

Synthesis of 1-phenyl -1, 2-cyclohexadiene and 1-(2-bromocyclohex-2-en-1-yl)benzene and Wurtz-like condensation products in the reaction of 1-(2,3-dibromocyclohex-1-en-1-yl) benzene with zinc

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The base-catalysed elimination of 1-(2-bromocyclohex-2-en-1-yl)benzene **1** and the zinc-catalysed elimination of 1-(2,3-dibromocyclohex-1-en-1-yl)benzene **9** have been used for the synthesis of 1-phenyl-1,2-cyclohexadiene **2**; reaction of **9** with zinc in THF resulted in the formation of two isomeric Wurtz-like condensation products **3** and **4**, but the reaction of **1** with *t*-BuOK gave the allene **2**.

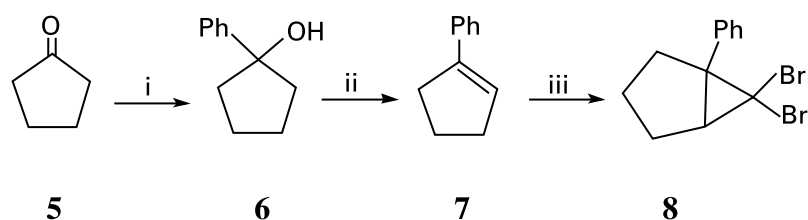
Keywords: 1-phenyl -1, 2-cyclohexadiene, 1-(2-bromocyclohex-2-en-1-yl) benzene, 1-(2,3-dibromocyclohex-1-en-1-yl) benzene, zinc

The first attempts to synthesise strained cyclic allenes were reported by Favorski³. The next pioneering work on strained allenes was carried out by Ball and Landor who successfully synthesised 1,2-cycloheptadiene and 1,2-cyclooctadiene⁴. Both of these readily dimerize and were not isolable. However, Balcı and Jones who isolated optically active cycloadducts by two different routes provided evidence for chirality in 1,2-cyclohexadiene and 1,2-cycloheptadiene⁵. Sütbeyaz has reported the synthesis of an allene unit in six and seven membered rings by fluoride-ion-promoted elimination of β -halogenosilane⁷.

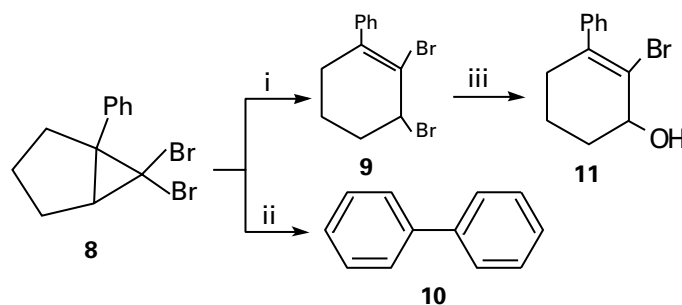
In addition, it is known that the reaction of 2,3-dihalocycloalkenes with zinc can give Wurtz-like condensation products. Previously, Balcı¹⁰ obtained the two Wurtz-like condensation products from the reaction of a dibromo derivative with zinc. Recently, we have reported¹¹ the synthesis of Wurtz-like dimeric products from the treatment of five, six, and seven membered 2,3-dibromocycloalkenes with zinc. In this paper, we have applied zinc-catalysed elimination to the

dibromo compound **9**, and dehydrohalogenation to monobromide **1** for generating allene **2**.

The dibromide **9** was synthesised by our published procedure.¹² We used cyclopentanone **5** as a starting material. Reaction of **5** with phenylmagnesium bromide¹³ followed by dehydration with 4-toluenesulfonic acid (*p*-TsOH) to afford alkene **7**.¹⁴ Dibromocarbene addition^{8,15} to **7** gave the adduct **8** (Scheme 1). The thermal rearrangement¹⁵ of **8** at 150°C and 180°C resulted in the formation of dibromoalkene **9** (74 %) and biphenyl **10** (88 %) as the sole isolable products, respectively. In addition, it was observed that compound **9** was converted into **10** by thermolysis at 180°C. Compound **9** was characterised by spectroscopic methods and chemical transformation. The treatment of **9** with aqueous silver nitrate gave alcohol **11** (Scheme 2). The reaction of **9** with activated zinc in THF at 65°C gave **3** and **4** in a combined yield of 80% instead of the expected allene **2** (Scheme 3). The structures of **3** and **4** were determined on the basis of spectral data. The ¹H- and ¹³C-NMR spectral patterns of **3** and **4** are very similar to each other and indicate that they are stereoisomers. The

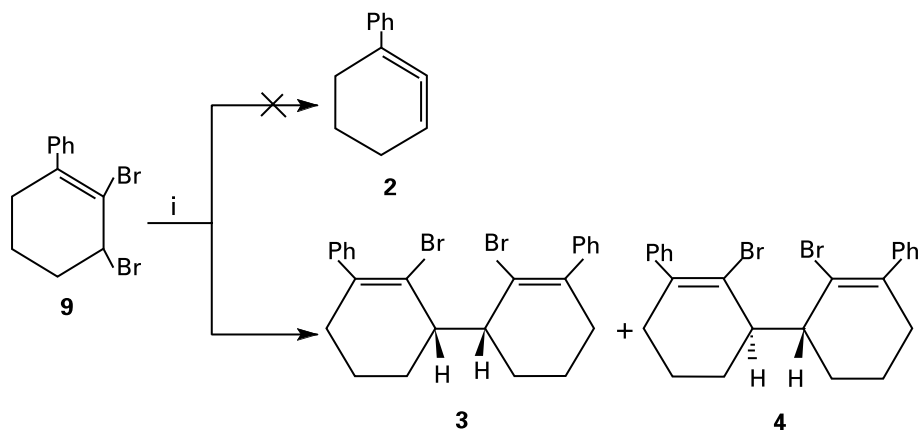


Scheme 1 Reagents and Conditions: (i) PhMgBr, H₂O, THF, (ii) *p*-TsOH, Benzene, (iii) K-*t*-BuO, CHBr₃, *n*-Hexane.

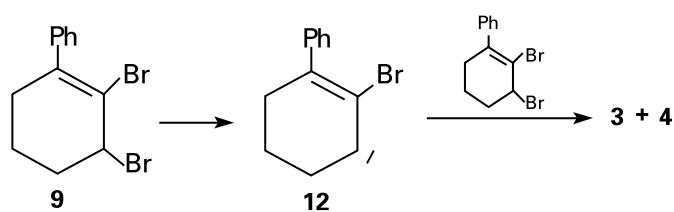


Scheme 2 Reagents and Conditions: (i) 150°C, (ii) 180°C, (iii) Acetone/H₂O(9:1), AgNO₃, 30°C.

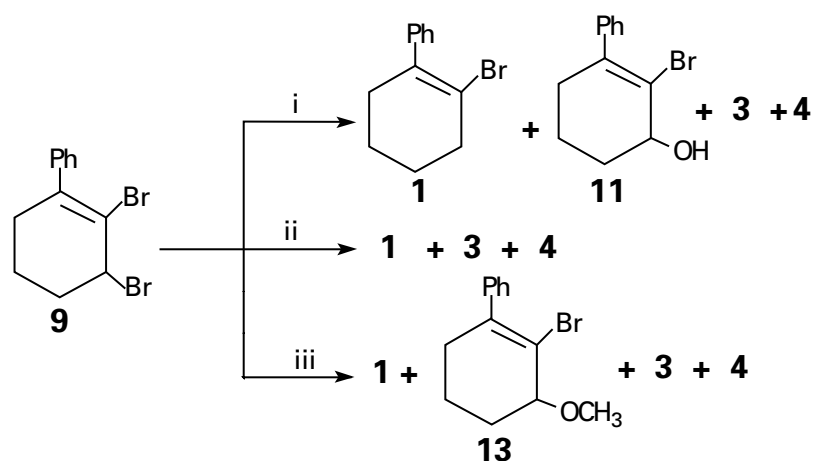
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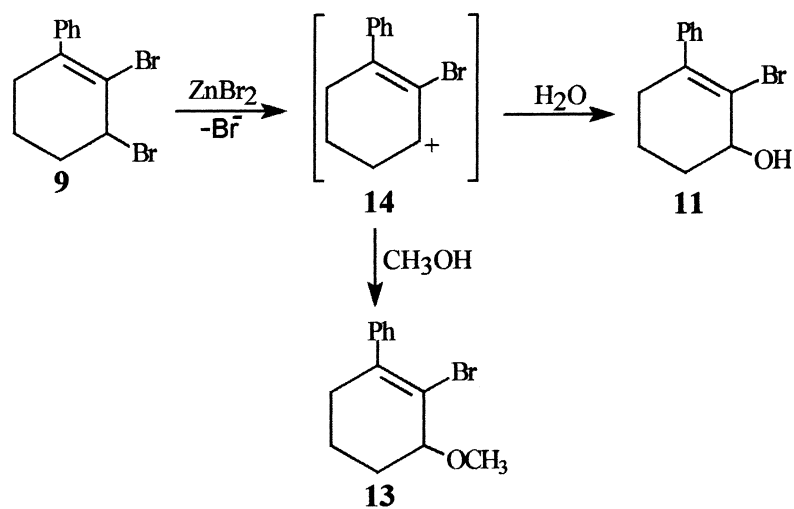
Scheme 3 Reagents and Conditions: (i) Zn , I_2 , 65°C , 16h.



Scheme 4



Scheme 5 Reagent and Conditions: (i) Zn , I_2 , THF, H_2O , 65°C , (ii) Zn , I_2 , THF, CH_3COOH , 65°C , (iii) Zn , I_2 , THF, CH_3OH , 65°C .



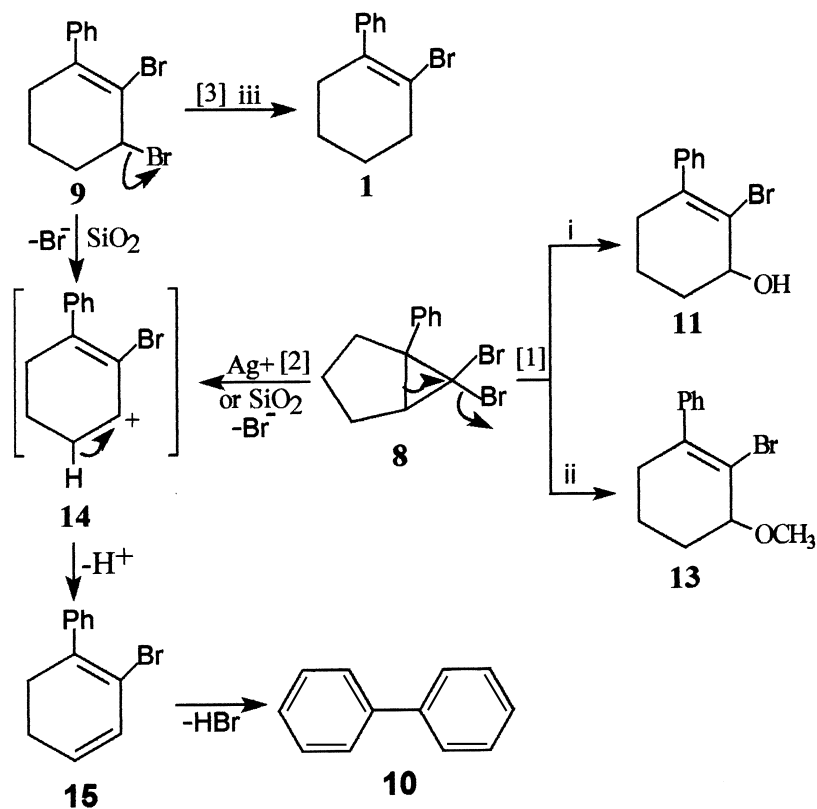
Scheme 6

formation of **3** and **4** can be reasonably explained by the intermediacy of the anion **12** (Scheme 4). The reaction of the dibromide **9** with zinc gave the compounds **1**, **3**, **4** in protic media (H_2O , CH_3OH , $\text{CH}_3\text{CO}_2\text{H}$). In addition, in the presence of H_2O and CH_3OH , the compounds **11** and **13** were obtained besides **1**, **3** and **4** (Scheme 5). Compounds **11** and **13** were characterized by spectroscopic methods and chemical transformation. Silver catalysed rearrangement of **8**¹⁶ in the presence of H_2O and CH_3OH gave the alcohol **11** and the methoxy compound **13**, respectively (Scheme 7 [1]). At the same time, the formation of **11** and secondary product, biphenyl **10**, was observed in the chromatography of **8** and **9** on silica gel, too. Additionally, compound **1** was obtained as a sole product by reduction of the products **9** with LiAlH_4 . Regarding the yield, this reduction is more advantageous than the reduction with zinc (Scheme 7 [3]).¹⁷ In this stage of the study, we aimed to form the intermediate **2** from **1**. The reaction of monobromide **1** with $t\text{-BuOK}$ in the presence of furan and without furan gave the rearrangement products **16** and **10** respectively, via the intermediate allene **2** (Scheme 8). 1-Phenylnaphthalene **16**^{18,19,22} and biphenyl **10**²⁰ were characterised by comparison with literature data. The formation of allene **2** was supported

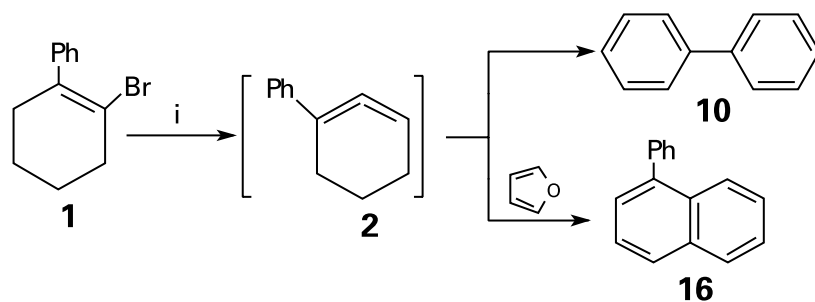
by the work done by Tolbert as shown in Scheme 9. He reported⁸ that the formation of the allene in the reaction of 2-chloro-3-phenylcyclohexene **17** with $t\text{-BuOK}$ at 50°C or in $h\nu$. In both conditions, the adduct products both furan and DBI of allene **2** and biphenyl **10** were isolated and in the absence of trapping reagent (furan or DBI), biphenyl **10** became the major product (Scheme 9). The mechanism of formation of biphenyl **10** and **16** can be explained by the base-catalysed rearrangement of the allene **2** to 1,3-diene **19** and by the rearrangement of adduct **20** to **21**, respectively. Then **19** aromatizes to **10**, and **21** is converted into **16** with aromatization via **22** (Scheme 10). A rearrangement mechanism similar to the latter mechanism has been reported in the literature.²¹ In conclusion, zinc-promoted reaction of **9** did not afford the expected allene **2** or its derivatives. However, we can say that allene **2** forms from the base-catalysed dehydrohalogenation of **1** according to the literature survey and spectroscopic data.^{8,18}

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

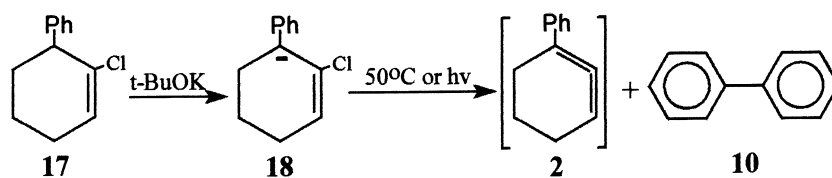
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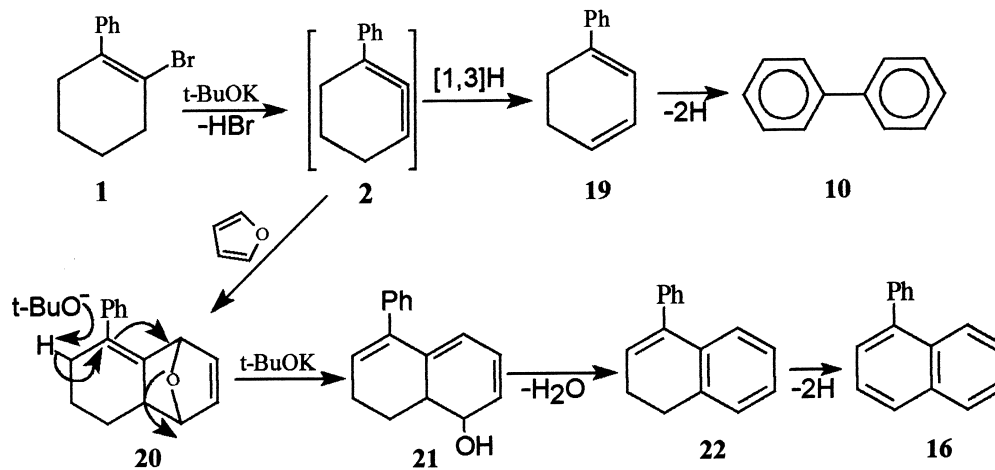
Scheme 7



Scheme 8 Reagents and Conditions: (I) $t\text{-BuOK}$, THF, 65°C .



Scheme 9



Scheme 10

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