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# Synthesis and Rearrangement of New Cage [4.3.2]Propellanes Containing Spiro Linkage

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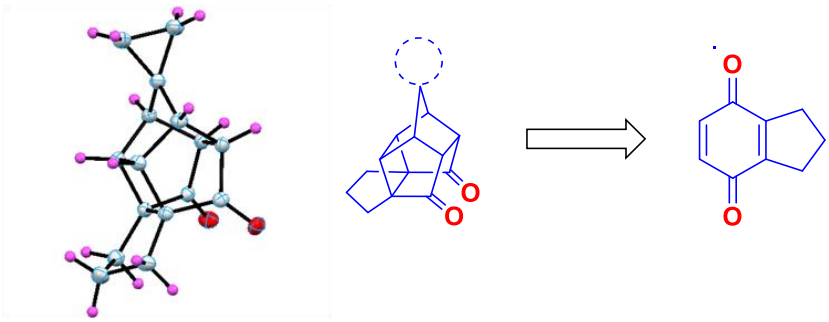
## Abstract

Rearranged cage ketones **6a** and **6b** are reported in eight linear synthetic steps starting with 2,5-dimethoxybenzaldehyde **9** without the involvement of protecting groups. In this regard, Diels–Alder reaction, [2+2] photocycloaddition and Lewis acid promoted rearrangement with $BF_3{\cdot}OEt_2$ has been used as key steps. Surprisingly, during the ring expansion process with Lewis acid, solvent incorporation occurred. This rearrangement approach has provided difficult complex targets via non-obvious synthetic routes. Rearrangement process demonstrated here opens up a new synthetic strategy to interesting and unusual cage molecules.




## Keywords:

Cage compounds, CAN oxidation, Diels–Alder reaction, [2+2]photocycloaddition, Lewis acid catalyzed rearrangement.

## Introduction

Carbocyclic cage compounds[1-5] have received the attention of synthetic chemists during the past four decades because of their applications in diverse areas of chemistry and these include: natural product synthesis,[3b,6] high energy materials,[5a,7] medicinal chemistry,[8] pharmaceutical applications,[9] polymers,[10] thermostable oils[11] and supramolecular chemistry.[12] Some of these molecules are also of theoretical interest because of their molecular symmetry, compact rigid

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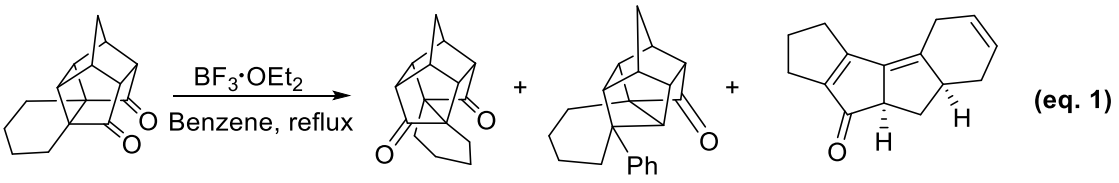
carbon framework, ready tendency to undergo skeletal rearrangements, unusual strain energy and deviation from normal C–C bond angles.[13]

Lewis acid-promoted rearrangement of various polycyclic cage diones as well as propellanes has received considerable interest due to their synthetic importance as well as mechanistic scrutiny.[14-16] Ring-rearrangement approach provide a non-conventional access to a variety of new and unusual cage systems.[17] As part of our ongoing programme, we are interested in developing novel strategies for the synthesis of new cage molecules which are suitable for rearrangement approach that provide intricate structures which are difficult to obtain by direct synthetic routes. In view of our current efforts in the synthesis of propellane derivatives,[23] here we report the synthesis and rearrangement of a rigid cage [4.3.2]propellanediones. Carbocation mediated rearrangement using $BF_3{\cdot}OEt_2$ gave solvent incorporated product. The structure of the product **6a** was unambiguously established by single-crystal X-ray diffraction studies.

## Results and Discussion

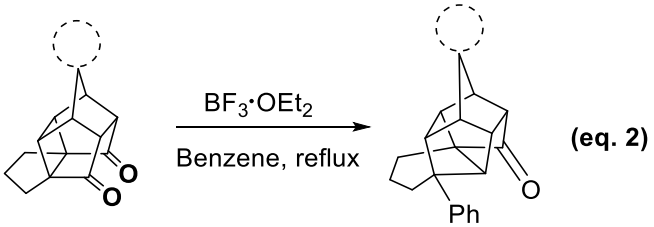
**Scheme 1. Synthesis of cage dione, rearranged cage ketones and polyquinane**

**Previous work**[14d]




**1** **2** (15%) **3** (25%) **4** (20%)

**Present work**




**5 a-b** **6 a-b** (up to 45-60%)

Previously (Scheme 1, eq. 1),[14d] carbocation mediated rearrangement of cage system **1** using $BF_3{\cdot}OEt_2$ was reported. In this regard, cage [4.4.2]propellanedione **1** has been prepared by Diels–Alder reaction of cyclopentadiene and 1,4-napthaquinone followed by [2+2]

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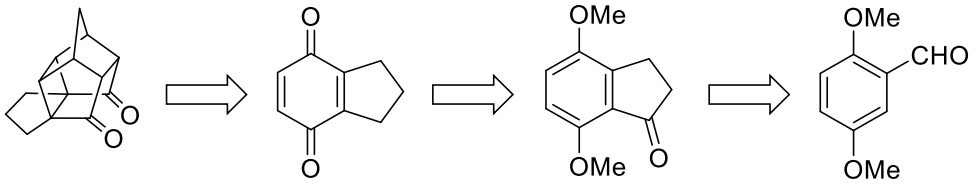
photocycloaddition and hydrogenation sequence which undergo $BF_3{\cdot}OEt_2$ mediated rearrangement in benzene to deliver **2, 3** and **4** in 15%, 25% and 20% selective yields, respectively. In our present strategy (Scheme 1, eq. 2), we disclose ring rearrangement of cage [4.3.2]propellanes such as **5a-b** with the aid of Lewis acid.

Retrosynthetic analysis of hexacyclic dione **5a** was depicted in Scheme 2. In this context the key building block, indane-based quinone **7** on Diels–Alder reaction may produce cycloadduct which on [2+2] photocycloaddition can generate the dione **5a**. The known indane derivative **7** was assembled from dimethoxy indanone **8** involving reduction of carbonyl group and CAN oxidation. The required indanone **8** was prepared from a readily available aldehyde **9** via unsaturated acid in two step sequence involving Fridel-Crafts cyclization as key step.

**Scheme 2**. **Retrosynthetic Analysis of target molecule 5a**




**5a** **7** **8** **9**

Our journey towards the synthesis of cage dione **5a** begin with the preparation of the key building block, quinone derivative **7.** Commercially available 2,5-dimethoxybenzaldehyde **9**, on treatment with malonic acid **10** under Knoevenagel reaction conditions afforded α, β-unsaturated acid **11**[18] in 75% yield (Scheme 3). Later the acid derivative **11** was smoothly transformed into saturated acid **12**[19] (92%) via hydrogenation with Pd-C. Next, 2,5-dimethoxybenzenepropanoic acid **12** was subjected to cyclization in the presence of $P_2O_5$ and $MeSO_3H$ afforded the corresponding indanone **8**[20] in 60% yield. Subsequently, carbonyl group was converted to methylene in the presence of trialkylsilane in $CF_3CO_3H$ media to deliver the 4,7-dimethoxy-indane **13**[21] in 55% yield. Oxidation of dimethoxy indane **13** was performed with CAN oxidation at 0 °C to afford the key building block **7,**[22] a useful dienophile in Diels–Alder sequence with various dienes like cyclopentadiene **14** as well as spirodienes **15** and **16** (Scheme 3). The required spirodienes **15** and **16** were prepared by adopting the known literature procedures.[24-25]

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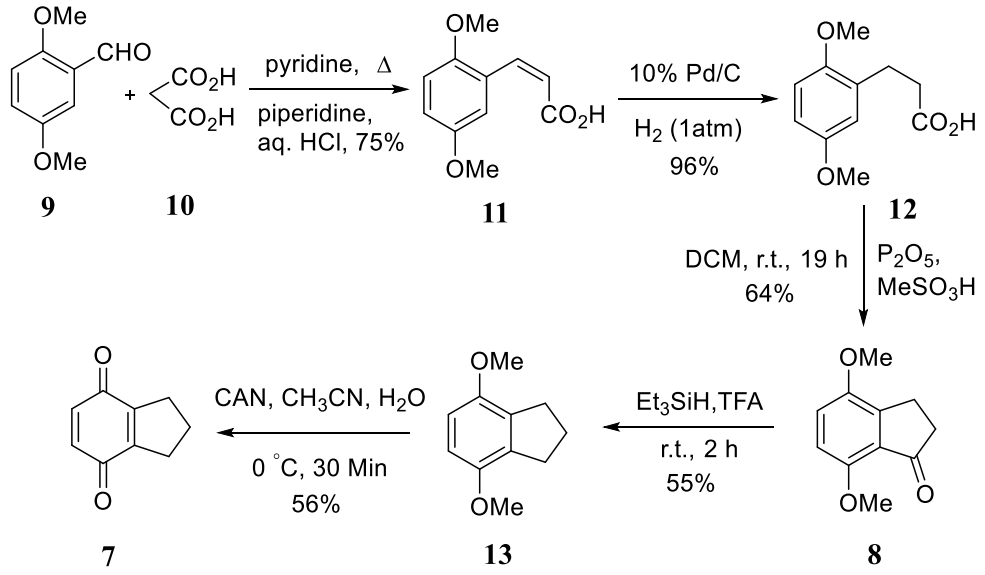
**Scheme 3. Synthesis of key building block 7**




Having prepared the building block **7**, next we directed our efforts to prepare the cage diones (Scheme 3). [4+2] Cycloaddition[20d,23] of quinone **7** with a freshly cracked 1,3-cyclopentadiene **14** at 0 °C delivered the DA adduct **17** (84%). Along similar lines, cycloaddition[26,27] of the quinone **7** with freshly generated spirodienes **15** and **16** under thermal conditions produced DA adducts **18** and **19** in good yields (Scheme 4). The stereochemistry of the DA adducts **17**, **18** and **19** has been expected to be *endo* and this observation found to be correct, when we realized that these DA adducts underwent a smooth intramolecular [2+2] photocycloaddition[23,26] upon exposure to UV light within 2 h. The formation of DA adducts **17**, **18** and **19** was strongly supported on the basis of $^{1}$H NMR, $^{13}$C NMR and HRMS data.

The DA adducts **17**, **18** and **19** derived from indanedione **7** undergo [2+2] photocycloaddition in dry ethyl acetate when they were irradiated with 125W UV lamp through a pyrex immersion well for 2 h under $N_2$ atmosphere to furnish the required cage diones **5a**, **5b** and **5c** in excellent yields (Scheme **4**). The structure of the cage propellanes **5a**, **5b** and **5c** were fully established on the basis of $^{1}$H NMR, $^{13}$C NMR, APT and further supported by HRMS data. The structure of the dione **5c** was further supported by single-crystal X-ray diffraction studies (Figure 1).[28]

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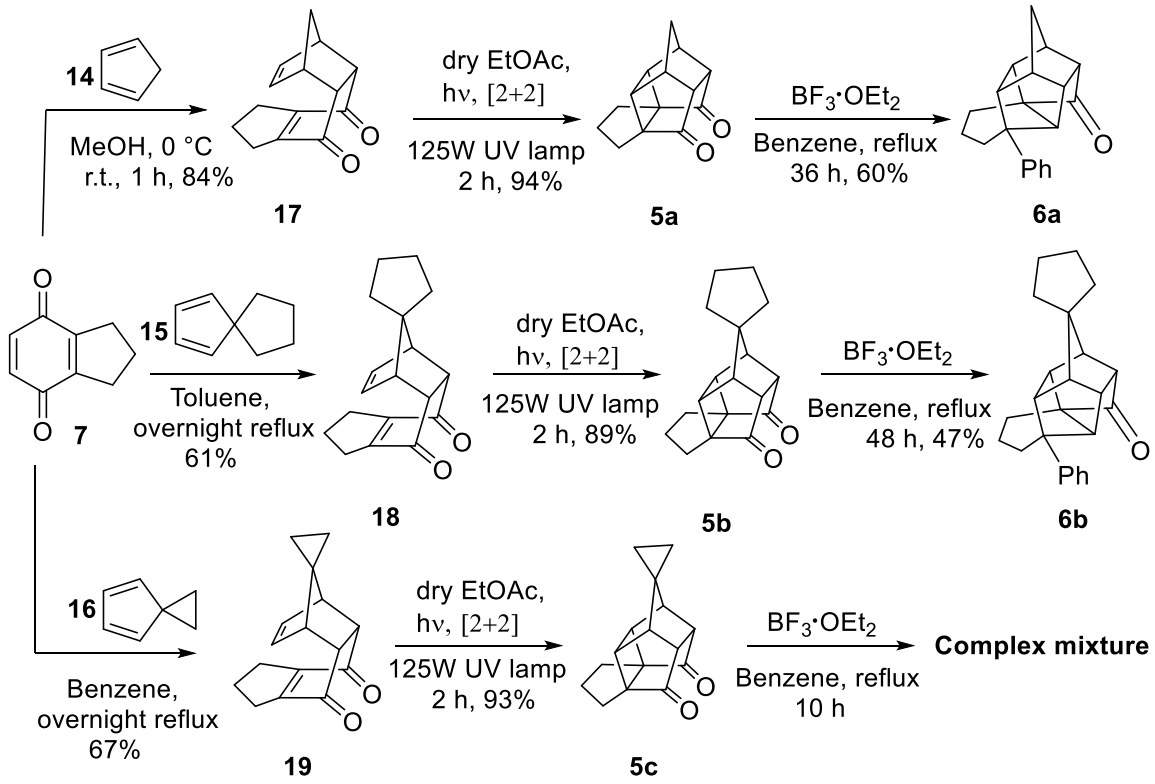
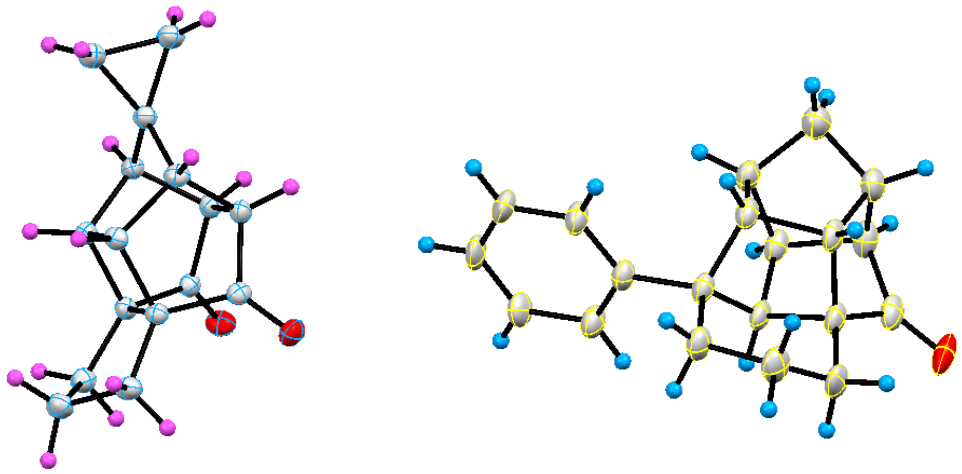
**Scheme 4. Synthesis of rearranged cage ketone's 6a, 6b and spiro cage dione 5c**



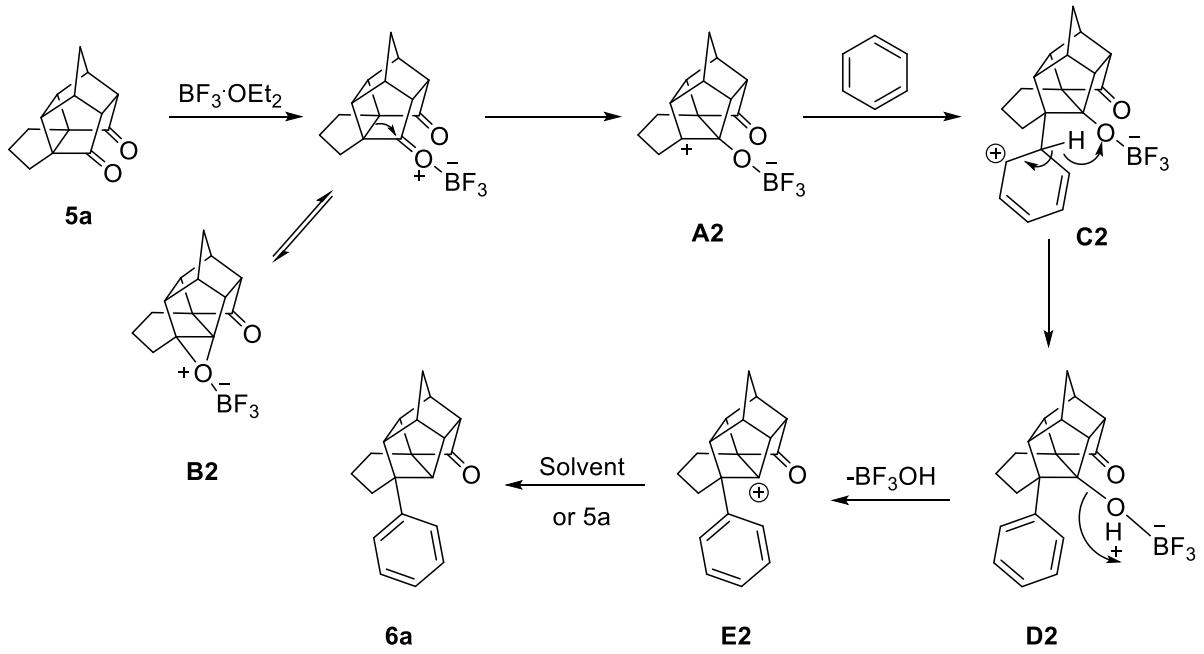
**5c** (CCDC 1481200) **6a** (CCDC 1481201)

**Figure 1**. Crystal structures of **5c** and **6a** with thermal ellipsoids drawn at the 50% probability level.

Based on previous literature reports,[14-16] we envisioned that hexa- as well as heptacyclic cage propellanediones **5a** and **5b** are useful candidates for carbocation rearrangements. Therefore, compounds **5a** and **5b** were treated with $BF_3{\cdot}OEt_2$ in dry benzene under reflux conditions to afford novel rearranged cage ketones **6a** and **6b** in a moderate to good yields. Along with

similar lines, compound **5c** was subjected to $BF_3{\cdot}OEt_2$ in dry benzene under reflux conditions and unfortunately, a complex mixture of products was obtained which could not be separated by column chromatography (Scheme 4). The structures of both these cage ketones **6a** and **6b** have been strongly confirmed by $^1H$ NMR, $^{13}C$ NMR, APT and HRMS data. Finally, the structure of ring-rearranged ketone **6a** was well established by single-crystal X-ray diffraction studies (Figure 1).[28]

**Scheme 5**. Plausible mechanism for the rearrangement of cage dione **5a** to **6a**




The proposed mechanism for the Lewis acid catalyzed rearrangement of cage dione **5a** with $BF_3.OEt_2$ is shown in Scheme 5. Initially, the Lewis acid attacks on the carbonyl group present in cage dione **5a**, and further migration of the cyclobutane bond in **5a** will generate carbocation intermediate **A2** which is trapped by the solvent (benzene) forms **C2**. Later aromatization followed by hydrogen transfer gives intermediate **D2**. Finally, elimination of $BF_3OH$ from **D2** will produce carbocation **E2** which on hydride transfer from **5a** (or from solvent) generates the rearranged product **6a** (Scheme 5).

Variation in results obtained from **1** and **5a-b** (Scheme 1) is attributed to the difference in flexibility and strain of the fused rings such as cyclohexane and cyclopentane rings. The migratory modes of propellane frame works might be influenced by their ring size as well as the presence of an incoming nucleophile. Since the six-membered ring in **1** is more flexible than the five-membered ring in **5a-b** and less strain involved in the cyclohexane ring more

favourable to formation of different products obtained from **1** such as **2, 3** and **4** (Scheme 1, eq. 1).

In case of **5a-b** such feasibility is not involved due to size of the fused ring. Because of less flexibility as well as more strain in **5a-b** causes the formation of exclusive rearranged product **6a-b** where solvent has been incorporated (Scheme 1, eq. 2). This is due to the reason where carbocation has formed immediately trapped by the solvent and does not accesses to the any other rearranged products. This approach has provided a new synthetic strategy to interesting and unusual cage systems.

## Conclusion

In summary, we have successfully demonstrated a concise and efficient synthetic route to various functionalized cage [4.3.2]propellanediones **5a**, **5b**, **5c** and rearranged cage ketones **6a** and **6b** from commercially available 2,5-dimethoxybenzaldehyde. Interestingly, solvent incorporation was observed in cage propellane framework during Lewis acid promoted carbocation rearrangement. This rearrangement strategy opens up new opportunities to create novel cage frameworks that are difficult to prepare via direct synthetic methodologies. Further studies to assemble other interesting functionalized caged systems will be reported in due course.

## Experimental Section

### General Experimental Details

All the required reagents, chemicals and solvents were purchased from the commercial grade and used as without any further purification. Analytical TLC was performed on (10×5) glass plates coated with Acme's silica gel (GF-254) containing 13% calcium sulfate as a binder. All the reactions were monitored by TLC using suitable solvent system and visualization was done under UV light, exposure to iodine vapour and by dipping in to a solution of $KMnO_4$. Dry reactions were performed in oven dried glassware under nitrogen atmosphere by using standard syringe-septum techniques. Acme's silica gel (100-200 mesh size) and neutral alumina was used for column chromatography and solvents were concentrated at vacuo on rotary evaporator. Benzene, Toluene, DCM were distilled from $P_2O_5$, $CaH_2$ and ethyl acetate was dried by using $K_2CO_3$.

IR spectra were collected on a Nicolet Impact-400 FTIR spectrometer and samples were prepared as a thin film between CsCl plates by dissolving the compound in DCM and chloroform and then evaporating the solvent. $^{1}$H NMR (400 and 500 MHz), $^{13}$C, $^{13}$C-APT NMR (100 and 125 MHz) spectra were recorded on Bruker spectrometer and samples were made in chloroform-d solvent. The chemical shifts are reported in parts per million (ppm) on delta scale with TMS as an internal standard and values for the coupling constants (*J*) are given in Hz. The standard abbreviations for $^{1}$H NMR spin couplings are given as s, d, t, q, dd, dt, td, and m for singlet, doublet, triplet, quartet, doublet of doublet, doublet of triplet, triplet of doublet and multiplet respectively. High-resolution mass spectra (HRMS) were recorded in a positive ion electrospray ionization (ESI). All melting points were recorded on veego VMP-CMP melting point apparatus and are uncorrected. Whatever all reported yields are isolated yields of the products after column purification. X-ray data were recorded on diffractometer equipped with graphite monochromated Mo Kα radiation and structure was solved by direct methods shelxl-97 and refined by full-matrix least-squares against $F^2$ using shelxl-97 software. Dihydroindanedione **7**[22] and spiro dienes **15**[25] and **16**[24] were prepared according to known literature procedures.

**Synthesis of Diels–Alder adduct 17**

A solution of dihydroindanedione **7** (500 mg, 3.37 mmol) in methanol (10 mL) was cooled in an ice-water bath at 0 ºC and freshly cracked cyclopentadiene **14** (0.3 mL, 3.54 mmol) was added dropwise manner. Then, the resulting reaction mixture was stirred at same temperature until all the starting material was consumed. After conclusion of the reaction (2 h, TLC monitoring), the solvent was evaporated under reduced pressure and the crude residue was directly purified by silica gel column chromatography without any further workup by using 5% ethyl acetate/petroleum ether as an eluent which afforded Diels–Alder adduct **17** as a pure pale yellow solid. Yield 84% (610 mg); m.p. 97-99 °C; IR (neat, cm$^{-1}$) 2932,1660; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.00 (s, 2H), 3.50 (s, 2H), 3.23 (s, 2H), 2.72-2.60 (m, 4H), 1.97-1.89 (m, 2H) 1.53, 1.43 (ABq, $J$ = 8.0 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 197.9, 155.2, 135.0, 50.7, 49.2, 48.6, 31.0, 21.5 ppm; HRMS (ESI) m/z calcd for $C_{14}H_{14}NaO_2$ $[M + Na]^+$ 237.0888; found: 237.0886.

**Synthesis of hexacyclic cage propellanedione 5a:**

The Diels–Alder adduct **17** (300 mg, 1.39 mmol) was dissolved in dry ethyl acetate (350 mL) and irradiated in a pyrex immersion well by using 125W medium pressure UV mercury-vapour lamp (Home-made) for 2 h under continuous flow of nitrogen at room temperature. After completion of the reaction (TLC monitoring), then the solvent was evaporated under reduced pressure and the crude residue was directly subjected to silica gel column chromatography by using 10% ethyl acetate/petroleum ether as an eluent which afforded **5a** as a pure white crystalline solid. Yield 93% (280 mg); m.p. 142-144 °C; IR (neat, $cm^{-1}$) 2963, 2869, 1741, 1728, 1450, 1218, 1023; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 2.92 (m, 2H), 2.67 (m, 4H), 2.02-1.97 (m, 2H), 1.92-1.84 (m, 2H), 1.79-1.72 (m, 2H), 1.52 (d, $J$ = 5.9 Hz, 1H), 1.50 (d, $J$ = 6.1 Hz, 1H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 212.6, 60.7, 55.2, 44.2, 41.1, 40.7, 27.2, 26.6 ppm; HRMS (ESI) m/z calcd for $C_{14}H_{14}NaO_2$ $[M + Na]^+$ 237.0886; found: 237.0882.

**Synthesis of Diels–Alder adduct 19**

A solution of dihydroindanedione **7** (200 mg, 1.35 mmol) in dry benzene was added to freshly made spiro[2.4]hepta-4,6-diene **16** (220 mg, 2.43 mmol) with stirring. Then the resulting reaction mixture was refluxed for overnight. At the end of the reaction (TLC monitoring), the solvent was removed under vacuo and the crude reaction mixture was directly subjected to silica gel column chromatography without any further workup by using 5% ethyl acetate/petroleum ether as an eluent to give the Diels–Alder adduct **19** as a pure light yellow crystalline solid. Yield 67% (220 mg); m.p. 119-122 °C; IR (neat, $cm^{-1}$) 2989, 2955, 1657, 1427, 1391, 1320, 1103, 702 ; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 6.09 (m, 2H), 3.40 (s, 2H), 2.86 (s, 2H), 2.70-2.64 (m, 4H),1.94-1.91 (m, 2H), 0.58-0.48 (m, 4H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 197.8, 155.6, 135.2, 53.6, 51.7, 45.1, 31.1, 21.6, 8.1, 7.1 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{16}NaO_2$ $[M + Na]^+$ 263.1043; found: 263.1047.

**Synthesis of heptacyclic cage propellanedione 5c**

The Diels–Alder adduct **19** (200 mg, 0.83 mmol) was dissolved in dry ethyl acetate (350 mL) and irradiated in a pyrex immersion well by using 125W medium pressure UV mercury-vapour lamp (Home-made) for 3 h under continuous flow of nitrogen at room temperature. After conclusion of the reaction (TLC monitoring, 2 h) the solvent was evaporated under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography using 8% ethyl acetate/petroleum ether as an eluent which afforded **5c** as a white crystalline solid. Yield 89% (178 mg); m.p. 176-178 °C; IR (neat, $cm^{-1}$) 2955, 1742, 1264, 1217, 1181; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 2.90-2.86 (m, 4H), 2.27-2.26 (m, 2H), 2.05-1.91 (m, 2H), 1.80

(td, $J$ = 13.0, 6.9 Hz, 2H), 1.56-1.53 (m, 2H), 0.73-0.63 (m, 4H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 212.5, 61.3, 55.7, 49.9, 41.5, 37.3, 27.3, 26.8, 5.5, 4.2 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{16}NaO_2$ $[M + Na]^+$ 263.1043; found: 263.1043.

**Synthesis of Diels–Alder adduct 18**

A solution of dihydroindanedione **7** (300 mg, 2.14 mmol) in dry toluene was added to freshly made spiro[4.4]nona-1,3-diene **15** (460 mg, 3.85 mmol) with stirring and this was kept refluxed for overnight. At the end of the reaction (TLC monitoring), the solvent was removed under vacuo and the crude reaction mixture was directly purified by silica gel column chromatography without any further workup by using 5% ethyl acetate/petroleum ether as an eluent to furnish the Diels–Alder adduct **18** as a pure pale yellow crystalline solid. Yield 61% (350 mg); m.p. 122-124 °C; IR (neat, cm$^{-1}$) 2949, 1659, 1429, 1391, 1319, 704; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 5.97 (m, 2H), 3.30-3.29 (m, 2H), 3.06 (s, 2H), 2.66-2.62 (m, 4H),1.93-1.88 (m, 2H), 1.58-1.41 (m, 8H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 198.3, 155.4, 135.7, 69.1, 56.1, 50.8, 31.9, 31.6, 30.9, 25.8, 25.3, 21.4 ppm; HRMS (ESI) m/z calcd for $C_{18}H_{20}NaO_2$ $[M + Na]^+$ 291.1356; found: 291.1355.

**Synthesis of heptacyclic cage propellanedione 5b**

The Diels–Alder adduct **18** (300 mg, 1.11 mmol) was dissolved in dry ethyl acetate (350 mL) and irradiated in a pyrex immersion well by using 125W medium pressure UV mercury-vapour lamp (Home-made) for 2 h under continuous flow of nitrogen at room temperature. After conclusion of the reaction (TLC monitoring, 2h), the solvent was evaporated under reduced pressure and the crude residue was directly purified by silica gel column chromatography without any workup by using 10% ethyl acetate/petroleum ether as an eluent which afforded **5b** as a white crystalline solid. Yield 95% (285 mg); m.p. 157-159 °C; IR (neat, cm$^{-1}$) 2949, 2328, 1740, 1723, 1263, 1217; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 2.81-2.77 (m, 4H), 2.47 (m, 2H), 2.02-1.85 (m, 2H), 1.78 (td, $J$ = 12.3, 6.5 Hz, 2H), 1.66-1.50 (m, 10H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 212.4, 64.6, 60.4, 55.0, 51.9, 41.3, 32.1, 28.6, 27.2, 26.8, 25.7,25.5 ppm; HRMS (ESI) m/z calcd for $C_{18}H_{20}NaO_2$ $[M + Na]^+$ 291.1356; found: 291.1351.

**$BF_3$.$OEt_2$-Promoted rearrangement of cage dione 5a**

Cage dione **5a** (150 mg, 0.69 mmol) was added to a stirred solution of distilled $BF_3{\cdot}OEt_2$ (1 mL) in dry benzene (10 mL) at room temperature. Then, the resulting reaction mixture was refluxed for 36 h. After completion of the reaction by TLC analysis, the reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution and this was extracted with benzene. The combined organic layer was washed with water, brine solution and dried over anhydrous $Na_2SO_4$. After removal of the solvent under vacuo, the resulting crude residue was subjected to silica gel column chromatography by using 3% ethyl acetate/petroleum ether as an eluent to give the desired rearranged caged molecule with a phenyl group **6a** as a colourless liquid, which is solidified as a white crystalline solid in the refrigerator upon storage for overnight in hexane solvent. Yield 47% (90 mg); m.p. 112-114 °C; IR (neat, $cm^{-1}$) 2942, 1759, 1217, 702, 666, 614; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.35-7.20 (m, 5H), 2.60-2.59 (m, 1H), 2.55 (q, *J* = 5.7 Hz, 1H), 2.49 (m, 1H), 2.38-2.36 (m, 1H), 2.21 (dd, *J* = 12.2, 4.7 Hz, 2H), 1.96-1.93 (m, 1H), 1.87 (dt, *J* = 4.0, 2.0 Hz, 1H), 1.72-1.66 (m, 2H), 1.59-1.44 (m, 4H), 1.31 (d, *J* = 10.5 Hz, 1H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 217.9, 147.4, 128.7, 126.7, 126.0, 58.2, 55.3, 53.1, 50.2, 49.3, 46.4, 44.0, 41.4, 40.4, 36.6, 35.2, 22.9, 21.2 ppm; HRMS (ESI) m/z calcd for $C_{20}H_{20}NaO$ $[M + Na]^+$ 299.1406; found: 299.1400.

**$BF_3.OEt_2$-Promoted rearrangement of cage dione 5b**

Cage dione **5b** (200mg, 0.74 mmol) was added to stirred solution of distilled $BF_3{\cdot}OEt_2$ (1 mL) in dry benzene (10 mL) at room temperature and the resulting reaction mixture was stirred at 90 ºC for 48 h. At the end of the reaction by TLC evident, the reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution and this was extracted with benzene. The combined organic layer was washed with water, brine solution and dried over anhydrous $Na_2SO_4$. After removal of the solvent under vacuo, the resulting crude reaction mixture was subjected to silica gel column chromatography by using 7 % ethyl acetate/petroleum ether as an eluent to afford the desired rearranged cage ketone **6b** as a pure colourless liquid, which is solidified as a white crystalline solid in the refrigerator upon storage for overnight in hexane solvent. Yield 60% (150 mg); m.p. 125-127 °C; IR (neat, $cm^{-1}$) 2952, 2925, 2864, 1742, 1459, 1376, 1218, 700; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.32-7.18 (m, 5H), 2.77-2.75 (m, 1H), 2.59-2.55 (m, 1H), 2.40 (td, *J* = 5.7, 1.5 Hz, 1H), 2.24 (dt, *J* = 5.5, 1.6 Hz, 1H), 2.08-2.00 (m, 2H), 1.94-1.91 (m, 1H), 1.87, 1.75-1.74 (m, 1H), 1.69-1.67 (m, 2H), 1.53-1.25 (m, 11H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 217.8, 147.5, 128.7, 126.9, 125.9, 58.1, 57.2, 55.8, 54.1, 53.0, 49.4, 49.1, 49.0, 44.8, 42.2, 36.8, 32.8, 26.3, 26.1, 22.9, 21.2 ppm; HRMS (ESI) m/z calcd for $C_{24}H_{26}NaO$ $[M + Na]^+$ 353.1876; found: 353.1871.

## Associated Content

### Supporting Information

Copies of NMR ($^{1}H$, $^{13}C$ & APT) spectra for all new compounds; X-ray crystallographic data (CIF files) for compounds **6a** and **5c**. This material is available free of charge via the internet at ……

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28. CCDC 1481200 (**5c**) and 1481201 (**6a**) contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ORTEPs of products **5c** and **6a**, please see the SI file.

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