–	–	121.41
H5(H6)–C5–C4	121.27	121.1	121.29	–
H5(H6)–C5–C1	–	–	–	115.94
H5(H6)–C5–C1–H1	–	–	–	65.21

[a] Structural parameters determined by electron diffraction (see ref 7). [b] All carbon–hydrogen bonds lengths were assumed to be the same. [c] Assumed to be the same as H3–C2–C3.

The energies of the π MO's of **5a**, **5s**, and **6** are given in Table IV, along with the observed PE ionization potentials of **5a**.[9]

2,5-Dimethyl-1,3,4-hexatriene (9).[10] 2,5-Dimethyl-1,3,4-hexatriene (**9**), prepared by the Pd(0)-catalyzed coupling of prop-1-en-2-ylmagnesium bromide with CMB, produces equilibrium mixtures of **9** and **10**. The structure of **10** was immediately evident from its NMR spectrum, which shows a characteristic resonance at δ 2.75 for the cyclobutene methylene hydrogens, along with resonances for two vinyl methyl groups and a single vinyl hydrogen. The equilibrium constants are given in Table V, and the thermodynamic parameters are given in Table VI.

5-Methyl-2-phenyl-1,3,4-hexatriene (11).[10] 5-Methyl-2-phenyl-1,3,4-hexatriene, prepared by the Pd(0)-catalyzed coupling of α-styrylmagnesium bromide with CMB, produces equilibrium mixtures of **11** and **12**; **12** was

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(4) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1988**, *53*, 4807.

(5) The substituted isopropylidenecyclobutenes formed on ring closure of **9**, **11**, and **13** are highly reactive and could not be successfully separated from the vinylallenes by chromatographic techniques. The 300-MHz NMR spectra of the equilibrium mixtures were well resolved, permitting unambiguous assignment of the structures of the ring-closed products by comparison with the NMR spectra of **12** and **14** formed by the cycloaddition of the substituted alkyne with 1,1-dimethylallene at 160 °C.

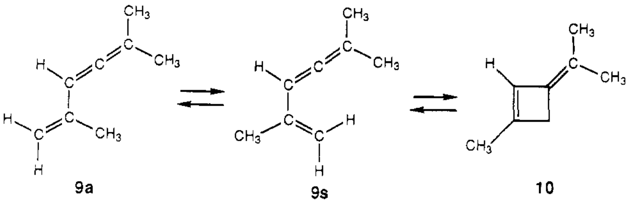
(6) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Reghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. C.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

(7) Traetteberg, M.; Bakken, P.; Hopf, H. *Acta Chem. Scand. A* **1980**, *34*, 461.

(8) Lefevre, F.; Martin, M. L.; LeBail, H.; Odiot, S. *Org. Magn. Reson.* **1975**, *7*, 315.

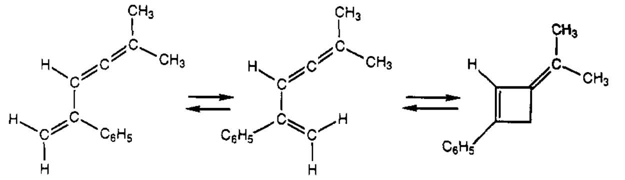
(9) Bischof, P.; Gleiter, R.; Hopf, H.; Lenich, F. T. *J. Am. Chem. Soc.* **1975**, *97*, 5467.

(10) Although **5** exists predominantly in the anti conformation, **9**, **11**, and **13** probably exist in equilibrium mixtures of anti and syn conformations and are thus shown as such in the chemical equations.



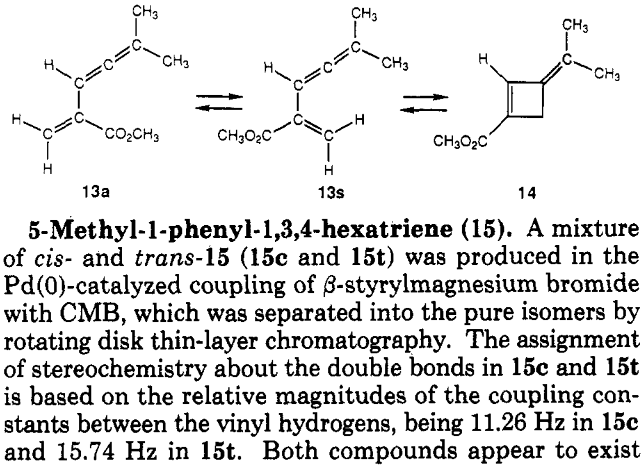
9a 9s 10

prepared independently by the cycloaddition of phenylacetylene with DMA at 160 °C,[4] conditions under which 12 does not undergo ring opening. The heating of 12 produces equilibrium mixtures of 11 and 12 identical in composition with those obtained from 11. The equilibrium constants are given in Table V, and the thermodynamic parameters are given in Table VI.



11a 11s 12

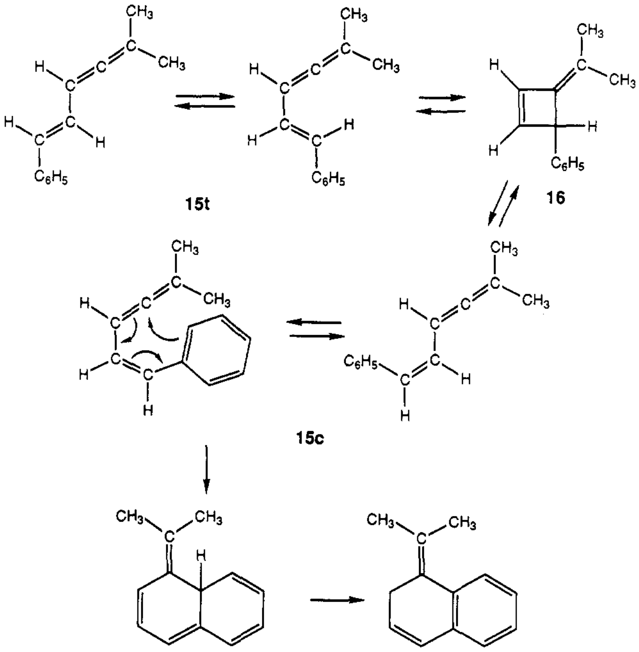
2-Carbomethoxy-5-methyl-1,3,4-hexatriene (13). Methyl 3-isopropylidenecyclobutenecarboxylate (14), prepared by the cycloaddition of methyl propiolate with DMA,[4] produces equilibrium mixtures of 13 and 14. Compound 14 was easily identified by its NMR spectrum, which showed three vinyl hydrogen resonances; a double-double-heptet at δ 5.86 (the allenyl hydrogen), and two double doublets at δ 5.69 and 6.08 (the terminal methylene hydrogens). The equilibrium constants are given in Table V, and the thermodynamic parameters are given in Table VI.



13a 13s 14

5-Methyl-1-phenyl-1,3,4-hexatriene (15). A mixture of *cis*- and *trans*-15 (15c and 15t) was produced in the Pd(0)-catalyzed coupling of β-styrylmagnesium bromide with CMB, which was separated into the pure isomers by rotating disk thin-layer chromatography. The assignment of stereochemistry about the double bonds in 15c and 15t is based on the relative magnitudes of the coupling constants between the vinyl hydrogens, being 11.26 Hz in 15c and 15.74 Hz in 15t. Both compounds appear to exist predominantly in the anti conformation as indicated by the similarity of the coupling constants between the allenyl and vinyl hydrogens of 11.26 Hz in 15c and 10.01 Hz in 15t. When 15c was passed through the heated tube once at 435 °C it was completely converted to a single product 18. When 15t was passed through the heated tube under identical conditions a mixture of 15c, 15t, and 18 was recovered. Repeated passes of this reaction mixture through the heated tube resulted in the final formation of only 18. The strucutre of 18 was assigned on the basis of characteristic spin patterns in its NMR spectrum, which indicate the presence of an ABCD spin system for the four aromatic hydrogens and an ABX_2 pattern for the $CH{=}CHCH_2$ fragment along with two vinyl methyl resonances.

2-Methyl-2,3,5-heptatriene (19). A 72:28 mixture of *cis*- and *trans*-2-methyl-2,3,5-heptatriene (19c and 19t) was produced by the Pd(0)-catalyzed coupling of prop-1-en-1-ylmagnesium bromide with CMB. This mixture could



not be separated into the pure cis and trans isomers by chromatographic techniques. The stereochemistry about the double bonds in 19c and 19t has been assigned on the relative magnitude of the vinyl hydrogen coupling constants, being 10.42 Hz in 19c and 15.19 Hz in 19t; 19c would appear to exist predominantly in the anti confirmation based on a comparison of the coupling constant between the allenyl and vinyl hydrogens (10.82 Hz) with those observed with 15c and 15t. In 19t, however, this coupling constant is considerably smaller (6.64 Hz), suggesting that the syn conformation is also populated to some degree.

A single pass of the mixture of 19c and 19t through the heated tube at 360 °C resulted in the complete disappearance of 19c and 19t with the formation of a complex mixture containing three major products 21, 22, and 23. There were no peaks present in the NMR spectrum of the reaction mixture suggestive of the presence of 20. When the mixture of 19c and 19t was passed through the column at 435 °C only 22 and 23 were formed in an 80:20 ratio. The structures of 21 and 22 were readily assigned from the NMR spectrum of the mixture using extensive double resonance studies. The structure of 21 is assigned on the basis of the coupling relationships shown in the structure in Figure 2. The stereochemistry about the central double bond is assigned as cis based on the magnitude of the vinyl hydrogen coupling constant of 10.41 Hz. The structure of 22 is assigned as shown based on the couplings shown in its structure in Figure 2. The structure of 23 is tentatively assigned as shown.

Discussion

The electrocyclic ring closure of 5 to 6 presents a very interesting thermodynamic situation. Our initial theoretical calculations indicated that 6 was favored over 5a on the basis of total energy (0.60 kcal/mol), yet experimentally 5 was observed to be favored. Further calculations indicated that 5a was favored entropically (4.49 eu at 298 °C). The thermodynamic parameters have also been calculated by the method of Benson,[11] giving a ΔH_{700K} of

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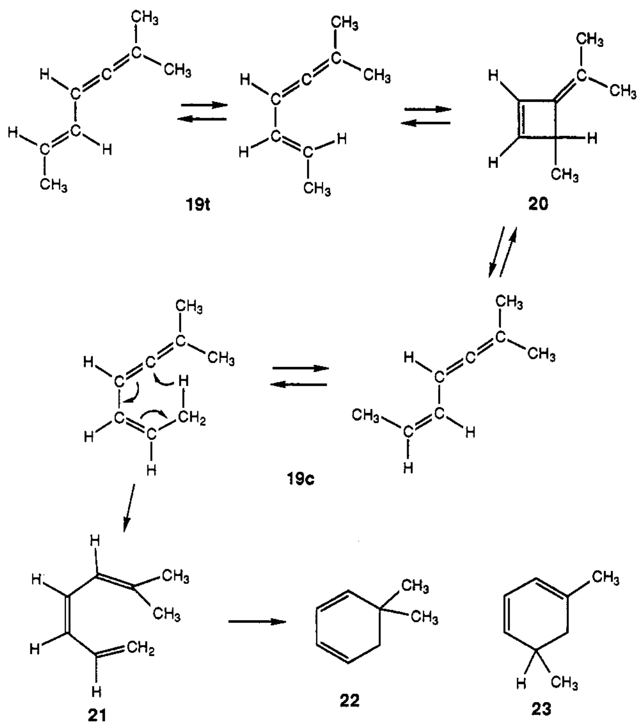
[11] Benson, S. W. *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; John Wiley & Sons: New York, 1976.



−4.8 kcal/mol and ΔS_{700K} of −8.58 eu. The experimental thermodynamic parameters determined for the equilibrium of **5** with **6** (see Table VI) are in rather good agreement with the results of these calculations. Compound **6** is favored enthalpically, but **5** is favored entropically, with the position of the equilibrium being entropically controlled at the temperatures that the equilibrium constants were measured.

An interesting correlation can be made of the thermodynamic parameters derived for the electrocyclization reactions of **5**, **9**, **11**, and **13**. The introduction of a methyl group at the 1-position of the alkylidenecyclobutene system as in **10** results in an increased enthalpic stabilization of the cyclized product. This can be attributed to the greater ability of the π-type MO's of the alkyl group to interact with a diene system to a greater extent when attached to a terminal position of the diene system compared to an internal position (e.g., the comparison of a thorough-conjugated system versus a cross-conjugated system). The presence of a carbomethoxy group at the 1-position of the alkylidenecyclobutene of **14** further enthalpically stabilizes the ring-closed structure. The phenyl group in **12** provides the greatest enthalpic stabilization of the ring-closed product. This sequence of stabilization of the through conjugated systems in the ring-closed structures interestingly parallels the stabilization afforded a radical center by these functional groups.[12]

The thermolysis of **15c** and **15t** resulted in the formation of the single product **18**. Experimentally, **15c** undergoes conversion much more rapidly to **18** than does **15t**. The incomplete thermolysis of **15t** produces a mixture of **15t**, **15c**, and **18**, suggesting that **15c** is an intermediate in the transformation of **15t** to **18**. A reasonable mechanism for the isomerization of **15t** to **15c** would be by reversible ring closure to **16**. Ring opening of **16** would be expected to favor the formation of **15t** due to steric reasons, but some **15c** should also be formed. Unfortunately, **16** could not be detected in the NMR spectra of mixtures obtained at partial conversions of **15** to **18**. At the temperatures involved in these thermolysis reactions, it is conceivable that the isomerization of **15t** to **15c** could occur via a diradical intermediate. Regardless of the mechanism of formation of **15c**, the formation of **18** can be easily envisioned as occurring via an electrocyclic ring closure of **15c** to form **17** followed by a [1,5]-sigmatropic suprafacial hydrogen migration.

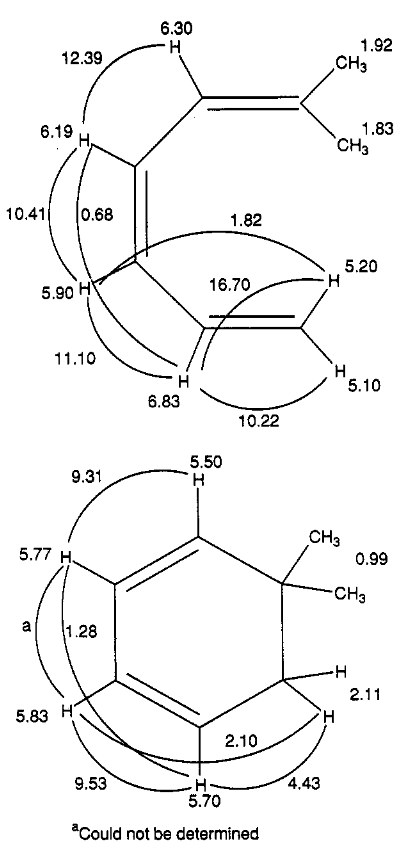


Figure 2. NMR parameters for structures **21** and **22**.

In order to reduce the possibility of cis,trans isomerization via a diradical intermediate, the thermal reaction of **19** was investigated, the reason being that the methyl group would stabilize an intermediate diradical involved in the isomerization much less than would a phenyl group, thereby decreasing the probability of such an isomerization mechanism. A single pass of the mixture of **19c** and **19t** through the column at 360 °C resulted in the formation of a mixture of **21** and **22**, along with a small amount of a compound believed to be **23**. The NMR spectrum of the reaction mixture indicated the complete disappearance of **19c** and **19t**, and the absence of resonances that would be characteristic of **20**. When the mixture is passed through the column at 435 °C only **21** and **22** are formed in an 80:20 ratio. The formation of **21** can be visualized as occurring via a [1,5]-sigmatropic hydrogen rearrangement[13] followed by electrocyclic ring closure to form **22**. The product tentatively assigned structure **23** would be formed by a [1,5]-sigmatropic rearrangement of a methyl group in **22**.

The results obtained with the thermolysis of **15** and **19** suggest that the isomerization of **15t** and **19t** to **15c** and **19c** occurs via the reversible formation of **16** and **20**, re-

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(12) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062.

(13) Numerous examples of [1,5]-hydrogen sigmatropic rearrangements of substituted vinylallenes have been reported (Crowley, K. T. *Proc. Chem. Soc. London* **1964**, 17. Minter, D. E.; Fonken, G. J.; Cook, F. T. *Tetrahedron Lett.* **1979**, 711. Condran, P., Jr.; Okamura, W. H. *J. Org. Chem.* **1980**, *45*, 4015. Sueiras, J.; Okamura, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 6255. Haces, A.; Okamura, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 6015. Condran, P.; Hammond, M. L.; Mourino, A.; Okamura, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 6259).

Table III. 6-31G* Calculated Total Energies and Entropies of 5a, 5s, and 6 at the 6-31G* Optimized Geometries

	5a	5s	6
E_{tot} (6-31G*)[a]	−192.74715 (0.0)[b]	−192.74270 (+2.79)	−192.74811 (−0.60)
E (MP2/6-31G*)[a]	−193.35901 (0.0)	−193.36516 (+2.42)	−193.37649 (−4.69)
E_{sum} (6-31G*)[c]	−192.64555 (0.0)	−192.64209 (+2.17)	−192.64525 (+0.19)
S_{298} (eu)[d]	72.42 (0.0)	70.04 (−2.38)	67.93 (−4.49)

[a] Total energies in au. [b] Relative energies in kilocalories per mole. [c] Sum of the HF and thermal energies. [d] Calculated at 298 K and 1 atm.

Table IV. Calculated π MO Energies (eV) of 5a, 5d, and 6 and the PE Ionization Potentials of 5a

	energy, eV			
MO	5a	5a (PE, IP)[a]	5s	6
2a″	−11.98	11.37	−11.90	−11.18
15a′	−10.26	10.04	−10.24	−
3a″	−8.70	8.88	−8.67	−8.64
4a″	+3.68	−	+3.46	+3.92
16a′	+4.91	−	+4.83	−
5a″	+6.89	−	+7.18	+6.59

[a] From ref 7.

Table V. Electrocyclic Equilibrium Constants of Substituted Vinylallenes

system	360 °C	435 °C
9 ⇄ 10	0.47	0.41
11 ⇄ 12	4.26	2.34
13 → 14	1.62	1.28

Table VI. Thermodynamic Parameters for the Electrocyclic Equilibria of the Substituted Vinylallenes

system	ΔH, kcal	ΔS, eu
5a ⇄ 6	−0.87	−6.20
9 ⇄ 10	−1.60	−4.03
11 ⇄ 12	−6.99	−8.20
13 ⇄ 14	−2.71	−3.33

Table VII. Calculated ΔH's, ΔS's, −TΔS's and ΔG's by the Benson Method for the Electrocyclic Equilibria of 1 ⇄ 2, 3 ⇄ 4, and 5 ⇄ 6

	system		
parameter	3 ⇄ 4	5 ⇄ 6	1 ⇄ 2
ΔH[a]	+10.54	−4.80	−29.14
ΔS[b]	−5.19	−8.58	−15.44
$-T\Delta S$[a]	+3.63	+6.01	+10.81
ΔG[a]	+14.17	+1.21	−18.33

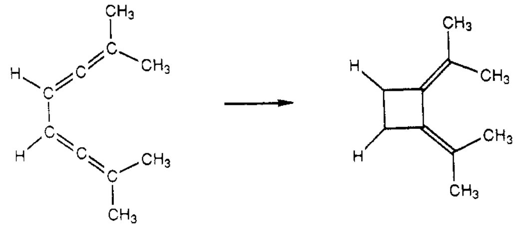
[a] Kilocalories per mole. [b] Calories per mole per degree Kelvin.

spectively. The lack of thermodynamic stability of these ring-closed structures compared to those in the equilibria involving **5**, **9**, **11**, and **13** would appear to be due to steric factors. In **16** and **20** the phenyl and methyl groups are relatively close to the inwardly oriented methyl group of the neighboring isopropylidene group resulting in steric congestion. In view of the fact that in **5**, **9**, **11**, and **13** the ring-closed products are favored only slightly enthalpically (but more highly disfavored entropically) the adverse steric interactions in **16** and **20** must strongly disfavor **16** and **20** in the equilibria with **15** and **19**.

Comparison of the Vinylallene–Alkylidenecyclobutene System with the Butadiene–Cyclobutene and Bisallene–Bisalkylidenecyclobutene Systems. As pointed out in the Introduction, in the butadiene–cyclobutene system the open-chain butadiene is heavily favored, while in the bisallene–bisalkylidenecyclobutene system the cyclic bisalkylidenecyclobutene is heavily favored. In the presently investigated systems, the 2-substituted 1,3,4-trienes **5**, **9**, **11**, and **13** form equilibrium mixtures of the vinylallene and alkylidenecyclobutene with equilibrium constants near unity, in between the two extremes of the other two systems.

An understanding of the factors giving rise to this trend is derived from an analysis of the thermodynamic parameters for the three systems relating the anti conformations of the acyclic compounds with the cyclic compounds. ΔH, ΔS, $-T\Delta S$, and ΔG have been calculated for the three systems at 700 K using the approach of Benson.[11] These values are given in Table VII. The ΔH's become markedly more negative across the series. This is due to the very highly positive group value for the heat of formation of an allenic carbon atom (+34.20 kcal/mol)[11] and is the dominant contributing factor that gives rise to the observed trend. The ΔS become slightly more negative across the series, but contributes less to ΔG than does ΔH except in the case of **5**.

A final interesting comparison of the vinylallene–alkylidenecyclobutene system with the bisallene–bisalkylidenecyclobutene system involves substantial differences in the mechanisms of the solution-phase electrocyclic ring-closure reactions. The solution-phase ring closure of **24** displays radical-chain properties and is accelerated by the presence of both electron-donating and electron-abstracting reagents. It is believed that the ring closure of **24** occurs via radical-anion and -cation intermediates in chain processes illustrated in the reactions in the following scheme. The facility of this reaction has been attributed to the near degeneracy of the HOMO's and LUMO's of **1** and **2**,[2] which are of the central diene chromophore in the syn-planar conformation of **1** and of the total triene chromophore of **2**. Similar behavior has not been observed with **5** or the substituted vinylallenes; electrocyclic ring-closure reactions of vinylallenes having not been observed in solution. We attribute this to the fact that the second propagation step for such a ring-closure mechanism for **5** is very endothermic because of the substantially higher energy of the LUMO of **6** versus **5** (10.6 kcal/mol, see Table IV).



24 **25**

$$\mathbf{24} + e^- \rightarrow \mathbf{24}^{\bullet -}$$
$$\mathbf{24}^{\bullet -} \rightarrow \mathbf{25}^{\bullet -}$$
$$\mathbf{25}^{\bullet -} + \mathbf{24} \rightarrow \mathbf{25} + \mathbf{24}^{\bullet -}$$

Experimental Section

Preparation of 1,2,4-Pentatriene (5).[14] To 40 mL of 1.0 M vinylmagnesium bromide in THF[15] at 0 °C was added 0.224 g of tetrakis(triphenylphosphine)palladium(0) (TPPd) dissolved in 10 mL of THF followed by 2 mL of propargyl bromide in toluene (80% by weight solution[15]). The reaction mixture was stirred at

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[14] Originally prepared by the base-catalyzed isomerization of 5-penten-1-yne (Grimaldi, J.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1971**, 947).

[15] Obtained from Aldrich Chemical Co.

15 °C for 0.5 h. The reaction mixture was directly subjected to distillation, and a distillate was collected (bp range 25–60 °C). Pure **5** was obtained by preparative GLC using a 12 ft, Carbowax 20M column: NMR ($CDCl_3$) δ 4.89 (dddd, J = 6.61, 1.62, 1.62, 1.05, Hz, 2 H), 4.96 (dtdd, J = 10.10, 1.62, 1.62, 0.67 Hz, 1 H), 5.15 (dtdd, J = 17.06, 1.62, 1.62, 0.62 Hz, 1 H), 5.81 (tddd, J = 6.61, 10.39, 0.67, 0.62 Hz, 1 H), 6.16 (dddt, J = 17.06, 10.39, 10.10, 1.05 Hz, 1 H).

Preparation of 2,5-Dimethyl-1,3,4-hexatriene (9). 2-Bromopropene (4.09 g, 33.4 mmol) in 5 mL of THF was added to 0.89 g of Mg suspended in 15 mL of THF at 45 °C. The reaction mixture was stirred for 2 h, and 0.236 g of TPPd dissolved in 10 mL of THF was added. 3-Chloro-3-methyl-1-butyne (CMB, 3.42 g, 33.4 mmol) dissolved in 3 mL of THF was slowly added at room temperature. During the addition the temperature slowly rose to 40 °C. The reaction mixture was stirred for 0.5 h. The reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl, and the aqueous phase was extracted with three 40-mL portions of pentane. The combined extracts were washed three times with cold water and dried over $MgSO_4$. The pentane was carefully removed by distillation, and the product was purified by column chromatography on silica gel giving 0.6 g of a highly reactive, colorless liquid.[16] The NMR spectrum of the product showed only peaks characteristic of **9** along with a very small amount of residual pentane. NMR ($CDCl_3$) δ 1.73 (d, J = 2.86 Hz, 6 H), 1.74 (dd, J = 0.83, 1.29 Hz, 3 H), 4.77 (m, 1 H), 4.85 (m, 1 H), 5.75 (heptet, J = 2.86 Hz, 1 H); MS extract *m/e* calcd for C_8H_{12} 108.0939, found 108.0940.

Preparation of 5-Methyl-2-phenyl-1,3,4-hexatriene (11). α-Bromostyrene (4.23 g, 20.8 mmol) in 5 mL of THF was slowly added dropwise to a suspension of 0.55 g of Mg in refluxing THF. After stirring for 1 h, the reaction mixture was cooled to 30 °C, and 0.224 g of TTPd was added followed by 2.15 g of CMB, and the reaction mixture was stirred for 1 h. The reaction mixture was worked up as described above. The crude product was purified by chromatography on silica gel, giving 0.013 g of colorless crystals identified as 2,7-dimethyl-2,3,5,6-octatetraene (from coupling of CMB), 0.960 g of **11**[16] as a highly reactive yellow liquid contaminated with approximately 10% of styrene, and 0.092 g of a yellow liquid identified as 2,3-diphenyl-1,3-butadiene (from coupling of α-styryl species). NMR of **11** (contaminated with $\sim$10% of styrene ($CDCl_3$) δ 1.64 (d, J = 2.94 Hz, 6 H), 5.12 (d, J = 1.52 Hz, 1 H), 5.17 (d, J = 1.52 Hz, 1 H), 5.94 (heptet, J = 2.94, 1 H), 7.1–7.5 (m, 5 H); MS exact *m/e* calcd for $C_{13}H_{14}$ 170.1095, found 170.1094.

Preparation of 5-Methyl-1-phenyl-1,3,4-hexatriene (15). β-Bromostyrene (2.62 g, 14.3 mmol, mixture of isomers) in 10 mL of THF was slowly added to 0.37 g of Mg suspended in 15 mL of refluxing THF. The mixture was stirred for 1 h and then cooled to 40 °C, and 0.51 g of TPPd was added followed by 1.70 g (16.6 mmol) of CMB. The reaction mixture was stirred at room temperature for 30 min and then worked up as described above. *cis*- and *trans*-**15** were isolated by rotating-disk, thin-layer chromatography on silica gel using Skelly-solve B as eluant. **15c** (colorless liquid): NMR (CDCl3) δ 2.01 (d, J = 2.77 Hz, 6 H), 6.33 (dd, J = 11.30, 11.30 Hz, 1 H), 6.50 (m, 1 H), 6.62 (dd, J = 0.89, 11.30 Hz, 1 H), 7.4–7.8 (m, 5 H). **15t** (colorless liquid): NMR ($CDCl_3$) δ 2.06 (d, J = 2.79 Hz, 6 H), 6.15 (m, 1 H), 6.75 (d, J = 15.79 Hz, 6.89 (dd, J = 10.01, 15.79 Hz, 1 H), 7.4–7.8 (m, 5 H); MS exact *m/e* calcd for $C_{13}H_{14}$ 170.1095, found 170.1093.

Preparation of 2-Methyl-2,3,5-heptatriene (19). 1-Bromo-1-propene (4.15 g, 34.3 mmol) in 5 mL of THF was added to a suspension of 0.88 g of Mg in 15 mL of THF at 45 °C. After stirring for 2 h, 0.226 g of TPPd was added followed by 3.64 g (35.5 mmol) of CMB dissolved in 3 mL of THF. The reaction mixture was stirred at room temperature for 0.5 h and worked up as described above. The mixture of *cis*- and *trans*-**19** (72:28) was purified by column chromatography on silica gel using Skelly-solve B as eluant giving a mixture of **19c** and **19t** (30%) as a colorless liquid. **19c**: NMR ($CDCl_3$) δ 1.64 (d, J = 2.78 Hz, 6 H), 1.65 (dd, J = 1.17, 7.03 Hz, 3 H), 5.34 (ddq, J = 10.42, 1.02, 7.03 Hz, 1 H), 5.72 (ddq, J = 10.82, 10.42, 1.71 Hz, 1 H), 5.83 (ddheptet, J = 10.82, 1.02, 2.78 Hz, 1 H). **19t**: NMR δ 1.63 (d, J = 2.80, 6 H), 1.66 (dd, J = 1.61, 6.62 Hz, 3 H), 5.51 (ddq, J = 15.19, 0.48, 6.62 Hz, 1 H) 5.83 and 6.64 obscured multiplets.

NMR Spectral Parameters for the Thermolysis Products. For the NMR spectral parameters of **21** and **22**, see Figure 2.

6: NMR ($CDCl_3$) δ 2.96 (br m, 2 H), 4.48 (br m, 1 H), 4.48 (br m, 1 H), 6.29 (br d, J = $\sim$2.4 Hz, 1 H), 6.63 (br d, J = $\sim$2.4 Hz, 1 H).

10: NMR ($CDCl_3$) δ 1.61 (s, 3 H), 1.69 (s, 3 H), 1.92 (s, 3 H), 2.75 (s, 2 H), 6.12 (s, 1 H).

14: NMR ($CDCl_3$) δ 1.76 (d, J = 2.93 Hz, 6 H), 3.78 (s, 3 H), 5.69 (dd, J = 0.62, 1.39 Hz, 1 H), 5.86 (ddheptet, J = 0.51, 0.62, 2.93 Hz, 1 H), 6.08 (dd, J = 0.51, 1.39 Hz, 1 H).

18: NMR ($CDCl_3$) δ 1.81 (br s, 3 H), 1.86 (t, J = 1.62 Hz, 3 H), 2.10 (m, 2 H), 6.00 (dt, J = 9.41, 4.30 Hz, 1 H), 6.37 (dt, J = 9.38, 1.98 Hz, 1 H), 7.1–7.3 (m, 4 H).

23: NMR ($CDCl_3$) δ 1.03 (d, J = 6.91 Hz, 3 H), 1.71 (d, J = 2.82 Hz, 3 H), 1.73 (m, 2 H), 2.41 (very broad resonance which appears as a broadened triplet on irradiation of the methyl group, 1 H), 5.63 (br dd, J = 10.58, 2.82 Hz, 1 H), 6.30 (br d, J = 14.99 Hz, 1 H), 6.50 (dd, J = 14.99, 10.58 Hz, 1 H).

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Supplementary Material Available: ^1H NMR spectra of **5**, **6**, **9–14**, **15c**, **15t**, **18**, and **19** (9 pages). Ordering information is given on any current masthead page.

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(16) Most of the substituted vinylallenes and alkylidenecyclobutenes used in this study are highly reactive substances which undergo partial or total polymerization on attempted distillation or isolation by preparative gas chromatography. The compounds undergo slow polymerization on standing, even in a freezer.