value for E_{ab} implies strong bonding between atoms a and b, while a positive value implies an anti-bonding interaction."

Energy partitioning has been applied to the study of the Cope rearrangement,[35] the basicity of heterocyclic amines,[36] and the investigation into nonclassical bonding in cations.[34]

When the total molecular energies of the cations (**2**) are partitioned within the MINDO/3 framework, as discussed, a net *bonding* interaction is observed between the bridgeheads in all cases. The MINDO/3 calculated energy components are displayed in Table IV, along with the calculated bond indices (W_{ab}).[11]

To our surprise, the MINDO/3 partitioned energies and bond indices suggested that both **2b** and **2c** are stabilized transannularly by approximately the same amount. The calculations indicate that E_{ab} for **2b** is −81.3 kcal·mol^{-1}, while the similar quantity for **2c** is −80.5 kcal·mol^{-1}. Inspection of Table IV reveals why this is so. The bicyclo[2.1.1]hexylium cation, **2b**, having the *shorter* bridgehead–bridgehead separation and the more favorable transannular angle (C_1C_4H = 154.1° in **2b**, C_1C_5H = 141.5° in **2c**) is advantaged with greater orbital overlap, reflected in the larger negative values for E_{ab}^{res} and E_{ab}^{V}, over **2c**. Conversely, **2b** is disadvantaged over **2c** with less favorable values for E_{ab}^{core} and E_{ab}^{el}, reflecting the closer proximity of both bridgehead nuclei and electrons in the case of **2b**. When all effects are taken into consideration, **2b** and **2c** are predicted to possess similar stabilization energies. The respective bond indices are 0.30 and 0.29.

Fischer and Kollmar[34] suggest that the bicentric terms (E_{ab}) should be used in a qualitative fashion, as the numerical values do not correspond to bond energy in the conventional sense, being often much larger than the observed bond dissociation energies. Thus, the observation that both **2b** and **2c** are stabilized by similar amounts is consistent with the conclusions drawn from the strain–reactivity relationship that **2b** is stabilized by about 25 kcal·mol^{-1} while **2c** is stabilized by approximately 30 kcal·mol^{-1}.

The calculations for **2a** suggest a greater degree of through-space stabilization. Thus, MINDO/3 suggests a bond index of 0.33[32] and a value of E_{ab} of −96.6 kcal·mol^{-1}. Clearly, in this case, the shorter bridgehead–bridgehead separation and ideal orbital angle (C_1C_3H = 180°) results in extremely favorable values for resonance (E_{ab}^{res}) and core–electron attraction (E_{ab}^{V}) terms; so favorable, in fact, as to more than compensate for the unfavorable repulsion terms (E_{ab}^{core} and E_{ab}^{el}). The calculated increase in the stabilization energy of **2a** over **2b** and **2c** of about 15 kcal·mol^{-1} is consistent with the ~20 kcal·mol^{-1} increase expected on the basis of the strain–reactivity relationship as previously discussed.

Thus, it would appear that the through-space stabilization energies, predicted on the basis of the strain–reactivity relationship, in the cations (**2**) are not unreasonable when compared with the MINDO/3 results in a qualitative sense. The observed trend in solvolysis rates (viz, **2c** > **2a** > **2b**) can be understood in terms of a delicate balance of opposing unfavorable strain energies and favorable transannular stabilization energies engendered in the cations (**2**). In **2a** the orbital effects dominate over strain considerations, thereby rationalizing the rapid solvolysis observed in the case of **1a**. As the strain decreases in progressing to the higher homologues, so does the favorable transannular stabilization. Considering that the stabilization effects are similar in **2b** and **2c**, and that the strain is markedly reduced in **2c**, it is not surprising that the higher homologue (**1c**) solvolyses the more rapidly. Clearly, strain considerations in **2b** dominate over the transannular orbital considerations, as **1b** is observed to solvolyse many orders of magnitude slower that either **1a** or **1c**.

Conclusions

As the data have shown, MINDO/3 appears to outperform both MNDO and AM1 in the description of the bicyclo[*n*.1.1]alkylium cations (**2**). When the MINDO/3 calculated energies are partitioned into mono- and bicentric components, the cations (**2**) are seen to be stabilized beyond the unfavorable strain engendered in their formation by favorable through-space effects. These effects can be invoked in rationalizing the unusual trends and rates of solvolysis observed for the 1-halobicyclo[*n*.1.1]alkanes.

Acknowledgment. We are indebted to the Australian Research Grants Scheme for financial support.

Registry No. **2a**, 22907-79-5; **2b**, 22907-78-4; **2c**, 113851-50-6.

Thermal Aromatization of Alkylidenecyclopentenes and Related Hydrocarbons

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3- and 4-alkylidenecyclopentenes (dihydrofulvenes) undergo thermal aromatization upon flash vacuum pyrolysis (FVP) at 700 °C. For example, toluene and *m*-xylene are the principal products formed from 3- and 4-isopropylidenecyclopentene. Similar behavior is observed for other dihydrofulvenes that have alkyl groups on the exocyclic methylene carbon. Cyclohexadienes are believed to be the intermediates immediately preceding the aromatics, and the aromatization step is believed to occur by a free radical process involving successive loss of an alkyl group and a hydrogen atom. Small amounts of secondary aromatics are formed from the primary products by free radical aromatic substitution, dealkylation, etc. Upon FVP, 6,6-dialkylbicyclo[3.1.0]hexenes give mixtures of aromatics which are very similar to those obtained from the isomeric dihydrofulvenes, and it is proposed that these bicyclic derivatives may be intermediates in the formation of cyclohexadienes from dihydrofulvenes. Other possible pathways from dihydrofulvenes to cyclohexadienes are presented.

Aromatization, the conversion of nonaromatic into aromatic substances, is an important process in petroleum refining and coal liquefaction. Aromatization may occur under the influence of heat alone, but it is usually accompanied by extensive side reactions. In the industrial processes catalysts are generally employed that increase

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Table I. Products from FVP of Alkylidenecyclopentenes, 700 °C

reactant	4	5	6	7	8	9/10
			Liquid Product[a]			
recovery, %	71.8	80.5	65.0	66.0	66.0	69.0
aromatics, %	52.0	61.0	71.0	77.0	69.0	82.0
cracking, %	8.8	8.3	13.0	15.7	15.0	13.5
unchanged, %	37.4	30.7	12.7	2.9	14.9	2.4
unidentified, %	0	0	3.0	4.2	1.5	2.1
			Composition of Aromatics,[b] %			
benzene	6.7	3.5	11.9	10.2	8.2	7.1
toluene	71.7	81.1	21.5	24.4	38.6	30.7
ethylbenzene	10.5	5.1	29.3	28.0	15.3	23.7
styrene	tr	tr	13.3	11.1	5.7	3.5
propylbenzene	0	0	3.1	2.7	1.4	1.7
p-xylene	tr	tr	1.8	1.8	} 10.2	} 9.9
m-xylene	11.1	10.3	4.3	5.6		
o-xylene	tr	tr	2.8	3.0	3.0	4.3
p-ethyltoluene	0	0	} 6.6	} 6.2	2.8	3.8
m-ethyltoluene	0	0			6.9	6.3
o-ethyltoluene	0	0	5.3	7.0	7.9	8.0

[a] Cracking refers to unidentified products with retention times shorter than benzene. Unchanged represents recovered starting material. Unidentified refers to unidentified compounds with retention times longer than benzene. [b] Tr = trace; a small peak appeared in the VPC tracing, but the amount was too small to activate the integrator. In some cases the *p*- and *m*-xylene peaks were incompletely resolved, and the integrator reported the total for the two isomers. In these cases, the combined percentage is indicated with a brace. The same is true for *p*- and *m*-ethyltoluene.

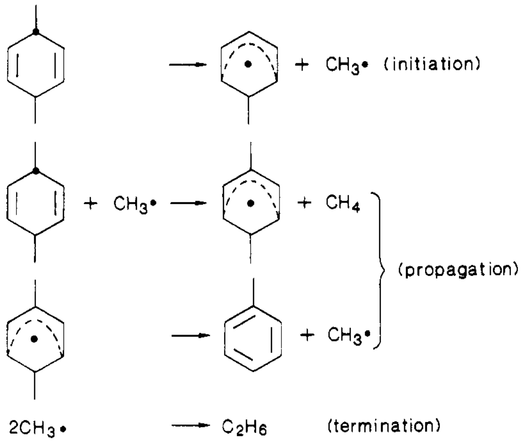
the rate of aromatization relative to these undesired side reactions. Thermal aromatization does constitute one source of aromatics in smokestack and exhaust emissions as well as other high-temperature processes.

The thermal aromatization of 1,3- and 1,4-cyclohexadienes has been studied by a number of groups.[1-11] 1,4-Cyclohexadiene itself and its *cis*-3,6-dimethyl derivative lose hydrogen by a concerted, Woodward–Hoffmann-allowed process giving hydrogen and *p*-xylene, respectively.[1,3] However, reactions involving the loss of an alkyl group are more complex, and, even though they can be formulated as allowed processes, they tend to follow multistep pathways involving free radical intermediates. For example, the pyrolysis of *trans*-3,6-dimethyl-1,4-cyclohexadiene yields toluene and methane, principally, along with a small amount of ethane.[4] The formation of ethane, as well as the fact that the reaction is inhibited by propylene, led Frey and co-workers to propose a free radical chain mechanism, as illustrated in Scheme I.

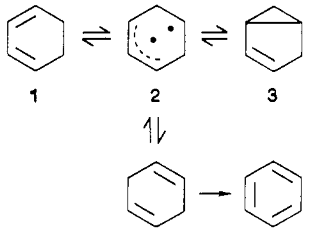
p-Xylene is formed by the pyrolysis of 3,3,6,6-tetramethyl-1,4-cyclohexadiene, and in the original paper the reaction was formulated in terms of the concerted loss of ethane.[5] However, later workers found that methane is formed in larger amounts than ethane, thus implicating methyl radicals as intermediates, and a mechanism involving the successive loss of two methyl radicals was proposed.[4]

The syn elimination of molecular hydrogen from 1,3-cyclohexadiene is orbital-symmetry forbidden, and it is found experimentally that drastic conditions are required to effect aromatization of this hydrocarbon and its alkyl derivatives.[2,6,9-11] The reaction follows a complex rate law at ordinary pressures, indicating a free-radical-chain mechanism, but it becomes first order at low pressure.[2] It has been suggested that at low pressure the reaction actually involves prior isomerization to 1,4-cyclohexadiene as illustrated in Scheme II.[6] The slow step is this sequence, 1 → **2**, is estimated to have an activation energy of 62 kcal/mol.

Scheme I



Scheme II



A few years ago we undertook a search for non-cyclohexadiene hydrocarbons that undergo thermal aromatization cleanly. Our ultimate goal was to elucidate some of the thermal pathways to aromatics. Among the compounds studied, the most promising results were obtained with 3- and 4-isopropylidenecyclopentenes (**4** and **5**). Upon flash vacuum pyrolysis (FVP) at 700 °C, both of these compounds underwent aromatization, giving toluene

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(1) Ellis, R. J.; Frey, H. M. *J. Chem. Soc. A* **1966**, 553–556.

(2) Benson, S. W.; Shaw, R. *J. Am. Chem. Soc.* **1967**, *89*, 5351–5354.

(3) Fleming, I.; Wildsmith, E. *J. Chem. Soc., Chem. Commun.* **1970**, 223–224.

(4) Frey, H. M.; Krantz, A.; Stevens, I. D. R. *J. Chem. Soc. A* **1969**, 1734–1738.

(5) Reusch, W.; Russell, M.; Dzurella, C. *J. Org. Chem.* **1964**, *29*, 2446–2447.

(6) Orchard, S. W.; Thrush, B. A. *J. Chem. Soc., Chem. Commun.* **1973**, 14–15.

(7) Pines, H.; Kozlowski, R. H. *J. Am. Chem. Soc.* **1956**, *78*, 3776–3783.

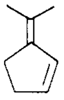
(8) Pines, H.; Chen, C.-T. *J. Am. Chem. Soc.* **1959**, *81*, 928–932.

(9) Schiess, P.; Dinkel, R.; Fuenfschilling, P. *Helv. Chim. Acta* **1981**, *64*, 787–800.

(10) Schiess, P.; Dinkel, R. *Helv. Chim. Acta* **1981**, *64*, 801–812.

(11) Schiess, P.; Dinkel, R. *Tetrahedron Lett.* **1975**, 2503–2506.

principally along with small amounts of *m*-xylene, ethylbenzene, and benzene, as shown in Table I.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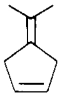
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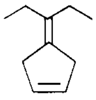
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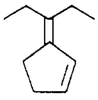
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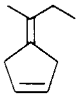
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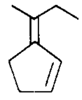
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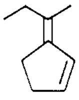
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This type of reaction is of interest for several reasons. Among them is the fact that cyclopentanes are formed as intermediates in the catalytic aromatization of alkanes,[12] a reaction of great importance in petroleum processing. The mechanism by which the cyclopentanes are converted to aromatics has not been established, and it is possible that the ring expansion is a thermal process comparable to that involved in the present study. Also of interest is the fact that dihydrofulvenes such as **4** and **5** can be obtained by pyrolysis of acyclic 1,2,5-trienes,[13] so the sequence 1,2,5-trienes → dihydrofulvenes → aromatics represents a pathway from open-chain hydrocarbons to aromatics.

FVP of Dihydrofulvenes. To gain some understanding of the scope of the aromatization reaction, other dihydrofulvenes, **6–10**, were synthesized and subjected to FVP. The results are presented in Table I. We were unable to separate **9** and **10**, so mixtures of the stereoisomers were used for the FVP studies.

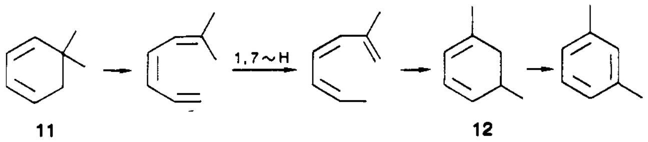
The FVP reactions were carried out by allowing degassed samples of hydrocarbon (10–50 μL) to effuse through a capillary leak into the evacuated pyrolysis tube. Condensable products were collected in a liquid nitrogen cooled receiver at the outlet of the pyrolysis tube. The exit line from the receiver was connected to a high-vacuum line capable of achieving 10^{-6} mm. The rate of sample addition was a function of the vapor pressure of the reactant, and ranged from 100 μL/h for C_8 to 50 μL/h for C_{10} reactants. The pressure in the pyrolysis tube was always less than 10^{-4} mm at the beginning of a run, but it rose during the reaction because of the formation of noncondensable gases—typically to ca. 0.1 mm for C_8 and 10^{-3} mm for C_{10} hydrocarbons. The pressure increase could be reduced significantly by placing an ice bath around the feed reservoir, which reduced the rate of addition, but experiments showed that this had a negligible effect on product composition.

The product distributions were not changed significantly when the surface area of the reactor was increased 4-fold by packing the pyrolysis tube with 1-mm quartz tubing, indicating the absence of an appreciable surface component in the aromatizations.

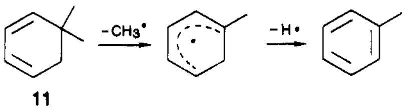
The weight of liquid products recovered was approximately 70% of the weight of reactant, and aromatics constituted 50–80% of the liquid. The remainder consisted of low-boiling cracking products, 6–15%, made up of at least 10 components, and minor amounts, 1–4%, of higher boiling, unidentified material. Some unchanged reactant was recovered in each case, ranging from ca. 2% for **9**/**10** to 37% for **4**. The recovered material showed no evidence for interconversion of the isomeric dihydrofulvenes.

Aromatization Step. Cyclohexadiene Intermediates. Toluene and *m*-xylene are formed in the flow-system pyrolysis of 6,6-dimethyl-1,3-cyclohexadiene (**11**) at 500 °C,[7] and the presence of these two compounds as the major aromatics from FVP of **4** and **5** leads us to postulate that cyclohexadienes are the immediate precursors of the primary aromatics formed from the dihydrofulvenes.

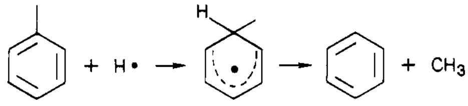
Scheme III



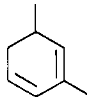
Scheme IV



Scheme V



In the flow system, toluene is formed from **11** presumably by a radical-chain process analogous to that shown in Scheme I, whereas *m*-xylene arises by a sequence involving preliminary ring opening and 1,7-hydrogen migration as illustrated in Scheme III.[10] (This sequence will be referred to as the ring-opening route in the subsequent discussion.) The immediate precursors of *m*-xylene are **12** and its 1,5-hydrogen-shift isomers **13** and **14**. Pines and Kozlowski found that the ratio of toluene to *m*-xylene was approximately 1:2 when **11** was pyrolyzed at 500 °C.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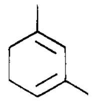
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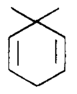
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Chain processes are not expected to be significant at the low pressures of the FVP experiments, and consequently the principal pathway for aromatization of cyclohexadienes such as **11** probably consists of two successive fragmentations as shown in Scheme IV. The ratio of fragmentation to ring opening is expected to increase with increasing reaction temperature, and consequently the ratio of toluene to *m*-xylene is expected to be greater in the FVP experiments than that found for the flow system. Furthermore, among the cyclohexadiene intermediates formed by ring opening, **12** and **13** should give toluene according to the successive fragmentation mechanism (Scheme IV), while **14** is expected to yield *m*-xylene. In addition, 3,3-dimethyl-1,4-cyclohexadiene (**15**), which is also a likely intermediate in the aromatization of **4** and **5** (see below), will give only toluene. These factors together may account for the fact that toluene formation actually exceeds *m*-xylene in the FVP of **4** and **5**, the ratio being ca. 7:1. When a sample of **11** was subjected to FVP in a separate experiment, the ratio of toluene to *m*-xylene in the product was approximately 4:1.

The remaining aromatics from FVP of **4** and **5** are believed to be secondary products, formed from toluene by reaction with free radicals liberated in the aromatization step. Thus, benzene is formed when toluene reacts with hydrogen atoms, as shown in Scheme V,[2] and, in view of the formation of hydrogen atoms in the aromatization reaction, this represents a likely mode of formation of benzene. Ethylbenzene, another minor aromatization product, and *o*- and *p*-xylene, which were formed in trace amounts, are believed to arise from the reaction of methyl radicals with toluene. The major pathway for this reaction

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[12] Pines, H.; Nogueira, L. *J. Catal.* **1981**, *70*, 391–403. Nogueira, L.; Pines, H. *Ibid.* **1981**, *70*, 404–408.

[13] Huntsman, W. D.; DeBoer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846–5850.

is known to be the abstraction of a benzylic hydrogen by a methyl radical, followed by recombination of methyl and benzyl radicals as shown in the following equations:[14]

$$\mathrm{PhCH_3 + CH_3^{\bullet} \rightarrow PhCH_2^{\bullet} + CH_4}$$

$$\mathrm{PhCH_2^{\bullet} + CH_3^{\bullet} \rightarrow PhCH_2CH_3}$$

The minor pathway involves substitution of methyl radicals into the aromatic ring and leads to the xylenes. For the reaction of methyl radicals with toluene at 281 °C, the ratio of ethylbenzene to the xylenes is 37:1, and the xylene isomers are formed in the ratio o:m:p = 37:42:21, which is very close to the statistically determined ratio.[14]

Styrene is known to be formed by the pyrolysis of ethylbenzene,[15,16] and it seems likely that this represents the mode of formation of the traces of styrene in the FVP of **4** and **5**. Examination of the other entries in Table I shows that only in those reactions in which ethylbenzene is a major product are significant amounts of styrene found.

The *gem*-diethylcyclohexadienes, the anticipated intermediates in the final stage of aromatization of **6** and **7**, are expected to show behavior similar to that of the dimethyl analogues. The product from direct fragmentation is ethylbenzene, whereas those from the ring-opening route are expected to be ethylbenzene, toluene, *o*-xylene, *o*-ethyltoluene, and 2,3-dimethylethylbenzene.

Consideration of the product distribution in Table I suggests that the ring-opening route is even less important for **6** and **7** than was found for **4** and **5**. Thus, the xylenes are minor products, and the amount of *o*-xylene is actually less than that of the meta isomer, not greater, as would be expected if significant reaction occurred by the ring-opening route. Similarly, the amount of *o*-ethyltoluene is not significantly greater than that of either of the other two isomers. Consequently, free-radical aromatic substitution appears to be the principal route to these disubstituted benzenes; two reactions are possible which lead to the ethyltoluenes, viz., reaction of ethyl radicals with toluene and reaction of methyl radicals with ethylbenzene. We did not identify 2,3-dimethylethylbenzene as a product, and it may have been present among the unidentified materials, but in view of the fact that the total amount of unidentified material was only 3–4%, we can conclude that 2,3-dimethylethylbenzene is not formed in significant amounts.

It seems likely that the bulk of the toluene in the product was formed by some route other than ring opening. The most likely mechanism is the degradation of ethylbenzene involving cleavage of the aliphatic carbon–carbon bond, followed by hydrogen abstraction by the benzyl radicals. Recombination of benzyl and ethyl radicals accounts for the *n*-propylbenzene, which was formed in small amounts.

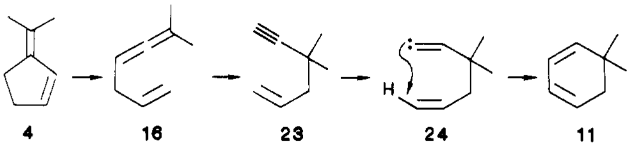
The composition of the FVP products from the ethyl–methyl derivatives **8–10** corresponds roughly to that expected on the basis of the behavior to the diethyl and dimethyl homologues. Thus, toluene and ethylbenzene are the principal products, with the former predominating as expected, based on the greater ease of cleavage of ethyl groups compared to methyl. The remaining products can be rationalized in terms of the free-radical processes described above.

Table II. Products from FVP of 1,2,5-Trienes, 700 °C

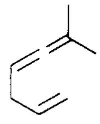
reactant	**16**	**17**	**18**
Liquid Product[a]			
recovery, %	87.5	77.3	87.0
aromatics, %	56.0	60.1	79.2
cracking, %	10.8	23.2	23.4
dihydrofulvenes, %	33.2[b]	10.4[c]	6.4[d]
unidentified, %	0	6.3	0
Composition of Aromatics,[e] %			
benzene	7.3	9.5	6.2
toluene	76.4	23.6	33.6
ethylbenzene	8.2	29.0	17.4
styrene	tr	10.6	6.8
propylbenzene	0	2.0	7.3
p-xylene	tr	1.8	} 9.6
m-xylene	8.2	5.0	
o-xylene	tr	2.7	3.8
p-ethyltoluene	0	} 7.3	2.1
m-ethyltoluene	0		5.3
o-ethyltoluene	0	8.5	7.8

[a] Cracking refers to unidentified products with retention times shorter than benzene. Unidentified refers to unidentified compounds with retention times longer than benzene. [b] 22.8% **4**, 10.4% **5**. [c] 7.2% **6**, 3.2% **7**. [d] 4.0% **8**, 2.4% **9/10**. [e] Tr = trace; a small peak appeared in the VPC chart, but the amount was too small to activate the integrator. In some cases the *p*- and *m*-xylene peaks were incompletely resolved and the integrator reported the total for the two isomers. In these cases the combined percentage is indicated with a brace. The same is true for *m*- and *p*-ethyltoluene.

Scheme VI



FVP of 1,2,5-Trienes. The dihydrofulvenes themselves were obtained by pyrolysis of the corresponding allylallenes at 350–400 °C,[13] e.g., **16** → **4** + **5**, **17** → **6** + **7**, and **18** → **8** + **9** + **10**. The results obtained by FVP of these trienes are shown in Table II, where it is seen that their behavior corresponds closely to that of the isomeric dihydrofulvenes.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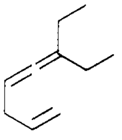
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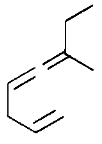
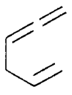

18

The presence of alkyl groups on the exocyclic methylene carbon seems to be a prerequisite for facile aromatization of the dihydrofulvenes. For example, FVP of 1,2,5-hexatriene (**19**) at 700 °C gave a mixture that contained only 17% benzene, the remainder consisting of **20** (38%), **21** (22%), and methylcyclopentadienes (24%). Similarly, Mazur and Berson found that **22** fails to aromatize under conditions comparable to those used in the present study.[17]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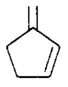
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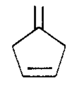
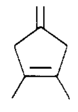

21


22

Possible Routes to the Cyclohexadienes. One of the possible mechanistic sequences for ring expansion of the dihydrofulvenes that we considered in the early stages of

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Table III. Products from FVP of Bicyclohexenes and 3-Isopropenylcyclopentene, 700 °C

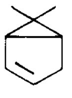
reactant	25	26	27	28	29[a]	30
			Liquid Product[b]			
recovery, %	85	76	86	71	78	84
aromatics, %	81.1	93.4	93.8	91.3	90.1	75.4
cracking, %	14.4	6.6	6.2	8.7	9.3	21.4
unidentified, %	4.5	tr	tr	tr	0.6	3.2
			Composition of Aromatics, %			
benzene	8.7	7.1	7.3	7.6	4.0	13.7
toluene	63.3	19.7	48.4	52.3	19.9	62.7
ethylbenzene	9.1	33.6	14.5	13.3	2.9	9.1
styrene	1.0	8.1	3.2	2.5	0.9	tr
p-xylene	tr	3.4	3.6	3.3	5.3	tr
m-xylene	16.7	1.7	5.9	5.7	48.2	13.6
o-xylene	1.2	9.8	6.2	5.0	3.1	0.9
p-ethyltoluene	0	} 5.8	} 4.8	tr	tr	0
m-ethyltoluene	0			1.6	8.5	0
o-ethyltoluene	0	4.3	tr	tr	2.6	0

[a] The aromatic fraction from **29** also contained 2.0% 1,2,4-trimethylbenzene and 2.7% 1,2,3-trimethylbenzene. [b] Tr = trace; a small peak appeared in the VPC chart, but the amount was too small to activate the integrator. Cracking refers to unidentified compounds with retention times shorter than benzene. Unidentified refers to unidentified compounds with retention times longer than benzene. In some cases the *p*- and *m*-xylene peaks were incompletely resolved and the integrator reported the total for the two isomers. In these cases, the combined percentage is indicated with a brace. The same is true for *p*- and *m*-ethyltoluene.

this study is shown in Scheme VI. The first step, reversal of the formation of the dihydrofulvene from the allylallene, is followed by [3,3]-rearrangement to the enyne **23**. 1,2-Hydrogen shift gives the vinylidenecarbene, **24**, which inserts in the distal C–H bond giving **11**. However, thermochemical calculations render this an unlikely pathway. The activation energy for the conversion of **16** to **4** is 37 kcal/mol,[18] and group additivity calculations indicate that the reaction is exothermic by ca. 30 kcal/mol.[19] Consequently, the activation energy for the reverse process, **4** → **16**, should be ca. 67 kcal/mol—a value that is too high for reactions occurring as rapidly as these aromatizations do.

Further considerations of possible pathways led us to postulate that bicyclo[3.1.0]hexenes are intermediates in the formation of cyclohexadienes. Two features that make this hypothesis attractive are the fact that the bicyclic system possesses both the five-membered ring of the reactants and the six-membered ring of the products; second, bicyclo[3.1.0]hexenes are known to rearrange thermally to cyclohexadienes.[1]

The five bicyclohexenes, **25**–**29**, were synthesized and subjected to FVP at 700 °C, and the results are presented in Table III. Comparison with the results in Table I shows that the correlation between the aromatics obtained from the bicyclohexenes and those from the corresponding dihydrofulvenes is sufficiently good to allow us to say that bicyclohexenes could be intermediates in the aromatization reactions.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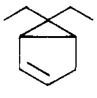
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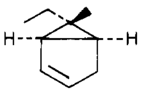

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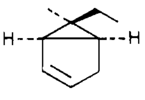

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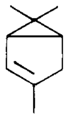
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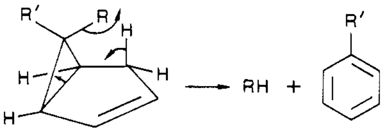
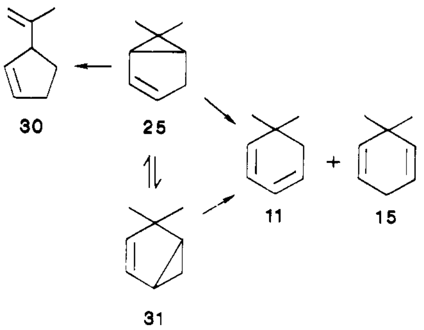
Scheme VII



Scheme VIII



There is an allowed pathway leading directly from the bicyclohexenes to aromatics that involves loss of the endo alkyl group at position 6 as shown in Scheme VII. If there is a significant contribution from this pathway, one would expect an increased proportion of ethylbenzene in the product from **27** and of toluene from **28**, provided, of course, that preliminary stereochemical equilibration of the reactants does not occur. As can be seen in Table III, the proportions of ethylbenzene and toluene from the two stereoisomers are not appreciably different. Unfortunately, the bicyclohexenes were completely consumed in the pyrolyses, so the possibility of stereochemical equilibration could not be checked.

A study of the thermal rearrangement of **25** at 280 °C provided an important clue to a possible pathway for the formation of bicyclohexenes from dihydrofulvenes. When **25** is heated at this lower temperature, **30** and **31** are formed initially, and **30** continues to form throughout the reaction while the concentration of **31** passes through a maximum and slowly declines to zero (Scheme VIII). The dimethylcyclohexadienes **11** and **15** as well as toluene are also formed, but at a much slower rate than **30**. The interconversion of **25** and **31** involves a vinylcyclopropane-type rearrangement, which has been shown to occur with this type of ring system.[20,21] The homo-1,5-

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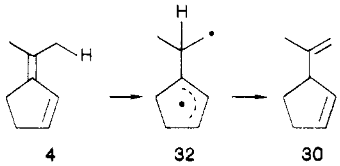
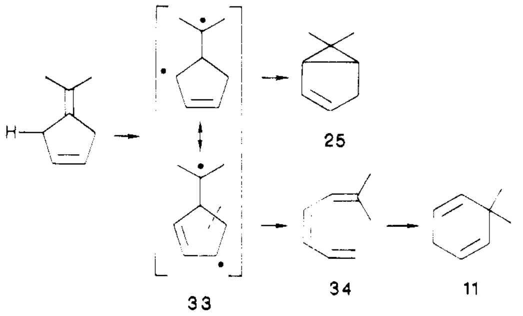
Scheme IX



Scheme X



hydrogen shift that is involved in the formation of **30** has been demonstrated with *cis*-1-methyl-2-vinylcyclopropane[22] and also with α-thujene.[20]

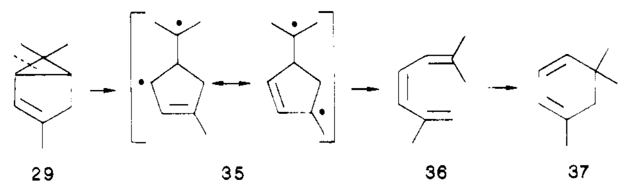
The pertinent clue for the aromatization studies came from the finding that, upon FVP, **30** gives a mixture of aromatics nearly identical with that from **25** (see Table III). The conversion of **25** to **30** is exothermic by only ca. 5 kcal/mol according to group additivities. Consequently the reverse process, **30** → **25**, should be rapid under FVP conditions, and this must represent the first step in the aromatization of **30**.

A pathway from the conjugated dihydrofulvene **4** to **30** can be formulated that involves two successive 1,2-hydrogen shifts comparable to the classical cyclopropane–propylene isomerization[23] (Scheme IX). The enthalpy change for the conversion of **4** to **32** is estimated to be 48 kcal/mol, and consequently **32** should be accessible under the FVP conditions. Thus the sequence for the rearrangement of the conjugated dihydrofulvenes to cyclohexadienes is represented as **4** → **30** → **25** → **11** + **15**.

In the case of the nonconjugated dihydrofulvene, **5**, it is also possible to devise a pathway to **30**, but here there are other routes to the cyclohexadienes that are simpler and more attractive and do not involve **30** directly (Scheme X). A 1,2-hydrogen shift leads to diradical **33**, which is both a 1,3- and a 1,4-diradical and has two modes of reaction available, viz., cyclization, giving **25**, or ring cleavage, giving the (*Z*)-triene **34**, which in turn will give cyclohexadiene **11** directly. Consequently, 1,3-cyclohexadienes may be formed from the nonconjugated dihydrofulvenes without passing through a bicyclohexene intermediate.

The initial step in the thermal rearrangement of bicyclo[3.1.0]hexenes may involve cleavage of either the internal (C_1–C_5) or external (C_1–C_6) cyclopropane ring bond. In the case of the unsubstituted derivative **3**, internal bond cleavage occurs, and at 320 °C, 1,3- and 1,4-cyclohexadiene are formed in the ratio 1.5:1, presumably by way of diradical **2**.[1] Cleavage of the external bond becomes competitive in 6-monosubstituted bicyclohexenes,[24,25] and it would be expected to become even more significant with the 6,6-disubstituted derivatives used in our studies. In fact, the results obtained with **29** indicate that it is the major pathway (Table III). Thus, *m*-xylene is the principal product from **29**, but there is no apparent way of obtaining this product by processes involving initial cleavage of the endocyclic ring bond. It can be rationalized readily, however, in terms of exocyclic cleavage as shown in Scheme XI. Diradical **35** should undergo cleavage of the central carbon–carbon bond in the same way that **33** does. Cyclization of the resulting triene **36** gives **37**, which will give *m*-xylene upon aromatization.

Scheme XI



Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer Model 237 or a Sargent Welch Model 3-200 infrared spectrophotometer. NMR spectra were determined with a JEOL FX 90Q spectrometer, with $CDCl_3$ as solvent and TMS as internal standard. All ^{13}C NMR spectra are noise decoupled. Analytical VPC determinations were carried out with an F & M Model 720 instrument with use of these columns: no. 1, 12 ft, silicone oil DC710; no. 2, 3 m, Carbowax 20M; no. 3, 15 ft, 2.8% bentone and 5% diisodecyl phthalate; no. 4, 2 m, thiodipropionitrile. Preparative-scale separations were performed with a Varian Aerograph Model 90P instrument with use of these $^3/_8$-in. columns: no. 5, 10 ft, Carbowax 20M; no. 6, 10 ft, silicone oil DC710.

Starting Materials. The synthesis of the bicyclo[3.1.0]hexenes **25**–**29** is described elsewhere.[26] The allylallenes **16**–**18** were synthesized from the appropriate allenyllithium and allylic bromide by a procedure modeled after Brandsma's general procedure for alkylation of allenyllithiums.[27]

6-Methyl-1,4,5-heptatriene (16). In a 300-mL, three-necked flask equipped with a mechanical stirrer, dropping funnel, and low-temperature thermometer, and with provisions for maintaining a nitrogen atmosphere, were placed 65 mL of dry THF and 0.5 mL of diisopropylamine.[28] The flask was cooled in a dry-ice bath, and 24 mL (60 mmol) of 2.6 M *n*-butyllithium in hexane was added. The temperature was maintained below −65 °C while a solution of 4.08 g (60 mmol) of 3-methyl-1,2-butadiene in 5 mL of THF was added dropwise, followed by 5 mL of HMPT. After the mixture had been stirred for 1 h, a solution of 6.05 g (50 mmol) of allyl bromide in 5 mL of THF was added dropwise. The temperature was maintained at −65 to −70 °C for 1 h and then allowed to rise to room temperature over a period of 2 h. The mixture was poured into saturated ammonium chloride, and the organic layer was separated. The aqueous layer was extracted with pentane, and the combined extracts were dried over magnesium sulfate. After the solvent had been stripped, the crude product was isolated by vacuum distillation, 0.74 g, bp 51–52 °C (75 mm), and shown by VPC (Column 1, 100 °C) to contain 82% **16**. Pure triene was obtained by preparative VPC (column 5, 90 °C) and exhibited ^1H NMR and IR spectroscopic properties identical with those reported:[29] ^{13}C NMR δ 20.7, 33.8, 86.9, 95.4, 114.7, 137.2, and 202.3.

6-Ethyl-1,4,5-octatriene (17). This compound was obtained in 40% yield from 3-ethyl-1,2-pentadiene and allyl bromide by the procedure described above, bp 73–79 °C (40 mm): ^1H NMR δ 0.98 (t, 6 H), 1.94 (q, 4 H), 2.71 (t, 2 H), 4.91–5.13 (m, 3 H), and 5.83 (m, 1 H); ^{13}C NMR δ 12.41, 25.68, 34.19, 91.02, 108.58, 114.65,

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137.35, and 200.75. Anal. Calcd for $C_{10}H_{16}$: C, 88.17; H, 11.83. Found: C, 88.01; H, 11.89.

6-Methyl-1,4,5-octatriene (18). By the same procedure as described above, **18** was obtained in 42% yield from 3-methyl-1,2-pentadiene and allyl bromide, bp 70–72 °C (70 mm): ^{1}H NMR δ 0.99 (t, 3 H), 1.68 (d, 3 H), 1.91 (m, 2 H), 2.71 (t, 2 H), 5.03 (m, 3 H), and 5.82 (m, 1 H); ^{13}C NMR δ 12.30, 19.18, 27.04, 33.97, 88.91, 101.70, 114.70, 137.30, and 201.47. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.30; H, 11.42.

Dihydrofulvenes 4–10 were obtained by pyrolysis of the corresponding allylallenes at 400 °C in a flow system as described previously.[13,29] The isomeric dihydrofulvenes were obtained in approximately equal amounts in each case and were separated by preparative VPC.

3- and 4-isopropylidenecyclopentene (4 and 5), obtained from **16**, were separated on column 5 at 120 °C. The IR and ^{1}H NMR spectra agreed with those reported:[29] ^{13}C NMR (**4**) δ 20.75, 21.29, 27.52, 31.91, 120.12, 131.17, 135.13, 140.11; (**5**) δ 21.02, 37.06, 122.72, 129.98, 131.93.

4-(1-Ethylpropylidene)- and 3-(1-ethylpropylidene)-cyclopentene (6 and 7) were obtained by pyrolysis of **17** and were separated by preparative VPC on column 5 at 135 °C. **6**: ^{1}H NMR δ 0.96 (t, 6 H), 2.03 (q, 4 H), 3.01 (s, 4 H), 5.79 (s, 2 H); ^{13}C NMR δ 12.30, 25.47, 36.41, 129.93, 131.39, 134.75. Anal. Calcd for $C_{10}H_{16}$: C, 88.17; H, 11.83. Found: C, 87.84; H, 11.80. **7**: ^{1}H NMR δ 0.98 (t, 6 H), 2.11 (q, 4 H), 2.48 (m, 4 H), 6.01 (m, 1 H), 6.37 (m, 1 H); ^{13}C NMR δ 12.41, 13.82, 25.19, 25.90, 26.82, 31.80, 131.12, 132.42, 135.29, 139.41. Anal. Calcd for $C_{10}H_{16}$: C, 88.17; H, 11.83. Found: C, 87.82; H, 12.06.

4-(1-Methylpropylidene)cyclopentene (8) and (*Z*)- and (*E*)-3-(1-methylpropylidene)cyclopentene (9 and 10) were obtained in the ratio 2:1.1:1 by pyrolysis of **18**. Separation of the nonconjugated isomer, **8**, was accomplished by preparative VPC on column 5 at 115 °C, but complete resolution of the stereoisomeric conjugated isomers, **9** and **10**, was not possible. Nevertheless, comparison of the spectra of a fraction 80% enriched in the *E* isomer **10** with those of a 50:50 mixture permitted the tentative assignment of proton and C-13 signals.[30] **8**: ^{1}H NMR δ 0.97 (t, 3 H), 1.62 (s, 3 H), 2.01 (q, 2 H), 2.98 (s, 4 H), 5.78 (s, 2 H); ^{13}C NMR δ 12.03, 18.10, 28.34, 37.22, 128.57, 129.92, 131.44. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.15; H, 11.73. **9**: ^{1}H NMR δ 0.99 (t, 3 H), 1.75 (s, 3 H), 2.16 (q, 2 H), 2.46 (m, 4 H), 5.99 (m, 1 H), 6.38 (m, 1 H); ^{13}C NMR δ 12.08, 17.88, 26.82, 28.55, 31.91, 126.03, 131.90, 135.34, 139.51. **10**: ^{1}H NMR δ 0.99 (t, 3 H), 1.68 (s, 3 H), 2.16 (q, 2 H), 2.47 (m, 4 H), 5.98 (m, 1 H), 6.38 (d, 1 H); ^{13}C NMR δ 13.33, 18.58, 27.58, 28.07, 31.75, 126.18, 130.79, 135.18, 139.68. **9** + **10** Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.71.

Thermal Aromatizations. The pyrolysis vessel consisted of a quartz tube 1.9 cm i.d. × 50 cm long, which was fitted with a thermocouple well, sample inlet tube, and product receiver. The outlet of the receiver was connected to a conventional high-vacuum line capable of achieving a vacuum of 10^{-6} mm, and the pressure was monitored with a McLeod gauge attached to the manifold of the line. The pyrolysis tube was heated in a vertical furnace, which was controlled with a Variac, and the temperature was measured with an iron-constantan thermocouple located at the center of the heated zone and connected to a Fluke 2176A digital thermometer. Temperature fluctuations were less than 1.5 °C during a run.

Weighed samples of reactant were placed in the sample reservoir and thoroughly degassed, and the vapor was allowed to effuse through a capillary leak into the pyrolysis tube. Condensable products were collected in the receiver, which was cooled in liquid nitrogen. At the end of a run, the product was allowed to warm to room temperature and was weighed and analyzed by VPC. Product identification was based on comparison of retention times with those of authentic samples, determined on columns 1–4. In cases where the identification was doubtful, products were isolated by preparative VPC and identified spectroscopically. The VPC instrument was equipped with a thermal conductivity detector, and peak areas were measured with a Hewlett-Packard 3390A recorder–integrator. The detector response was corrected for the aromatics, relative to toluene, by determining known mixtures of each of the aromatics and toluene. No correction was made for the nonaromatic components. The results are presented in Tables I–III, where the values given are the averages of two or more runs.

Thermal Rearrangement of 6,6-Dimethylbicyclo[3.1.0]-hex-2-ene (25). A 47.5-mg sample of **25** was placed in a glass ampoule, degassed and sealed under vacuum. After the material had been heated for 2.5 h at 280 °C, VPC analysis showed the presence of 10.2% unchanged **25**, 7.8% of a mixture of dimethylcyclohexadienes, 11.2% 4,4-dimethylbicyclo[3.1.0]hex-2-ene (**31**), 62.1% 3-isopropenylcyclopentene (**30**), and 8.7% toluene.

In separate experiments carried out in a static, gas-phase reactor, with provisions for monitoring the composition, it was found that **30** and **31** were formed initially, and the concentration of **30** continued to rise throughout the reaction while that of **31** passed through a maximum and slowly declined to zero. The dimethylcyclohexadienes increased steadily, but at a much slower rate than **30**.

Acknowledgment. Support of this research by the National Science Foundation under Grant CHE-8304223 is gratefully acknowledged.

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(30) Assignment of configurations was based on the report of Mach et al.[31] that the allylic methyl signal of (*Z*)- and (*E*)-3-ethylidenecyclopentene appears at 1.66 and 1.69 ppm, respectively.

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