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Synthesis of 1-Cyclohept-1,2-dien-1-yl Benzene from 1-(2-iodo-, chlorocyclohept-1-en-1-yl)benzene and 1-(2-iodo-, chlorocyclohept-2-en-1-yl)benzene: Its Trapping with Diphenylisobenzofuran

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The key compounds vinyl iodides **12a** and **13a**, for the generation of 1-cyclohept-1,2-dien-1-ylbezene (**1**), were synthesized from cycloheptanone (**5**). Bromobenzene was converted to the Grignard reagent, which was condensed with **5**. Dehydration of alcohol **6** gave alkene **7**. Hydroboration of **7** followed by oxidation with PCC afforded ketone **9**, which was converted to hydrazone **10**. Treatment of **10** with iodine resulted in the formation of **12a** and **13a**. The other precursors, **12b** and **13b,** were synthesized from the reaction of **9** with PCl_5. Reactions of **12a, b** and **13a, b** with KO*t*Bu in a sealed tube at 185 °C gave the [2+4] and [2+2] dimer products **20** and **21**, respectively. In addition, reactions of **12a, b** and **13a, b** with KO*t*Bu under the same conditions in the presence of diphenylbenzoisofuran (DBI) as a trapping reagent afforded the [2+4] cycloadducts **24** and **25** in good yields.

Key Words: Substituted cyclic allene, dehydroiodination, dehydrochloration, dimerization, cycloaddition

Introduction

Strained allenes have provided fruitful ground for a number of theoretical and experimental investigations into the effect of strain on reactivity.[1−4] Favorski[5,6] reported the first attempts to synthesize strained cyclic allenes; however, the pioneering work on strained allenes, the generation of 1,2-cycloheptadiene, was carried out by Ball and Landor[7], who employed a dehydrohalogenation route and isolated the [2+2] dimer. Further work on 1,2-cycloheptadiene showed that it is too reactive to be isolated or observed spectroscopically.[8,9] Evidence for the chirality of 1,2-cycloheptadiene was provided by Balci and Jones,[10] who isolated optically active cycloadducts by 2 different routes. One other approach to 1,2-cycloheptadiene has been the photolysis of vinyl iodide, a reaction reported by Kropp.[11] Jones[12,13] and co-workers have reported the first crystal

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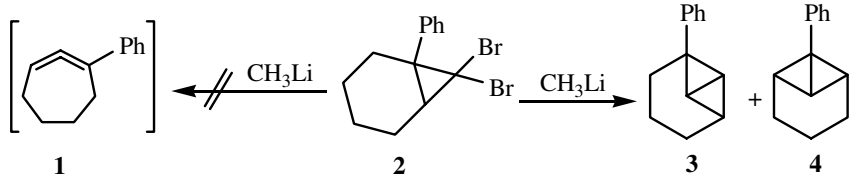
structure of a 1,2-cycloheptadiene-iron complex. Recently, Sütbeyaz et al.[14] reported the synthesis of 1,2-cycloheptadiene via a β-halosilan elimination.

Taylor et al.[15] isolated the methoxy derivative of 1,2-cycloheptadiene as a dimer using the carbenoid method. Christl et al.[16] employed the same method for 7,7-dibromo-1-phenylbicycloheptane (**2**), but they have obtained 2 C-H insertion products (**3** and **4)** instead of the phenyl derivative of 1,2-cycloheptadiene (**1**).

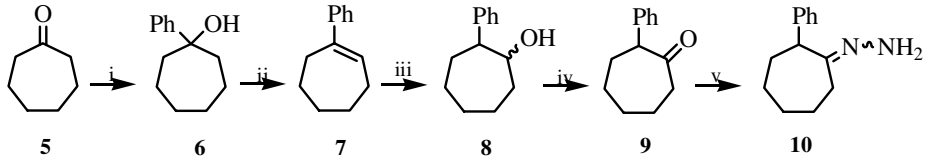


In this paper, we report the synthesis of 1-cyclohept-1,2-dien-1-ylbenzene (**1**) via β-elimination of HI and HCl from 1-(2-iodo-, chlorocyclohept-1-en-1-yl) benzene (**12a, b**) and g-(2-iodo-, chlorocyclohept-2-en-1-yl) benzene (**13a, b**).

Results and Discussion

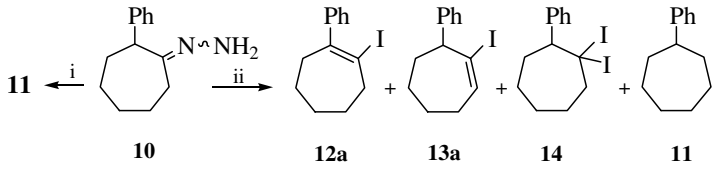
Firstly, for the synthesis of **12a** and **13a**, which are key compounds for the preparation of **1**, cycloheptanone (**5**) was used as the starting material. Bromobenzene was converted to the Grignard reagent,[17] which was condensed with cycloheptanone (**5**). Dehydration[18] of the crude alcohol **6** with *p*-TsOH in benzene gave alkene **7** in 93% yield, and hydroboration[19,20] of **7** gave trans- and cis-alcohol **8** in the ratio of ca. 8:2, followed by oxidation[21] with PCC, which led to ketone **9** in a yield of 97%. Ketone **9** was converted to the hydrazone derivative **10** by treatment with hydrazine hydrate at 90-95 °C (Scheme 1). Product **10** was estimated to be a 2:1 mixture of *E*- and *Z*-isomers. Treatment of this mixture with iodine[22,23] in the presence of NEt_3 in THF, resulted in the formation of 4 products, **12a**, **13a**, **14,** and **11**, in a ratio of 8:9:1:2 (58% total yield), which were separated by silica gel column chromatography (Scheme 2).

Diiodide **14** was converted to **12a** and **13a** in a ratio of 1:1 with a short reaction time at room temperature.



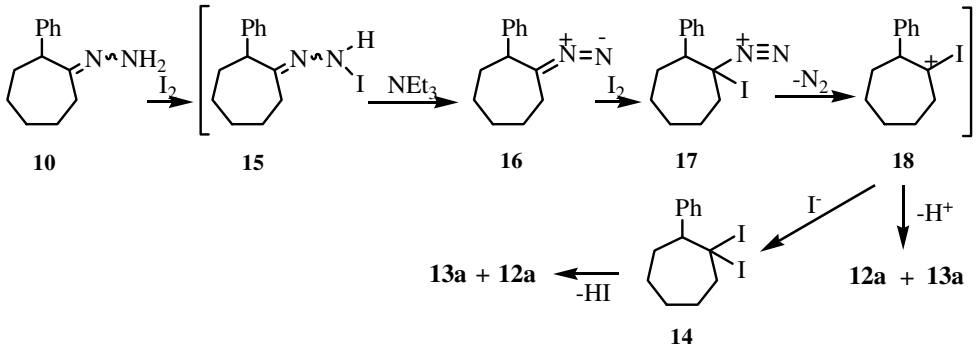
Scheme 1. Reagent and conditions: (i) PhMgBr, THF, 0 °C, 92%, (ii) *p*-TsOH, Benzene, reflux, 93%, (iii) a) $NaBH_4$, BF_3, THF, 0 °C; b) H_2O_2, NaOH, 84%, (iv) PCC, CH_2Cl_2, r.t., 97%, (v) $H_2NNH_2.H_2O$, NEt_3, EtOH, 90-95 °C, 93%.

Compound **11** was characterized by spectroscopic methods and chemical transformation. The treatment of **10** with KO*t*Bu and EtOH in DMSO (Wolf-Kishner reduction) gave compound **11** in a yield of 58% (Scheme 2).



Scheme 2. Reagent and conditions: (i) KO*t*Bu, DMSO, EtOH, 185 °C, 58%, (ii) NEt_3, THF, I_2, 0-25 °C.

The formation of the key compounds **12a** and **13a** can be accounted[22] for as shown in Scheme 3. The hydrazone **10** is oxidized, possibly via the *N*-iodo derivative **15**, to the aliphatic diazo compound **16**. Iodine, acting as an electrophile, converts the diazo compound **16**, possibly via an intermediate iododiazonium compound (**17**), into an iodocarbonium ion (**18**), which then gives the products **14** and **12a**, and **13a** by attack of the iodide ion or elimination of a proton, respectively. The subsequent conversion of the *gem*-diiodide **14** into the vinyl iodides **12a** and **13a** by *β*-elimination of the hydrogen iodide was considered (Scheme 3).

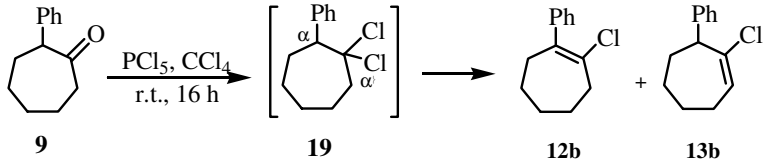


Scheme 3

The structures of **12a** and **13a** were determined on the basis of spectral data and comparison with the literature.[24] The characteristic =CI signals (at 105.26 and 101.69 ppm, respectively) in the ^{13}C-NMR spectra of **12a** and **13a** are in good agreement with the proposed structure of **12** and **13**.

Secondly, **12b** and **13b**, the other precursors of **1**, were synthesized from the reaction of **9** with PCl_5 in CCl_4 at r.t. for 16 h.[25] The mixture of **12b** and **13b** was separated on silica gel column chromatography eluting with *n*-hexane (Scheme 4).

The structures of **12b** and **13b** were determined on the basis of spectral data. In the ^{1}H NMR spectrum of **13b**, the benzylic proton appears as a triplet (J = 2.45 Hz) at 3.95 ppm and the olefinic proton resonates as a triplet (J = 6.36 Hz) at 6.24 ppm. The carbon NMR spectra of these isomers showed 11 lines, which supported the structures.



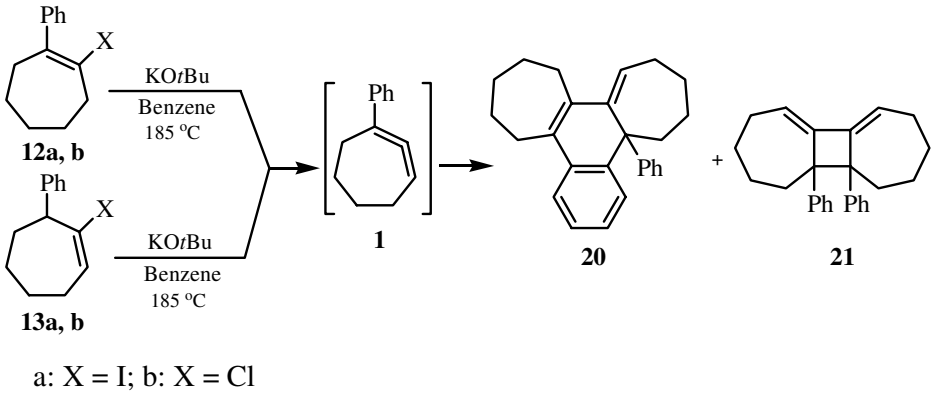
Scheme 4

The formation of **12b** and **13b** can be explained by the formation of *gem*-dichloride (**19**), which converts to the vinyl chlorides **12b** and **13b** by β-elimination of the hydrogen chloride from α and α' position, respectively (Scheme 4).

After the successful synthesis of the key compounds **12a** and **12b,** they were submitted to the base-induced HI and HCl-elimination reaction, separately. The reactions of **12a, b** and **13a, b** with KO*t*Bu in benzene (sealed tube, 185 °C) gave the 2 dimeric products, **20** and **21,** in different yields (Scheme 5, Table 1).

Table 1. Products and yields from the reaction of vinyl halides with KO*t*Bu, without DBI and in the presence of DBI.

Vinyl halides	Products			
	20	**21**	**24**	**25**
12a	52	9	39	8
12b	38	8	48	10
13a	48	8	43	9
13b	35	7	36	8

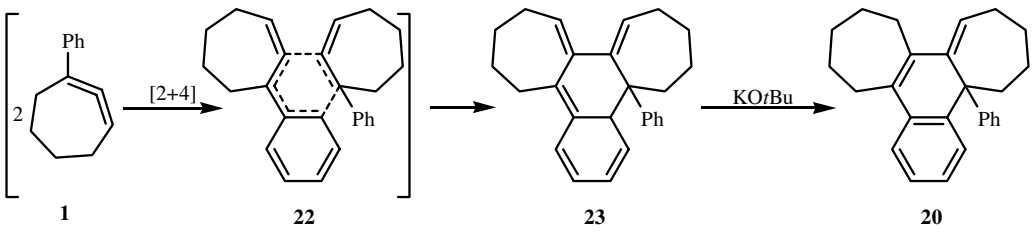


Scheme 5

The mixture was separated on silica gel column chromatography. The elemental analysis and the molecular peak of 340 (M^+) of the products clearly indicated the presence of an allene dimer. The structures of the products were explained on the basis of their NMR data. The observation of only 5 signals in the sp^3 region of the ^{13}C-NMR spectrum of **21** and tail-to-tail dimerization product is evidence of its symmetrical structure.

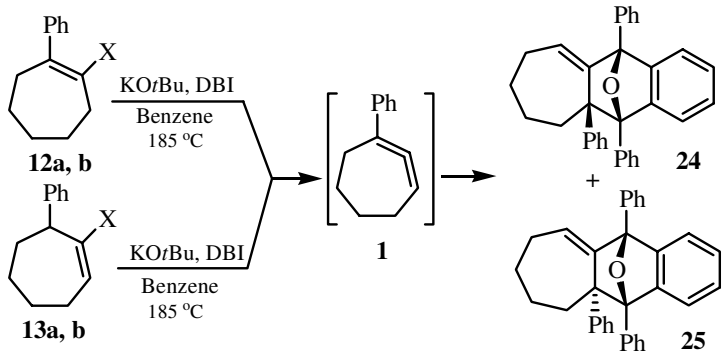
In the ^{1}H-NMR spectrum of the main product (**20**), the olefinic proton signal appears as a doublet of doublet (J = 6.05, 7.88 Hz, 1H) at 6.19-6.16 ppm. The asymmetrical structure of **20** was established by the observation of 24 signals of its ^{13}C-NMR spectrum, as required by the asymmetry in the molecule.

The formation of **20** was accounted for as shown in Scheme 6. Intermediate allene **1** cyclizes via transition state **22,** which is formed by [2+4] synchron addition with participation of a phenyl group and furnishes the methylene-1,3-cyclohexadiene derivative **23**, which is isomerized to yield **20** under the influence of KO*t*Bu (Scheme 6).



Scheme 6

Additionally, we investigated the reaction of **12a, b** and **13a, b** with KO*t*Bu in the presence of 1,3-diphenylisobenzofuran (DBI) as a trapping reagent. Reaction of **12a, b** and **13a, b** with KO*t*Bu in the presence of DBI (in benzene, sealed tube, at 185 °C) afforded the cycloadducts **24** and **25** (in a ratio of 4:1) in good yields (Scheme 7, Table 1). Constitution and configuration of **24** and **25** were established by the typical NMR spectroscopic data in comparison to the DBI adducts of 1,2-cycloheptadiene.[8,14,26] The major product (**24)** was characterized as the *endo* adduct of DBI and 1-cyclohept-1,2-dien-1-ylbenzene (**1**), and the minor product (**25)** was the *exo* adduct (Scheme 7). Formation of the cycloaddition products **24** and **25** can only be explained by the strained allene intermediate (**1)**. Although the intermediate (**1)** has 2 active sides for the cycloaddition reaction, the exclusive formation of **24** and **25** shows that the trapping occurs with a high degree of regioselectivity. All spectral data (elemental analysis, GC-MS, ^{1}H- and ^{13}C-NMR, and IR) are in good agreement with the assumed structures.



Scheme 7

We have demonstrated that the title intermediate (**1**), a strained substituted cyclic allene, can be generated from 1-(2-iodo-, chlorocyclohept-1-en-1-yl) benzene (**12a, b**) and 1-(2-iodo-, chlortocyclohept-2-en-1-yl) benzene (**13a, b**) by β-elimination of HX (HI and HCl) with KO*t*Bu.

Experimental

^{1}H- and ^{13}C-NMR spectra were recorded with Varian 200, Varian Mercury 400, and Bruker AC 400 instruments. TMS (δ 0.00) and $CDCl_3$ (δ 77.00) served as internal standards; Jvalues are given in Hz. The multiplicities of the signals in the ^{1}H-NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and 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. Quadrupole, 70 eV) equipped with an SGE-BPX5 MS capillary column (30 m × 0.25 mm i.d., 0.25

μm). 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. Column chromatography was performed on silica gel (60-230 mesh, Merck) or Al_2O_3-90 (70-230 mesh, Merck).

1-Phenylcycloheptanol 6: To a stirred solution of Mg (3.5 g, 0.15 mol) in 100 mL dry THF at r.t. were added 1 mL of bromobenzene and a small amount of I_2, and the mixture was heated to a bath temperature of 65 °C. To the mixture was added bromobenzene (21 g, 0.13 mol) in 30 mL of THF over 2 h, and stirred for 1 h at the same temperature. The mixture was cooled to r.t. and cycloheptanone (**5)** (15 g, 0.13 mol) was added, followed by stirring 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 **6** (23 g, 92%); ^{1}**H-NMR** (400 MHz, $CDCl_3$) δg.50-7.47 (m, aromatic, 2H), 7.33-7.22 (m, aromatic, 2H), 7.21-7.17 (m, aromatic, 1H), 2.48-2.41 (m, 2H), 2.33-2.13 (brs, -OH, 1H), 2.12-2.03 (m, 2H), 1.92-1.76 (m, 3H), 1.74-1.52 (m, 5H); ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδg1.11, 128.32, 126.65, 124.76, 76.98, 43.42, 29.38, 22.80; **IR** (CCl_4) 3372, 3067, 3027, 2928, 2856, 1598, 1492, 1448, 1106, 1060, 1029, 786, 755, 692 cm^{-1}.

1-Cyclohept-1-en-1-ylbenzene 7: To a stirred solution of crude alcohol (**6)** (20 g, 0.11 mol) in 200 mL of benzene was added 4-toluenesulfonic acid (*p*-TsOH) (50 mg) and the resulting mixture was refluxed for 3 h. The mixture was washed with water (100 mL) and dried ($MgSO_4$). Removing the solvent and distilling (20 mm-Hg, 184 °C) gave 1-cyclohept-1-en-1-ylbenzene **7** (16.8 g, 93%); ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.42-7.22 (m, aromatic, 5H), 6.16-6.13 (t, J = 6.78 Hz, olefinic, 1H), 2.68-2.65 (m, 2H), 2.36-2.32 (m, 2H), 1.95-1.83 (m, 2H), 1.73-1.64 (m, 2H), 1.63-1.59 (m, 2H); ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 145.25, 130.65, 128.38, 127.10, 126.52, 125.93, 33.06 (2C), 29.17, 27.22, 27.10; **IR** (CCl_4) 3056, 3027, 2923, 2848, 1598, 1473, 1442, 1336, 1160, 848, 781, 755, 698 cm^{-1}; **Anal.** Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.48; H, 9.16.

Trans- and *cis*-2-phenylcycloheptanol 8: To a slurry of $NaBH_4$ (3.5 g, 92 mmol) in THF (80 mL) was added alkene **7** (15 g, 87 mmol) in THF (40 mL) at room temperature under N_2. The reaction mixture was cooled to 0 °C and BF_3-OEt_2 (13 g, 92 mmol) was added over 30 min. The resulting mixture was stirred at room temperature for 3 h. Then, NaOH (35 mL, 3 N) and H_2O_2 (53 mL, 35%) were added to the mixture, warmed to 50 °C, and stirred for 30 min. The aqueous layer was extracted with diethyl ether (3 × 150 mL). The combined organic extracts were washed with Na_2SO_3 solution (2%) and dried ($MgSO_4$). Removing the solvent gave the *trans*- and *cis*-2-phenylcycloheptanol **8** in a ratio of ca. 8:2 (colorless liquid, 13.9 g, 84%); ^{1}**H-NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, aromatic, 2H), 7.25-7.17 (m, aromatic, 3H), 3.84-3.75 (m, 1H), 2.59-2.53 (m, 1H), 2.06-1.96 (m, 2H), 1.94-1.84 (m, 1H), 1.83-1.70 (m, 3H), 1.69-1.52 (m, 4H), 1.46-1.37 (m, 1H); ^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 146.08, 129.05, 127.91, 126.85, 77.80, 76.98, 55.64, 37.79, 35.59, 32.34, 28.34, 27.62, 27.04, 22.87, 22.11; **IR** (CCl_4) 3586, 3424, 3081, 3062, 3023, 2927, 2857, 1598, 1448, 1317, 1068, 962, 786, 748, 698 cm^{-1}; **Anal.** Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.01; H, 9.18.

2-Phenylcycloheptanone 9: To a stirred solution of pyridinium-chlorochromate (PCC) (15 g, 70 mmol) in 100 mL of CH_2Cl_2 was added alcohol **8** (13 g, 68 mmol) in 40 mL of CH_2Cl_2 at 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 (100 mL) and dried (Na_2SO_4). Removing the solvent gave 2-phenylcycloheptanone **9** (colorless crystals, mp 56-69 °C, 12.5 g, 97%); ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.32-7.28 (m, aromatic, 2H), 7.24-7.19 (m, aromatic, 3H), 3.74-3.70 (dd, J = 4.03, 11.36 Hz, 1H), 2.71-2.64 (m, 1H), 2.53-2.48 (m, 1H), 2.16-2.09 (m, 1H), 2.06-1.91 (m, 4H), 1.68-1.59 (m, 1H), 1.42-1.38 (m, 2H); ^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 213.52, 140.61, 128.73, 128.11, 127.10, 58.99, 42.89, 32.20, 30.23, 28.77, 25.58; **IR** (KBr) 3062, 3027, 2929, 2857, 1702, 1592, 1492, 1548, 1316, 1160, 1124, 1024, 937, 786, 755, 692 cm^{-1}; **Anal.** Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.64; H, 8.27.

***Syn*- and *anti*-2-phenylcycloheptan-1-one hydrazones 10**: A solution of hydrazine hydrate (12.75 g, 210 mmol) and triethylamine (5.5 g, 53 mmol) was added to a vigorously stirred solution of 2-phenylcycloheptanone (**9)** (10 g, 53 mmol) at room temperature over 3 h. The reaction mixture was stirred at 90-95 °C for 1 h, cooled to room temperature, and extracted with chloroform (3 × 50 ml). The combined extracts were dried with K_2CO_3 and the solvent was evaporated to yield an essentially pure mixture consisting of *syn*- and *anti*-hydrazones (**10)** (colorless liquid, 10 g, 93%). ^{1}**H-NMR** (200 MHz, $CDCl_3$) δ 7.39-7.12 (m, aromatic, 10H), 4.89-4.12 (brs, -NH_2, 4H), 3.87-3.82 (m, 1H), 3.78-3.70 (m, 1H), 2.80-2.47 (m, 5H), 2.26-2.19 (m, 2H), 2.12-2.01 (m, 4H), 1.99-1.82 (m, 5H), 1.79-1.49 (m, 4H);g^{13}**C-NMR** (50 MHz, $CDCl_3$)gδ 169.04, 167.10, 150.02, 144.76, 129.44, 128.72 (2C), 128.67, 128.56 (2C), 128.51, 127.91, 124.94, 124.78, 52.65, 49.44, 47.35, 43.74, 37.12, 37.10, 31.27, 30.23, 29.75, 28.27, 27.54, 24.81; **IR** (CCl_4) 3403, 3378, 3087, 3062, 2923, 2854, 1623, 1598, 1492, 1448, 1068, 1024, 786, 755, 698 cm^{-1}.

Treatment of *syn*- and *anti*-2-phenylcycloheptan-1-one hydrazones (10) with I_2: A saturated solution of iodine (27.5 g, 0.11 mol) in dry THF was added rapidly to a stirred solution of isomeric **10** (10 g, 50 mmol) in 45 mL of triethylamine under a nitrogen atmosphere at 0 °C. The reaction mixture was stirred for an additional 1 h at room temperature. After diluting the reaction mixture with 300 mL of distilled water, it was extracted with hexane (3 × 150 mL). The combined organic layers were washed with HCl (3 × 50 mL, 1N), saturated $NaHCO_3$, a NaCl solution, then dried and evaporated to yield a mixture (9.5 g) consisting of **12a**, **13a**, **14,** and **11**. The residue was submitted to silica gel column chromatography (100 g), eluting with hexane. The first fraction yielded pure phenylcycloheptane (**11**) (colorless liquid, 0.26 g, 3%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.29-7.27 (m, aromatic, 2H), 7.21-7.14 (m, 3H), 2.70-2.63 (pentet, 1H), 1.95-1.89 (m, 2H), 1.85-1.76 (m, 2H), 1.74-1.64 (m, 4H), 1.61-1.51 (m, 4H); ^{13}**C-NMR** (100 MHz, $CDCl_3$) δ 150.25, 128.52, 126.90, 126.72, 47.29, 37.06, 28.19, 27.47; **IR** (CCl_4) 3057, 3025, 2935, 2856, 1492, 1446, 788, 700 cm^{-1}; **Anal.** Calcd for $C_{12}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.36; H, 10.10.

The second fraction was 1,1-diiodo-2-phenylcycloheptane (**14**) (colorless liquid, 1 g, 5%), but this compound (**14)** converted to **12a** and **13a** in the ratio of 1:1 in a short time at room temperature.

The third fraction yielded pure 1-(2-iodocyclohept-1-en-1-yl) benzene (**12a**) (colorless crystals, mp 50-55 °C, 3.4 g, 23%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.39-7.35 (m, aromatic, 2H), 7.32-7.25 (m, aromatic, 3H), 3.13-3.10 (m, 2H), 2.66-2.63 (m, 2H), 2.28-2.20 (m, 2H), 2.01-1.88 (m, 2H), 1.54-1.44 (m, 2H); ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 149.44, 143.93, 128.73, 128.49, 127.50, 105.26, 46.37, 36.32, 31.89, 27.51, 25.71; **IR** (CCl_4) 3077, 3025, 2935, 2850, 1490, 1444, 1247, 1124, 1004, 976, 794, 700 cm^{-1}; **Anal.** Calcd for $C_{13}H_{15}I$: C, 52.37; H, 5.07. Found: C, 52.19; H, 4.98.

Later fractions were a mixture of **12a** and **13a**. The mixture was resubmitted to a silica gel column. The last fraction yielded pure 1-(2-iodocyclohept-2-en-1-yl) benzene (**13a**) (colorless crystals, mp 67 °C,

3.98 g, and 27%). ^{1}**H-NMR** (200 MHz, $CDCl_3$)gδ 7.38-7.36 (m, aromatic, 2H), 7.32-7.29 (m, aromatic, 2H), 7.22-7.19 (m, aromatic, 1H), 6.82-6.78 (dd, J = 5.86, 6.97 Hz, olefinic, 1H), 4.14-4.11 (dd, J= 4.03, 6.96 1H), 2.19-2.13 (m, 4H), 1.73-1.66 (m, 4H), 1.64-1.56 (m, 2H); ^{13}**C-NMR** (50 MHz, $CDCl_3$)gδ 150.26, 143.89, 128.69, 128.54, 126.93, 101.69, 60.59, 34.12, 30.55, 26.25, 24.38; **IR** (CCl_4) 3079, 3054, 3023, 2923, 2850, 1486, 1442, 988, 962, 817, 792, 698 cm^{-1}; **Anal.** Calcd for $C_{13}H_{15}I$: C, 52.37; H, 5.07. Found: C, 52.21; H, 4.97.

Phenylcycloheptane 11: To a solution of **10** (0.2 g, 1 mmol) in DMSO (5 mL) and EtOH (0.5 mL) was added KO*t*Bu (0.5 g, 4 mmol), followed by heating at 185 °C for 14 h. The mixture was extracted with hexane and dried over $MgSO_4$. The solvent was evaporated and the residue submitted to silica gel (10 g) column chromatography, eluting with hexane. Removal of the solvent under reduced pressure gave pure phenylcycloheptane (**11**) (colorless liquid, b.p. 240 °C, 100 mg, 58%).

Reaction of 2-Phenylcycloheptanone (9) with PCl_5: To a stirred solution of **9** (1 g, 5.3 mmol) in 30 mL of CCl_4 at room temperature was added PCl_5 (1.1 g, 5.3 mmol), and the resulting mixture was stirred for 16 h at r.t. Then, the mixture was washed with water (2 × 50 mL) and dried over $MgSO_4$. Concentration in a rotatory evaporator gave the crude product, which was submitted to silica gel column chromatography (40 g) eluting with n-hexane/$CHCl_3$, 9:1. The first fraction yielded pure 1-(2-chlorocyclohept-1-en-1-yl) benzene (**12b**) (colorless liquid, 0.48 g, 44%). ^{1}**H-NMR** (200 MHz, $CDCl_3$)gδ 7.36 (m, 5H), 2.58 (t, 4H; J= 5.31 Hz), 1.90 (m, 4H), 1.64 (m, 2H). ^{13}**C-NMR** (50 MHz, $CDCl_3$) δ 141.94, 130.77, 130.63, 128.80, 128.75, 127.60, 42.28, 41.95, 31.72, 28.92, 26.45. **IR** (liquid): 3062, 3027, 2923, 2848, 1639, 1598, 1494, 1450, 1076, 1022, 916, 782, 748, 701, 408 cm^{-1}; **Anal.** Calcd for ($C_{13}H_{15}Cl$): C, 75.54; H, 7.31. Found: C, 75.44; H, 7.46.

The last fraction yielded pure 1-(2-chlorocyclohept-2-en-1-yl) benzene (**13b**) (colorless liquid, 0.26 g, 24%). ^{1}**H-NMR** (200 MHz, $CDCl_3$) δ 7.26 (m, 5H), 6.24 (t, 1H; J= 6.36), 3.95 (t, 1H; J= 2.45), 2.77 (m, 1H) 2.25 (m, 2H), 2.11 (m, 2H), 1.67 (m, 3H). ^{13}**C-NMR** (50 MHz, $CDCl_3$)gδ 143.18, 132.31, 130.39, 129.98, 129.76, 128.40, 56.60, 35.07, 28.36, 28.23, 25.92. **IR** (liquid): 3062, 2933, 2857, 1724, 1494, 1444, 1315, 1155, 1126, 941, 723, 688, 622, 572, 408 cm^{-1}; **Anal.** Calcd for ($C_{13}H_{15}Cl$): C, 75.54; H, 7.31. Found: C, 75.60; H, 7.64.

Reaction of 12a with KOtBu in benzene: A solution of **12a** (2 g, 6.7 mmol) in 10 mL of dry benzene and KO*t*Bu (0.8 g, 7 mmol) was placed in a glass tube. After sealing the tube, it was heated to 180 °C for 16 h. The solvent was evaporated and the residue was submitted to silica gel (60 g) column chromatography, eluting with hexane. The first fraction was pure 10a,10b-diphenyl-1,2,3,4,7,8,910,10a,10b-decahydro-dicyclobuta[1,2:3,4]dicycloheptene (**21**) (white crystals from hexane, mp 163-167 °C, 105 mg, 9%); ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.47-7.33 (m, aromatic, 5H), 7.32-7.19 (m, aromatic, 5H), 6.21-6.18 (dd, J = 4.76, 8.06 Hz, olefinic, 2H), 2.08-1.95 (m, 2H), 1.93-1.55 (m, 2H), 1.73-1.68 (m, 2H), 1.56-1.49 (m, 2H), 1.34-1.17 (m, 4H), 1.14-1.07 (m, 4H); ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 146.35, 141.95, 129.41, 128.32, 127.25, 120.79, 61.24, 37.53, 28.49, 28.19, 27.68; **IR** (KBr) 3054, 3021, 2923, 2852, 1617, 1595, 1490, 1444, 1248, 817, 727 cm^{-1}; **MS** (70 eV) 340.6 (M^+,3), 272.4 (3), 216.3 (100), 170.2 (44), 141.2 (85), 90.1 (69), 77.1 (31); **Anal.** Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.45; H, 8.33.

The second fraction yielded pure 4b-phenyl-4b,5,6,7,8,10,11,12,13,14-decahydro-dicyclohepta[a, c]naphthalene (**20**) (colorless crystals from hexane, mp 157-159 °C, 590 mg, 52%); ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.63-

7.59 (m, aromatic, 1H), 7.35-7.28 (m, aromatic, 4H), 7.17-7.08 (m, aromatic, 3H), 7.00-6.97 (m, aromatic, 2H), 6.19-6.16 (dd, J = 6.05, 7.88 Hz, olefinic, 1H), 2.69-2.59 (m, 2H), 2.57-2.50 (m, 1H), 2.49-2.46 (m, 2H), 2.42-2.29 (m, 3H); 1.94-1.70 (m, 4H), 1.66-1.52 (m, 3H), 1.49-1.34 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$)gδ 149.41, 144.76, 140.74, 140.32, 137.24, 133.48, 129.57, 128.57, 127.54, 126.94, 126.59, 125.73, 125.38, 123.42, 55.11, 34.83, 33.49, 32.41, 29.02, 26.83, 26.17, 25.47, 24.64, 21.66; **IR** (KBr) 3054, 3021, 2933, 2857, 1617, 1592, 1261, 892, 748, 698 cm^{-1}; **MS** (70 eV) 340.6 (M^+,1), 272.4 (1), 217.3 (18), 216.3 (59), 170.2 (27), 169.2 (100), 141.2 (89), 115.1 (42), 91.0 (68), 77.1 (14); **Anal.** Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.38; H, 8.10.

The above reaction was employed for **13a, 12b,** and **13b**, and the same products, **20** and **21,** were obtained.

Reaction of 12a with KO*t*Bu in the presence of DBI: A solution of **12a** (0.7 g, 2.3 mmol) in 8 mL of dry benzene, KO*t*Bu (0.35 g, 3 mmol), and DBI (0.63 g, 2.3 mmol) were placed in a glass tube. After sealing the tube, it was heated to 180 °C for 16 h. The mixture was extracted with CH_2Cl_2, and dried over $MgSO_4$. Then, the solvent was removed in a vacuum. The residue was submitted to Al_2O_3 (active basic, grade III, 40 g.) column chromatography eluting with hexane/benzene (9:1). The first fraction was the excess of DBI. The second fraction yielded pure *endo* adduct (**24**) (colorless crystals, mp 143-144 °C, 0.41 g, 39%); **^{1}H-NMR** (400 MHz, $CDCl_3$)gδ 8.01-7.99 (m, aromatic, 2H), 7.72-7.68 (m, aromatic, 2H), 7.63-7.57 (m, aromatic, 2H), 7.53-7.48 (m, aromatic, 2H), 7.47-7.42 (m, aromatic, 2H), 7.39-7.36 (m, aromatic, 1H), 7.29-7.17 (m, aromatic, 4H), 6.97 (brs, aromatic, 1H), 6.10-6.06 (dd, J = 4.40, 9.17 Hz, olefinic, 1H), 2.76-2.71 (ddd, J = 2.57, 5.15, 13.65 Hz, 1H), 1.95-1.89 (m, 1H), 1.70-1.66 (m, 1H), 1.60-1.49 (m, 2H), 1.46-1.42 (m, 1H), 1.01-0.92 (dt, J = 2.15, 13.56 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.72, 147.28, 145.93, 139.69, 137.55, 136.69, 129.58, 128.71, 128.05, 127.77, 127.41, 127.23, 127.08, 126.95, 126.27, 125.65, 124.09, 122.07, 118.81, 93.41, 89.27, 61.55, 34.23, 27.29, 26.87, 26.44; **IR** (KBr) 3062, 3025, 2931, 2852, 1596, 1548, 1452, 1442, 1165, 1115, 1020, 995, 792, 754, 698 cm^{-1}; **MS** (70 eV) 440.7 (M^+, 5), 422.8 (3), 331.6 (7), 271.5 (21), 270.4 (66), 252.4 (12), 165.2 (40), 115.1 (28), 105.1 (100), 91.2 (53), 77.1 (66); **Anal.** Calcd for $C_{33}H_{28}O$: C, 89.96; H, 6.41. Found: C, 89.76; H, 6.21.

The third fraction yielded pure *exo* adduct (**25**) (colorless crystals, mp 160-164 °C, 85 mg, 8%); **^{1}H-NMR** (400 MHz, $CDCl_3$)gδ 7.96-7.94, (m, aromatic, 2H), 7.65-7.63 (m, aromatic, 2H), 7.60-7.56 (brt, J= 7.69 Hz, aromatic, 2H), 7.54-7.52 (brd, J = 7.33 Hz, aromatic, 1H), 7.47-7.43 (brt, J = 7.56 Hz, aromatic, 2H), 7.40-7.36 (m, aromatic, 1H), 7.34-7.29 (m, aromatic, 1H), 7.25-7.23 (m, aromatic, 2H), 7.18-7.10 (m, aromatic, 2H), 6.90-6.86 (m, aromatic, 1H), 6.83-6.78 (m, aromatic, 2H), 6.08-6.06 (brd, J = 8.06 Hz, aromatic, 1H), 5.97-5.94 (dd, J = 5.49, 9.16 Hz, olefinic, 1H), 1.93-1.88 (m, 2H), 1.82-1.73 (m, 1H), 1.72-1.65 (m, 1H), 1.63-1.58 (m, 2H), 1.56-1.47 (m, 1H), 1.40-1.35 (m, 1H), 1.20-1.11 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$)gδ 150.46, 146.57, 144.56, 140.09, 137.51, 137.15, 129.44, 128.58, 128.52, 128.02, 127.85, 127.80, 127.51, 127.04, 126.97, 126.74, 126.31, 126.28, 123.56, 121.45, 119.42, 92.77, 90.22, 60.23, 32.91, 27.07, 26.80, 26.59; **IR** (KBr) 3062, 3034, 2929, 2854, 1554, 1538, 1445, 1154, 1012, 991, 794, 757, 701 cm^{-1}; **MS** (70 eV) 440.5 (M^+, 0.2), 335.5 (9), 307.5 (13), 270.4 (65), 165.2 (38), 115.1 (28), 105.1 (100), 77 (57); **Anal.** Calcd for $C_{33}H_{28}O$: C, 89.96; H, 6.41. Found: C, 89.68; H, 6.28.

The above reaction was employed for **13a, 12b** and **13b**, and the same products, **24** and **25,** were obtained.

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