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Attempted Synthesis of Cyclopenta-1,2-diene and Wurtz-like Condensation Products in the Reaction of 2,3-Dibromocycloalkenes with Zinc

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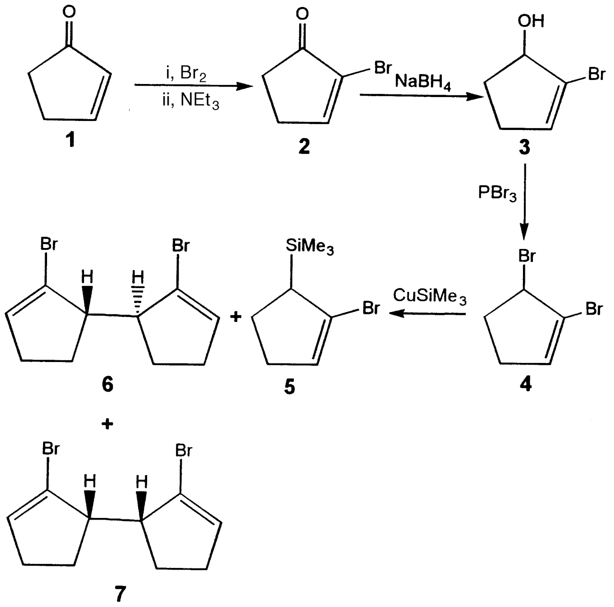
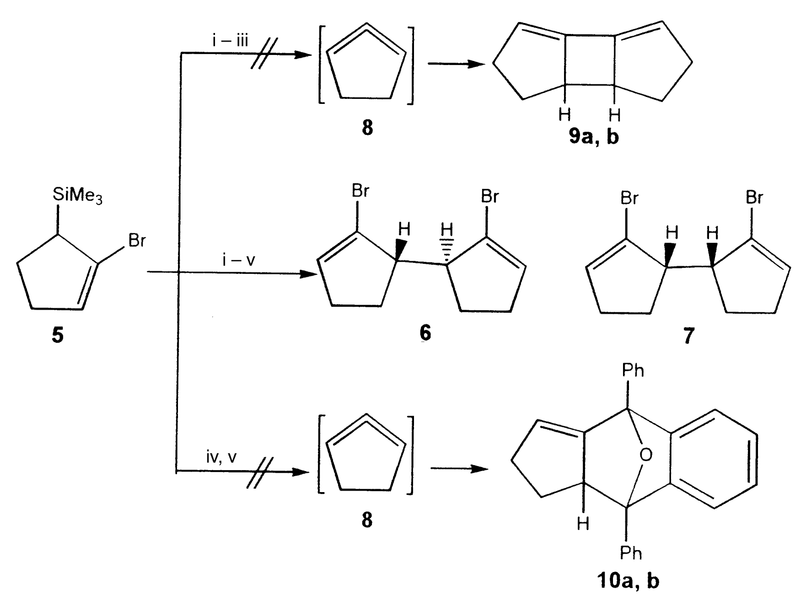
Fluoride ion-promoted elimination of 2-bromo-3-trimethylsilylcyclopentene **5** and the reaction of five-, six- and seven-membered 2,3-dibromocycloalkenes with zinc gave Wurtz-like dimeric products instead of the expected cyclic allenes.

Allenes are an important class of unsaturated hydrocarbons which contain two cumulative orthogonal double bonds. In cyclic allenes, ring constraints bend and twist the normally linear, perpendicular allene and result in substantial strain and kinetic reactivity.[1] Recently, we reported the synthesis of an allene unit in six- and seven-membered rings by fluoride ion-promoted elimination of a β-halogenosilane.[4] In this paper, we applied fluoride ion-promoted elimination of halogenosilane to **5** and zinc catalysed elimination to **4** to synthesise the highly strained cyclic allene cyclopenta-1,2-diene **8**. In addition, we applied zinc catalysed elimination to **12** and **13**. To synthesise **5**, cyclopent-2-enone **1** as starting material was used. Addition of bromine and triethylamine to **1** followed by reduction of **2** with $NaBH_4$ afforded the bromoalcohol **3**. Substitution of **3** with PBr_3 gave dibromoalkene **4**. To convert **4** to **5**, a published procedure was used.[4] In this reaction, **6** and **7** were also obtained in a combined yield of 13%. When the same reaction was carried out at -70 °C, the yield of **6** and **7** increased to 55% (Scheme 1).

Treatment of **5** with tetrabutylammonium fluoride (Bu_4NF) and KF under different conditions resulted in the formation of two isomeric Wurtz-like condensation products **6** and **7** in a combined yield of 48–50% (Scheme 2).



Scheme 1



Scheme 2 *Reagents and conditions:* i, Bu_4NF, DMSO, 85 °C; ii, Bu_4NF, toluene, 110 °C; iii, KF, $AgNO_3$, HMPA, 110 °C; iv, Bu_4NF, THF, DBI, 65 °C; v, Bu_4NF, toluene, DBI, 110 °C

Treatment of **4** with activated zinc in DMSO at 85 °C gave **6** and **7** in a combined yield of 58% (Scheme 3).

The structures of **6** and **7** were determined on the basis of ^{1}H and ^{13}C NMR spectral data. The identical product distribution from the three different reactions, implies a common intermediate **11**. **12** and **13** were synthesised according to literature procedures.[4,6] Treatment of **12** and **13** with activated zinc in THF at 65 °C resulted in the formation of two isomeric Wurtz-like condensation products **18**,**19** (combined yield, 73%) and **20**,**21** (combined yield, 68%), respectively. The same condensation products **18**, **19**, **20**, **21** were also obtained in the synthesis of silyl compounds **16**[7] and **17**[4] from

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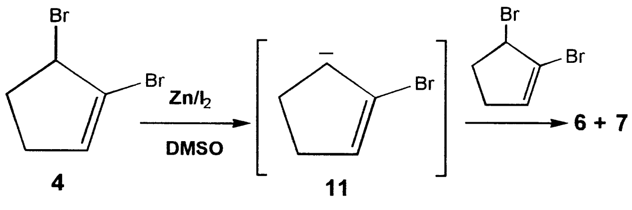
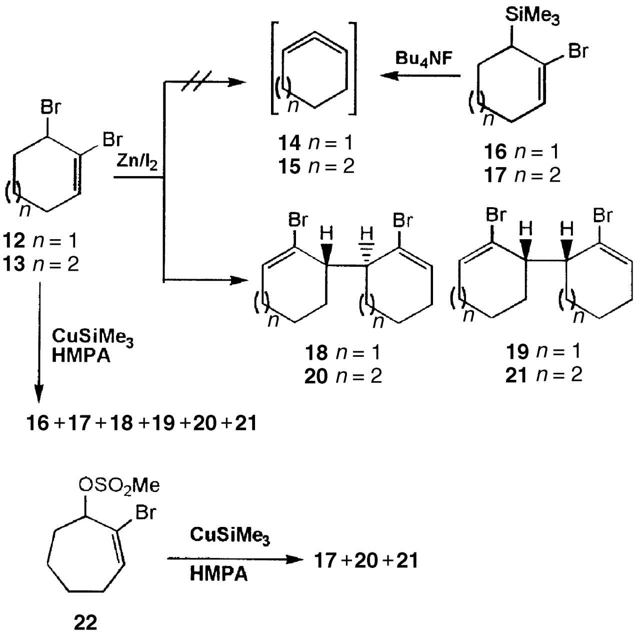


Scheme 3



Scheme 5

dibromides **12** and **13** and the mesylate compound **22** which was synthesised by a literature procedure.[3a,8] Treatment of **12** and **13** with trimethylsilylcopper (CuSiMe$_3$) gave the silyl compounds **16** (54%) and **17** (20%) and the condensation products **18**,**19** (combined yield, 10%) and **20**,**21** (combined yield, 28%), respectively. In addition, treatment of **22** with trimethylsilylcopper at -40 °C also gave **17** (6%) and **20**,**21** (combined yield, 35%). In contrast, reaction of **16** and **17** with Bu$_4$NF had resulted in the formation of **14** and **15** in good yield[4] (Scheme 5).

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Techniques used: ^{1}H and ^{13}C NMR, IR spectrometry

References: 8

Schemes: 5

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