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Intramolecular Cationic Cyclizations Initiated by Electrocyclic Cleavage of Cyclopropanes. Synthesis of Trienic Cyclopentane Derivatives

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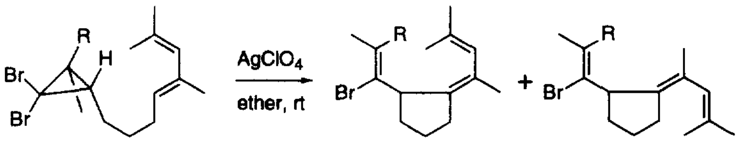
Abstract: *The electrocyclic opening of dibromocyclopropane derivatives containing a tethered diene unit provides a good route to trienic cyclopentane derivatives. In one instance a bicyclic product arising from a formal 4 + 2 cycloaddition process was observed.*

Although it is well known that allyl cations can be generated from the disrotatory electrocyclic cleavage of cyclopropane derivatives,[2] only a few examples have described the use of these allyl cations in cyclization reactions.[3] As part of our study of both the intramolecular[4] and intermolecular[5] cyclization reactions of allyl cations, we have explored the intramolecular addition of allyl cations generated from dibromocyclopropane derivatives to dienes. We now report that trienic cyclopentanes can be formed in moderate to good yields through this cationic cyclization reaction at room temperature.

Substrates **1a**[6,7] and **1b**,[6,7] each containing a diene and dibromocyclopropane subunit, gave the cleanest product mixtures of all of the substrates studied. In a typical procedure, a dry diethyl ether solution of **1a** was treated with 1.1 equiv of silver perchlorate at room temperature 14 h. Cyclopentane derivatives **2a**[7] and **3a**[7] were isolated as a mixture in 89% yield following flash chromatography. The ratio of **2a** to **3a** was determined to be 1.4:1 by both GLC and ^{1}H NMR spectral analysis. Analytical sample of **2a** and **3a** were obtained by separating the mixture by preparative gas chromatography. The olefin geometries were assigned through NOE studies. Similar treatment of **1b** in diethyl ether at room temperature with 1.1 equiv of silver perchlorate gave 74% of **2b**[7] and **3b**[7] (1:1).



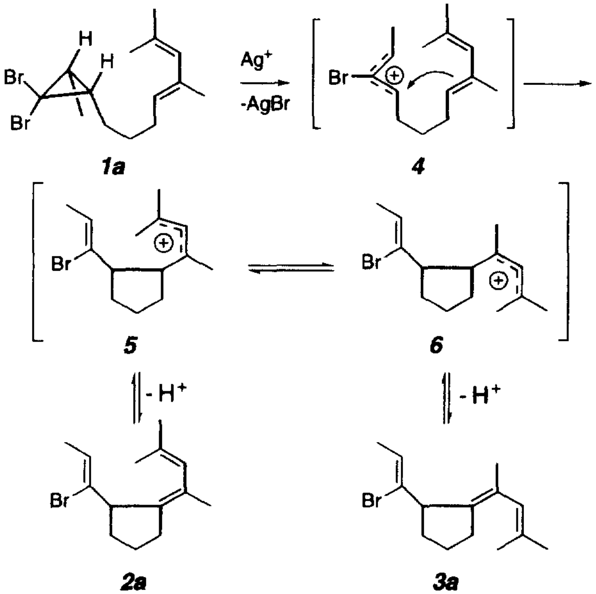
1a *1b*

a R = H
b R = Me

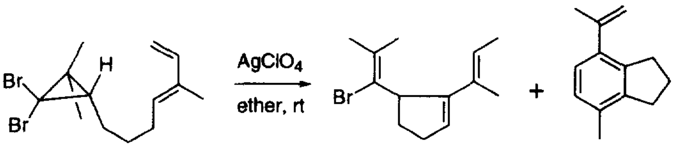
2a *2b*

3a *3b*

The formation of the cyclopentane derivatives can be explained by an ionic mechanism. Silver-assisted electrocyclic cleavage of the dibromocyclopropane in **1a** would produce the allyl cation **4**. Addition of the allyl cation to the tethered diene could give the new allyl cation intermediate **5**, which might be in equilibrium with the rotamer **6**. Elimination of a proton from the allyl cation **5** or **6** would then produce the final product **2a** or **3a**. The formation of **2b** and **3b** can be explained in the same way. Theoretically, bicyclic skeletons (formal Diels-Alder products) could be formed from the cyclization of allyl cations such as **5** and **6**. Such products were not isolated from the reactions of either **1a** or **1b**. The mixture of **2a** and **3a** (1.4:1) was treated with *p*-toluenesulfonic acid in dry methylene chloride in an attempt to regenerate allyl cations **5** and **6** and to force the formation of bicyclic products. However, no bicyclic products were observed; the ratio of **2a** to **3a** changed to 2.4:1. We hypothesized that the steric hindrance of the *gem*-dimethyl groups on the diene terminus was partially responsible for the failure of these systems to undergo further cyclization.

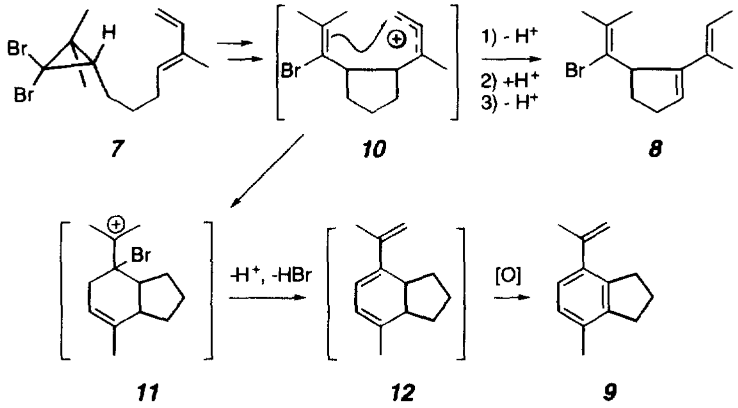


Indeed, treatment of **7**,[6,7] a precursor with the *gem*-dimethyl groups on the diene removed, with 1.5 equivalent of silver perchlorate in anhydrous diethyl ether at room temperature for 24 h gave, in addition to 50% of the cyclopentene derivative **8**,[7] 13% of the bicyclic product **9**[7] along with several other unidentified products. Both compounds **8** and **9** can be derived from allyl cation **10**, which would arise from the silver-assisted electrocyclic cleavage of the dibromocyclopropane in **7** followed by cyclization of the allyl cation

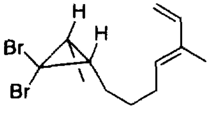


7 **8** **9**

to the diene. Elimination of a proton from **10** followed by acid-catalyzed diene isomerization would produce **8**. On the other hand, the allyl cation in **10** might add to the vinyl bromide to give the bicyclic skeleton **11**. Upon loss of a proton and hydrogen bromide from **11**, the bicyclic compound **12** might be obtained. Apparently, this triene system is not stable. It is oxidized *in situ* to generate the more stable aromatic indane **9**. However, it is curious that triene **12**, if formed, did not undergo simple acid-catalyzed isomerization to the isopropyl-substituted indane (i.e., compound **9** in which the alkene is saturated).



Several additional diene-containing bromocyclopropanes **13-16** were studied.[7] Each gave rise to more complex product mixtures. However, among all the products identified from these reactions, none contained bicyclic skeletons.



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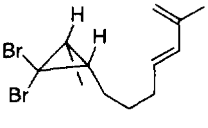

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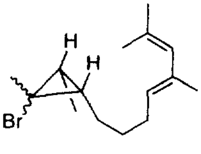

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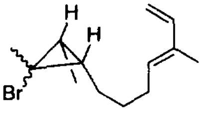

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In summary, we have demonstrated that allyl cations generated from bromocyclopropane derivatives bearing a tethered diene can effectively produce trienic cyclopentane derivatives. However, this is not a generally applicable strategy for creation of formal Diels-Alder adducts.

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References and Notes

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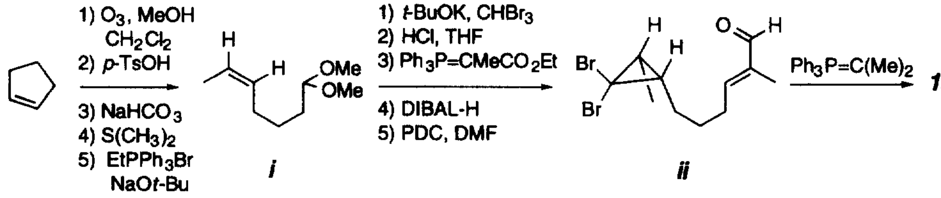
6. (a) Compound **1a** was prepared from cyclopentene in a total of eight steps. Ozonolysis^{6b} of cyclopentene followed by a lithium-salt-free Wittig reaction with ethylidenetriphenylphosphorane, generated *in situ* from ethyltriphenylphosphonium bromide and sodium *tert*-butoxide, gave (*Z*)-7,7-dimethoxy-2-heptene (**i**) in 52% overall yield. Treatment with dibromocarbene gave 85% of (±)-(2α,3α)-1,1-dibromo-2-methyl-3-(4,4-dimethoxybutyl)cyclopropane. Acid hydrolysis of the dimethylacetal group and reaction with (carbethoxymethylene)triphenylphosphorane produced ethyl (±)-(2*E*,1'α,3'α)-6-(2,2-dibromo-3-methylcyclopropyl)-2-methylhexenoate in 73% overall yield. Reduction of the ester with DIBAL-H followed by oxidation of the alcohol with PDC in DMF at 0 °C gave 96% of (±)-(2*E*,1'α,3'α)-6-(2,2-dibromo-3-methylcyclopropyl)-2-methylhexenal (**ii**). Addition of isopropylidenetriphenylphosphorane to the aldehyde gave 78% of **1a**. A similar synthetic sequence starting from 5,5-dimethoxypentanal provided **1b** and **7** in 28% and 34% yield, respectively.
   (b) Schreiber, S. L.; Claves, R. E.; Reagar, S. *Org. Synth.* Coll. Vol. 7, 168.



7. All new compounds were completely characterized by appropriate spectroscopic methods. All gave satisfactory elemental analyses and/or exact mass molecular weights. Tan, L. Ph. D. Dissertation, University of Minnesota, 1995.

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