SHORT PAPER

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Attempted synthesis of 1-pheny-1, 2-cyclohexadiene and Wurtz-like condensation products in the reaction of 1-(2,3-dibromocyclohex-1-en-1-yl) benzene with zinc

Mustafa Ceylan* and Yakup Budak

Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpaşa University, 60250 Tokat, Türkïye

The thermal rearrangement of **8** at 150 °C and 180 °C gave **9** and **10**, respectively. The reaction of 1-(2,3-dibromocyclohex-1-en-1-yl)benzene 9 with activated zinc gave Wurtz-like dimeric products **3** and **4** instead of expected allene **2**.

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

The chemistry of strained cyclic allenes is of considerable interest both for preparative[1] and theoretical[2] organic chemistry. The first attempts to synthesise strained cyclic allenes were reported by Favorski.[3] The next pioneering work on strained allenes was carried out by Ball and Landor who successfully synthesised 1,2-cycloheptadiene and 1,2-cyclooctadiene.[4] Both of these readily dimerise 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-cycloheptadiene.[5] Since this time, numerous strained cyclic allenes have been described, either as putative reaction intermediates or isolable substances.[6] Recently, we have reported the synthesis of an allene unit in six and seven membered rings by fluroide ion-promoted elimination of β-halogenosilane.[7]

During the last years, however, there has been renewed interest in the study of synthesis of substituted cyclic allenes. Tolbert,[8] accomplished the synthesis of 1-phenyl-1,2-cyclohexadiene 2 *via* photo elimination from 1-chloro-2-phenylcyclohexene. The zinc-catalysed elimination is one of the methods used for the synthesis of cyclic allenes.[9]

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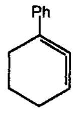

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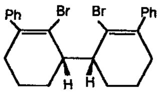

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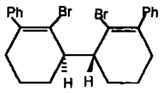

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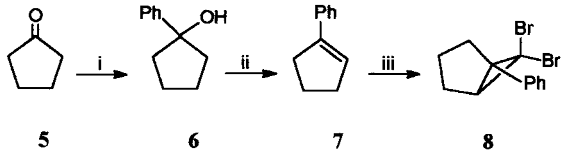
In addition, it is known that the reaction of 2,3-dihalocycloalkenes with zinc can give Wurtz-like condensation products. Previously, Balcı,[10] obtained the two Wurtz-like condensation products from the reaction of 2,3-dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene with zinc. Recently, we have reported[11] synthesis of Wurtz-like dimeric products from the treatment of five, six and seven membered 2,3-dibromocyloalkenes with zinc. In this paper, we have applied zinc-catalysed elimination to the dibromo compound **9** a reaction which resulted in the formation of the Wurtz-like products **3** and **4**.

By our approach, we envisaged that zinc mediated elimination from **9** could give allene **2**. To synthesise **9** we used cyclopentanone **5** as a starting material. Reaction of **5** with phenyl-magnesium bromide[12] followed by dehydration[12] with 4-toluenesulfonic acid (*p*-TsOH) to afford alkene **7**. Dibromocarbene addition[13] to **7** gave the adduct product **8** (Scheme 1).



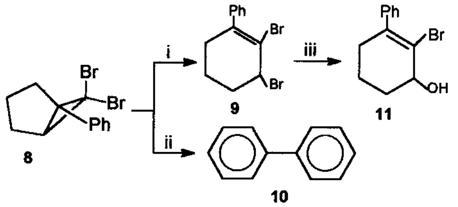
Scheme 1 *Regents and conditions:* (i) PhmgBr,H_2O,THF; (ii) *p*-TsOH, benzene; (iii) *t*-BuOK, $CHBr_3$, *n*-Hexane.

The thermal rearrangement[14] 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 to **10** with the thermolysis of **9** 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).

In the present work, we tried to use the zinc mediated elimination method for generating the strained phenyl substituted cyclic allene **2**. The reaction of **9** with activated zinc in the THF at 65 °C gave **3** and **4** in a combined yield of 80%. Not even a trace of the expected allene **2** was detected in this reaction (Scheme 3).

The structures of **3** and **4** were determined on the basis of spectral data. The ^1H- and ^{13}C-NMR Spectral patterns of **3** and **4** are very similar to each other and indicate that they are stereoisomers. On the other hand, a 10 line ^{13}C-NMR spectrum is in good agreement with the structures of **3** and **4**, which posses a symmetry element. From all of these spectroscopic findings, we conclude that **3** and **4** are diastereoisomers of each other with two stereocenters at the points of attachment of two rings.

The formation of **3** and **4** can be reasonably explained by the intermediacy of the anion **12**, which is formed by the initial



Scheme 2 *Regents and conditions:* (i) 150°C, (ii) 180°C, (iii) acetone/H_2O (9:1), $AgNO_3$, 30°C.

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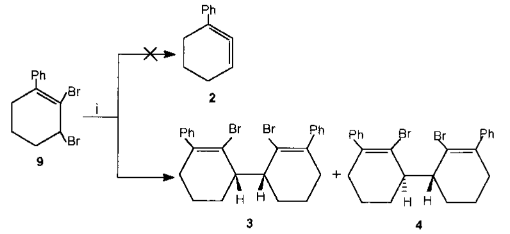
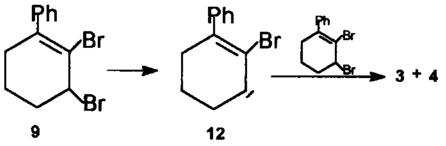
* To receive any correspondence. E-mail: mceylan@gop.edu.tr

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 3 *Reagents and conditions:* (i) Zn, I$_2$, 65°C, 16h.



Scheme 4

reduction of **9** with zinc. Subsequent displacement of the allylic bromine atom in **9** by the formed anion **12** leads to the Wurtz-type condensation products **3** and **4** (Scheme 4).

In conclusion, the thermal rearrangement 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. Zinc-promoted reaction of **9** gave the Wurtz-like dimeric products **3** and **4** instead of the expected allene **2** or some derivatives of **2**.

Experimental

6,6-Dibromo-1-phenyl bicyclo [3.1.0] hexane **8**: To a stirred solution of 7 (4g, 27.6 mmol), and potassium *t*-butoxide (6.33 g, 55.6 mmol) in 50 ml *n*-hexane was added to a solution of CHBr$_3$ (14.0 g, 55.6 mmol) in 50 ml *n*-hexane at 0°C for 1h. 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 **8** (5.6g, 67%) as a colourless liquid. ^{1}H-NMR (200 MHz, CDCl$_3$) δ = 7.25 (m, 5H), 2.62 (t, 2H), 2.43 (m, 2H) 2.25 (m, 2H), 1.86 (1H). ^{13}C-NMR (50 MHz, MHz, CDCl$_3$) δ = 143.21, 131.52 (2C), 129.25, 114.12 (2C), 51.92, 45.23, 40.04, 32.52, 28.32, 26.84.

1-(2,3-Dibromocyclohex-1-en-1-yl) benzene **9**: Compound **8** (1.17 g, 3.69 mmol) was heated at 150°C for 3h. The crude product, filtered through a short silica gel column with CCl$_4$. Evaporation of the solvent gave **9** (0.9g, 74%) as a colourless liquid (^{1}H-NMR (200 MHz, CDCl$_3$) δ = 7.32 (m, 5H), 5.04 (m, 1H), 2.58 (m, 2H), 2.32 (m, 2H), 1.91 (m, 2H). ^{13}C-NMR (50 MHz, CDC1$_3$) δ = 144.27, 144.07, 130.16 (2C), 129.66, 129.40 (2C), 127.82, 58.04, 36.05, 35.88, 20.18 IR (liquid) 3050, 3020, 2950, 1634, 1490, 1440, 1186, 950, 755, 694, 540. Anal calc. for C12H12Br2 (316.0348) C, 45.60; H, 3.82. Found: C, 45.53; H, 3.64.

Biphenyl **10**: Compound **8** (0.2g, 0.63 mmol) was heated at 180°C for 3h. The crude product, filtered through a short silica gel column with CCl$_4$. Removal of the solvent gave **10** (0.085g, 85%) as a white needles solid (m.p. 68–71°C; Lit. m.p. 70°C) ^{1}H-NMR (200 MHz, CDCl$_3$) δ = 7.72 (m, 4H), 7.54 (m, 6H). ^{13}C-NMR (50 MHz, CDCl$_3$) δ = 143.36, 130.89, 129.37, 129.28.

2-Bromo-3-phenylcyclohex-2-en-1-o1 **11**: To a solution of **9** (0.3g, 0.95 mmol) in 5 ml acetone was added solution of AgNo$_3$ (0.16g, 0.95 mmol) in 5 ml acetone/H$_2$O (9:1). The mixture was stirred at 30°C for 0.5h, filtered, and dried (MgSO$_4$). Removal of the solvent gave **11** (0.17g, 70%) as a colourless oil. ^{1}H-NMR (200 MHz, CDCl$_3$) δ = 7.35 (m, 5H), 4.44 (m, 1H), 2.45 (m, 3H), 2.00 (m, 2H), 1.72 (m, 2H) ^{13}C-NMR (50 MHz, CDCl$_3$) δ = 1.44.28, 143.68, 130.22 (2C), 129,63 (2C), 129.47, 127.91, 73.46, 36.53, 33.76, 20.59. IR (liquid), 3560, 3053, 3021, 2938, 2868, 1602, 1486, 1442, 1071, 1060, 980, 790, 694.

Reaction of 1-(2,3-dibromocyclohex-1-en-1-yl) benzene **9** *with zinc:* To a solution of **9** (0.3g, 0.9mmol) in 15 ml of anhydrous THF was added Zn dust (0.08g, 0.9mmol) and a small amount of I$_2$. The reaction mixture was heated at a bath temperature of 65°C for 16h. 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$_2$Cl$_2$ (9:1), and **3** and **4** were separated in the ratio of 1:1 (180 mg, combined yield 80%). One of the products is white needles solid (**3** or **4**) (m.p. 188–189°C). ^{1}H-NMR (200 MHz, CDCl$_3$) δ = 7.33 (m, 10H), 3.43 (m, 2H), 2.42, (m, 4H), 1.98 (m, 4H), 1.76 (m, 4H). ^{13}C-NMR (50 MHz, CDCl$_3$) δ = 146.09 (2C), 143.73 (2C), 130.19 (4C), 129.05 (2C), 127.00 (2C), 48.14 (2C), 36.92 (2C), 26.89 (2C), 24.11 (2C). IR (KBr) 3025, 2930, 2860, 1680, 1630, 1590, 1480, 1440, 780, 720, 690, 535. Anal calc. for C$_{24}$H$_{24}$Br$_2$ (472.25) C, 61.03; H, 5.12. Found: C, 60.92; H, 4.98.

The other product is colourless liquid (**3** or **4**) 1H-NMR (200 MHz, CDCl$_3$) δ = 7.35 (m, 10H), 3,24 (m, 2H), 2.43 (m, 4H), 2.12–1.77 (m, 8H). ^{13}C-NMR (50 MHz, CDCl$_3$) δ = 146.32 (2C), 142.33 (2C), 130.14 (4C), 129.84 (4C), 128.89 (2C), 49.68 (2C), 36.67 (2C), 31.37 (2C), 24.33 (2C). IR (liquid) 3021, 2955, 1685, 1634, 1595, 1480, 1442, 789, 722, 694, 534. Anal calc. for C$_{24}$H$_{24}$Br$_2$ (472.25) C, 61.03; H, 5.12. Found C, 60.94; H, 4.96.

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