



The first generation and trapping of a five-membered ring allene: 2-dehydro-3a,4,5,6,6a-pentahydropentalene

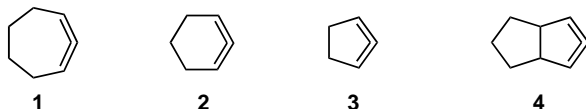
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Abstract—3-Bromo-3-fluorotricyclo[3.3.0.0^{2,4}]octane (**8**) was prepared by addition of bromofluorocarbene to bicyclo[3.2.0]hept-6-ene (**5**). Treatment of a solution of **8** in ether with MeLi in the presence of furan afforded the trapping product **11**. The formation of the trapping product is consistent with the first generation of a five-membered ring allene, namely, 2-dehydro-3a,4,5,6,6a-pentahydropentalene (**4**), a reactive intermediate. © 2002 Elsevier Science Ltd. All rights reserved.

Allenes are an important class of unsaturated hydrocarbons, which contain two cumulated double bonds with an orthogonal geometry. Incorporation of an allene unit in small carbocyclic rings causes considerable deformation from the linear geometry and, furthermore, the ring constraints exert torsion towards the planar arrangement of ligands.¹



Enormous effort has been devoted toward the synthesis of 1,2-cycloheptadiene (**1**) and 1,2-cyclohexadiene (**2**), and a number of their derivatives.¹ Among the cyclic allenes, experimental evidence for 1,2-cyclopentadiene (**3**) has remained elusive.² Favorskii first attempted to generate this strained allene by treatment of 1,2-dibromocyclopentene with metallic sodium and isolated 1,3-cyclopentadiene.³ Dehydrobromination reactions of 1-bromocyclopentene^{3,4} and 1-chlorocyclopentene⁵ resulted in the formation of cyclopentyne rather than the cyclic allene **3**. Fluoride ion-promoted elimination of 2-bromo-3-trimethylsilylcyclopentene⁶ gave Wurtz-like dimers⁷ instead of the cyclic allene **3**. In this communication, we describe a possible generation of a

five-membered ring allene, namely 2-dehydro-3a,4,5,6,6a-pentahydropentalene (**4**).

In principle, one of the best ways to generate allenes directly is rearrangement of cyclopropylidenes to cyclic allenes. This method has been successfully applied to the synthesis of six-⁸ and seven-membered⁹ ring allenes.

For the generation of a five-membered ring allene, the addition of a dihalocarbene to a cyclobutene unit is necessary. Only a few dihalocarbene addition reactions to cyclobutenes are reported in the literature.¹⁰ However, in no case could the addition products be isolated or their structures proven spectroscopically.

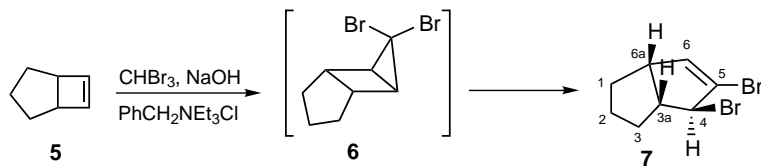
First of all, we studied the addition of dibromocarbene¹¹ generated from CHBr_3 and NaOH under phase-transfer conditions to bicyclo[3.2.0]hept-6-ene (**5**)¹² and isolated the rearranged product **7** in 35% yield (based on recovered starting material) (Scheme 1).

The structure of **7** was elucidated on the basis of NMR spectroscopic data. The stereochemistry of the allylic bromide defines the stereochemistry of the carbene addition. The *exo*-configuration of the bromide implies an *exo*-addition of dibromocarbene to **5**. Since the dibromocarbene adduct **6** undergoes a ring-opening reaction, we decided to add fluorobromocarbene to bicyclo[3.2.0]hept-6-ene (**5**) to prevent the ring-opening reaction at least in one of the isomers. Addition of fluorobromocarbene, generated from CHFBr_2 ¹³ under similar conditions to **5**, afforded the expected addition product, fluorobromocyclopropane derivative **8**, and the ring-opened product **9** in a ratio of 1:5 and in a total yield of 45% (based on recovered starting material) (Scheme 2). The symmetrical structure of the

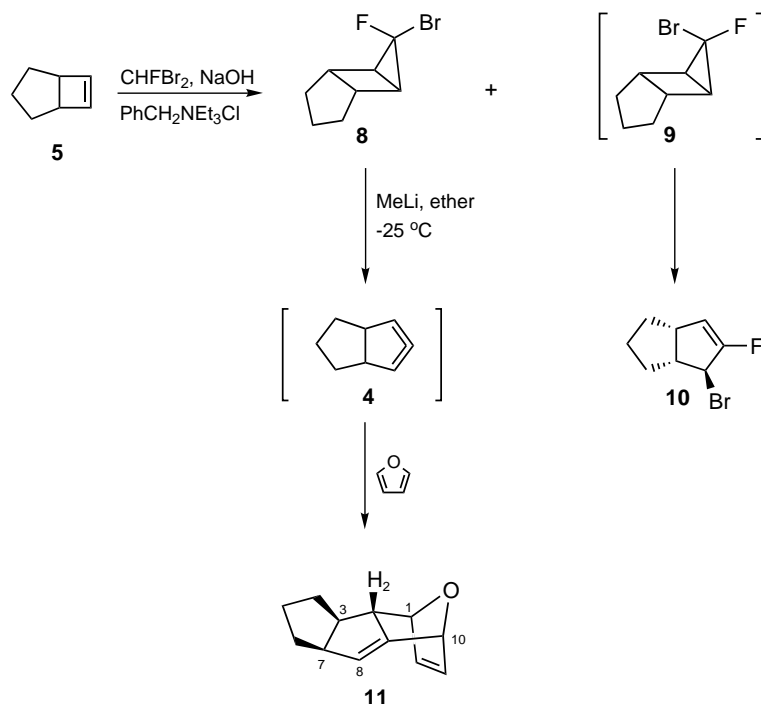
Keywords: cyclic allenes; carbenes and carbenoids; Diels–Alder reactions.

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Scheme 1.



Scheme 2.

exo,exo-isomer **8** was established by the observation of five signals in its ^{13}C NMR spectrum, as required by the symmetry in molecule. The initially formed *exo,endo*-isomer **9** underwent a ring-opening reaction to give **10**. The *exo*-orientation of allylic bromide was determined by measuring the coupling constant between protons H_{3a} and H_4 .

After the successful synthesis and characterization of **8**, it was submitted to the Doering–Moore–Skatebol reaction.¹⁴ Treatment of bromofluorocyclopropane **8** with MeLi in ether at -25°C in the presence of furan as the trapping reagent afforded **11** as the major product that was an isomer of **11**. The structural assignment of **11**¹⁵ was based on ^1H and ^{13}C NMR data including the 2D NMR spectra COSY, HMQC and HMBC. The *exo*-orientation of proton H_2 in **11** was apparent from the value $J_{1,2}=4.1$ Hz (dihedral angle = 47° determined after AM1 geometry optimization). In the case of the *endo*-orientation of proton H_2 , the determined dihedral angle would have been 96° . The lack of a measurable coupling between protons H_2 and H_3 and the large coupling observed between the protons H_7 and H_8 , ($J_{7,8}=8.0$ Hz) support the *exo*-orientation of the cyclopentane ring.

In summary, we believe that we have generated the title compound **4**, which is the first example of a five-membered cyclic allene, by α -elimination of Br and F from bromofluoro cyclopropane compound **8** with MeLi.

Acknowledgements

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15. 13-Oxatetracyclo[8.2.1.0^{2,9}.0^{3,7}]trideca-8,11-diene **11**: ¹H NMR (400 MHz, CDCl₃) δ 6.32 (dd, A part of AB system, $J_{11,12}=5.6$, $J_{10,11}=1.6$ Hz, H₁₁), 6.17 (dd, B part of AB system, $J_{11,12}=5.6$, $J_{1,12}=1.5$ Hz, H₁₂), 5.62 (dd, $J_{8,7}=8.0$, $J_{8,2}=2.5$ Hz, H₈), 5.20 (bs, H₁₀), 5.01 (br. d, $J_{1,2}=4.1$, H₁), 2.90 (m, H₂), 2.75 (ddd, $J_{7,3}=11.0$, $J_{7,8}=8.0$, $J_{7,6}=1.7$ Hz, H₇), 2.27 (dt, $J=4.2$ and 11.0 Hz, H₃), 1.15–1.60 (m, 6H); ¹³C NMR δ 146.5 (C9), 136.2 (C11), 130.2 (C12), 117.7 (C8), 82.2 (C1), 80.9 (C10), 49.5 (C7), 48.9 (C3), 38.5 (C2), 33.3 (CH₂), 33.2 (CH₂), 25.6 (CH₂); IR (CHCl₃): 2997, 2934, 2808, 2801, 1220, 1217, 1213, 1208, 785, 780, 773, 770, 760, 750, 737, 669 cm⁻¹.