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1,5-Disubstituted Cyclooctatetraenes

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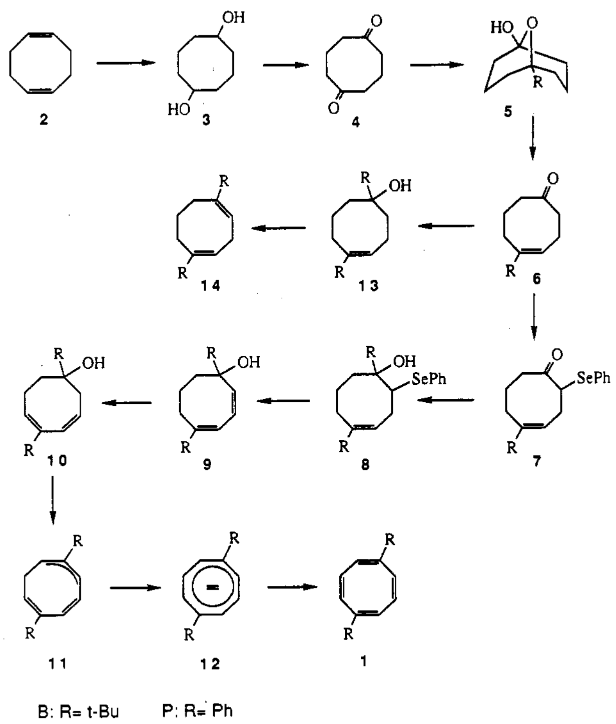
1,5-Di-*tert*-butylcyclooctatetraene (**1B**) and 1,5-diphenylcyclooctatetraene (**1P**) have been prepared from 1,5-cyclooctadiene in 10 steps and in 11% and 1% overall yield, respectively. An alternative route gave **1P** in 10% overall yield in eight steps, but this route was not effective for **1B**. Both pathways share a common appropriately substituted intermediate, 5-phenyl-9-oxobicyclo[3.3.1]nonan-1-ol, **5P**, and 5-*tert*-butyl-9-oxabicyclo[3.3.1]nonan-1-ol, **5B**. 1,1′,5,5′-Tetra-*tert*-butyluranocene prepared from **1B** was stable to water and substantially insensitive to air.

For many years cyclooctatetraene (COT) and compounds containing the COT ring have been the focus of theoretical interest as well as a source of synthetic challenge. Most of the synthetic work toward substituted COTs has been done to investigate the ring inversion and bond shift isomerization phenonema exhibited by these compounds.[1] Our interest has been in the preparation of substituted uranocenes and related actinide and lanthanide sandwich complexes.[2] These compounds are generally air sensitive, but the reaction with oxygen is slowed by the presence of bulky groups on the [8]annulene rings. The uranocene prepared from 1,3,5,7-tetraphenylcyclooctatetraene is particularly stable[3] and it was of interest to determine the effect of fewer bulky groups. In this paper we present a new route to 1,5-di-*tert*-butyl- and 1,5-diphenylcyclooctatetraenes, **1B** and **1P**, respectively.

Two methods have been used for the preparation of 1,5-disubstituted cyclooctatetraenes. 1,5-Dimethylcyclooctatetraene has been prepared by pyrolysis of bridgehead dimethylated semibullvalene,[4] in which the substituent methyl groups stem from the starting material biacetyl.[5] Accordingly, this route lacks generality and was considered to be inappropriate for the *tert*-butyl and phenyl substituents. The syntheses of 1,5-dicarbomethoxy-, 1-carbomethoxy-5-cyano-, and 1,5-dicyanocyclooctatetraenes have been reported in which the key step is a regioselective $({}_2\pi_s + {}_2\sigma_s + {}_2\sigma_s)$ addition of a monosubstituted acetylene to a substituted quadricyclanone. Thermal extrusion of carbon monoxide and carbocyclic rearrangement gave the 1,5-disubstituted cyclooctatetraenes in low yield.[6] This method also lacks generality because it appears to be limited to electron-attracting substituents.

Scheme I



The synthesis developed here starts with inexpensive commercially available 1,5-cyclooctadiene, **2**, and is outlined in Scheme I. Although the subsequent transformations make use of known reactions, the 8-membered ring provides conformation and proximity effects that make the sequence less straightforward and add significant interest. Hydroboration of **2** following Knights and Brown[7] gave 1,5-cyclooctanediol, **3**, which was oxidized with PCC to 1,5-cyclooctanedione, **4**, in 80% overall yield. The Rapoport group at Berkeley prepared **4** in the 60s by condensing 2 equiv of acrylonitrile with acetone followed by hydrolysis and decarboxylation of the resulting 4-cyano-5-iminocyclooctan-1-one.[8] The dione can also be prepared by Collins oxidation of the hemiketal, 9-oxabicyclo[3.3.1]nonan-1-ol (**15**; **5**, R = H).[9] The oxidation of **3** is not straightforward because of transannular interactions. Collins oxidation of **3** gave **4** and the hemiketal **15** in roughly equal amounts. Normal oxidation of **3** with PCC gave only **15**. The use of 7 equiv of PCC (3.5 equiv per alcohol functionality) and refluxing for 3 days in methylene chloride led to the desired dione in good yield. We also attempted to oxidize 9-BBN to the dione directly, using chromic acid in a manner similar to that reported by Brown and Garg[10] for the conversion of alkylboranes into ketones, but to our surprise, only cyclooctanone was isolated, in good purity and yield.

Treatment of **4** with *tert*-butyl- or phenyllithium reagents gave the 5-substituted 9-oxabicyclo[3.3.1]nonan-1-ol, **5**, in good yield. The presence of only five sp^3-hybridized

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(1) For leading references, see: Paquette, L. A.; Wang, T. Z. *J. Am. Chem. Soc.* **1988**, *110*, 3663, 8192. Paquette, L. A.; Gardlik, J. M.; McCullough, K. J.; Samodral, R.; DeLucca, G.; Ouellette, R. J. *Ibid.* **1983**, *105*, 7649.

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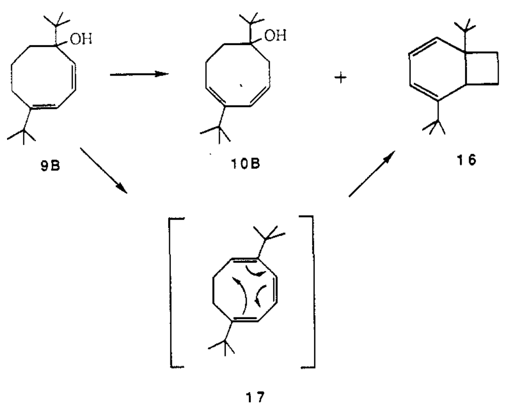
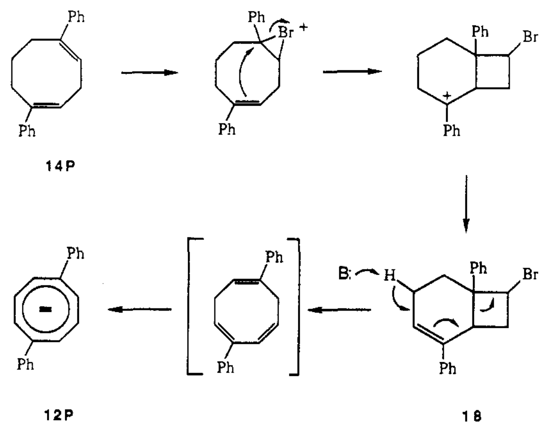
Scheme II



Scheme III



carbon resonances in the CMR spectrum of **5P** supports the structure, which possesses a mirror plane. The hemiketal alkoxide is stable and will not react with excess lithium reagent. Thus, further reaction required removing the ether link to free the carbonyl group. This approach also provided an opportunity to introduce the necessary third double bond.

Dehydration of **5** with small amounts of *p*-toluenesulfonic acid in benzene in a Dean–Stark apparatus gave the 5-substituted 4-cycloocten-1-one, **6**, in fair yield. Treatment of these unsaturated ketones with lithium diisopropylamide (LDA) followed by phenylselenyl bromide[11] gave the corresponding 2-phenylseleno compounds, **7**, after aqueous workup and chromatography. The yield of **7B** was satisfactory (75%), but that of **7P** was not (24%). In both cases only one isomer was formed, as evidenced by NMR data and subsequent chemistry. Molecular models of **6** show a hydrogen in the 2-position as being the most periplanar with the carbonyl carbon p orbital and should make the enolates leading to the observed products kinetically favored. An important difference between **6B** and **6P** is that **6P** is a styrene, which would be more subject to reduction and polymerization; a large amount of high molecular weight material accompanied the formation of **7P**.

The selenium compounds **7B** and **7P** were treated with *tert*-butyllithium and phenyllithium, respectively, to give the corresponding alcohols, **8**. The yield of **8B** was moderate (56%) whereas that of **8P** was poor (16%). The low yield of **8P** was again accompanied by much high molecular weight material. In both reactions very little of the starting ketones were recovered. As far as NMR spectroscopy could tell, both **8B** and **8P** were single diastereomers. Oxidation and elimination of the phenylseleno group[11] furnished the unsaturated alcohols **9** in good yields. A 180-MHz ^{1}H NMR spectrum of the *tert*-butyl compound, **9B**, shows an ABC pattern in the vinyl region, which suggests a conjugated diene system unsplit by sp^3 protons. The ultraviolet spectrum shows a λ_{max} of 228 nm; 1,3-cyclooctadiene also has λ_{max} = 228 nm.[12]

Attempted dehydration of **9B** with thionyl chloride/pyridine gave no hydrocarbon product. When **9B** was heated above 200 °C in another attempt at dehydration, it produced instead a mixture of 1,5-di-*tert*-butylbicyclo[4.2.0]-1,3-octadiene, **16**, and 1,5-di-*tert*-butyl-3,6-cyclooctadien-1-ol, **10b**; **16** probably arises by a six-electron cyclization of 1,5-di-*tert*-butyl-1,3,5-cyclooctatriene, **17**, formed by the dehydration of **9B** (Scheme II). The complete isomerization of the triene **17** into the bicyclic diene **16** is unusual because the parent unsubstituted 1,3,5-cycloootatriene is in equilibrium with only about 10% of bicyclo[4.2.0]octa-1,3-diene.[13] The preference for the bicyclo isomer in the *tert*-butyl case undoubtedly is due to a relaxation of steric compression. When **16** was treated with potassium amide, no color indicative of the formation of a COT dianion was observed. It was hoped that a small amount of **17** would be present in a mobile equilibrium with **16**; its deprotonation would then result in conversion of all of the material to the dianion.

Boiling **9B** or **9P** in toluene overnight gave the corresponding rearranged dienol **10** in quantitative yield. The isomeric dienols were cleanly dehydrated to mixtures of the corresponding disubstituted 1,3,5- and 1,3,6-cyclooctatrienes, **11**, by treatment with thionyl chloride and pyridine. Reaction of **11** with potassium amide in a mixture of tetrahydrofuran (THF) and liquid ammonia at −33 °C gave deeply colored solutions, which after treatment with iodine gave the desired 1,5-disubstituted cyclooctatetraenes **1**. The yield of **1B** was fair (70%), but **1P** was obtained in mediocre yield (39%). The use of sodium amide in THF at room temperature gave better results; a 70% yield of **1P** was obtained. The overall yield of **1B** was 11%, but that of **1P** was an unacceptable 1%.

An alternative route to **1B** was based on the known reaction of 1,5-cyclooctadiene with butyllithium and tetramethylethylenediamine (TMEDA) to give COT dianion.[14] Treatment of **6B** with *tert*-butyllithium gave 1,5-di-*tert*-butyl-4-cycloocten-1-ol, **13B**, as a low-melting solid. Dehydration gave a product, which did not give a COT dianion on treatment with butyllithium and TMEDA. Diene **14B** was allowed to react with *N*-bromosuccinimide (NBS) followed by base, but the products were viscous tars from which no characterizable hydrocarbon could be isolated. A different approach did work to prepare the phenyl analogue. 1,5-Diphenyl-1,4-cyclooctadiene, **14P**, prepared from **6P**, was treated with 1 equiv of bromine followed by reflux with excess sodium amide in THF to give a black solution from which **1P** was obtained in 35% yield on chromatography after treatment with iodine. The overall yield of **1P** was 10% from 1,5-cyclooctadiene using these steps.

When the bromine adduct of **14P** was treated with a solution of sodium hydroxide in methanol, a white crystalline solid was obtained. Analysis and mass spectroscopy showed the presence of only one bromine. The only structure that fits the NMR data is that of 1,5-di-

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phenyl-8-bromo-bicyclo[4.2.0]oct-4-ene, **18**. This product may be an intermediate in the conversion of diene **13P** into **1P** because **18** reacts with sodium amide to give black solutions from which 1,5-diphenylcyclooctatetraene was obtained. One rationalization (Scheme III) for the formation of **18** is that an initially formed bromonium ion is transannularly attacked by the double bond on the other side of the ring to give a benzylic cation that loses a proton to yield the observed product. Subsequent elimination with strong base could occur as shown in Scheme III to give a disubstituted cyclooctatriene, which is easily deprotonated to give 1,5-diphenylcyclooctatetraene dianion, **12P**.

Reduction of **1B** with potassium gave the dianion, which was treated with uranium tetrachloride to give the corresponding uranocene as black crystals melting without decomposition at 338–340 °C. The compound is stable to water or acetic acid in THF. Crystals could be exposed to air for 24 h with little effect. Some oxidation did occur because the exposed crystals would only partially dissolve and left brown material behind. Nevertheless, this behavior is far different from most uranocenes that decompose immediately on exposure to air.

Experimental Section

General. Unless otherwise noted all NMR spectra are in $CDCl_3$, ultraviolet spectra are in ethanol, and infrared spectra are on liquid films. Melting points are uncorrected. Combustion and mass spectral analyses were done at the Analytical Services Facility, College of Chemistry, UCB.

1,5-Cyclooctanedione (4). A solution of 250 mL of 1 M borane–THF complex in THF was cooled to 0 °C in a dried flask fitted with a condenser, dropping funnel, and nitrogen bubbler. To the cooled, nitrogen-filled apparatus was slowly added a mixture of 25 g (0.23 mmol) of 1,5-cyclooctadiene in 50 mL of THF. After addition was complete, the clear solution was refluxed for 1 h and allowed to cool. To this mixture was slowly added 50 mL of 3 M sodium hydroxide, followed by 50 mL of 30% hydrogen peroxide, which was added dropwise at a rate which caused the solution to reflux gently. The cloudy mixture was allowed to cool for 0.5 h and saturated with potassium carbonate. The layers were separated, and the aqueous phase was extracted with 200 mL of ether. The combined organic layers were dried over magnesium sulfate and evaporated to a clear tar. This product was dissolved in 1500 mL of methylene chloride in a flask equipped with a condenser and mechanical stirrer. To this was cautiously added 350 g (1.62 mol) of pyridinium chlorochromate (PCC) in small portions with stirring. The solution became black and was refluxed for 1 day. The black mixture was cooled and poured through a large column packed with silica in 1:1 ether–hexane. The column was rinsed with an additional liter of this solvent. The elutant was evaporated to a semisolid mass, which was distilled, bp 100 °C (0.15 Torr); the yield was 26 g (80%) of a white semisolid material. Recrystallization of a small amount of the material from a 2:1 ether–petroleum ether mixture gave crystals: mp 68.8–69.6 °C (lit.[8] mp 71–72 °C); ^{1}H NMR (60 MHz, δ ppm, CCl_4) 2.1 (m, 4 H), 2.4 (m, 8 H); UV λ_{max} 297 nm (ϵ 29.5, $CHCl_3$); IR 5.85 μm. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.68; H, 8.47.

5-Phenyl-9-oxabicyclo[3.3.1]nonan-1-ol (5P). To a solution of 16 g (0.114 mol) of 1,5-cyclooctanedione (4) in 500 mL of dry THF under N_2 was slowly added 65 mL (0.12 mol) of phenyllithium (1.85 M in pentane and ether). The mixture was stirred for 1 h and allowed to warm to room temperature. It was then quenched with 100 mL of ammonium chloride solution. Next, 200 mL of ether was added, and the yellow solution was washed with 200 mL of water followed by 100 mL of brine. The solution was dried with potassium carbonate, and the solvent was removed under vacuum to yield 23.2 g (93%) of tan crystals. A small amount was recrystallized from ether–hexane: ^{1}H NMR (60 MHz) δ 1.2–2.6 (m, 12 H), 3.4 (s, 1 H), 7.0–7.6 (m, 5 H); IR 3400 cm^{-1}; mass spectrum, *m/z* (rel intensity) 218 (M^+, 37.85), 120 (100), 105 (62.88), 77 (28.34); ^{13}C NMR 149, 127, 126, 123, 95, 78, 35.5, 35.3, 21. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.17; H, 8.31.

An analogous procedure with 4.2 g (30 mmol) of **4** and 23 mL of 1.9 M *tert*-butyllithium in pentane gave 5.5 g (93%) of 5-*tert*-butyl-9-oxabicyclo[3.3.1]nonan-1-ol, **5B**, as a semicrystalline solid. One sample crystallized: mp 79.5–81.0 °C; ^{1}H NMR (60 MHz, δ CCl_4), 1.9 (s, 9 H), 1.1–1.5 (m, 8 H), 1.5–1.9 (m, 4 H), 2.35 (broad s, 1 H); IR (CCl_4) 2.81, 2.94, 3.41 μm; mass spectrum, *m/z* (rel intensity) 198 (M^+, 9.3), 170 (17), 155 (19), 141 (59), 113 (71), 97 (48), 95 (54), 83 (85), 71 (70), 57 (79), 41 (100).

5-Phenyl-4-cycloocten-1-one (6P). A mixture of 23.15 g (0.106 mol) of **5P** and 2 g of toluenesulfonic acid in 1.5 L of benzene was refluxed for 2 h in a flask fitted with a Dean–Stark trap and condenser. About half of the solvent was removed from the cooled deep blue solution. The remaining portion was mixed with 500 mL of ether and filtered through a 5 × 25 cm column of silica gel wetted with a 1:1 mixture of hexane and ether. The column was rinsed with an additional 1 L of this same solvent. The combined organic elutant was treated with 2 mL of triethylamine and evaporated to a dark yellow oil, which was distilled in a Kugelrohr apparatus at 100 °C (1 Torr) to give 16.37 g (77% yield) of a light yellow odorless oil: ^{1}H NMR (60 MHz) δ 1.7–2.0 (m, 2 H), 2.4–2.7 (m, 8 H), 5.8–6.2 (m, 1 H), 7.1 (s, 5 H); ^{13}C NMR (ppm) 213, 142, 141, 127, 126, 125, 47, 40, 29.5, 23.2, 23.0; IR 1700 cm^{-1}; mass spectrum, *m/z* (rel intensity) 200 (100), 185 (13.42), 171 (42.0), 143 (55.51), 129 (88.28), 115 (76.22), 91 (47.74), 77 (31.21). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.64; H, 8.02.

A similar procedure with 9 g of **5B** gave 5.3 g (66%) of **6B**: bp 100 °C (0.1 Torr); ^{1}H NMR (CCl_4, 60 MHz, δ) 1.05 (s, 9 H), 1.4–2.0 (m, 4 H), 2.1–2.5 (m, 6 H), 5.45 (m, 1 H); IR 5.85 1 μm (neat); mass spectrum, *m/z* (rel intensity) 180 (M^+, 27), 156 (10), 152 (21), 147 (18), 137 (15), 123 (53), 106 (68), 95 (50), 81 (44), 67 (41), 57 (50), 55 (51), 51 (100).

2-(Phenylseleno)-5-phenyl-4-cycloocten-1-one (7F). A solution of lithium diisopropylamide was prepared by adding 24.5 mL (42 mmol) of 1.72 M butyllithium in pentane to 6.44 mL (4.64 g, 46 mmol) of diisopropylamine in 200 mL of dry THF under argon at −78 °C. The solution was stirred for 20 min, and 7 g (35 mmol) of **6P** dissolved in 15 mL of THF was added slowly. The solution was stirred for 15 min, during which time it turned green. To this was quickly added a mixture of 6.58 g (21 mmol) of diphenyl diselenide and 1.1 mL (3.43 g, 21 mmol) of bromine in 10 mL of dry THF. The black phenylselenyl bromide solution was decolorized as rapidly as it was added, resulting in a yellow solution, which was immediately quenched with 50 mL of saturated ammonium chloride solution. The mixture was allowed to warm to room temperature, and 100 mL of ether was added. The resulting two-phase mixture was separated, and the organic layer was washed successively with 1 N HCl, saturated sodium bicarbonate, and brine. The yellow solution was dried over potassium carbonate and evaporated to an orange oil having a strange odor. The crude product, 7 g, was chromatographed on silica eluted with a 5:1 mixture of hexane and ether. The first fraction was 3 g of diphenyl diselenide. The last fraction was 3.0 g of the desired product contaminated with an unknown substance: ^{1}H NMR (250 MHz) δ 2.2–2.4 (m, 2 H), 2.5–2.7 (m, 4 H), 2.7–3.0 (dt, $J = 10, 3$, 1 H), 3.0–3.2 (dt, $J = 12, 3$, 1 H), 3.8–4.0 (dd, $J = 12, 4.5$, 1 H), 5.7–6.0 (dd, $J = 10, 3$, 1 H), 7.1–7.6 (m, 10 H); ^{13}C NMR (25 MHz, ppm) 208.5, 143, 142.7, 134.6, 134.3, 129, 128.6, 128.4, 128.1, 127.1, 125, 54.5, 37.7, 31, 29.5, 24.7; both spectra also had small peaks due to the impurity; IR 1690 cm^{-1}; mass spectrum, *m/z* (rel intensity) 356 (6.17), 314 (1.93), 279 (1.15), 199 (23), 157 (13.7), 155 (15), 105 (28.5), 91 (58), 77 (36.5); high-resolution mass spectrum (HRMS) calcd for $C_{20}H_{20}OSe$ 356.0679, found 356.0680.

A similar procedure was applied to 1 g (5.6 mmol) of **6B** to give 1.4 g (75%) of **7B** as a light yellow oil: ^{1}H NMR (60 MHz) δ 1.0 (s, 9 H), 1.8–3.3 (m, 8 H), 3.5–3.8 (dd, $J = 12, 7.5$, 1 H), 5.2–5.65 (dd, $J = 8.5, 10$, 1 H), 7.0–7.5 (m, 5 H); ^{13}C NMR (25 MHz, ppm) 151.3, 134.1, 129.0, 128.3, 127.8, 119.1, 53.9, 37.6, 36.7, 28.9, 27.2, 25.9, 9.4 (carbonyl carbon not seen); IR 1700 cm^{-1}; mass spectrum, *m/z* (rel intensity) 336 (3.64), 334 (1.67), 179 (16.65), 123 (16.75), 121 (17.32), 57 (100). Anal. Calcd for $C_{18}H_{24}OSe$: C, 64.47; H, 7.21. Found: C, 64.88; H, 7.38.

1,5-Diphenyl-2-(phenylseleno)-4-cycloocten-1-ol (8P). To a solution of 3 g (8.5 mmol) of **7P** in 200 mL of dry THF cooled under N_2 to −78 °C was slowly added 4.5 mL (8.5 mmol) of 1.89 M phenyllithium in an ether–pentane mixture. The solution was stirred, allowed to warm to room temperature, and quenched with 50 mL of ammonium chloride solution. After addition of 100 mL of ether the layers were separated, and the organic phase was washed with water and brine. The resulting yellow solution was dried over potassium carbonate and evaporated to give 4 g of a yellow oil, which was dissolved in a mixture of hexane and ether and allowed to stand at room temperature for a week to yield 600 mg (16%) of white solid. A small amount was recrystallized from a hexane–ether mixture, yielding tan crystals: mp 160 °C; ^1H NMR (250 MHz) δ 1.7–1.9 (m, 1 H), 1.0–2.2 (m, 2 H), 2.2–2.4 (m, 1 H), 2.6–3.0 (m, 4 H), 4.0 (dd, J = 3.3, 7.9, 1 H), 6.3–6.4 (t, J = 8, 1 H), 7.1–7.5 (m, 15 H); mass spectrum, m/z (rel intensity) 434 (M^+, 7.64), 277 (39.35), 259 (28.8), 157 (100), 105 (97.18), 91 (87.71), 77 (71.82). Anal. Calcd for $C_{26}H_{26}OSe$: C, 72.05; H, 6.05. Found: C, 71.67; H, 6.22.

A similar procedure using 0.4 g (1.4 mmol) of **7B** gave **8B** as a yellow oil that was chromatographed on a silica column eluted with a 2:1 mixture of hexane–ether to give 262 mg (56%) of an oil which crystallized to a yellow solid on standing: ^1H NMR (60 MHz) δ 1.1 (s, ca. 16 H), 1.5–2.8 (br m, ca. 13 H; probably includes impurities), 3.8–4.0 (dd, 1 H), 5.6–6.0 (m, 1 H), 7.1–7.8 (m, 5 H); ^{13}C NMR (25 MHz, ppm) 138.9, 124.6, 122.1, 120.1, 188.6, 113.8, 79.5, 59.6, 46.9, 43.5, 42.0, 39.3, 36.9, 36.3, 35.7, 34.1; IR 3500 cm^{-1}; mass spectrum, m/z (rel intensity) 394 (2.67), 392 (1.47), 337 (1.35), 317 (0.97), 259 (1.53), 237 (5.34), 57 (100). Anal. Calcd for $C_{22}H_{34}OSe$: C, 67.16; H, 8.71. Found: C, 67.49; H, 8.89.

1,5-Diphenyl-2,4-cyclooctadien-1-ol (9P). A solution of 760 mg of **8P** in 200 mL of methanol and 10 mL of water was treated with 0.5 g of sodium bicarbonate, which did not all dissolve. The mixture was stirred, and 750 mg of sodium periodate (3.5 mmol) was added in small portions. The cloudy white mixture was stirred for 24 h, but TLC revealed the presence of starting mateial. An additional 750 mg of sodium periodate was added, and TLC showed that the starting material was gone after 1 h. The mixture was poured into 100 mL of hexane and extracted twice with 100-mL portions of water. The clear colorless solution was washed with 60 mL of brine and dried over potassium carbonate. The solution was evaporated to a light yellow oil and chromatographed on silica eluted with a 6:1 mixture of hexane and ether. The yield was 480 mg (99%) of an odorless colorless liquid: ^1H NMR (250 MHz) δ 1.3–1.5 (m, 1 H), 1.7–2.35 (m, 4 H), 2.6–2.8 (m, 2 H), 5.6–5.7 (d, J = 12.4, 1 H), 5.9–6.1 (dd, J = 12.4, 5, 1 H), 6.5 (d, J = 5, 1 H), 7.0–7.7 (m, 10 H); UV λ_{max} 286 nm (EtOH, ϵ = 12500); mass spectrum, m/z (rel intensity) 276 (M^+, 6.35), 258 (7.08), 156 (28.47), 177 (100), 105 (39), 91 (42.64), 77 (33.25); HRMS calcd for $C_{20}H_{20}O$ 276.1514, found 276.1527.

1,5-Di-*tert*-butyl-2,4-cyclooctadien-1-ol (9B). A mixture of 100 mg (0.25 mmol) of **8B**, 200 mg of sodium bicarbonate, 50 mL of THF, and 3 mL of water and cooled to 0 °C with stirring. To this was slowly added 3 mL of 30% hydrogen peroxide. The mixture was allowed to warm, stirred overnight, and then poured into a separatory funnel, which contained a mixture of 20 mL of water and 60 mL of ether, shaken, and separated. The organic phase was washed successively with two 60-mL portions of water and one 60-mL portion of brine. The clear colorless solution was dried over magnesium sulfate and evaporated to a cloudy oil. The residue was chromatographed on a silica column eluted with a 2:1 mixture of hexane and ether, which resulted in a yield of 58 mg (97%) of a clear oil. ^1H NMR (180 MHz) δ 0.95 (s, 9 H), 1.1 (s, 9 H), 1.2–2.5 (m, 7 H), 5.7 (d, J = 12, 1 H), 5.8 (dd, J = 12, 3, 1 H), 6.0 (d, J = 3, 1 H); ^{13}C NMR (25 MHz) ppm 150.8, 134.2, 126.3, 120.1, 77.7, 38.9, 36.6, 29.3, 27.8, 27.0, 25.1, 21.0; IR 3500 cm^{-1}; mass spectrum, m/z (rel intensity) 236 (1.77), 218 (4.71), 203 (2.57), 179 (59.68), 57 (100); UV λ_{max} 228 nm (ϵ = 5800); HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2147.

When about 50 mg of **9B** was heated without solvent at 200 °C for 30 min, the sample turned brown, and TLC revealed the presence of two products, one polar (1,5-di-*tert*-butyl-3,5-cyclooctadien-1-ol, **10B**) and one nonpolar, which was isolated by filtering the sample through a silica column eluted with hexane. About 20 mg of 1,5-di-*tert*-butylbicyclo[4.2.0]octa-1,3-diene, **16**, was isolated as a clear colorless oil: ^1H NMR (250 MHz) δ 0.82 (s, 9 H), 1.0 (s, 9 H), 1.65–1.8 (m, 1 H), 1.8–1.9 (m, 1 H), 1.95–2.1 (quintet, J = 9.7, 1 H), 2.2–2.4 (quartet, J = 9.0, 1 H), 3.0–3.1 (t, J = 9.1, 1 H), 5.5–5.6 (m, 2 H), 5.9–6.0 (dd, J = 5.7, 9.8, 1 H). Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.93; H, 11.98.

1,5-Diphenyl-3,5-cyclooctadien-1-ol (10P) and 2,6-Diphenyl-1,3,6-cyclooctatriene + 1,5-Diphenyl-1,3,5-cyclooctatriene (11P). A solution of 500 mg (1.8 mmol) of **9P** in 100 mL of toluene was refluxed for 36 h. The solvent was removed from the cooled solution, resulting in 500 mg of **10P** as a white solid: mp 108 °C; ^1H NMR (250 MHz) δ 1.6–2.2 (m, 3 H), 2.3–2.6 (m, 2 H), 2.6–2.8 (m, 2 H), 6.0–6.2 (m, 1 H), 6.3–6.6 (m, 2 H), 7.2–7.6 (m, 10 H); UV λ_{max} 254 nm, (EtOH, ϵ = 12000).

To a solution of 350 mg (1.27 mmol) of **10P** in 100 mL of dry ether under N_2 at 0 °C was added 2 mL of pyridine followed by 0.2 mL of thionyl chloride. The cloudy mixture was stirred for 1 h, and another 0.2 mL of thionyl chloride was added. The mixture was separated, and the yellow organic phase was washed with 100 mL of water followed by 60 mL of brine. The solution was dried over potassium carbonate and evaporated to a yellow oil. This oil was chromatographed on silica eluted with hexane, resulting in 200 mg (60% yield) of a clear oil: ^1H NMR (250 MHz) δ 2.7–2.9 (m, 2 H), 3.0–3.1 (t, J = 6.8, 1 H), 3.1 (d, J = 7.7, 1 H), 5.8–6.1 (m, 2 H), 6.2 (m, 1 H), 6.3 (t, J = 6.7, 0.5 H), 6.5 (d, J = 9.9, 0.5 H), 7.2–7.6 (m, 10 H); mass spectrum, m/z (rel intensity) 258 (M^+, 26.78), 230 (100), 154 (42.06), 105 (36.47), 91 (24.78), 77 (23.35); HRMS calcd for $C_{20}H_{18}$ 258.1409, found 258.1401.

1,5-Di-*tert*-butyl-3,5-cyclooctadien-1-ol (10B) and 2,6-Di-*tert*-butyl-1,3,6-cyclooctatriene + 1,5-Di-*tert*-butyl-1,3,5-cyclooctatriene (11B). A solution of 70 mg of **9B** in 40 mL of toluene was refluxed overnight. The solvent was removed, yielding 70 mg of **10B** as a colorless oil: ^1H NMR (250 MHz) δ 0.94 (s, 9 H), 1.04 (s, 9 H), 1.2–1.4 (m, 3 H), 1.8–1.95 (dd, J = 7.2, 12.6, 1 H), 5.6 (t, J = 7.9, 1 H), 5.7–5.8 (m, 1 H), 6.2 (d, J = 10.8, 1 H); mass spectrum, m/z (rel intensity) 236 (3.17), 218 (1.46), 203 (1.27), 179 (31.7), 57 (100); UV λ_{max} 206 nm (ϵ = 5800).

To a solution of 200 mg (90.85 mmol) of **10B** in 150 mL of dry ether and 2 mL of pyridine at 0 °C under nitrogen was added 0.2 mL of thionyl chloride slowly and dropwise. The mixture developed a white precipitate immediately and was stirred for 0.5 h. A small amount of water was added, along with 60 mL of hexane. The mixture was washed successively with 2 60-mL portions of water and one portion of brine. The clear solution was dried over magnesium sulfate and evaporated. The residue was chromatographed on a silica column eluted with hexane to give 140 mg (75%) of **11B** as a clear oil: ^1H NMR (250 MHz) δ 1.03 (s, 9 H), 1.07 (s, 9 H), 3.6–3.7 (m, 4 H), 5.2 (t, J = 7.4, 1 H), 5.5 (m, 2 H), 6.3 (d, J = 10.1, 1 H); mass spectrum, m/z (rel intensity) 218 (8.96), 203 (6.01), 190 (10.71), 175 (68.25), 161 (31.75), 57 (100); Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 88.00; H, 12.08.

1,5-Di-*tert*-butylcyclooctatetraene (1B). Into an oven-dried nitrogen-filled flask containing 1 mg of dry iron trichloride and fitted with a filled dry ice condenser cooled to −78 °C under positive argon pressure was introduced 30 mL of dry liquid ammonia. Next, 120 mg of potassium (3 mmol) was added, and the resultant blue solution was allowed to warm until it became gray. To this was added 10 mL of dry THF followed by a solution of 100 mg (0.145 mmol) of **11B** in 10 mL of THF. The mixture slowly turned orange, and the ammonia was allowed to evaporate. To the resulting green solution was cautiously added 0.5 g of iodine (NOTE: such a mixture should not be allowed to evaporate to dryness, because the explosive nitrogen triiodide would undoubtedly be formed). The brown mixture was poured into 100 mL of saturated sodium thiosulfate and extracted with 100 mL of hexane. The organic phase was washed with 60 mL of water and 60 mL of brine. The solution was dried over magnesium sulfate and evaporated. The residue was filtered through silica with hexane as the solvent, yielding 70 mg (70%) of a clear colorless oil: ^1H NMR (250 MHz) δ 1.04 (s, 18 H), 5.6 (d, J =2.5, 2 H), 5.8 (dd, J = 2.5, 11.5, 2 H), 5.9 (d, J = 11.5, 2 H); mass spectrum, m/z (rel intensity) 216 (16.52), 201 (28.01), 159 (90.99), 145 (79.37), 57 (100). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 89.01; H, 11.25.

1,5-Diphenyl-4-cycloocten-1-ol (13P). A solution of 15.5 g (77.5 mmol) of **6P** in 250 mL of dry THF was cooled to −78 °C under N_2, and 77 mL (138.5 mmol) of 1.8 M phenyllithium was added slowly. The clear brown solution was stirred for 1 h and was then quenched with 50 mL of saturated ammonium chloride solution. To this light yellow solution was added 200 mL of ether, the mixture was separated, and the organic phase was washed with 200 mL of water followed by 100 mL of brine. It was then dried over potassium carbonate and evaporated to a yellow oil, 21.1 g (98%): ^{1}H NMR (250 MHz) δ 1.6–1.8 (m, 1 H), 1.8–2.1 (m, 5 H), 2.2–2.4 (m, 2 H), 2.5–2.7 (m, 2 H), 2.8–3.0 (m, 1 H), 6.2 (t, J = 7, 1 H), 7.1–7.5 (m, 10 H); IR 3450 cm^{-1}; mass spectrum, m/z (rel intensity) 278 (33.72), 260 (78.47), 231 (32.81), 183 (2.76), 129 (76.11), 105 (100), 91 (97.92), 77 (68.19). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 85.95; H, 7.45.

1,5-Diphenyl-1,4-cyclooctadiene (14P). To a solution of 21 g (75.5 mmol) of **13P** in 1600 mL of dry ether at 0 °C under N_2 was added 20 mL of dry pyridine. Thionyl chloride was then added slowly (5 mL over 10 min), and the resulting cloudy white suspension was stirred for 16 h. The reaction mixture was quenched with 50 mL of water, and the layers were separated. The organic phase was washed with 1.2 M HCl and twice with saturated sodium bicarbonate. The yellow solution was washed with brine and dried over potassium carbonate. The solution was evaporated to a yellow oil and filtered through a silica column eluted with hexane. The solvent was evaporated, resulting in 13.6 g (69% yield) of a clear colorless oil: ^{1}H NMR (250 MHz) δ 1.6–1.8 (m, 2 H), 2.8 (t, J = 6.2, 4 H), 3.1 (t, J = 5.9, 2 H), 6.0 (t, J = 5.9, 2 H), 7.1–7.5 (m, 10 H); mass spectrum m/z (rel intensity) 260 (100), 232 (42.36), 156 (32.64), 128 (69.85), 91 (90.33), 77 (35.34). Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.42; H, 7.70.

1,5-Diphenylcyclooctatetraene (1P). From 11P. A suspension of 1 g of sodium amide in 200 mL of dry THF under argon was combined with 337 mg (1.3 mmol) of **11P**. The mixture was stirred for 2 days, during which time it gradually changed in color from light yellow to deep purple. The reaction was quenched by adding iodine until the mixture ceased to bubble. The red solution was poured into 100 mL of saturated sodium thiosulfate solution and extracted with 100 mL of hexane. The yellow organic phase was washed with 60 mL of brine and dried over potassium carbonate. The solvent was evaporated, and the residue was filtered through a short column of silica eluted with hexane. The yield was 250 mg (75%) of a yellow oil: ^{1}H NMR (250 MHz) δ 6.1–6.2 (d, J = 11.2, 2 H), 6.2–6.3 (dd, J = 11.2, 3.4, 2 H), 6.3–6.4 (d, J = 3.4, 2 H), 7.2–7.4 (m, 10 H); mass spectrum, m/z (rel intensity) 256 (M$^+$, 100), 230 (54.39), 178 (26.21), 154 (31.89), 115 (30.24), 91 (25.7), 77 (18.16). Crystals were obtained by dissolution of the oil in hexane and cooling, mp 95–96 °C. Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.41; H, 6.45.

From 14P. A solution of 500 mg (1.9 mmol) of **14P** in 100 mL of carbon tetrachloride was treated with 1.9 mL of 1 M bromine in carbon tetrachloride (1.9 mmol) over 5 min, and the solvent was then removed. The resulting brown oil was subjected to a 1-μm vacuum for 5 m, and 100 mL of dry THF was added. About 1 g of sodium amide was added, and the mixture was refluxed under argon for 2 days. The now black solution was cooled, and iodine was added until the solution no longer bubbled. The mixture was shaken with saturated sodium thiosulfate solution and with hexane. The layers were separated, and the yellow organic phase was washed with water and brine. The solution was dried over potassium carbonate and evaporated to an oily solid. This material was filtered through a short column of silica gel eluted with hexane. The solvent was evaporated to give 180 mg (36% yield) of **1P** identical with that obtained above.

1,5-Diphenyl-8-bromobicyclo[4.2.0]oct-4-ene (18). To a solution of 3.31 g (12.7 mmol) of **14** in 400 mL of carbon tetrachloride was added 0.66 mL (13 mmol) of bromine dropwise over 20 min. The bromine was decolorized as it was added. The resulting yellow solution was evaporated, and the brown solid was subjected to high vacuum. This material was dissolved in 200 mL of methanol, and a few sodium hydroxide pellets were added. The solution was stirred overnight and then poured into 500 mL of water. The cloudy solution was extracted twice with hexane, and the combined organic layers were washed with 100 mL of brine and dried over magnesium sulfate. The solution was filtered and evaporated to about 40 mL in volume. Chilling of this solution gave 1.1 g (25% yield) of brown rocky crystals. This material was recrystallized from hexane to give white needlelike crystals: mp 119 °C; ^{1}H NMR (250 MHz) δ 1.8 (m, 1 H), 2.0 (m, 1 H), 2.2–2.4 (m, 2 H), 3.0 (dt, J = 7.9, 9, 1 H), 3.3 (t, J = 8.6, 1 H), 4.7 (t, J = 8, 1 H), 7.4 (d, J = 6, 1 H), 7.12–7.6 (m, 10 H); ^{13}C NMR (25 MHz) ppm 148.1, 140.0, 138.2, 128.4, 128.3, 127.2, 126.5, 125.9, 124.7, 51.4, 51.0, 39.4, 38.4, 31.2, 21.7; mass spectrum, m/z (rel intensity) 340 (9.17), 338 (8.83), 259 (26.98), 232 (100), 154 (39.42), 91 (93.61), 77 (61.64). Anal. Calcd for $C_{20}H_{19}Br$: C, 70.81; H, 5.64. Found: C, 70.70; H, 5.64.

Bis(1,5-di-*tert*-butyl[8]annulene)uranium(IV). Commercial uranium tetrachloride (Alfa) was purified by refluxing in thionyl chloride for 24 h, removing the thionyl chloride under high vacuum, dissolving in THF under inert atmosphere, filtering, and evaporating the solvent. To a solution of 360 mg (1.66 mmol) of **1B** in 200 mL of dry THF under argon was added 200 mg (5.1 mmol) of clean potassium. The mixture was stirred overnight, and the unreacted potassium was removed mechanically. To the resulting green solution was added 313 mg (0.83 mmol) of purified uranium tetrachloride. After stirring the dark solution for 1 h the solvent was removed by vacuum transfer. The resulting black tar was washed three times with hexane, and the combined hexane solutions were filtered. Removal of solvent by vacuum transfer left a green powder that was recrystallized from hexane to give 400 mg (71%) of shiny black crystals, mp 338–340 °C. An analytical sample was prepared by sublimation at 120 °C (1 Torr): ^{1}H NMR (THF-d_8, 25 °C) δ −11.7 (s, 36 H), −33.3 (s, 4 H), −35.8 (s, 8 H); mass spectrum, m/z (relative intensity) 670 (M$^+$, 100.00), 454 (49.73), 422 (25.58), 340 (19.88), 159 (23.57), 119 (10.33), 91 (10.67), 57 (93.20); visible spectrum, λ_{max} 632, 662, 682 nm. Anal. Calcd for $C_{32}H_{48}U$: C, 57.30; H, 7.21. Found: C, 57.47; H, 7.22.

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