

Communications to the Editor

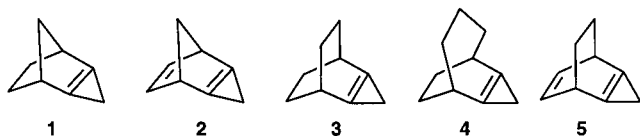
Isomerization of Tricyclo[3.2.2.0^{2,4}]nona-2(4),6-diene to the Anti-Bredt Compound 8-Methylenebicyclo[3.2.1]octa-1,6-diene

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Although the existence of cyclopropenes has been known for over a century, and the first authenticated synthesis of cyclopropene was reported by Dem'yanov and Doyarenko in 1922,¹ the cyclopropenes continue to fascinate both theoretical and experimental chemists because of their unique structure, high degree of ring strain, and difficult synthesis.² Cyclopropenes undergo many unusual processes such as ring opening reactions to form vinyl carbenes and [2 + 2] cycloadditions to give tricyclo[3.1.0.0^{2,4}]hexanes in order to release strain energy.³ Fused bicyclic cyclopropenes, which are more energetic than cyclopropene itself, have been well studied.^{3,4} Four 1,2-fused tricyclics with a cyclopropene fused to a bicyclic ring skeleton, **1**,^{5,6} **2**,^{5,7} **3**,⁸ and **4**,⁹ have been synthesized and trapped. However, the chemistry of **1**, **2**, **3**, and **4** is unknown. In these compounds, the strain energies of compounds **1** and **2** are very high, and therefore, their isomerization becomes complicated. The stereochemistry of the Diels–Alder reactions of **1** and **2** with diphenylisobenzofuran (DPIBF) is different, but only exo addition (from the view of bicyclic systems) adducts are formed, and the effects of CH₂–CH₂ and CH=CH bridges in these reactions are not clear. To better understand these effects in this type of Diels–Alder reaction, we have synthesized tricyclo[3.2.2.0^{2,4}]nona-2(4),6-diene (**5**) and trapped it with DPIBF.



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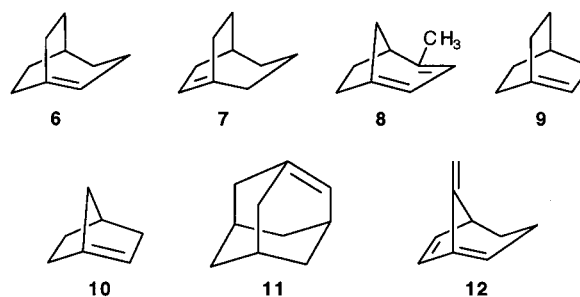
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The twisting distortion of π bonds was not given much attention until the early part of this century when J. Bredt studied it.¹⁰ Although his conclusions were aimed at bicyclic systems of the camphane and pinene series, Bredt's Rules came to imply a complete prohibition of bridgehead double bonds.^{4a,11} On the other hand, bicyclo[3.2.2]non-1-ene (**6**) and bicyclo[3.2.2]non-1(7)-ene (**7**), whose largest ring containing the double bond is *trans*-cycloheptene, have been prepared by Hofmann elimination of bicyclo[3.2.2]non-1-yl trimethylammonium hydroxide.¹² 4-Methylenebicyclo[3.2.1]octa-1,3-diene (**8**) was synthesized by the Wittig reaction of cyclopenten-3-one with butenylidetriphenylphosphorane.¹³ The smaller system, bicyclo[2.2.2]oct-1-ene (**9**), a *trans*-cyclohexene derivative, has been generated both by insertion of bicyclo[2.2.1]hept-1-yl carbene and elimination of 2-bromo-1-ethoxybicyclo[2.2.2]octane.¹⁴ When 1-iodo-2-chlorobicyclo[2.2.1]heptane or 1-iodo-2-bromobicyclo[2.2.1]heptane was treated with butyllithium, the bicyclo[2.2.1]hept-1-ene (**10**) was formed.¹⁵ Adamantene (**11**), which can be regarded as a methylene-bridged bicyclo[3.3.1]non-1(9)-ene containing the *trans*-cyclohexene skeleton, was synthesized by thermally induced fragmentation of the di-*tert*-butyl ester of 1,2-adamantanediperoxycarboxylic acid, by elimination of 1,2-dihaloadamantane and by irradiation of 1-adamantyl phenylacetate, 2-adamantyl phenylacetate, or protoadamantan-4-one hydrazone.¹⁶ In this paper, we utilize the unusual properties of cyclopropenes to synthesize the anti-Bredt compound 8-methylenebicyclo[3.2.1]octa-1,6-diene (**12**) which was formed from the isomerization of **5**.



The synthesis of the starting material 2-bromo-4-chlorotricyclo[3.2.2.0^{2,4}]non-6-ene (**13**) is illustrated in Scheme 1. Compound **13** is synthesized by the reaction of cyclohexa-1,3-diene with 1-bromo-2-chlorocyclopropene which was generated by the fluoride-induced elimination of 1-bromo-2,2-dichloro-1-trimethylsilylcyclopropane in dichloromethane.⁵ Elimination of **13** with methylolithium in ether solution at 0 °C yielded the desired compound, tricyclo[3.2.2.0^{2,4}]nona-2(4),6-diene (**5**), which was trapped with DPIBF. Theoretically, four isomers are possible in this Diels–Alder reaction, but only one isomer **14** was generated.

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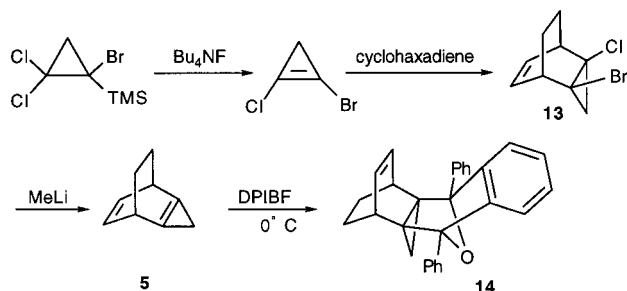
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Scheme 1

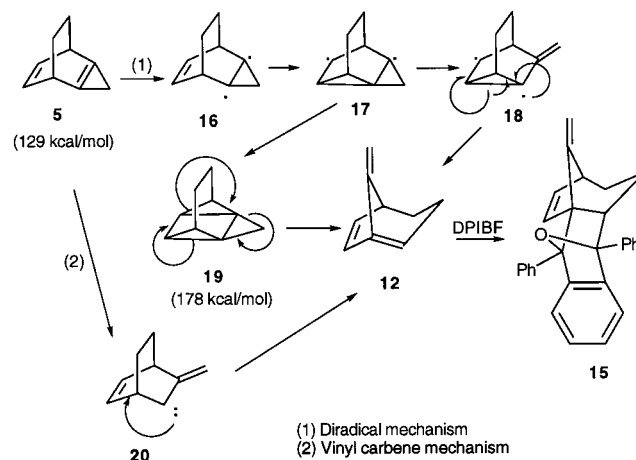


Its structure was determined by single-crystal X-ray analysis. The stereochemistry of **14** shows that the Diels–Alder reaction occurs via exo addition from the view of cyclopropene and endo addition from the view of bicyclo[2.2.2]oct-2,5-diene (exo–endo adduct). This finding leads us to conclude that the repulsion of H₂C–CH₂ and DPIBF is larger than HC=CH and DPIBF and that the repulsion between HC=CH and the oxygen atom is greater than that between HC=CH and the benzene ring at DPIBF. The result is different from that of the Diels–Alder cycloadditions of tricyclo[5.2.2.0^{2,6}]undeca-2,5,8-triene with dienophiles.¹⁷

When compound **13** was reacted with methyllithium at 0 °C for 30 min and the solution of DPIBF in ether was then added to the mixture, two compounds, **14** and **15**, were obtained. To define the origin of compound **15**, compound **14** was subjected to the reaction conditions but underwent no change. The structure of **15** was shown by single-crystal X-ray analysis. Thus, **15** was formed by DPIBF with 8-methylenebicyclo[3.2.1]octa-1,6-diene (**12**) which was produced by the isomerization of **5**.

According to the literature, cyclopropenes can undergo [2 + 2] cycloaddition to give dimers via a stepwise diradical¹⁸ and cyclopropene/vinylcarbene rearrangement¹⁹ to release the strain energy. There are two possible mechanisms in this isomerization—the diradical mechanism and the vinyl carbene mechanism. In the diradical mechanism, compound **5** undergoes electrocyclic opening of the cyclopropyl radical **17**, formed from **16**, to give a new 1,4-diradical **18** which is transformed to **12** by breaking the 2,3-bond, or the cyclopropyl radical **17** undergoes a coupling reaction to give pentacyclo[3.2.2.0.^{2,4}0.^{2,7}0^{4,6}]nonane (**19**) followed by ring opening rearrangement to form **12**. In the vinyl carbene

Scheme 2



mechanism, compound **5** isomerizes to **12** via the cyclopropene/vinyl carbene rearrangement to yield carbene **20** followed by intramolecular insertion. (Scheme 2)

To understand the mechanism of this isomerization, we used UV light to irradiate the reaction mixture, causing the yield of **15** to be higher than in the control reaction. As a result, we propose that this reaction proceeds via a diradical mechanism. Furthermore, theoretical calculations show that the heat of formation of compound **19** (178 kcal/mol) is higher than that of compound **5** (129 kcal/mol).²⁰ Therefore, it is proposed that compound **5** rearranges to 1,3-diradical **17** followed by electrocyclic opening to generate 1,4-diradical **18** which converts to **12**.

In conclusion, we have demonstrated a facile route to synthesize the highly strained compound **5**, which forms a sole adduct **14** with DPIBF. Furthermore, compound **5** rearranges to another highly strained anti-Bredt compound **12**, via diradicals **17** and **18**. This methodology may open up an avenue for the synthesis of bicyclic [n.2.1] systems containing bridgehead double bonds.

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Supporting Information Available: Experimental procedures, spectral data of the new compounds, and crystal structures of **14** and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) Using HyperChem, single point, SemiEmpirical, molecule, AM1, convergence limit = 0.01, iteration limit = 50, accelerate convergence = YES, RHF calculation = singlet state calculation, number of electrons = 46, number of double occupied levels = 23, charge on the system = 0, total orbitals = 46.