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Attempted Synthesis of 1-Cyclohepta-1,2-dien-1-ylbenzene and Wurtz-Like Condensation Products in the Reaction of 1-(2,3-Dibromocyclohept-1-en-1-yl)benzene with Zinc

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7,7-Dibromo-1-phenylbicyclo[4.1.0]heptane **4** was synthesized and its thermal and silver ion-catalyzed rearrangements were studied. Alcohol **8** was converted to 1-(2,3-dibromocyclohept-1-en-1-yl)benzene **6.** The zinc-mediated elimination of 1-(2,3-dibromocyclohept-1-en-1-yl)benzene **6** resulted in the formation of 2 isomeric Wurtz-like condensation products **15** and **16** (whose structural assignments were based on ^{1}H-and ^{13}C-NMR spectral data) instead of the expected 1-cyclohepta-1,2-dien-1-ylbenzene **14**.

Key Words: Substituted strained cyclic allene, dehydrobomination, Wurtz-like condensation, zinc.

Introduction

The chemistry of strained cyclic allenes is of considerable interest for both preparative and theoreticalorganic chemistry.[1−5] Favorski[6,7] reported the first attempts to synthesize strained cyclic allenes. The next work on strained allenes, the generation of cyclohepta-1,2-diene, was carried out by Ball and Landor,[8,9] who employed a dehydrohalogenation route and isolated a [2 + 2] dimer. Further work on cyclohepta-1,2-diene showed that it is too reactive to be isolated or observed spectroscopically.[10] We have reported the synthesis of an allene unit in 6- and 7-membered rings by fluoride ion-promoted elimination of β halogenosilane.[11]

An allene unit in a 6- or 7-membered ring is bent and twisted away from its optimum geometry.[12] Evidence for the chirality of cyclohepta-1,2-diene was provided by Balcı and Jones.[13,14] They treated optically active bromide with potassium *tert*-butoxide and trapped a chiral intermediate presumed to be cyclohepta-1,2-diene.

Since that time, numerous strained cyclic allenes have been described, either as putative reaction intermediates or as isolable substances. In recent years, however, there has been renewed interest in the

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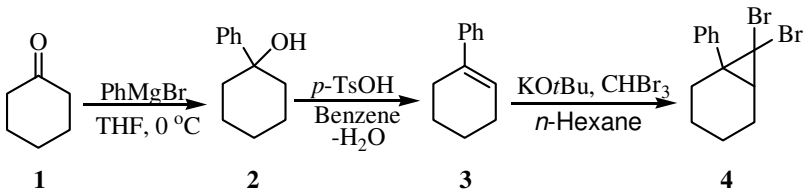
study of the synthesis of strained and substituted cyclic allenes.[15−18] Azizoğlu et al.[19] have reported the formation of methyl substituted bicyclic allene from α-pinene using the Doering-Moore-Skattebol method.

In addition, it is known that the reaction of 2, 3-dihalocycloalkenes with zinc can give allene[20,21] and Wurtz-like condensation products. Previously, Taskesenligil et al.[22] obtained 2 Wurtz-like condensation products from the reaction of 2,3-dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene with zinc. In addition, we have reported[23,24] the synthesis of Wurtz-like dimeric products from the treatment of 5-, 6-, and 7-membered 2,3-dibromocyloalkenes and 1-(2,3-dibromocyclohex-1-en-1-yl)benzene with zinc. In the present study, we applied zinc-mediated elimination to 1-(2,3-dibromocyclohept-1-en-1-yl)benzene, a reaction that resulted in the formation of the Wurtz-like condensation products **15** and **16**.

Results and Discussion

For the synthesis of 1-(2,3-dibromocyclohept-1-en-1-yl)benzene, the key compound for **13**, cyclohexanone **1** was used as the starting material. Bromobenzene was converted to the Grignard reagent,[25] which was condensed with cyclohexanone **1**. Dehydratation[26] of the crude alcohol **2** with 4-toluenesulfonic acid (*p*-TsOH) affords the alkene **3**. Dibromo adduct **4** was prepared by the published procedure.[27]In the published procedure, alkene **3** was not consumed; therefore we used 1 mol of alkene **3** to 2 mol of bromoform. Furthermore, the reaction time was increased to 16 h (Scheme 1).

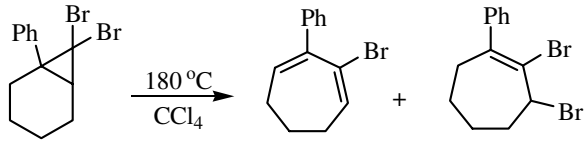


1 **2** **3** **4**

Scheme 1

The structure of **4** was determined by comparison of its published ^{1}H-NMR and elemental analysis data. On the other hand, an 11-line ^{13}C-NMR spectrum is in good agreement with the structure of **4**.

The thermal rearrangement of **4** at 180 °C in CCl_4 resulted in the formation of 1, 3-diene **5** (80%) and dibromo alkene **6** (5%) as the sole isolable products (Scheme 2). The structures of **5** and **8** were determined on the basis of spectral data and the literature.[25,28]

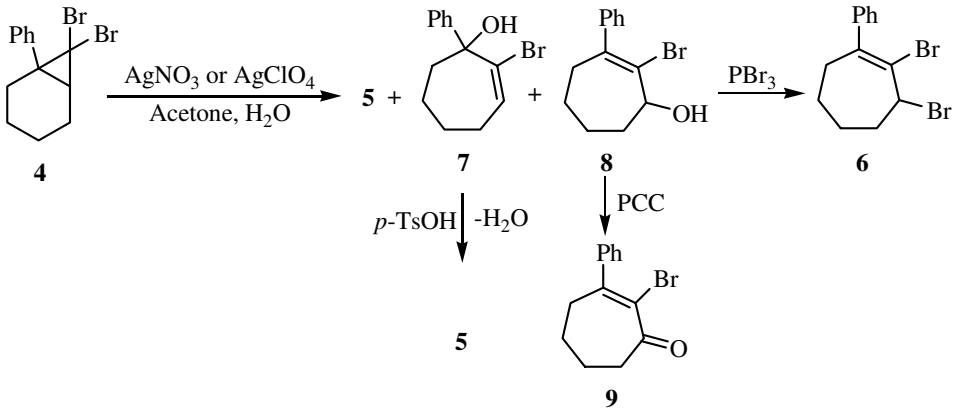


4 **5** **6**

Scheme 2

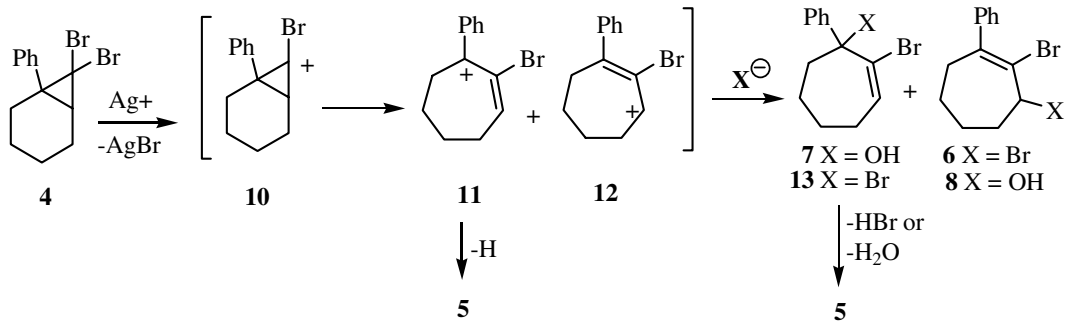
Because the dibromide **6** was obtained in low yield from the above reaction (Scheme 2), we aimed to synthesize **6** by another way. For this, the electrophilic rearrangement of **4** was carried out with silver nitrate[25,29] in aqueous acetone (8:2) at 80 °C for 5 h to give **5**, **7**, and **8** in yields of 2%, 37%, and 42%, respectively. In addition, silver ion-catalyzed rearrangement of **4** was employed with silver

perchlorate under the same conditions to afford the same products, **5**, **7,** and **8,** in different yields (13%, 71%, and 12%, respectively). Compounds **7** and **8** were characterized by spectroscopic methods and chemical transformations. The dehydratation of **7** with *p*-TsOH in benzene gave the bromo 1, 3-diene **5**. Pyridinium chlorochromate (PCC) oxidized **8** smoothly to bromo ketone **9.** In addition, alcohol **8** was converted to the corresponding dibromide **6**, the key compound for 1-cyclohepta-1,2-dien-1-ylbezene **14**, by reaction with PBr_3in benzene (yield 40%) (Scheme 3).



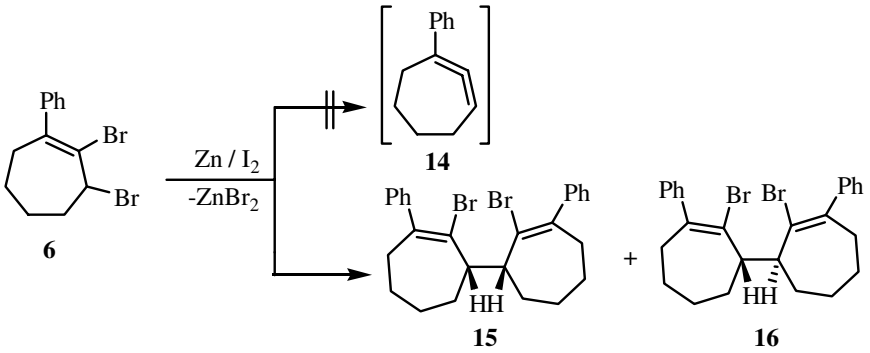
Scheme 3

The formation of **5**, **6,** and **7** can be accounted for as shown in Scheme 4. We assume that the dibromocyclopropane ring in **4** is rearranged with heat and the action of the Ag^+ ion to form allylic cations **11** and **12**. These cations are extracted with H_2O and the Br^- ion. The nucleophilic attack of H_2O and Br^- on allylic cations **11** and **12** yields **7**, **8**, **13,** and **6**. Moreover, removal of the H^+ ion from cation **11** and elimination of HBr and H_2O from **13** and **6** give bromo 1,3-diene **5** (Scheme 4).



Scheme 4

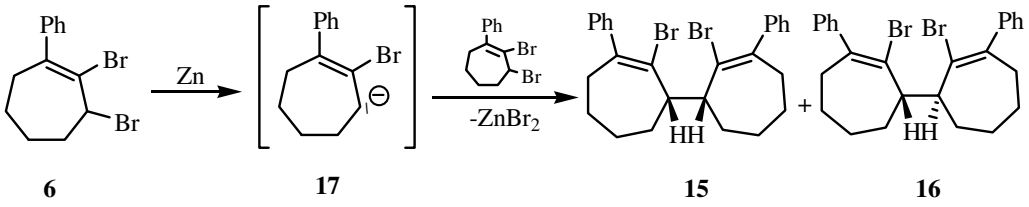
In the present work, we tried to use zinc-mediated elimination to generate the phenyl substituted cyclic allene **14**. The reaction of **6** with zinc in THF at 65 °C gave **15** and **16** in a combined yield of 68% (Scheme 5). The products **15** and **16** were separated with crystallization from *n*-hexane/CH_2Cl_2 (9:1). The same reaction was carried out in the presence of diphenylisobenzofuran (DPIBF) as a trapping reagent, but not even a trace of the expected allene adduct was detected.



Scheme 5

The structures of **15** and **16** were determined on the basis of spectral data. The ^{1}H- and ^{13}C-NMR spectrum patterns of **15** and **16** are very similar to each other, which indicates that they are stereoisomers. The mass spectra of **14** and **15** (M^{+} = 498/500/502) and elemental analysis indicated the existence of 2 bromine atoms. Eleven-line ^{13}C-NMR spectra are in good agreement with the structures of **15** and **16**, which possess a symmetry element. From all these spectroscopic findings, we conclude that **15** and **16** are diastereomers of each other with 2 stereocenters at the attached points of 2 rings. On the basis of the spectral data, we were not able to make a clear-cut differentiation between these diastereomer pairs (DL and meso). For exact assignment of the correct configuration to these isomers, X-ray analysis should be carried out on one of these isomers.

The formation of **15** and **16** can be reasonably explained by the intermediacy of the anion **17**, which is formed by the initial reduction of **6** with zinc. Subsequent displacement of the allylic bromine atom in **6** by the intermediate **17** leads to the Wurtz-type condensation products **15** and **16** (Scheme 6).



Scheme 6

Experimental

^{1}H and ^{13}C NMR spectra were recorded with Varian Mercury 400 (Atatürk University) and Bruker Avance DPX-400 (TÜBİTAK Analysis and Test Laboratory) instruments. As internal standards TMS (δ 0.00) was used for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR spectroscopy. J values are given in Hertz. The multiplicities of the signals in the ^{1}H NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) and combinations thereof. IR spectra were recorded on a Jasco FT/IR-430 spectrometer. Mass spectra were recorded on a Thermofinnigan Trace GC/Trace DSQ / A1300, (E.I Quadrapole, 70 eV) equipped with a SGE-BPX5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm) (Atatürk University). Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer. Melting points were measured on an Electrothermal 9100 apparatus.

All reactions were conducted in anhydrous solvents in an atmosphere of dry nitrogen. All column chromatographies were performed on silica gel (60-230 mesh, Merck) and Al_2O_3-90(70-230 mesh, Merck).

1-Phenylcyclohexanol 2[25]: To a stirred solution of Mg (2.5 g, 0.11 mol) in 100 mL of dry THF at r.t. were added 1 mL of bromobenzene and a small amount of I_2, and the mixture was heated at a bath temperature of 65 °C. To the mixture was added bromobenzene (17 g, 0.11 mol) in 30 mL of THF over 2 h, followed by stirring for 1 h at the same temperature. The mixture was cooled to r.t., cyclohexanone **1** (10 g, 0.1 mol) was added, and it was stirred for 3 h. The mixture was extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with water (300 mL) and dried ($MgSO_4$). Evaporation of the solvent (30 °C, 20 mmHg) gave alcohol **2** (17 g, 95%). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.54-7.50 (m, aromatic, 2H), 7.38-7.31 (m, aromatic, 3H), 1. 92-1.71 (m, 9H), 1. 68-1.63 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 149.7, 128.5, 126.9, 124.8, 73.4, 39.1, 25.8. **IR** (CCl_4) 3580, 3060, 3030, 2931, 2857, 1446, 1056, 1014, 710 cm^{-1}.

1-Cyclohex-1-en-1-ylbenzene 3[26]: To a stirred solution of alcohol **2** (10 g, 57 mmol) in 100 mL of benzene was added 4-toluenesulfonic acid (*p*-TsOH) (50 mg), followed by refluxing for 3 h. The mixture was washed with water (100 mL) and dried ($MgSO_4$). Removal of the solvent and distilling (bp 85 °C, 17 mmHg) gave 1-Cyclohex-1-en-1-ylbenzene **3** (8.5 g, 94%); ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.42-7.38 (m, aromatic, 2H), 7.36-30 (m, aromatic, 2H), 7.26-21 (m, aromatic, 1H), 6.16-6.13 (m, olefinic, 1H), 2.44-2.42 (m, 2H), 2.26-2.21 (m, 2H), 1.84-1.78 (m, 2H), 1.72-1.66 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 142.9, 136.8, 128.4, 126.7, 125.2, 124.9, 27.6, 26.1, 23.3, 22.4. **IR** (CCl_4) 3050, 3030, 2950, 2840, 1620, 1490, 1440, 1310, 1020, 680 cm^{-1}. **Anal. Calcd** for $C_{12}H_{14}$: C 91.08, H 8.92. Found: C 90.98, H 8.88.

7,7-Dibromo-1-phenylbicyclo[4.1.0]heptane 4: To a stirred solution of **3** (8 g, 55.2 mmol), and potassium *t*-butoxide (12.5 g, 110.4 mmol) in 150 mL *n*-hexane was added a solution of $CHBr_3$ (28 g, 111 mmol) in 50 mL of *n*−hexane at 0 °C over 1 h. Stirring was continued overnight at room temperature. The reaction mixture was extracted with n-hexane (3 × 100 mL). The combined organic extracts were washed with water (3 × 100 mL) and dried ($MgSO_4$). Evaporation of the solvent gave **4** (11.2 g, 67 %) as a viscous oil (**4** is solid below 20 °C). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.41-7.34 (m, 2H), 7.32-7.26 (m, 3H), 2.31-2.13 (m, 4H), 1.85-1.77 (m, 1H), 1.63-1.51 (m, 2H), 1.54-1.32 (m, 2H). ^{13}**CNMR** (100 MHz, MHz, $CDCl_3$) 146.5, 128.3, 127.4, 127.1, 47.5, 36.4, 32.3, 31.2, 21.2, 21.1, 20.3. **IR** (CCl_4) 3058, 3023, 2942, 2857, 1600, 1494, 1444, 765, 696, 661 cm^{-1}. **Anal. Calcd** for $C_{13}H_{14}Br_2$: C 47.31, H, 4.28. Found: C 47.29, H, 4.26.

Thermolysis of 4: Solution of **4** (2 g, 6.06 mmol) was heated in a sealed tube at 180 °C for 5 h. To the mixture was added 10 mL of CCl_4 and it was washed with water and $NaHCO_3$ (1%, 20 mL), and dried over $MgSO_4$. The solvent was removed and the residue was chromatographed on a silica gel column, eluting with petroleum-ether (40-60 °C).

The first fraction gave 2-bromo-3-phenyl-cyclohepta-1,3-diene **5** (1.2 g, 80%, colorless liquid). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.46-7.32 (m, 5H), 6.85 (t, J = 7.3 Hz, 1H), 6.54 (t, J = 7.3 Hz, 1H), 2.22-2.16 (m, 4H), 2.09-2.03 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 142.8, 138.9, 138.1, 133.4, 128.4, 127.8, 127.7, 120.4, 37.3, 27.5, 26.6. **IR** (CCl_4) 3058, 3025, 2946, 1612, 1523, 1492, 1446, 696, 655, 572, 547 cm^{-1}. **Anal. Calcd** for $C_{13}H_{13}Br$: C 62.67, H 5.26. Found: C 62.65, H 5.24.

The second fraction gave 1-(2,3-dibromocyclohept-1-ene-1-yl)benzene **6** (0.1 g, 5%, colorless crystals, mp 71-73 °C). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.37−7.31 (m, 3H), 7.27−7.14 (m, 2H) 5.52 ?(t, J = 4.2 Hz, 1H), 2.94 (ddd, A part of AB system, J = 16.4, 10.5, 1.8 Hz, 1H (allylic –CH_2)), 2.66 (ddd, B part of AB

system, J = 16.4, 7.5, 1.8 Hz, 1H (allylic –CH_2)), 2.32-2.27 (m, 2H), 2.25-2.11 (m, 2H); 1.95-1.87 (m, 1H), 1.81-1.71 (m, 1H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 151.22, 147.7, 140.4, 129.1, 128.9, 126.2, 49.1, 34.9, 33.9, 25.2, 25.1. **IR** (liquid) 3058, 3025, 2923, 2854, 1612, 1514, 1476, 1434, 1172, 934, 741, 674, 540 cm^{-1}. **Anal. Calcd** for $C_{13}H_{14}Br$: C 47.31, H 4.28. Found: C 47.30, H 4.25.

Rearrangement of 4 with aqueous silver nitrate: To a solution of $AgNO_3$(5.5 g, 32 mmol) in acetone/water (36 mL, 9:1) was added solution of **4** (10 g, 30 mmol) in 10 mL of acetone. The mixture was refluxed for 24 h. The insoluble materials were separated by filtration, and the mixture was extracted with $CHCl_3$, and dried over $MgSO_4$. After removal of the solvent, the crude product was chromatographed on a silica gel column (70 g), eluting with CH_2Cl_2/petroleum-ether (5:1). The first fraction gave **5** (0.2 g, 3%). The second fraction gave 2-bromo-1-phenylcyclohept-2-en-1-ol **7** (3 g, 37%, yellow oil). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.39-7.37 (m, 2H), 7.27-7.23 (m, 2H), 7.19-7.17 (m, 1H), 6.46 (t, J = 6.7 Hz, 1H), 2.76-2.75 (br. s, and m, -OH and 1H), 2.17-2.07 (m, 3H), 1.65-1.51 (m, 3H), 1.21-1.15 (m, 1H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 144.7, 135.2, 133.3, 128.3, 127.6, 125.8, 81.7, 38.7, 26.4, 24.3, 20.4. **IR** (liquid) 3442, 3058, 3027, 2937, 2861, 1693, 1444, 1029, 700 cm^{-1}. **Anal. Calcd** for $C_{13}H_{15}BrO$: C 58.44, H 5.66. Found: C 58.41, H 5.63.

The third fraction gave 2-bromo-3-phenylcyclohept-2-en-1-ol **8** (3.4 g, 42%, yellow oil). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.28-7.18 (m, 4H), 7.08-7.06 (m, 1H), 4.72 (dd, J = 7.7, 2.2 Hz, 1H), 3.06 (br. s, -OH), 2.69 (ddd, A part of AB system, J = 15.3, 8.8, 2.6 Hz, 1H (allylic –CH_2)), 2.41 (ddd, B part of AB system, J = 15.3, 8.1, 2.6 Hz, 1H (allylic –CH_2)), 2.07-1.88 (m, 3H), 1.81-1.66 (m, 3H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 153.1, 141.9, 139.9, 128.7, 128.3, 126.1, 70.2, 34.2, 32.9, 25.4, 24.2. **IR** (liquid) 3559, 3062, 3027, 2938, 2865, 1602, 1490, 1446, 1024, 980, 790, 694 cm^{-1}. **Anal. Calcd** for $C_{13}H_{15}BrO$: C 58.44, H 5.66. Found: C 58.42, H 5.64.

2-Bromo-3-phenylcyclohepta-1,3-diene 5: To a stirred solution of alcohol **7** (0.4 g, 1.5 mmol) in benzene (10 mL) was added *p*-toluenesulfonic acid (20 mg) and the mixture was refluxed for 3 h. The mixture was washed with water and dried ($MgSO_4$). Removal of the solvent in vacuum gave **5** (0.32 g, 86%).

2-Bromo-3-phenylcyclohept-2-en-1-one 9: To a stirred solution of pyridinium-chlorochromate (PCC) 0.8 g, 3.7 mmol) in 20 mL of CH_2Cl_2 was added the alcohol **8** (1 g, 3.7 mmol) in 5 mL of CH_2Cl_2at 0 °C over 30 min. The mixture was stirred for 3 h at room temperature and then filtered. The organic layer was washed with water (50 mL) and dried (Na_2SO_4). Removal of the solvent gave 2-bromo-3-phenylcyclohept-2-en-1-one **9** (0.8 g, 81%, colorless crystals, mp 81-83 °C). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.42-7.38 (m, 2H), 7.35-7.31 (m, 1H), 7.26-7.24 (m, 2H), 2.81-2.77 (m, 4H), 1.94-1.87 (m, 4H).^{13}**C-NMR** (100 MHz, $CDCl_3$) 199.1, 144.1, 128.6, 128.4, 126.9, 126.9, 123.6, 40.7, 35.8, 24.4, 21.2. **IR** (KBr) 3060, 3029, 2944, 2867, 1716, 1685, 1455, 1442, 1024, 794, 763 cm^{-1}. **Anal. Calcd** for $C_{13}H_{13}BrO$: C 58.89, H 4.94. Found: C 58.87, H 4.91.

1-(2,3-Dibromocyclohept-1-en-1-yl)benzene 6: To a stirred solution of alcohol **8** (2 g, 7.5 mmol) and pyridine (1.18 g, 15 mmol) in 30 mL of benzene was added the solution of PBr_3 (2.5 g, 9.2 mmol) in 15 mL of benzene at 0 °C over 1 h. The reaction mixture was stirred at room temperature for 6 h. The mixture was added to 30 mL of water and the organic layer was extracted with benzene (2 × 30 mL). The combined organic extracts were washed with water (50 mL) and dried ($MgSO_4$). Removal of the solvent gave 1-(2,3-dibromocyclohept-1-en-1-yl)benzene **6** (1 g, 40%).

Reaction of 1-(2,3-Dibromocyclohept-1-en-1-yl)benzene 9 with Zinc: To solution of **9** (0.45

g, 1.4 mmol) in 20 mL of anhydrous THF was added Zn dust (0.1 g, 1.6 mmol) and a small amount of I_2. The reaction mixture was heated at a bath temperature of 65 °C for 16 h. After the mixture was cooled to r.t., the insoluble materials were separated by filtration. The solvent was removed, and the residue was crystallized from *n*-hexane/CH_2Cl_2 (9:1), and **15** and **16** were separated in a ratio of 6:5 (220 mg, combined yield 68%). One of the products is white needles, solid (**15** or **16**) (mp 250-253 °C). ^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.31-7.23 (m, 6H), 7.14-7.7.09 (m, 4H), 3.89 (m, 2H), 2.83-2.75 (m, 2H), 2.41-2.36 (m, 2H), 2.07-1.95 (m, 4H), 1.94-1.81 (m, 6H), 1.66-1.56 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 152.4, 144.7, 141.6, 128.8, 128.1, 125.9, 39.2, 34.8, 27.9, 25.4, 24.6. **IR** (KBr) 3060, 3027, 2925, 2860, 1600, 1590, 1492, 1452, 780, 720, 698, 539 cm^{-1}. **MS** *m/z* (relative intensity): 498/500/502 (M^+, 1), 342.5 (4), 341.4 (28), 340.4 (100), 298.4 (8), 297.3 (22), 283.3 (48), 241.2 (56), 229.2 (68), 215.2 (65), 179.2 (47), 178.2 (50), 165.1 (51). 91.2 (38), 77.1 (11). **Anal. Calcd** for $C_{26}H_{28}Br_2$: C 62.42, H 5.64. Found: C 62.40, H 5.62.

The other product is white needles, solid (**15** or **16**) (mp 156-159 °C).^{1}**H-NMR** (400 MHz, $CDCl_3$) 7.36-7.7.27 (m, 6H), 7.15-7.12 (m, 4H), 3.76 (m, 2H), 2.83-2.75 (m, 2H), 2.47-2.42 (m, 2H), 2.07-2.06 (m, 4H), 1.88-1.81 (m, 2H), 1.76-1.69 (m, 2H); 1.66-1.47 (m, 4H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 152.6, 143.4, 140.8, 129.1, 128.4, 126.1, 41.9, 34.2, 28.9, 25.9, 23.9. **IR** (KBr) 3054, 3055, 2927, 2855, 1664, 1598, 1494, 1450, 748, 741, 694, 524 cm^{-1}. **MS** *m/z* (relative intensity): 498/500/502 (M^+, 1), 342.5 (4), 341.4 (28), 340.4 (100), 298.4 (8), 297.4 (21), 283.2 (45), 241.3 (55), 229.2 (68), 215.2 (65), 179.2 (47), 178.2 (50), 165.1 (53). 91.2 (39), 77.1 (14). **Anal. Calcd** for $C_{26}H_{28}Br_2$: C 62.42, H 5.64. Found: C 62.41, H 5.61.

Conclusion

Consequently, while the thermal rearrangement of **4** at 160 °C gave the 1,3-diene **5** and dibromide **6**, the silver ion-catalyzed rearrangement of **4** afforded the 1,3-diene **5** and alcohols **7** and **8**. Alcohol **8** was converted to the dibromide **6** by the reaction of PBr_3. Zinc-mediated reaction of **6** resulted in the formation of 2 Wurtz-like condensation products (**15** and **16**) instead of the expected allene **14** and its derivatives.

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