

Ring Closure Reactions of Allyl to Cyclopropylcarbinyl Cations^{1a}

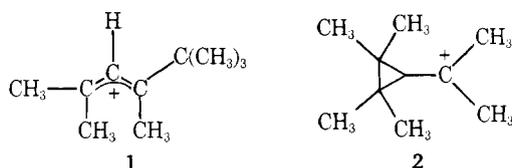
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Abstract: The rearrangements of the allyl cations $\text{CH}_3\text{CHRC}^+\text{HCR}'=\text{CH}_2$ to the isomeric cyclopropylcarbinyl cations $\text{R}'\text{-c-C}_3\text{H}_4\text{C}^+\text{CH}_3\text{R}$ ($\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$; $\text{R}, \text{R}' = \text{CH}_3$; $\text{R}, \text{R}' = \text{H}$) have been observed in SO_2ClF solution at -78 and -120 °C. At higher temperatures ring opening reactions leading to more highly substituted allyl cations took place. The general order of thermodynamic stability of ions was derived as $\text{R}(\text{C}_3\text{H}_5)^+ < \text{c-C}_3\text{H}_5\text{C}^+\text{R}_2 < \text{R}(\text{C}_3\text{H}_5)^+\text{R}$. The stabilizing effect of a cyclopropyl group on a carbenium center is estimated to be 11–17 kcal/mol larger than that of a vinyl group.

Roberts and Mazur observed in 1951 that cyclopropylcarbinyl derivatives are generally solvolyzed faster than analogously substituted allyl compounds.² Their conclusion that a neighboring cyclopropyl group possesses an exceptional ability to stabilize positive charge has been emphasized by numerous kinetic studies.^{3a} More recently, ¹³C NMR studies of substituted cyclopropylcarbenium ions demonstrated that the stabilizing effect of a cyclopropyl group on a carbenium center is comparable to the effect of a phenyl group.^{1a}

Identical values of the appearance potentials of the cyclopropylcarbinyl cation⁴ and the allyl cation,⁵ each 2.52 eV lower than that of the methyl cation (14.4 eV),⁶ indicate similar stabilizing abilities of vinyl and cyclopropyl groups in the gas phase. However, no evidence has been obtained that cyclopropylcarbinyl cations exist in an observable equilibrium concentration with their isomeric allyl cations. From kinetic data Winstein and Poulter concluded that the tetraalkylallyl cation **1** is at least 6 kcal/mol more stable than the corresponding cyclopropylcarbenium ion **2**.⁷



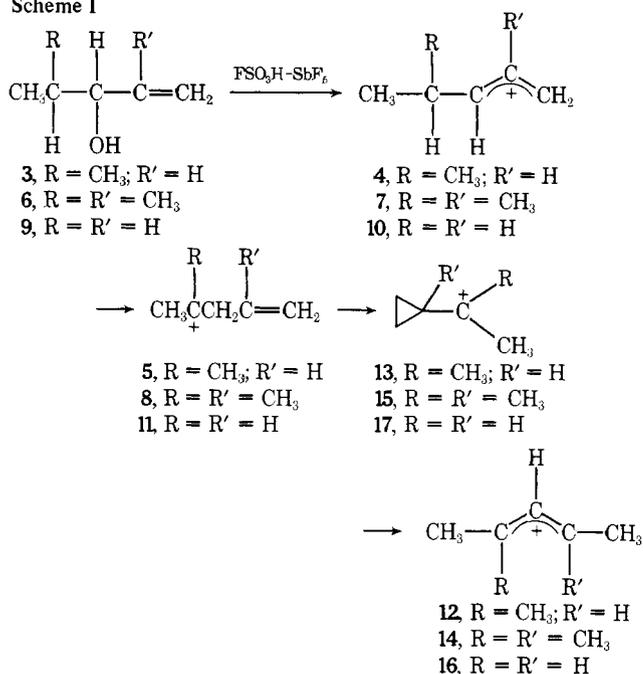
The observed rearrangement of the α,α -dimethylcyclopropylcarbenium ion (**13**) to the 1,1,3-trimethylallyl cation (**12**) also indicates a higher thermodynamic stability of the allylic system.⁷ Whereas ring closure reactions accompanying the solvolysis of homoallylic derivatives are well known,^{3b} this reaction type has not yet been observed from allylic precursors. Recently we observed the formation of **13** upon protonation of 4-methyl-1-pentyne and postulated its formation via the intermediacy of an allylic cation.⁹ We now wish to present the first systematic study of ring closure reactions of allyl to cyclopropylcarbinyl cations.

Results and Discussion

1. α,α -Dimethylcyclopropylcarbinyl Cation (13**).** When 4-methyl-1-penten-3-ol (**3**) was treated with $\text{FSO}_3\text{H-SbF}_5$ in SO_2 or SO_2ClF solution at -78 °C, the quantitative formation of **13**⁸ was observed (Scheme I). At 0 °C, the reported rearrangement of **13** to **12** took place as a slow reaction.^{7,9}

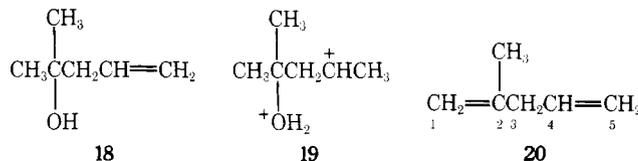
As the preparation of allyl cations from the corresponding allyl alcohols is well known,¹⁰ we interpret the formation of **13** as a rearrangement of the intermediate allyl cation **4**. Moreover, the rearrangement of **4** to **13** was also indicated by the formation of **13** through protonation of 4-methyl-1-pentyne.⁹ In analogy to observation on cation **1**,⁷ **4** might isomerize to

Scheme I



the homoallylic ion **5**, which then undergoes ring closure to **13**.

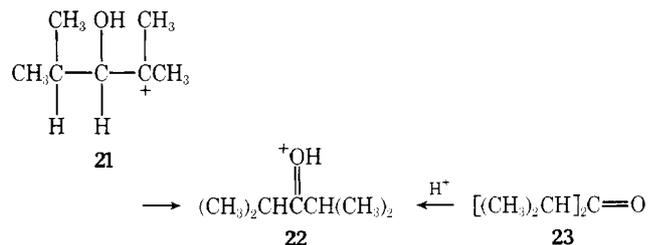
To establish the intermediacy of **5** we attempted its preparation from homoallyl alcohol **18** with $\text{FSO}_3\text{H-SbF}_5$ in SO_2ClF solution. However, only the allyl cation **12** was obtained, even at -78 °C. **18** probably becomes protonated in the CC double bond prior to dehydration. The allyl cation **12** is then formed directly, possibly via the diprotonated species **19**. **13** was obtained, however, in approximately 40% yield when **18** was treated with SbF_5 in SO_2ClF solution at -78 °C.



Another possibility of generating **5** is the protonation of 2-methyl-1,4-pentadiene (**20**), since the tertiary carbenium ion **5** is expected to be more stable than the secondary ion which might arise from protonation on C5. However, when **20** was treated with $\text{FSO}_3\text{H-SbF}_5$ in SO_2ClF at -78 °C, no evidence for the formation of **13** was obtained. The ¹H NMR spectrum consisted of broad, unresolved resonances, indicating the presence of polymers. Utilizing the observation that raising the

temperature generally favors intramolecular to intermolecular reactions,⁹ we obtained **13** in high yield (~80%) when neat **20** was added to a solution of FSO₃H-SbF₅ in SO₂ClF at 0 °C. Therefore the intermediacy of the homoallylic ion **5** seems to be indicated, though the ring closure reactions of these ions have not yet been observed under stable ion conditions.

2. α,α,1-Trimethylcyclopropylcarbinyl Cation (15). Since the stability of an allylic cation is not affected significantly by substitution at the central carbon atom, **7** was expected to undergo ring closure similar to **4**. Indeed, when 2,4-dimethyl-1-penten-3-ol (**6**) was reacted with FSO₃H-SbF₅ in SO₂ClF at -120 °C, a 1:1 mixture of **15** and **22** was obtained. **15** showed identical NMR spectra with those reported previously,¹¹ while the formation of **22** was verified by its independent preparation from 2,4-dimethyl-3-pentanone (**23**) and FSO₃H-SbF₅-SO₂ClF.

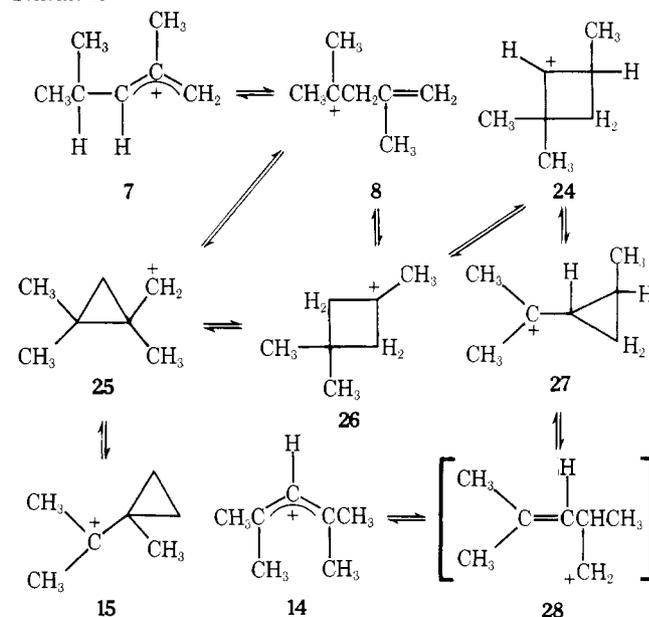


The formation of **22** is rationalized by the protonation of **6** at the C=C double bond to give **21**, which then undergoes 1,2-hydrogen migration to give **22**. This is in accordance with the observation that ion **15** was exclusively formed when **9** was treated with SbF₅ in SO₂ClF at -120 °C.

The ring opening reaction of **15** to **14**,¹² which takes place at -78 °C in FSO₃H-SbF₅-SO₂ClF was previously observed in our work (FSO₃H-SO₂ClF at -78 °C).¹³

A mechanism for the formation of **15** and **14** is suggested in Scheme II. The primary allyl cation **7** undergoes a 1,2-

Scheme II



hydrogen shift to give the homoallylic ion **8**, as already indicated in Scheme I. Ring closure of **8**, either directly or via the cyclobutyl cation **26**, leads to **25**, which undergoes a cyclopropylcarbinyl to cyclopropylcarbinyl ion rearrangement to yield **15**.

As the isomerization of **13** in FSO₃D-SO₂ClF yielded **12** without deuterium incorporation,⁷ we can conclude that the formation of **14** from **15** is not initiated by protolysis of **15**. The

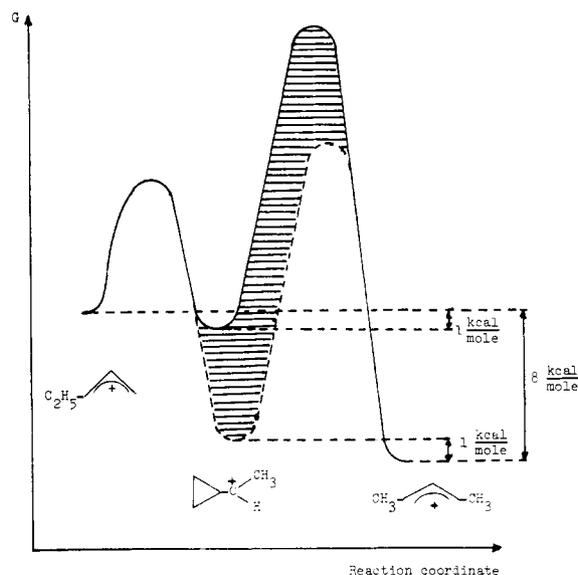
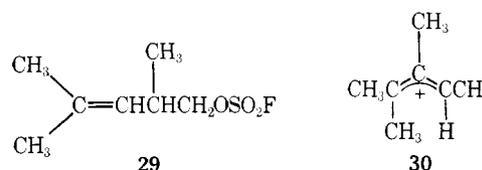


Figure 1. Energy profile of the rearrangements **10** → **17** → **16** (high energy intermediates not included).

cyclobutyl cation **26**, which might be present in low concentration in equilibrium with **15**, might undergo a 1,2-hydrogen shift to **24**. Ring contraction of **24** and subsequent ring opening of **27** yields the homoallylic cation **28**. Finally, the tetramethylallyl cation **14** is formed by a 1,2-hydrogen shift from **28**.

The observation that ring opening reactions of cyclopropylcarbinyl cations occur more readily in the presence of FSO₃H than in FSO₃H-SbF₅ indicates that the process leading to **14** might be more complicated than the mechanism of Scheme II. Possibly **27** is attacked by FSO₃⁻ to yield **29**, which then ionizes to **28** and **14**.

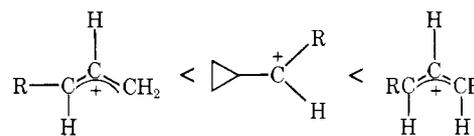


The direct ring opening of **15** (prior to rearrangement to **27**) does not appear to take place, since the cation that would be expected from such a process (**30**) was not detected. Since **30** does not isomerize to **14** under the reaction conditions,^{9,14} the formation of **14** must be due to kinetic control.

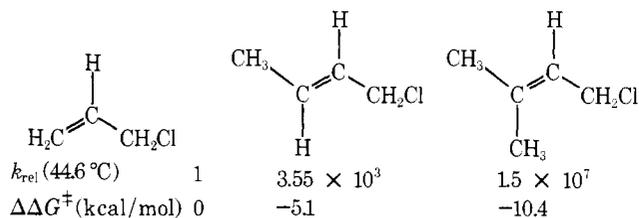
To save space, no detailed mechanistic scheme is presented for the formation and decomposition of **13** and **17**. Scheme II can, however, analogously be applied to these cases with the only difference that some formula become identical.

3. α-Methylcyclopropylcarbinyl Cation (17). The quantitative formation of **17**¹⁵ from 1-penten-3-ol (**9**) and FSO₃H-SbF₅ in SO₂ClF at -78 °C indicates the rearrangement of the allyl cation **10** to the cyclopropylcarbinyl cation. When this solution was warmed to -50 °C **17** rearranged within 1 h quantitatively to the 2-penten-4-yl cation **16**.¹⁶

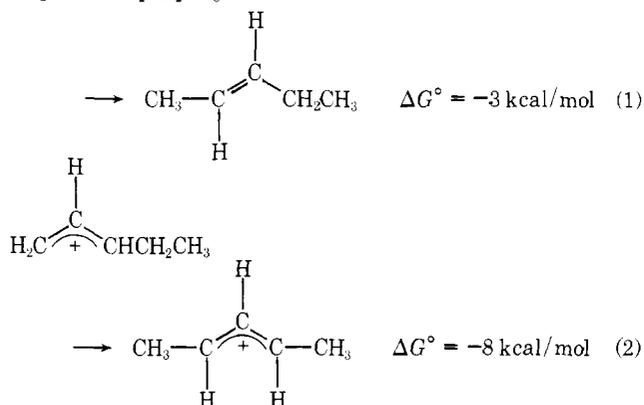
The relative thermodynamic stabilities of ions **10**, **16**, and **17**, which can be derived from this reaction sequence, are depicted in Figure 1. Since the stabilizing effect of a methyl or ethyl substituent upon allylic cations is very similar,¹⁷ the following general order of stabilities is indicated. The energy



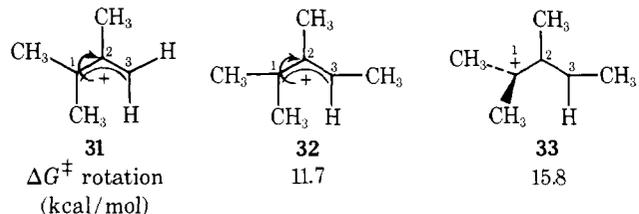
difference between the ions **10** and **16** (i.e., ΔG° of eq 2) can be estimated from the relative solvolysis rates of the following allylic chlorides.^{18a} The decrease of the activation barrier in-



dicates that each methyl group stabilizes the transition state (which is energetically close to the allyl cation) by about 5 kcal/mol relative to the ground state. Therefore it is concluded that reaction 2 is favored by 5 kcal/mol compared to the isomerization of 1-pentene to 2-pentene (eq 1).¹⁹ A similar $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$



value can be obtained by comparison of the rotational barriers of the allylic ions **31** and **32**.^{18b} The difference of 4 kcal/mol

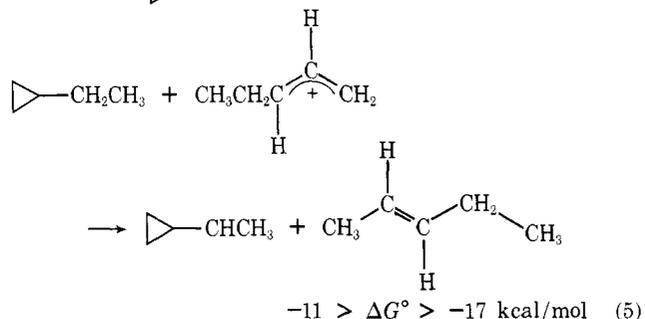
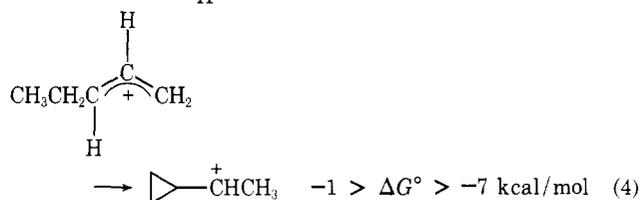
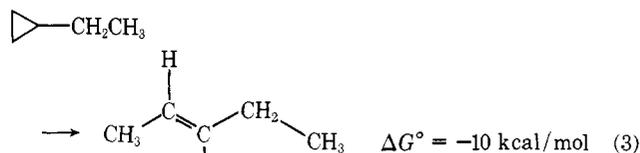


arises from the fact that the additional methyl group stabilizes the planar cation **32** more than the perpendicular transition state of the rotation (**33**). Since the stabilizing effect of the 3- CH_3 upon **33** can be expected to be about the same as on a neutral double bond (3 kcal/mol), a total methyl stabilization of 7 kcal/mol can be estimated.

When **9** was treated with magic acid at -78°C , the allylic cation **10** was not observed in addition to **17**. Assuming that a minimum of 10% of **10** would be detectable in the NMR spectra, it can be concluded that **17** is at least 1 kcal/mol more stable than **10** (Figure 1). Similarly it can be derived that **17** is more than 1 kcal/mol higher in energy than **16**. Thus the solid and the dashed lines in Figure 1 are the extreme boundaries for the rearrangements $\mathbf{10} \rightarrow \mathbf{17} \rightarrow \mathbf{16}$. The true reaction coordinate must lie in the shaded area.

In order to estimate the differing stabilization of a carbenium center by vinyl and cyclopropyl groups, it is necessary to consider the different strain energies of the cyclic and linear ions. ΔG° of the isomerization according to eq 3 was calculated from the standard group increments¹⁹ and ΔG° of eq 4 was obtained from Figure 1.

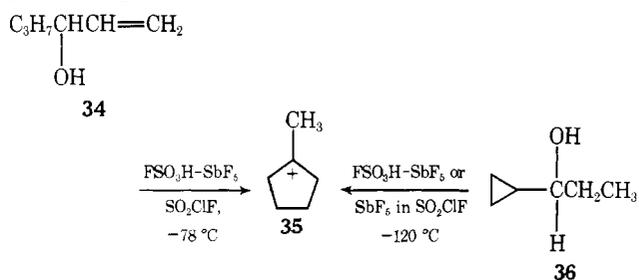
The isodesmic reaction 5, which is obtained by the summation of eq 3 and 4, shows that the proton transfer from ethylcyclopropane to the 2-penten-1-yl cation is favored by -11 to -17 kcal/mol. Therefore it can be concluded that a



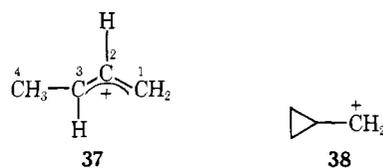
cyclopropyl group stabilizes a carbenium ion center by 11–17 kcal/mol more than a vinyl group. The higher thermodynamic stability of **17** relative to **10** (-1 to -7 kcal/mol), therefore, reflects both the higher resonance energy (-11 to -17 kcal/mol) and the higher strain (10 kcal/mol) of **17**.

4. Related Systems, Not Giving Cyclopropylcarbiny Ions.

In analogy to **9**, 1-hexen-3-ol (**34**) was expected to yield the α -ethylcyclopropylcarbiny ion when treated with magic acid at low temperature. However, even at -78°C quantitative formation of the 1-methyl-1-cyclopentyl cation was observed. This reaction might proceed via a subsequent 1,2-hydrogen shift in the 1-hexen-4-yl cation to form the 1-hexen-5-yl cation, which might undergo ring closure to the cyclopentyl system.⁹ The intermediacy of the α -ethylcyclopropylcarbiny ion is, however, possible, since 1-cyclopropyl-1-propanol (**36**) reacted with magic acid or SbF_5 in SO_2ClF to yield **36**, even at -120°C .²⁰



From the comparison of **16** and **17** it would be expected that **37** is more stable than **38**, though the rearrangement $\mathbf{38} \rightarrow \mathbf{37}$ has not yet been observed under stable conditions. The reason might be a kinetic barrier or the unusually high stability of **38**. In order to check the second explanation, we prepared **37** by the reaction of 3-buten-2-ol with $\text{FSO}_3\text{H-SbF}_5$ in SO_2ClF at -120°C . The rearrangement of **37** to **38** was not observed below -20°C , at which temperature decomposition to polymeric materials occurred. The question, whether **37** or **38** is thermodynamically favored, therefore, remains to be solved.



Experimental Section

All allyl alcohols were commercially available (Chemical Samples Co.) and were used without further purification. 1-Cyclopropyl-1-propanol²¹ was prepared by the reaction of cyclopropylmagnesium bromide with propionaldehyde in THF in 28% yield (bp 80–84 °C (95 Torr)). Magic acid was prepared from triply distilled FSO₃H and doubly distilled SbF₅. The 1:1 molar ratio was used in all experiments.

Preparation of Ions. A dilute (~10%) solution of the alcohol in SO₂ClF at –78 °C was added dropwise, with efficient stirring, to an approximately 1:1 (by volume) solution of FSO₃H–SbF₅ at –78 or –120 °C. To avoid the ring opening of **15** and **17** the addition had to be carried out very slowly. The solutions were transferred to precooled NMR tubes for study.

Protonated Diisopropyl Ketone. The ¹H NMR spectrum obtained of **22** in FSO₃H–SbF₅–SO₂ClF solution did not show the nonequivalence of the methyl groups observed in SO₂ solution.²² The ¹³C NMR spectrum obtained after protonation of **23** with magic acid in SO₂ClF (δ_C 17.0 (q), 18.2 (q), 40.3 (d), 43.0 (d), 258.4 (s)) proved the identity of **22** as a by-product of **15** when **6** was treated with magic acid.

1-Buten-3-ylum Cation (37). ¹H NMR δ 3.53 (d, J = 6 Hz, CH₃), 8–9 (m, allyl H, partially overlapping with H₃O⁺); ¹³C NMR δ_C 255.1 (d, J = 168 Hz, C3), 201.5 (t, J = 172 Hz, C1), 149.8 (d, J = 177 Hz, C2), 36.3 (q, J = 130 Hz, C4).

Proton Magnetic Resonance Spectra. ¹H NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer equipped with a variable temperature probe. External Me₄Si was used as a reference.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broad band decoupler and a variable temperature probe. All shifts are from external Me₄Si.

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Annulation of Tricarbonyliron Complexes of Ortho-Disubstituted [4]Annulenes. Synthesis of Tricarbonyliron Complexes of Derivatives of Bicyclo[6.2.0]decapentaene via Wittig Cycloolefination

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Abstract: Wittig cycloolefination of dialdehyde **4** has been studied as a route to tricarbonyliron complexes of derivatives of bicyclo[6.2.0]decapentaene. Treatment of **4** with ylides derived from bisphosphonium salts **5**, **7**, **11**, and **14** afforded benzo, furo, dihydro, and tropono derivatives **6**, **8**, **12**, and **15** in modest yields. Diels-Alder addition of *N*-phenylmaleimide to **8** led to the (syn,endo), (syn,exo), and (anti,exo) stereoisomers of **10**. All attempts to dehydrogenate **12** or to cycloolefinate **4** with the ylide derived from *cis*-2-butene-1,4-bis(triphenylphosphonium chloride) (**13**) to give parent complex **9** failed as did attempted ring expansion of tropono complex **15** with diazomethane. The enhanced intensities and bathochromic shifts observed in the electronic spectra of **6**, **8**, and stereoisomers of **10** are additional examples of the 1,2:5,6 bisannulation effect in [8]annulenes, the origin of which may be increased conjugation through flattening of the eight-membered ring. Conformational analysis of a model of the bicyclo[6.2.0]decapentaene ring system in which the four-membered ring is complexed to a tricarbonyliron group suggests a strong preference for the conformer in which the metal is on the convex face of a tub form.

Introduction

Bicyclo[6.2.0]deca-1,3,5,7,9-pentaene, (**1**), an isomer of naphthalene and azulene, is an intriguing representative of systems comprising fused 4n π -electron systems. In view of the

conformational flexibility of cyclooctatetraene and the contrasting conformational rigidity of cyclobutadiene, respectively, a central question concerning the nature of **1** is how ground-state geometry reflects a compromise between elec-