REACTION OF 1-PHENYLCYCLOOCTENE WITH NBS. SYNTHESIS OF ALLYLIC ALCOHOLS AND 1,3-DIENES

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Abstract

Reaction of 1-phenylcyclooctene (**3**) with NBS resulted in the formation of a mixture of products (**4-8**). After column chromatography, we isolated the vinyl bromide **14** and 1,3-dienes **9**, **10**, bromo-1, 3-dienes **11**, **12** and allylic alcohol **15**. Reaction of the mixture (**4-8**) with $AgClO_4$ afforded compounds **9**, **14**, **15** and α,β-unsaturated ketones **21** and **22**.

Introduction

The unique symmetry of eight-membered rings and their intriguing conformational properties have attracted much theoritecal interest over years. The synthesis of compounds containing ring of this size has been a long-standing problem because of difficulties stemming from the high degree of ring strain and transannular interactions.[1]

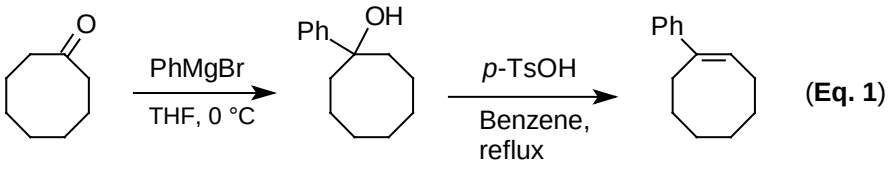
In recent years, interest has grown considerably in the synthesis of eight-membered rings.[2-4] In addition, the discovery of more than 100 cyclooctanoid-based sesqui-, di-, and sesterterpenes have spurred extensive activity in the total synthesis of this class of natural products.[1]

However, neither of these endeavours have provided the occasion for scrutinizing the degree to which an eight-membered ring can be functionalized without postering one or another unwanted transannular process. Paquette has reported[4] that the derivation of cyclooctene gave the polybrominated products. In the present work, we investigated the reaction of 1-phenylcyclooctene (**3**) with NBS.

Results and discussion

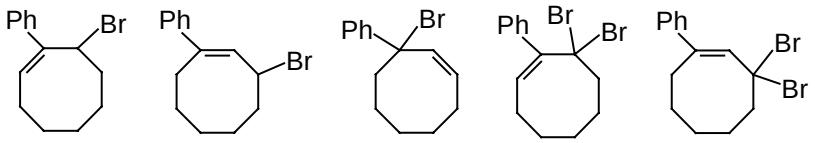
In the present work we investigated the reaction of 1-phenylcyclooctene (**3**) with *N*-bromosuccunimide (NBS). Compound **3** was synthesized by the procedure described in literature.[5] We used cyclooctanone (**1**) as a starting material. The reaction of **3** with

phenylmagnesium bromide was followed by dehydration with 4-toluenesulfonic acid (*p*-TsOH) resulted in cycloocten-1-ylbenzene (**3**) in good yield (Eq. 1).



1 **2** **3** (**Eq. 1**)

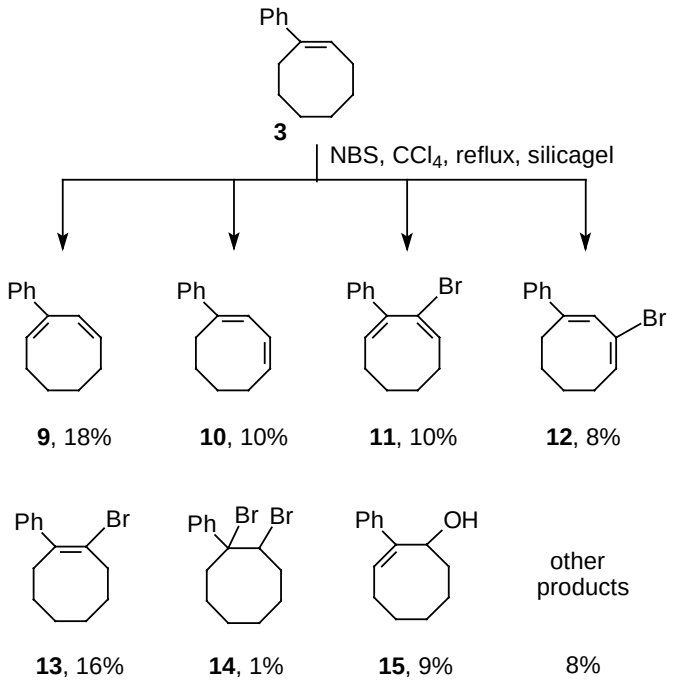
The reaction of **3** with 1 equivalent of NBS was carried out in CCl_4 at 65 °C. Examination of the reaction mixture by ^{1}H NMR spectroscopy revealed that many different compounds were indeed present in the reaction mixture. We determined that the five compounds were the allylic bromides **4**-**8**, which are expected compounds, shown in Figure 1. Confirmation of the proposed structure for compounds **4**-**8** comes from the ^{13}C NMR study of the products (C-Br Shifts: δ 62.84, 62.50, 55.79, 51.22, 50.51 ppm). Additionally, from the proton NMR studies it was determined that the compounds **4** and **5** were the main products. Purification of the reaction mixture by column chromatography on silica gel did not lead to the isolation of these compounds.



4 **5** **6** **7** **8**

Figure 1

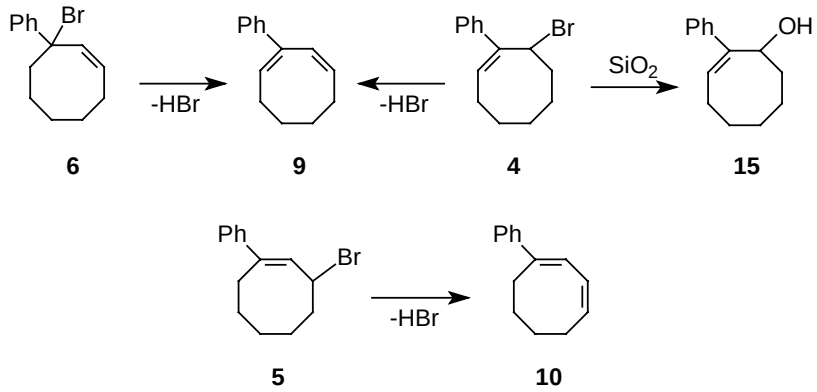
Instead, after repeated column chromatography, we isolated compounds **9**-**13** and **15**. These products were presumably formed from compounds **4**-**8** on silica gel during the chromatographic seperation (Scheme 1). The compounds **4**-**8** are moisture and heat sensitive and easily liberate bromine atom, and convert into the corresponding alcohols **15** and alkenes **9**-**12** on column material. In addition, the alkenes **9**-**12** can also be formed in the reaction medium. In Scheme 1 we also indicated that small amounts of saturated dibromide **14** were formed. The structure of **14** was elucidated from the NMR spectra and it was not isolated in a pure form since during the chromatographic separation **14** eluted together with the unreacted **3**.



Scheme 1

The structures of the isolated products (**9**-**13**, **15**) have been elucidated on the basis of NMR data and the chemical transformations. IR analysis showed that a hydroxyl group was incorporated into compound **15**. Therefore, we assume that this product was formed by a partial hydrolysis of compound **4**. Compound **4** contains allylic bromine atom which can be easily hydrolized on column material to the corresponding alcohol **15** (Scheme 2). Similar rearrangements have been reported in the literature.[5-7]

Alcohol **15** was distinguished easily. The proton NMR spectrum of **15** showed the olefinic proton at δ 5.63 ppm, which arises as a triplet (J = 8.5 Hz) and a proton (*H*C-OH) at δ 4.85 ppm as a doublet of doublet (J = 4.93 and 11.19 Hz). Additionally, the carbon NMR spectrum of **15** showed 12 resonances (C-OH shift: 70.45 ppm). All these findings are in good agreement with the structure of **15**. Additionally, two products were obtained in 8% yield, which can not be identified clearly. We speculated that these products may be similar to 1-hydroxy-3-phenylcycloocta-2-ene according to the NMR studies (^{13}C Shifts:(C-OH), δ 77.03 and 75.83)).

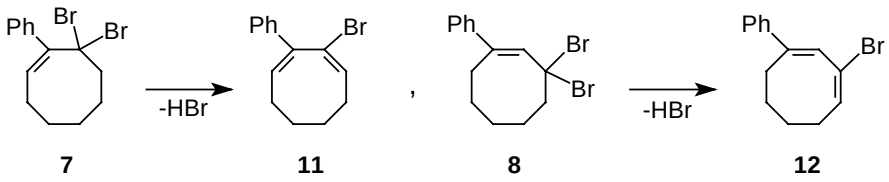


Scheme 2

2-Phenyl-1,3-cyclooctadiene (**9**) was one of the major products. The formation of **9** can be explained by the elimination of HBr from the allylic bromides **4** and **6** in the reaction medium or during the chromatography. The other 1,3-diene **10** can be formed from **5** in a similar way (Scheme 2).

The structures of **9** and **10** were determined on the basis of spectral data. The ^{1}H NMR spectra of **9** and **10** showed the olefinic proton (H_1) of **9** at δ 6.03 ppm as a triplet (J = 8.15 Hz.) and of **10** the olefinic proton (H_2) at δ 6.14 as a doublet (J = 7.79 Hz). Furthermore, twelve resonances in ^{13}C NMR spectra for each compound were in a good agreement with the structures of **9** and **10**.

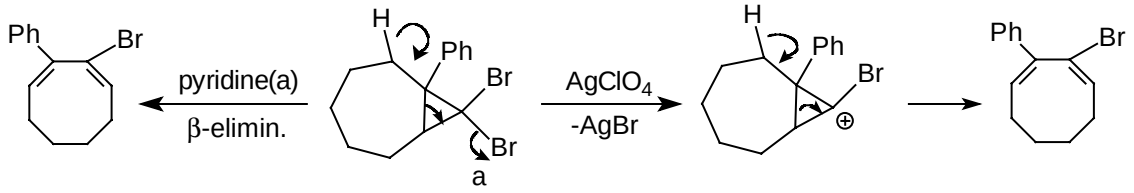
The other 1,3-dienes, **11** and **12** which contain bromine atom, were isolated in 10% and 8% yield, respectively. We assume that the **11** and **12** were formed by the elimination of HBr from the allylic dibromides **7** and **8**, respectively, in the reaction medium or during the chromatography (Scheme 3).



Scheme 3

In addition, **11** was also synthesized by the rearrangement of **16** with pyridine and $AgClO_4$. It was reported[8,9] that the 2-halo-1,3-dienes were obtained by rearrangement of the dihalocarbene adducts with pyridine. For this reason, in two separate experiments

1-phenyl-8,8-dibromobicyclo[5.1.0]octane **16** was reacted with pyridine and $AgClO_4$, respectively. In both cases, **11** was isolated as the sole product and not even a trace of **12** was detected in these reactions (Scheme 4).

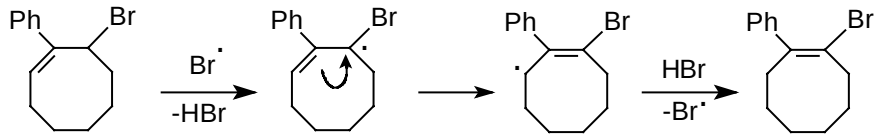


11 **16** **17** **11**

Scheme 4

The compounds **11** and **12** were easily distinguished from the NMR spectra. The proton NMR spectra of **11** and **12** showed the olefinic protons of **11** at δ 6.48 ppm (J = 8.3 Hz) and at δ 6.20 ppm as a triplet (J = 8.28 Hz), and of the **12** at δ 6.41 as a singlet and at δ 6.03 ppm as a triplet (J = 8.25 Hz). Additionally, the carbon NMR spectra showed twelve signals for each compound. All these findings supported the purposed structures of **11** and **12**.

The formation of products **13** and **14** is surprising. The formation of **13** can reasonably be explained by the intermediacy of the radical **18**, which is formed by the abstraction of the α-hydrogen relative to bromine in **4** with bromine radical. The radical **18** converts into radical **19** with π-bond shift. The abstraction of hydrogen of **19** from HBr in the reaction medium leads to the formation of **13** (Scheme 5).

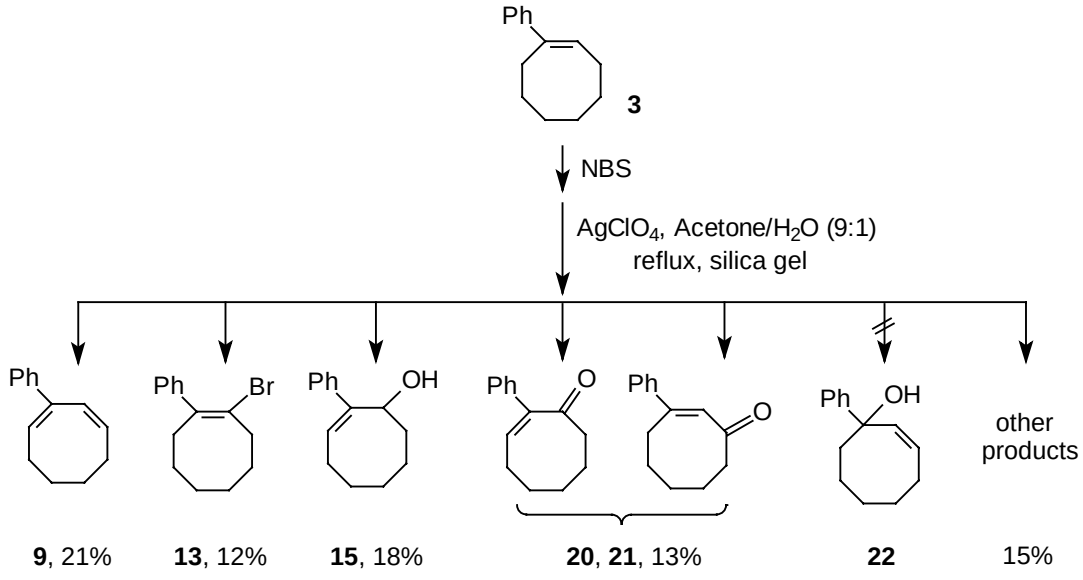


4 **18** **19** **13**

Scheme 5

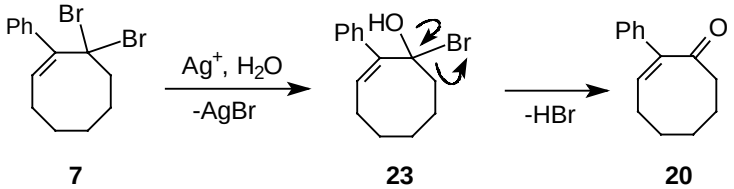
Furthermore, benzylic and allylic bromides give the corresponding alcohols by the hydrolysis in the presence of Ag^+ salts.[10] Additionally, it is known that the geminal dibromides can be converted into the corresponding ketones by hydrolysis with SiO_2[7] and/or Ag^+ salt.

Thus, to further support of the formation of allylic dibromides **4-8**, the mixture of compounds obtained from the reaction of **3** with NBS was let to react with $AgClO_4$. NMR studies have indicated that the resulting reaction mixture was very complex and consisted of at least seven products. However, ^{13}C NMR spectrum showed that the two of them were α,β-unsaturated ketones **20** and **21** (C = O shifts: δ 200.91, 200.66 ppm and C=C shifts: δ 163.35 and 161.46 ppm, characteristic for α,β-unsaturated ketones), one of them was alcohol **15** (C-OH shift: δ 70.45 ppm), and the others were **9** and **13**. This mixture was submitted to silica gel column chromatography. After repeated column chromatography, we isolated compounds **9**, **13**, and **15**. But we could not separate the α,β-unsaturated ketones **20** and **21** as sufficiently pure. Even a trace of the **22** was not detected in this reaction (Scheme 6).



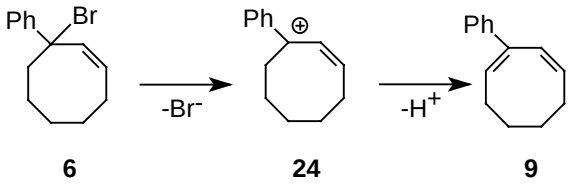
Scheme 6

The formation of **20** and **21** can be explained by the hydrolysis of **7** and **8** in the presence of Ag^+ (Scheme 7).



Scheme 7

As the compound **6** contains both benzylic and allylic bromine atom, we estimated that the cation **24** was easily formed by removal of the bromine atom in **6**. As the cation **24** is very stable, it can easily be converted to 2-phenyl-1,3-cyclooctadiene (**9**) by removal of proton (Scheme 8).



6 **24** **9**

Scheme 8

Conclusions

Five allylic bromides **4-8** were primarily formed in the reaction of **3** with NBS. An attempt to isolate these compounds which are moisture and heat sensitive, led instead to the formation of new compounds **9-12**. The formation of these can be explained by the elimination of HBr from the allylic bromides **4-8**. Compound **15** was formed by the addition OH to the allylic system **4** whereas compounds **20** and **21** were formed by the hydrolysis of **7** and **8** in the presence of Ag^+. In addition, we isolated the vinyl bromide **13** and saturated dibromide **14**. Similar rearrangements have been reported in literature.[11]

Experimental

All solvents were dried and distilled by standard procedures. Compound **18** was synthesized by the literature procedure.[10] Infrared spectra were obtained from films on NaCl plates of solutions (CCl_4) in 0.1 mm cell on a Jasco FT/IR-430 Spectrometer. ^1H and ^{13}C NMR spectra were recorded on 200 (50) MHz Varian and 400 (100) MHz Bruker WP-200 Spectrometers, and we reported δ units with TMS as an internal standard. All column chromatographies were performed on silica gel (60 mesh, Merck). The elemental analyses were carried out on a CHNS-932 (LECO) analyzer.

1-Phenylcyclooctene (3). To a stirred Mg (0.95 g, 39.68 mmol) in 25 mL dry tetrahydrofuran (THF) at room temperature bromobenzene 2 mL and a small amount of I_2 were added. The mixture was treated to a solution of bromobenzene (6.23 g, 39.68 mmol) in THF (15 mL) over 2 h at 65 °C and stirred for 1 h. then it was cooled to room

temperature Cyclooctanone **1** (5 g, 39.68 mmol) was added into this mixture and stirred for 3 h. The resulting mixture was extracted with Et_2O (3×150 mL). The combined organic extracts were washed with water (300 mL), and dried over $MgSO_4$. The evaporation of the solvent (30 °C, 20 mmHg) gave alcohol **2** (7.40 g, 90%). To 50 mL of a stirred solution of **2** (7.49 g, 36.27 mmol) in benzene was added 4-toluenesulfonic acid (*p*-TsOH) (50 mg) and the mixture was refluxed for 3 h. The reaction mixture was washed with water (50 mL) and dried ($MgSO_4$). The solvent was removed and the crude product was filtered through a short silica gel column with *n*-hexane. Evaporation of the solvent gave **3** (4.0 g, 60%) as a colurless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.24 (m, 3H), 5.96 (t, 1H, *J* 8.28 Hz), 2.57 (m, 2H), 2.23 (m, 2H), 1.58 (m, 2H), 1.47 (m, 6H). **^{13}C NMR**, (100 MHz, $CDCl_3$) δ 143.66, 140.73, 128.68 (2C), 128.41, 126.91, 126.25 (2C), 30.50, 29.97, 28.97, 27.93, 27.43, 26.67. **IR** (CCl_4) ν 3072, 3055, 3024, 2925, 2850, 1597, 1493, 1473, 1448, 1355, 1282, 1072, 1022, 937, 898, 843, 764, 696 cm^{-1}. Anal. Calcd for $C_{14}H_{18}$: C 90.26, H 9.74. Found: C 90.30, H 9.76.

Reaction of 1-phenylcyclooctene (3) with NBS. A mixture of **3** (1 g, 5.4 mmol), *N*-bromosuccinimide (0.95 g, 5.40 mmol), AIBN (20 mg), and CCl_4 (20 mL) was heated at reflux for 5 h, cooled, and filtered to remove succinimide. The filtrate was washed with water (20 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure. The residue (1.46 g) was chromatographed on silica gel (60 g) eluted with *n*-hexane. The first fraction: **2-phenyl-1,3-cyclooctadiene (9)**, (180 mg, 18%), colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.22 (m, 2H), 7.14 (m, 1H), 6.03 (t, 1H, *J* 8.15 Hz), 5.94 (d, 1H, *J* 11.3 Hz), 5.88 (dt, 1H, *J* 7.04 and 11.30 Hz), 2.22 (m, 2H), 2.14 (m, 2H), 1.45 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.51, 137.07, 133.98, 129.07, 128.65 (2C), 127.32, 126.99, 126.88 (2C), 28.96, 28.85, 24.63, 22.88. **IR** (CCl_4) ν 3078, 3055, 3005, 2952, 2850, 1497, 1492, 1442, 1077, 1022, 918, 862, 781, 696, 523 cm^{-1} Anal. Calcd for $C_{14}H_{16}$: C 91.25, H 8.75. Found: C 91.22, H 8.77.

The second and third fraction consisted of a mixture of **10**, **11** and **12**. This mixture was chromatographed on silica gel, eluted with hexane. The first: **1-Phenyl-1,3-cyclooctadiene (10)**, (100 mg, 10%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (m, 5H), 6.14 (d, 1H, *J* 7.79 Hz), 5.87 (dd, 1H, *J* 7.52 and 10.88 Hz), 5.66 (dt, 1H, *J* 6.11 and 11.95 Hz), 2.18 (m, 4H), 1.43 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.71, 139.97,

138.11, 138.01, 129.07 (2C), 128.09, 127.68 (2C), 126.37, 30.37, 30.10, 26.33, 24.90. **IR** (CCl_4) ν 3080, 3058, 3015, 2958, 2855, 1499, 1494, 1443, 1079, 1021, 916, 864, 783, 697, 525 cm^{-1}. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.23; H, 8.78. The second: **2-Bromo-3-phenyl-1,3-cyclooctadiene (11),** (140 mg, 10%). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.34 (m, 5H), 6.48 (t, 1H, *J* 8.32 Hz), 6.20 (t, 1H, *J* 8.28 Hz), 2.41 (m, 4H), 1.79 (m, 4H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 140.27, 138.27, 134.39, 130.36 (2C), 130.09, 129.58, 129.05 (2C), 121.76, 31.46, 30.41, 25.38, 24.96. **IR** (CCl_4) ν 3078, 3058, 3024, 2923, 2854, 1598, 1494, 1460, 1444, 1111, 972, 787, 752, 698, 638, 559, 526 cm^{-1}. Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74. Found: C, 63.87; H, 5.76. The third: **2-Bromo-4-phenyl-1,3-cyclooctadiene (12)**, (110 mg, 8%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (m, 5H), 6.41 (s, 1H), 6.01 (t, 1H, *J* 8.25 Hz), 2.63 (m, 2H), 2.18 (m, 2H), 1.55 (m, 4H): **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.95, 135.14, 132.59, 127.95 (2C), 127.31 (2C), 126.05, 125.90, 124.91, 28.16, 27.13, 26.99, 25.60. Anal. Calcd for $C_{14}H_{15}Br$: C 63.89, H 5.74. Found: C 63.88, H 5.74.

The fourth fraction: 1-bromo-2-phenylcyclooctene (**13)**, (230 mg, 16%), colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.14 (m, 1H), 7.10 (m, 2H), 2.74 (t, 2H, *J* 5.99 Hz), 2.45 (t, 2H, *J* 5.67 Hz), 1.67 (m, 2H), 1.54 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.32, 140.34, 128.10 (2C), 128.01 (2C), 126.85, 122.44, 37.85, 34.98, 28.95, 28.49, 26.67, 26.17. **IR** (CCl_4) ν 3080, 3055, 3024, 2923, 2856, 1597, 1493, 1462, 1442, 1110, 792, 762, 692, 611, 542 cm^{-1}. Anal. Calcd for $C_{14}H_{17}Br$: C 63.41, H 6.46. Found: C 63.40, H, 6.43.

The fifth fraction: **2-Phenylcyclooct-2-ene-1-ol (15)**, (95 mg, 9%), pale yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (m, 5H), 5.63 (t, 1H, *J* 8.51 Hz), 4.85 (dd, 1H, *J* 4.93 and 11.19 Hz), 2.12 (m, 2H), 1.97 (m, 2H), 1.60 (m, 4H), 1.32 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.52, 140.55, 130.21, 128.65 (2C), 128.49 (2C), 127.33, 70.45, 39.27, 30.52, 27.65, 27.29, 24.75. **IR** (CCl_4) ν 3444, 3080, 3049, 3024, 2918, 2856, 1683, 1628, 1597, 1493, 1448, 1352, 1285, 1078, 1071, 758, 657 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O$: C 83.12, H 8.97. Found: C 83.14, H, 8.97.

The sixth fraction: **Other products,** (87 mg, 8%), pale yellow viscous oil**.**

8,8-Dibromo-1-phenylbicyclo[5.1.0]octane (16). To 75 mL of a stirred solution of 1-phenylcycloheptene (4.00 g, 23.25 mmol), and potassium *t*-butoxide (6.50 g, 58.00 mmol) in hexane a solution of $CHBr_3$ (14.0 g, 55.0 mmol) in 25 mL hexane at 0 °C for

1 h was added. Stirring was continued overnight at room temperature. The reaction mixture was added to 100 mL of water with ice and extracted with hexane (3×75 mL). The combined extracts were washed with water (3×50 mL) and dried $CaCl_2$. The solvent was removed under reduced pressure and the residue was crystallized from *n*-hexane/CH_2Cl_2 (9:1), and **16** was obtained as a colorless solid (5.60 g, mp 42-45 °C, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (m, 5H), 2.36 (m, 1H), 2.18 (m, 1H), 1.95 (m, 1H), 1.82 (m, 3H), 1.45 (m, 2H), 1.31 (m, 1H), 1.18 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.19, 131.56, 130.10 (2C), 128.97 (2C), 49.65, 44.94, 40.99, 39.52, 33.78, 31.48, 29.96, 27.97. **IR** (KBr) ν 3080, 3055, 3024, 2917, 2886, 1602, 1493, 1454, 1443, 1103, 974, 788, 750, 702, 640, 559, 522 cm^{-1}. Anal. Calcd for $C_{14}H_{16}Br_2$: C 48.87, H 4.69. Found: C 48.88, H 4.67.

Reaction of 16 with pyridine. A mixture of **16** (0.50 g, 1.45 mmol) and pyridine (10 mL) was heated at reflux for 1h, cooled and added to 50 mL of water. The mixture was washed with Et_2O washed with dilute HCl (150 mL, 1%) and water (100 mL), and dried over $CaCl_2$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel, eluted with hexane. Compound **11** was obtained in the yield of 45%.

Reaction of 16 with $AgClO_4$. To 20 mL of a stirred solution of **16** (0.50 g, 1.45 mmol) in acetone/H_2O (9:1) $AgClO_4$ (0.30 g, 1.45 mmol) was added. The mixture was refluxed overnight, filtered and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was chromatographed on silica gel, eluted with hexane. 2-Bromo-3-phenyl-1,3-cyclooctadiene (**11**) was obtained in the yield of 12%. The same reaction was also carried out with dioxane/H_2O at reflux temperature and **12** was obtained in the yield of 25%.

Reaction of 3 with NBS and $AgClO_4$. A mixture of **3** (1 g, 5.4 mmol), *N*-bromosuccinimide (0.95 g, 5.4 mmol), AIBN (20 mg), and CCl_4 (20 mL) was heated at reflux for 5 h, cooled, and filtered to remove succinimide. The filtrate was washed with water (20 mL) and dried over $CaCl_2$. The solvent was removed under reduced pressure. The crude product (1.40 g) was dissolved in acetone/H_2O (40 mL, 9:1), and

added $AgClO_4$ (1.30 g, 6.28 mmol). The mixture was heated at 30 °C for 2 h. The reaction mixture was filtered and dried over $MgSO_4$. After removal of the solvent, the crude product was chromatographed on silica gel column eluted with hexane/$CHCl_3$ (9:1).

The first fraction: **2-Phenyl-1,3-cyclooctadiene (9)**, (210 mg, 21%), colorless liquid. The second fraction: **1-Bromo-2-phenylcyclooctene (13)**, (160 mg, 12%), colorless liquid. The third fraction: **2-Phenylcyclooct-2-ene-1-ol (15)**, (190 mg, 18%), pale yellow viscous oil. The fourth fraction: **Other products**, (160 mg, 15%), pale yellow viscous oil.

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References

1. N. A. Petasis, M. A. Patane, *Tetrahedron* **1992**, *48*, 5757–5821.
2. L. A. Paquette, *Tetrahedron* **1975**, *31*, 2855–2883.
3. G. I. Fray, R. G. Savton, *The Chemistry of Cyclooctatetraene Derivatives*; Cambridge University Press; Cambridge, **1978**.
4. L. A. Paquette, T. J. Watson, D. Friedrich, *J. Org. Chem*. **1993**, *58*, 776–778.
5. (a) M. Ceylan, Y. Budak, *J. Chem. Research (M)* **2002**, *9*, 937-946. (b) M. Ceylan, Y. Budak, *J. Chem. Research (S)* **2002**, *9*, 416–419.
6. A. Daştan, M. Balcı, T. Hökelek, D. Ülkü, O. Büyükgüngör, *Tetrahedron* **1994**, *35*, 10555–10578.
7. A. Daştan, Y. Taşkesenligil, F. Tümer, M. Balcı, *Tetrahedron* **1996**, *52*, 14005–14020.
8. W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kunel, R. M. Dodson, *J. Am. Chem. Soc*. **1965**, *87*, 321–323.
9. W. E. Parham, R. J. Sperley, *J. Org. Chem*., **1967**, *32*, 926–931.
10. M. Ceylan, Y. Budak, *J. Chem. Research (S)* **2001**, *9*, 368–369.
11. J. S. Pizey, *Synthetic Reagents*; Vol. *II*, Chapter 1, Ellis Horwood: Chichester, **1974**.

Povzetek

Reakcija 1-fenilciklooktena (**3**) z NBS je dala zmes produktov (**4**-**8**). S kolonsko kromatografijo smo izolirali vinil bromid **14** in 1,3-diena **9**, **10**, bromo-1,3-diena **11**, **12** in alilni alkohol **15**. Reakcija zmesi **4**-**8** z $AgClO_4$ je dala spojine **9**, **14**, **15** in α,β-nenasičena ketona **21** in **22**.