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The key compounds, 1-(2-iodocyclohex-1-en-1-yl) benzene (**12**) and 1-(2-iodocyclohex-2-en-1-yl) benzene (**13**), for the generation of 1-cyclohex-1,2-dien-1-ylbezene (**20**) were synthesized starting with cyclohexanone. Separate reactions of **12** and **13** with KO*t*Bu in benzene in a sealed tube at 180 °C gave 6 products: 1-cyclohex-1-en-1-ylbenzene (**8**), 2-phenylcyclohexanone (**10**), 1,8-diphenyl-2,3,4,4a,4b,5,6,7-octahydrobiphenylene (**21**), 8a-phenyl-1,2,3,4,6,7,8,8a-octahyd-rotriphenylene (**22**), 1,2-diphenylcyclohexene (**23**), and 1-(2-tert-butoxycyclohex-1-enyl) benzene (**24**). In addition, reactions of **12** and **13** under the same conditions in the presence of diphenylisobenzofuran and furan as trapping reagents afforded the [4 + 2] cyclo-adducts **30**, **31**, and **32** in good yields, respectively.

Key Words: Cyclic strained allenes, dehydroiodination, dimerisation, cycloaddition.

Introduction

Early attempts to synthesise and isolate cyclohexa-1,2-diene were made around 1935 by Favorski.[1,2] The next pioneering work on cyclohexa-1,2-diene was carried out by Ball and Landor,[3] who successfully generated cyclohexa-1,2-diene. The first clear demonstration of the existence of cyclohexa-1,2-diene was reported by Wittig and Fritze[4] in 1968. Moore and Moser[5] have prepared cyclohexa-1,2-diene using a carbenoid route. Balci and Jones[6] optically isolated active cycloadducts by 2 different routes providing evidence for chirality in cyclohexa-1,2-diene. Sütbeyaz et al.[7] reported the synthesis of cyclohexa-1,2-diene by fluoride ion-promoted elimination of β-halogenosilane.

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Previously we applied the base-induced HI-elimination reaction to **1** for the generation of **2.**[8] As a result of the reaction of **1** with KO*t*Bu in benzene, deuterated benzene, and toluene, we obtained the products **4** and **5** via transient allene **2**. Due to the high reaction temperature (240 °C), the intermediate allene **2** formed by HI-elimination might have been in equilibrium with the corresponding diradical **3**. Thus, the addition of benzene to diradical **3** could give the phenyl alkene **4** and diphenyl alkene **5** (Figure).

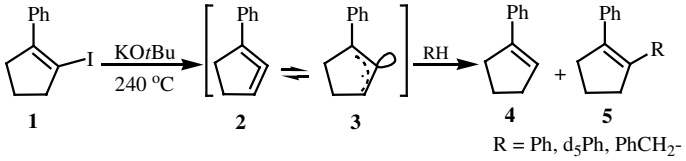
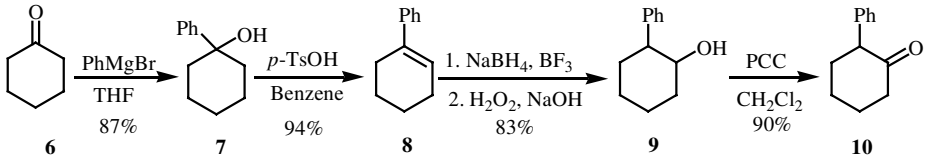


Figure 1. Synthesis of 1-cyclopent-1,2-dien-1-ylbezene.

In order to get more information about the possibility of the formation of **2**-like transient allenes, we decided to synthesize **1**-like allene precursors with a 6-membered ring and to study its elimination with base.

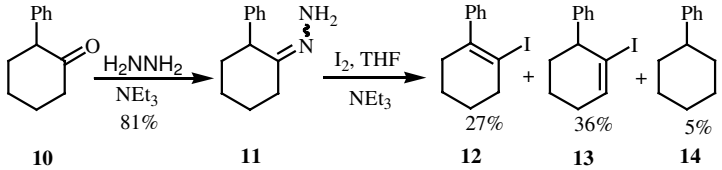
Results and Discussion

For the synthesis of **12** and **13**, key compounds for the preparation of 1-cyclohex-1,2-dien-1-ylbenzene (**20**), cyclohexanone **6** was used as the starting material. Bromobenzene was converted to the Grignard reagent,[9] which was condensed with cyclohexanone **6** to give 1-phenylcyclohexanol (**7**). Dehydration[10] of the crude alcohol **7** with *p*-TsOH in benzene gave alkene **8** in 94% yield, and hydroboration[11,12] of **8** followed by oxidation[13] with PCC led to ketone **10** in a yield of 81% (Scheme 1).



Scheme 1

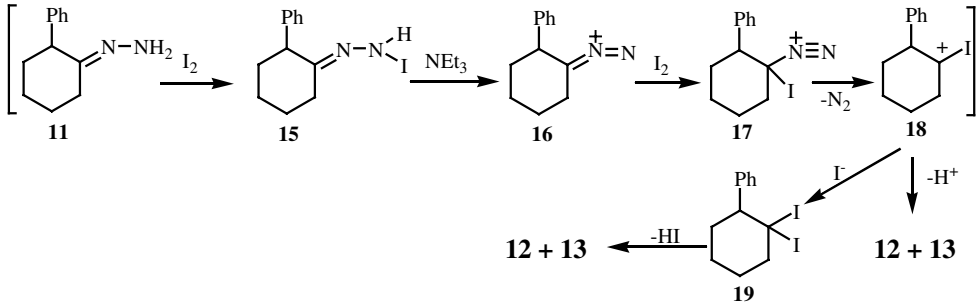
Ketone **10** was converted to the hydrazone derivative **11** by treatment with hydrazine hydrate[14] at 90-95 °C. Product **11** was estimated to be a 1.5:1 mixture of *E* and *Z* isomers. Treatment of this mixture with iodine[15] in the presence of NEt_3 in THF resulted in the formation of 3 products (**12**, **13**, and **14)** in a ratio of 5.5:7:1 (68% total yield), which were separated by silica gel column chromatography and recrystallisation (Scheme 2).



Scheme 2

The formation of compound **14** can be explained by the Wolf-Kishner reduction of hydrazone **11**. The structure of **14** was identified by comparison with authentic samples.[16,17]

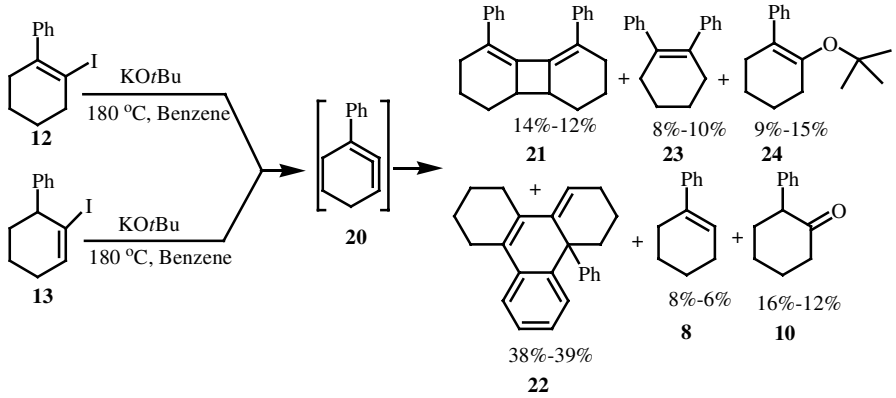
The formation of the key compounds **12** and **13** can be explained[14,15] as shown in Scheme 3. The hydrazone **11** is oxidised, possibly via the *N*-iodo derivative **15**, to the aliphatic diazo compound **16**. Iodine, acting as an electrophile, converts the diazo compound **16**, possibly via an intermediate iododiazonium compound **17**, into an iodocarbonium ion **18,** which gives the products **19** or **12** and **13** together by the attack of the iodide ion or the elimination of a proton, respectively. The subsequent conversion of the *gem*-diiodide **19** to the vinyl iodides **12** and **13** occurred by β-elimination of the hydrogen iodide.



Scheme 3

The structures **12** and **13** were determined on the basis of spectral data and by comparison with literature data.[8] The characteristic ^{13}C signals of =C-I signals (at 98.73 and 103.33 ppm, respectively) in the ^{13}C-NMR spectra of **12** and **13** are in good agreement with the proposed structure of **12** and **13**.

After the successful synthesis of the key compounds **12** and **13**, they were submitted separately to the base-induced HI-elimination reaction. No reaction was observed when the dehydroiodination was carried out in different solvents and at different temperatures (60-160 °C). When more drastic conditions (sealed tube, benzene or THF, at 180-185 °C) were employed, dehydroiodination occurred. The reaction of **12** or **13** with KO*t*Bu afforded 6 products (**8**, **10**, and **21-24)** (Scheme 4). In addition, we also observed that the yield of ether **24** increased when we used 2 mol equiv of KO*t*Bu. Temperature is also important for the product distribution: above 200 °C, the yield of diphenylcyclohexene (**23**) increased. From this latter finding, we conclude that the allenic structure might be converted to a diradicalic structure (Scheme 6) by increasing the reaction temperature.



Scheme 4

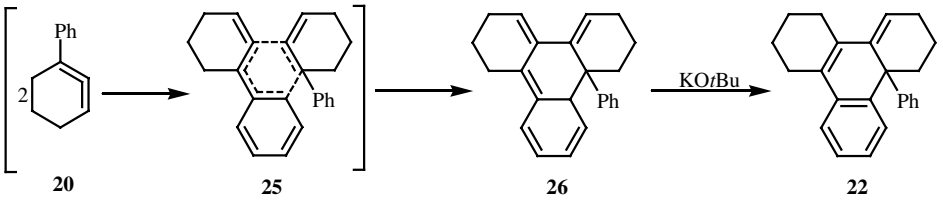
The mixture was separated by a silica gel column chromatography. The elemental analysis and molecular peak of 312 (M+) of the products **21** and **22** clearly indicated the presence of an allene dimer.

The head-to-head dimerisation product **21** was isolated in yields of 14% from **12** and 12% from **13**. The observation of only 4 signals in the sp^3 region of the ^{13}C-NMR spectrum of **21** is evidence for its symmetrical structure.

Other dimerisation products of **20** were isolated in yields of 38% from **12** and 39% from **13**.

The structure of **22** was explained on the basis of its NMR data. The asymmetrical structure of **22** was established by the observation of 22 signals of its ^{13}C-NMR spectrum as required by the asymmetry in the molecule.

The formation of **22** was outlined as shown in Scheme 5.[18] Intermediate allene (**20)** cyclises via transition state **25**, which is formed by [2+4] synchron in addition with the participation of a phenyl group and furnishes a methylene-1,3-cyclohexadiene derivative (**26)**, which is isomerised to yield **22** under the influence of KO*t*Bu (Scheme 5).

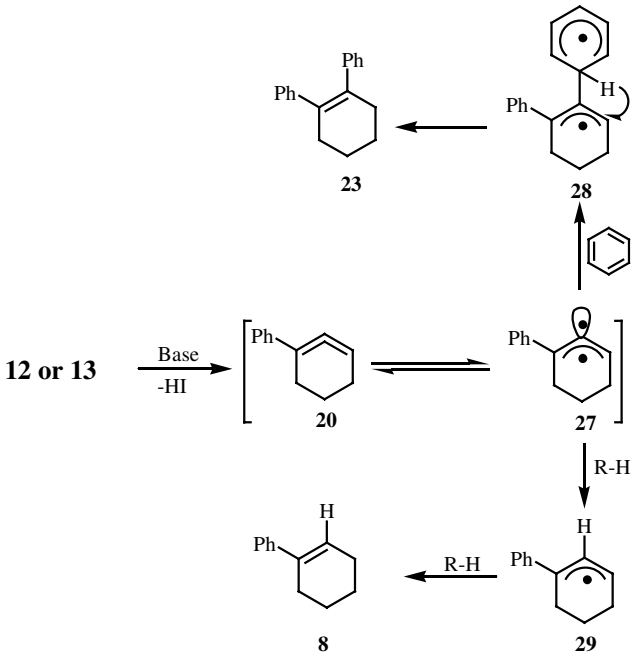


Scheme 5

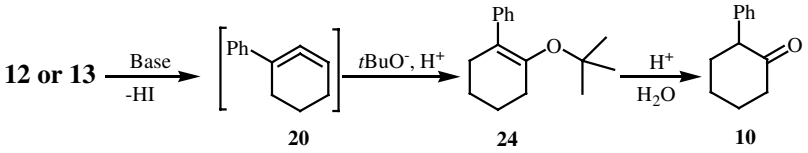
The structures of **23** and **8** were established by comparison of the NMR data with the literature. The latter is the result of a reductive elimination reaction. The formation of **8** and **23** can be explained by the following mechanism[8] (Scheme 6). Firstly, base-induced elimination of HI from **12** or **13** gives the intermediate, allene **20**, which will be in equilibrium with the corresponding diradical **27** (Scheme 6). The latter reacted with benzene to give the intermediate (**28)**, which can be easily transformed to the neutral compound, diphenylalkene **23**, by a hydrogen transfer. The theoretical calculations show that cyclohexa-1,2-diene may exist as a chiral allenic structure,[19] but it can easily racemise through a species best described as a diradical. The effect of temperature on racemisation of the allenic structure was also demonstrated in the case of 6- and 7-membered ring allenes.[6]

The formation of etheric compound **24** can be explained by the addition of tBuO$^-$ to allene **20**. The nucleophilic attack at the central allenic carbon atom and the protonation of the resulting ally anion by HO*t*Bu leads to the enol ether[20] **24** (Scheme 7), and the ketone **10** was formed by the hydrolysis of the enol ether **24**. The identification of **24** revealed its structure by the characteristic NMR signals of the enol ether subunit.

In this stage of the study, we examine the reactions of **12** and **13** with KO*t*Bu in benzene (in a sealed tube, at 180 °C) in the presence of 1,3-diphenylisobenzofuran (DBI) as a trapping reagent. Reactions of **12** with KO*t*Bu in the presence of DBI yielded allene cycloadducts **30** and **31** in a ratio of 4:1. The allene cycloadducts **30** and **31** were characterised by spectroscopic studies and by comparison to the DBI adducts of cyclohexa-1,2-diene.[4,7,21]

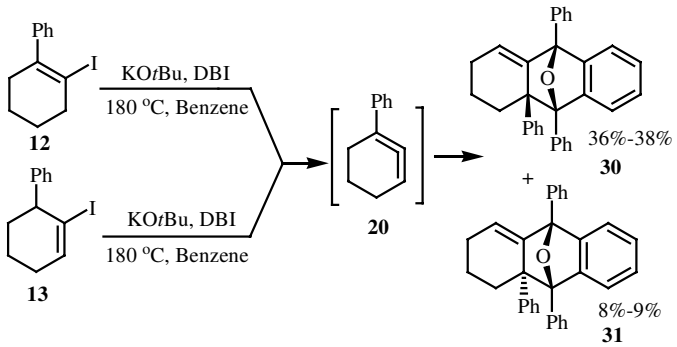


Scheme 6



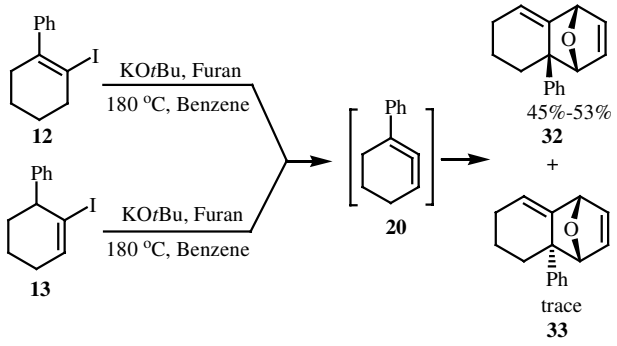
Scheme 7

The major product **30** (36%) was determined as an *endo* adduct of DBI and 1-cyclohex-1,2-dien-1-ylbenzene (**20**) and **31** (8%) were *exo* adducts. Reaction of **13** with KO*t*Bu in the same conditions afforded the same products in yields of 38% and 9%, respectively (Scheme 8). Formation of the cycloaddition products **30** and **31** can only be explained by the strained allene intermediate **20**. Although the intermediate **20** has 2 active sides for the cycloaddition reaction, the exclusive formation of **30** and **31** shows that the trapping occurs with a high degree of regioselectivity.



Scheme 8

In addition, the reactions of **12** and **13** with KO*t*Bu in benzene (in a sealed tube, at 180 °C) in the presence of furan as a trapping reagent afforded known cycloadduct **32** as a major product and **33** in trace amount (Scheme 9).



Scheme 9

The major product **32** was characterised by comparison of the NMR data with those reported in the literature[21] as an *endo* adduct of furan and 1-cyclohex-1,2-dien-1-ylbenzene (**20**)**.** Although compound **33** was observed in the NMR spectrum of the mixture (**32** and **33**), it was not isolated in sufficient amount for full characterisation. The outcomes of these reactions are rationalised by assuming the β-elimination of HI from **12** and **13** with the formation of the desired intermediate **20**.

Conclusions

We have demonstrated that the title intermediate **20**, a strained cyclic allene, can be generated from 1-(2-iodocyclohex-1-en-1-yl) benzene (**12**) and 1-(2-iodocyclohex-2-en-1-yl) benzene (**13**) by β-elimination of HI with KO*t*Bu. Furthermore, the formation of compound **23** showed that allene **20** is equilibrium with the diradical form **27** at especially high temperatures.

Experimental

^{1}H- and ^{13}C-NMR spectra were recorded with Varian 200, Varian 400, and Bruker AC 400 instruments. As internal standards, TMS (δ 0.00 ppm) was used for ^{1}H-NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C-NMR spectroscopy, and J values 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), 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). Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyser. Melting points were measured on an Electrothermal 9100 apparatus.

All reactions were conducted in anhydrous solvents in an atmosphere of dry N_2. All column chromatographies were performed on silica gel (60-230 mesh, Merck) and Al_2O_3-90 (70-230 mesh, Merck).

1-Phenylcyclohexanol 7: To a stirred mixture of Mg (2.5 g, 0.11 mol) in 100 mL of dry THF at r.t. were added bromobenzene (2 mL) and a small amount of I_2, and the mixture was heated to 65 °C. To the mixture was added bromobenzene (18 g, 0.11 mol) in 30 mL of THF within 2 h, followed by stirring for

1 h at the same temperature. The mixture was cooled to r.t., cyclohexanone **6** (10 g, 0.1 mol) was added, and the mixture was stirred for 3 h. The mixture was extracted with Et_2O (3 × 100 mL), and the combined org. extracts were washed with H_2O (300 mL) and dried ($MgSO_4$). Evaporation of the solvent (30 °C, 20 mm Hg) gave alcohol **7** (15 g, 87%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)δg.54-7.50 (m, aromatic, 2H), 7.38-7.30 (m, aromatic, 3H), 1.92-1.71 (m, 9H), 1.68-1.60 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)δ 149.66, 128.45, 126.93, 124.81, 73.38, 39.07, 25.76. **IR** (CCl_4)ν 3600, 3060, 3020, 2940, 2860, 1450, 1080, 1020, 710 cm^{-1}.

1-Cyclohex-1-en-1-ylbenzene 8: To a stirred solution of alcohol **7** (10 g, 57 mmol) in 100 mL of benzene was added 4-toluenesulfonic acid (*p*-TsOH) (50 mg) and the mixture was refluxed for 3 h. The mixture was then washed with water (100 mL) and dried ($MgSO_4$). Removal of the solvent and distillation (20 mmHg, 180 °C) gave 1-cyclohex-1-en-1-ylbenzene **8** (8.5 g, 94%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.42-7.37 (m, aromatic, 2H), 7.35-7.30 (m, aromatic, 2H), 7.26-7.21 (m, aromatic, 1H), 6.16-6.13 (m, olefinic, 1H), 2.44-2.42 (m, 2H), 2.25-2.22 (m, 2H), 1.84-1.78 (m, 2H), 1.72-1.66 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 142.94, 136.84, 128.42, 126.75, 125.18, 124.99, 27.65, 26.13, 23.33, 22.42. **IR** (CCl_4)g 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.

2-Phenylcyclohexanol 9: To a slurry of $NaBH_4$ (2 g, 52.6 mmol) in THF (60 mL) was added alkene **8** (8 g, 50.06 mmol) in THF (30 mL) at room temperature under N_2. The reaction mixture was cooled to 0 °C and BF_3-OEt_2 (7.5 g, 52.6 mmol) was added over 30 min. The resulting mixture was stirred at room temperature for 3 h. Then, to the mixture were added NaOH (20 mL, 3 N) and H_2O_2 (30 mL, 35%), followed by warming to 50 °C and stirring for 30 min. The aqueous layer was extracted with diethyl ether (2 × 150 mL). The combined organic extracts were washed with Na_2SO_3 solution (2%) and dried ($MgSO_4$). Removal of the solvent gave 2-phenylcyclohexanol **9** (colourless crystal, mp 67-69 °C, Lit.[11,12] 64-65 °C, 7.2 g, 83%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.39-7.35 (m, aromatic, 2H), 7.32-7.24 (m, aromatic, 3H), 3.70-3.64 (m, 1H), 2.65-2.60 (br. s, -OH), 2.51-2.41 (m, 1H), 1.94-1.80 (m, 4H), 1.62-1.34 (m, 4H). ^{13}**C-NMR** (100 MHz, $CDCl_3$) 143.87, 128.94, 128.28, 126.98, 74.59, 53.42, 34.85, 33.74, 26.39, 25.43. **IR** (CCl_4) νg382, 3027, 2929, 2856, 1600, 1448, 1058, 962, 786, 736, 700 cm^{-1}. **Anal. Calcd** for $C_{12}H_{15}O$: C 81.77, H 9.15. Found: C 81.65, H 9.23.

2-Phenylcyclohexanone 10: To a stirred solution of pyridiniumchloro-chromate (PCC) (9.5 g, 44 mmol) in 50 mL of CH_2Cl_2 was added the alcohol **9** (prepared above) (7 g, 40 mmol) in 20 mL of CH_2Cl_2 at 0 °C for 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). Removal of the solvent gave 2-phenylcyclohexanone **10** (colourless crystals, mp 56-59 °C, 6.3 g, 90%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.27-7.23 (m, aromatic, 2H), 7.18-7.15 (m, aromatic, 1H), 7.07-7.05 (m, aromatic, 2H), 3.54-3.50 (dd, J = 5.38, 12.79 Hz, 1H), 2.45-2.31 (m, 2H), 2.19-2.14 (m, 1H), 2.07-1.98 (m, 1H), 1.95-1.87 (m, 2H), 1.78-1.66 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$): 210.34, 138.92, 128.64, 128.39, 126.92, 57.40, 42.26, 35.21, 27.89, 25.37. **IR** (KBr) ν 3029, 2935, 2859, 1714, 1448, 1126, 1068, 786, 698 cm^{-1}. **Anal. Calcd** for $C_{12}H_{14}O$: C 82.72, H 8.10. Found: C 82.67, H, 8.08.

Syn- and anti-2-phenylcyclohexan-1-one hydrazone 11: A solution of hydrazine hydrate (8.5 g, 140 mmol) and triethylamine (3.6 g, 35 mmol) was added to a vigorously stirred solution of 2-phenylcyclohexanone (**10**) (6 g, 35 mmol) at room temperature over 3 h. The reaction mixture was stirred at 90-95 °C for 1 h. The reaction mixture was cooled to room temperature and extracted with chloroform (3 × 50 mL). The combined extract was dried with K_2CO_3 and the solvent was evaporated to yield an essentially pure mixture consisting of *syn*- and *anti*-hydrazone **11** (colourless liquid, 5.3 g, 81%). ^{1}**H-NMR**

(200 MHz, $CDCl_3$)gδ 7.41-7.21 (m, aromatic, 10H), 4.87-4.72 (br. s, -NH_2, 4H), 3.74-3.68 (dd, J = 5.09, 7. 97 Hz, 1H), 3. 61-3.54 (dd, J = 5.27, 8.35 Hz, 1H), 2.58-2.46 (m, 2H), 2.38-2.29 (m, 2H), 2.27-2.04 (m, 4H), 1.88-1.73 (m, 4H), 1.71-1.63 (m, 4H).g^3**C-NMR** (50 MHz, $CDCl_3$)gδ 166.80, 157.69, 144.19, 143.58, 130.39, 130.33, 130.19, 128.19, 51.88, 51.72, 35.29, 35.01, 29.29, 28.69, 28.59, 27.69, 26.14, 25.71. **IR** (CCl_4)ν 3365, 3025, 2935, 2859, 1600, 1494, 1448, 1051, 788, 698 cm^{-1}. Isomeric hydrazone **6** was used without further purification.

Treatment of syn- and anti-2-phenylcyclohexan-1-one hydrazone 11 with I_2. A saturated solution of iodine (15 g, 0.06 mol) in dry THF was added rapidly to a stirring solution of isomeric **11** (5 g, 27 mmol) in 25 mL of triethylamine under nitrogen atmosphere at 0 °C. The reaction mixture was stirred for an additional hour at room temperature. After diluting the reaction mixture with 150 mL of distilled water, it was extracted with hexane (3 × 100 mL). The combined organic layers were washed with HCl (3 × 30 mL, 1 N), saturated with $NaHCO_3$ and NaCl solution, dried and evaporated to yield a mixture (5.5 g) consisting of **12**, **13**, and **14**. The residue was submitted to a silica gel column chromatography (70 g), eluting with hexane. The first fraction yielded pure phenylcyclohexane (**14**) (colourless liquid at r.t. (lit.[16]) but **14** is solid below 8 °C lit,[17] 0.5 g, 5%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.32-7.26 (m, aromatic, 2H), 7.23-7.16 (m, 3H), 2.54-2.50 (m, 1H), 1.91-1.81 (m, 4H), 1.46-1.35 (m, 6H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 148.35, 128.52, 127.07, 126.02, 44.84, 34.71, 27.17, 26.42. **IR** (CCl_4)g 3027, 2925, 2852, 1492, 1452, 784, 698 cm^{-1}. **Anal. Calcd** for $C_{12}H_{16}$: C 89.84, H 10.06. Found: C 89.76, H, 10.10.

Second fraction yielded pure 1-(2-iodocyclohex-1-en-1-yl)benzene (**12**) (colourless crystals, mp 50-55 °C, 2.1 g, and 27%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.31-7.27 (m, aromatic, 3H), 7.10-7.08 (m, aromatic, 2H), 2.74-2.70 (m, 2H), 2.40-2.36 (m, 2H), 1.81-1.76 (m, 2H), 1.71-1.65 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 146.91, 144.27, 127.87, 127.21, 127.10, 98.71, 41.57, 34.07, 25.57, 22.96. **IR** (CCl_4)νg029, 2938, 2865, 1540, 1448, 1247, 1124, 1004, 794, 698, 547 cm^{-1}. **Anal. Calcd** for $C_{12}H_{13}I$: C 50.73, H, 4.61. Found: C 50.69, H 4.57.

Later fractions were mixtures. The last fraction yielded pure 1-(2-iodocyclohex-2-en-1-yl)benzene (**13**) (colourless crystals, mp 67 °C, 2.7 g, and 36%). ^{1}**H-NMR** (200 MHz, $CDCl_3$)gδ 7.40-7.19 (m, aromatic, 5H), 6.70-6.65 (dt, olefinic, J = 1.47, 4.03 Hz, 1H), 3.74-3.68 (m, 1H), 2.24-2.10 (m, 3H), 1.88-1.70 (m, 1H), 1.68-1.58 (m, 2H). ^{13}**C-NMR** (50 MHz, $CDCl_3$)gδ 146.16, 142.23, 131.32, 130.33, 128.60, 103.33, 54.67, 35.69, 31.36, 19.83. **IR** (CCl_4)ν 3025, 2933, 1490, 1450, 983, 754, 700 cm^{-1}. **Anal. Calcd** for $C_{12}H_{13}I$: C 50.73, H 4.61. Found: C 50.69, H 4.57.

Reaction of 12 with KO*t*Bu in benzene. A solution of **12** (1 g, 3.5 mmol) in 5 mL of dry benzene and 0.45 g (4 mmol) of KO*t*Bu was placed in a glass tube. After sealing the tube, it was heated to 180 °C over 16 h. Benzene was evaporated and the residue was submitted to silica gel (60 g) column chromatography, eluting with hexane. The first fraction was pure 1-cyclohex-1-en-1-ylbenzene (**8**) (40 mg, 8%).

The second fraction gave 1,8-diphenyl-2,3,4,4a,4b,5,6,7-octahydrobiphenylene (**21**) (colourless solids from hexane, mp 148-151 °C, 80 mg, 14%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.38-7.13 (m, aromatic, 10H), 2.55-2.51 (m, 2H), 2.29-2.25 (m, 1H), 2.17-2.05 (m, 1H), 2.03-1.98 (m, 2H), 1.86-1.70 (m, 4H), 1.36-1.28 (m, 4H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 138.97, 131.15, 130.86, 129.04, 127.15, 113.91, 55.72, 38.93, 23.95, 23.24. **IR** (KBr) νg060, 3021, 2931, 2861, 1550, 1484, 1440, 1247, 1214, 1002, 817, 727 cm^{-1}. **MS** m/z (relative intensity): 312.2 (M+H,7), 235.2 (13), 154.1 (100), 129 (44), 105 (35), 90.1 (29), 77.1 (31). **Anal. Calcd** for $C_{24}H_{24}$: C 92.26, H 7.74. Found: C 92.22, H 7.73.

The third fraction yielded pure 1-(2-phenylcyclohex-1-en-1-yl)benzene (**23**) (colourless crystals from

methanol, mp 48-50 °C, Lit.[22] 47-48 °C 65 mg, 8%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.39-7.22 (m, aromatic, 10H), 2.47-2.44 (m, 4H), 1.88-1.82 (m, 4H).g^3**C-NMR** (100 MHz, $CDCl_3$) δ 144.10, 135.21, 129.28, 127.81, 125.89, 38.37, 32.15. **IR** (KBr) νg065, 3019, 2910, 2840, 1689, 1485, 1440, 1248, 1154, 1025, 905, 690 cm^{-1}. **Anal. Calcd** for $C_{18}H_{18}$: C 92.26, H 7.74. Found: C 92.25, H 7.75.

The fourth fraction gave 8a-phenyl-1,2,3,4,6,7,8,8a-octahydrotriphenylene (**22**) (colourless solids from hexane, mp 143 °C, 210 mg, 38%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.70-7.68 (m, aromatic, 1H), 7.29-7.06 (m, aromatic, 9H), 6.21-6.19 (t, J = 4.25 Hz, 1H), 2.74-2.69 (m, 1H), 2.49-2.44 (m, 2H), 2.28-2.19 (m, 3H), 2.16-2.12 (m, 1H); 1.83-1.73 (m, 2H), 1.66-1.55 (m, 2H); 1.52-1.32 (m, 2H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 147.54, 142.44, 139.09, 135.95, 132.04, 128.45, 127.82, 127.51, 126.53, 125.99, 125.79, 125.66, 125.39, 122.65, 46.12, 36.66, 27.18, 26.12, 25.78, 23.15, 22.69, 18.53. **IR** (KBr) ν 3064, 3018, 2933, 2867, 1544, 1484, 1249, 1213, 1002, 815, 725 cm^{-1}. **MS** m/z (relative intensity): 312.3 (M+H, 65), 235.2 (100), 178.1 (58), 165.1 (73), 149.0 (51), 91.0 (49), 77.1 (32). **Anal. Calcd** for $C_{24}H_{24}$: C 92.26, H 7.74. Found: C 92.24, H 7.72.

The fifth fraction yielded 1-(2-*tert*-butoxycyclohexenyl)benzene (**24**) (colourless liquid, 75 mg, 9 %). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.35-7.33 (m, aromatic, 2H), 7.29-7.26 (m, aromatic, 2H), 7.18-7.14 (m, aromatic, 1H), 2.40-2.36 (m, 2H), 2.24-2.20 (m, 2H); 1.77-1.67 (m, 4H), 1.06 (s, 9H).g^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 147.35, 142.36, 129.21, 127.71, 125.88, 124.28, 77.67, 31.77, 30.51, 29.76, 23.78, 23.48. **IR** (liquid) ν 3054, 3023, 2973, 2933, 1646, 1490, 1440, 1365, 1153, 1122, 896, 781, 755, 696 cm^{-1}. **Anal. Calcd** for $C_{16}H_{22}O$: C 83.43, H 9.63. Found: C 83.41, H 9.61. The sixth fraction was 2-phenylcyclo-hexanone (**10**) (100 mg, 16%).

The above reaction was employed for **13** and the same products, **8**, **10,** and **21-24**, were obtained in the yields of 6%, 12%,12%, 39%, 10%, and 15%, respectively.

Reaction of 12 with KO*t*Bu in the presence of DBI. A solution of **12** (0.5 g, 1.76 mmol) in 6 mL of dry benzene, 0.2 g (1.78 mmol) of KO*t*Bu, and 0.5 g (1.8 mmol) of DBI was placed in a glass tube. After sealing the tube, it was heated to 180 °C over 16 h. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$, and the solvent was removed in vacuum. The residue was submitted to Al_2O_3 (active basic, grade III, 30 g) column chromatography, eluting with hexane/benzene (9:1). The first fraction was the excess of DBI. The second fraction yielded pure *endo* adduct (**30**) (colourless solid, mp 185 °C, 0.29 g, 36%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 8.03-8.00 (m, 2H), 7.63-7.49 (m, 4H), 7.45-7.43 (m, 2H), 7.31-7.12 (m, 6H), 6.98-6.94 (m, 5H), 5.96-5.94 (dd, J = 2.94, 4.67 Hz, 1H), 2.70-2.65 (dt, J = 3.42, 11.64 Hz, 1H), 2.01-1.83 (m, 2H), 1.55-1.46 (m, 1H), 1.32-1.21 (m, 1H), 0.99-0.91 (dt, J = 4.16, 11.98 Hz, 1H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)δ 150.26, 147.79, 145.36, 142.36, 138.05, 135.34, 129.81, 128.92, 128.83, 128.64, 128.04, 127.57, 127.15, 126.92, 125.85, 125.68, 125.51, 123.58, 122.16, 117.63, 93.84, 89.12, 56.79, 32.17, 24.25, 18.91. **IR** (KBr) ν 3060, 3025, 2927, 1600, 1544, 1492, 1452, 1155, 1305, 1000, 786, 754, 698 cm^{-1}. **MS** m/z (relative intensity): 427 (M+H, 0.2), 409 (0.25), 321 (15), 215 (22), 165 (38), 115 (23), 105 (100), 77 (66).

The third fraction yielded pure *exo* adduct (**31**) (colourless solid, mp 230 °C, 0.70 mg, 8%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)gδ 7.87-7.85, (br d, J = 7.10 Hz, 2H), 7.76-7.74 (br d, J = 7.19 Hz, 2H), 7.61,7.57 (br t, J= 7.48 Hz, 2H), 7.52-7.47 (br t, J = 7.88 Hz, 2H), 7.45-7.36 (m, 5H), 7.13-7.05 (m, 3H), 6.90-6.84 m, 3H), 5.79-5.77 (dd, J = 2.57, 6.96 Hz, 1H), 1.98-1.90 (m, 1H), 1.89-1.85 (m, 1H),1.55-1.38 (m, 3H), 1.312-1.17 (m, 1H). ^{13}**C-NMR** (100 MHz, $CDCl_3$)gδ 148.94, 147.03, 144.92, 141.44, 137.69, 136.64, 128.72, 128.19, 127.69, 127.58, 127.13, 126.85, 126.59, 126.47, 126.15, 120.95, 119.81, 119.27, 92.05, 90.03, 56.36, 30.58, 21.37, 17.71. **IR** (KBr) ν 3029, 2938, 1544, 1494, 1448, 1303, 998, 786, 744, 700 cm^{-1}. **MS** m/z (relative intensity): 427 (M+H, 0.2), 409 (0.25), 321 (15), 215 (22), 165 (38), 115 (23), 105 (100), 77 (66).

The above reaction was employed for **13** and the same products (**30** and **31)** were obtained in the

yields of 38% and 9%, respectively.

Reaction of 12 with KOtBu in the presence of furan. A solution of **12** (0.5 g, 1.76 mmol) in 6 mL of dry benzene, 0.2 g (1.78 mmol) of KO*t*Bu and 0.24 g (3.5 mmol) of furan was placed in a glass tube. After sealing the tube, it was heated to 180 °C over 16 h. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and the solvent was removed in vacuum. The residue was submitted to Al_2O_3 (active basic, grade III, 40 g) column chromatography, eluting with hexane/benzene (9:1), to give the pure *endo* adduct (**32**) (colourless solid, mp 91-94 °C, lit.[21] 92-93 °C, 155 mg, 45%). ^{1}**H-NMR** (400 MHz, $CDCl_3$pgδgg.28-7.06gm, aromatic, 5H), 6.39-6.37 (dd, J = 1.73, 5.62 Hz, 1H), 6.23-6.21 (dd, J = 1.61, 5.62 Hz, 1H), 5.78-5.58 (dd, J = 2.73, 4.56 Hz, 1H), 5.10 (s, 1H), 4.95 (d, J = 1.25 Hz, 1H), 2.14-2.09 (dt, J = 3.42, 11.67 Hz, 1H), 2.02-1.96 (dd, J = 8.36, 18.91 Hz, 1H), 1.93-1.87 (m, 1H), 1.43-1.32 (m, 1H), 1.23-1.05 (m, 1H), 0.86-0.64 (m, 1H). ^{13}**C-NMR** (100 Mz, $CDCl_3$)gδ 145.92, 141.57, 137.50, 131.12, 128.28, 126.20, 121.06, 88.26, 80.19, 51.13, 34.94, 24.36, 19.09. **IR** (KBr) ν 3060, 2935, 2859, 1600, 1492, 1446, 1261, 1097, 1014, 896, 794, 767 cm^{-1}. **MS** m/z (relative intensity): 224 (M+H, 33.4), 196 (25.5), 195 (100), 181 (18.4), 167 (32.3), 115 (18.7), 91 (25.3), 77 (11.7).

The above reaction was employed for **13** and the same product (**32)** was obtained in the yield of 53%.

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