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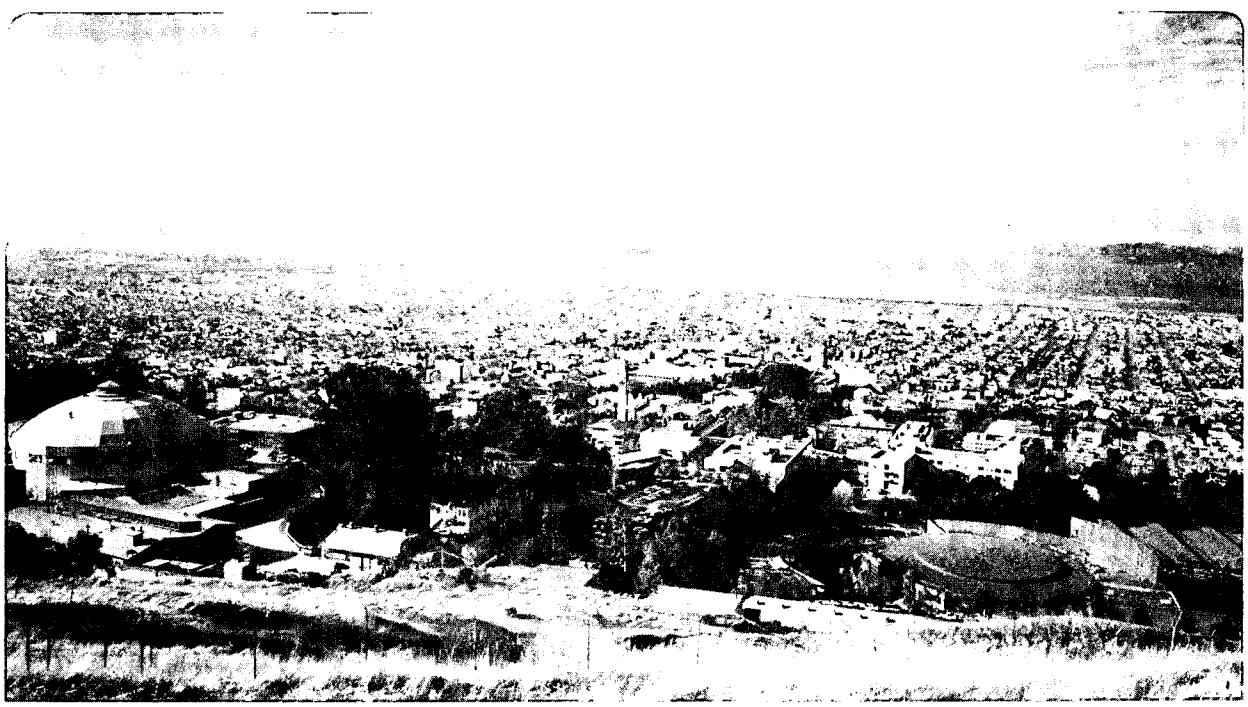

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Two Complementary Syntheses of Symmetrically-Tetrasubstituted Cyclooctatetraenes

Thomas R. Boussie and Andrew Streitwieser*

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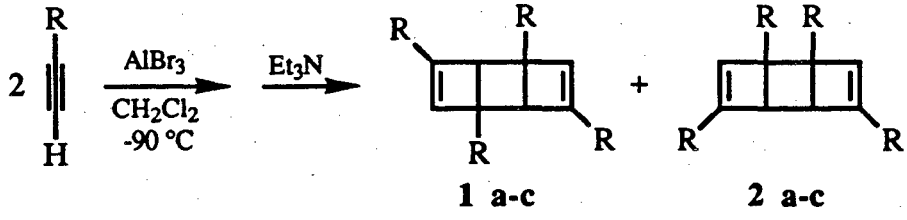
Abstract: Two complementary synthetic approaches to tetrasubstituted cyclooctatetraenes (COT's) have been developed. The first approach involves reaction of terminal acetylenes with $AlBr_3$ and Et_3N to generate mixtures of 1,3,5,7- and 1,2,5,6-substituted *syn*-tricyclo[4.2.0.$0^{2,5}$]octadienes (TCOD's) in high yield. These TCOD's can then be thermally or photolytically ring opened to 1,3,5,7- and 1,2,5,6-substituted COT's. Bulky substituents (e.g. *tert*-butyl, isopropyl) give exclusively 1,3,5,7-substituted TCOD and COT products. In the second approach, 1,3,5,7- (**4**) and 1,2,5,6- (**5**) tetrakis(hydroxymethyl) COT's are generated and isolated in good yield from the Ni(0)-catalyzed tetramerization of propargyl alcohol. These isomers are converted to their corresponding tetrakis(bromomethyl)COT's **7** and **8**. Reduction of **7** and **8** with $LiAlH_4$ affords 1,3,5,7-tetramethyl COT (**9**) and 1,2,5,6-tetramethyl COT (**10**).

As part of an effort to synthesize ligand precursors for actinide and lanthanide organometallic complexes, we have developed two complementary synthetic approaches to tetraalkyl-substituted cyclooctatetraenes (COT's). For purposes of ligand design, we are particularly interested in highly symmetric 1,3,5,7- and 1,2,5,6-substituted isomers. The synthesis of representative molecules of these types are the subject of this report. The only general synthetic approach to 1,3,5,7-tetraalkyl-substituted COT's reported to date, that of DeMayo and Yip,[1] suffers several disadvantages. The approach is multi-step (five or more steps depending on the nature of the ring substituent), low yield, and not applicable to bulky substituents such as *tert*-butyl.[2] We describe herein two approaches to tetraalkyl substituted COT's that offer clear advantages of ease and flexibility over previously reported synthetic methodologies.

First Approach: $AlBr_3$-Mediated Cyclotetramerization of Termi Acetylenes

It is well known that cyclobutadiene cannot be isolated at room temperature; it dimerizes in a Diels-Alder fashion to yield *syn*-tricyclo[4.2.0:$0^{2,5}$]octadiene (TCOD),[3] which can in turn be thermally or photolytically ring-opened to COT.[4] Substituted cyclobutadienes react in an analogous fashion; 1,2-substituted cyclobutadienes provide a mixture of 1,2,4,6-, 1,2,4,5-, and 1,2,5,6-substituted products[5] and 1,3-substituted cyclobutadienes give 1,3,5,7- and 1,2,4,7-substituted products (Scheme I). To our knowledge, the only example of the latter reaction in the literature is the dimerization of 1,3-diphenylcyclobutadiene generated from the Hofmann elimination of the bis-quaternary ammonium salt of diphenylcyclobutane.[6] Presumably, extension of this approach to the synthesis of other tetrasubstituted TCOD's and corresponding COT's has been inhibited by the lack of a general route to 1,3-disubstituted cyclobutadienes. Recently, however,

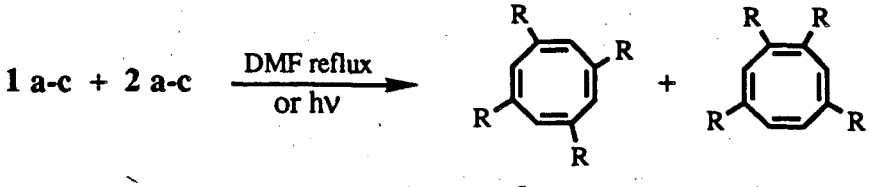
Hogeveen[7] has demonstrated that aluminum halide salts of cyclobutene cations, conveniently synthesized via $AlCl_3$- or $AlBr_3$-mediated dimerization of alkyl-substituted acetylenes, react with Lewis bases apparently to liberate free cyclobutadienes (Scheme II). An important feature for our purposes is that the reaction of monosubstituted acetylenes with $AlBr_3$ shows remarkable regioselectivity, yielding exclusively 1,3-substituted isomers of cyclobutene cation complexes and, on reaction with Lewis bases, exclusively 1,3-substituted cyclobutadienes.[7a] We have found that this route to 1,3-disubstituted cyclobutadienes can be exploited in the synthesis of tetrasubstituted *syn*-tricyclo[4.2.0.0^{2,5}]octadienes (Eq. 1) and subsequent conversion to their corresponding tetrasubstituted COT's (Eq. 2).



(1)

1 a-c **2 a-c**

	Compound	% 1	% 2
a	R = *tert*-butyl	100	0
b	R = isopropyl	100	trace
c	R = propyl	77	23



(2)

3 a-c **4 a-c**

Note that we observed fewer brominated side products using an excess of triethylamine (TEA) as the Lewis base (Eq. 1) rather than DMSO, as favored by

Hogeveen. Also, despite several attempts, no isolable compounds could be obtained from the reaction of propyne under the conditions of Equation 1. However, the desired product of this reaction, 1,3,5,7-tetramethyl COT, is available from an alternative route (*vida infra*).

The difference in the product distribution for various alkyl substituents (Eq. 1) can be rationalized as follows. For cyclobutadienes bearing bulky substituents, the transition state leading to the 1,2,4,6-substituted product is of significantly higher energy than that leading to the 1,3,5,7-substituted product (Scheme I), resulting in the formation of a single product. For the less sterically demanding substituents (e.g. phenyl and *n*-propyl) both transition states are accessible and a mixture of products results.

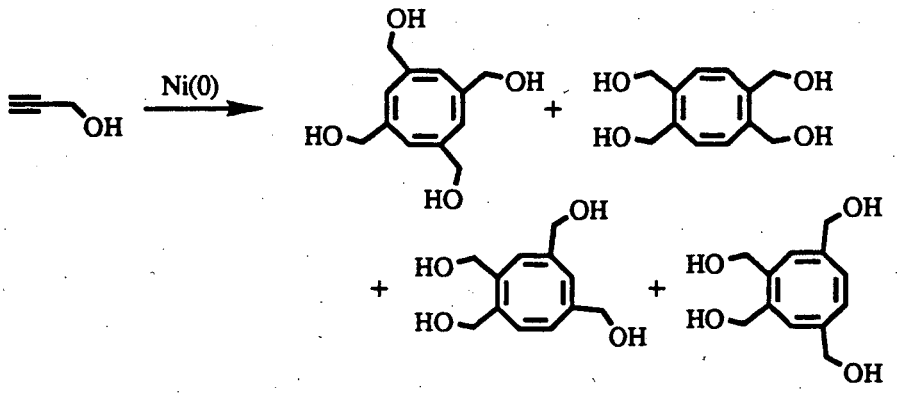
Unfortunately, extension of this approach to other substituted acetylenes was not successful. As reported by Hogeveen,[7b] reaction of phenylacetylene and trimethylsilylacetylene under the reaction conditions of Equation 1 resulted in formation of polymeric material only.

Second Approach: Ni(0)-Catalyzed Cyclotetramerization of Propargyl Alcohol

The above-described approach to 1,3,5,7-tetrasubstituted COT's from terminal acetylenes is best suited for the synthesis of COT's bearing relatively bulky alkyl groups, e.g. from acetylenes with quarternary or tertiary carbon substituents (see Eq. 1). The reaction is not particularly useful for acetylenes with secondary carbon substituents because of the production of mixtures of isomers that can be difficult to separate. The reaction fails with propyne. However, we have developed a second approach to the synthesis of tetrasubstituted COT's bearing primary and secondary carbon substituents that serves to complement the direct cyclotetramerization of alkyl-substituted acetylenes. The critical feature of this synthesis is the

remarkable nickel-catalyzed cyclotetramerization of propargyl alcohol. A variety of Ni(II) catalysts have been reported for the cyclotetramerization of acetylene to cyclooctatetraene,[8] but these catalysts generally convert alkyl-substituted acetylenes to mixtures of linear polymers and benzenes.[9] Direct cyclotetramerization of both acetylene[10] and propyne[11] over finely divided Ni metal have been reported; however, there is considerable (~50%) trimer and linear oligomer formation in both examples. Moreover, in the case of propyne, little regiospecificity is observed within the cyclotetramer fraction and the resultant mixture of isomers is difficult to separate. Cyclooligomerizations of "activated" acetylenes (such as propargylic acetylenes) mediated by transition metal catalysts have been long known to produce cyclotetramers.[12] The low-yield catalyst system of $Ni(acac)_2$ in benzene at reflux was reported[12a] in 1962, followed by reports of the more active Ni(0) catalysts of tom Dieck,[12b] and, more recently, that of Walther, et al.[12c] In the latter example, finely-divided nickel metal was reported to catalyze the quantitative conversion of propargyl alcohol to cyclic tetramers. We undertook to exploit this reaction in the synthesis of isomeric tetrakis(hydroxymethyl)-cyclooctatetraenes (THMCOT's) and conversion to substituted COT derivatives.

As reported by Walther, et al.,[12c] addition of $NaBH_4$ to a dilute solution of $(DME)NiBr_2$ in propargyl alcohol resulted in an astonishingly exothermic reaction that resulted in quantitative consumption of propargyl alcohol and conversion to >95% cyclotetramers (Eq. 3).

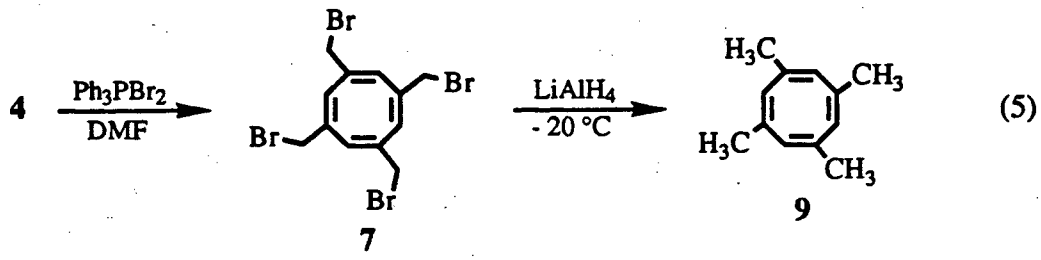


(3)

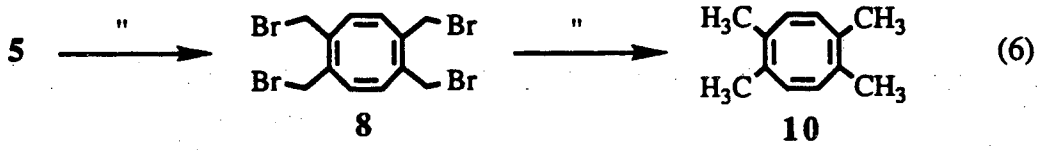
This mixture of isomeric THMCOT's proved resistant to separation by standard techniques. However, we have found that dissolution of the product mixture in acidic 2,2-dimethoxypropane (DMP) results in the conversion of all sites of 1,2-bis(hydroxymethyl) substitution to cyclic acetonides (Scheme III). The resultant mixture of derivatized isomers can be readily separated through fractional recrystallization. The 1,3,5,7-THMCOT (**4**) isomer is available directly, while 1,2,5,6-THMCOT (**5**) is regenerated from the hydrolysis of the bis(acetonide) **6** (Eq. 4).

$$\mathbf{6} \xrightarrow[H^+]{MeOH/H_2O} \mathbf{5} + 2\,(CH_3)_2CO \qquad (4)$$

Compounds **4** and **5** can be converted to the corresponding tetrakis-(chloromethyl) COT's on reaction with PCl_5 in DMF. We found, however, that the analogous tetrakis(bromomethyl) COT's (TBrMCOT's) are better suited for further derivatization. Reaction of **4** and **5** with Ph_3PBr_2 affords 1,3,5,7-TBrMCOT (**7**) and 1,2,5,6-TBrMCOT (**8**), respectively, which can in turn be reduced with cold $LiAlH_4$ to 1,3,5,7-TMCOT (**9**) and 1,2,5,6-TMCOT (**10**) (Eqs. 5 and 6).



(5)



(6)

Although unexplored to date, TBrMCOT's **7** and **8** should be suitable for conversion to other alkyl-substituted COT's.

Experimental Section

Reagents 2,2-dimethoxypropane (DMP), $AlBr_3$, 3,3-dimethyl-1-butyne, and 1-hexyne (Aldrich Chemical Co.), 3-methyl-1-butyne and propyne (Farchan Chemical Co) were either sublimed or fractionally distilled before use. Propargyl alcohol was vacuum distilled at temperatures <50 °C and stored under Ar. Methylene chloride (CH_2Cl_2), triethylamine (TEA), diethyl ether (Et_2O) and dimethyl formamide (DMF) were distilled from CaH_2 and degassed in three freeze-pump-thaw cycles before use. The complex (DME)$NiBr_2$ was prepared by the method of Ward.[13] All other reagents, unless otherwise noted, were used as received from commercial suppliers. Air-sensitive manipulations were carried out in an Ar atmosphere using standard Schlenk techniques.

1,3,5,7-Tetra-*tert*-butyl-*syn*-tricyclo[4.2.0.0^{2,5}]octadiene (1a). T 26.67 g (100 mmol) of $AlBr_3$ in a 250 mL, Ar-filled, 1-necked Schlenk flask equipped with a magnetic stir bar and capped with a septum was added 100 mL of CH_2Cl_2 (precooled to -78°C) and the resultant slurry was cooled to -90 °C. A

solution of 8.22 g (100 mmol) of 3,3-dimethyl-1-butyne in 10 mL of CH_2Cl_2 was added dropwise by syringe over 1 h. The solution was warmed to -78 °C and stirred for 30 min. Into this solution was cannulated 42 mL (300 mmol) of cold (-78 °C) TEA, and the resultant slurry was warmed slowly to room temperature. The ppt was collected by vacuum filtration and washed with CH_2Cl_2. The filtrate was washed with 2 50 mL portions of saturated NH_4Cl and 2 50 mL portions of water. The organic layers were combined, dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by flash chromatography (pentane, 150 mesh alumina) to yield 6.5 g (79%) of **1a** as a colorless oil: R_f (pentane, silica tlc) = 0.95; ^1H NMR ($CDCl_3$) δ 5.63 (d, J = 3.3 Hz, 2H), 2.75 (d, J = 3.3 Hz, 2H), 0.97 (s, 18 H), 0.88 (s, 18 H) (matches previously reported[3] spectrum).

1,3,5,7-Tetra-*tert*-butylcyclooctatetraene (3a). A solution of 2.0 g (6.0 mmol) of **1a** in 30 mL of DMF was heated at reflux (153 °C) for 12 h, cooled to room temperature, and poured into 200 mL of a 1:1 mixture of pentane and water. The pentane layer was collected and washed with 4 50 mL portions of water. The combined pentane layers were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography (pentane, 150 mesh alumina) to yield 1.2 g (60%) of **3a** as a colorless oil. This material was used for subsequent reactions. Further purification by prep. gc gave material that was pure by ^1H NMR standards: ^1H NMR ($CDCl_3$) d 5.67 (s, 4H), 1.52 (s, 36H) (matches previously reported[2] spectrum). Note that photolysis (450 W Hg lamp) of a cooled (0 °C) pentane solution of **1a** for 12 h affected conversion to **3a** in higher (80-90%) yield.

1,3,5,7-Tetraisopropyl-*syn*-tricyclo[4.2.0.0^{2,5}]octadiene (1b). Followin the procedure for the synthesis of **1a** above, 3.41 g (50 mmol) of isopropylacetylene yielded after chromatography 2.3 g (68%) of **1b** as a colorless

oil: R_f (pentane, silica tlc) = 0.95; ^1H NMR ($CDCl_3$) δ 5.62 (dd, J = 2.5 Hz, 2H), 2.44 (d, J = 2.5 Hz, 2H), 2.30 (m, 2H), 1.74 (m, J = 6.6 Hz, 2H), 1.02 (d, J = 6.6 Hz, 12 H) 0.93 (d, J = 6.6 Hz, 6 H), 0.89 (d, J = 6.6 Hz, 6 H). Anal. Calcd. for $C_{20}H_{32}$: C, 88.17; H, 11.83. Found: C, 88.01; H, 11.55.

1,3,5,7-Tetraisopropylcyclooctatetraene (3b). Following the procedure fc **3a** above, 2.0 g (7.3 mmol) of **5** yielded, after chromatography, 1.4 g (70%) of **3b** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.45 (s, 4H), 2.21 (m, J = 6.8 Hz, 4H), 0.934 (d, J = 6.9 Hz, 12H), 0.925 (d, J = 6.8 Hz, 12 H). Anal. Calcd. for $C_{20}H_{32}$: C, 88.17; H, 11.83. Found: C, 88.21; H, 11.61.

1,3,5,7-Tetra-*n*-butylcyclooctatetraene (3c) and 1,2,5,6-Tetra-*n*-butylcyclooctatetraene (4c). Following the procedure for the synthesis of **1a** above, 3.41 g (50 mmol) of *n*-butylacetylene yielded after chromatography 1.9 g (56%) of a mixture of **1c** and **2c** as a colorless oil: R_f (pentane, silica tlc) = 0.95, 0.90. This material was heated at reflux in DMF for 5 h and worked up as described for **3a** above to afford after chromatography 1.4 g (41% from *n*-butylacetylene) of a 3.4:1 mixture of **3c** and **4c**: ^1H NMR of **3c** ($CDCl_3$) δ 6.22 (s, 4H), 2.45 (t, J = 8 Hz, 2H), 0.9 (overlapping m); ^1H NMR of **4c** ($CDCl_3$) δ 6.80 (s, 2H), 6.72 (s, 2H), 2.52 (t, J = 8 Hz, 2H), 0.9 (overlapping m).

Tetramerization of propargyl alcohol by Ni metal generated in situ A 100 mL 2-necked flask equipped with a reflux condenser capped with an Ar bubbler and a ground-glass stopper was charged with a solution of 0.01 g (0.03 mmol) of $(DME)NiBr_2$ in 30 g (534 mmol) of propargyl alcohol. To this solution was added 0.006 g (0.15 mmol) of $NaBH_4$ in several portions. Care must be taken as the reaction is extremely exothermic. After stirring for 3 h the solution was diluted

with THF, filtered through a bed of Celite, and the THF and unreacted propargyl alcohol were removed *in vacuo*.

Treatment of mixed THMCOT isomers with DMP. Isolation of 1,2,5, THMCOT Diacetonide (6). To 10 g of the mixture of cyclotetramers and cyclotrimers resulting from the nickel-catalyzed reaction described above was added 30 g of DMP, 20 mL of methanol and 0.1 g of *p*-toluenesulfonic acid and the mixture was mechanically stirred for 18 h. The resulting suspension was cooled to 0 °C for 2 h, the precipitate was collected by vacuum filtration, and the filtrate was set aside (see directly below). Dissolution of the precipitate in $CHCl_3$ followed by filtration and evaporation of the filtrate to dryness yielded 3.0 g (22% based on 1,2,5,6-THMCOT) of **6** as a white powder. Recrystallization from acetone afforded colorless crystals: mp 121-122 °C; ^{1}H NMR ($CDCl_3$) δ 5.71 (s, 4H), 4.12 (d, J = 12.6 Hz, 4 H), 3.87 (d, J = 12.6 Hz, 4 H), 1.27 (s, 12H). Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.94. Found: C, 71.19; H, 7.90.

Isolation of 1,3,5,7-THMCOT (4). The methanol and unreacted DMP were removed from the filtrate *in vacuo*, then 20 mL of DMP was added and the mixture was mechanically stirred for 4 h. Cooling of the resulting suspension at 0 °C for 24 h followed by collection of the precipitate by vacuum filtration afforded 4.3 g (43%) of **2** as a white powder. This material is suitable for subsequent reactions. Recrystallization from acetone yielded **4** as small, colorless crystals: mp >360 °C; ^{1}H NMR (D_2O, 25 °C) δ 5.75 (s, 4H), 3.91 (s, 8H); (CD_3OD, 25 °C) δ 5.84 (s, 4H), 3.95 (s, 8H); (CD_3OD, -77.5 °C) δ 5.81 (s, 4H), 3.95 (dd, J = 12.1, 14.6 Hz, 8H). The spectrum in CD_3OD matches that reported by tom Dieck.[5b]

Conversion of 1,2,5,6-THMCOT Diacetonide (6) to 1,2,5,6-THMCOT (5 Into 50 mL of a solution of 10% water in methanol containing 0.1 g of *p*-toluenesulfonic acid was mixed 3.0 g (9.9 mmol) of **6**, and the suspension was stirred at 50 °C until a clear solution resulted (2-3 h). The solution was filtered and evaporated to dryness *in vacuo*. Recrystallization from methanol yielded 1.8 g (81%) of **5** as colorless crystals: mp 162-163 °C; ^{1}H NMR (D_2O, 25 °C) δ 5.90 (s, 4H), 4.08 (d, J = 12.8 Hz, 4H), 3.98 (d, J = 12.8 Hz, 4H); (CD_3OD, 25 °C) δ 5.90 (s, 4H), 4.10 (d, J = 12.8 Hz, 4H), 3.96 (d, J = 12.8 Hz, 4H). Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 63.97; H, 7.29.

1,3,5,7-Tetrakis(bromomethyl)cyclooctatetraene (7). To a solution 9.36 g (35.7 mmol) of PPh_3 in 200 mL of dry DMF at 0°C was added 5.71 g (35.7 mmol) of Br_2 dropwise over 1 h. After stirring for an additional 1 h, a suspension of 2.0 g (8.9 mmol) of **4** in 100 mL of DMF was added over 30 min. The solution was warmed to 25 °C and stirred for 18 h. After quenching with ice and extraction with Et_2O, the organic layer was washed with 2 50 mL portions of saturated brine and 2 50 mL portions of water. The combined organic layers were dried over $MgSO_4$, the volume was reduced to ca. 40 mL and the solution was cooled to -20 °C to precipitate Ph_3PO. The solution was then pulled through a 10 cm plug of silica and washed with Et_2O. Removal of the Et_2O afforded 2.3 g (60%) of **7** as a white powder. ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 4H), 3.98 (d, J = 10.1 Hz, 4H), 3.91 (d, J = 10.1 Hz, 4H). Anal. Calcd. for $C_{12}H_{12}Br_4$: C, 30.29; H, 2.54. Found: C, 30.44; H, 2.43.

1,2,5,6-Tetrakis(bromomethyl)cyclooctatetraene (8). Following th procedure for the synthesis of **4** above, 2.00 g (8.9 mmol) of **5** yielded after chromatography 1.7 g (45%) of **8** as a white powder. ^{1}H NMR ($CDCl_3$) δ 6.14 (s, 4H),

4.14 (d, J = 10.9 Hz, 4H), 4.00 (d, J = 10.9 Hz, 4H). Anal. Calcd. for $C_{12}H_{12}Br_4$: C, 30.29; H, 2.54. Found: C, 30.11; H, 2.41.

Reduction of 7 to 1,3,5,7-TMCOT (9) with $LiAlH_4$. To a suspension of 0.2 g (6.3 mmol) of $LiAlH_4$ in 25 mL of anhydrous ether at -20 °C was added a solution of 1.0 g (2.1 mmol) of **7** in 20 mL of ether over 1 h. After allowing to warm slowly to room temperature and quenching with I_2 (1.6 g, 25.2 mmol), 50 mL of water and 50 mL of ether was added, followed by 50 mL of 10% aqueous HCl. The organic layer was separated and washed with sat. $Na_2S_2O_3$ and 3 50 mL of 10% HCl. After drying over $MgSO_4$, the ether was removed *in vacuo* to afford a yellow oil. Flash column chromatography (pentane, 150 mesh alumina) of this material gave, after removal of solvent, 0.14 g (42%) of **9** as a pale yellow oil, suitable for further reactions. Prep. gc affords **9** as a waxy white solid; ^1H NMR ($CDCl_3$) δ 5.40 (s, 4H) 1.66 (s, 12H) (matches reported[14, 34b] spectra).

Reduction of 8 to 1,2,5,6-TMCOT (10) with $LiAlH_4$. By a procedur analogous to the reduction of **7** described above, 1.0 g of **8** afforded after chromatography 0.19 g (57%) of **10** as a colorless oil. Prep. gc affords **10** as a clear viscous oil; ^1H NMR ($CDCl_3$) δ 5.50 (s, 1H), 1.75 (s, 3H); Anal. Calcd. for $C_{12}H_{16}$: C, 89.95; H, 10.05. Found: C, 89.77; H, 9.89.

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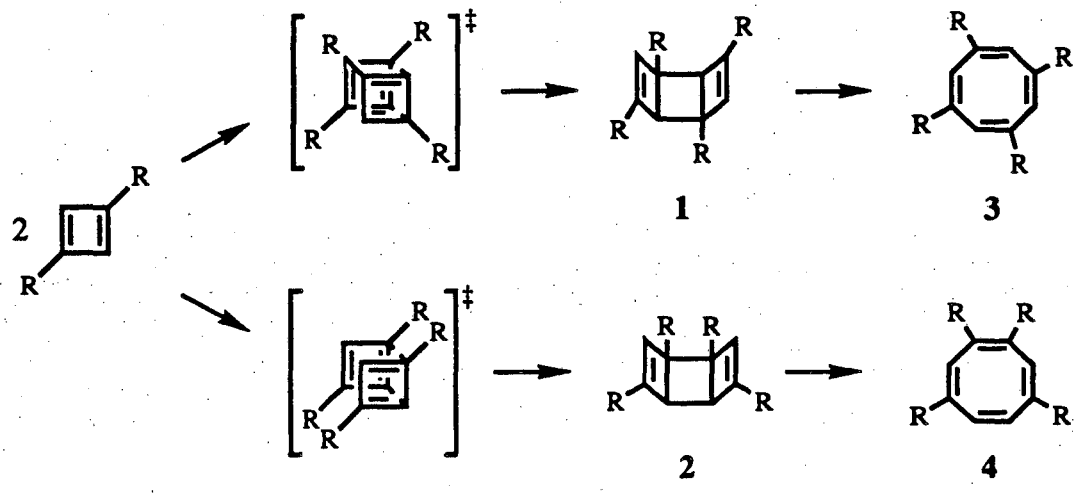
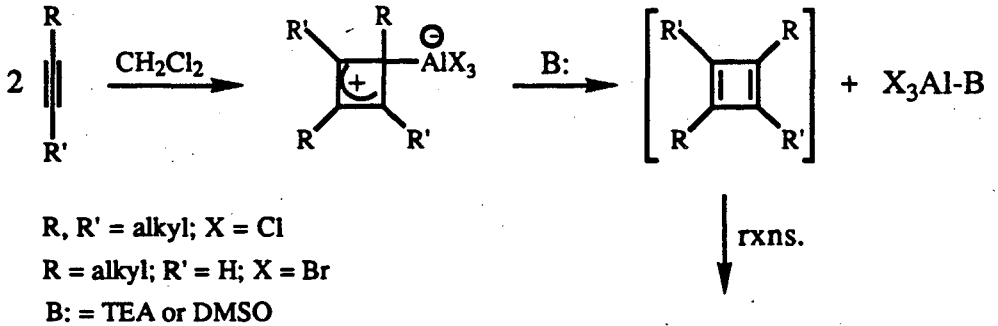
Scheme I. Dimerization of 1,3-Substituted Cyclobutadienes

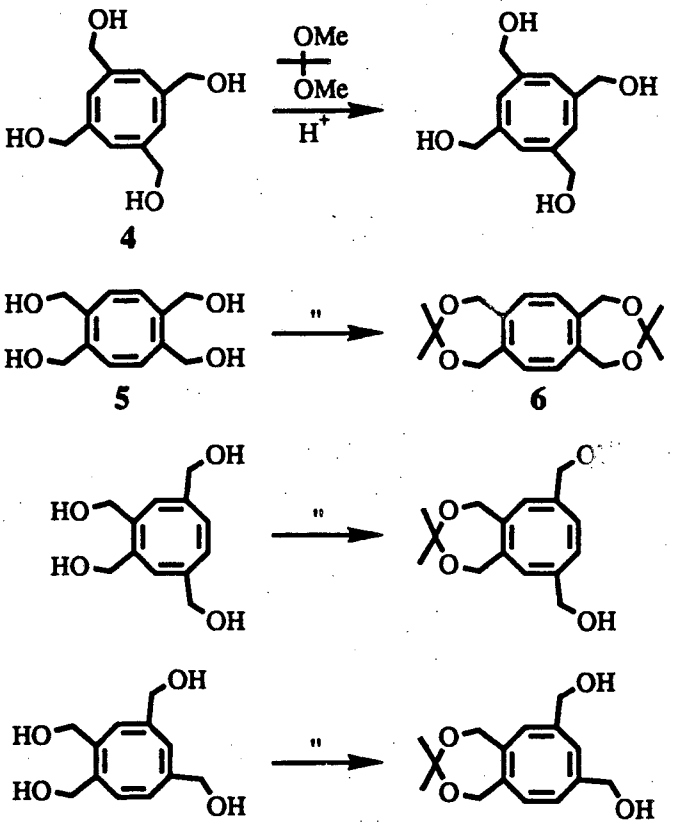


Scheme II. In Situ Generation of Substituted Cyclobutadienes from Acetylenes



R, R' = alkyl; X = Cl
R = alkyl; R' = H; X = Br
B: = TEA or DMSO

Scheme III. Conversion of Isomeric THMCOT's to Acetonides



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