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Impact of High-Lying σ Orbitals and Extensive Through-Bond Interaction on Chemical Reactivity. 1. Convenient Syntheses of Hypostrophene and Its Susceptibility to Rearrangement under Electrophilic Conditions

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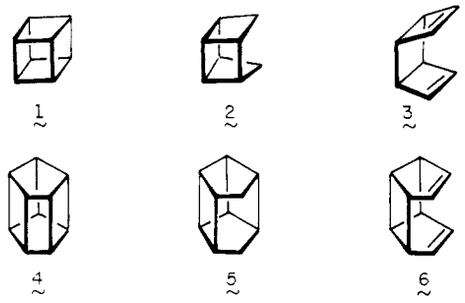
Two practical syntheses of hypostrophene (**6**) beginning with cyclopentadiene (14.6% overall) and cyclopentanone (21.6%) are reported. Both routes converge at the stage of keto ketal **8**, which is subsequently photocyclized and transformed to diiodide **14**. Exposure of **14** to sodium–potassium alloy delivers the title diene. When **6** was treated with elemental bromine or *N*-bromosuccinimide in aqueous dimethyl sulfoxide, extensive structural rearrangement occurred with formation of the *endo*-dicyclopentadiene derivatives **17** and **23**, respectively. Under acidic conditions, epoxide **26** was similarly isomerized to diol **30**, the skeletal rearrangement again involving eight of the ten carbon atoms contained in the hypostrophene framework. A possible correlation between the high-lying σ orbitals present in **6**, its marked preference for through-bond instead of through-space interaction, and strain relief is presented in rationalization of this proclivity for deep-seated structural change.

In molecules such as cubane (**1**) and pentaprismane (**4**), two identical alicyclic rings are brought together in face-to-face proximity within a rigid prismatic molecular framework. At least in the case of **1** (**4** remains unknown), such a bonding arrangement engenders sizable strain energy[2] with resultant high chemical reactivity.[3] The state of hybridization demanded by the novel geometry of **1**[4a] is reflected in the high acidity of its protons,[4b] its very low (8.74 eV) first ionization potential,[5] and its behavior on electron impact.[6] Progression through the series **1**–**3** and **4**–**6** results in substantial strain



1 **2** **3**

4 **5** **6**

amelioration. The pair of internal hydrogens in secocubane (**2**) are known to cause outward puckering of the upper and lower cyclobutene rings.[7] A comparable steric situation likely prevails in **5**.

The removal of two contiguous lateral bonds in **1** and **4** leads to **3**[8] and **6**,[9] respectively, having pairs of nonconjugated cisoid π orbitals whose inner lobes are tightly compressed. Despite their obvious proximity, however, the double bonds in *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene[10] and hypostrophene[11] experience vastly more effective through-bond interaction than through-space coupling. This results because of the continued presence of exceptionally high-lying σ orbitals which serve to reverse the normal ordering, wherein the out-of-phase linear combination of the two π orbitals is located at higher energy than the in-phase combination.[12] Since few known organic molecules possess structural and stereoelectronic features capable of effectively overriding customary through-space interaction, the reactivities of **3**, **6**, and suitable derivatives thereof merit serious experimental investigation.

Although these interesting molecules hold promise as possible sources of new theoretical and mechanistic understanding, they have been subjected to very limited scrutiny, apparently due to their relative inaccessibility. It is currently recognized that neither diene is capable of ($\pi 2_s + \pi 2_s$) photochemical cyclization, since through-bond coupling destroys the usual symmetry allowedness of this closure. In contrast, the capability of both molecules for sequential degenerate Cope rearrangement of low temperatures is not inhibited.[9,13] Therefore, these substances can endlessly interchange two sets of carbon atoms with regeneration of the original structures. At somewhat more elevated temperatures, **3** is transformed into cyclooctatetraene[14] and **6** gives rise to an isomeric $(CH)_{10}$ hydrocarbon.[9]

In this and the two accompanying reports,[15,16] we have attempted to relieve this imbalance through development of practical synthetic routes to **6**, analysis of its response to electrophilic reagents, and investigation of the solvolytic behavior of appropriately functionalized derivatives of **3** and **6**.

Results

Synthetic Considerations. Pettit's original synthesis of hypostrophene provides the hydrocarbon in 0.7% yield from cyclooctatetraene and is not only costly but also tedious. Therefore, the development of rather less expensive and more flexible routes to **6** was initially investigated. Two series of interconversions were developed to gain access to the pivotal intermediate **8** (Scheme I). The first of these began with cy-

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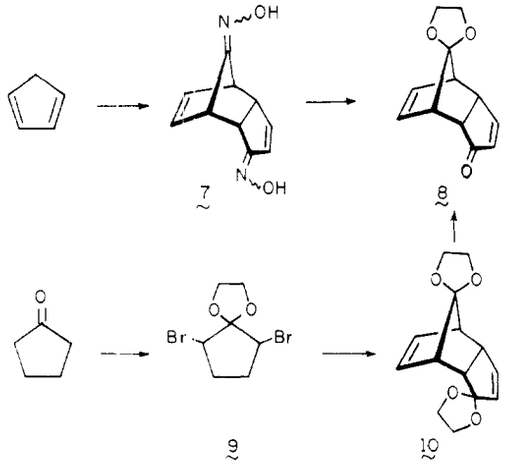
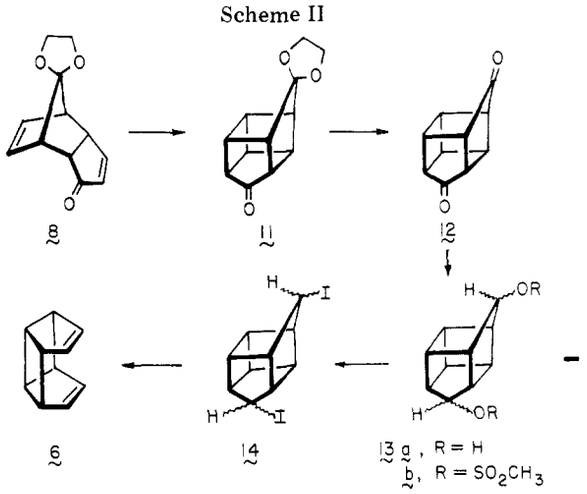
Scheme I



Scheme II



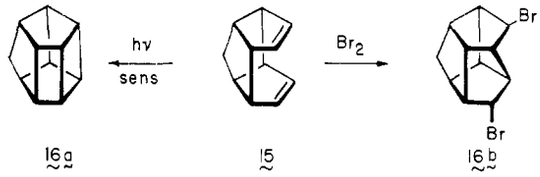
clopentadiene,[17] nitrosation of which provided dioxime **7**.[18] Through sequential transoximation with levulinic acid[19] and selective ketalization with ethylene glycol in benzene containing *p*-toluenesulfonic acid,[20] this dioxime was efficiently converted to **8**. Although this sequence is quite satisfactory for either small- or large-scale preparations of **8**, there remain undesirable economic and technical problems in the handling of bulk quantities of levulinic acid. These drawbacks were totally eliminated through use of cyclopentanone as starting material. Conversion to its ethylene ketal[21] followed by dibromination with elemental bromine in dioxane[20b] gave **9**. To achieve maximum yields in the latter step, **9** should be isolated immediately without unnecessary heating during solvent removal and used directly. When left at room temperature for any length of time, the dibromo ketal is transformed to a dense black oil. Dehydrobromination of **9** and in situ dimerization were achieved through the use of refluxing sodium methoxide in methanol,[20b] or preferably sodium or potassium *tert*-butoxide in *tert*-butyl alcohol. Partial hydrolysis of **10** to **8** could be reproducibly achieved in 95% yield by stirring with hydrochloric acid in tetrahydrofuran at room temperature for 2 h. Extension of the reaction time to 4–5 h invariably caused drastic reductions in yield.

Upon irradiation of **8** in ether through Pyrex with a Hanovia 450-W lamp, photoclosure to **11** was routinely realized in 95% yield. Although the subsequent hydrolysis of **11** to **12** is somewhat capricious and requires careful attention to detail, this approach to **12** is vastly superior to that involving direct photocyclization of dicyclopentadienone,[22] since no photochemical side reactions compete. Lithium aluminum hydride reduction of **12**, treatment of diol mixture **13a** with sulfene,[23] and S_N2 displacement with sodium iodide in anhydrous hexamethylphosphoramide afforded the nicely crystalline **14** as a mixture of epimers (Scheme II).

Initially, the conversion of diiodide **14** to hypostrophene was effected with sodium–potassium alloy in anhydrous tetrahydrofuran at room temperature (54% yield). To remove the last traces of solvent and some polymerization product, the impure **6** was generally sublimed. But contamination with a saturated hydrocarbon byproduct of comparable volatility persisted. These complications do not arise if ether is originally employed as solvent. Under these conditions, chromatography on silica gel (unfeasible earlier) suffices to provide pure hypostrophene (61%). Other methods such as those involving sodium naphthalenide or sodium phenanthrenide suffer from the problem of ultimate separation of volatile **6** from aromatic compounds and are substantially less desirable.

These procedures therefore permit the ready production of hypostrophene in 14.6% overall yield from cyclopentadiene or, more impressively, in 21.6% yield from cyclopentanone.

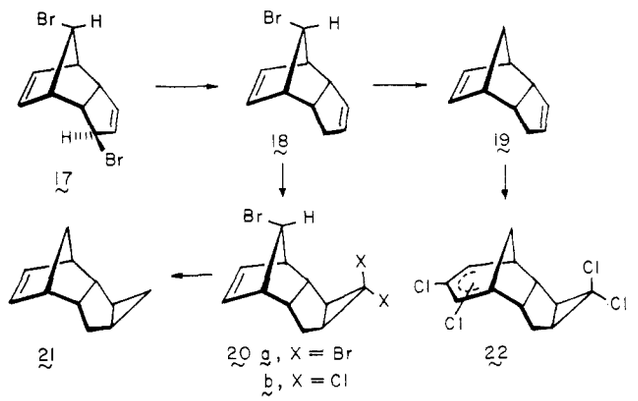
Chemical Consequences of Through-Bond Interaction. To assess in reasonably systematic fashion the degree of control that high-lying σ orbitals can exert upon chemical reactivity, comparisons with one or more compounds lacking through-bond interaction are warranted. For the present purposes, homohypostrophene (**15**) is considered particularly attractive because of its close structural similarities to **6**. Although photoelectron spectroscopic analysis of **15** has yet to be reported, this diene lacks laterally fused cyclobutane rings and probably is endowed with normal orbital ordering. That through-space interaction does dominate in **15** is suggested by its closure to homopentaprismane (**16a**) upon ultraviolet



irradiation in the presence of xanthone or acetone.[24] A further chemical test in support of this conclusion is found in the bromination of **15**, which proceeds straightforwardly by 1,4 addition to give exclusively **16b**.[25,26]

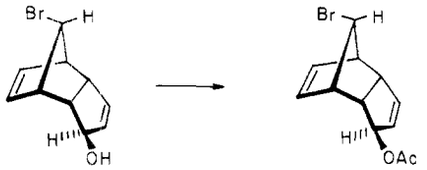
Reaction of **6** at 0 °C in carbon tetrachloride with 1 equiv of bromine gave a single oily dibromide (**17**) in excellent yield. The ^1H NMR spectrum of **17** displays four olefinic protons, thereby ruling out the operation of simple transannular chemistry as exhibited by **15**. Because reduction of **17** with lithium aluminum hydride afforded an isomerically pure monobromide, it became immediately apparent that its halogens are situated in differing chemical environments. The finding that further dehalogenation with sodium in liquid ammonia furnished *endo*-dicyclopentadiene (**19**) implicated the prior formation of **17** and **18** (Scheme III). The syn stereochemical assignment to the 8-bromo substituent in these

Scheme III



molecules is founded upon the selective reactivity of **18** toward dihalocarbenes generated under phase-transfer conditions[28] and upon mechanistic reasoning (vide infra).[29] The steric shielding which arises with this substitution plan causes **18** to be subject only to monoaddition with formation of **20a** and **20b** under conditions where parent hydrocarbon **19** undergoes reaction at both olefinic sites to give **22.** Upon reductive dehalogenation, **20a** and **20b** were transformed to the known hydrocarbon **21.**[30]

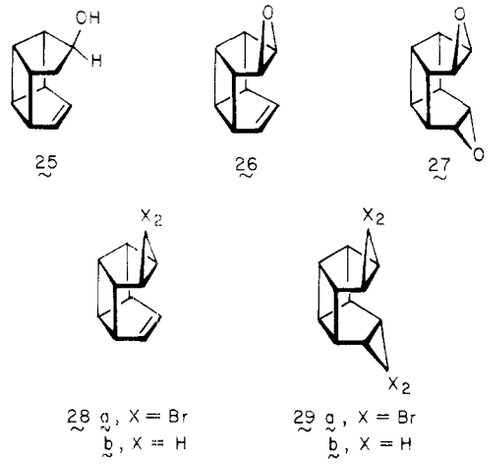
When hypostrophene was treated with *N*-bromosuccinimide in wet dimethyl sulfoxide, a reagent known to lead regio- and stereospecifically to bromohydrins[31a] with skeletal rearrangement occurring only infrequently,[31b] there was isolated only the extensively isomerized bromo alcohol **23.** The identity of **23** is based upon its formation by hydrolysis of **17** and the spectral properties of its more stable acetate derivative **24** (see



23 24

Experimental Section). These results are taken as an indication that hypostrophene possesses a powerful latent drive for rearrangment that is accompanied by strain release and made possible by its electron-rich lateral bonds.

Nonetheless, reagents such as 9-borabicyclononane (9-BBN),[32] *m*-chloroperbenzoic acid, dibromocarbene, and iodomethylzinc iodide engage **6** in chemical reaction (exo attack only) without inducing skeletal isomerization. With 9-BBN, the multiplicity of addition could be controlled to give alcohol **25** in >70% isolated yield. We have directed efforts toward the maximization of monoaddition in all instances, but the 70+% limit has been repeatedly realized under individually tailored experimental circumstances. For example, *m*-chloroperbenzoic acid in chloroform at 0 °C provided monoepoxide **26** (73%) and diepoxide **27** (15%). With potassium *tert*-butoxide and bromoform in pentane at −30 °C, there was isolated 77% of **28a** and 15% of **29a.** Simmons–Smith cyclopropanation



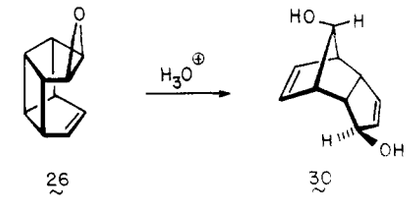
25 26 27

28 a, X = Br
b, X = H

29 a, X = Br
b, X = H

similarly gave a mixture of **28b** and **29b,** and the need for preparative VPC separation substantially lowered the isolated yields in this case. Reductive debromination[33] of **28a** is the preferred route to **28b.**

No rearrangement products are formed in the above reactions due to the absence of mechanistic requirements that cationic intermediates intervene. When this is purposefully undertaken as, for example, when **26** is dissolved in 10% aqueous perchloric acid at room temperature, rapid conversion to the known 1-*exo*-8-*syn*-diol **30** does occur.



26 30

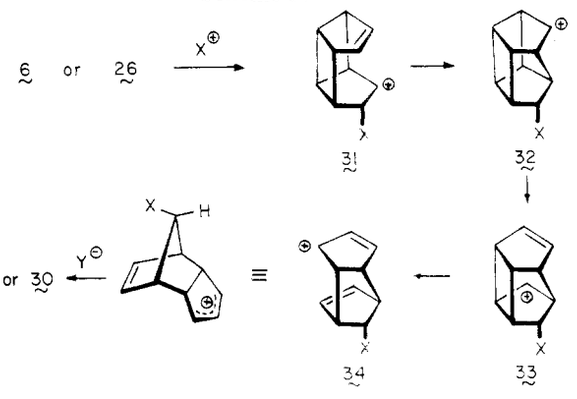
Discussion

An intriguing feature of the conversion of hypostrophene to **17** and **23** is the involvement of *eight* of this hydrocarbon's ten constituent carbon atoms in the skeletal rearrangement. We believe that electrophilic attack begins with exo approach to generate **31.** This intermediate subsequently experiences transannular bonding with the normal kinetic preference for 5-ring closure (Scheme IV) to deliver **32.** Two sequential cyclobutane bond cleavages follow. The first phase leading to **33** is quite likely facilitated by the electron-rich nature of the lateral bond and controlled by strain release since the new cationic center does not appear to be particularly stabilized relative to that in **32.** The energetic value of the second phase which gives rise to **34** probably lies chiefly in the development of allylic resonance, although a further diminution in strain also obtains. As a direct consequence of the prevailing symmetry in **34,** nucleophilic capture can take place with equal probability at either allylic terminus.

The behavior of epoxide **26** in acidic solution is entirely comparable. Here, electrophilic ring opening leads to **31** (X = OH) which then proceeds to **30** in the predescribed manner.

We have been singularly unsuccessful in our attempts to intercept such hypostrophene rearrangements even with most reactive uniparticulate electrophiles[34] such as TCNE and CSI. Due to the geometric limits imposed upon intramolecular charge annihilation when uniparticulate reagents are involved, only the capture of **31** and **33** becomes feasible under such circumstances. However, tarry polymeric substances which defied characterization were produced with CSI under the various conditions examined. TCNE proved unreactive. It is, therefore, perhaps more reasonable to view the conversion of **31** to **34** as a concerted electronic reorganization, although we recognize that this hypothesis is based upon negative rather than positive evidence. In this interpretation, the synchronous flow of electron density which undulates between the two "wafered" cyclopentane rings such that 80% of the carbon atoms experience rehybridization can be viewed as the result of the extensive $\sigma\pi$ orbital mixing which prevails. Certainly, if any barriers to bond making and bond breaking do exist on this energy profile, their magnitudes have been greatly reduced as compared to the situation in **15** and other structurally related molecules.

Scheme IV



Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained on Varian T-60A and HA-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were obtained with Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were measured with an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***endo*-Dicyclopentadienone.** A substantial quantity of bisoxime **7** was prepared in 77% yield by the method of Doering and DePuy.[18] The crude solid obtained by Soxhlet extraction of the reaction mixture was used without further purification. Its infrared spectrum was identical with that reported.

A mixture of 20 g (105 mmol) of bisoxime **7** in 480 mL of freshly distilled levulinic acid and 54 mL of hydrochloric acid was stirred at room temperature for 3 h during which time the solids dissolved. The orange solution was heated on a steam bath for 3 h, cooled, diluted with 1000 mL of water, and extracted with four portions of methylene chloride totalling 2000 mL. The combined organic layers were carefully neutralized with saturated sodium bicarbonate solution, followed by washing with 100 mL of 20% sodium hydroxide solution and finally with water until color was no longer extracted. The dried solution was filtered and evaporated to leave a yellow solid which was purified by column chromatography on neutral alumina (benzene elution). There was isolated 13.13 g (78%) of dicyclopentadienone as off-white crystals whose spectral properties proved identical with the reported data.[18]

***endo*-Dicyclopentadienone 8-Ethylene Ketal (8). A. Selective Ketalization of *endo*-Dicyclopentadienone.** A solution of 5.10 g (31.8 mmol) of *endo*-dicyclopentadienone, 3.95 g (63.7 mmol) of ethylene glycol, and 100 mg of *p*-toluenesulfonic acid in 50 mL of benzene was heated under reflux while water was azeotropically removed in a Dean–Stark trap. After 22 h the mixture was cooled, extracted with equal volumes of saturated sodium bicarbonate solution and water, and dried. Elution of the filtrate through 10 g of neutral alumina and evaporation of solvent gave 5.15 g (81%) of **8** as a white solid. This material could be recrystallized from carbon tetrachloride to a melting point of 94–95 °C (lit.[20a] mp 94–95 °C), or used without further purification.

B. Partial Hydrolysis of 10. Cyclopentanone ethylene ketal (87% yield) and 2,5-dibromocyclopentanone ethylene ketal (96% yield) were prepared according to literature procedures.[20b,21]

To 2000 mL of dry *tert*-butyl alcohol was added 141 g (3.6 g-atom) of potassium metal portionwise during 1 h under a nitrogen atmosphere with mechanical stirring. The mixture was gently refluxed to achieve reaction of the last amounts of potassium. To this potassium *tert*-butoxide solution was added 281.28 g (0.98 mol) of **9** dropwise under nitrogen. The resultant black mixture was heated gently for 12 h and diluted with 2000 mL of water. The *tert*-butyl alcohol was removed under reduced pressure and the black aqueous mixture was diluted to 5000 mL and extracted continuously with diethyl ether to give 104 g (86%) of **10** as light yellow crystals. Recrystallization from ether gave colorless crystals: mp 91–92 °C (lit.[20b] mp 92 °C); NMR 6.10–6.33 δ_{Me_4Si} ($CDCl_3$) (m, 1), 5.5–5.97 (m, 3), 3.82–4.07 (m, 8), 3.33–3.62 (m, 1), and 2.58–3.05 (m, 3).

A solution of 60.8 g (0.245 mol) of **10** in a mixture of 96 mL of concentrated hydrochloric acid and 960 mL of tetrahydrofuran was allowed to stand at room temperature for 2 h and no longer. Water (1 L) was added and the aqueous mixture was neutralized carefully with sodium carbonate. The tetrahydrofuran was removed on a rotary evaporator and the aqueous layer was diluted to 1000 mL, extracted exhaustively with diethyl ether, and dried. Filtration and evaporation gave 49.36 g (100%) of **8** as colorless crystals, mp 94–95 °C.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 6-Ethylene Ketal (11).[20] A solution of 28.6 g (0.14 mol) of **8** in 1500 mL of dry benzene was placed in a large Pyrex vessel and irradiated with a 450-W Hanovia lamp contained in a quartz immersion well equipped with a Pyrex filter for 36 h. Filtration of the resultant yellow solution through 10 g of Florisil removed colored impurities and led to the isolation of 27.0 g (94%) of **11** as a colorless oil. If desired, crystallization could be achieved at −60 °C from diethyl ether.

Pentacyclo[5.3.0.0.^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione (12). A heterogeneous mixture of 2.39 g (11.7 mmol) of **11**, 110 mL of 10% aqueous sulfuric acid, and 20 mL of tetrahydrofuran was heated at 80–90 °C for 3 h with stirring. After cooling, the mixture was poured onto 100 g of ice and carefully neutralized with solid sodium bicarbonate. The contents of the flask was diluted to 700 mL with water and extracted continuously with methylene chloride. Evaporation of the organic phase gave 1.71 g of orange oil, chromatography of which on silica gel (elution with benzene/ethyl acetate, 4:1) gave **12** as colorless crystals (1.42 g, 76%). The physical and spectral properties of **12** coincided with those described in the literature.[22]

This diketone, on standing open to the air, gradually forms a hydrate which appears as a white powder.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-diol (13a). To a stirred suspension of 9.9 g (0.26 mol) of lithium aluminum hydride in 300 mL of dry tetrahydrofuran under nitrogen was added dropwise a solution of 20.7 g (0.13 mol) of **12** in 400 mL of dry tetrahydrofuran. The resultant mixture was heated under reflux for 24 h, cooled, and treated carefully with 10 mL of water, 10 mL of 15% sodium hydroxide solution, and 30 mL of water. The mixture was suction filtered and the solids were leached repeatedly with diethyl ether. The combined organic filtrates were evaporated under reduced pressure to give 19 g (90%) of a pale yellow oil. Recrystallization from benzene gave 6.84 g of colorless crystals: mp 185–197 °C (mixture of epimers); NMR δ_{Me_4Si} ($CDCl_3$) 2.10 (br s, 2), 2.68 (m, 4), 2.88 (m, 4), and singlets at 3.98, 4.20, and 4.36 (total 2 H) (the three methine signals appeared in the ratio 5:16:4); IR ν_{max} (neat) 3320 cm^{-1}.

6,10-Bis(methanesulfonyloxy)pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decane (13b). To a solution of 1.61 g (9.8 mmol) of **13a** in 200 mL of methylene chloride at 0 °C was added 2.52 g (22 mmol) of triethylamine under nitrogen. Methanesulfonyl chloride (3.0 g, 29.7 mmol) was added dropwise over 30 min at 0 °C and the resultant clear solution was maintained at 0 °C for an additional 20 min before being poured into 200 mL of ice water. The aqueous phase was extracted with 100 mL of methylene chloride and the combined organic layers were washed consecutively with cold 5 N hydrochloric acid (200 mL) and saturated sodium bicarbonate solution, prior to drying and evaporation. There was obtained 2.68 g (85%) of a white crystalline solid, recrystallization of which from ethyl acetate gave colorless blades: mp 151.5–153 °C; NMR δ_{Me_4Si} ($CDCl_3$) 2.8 (m, 4), 3.02 (s, 6), 3.2 (m, 4), and singlets at 4.74, 4.90, and 5.04 (total 2 H).

Anal. Calcd for $C_{12}H_{16}O_6S_2$: C, 44.99; H, 5.03; S, 20.02. Found: C, 44.93; H, 5.06; S, 19.81.

6,10-Diiodopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (14). A mixture of 200 mg (0.6 mmol) of dimesylate **13b** and 1.88 g (12.5 mmol) of sodium iodide in 4 mL of anhydrous hexamethylphosphoramide was heated to 130–140 °C under nitrogen for 2 days. The resultant black solid mixture was cooled and treated with 50 mL of water. The suspension was extracted with diethyl ether followed by washing of the combined organic phases with 6 N hydrochloric acid, water, and saturated sodium bicarbonate solution. Drying, filtration, and evaporation left 230 mg of orange oil which solidified on standing. The diiodide was purified by column chromatography on silica gel (pentane elution). The colorless crystals so obtained (216 mg, 90%) were recrystallized from petroleum ether: mp 171–173 °C; NMR δ_{Me_4Si} ($CDCl_3$) 2.44–3.60 (br m, 8) together with singlets at 3.76, 3.88, and 4.02 (total 2 H).

Anal. Calcd for $C_{10}H_{10}I_2$: C, 31.28; H, 2.63. Found: C, 31.56; H, 2.77.

Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene (6). Method A. A dry 250-mL three-neck, round-bottom flask was charged with 2 g (87 mg-atom) of sodium and 2 g (51 mg-atom) of potassium under nitrogen. The flask was evacuated to 0.1 mm and the metals were fused by heating with a Bunsen burner. The flask was permitted to cool and the vacuum was carefully released under nitrogen. The sodium–potassium alloy was treated with 50 mL of dry tetrahydrofuran followed by the dropwise addition of 4.95 g (12.9 mmol) of **14** in 100 mL of the same solvent. The resultant gray suspension was stirred for 12 h and allowed to settle. The supernatant solution was removed by syringe and the flask was rinsed with 25 mL of pentane which was again removed by syringe. The combined organic layers were suction filtered through a pad of Celite to remove inorganic solids and the filtrate was carefully concentrated under reduced pressure (80 mm) at 10 °C to a volume of 25 mL. The dark solution was diluted to 250 mL with water and extracted with three 100-mL portions of pentane. The combined organic extracts were washed several times with water and brine prior to drying. After filtration, the volume of solution was reduced to 10 mL as before and the solution was placed in a sublimator where the remainder of the solvent was removed under vacuum. Sublimation of hypostrophene from the resultant orange oil was achieved at 25 °C and 0.1 mm with the use of a dry ice cooled cold finger to give 890 mg (54%) of **6** as pungent colorless plates. The spectra of this hydrocarbon were identical with those described earlier.[9]

Method B. A dry 1-L round-bottom flask was charged with 8.0 g of sodium and 8.0 g of potassium. After evacuation, the alloy was prepared as described above. After cooling, anhydrous ether (200 mL) was added under a nitrogen atmosphere. The resulting mixture was

stirred magnetically. A solution of **14** (20 g) in 400 mL of ether was added dropwise, and stirring was maintained at room temperature for 15 h. Workup in the predescribed manner (except washing with ether) followed by careful removal of solvent left 5.2 g of a low melting solid which was chromatographed on silica gel (pentane elution). The amount of hypostrophene recovered was 4.1 g (61%).

Bromination of Hypostrophene. To an ice-cold solution of **6** (0.5 g) in 20 mL of carbon tetrachloride was slowly added 0.62 g of bromine with a syringe. Stirring was continued for 30 min prior to washing with water and drying. Removal of the solvent left 1.12 g (95%) of **17** as a pale yellow oil which turned dark green after several hours at room temperature: NMR δ_{Me_4Si} ($CDCl_3$) 5.92 (m, 2), 5.72 (m, 2), 3.92 (m, 1), and 3.70–3.0 (m, 4); *m/e* calcd 287.9150, found 287.9156.

***syn*-8-Bromo-*endo*-dicyclopentadiene (18).** A solution of **17** (1.0 g) in 5 mL of anhydrous ether was added dropwise to a stirred suspension of lithium aluminum hydride (0.3 g) at 20 °C, cooled to 0 °C, and treated sequentially with 0.3 mL of water, 0.3 mL of 15% sodium hydroxide solution, and 0.9 mL of water. The precipitated salts were removed by filtration and rinsed well with ether. The filtrate was washed with brine, dried, and evaporated to give 0.57 g (80%) of **18:** NMR δ_{Me_4SI} ($CDCl_3$) 5.93 (m, 2), 5.48 (m, 2), 3.92 (m, 1), 3.42–2.40 (m, 5), and 2.27–1.98 (m, 1); *m/e* calcd 210.0045, found 210.0048.

***endo*-Dicyclopentadiene (19).** To a stirred solution of 0.40 g of sodium in 40 mL of liquid ammonia maintained at −78 °C was added dropwise 900 mg of **18** dissolved in 10 mL of ether. After 30 min, solid ammonium chloride was added to discharge the blue color, the ammonia was allowed to evaporate, water (25 mL) was added, and the product was extracted into ether (3 × 20 mL). The combined organic layers were dried and evaporated to give 510 mg (92%) of hydrocarbon **19,** the spectral properties of which were identical with those of an authentic sample.

Dibromocarbene Addition to 18. To a solution containing 250 mg of **18,** 50 mg of triethylbenzylammonium bromide, 7.6 g of bromoform, and 3 mL of benzene was added 1.6 mL of 50% sodium hydroxide solution and the mixture was stirred at room temperature for 48 h. Water (10 mL) was added and a small amount of tarry solid was removed by filtration. The layers were separated and the aqueous phase was extracted with chloroform (3 × 25 mL). The combined organic solutions were washed with brine, dried, and evaporated. There was obtained 0.4 g of an oil which solidified on overnight storage in a refrigerator. Two recrystallizations from ethanol afforded 250 mg (55%) of pure **20a:** mp 105–106 °C; NMR δ_{Me_4Si} ($CDCl_3$) 6.17 (m, 2), 3.90 (m, 1), 3.30–3.10 (m, 1), 3.10–2.28 (m, 3), and 2.25–1.57 (m, 4).

Anal. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90. Found: C, 34.84; H, 3.05.

Dichlorocarbene Addition to 18. The identical procedure was followed, except for substitution of bromoform by chloroform. There was obtained a 71% yield of **20b,** mp 78–79 °C, after two recrystallizations from ethanol. The ^1H NMR spectrum of **20b** was similar in many respects to that of **20a.**

Reduction of 20a. A solution of **20a** (200 mg) in 3 mL of ether was added dropwise to a solution of sodium metal (300 mg) in liquid ammonia (50 mL) maintained at −70 °C. After 30 min, the excess sodium was destroyed by addition of solid ammonium chloride. The ammonia was allowed to evaporate, water was carefully added, and the aqueous mixture was extracted with ether (3 × 25 mL). The combined organic layers were dried and carefully evaporated to leave 70 mg (70%) of **21:** NMR δ_{Me_4Si} ($CDCl_3$) 6.15 (m, 2), 3.0–2.15 (m, 4), 1.84–0.71 (m, 6), 0.61–0.31 (m, 1), and 0.19 to −0.42 (m, 1).[29]

Dichlorocarbene Addition to 19. A mixture of *endo*-dicyclopentadiene (0.70 g), triethylbenzylammonium bromide (50 mg), and chloroform (5 mL) was treated with 3.5 mL of 50% sodium hydroxide solution and stirred at room temperature for 60 h. Workup in the predescribed fashion furnished 1.0 g of **22:** NMR δ_{Me_4Si} ($CDCl_3$) 6.04 (m, 1), 4.42 (m, 1), and 3.05–1.40 (m, 10); *m/e* calcd 295.9693, found 295.9696.

***syn*-8-Bromo-*exo*-1-hydroxy-*endo*-dicyclopentadiene (23). A. By Rearrangement of Hypostrophene.** An ice-cold solution of hypostrophene (100 mg) in 1 mL of dimethyl sulfoxide was treated with 0.2 mL of water and 140 mg of *N*-bromosuccinimide and stirred at 0 °C for 2 h. Saturated sodium bicarbonate solution (20 mL) was added, the mixture was extracted with ether (3 × 20 mL), and the combined organic layers were washed with brine and dried. Evaporation of solvent left 130 mg (74%) of **23** as a colorless oil: NMR δ_{Me_4Si} ($CDCl_3$) 5.90 (m, 2), 5.70 (m, 2), 4.09 (m, 1), 3.95 (m, 1), 3.55–3.20 (m, 2), 3.20–2.95 (m, 1), 2.68–2.45 (m, 1), and 2.40 (br s, 1).

The bromo alcohol was converted to its crystalline acetate **24,** mp 90–91 °C (from pentane–ether, 9:1), for further characterization: NMR δ_{Me_4Si} ($CDCl_3$) 6.20–5.55 (m, 4), 4.95 (m, 1), 3.98 (m, 1), 3.60–3.25 (m, 2), 3.25–3.0 (m, 1), 2.60–2.45 (m, 1), and 2.02 (s, 3).

Anal. Calcd for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87. Found: C, 53.61; H, 5.03.

B. Hydrolysis of 17. A mixture of **17** (500 mg), water (6 mL), acetone (12 mL), and calcium carbonate (500 mg) was stirred at 20 °C for 24 h. The acetone was removed under reduced pressure, the residue was diluted with water and extracted with ether (3 × 25 mL), and the combined organic layers were washed with brine and dried. After solvent removal, there remained 350 mg (80%) of **23** which also was directly converted to its acetate, mp 90–91 °C.

***exo*-Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]dec-4-en-8-ol (25).** A solution of 2.6 g (20 mmol) of **6** in 40 mL of dry tetrahydrofuran was cooled to 0 °C under nitrogen and 9-borabicyclononane in tetrahydrofuran solution (0.5 M, 40 mL, 20 mmol) was added dropwise during 2 h. The resultant mixture was allowed to warm to ambient temperature during 1.5 h and cooled again to 0 °C. Sodium hydroxide solution (15%, 10 mL) was added, followed by 8 mL of 30% hydrogen peroxide. This mixture was stirred for 8 h prior to saturation with potassium carbonate and separation of the layers. The aqueous phase was extracted with 100 mL of ether and the combined organic phases were dried. Filtration and solvent evaporation gave a large quantity of yellow oil which was chromatographed on Florisil (elution with ligroin–ether). Recovered hypostrophone amounted to 0.72 g while later fractions yielded 1.58 g (73%) of exo alcohol **25** as a low-melting, semicrystalline material. Purification could be achieved by gas chromatography on a 6 ft SE-30 column at 110 °C: NMR δ_{Me_4Si} ($CDCl_3$) 6.31 (m, 2), 4.20 (dd, J_{syn} = 7 Hz, 1), 3.32 (m, 5), 2.92 (m, 1), 2.15 (dd, J_{gem} = 15, J_{syn} = 7 Hz, 1), 1.89 (s, 1), and 1.56 (m, 1).

The 3,5-dinitrobenzoate of **25,** prepared by the customary procedure and recrystallized from ether, was obtained as off-white crystals, mp 136–137 °C.

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.19. Found: C, 59.76; H, 4.20; N, 8.03.

Epoxidation of Hypostrophene. A solution of 890 mg (6.85 mmol) of **6** in 25 mL of chloroform was cooled to 0 °C under nitrogen and a solution of 1.18 g (6.85 mmol) of *m*-chloroperbenzoic acid in 10 mL of chloroform was added dropwise during 30 min. The reaction mixture was allowed to warm to room temperature with stirring for 12 h prior to washing with saturated sodium bicarbonate solution and drying. The solvent was evaporated under reduced pressure and the resultant yellow oil was taken up in pentane and deposited on a Florisil column. Chromatography (elution with pentane) provided 78 mg of recovered hypostrophene, 667 mg of monoepoxide **26,** and 170 mg of bisepoxide **27.** The yield of monoepoxide based on recovered **6** was 73%, while that of **27** was 15%.

The monoepoxide was recrystallized from pentane and obtained as colorless crystals: mp 170 °C dec; NMR δ_{Me_4Si} ($CDCl_3$) 6.14 (s, 2), 2.84–3.44 (br m, 5), 3.36 (s, 2), and 2.64–2.80 (m, 1).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.02; H, 6.99.

The bisepoxide when recrystallized from ether was isolated as colorless needles which sublimed slowly above 150 °C and decomposed above 200 °C; NMR δ_{Me_4Si} ($CDCl_3$) 3.51 (s, 4), 3.08 (m, 4), and 2.56 (m, 2).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.80; H, 6.25.

9,9-Dibromopentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{8,10}]undec-4-ene (28a). A solution of 170 mg (1.31 mmol) of **6** in 5 mL of pentane was cooled to −30 °C and 291 mg (2.6 mmol) of potassium *tert*-butoxide (sublimed) was added in one portion. The resultant slurry was treated slowly while magnetically stirred with 329 mg (1.30 mmol) of bromoform in 2 mL of pentane. The ten colored suspension was stirred under nitrogen for 12 h at room temperature prior to addition of 25 mL of pentane and 50 mL of water. The layers were separated and the aqueous phase was further extracted with 10 mL of pentane. The combined pentane extracts were washed once with water and dried. Distillation of the pentane at 60 °C through a short Vigreux column left a colorless solution (5 mL) which deposited colorless crystals upon standing in a freezer overnight. The crystalline precipitate was filtered to give 35.5 mg (15%) of bisadduct **29a.** Recrystallization from hexane gave off-white plates which decomposed between 175 and 205 °C: NMR δ_{Me_4Si} ($CDCl_3$) 3.18 (dd, 4), 2.78 (m, 2), and 2.35 (s, 4).

Anal. Calcd for $C_{12}H_{10}Br_4$: C, 30.41; H, 2.13. Found: C, 30.52; H, 2.20.

The mother liquors were evaporated under reduced pressure to give a yellow oil from which was sublimed 100 mg of hypostrophene [50–60 °C (20 mm)] and finally 126 mg (77%) of **28a** [60 °C (0.05 mm)] as white crystals which turned yellow on standing. Recrystallization from pentane provided large, colorless crystals: mp 79–80 °C; NMR δ_{Me_4Si} ($CDCl_3$) 6.23 (s, 2), 3.10–3.48 (br m, 4), 3.01 (m, 1), 2.76 (m, 1), and 2.03 (s, 2).

Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.74; H, 3.34. Found: C, 43.84; H, 3.37.

Pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{8,10}]undec-4-ene (28b). A. Simmons–Smith Reaction of Hypostrophene. A zinc–silver couple was prepared as follows: a mixture of 2 mg of silver acetate in 1 mL of glacial acetic acid was heated to boiling and 144 mg (2.2 mg-atom) of 30 mesh granulated zinc was added in one portion with stirring under nitrogen. After 30 s, the acetic acid solution was pipetted from the mixture and the couple was washed with 1 mL of fresh acetic acid followed by five 1-mL portions of anhydrous diethyl ether. Finally, 1.5 mL of dry diethyl ether was added as the reaction solvent.

The ether suspension of the gray-brown couple was treated with 100 mg (0.77 mmol) of **6**. While under nitrogen, a solution of 295 mg (1.1 mmol) of diiodomethane in 1.5 mL of ether was added dropwise during 10 min. The mixture was refluxed while the progress of the reaction was followed by gas chromatography. After 88 h, the mixture was cooled to 0 °C and pyridine was added dropwise to precipitate zinc salts. After suction filtration, the clear filtrates were again treated with pyridine until no more precipitate formed. The mixture was filtered and reduced in volume to 1 mL. Preparative gas chromatography on a 2 ft SE-30 column at 65 °C gave three components: 10 mg of recovered hypostrophene, 17 mg (17% yield) of **28b**, and 15 mg (14%) of **29b**. For **28b**: NMR δ_{Me_4Si} ($CDCl_3$) −0.24 (dd, 1), 0.25 (dt, 1), 1.19 (dd, 2), 2.48–3.46 (br m, 6), and 6.28 (br s, 2).

Anal. Calcd for $C_{11}H_{12}$: C, 91.08; H, 8.92. Found: C, 91.48; H, 9.07.

For **29b**: NMR δ_{Me_4Si} ($CDCl_3$) −0.33 (dd, 2), 0.36 (dt, 2), 1.42 (dd, 4), 2.36–2.64 (m, 4).

Anal. Calcd for $C_{12}H_{14}$: C, 91.61; H, 8.39. Found: C, 91.26; H, 8.77.

B. Reductive Debromination of 28a. A solution of 50 mg (0.165 mmol) of **28a** in 1 mL of dry tetrahydrofuran was treated with 50 mg of lithium wire and 0.5 mL of dry *tert*-butyl alcohol portionwise over 30 min. After 1 h, a cloudy precipitate had formed and the lithium was visibly reacting. After an additional 3 h, the mixture was decanted to remove lithium pieces and the solution was diluted with 25 mL of water. The aqueous mixture was extracted with two 25-mL portions of diethyl ether followed by washing of the combined organic layers with water and drying. The mixture was filtered and concentrated by distillation through a short Vigreux column (60 °C bath) to a volume of 1 mL. Preparative gas chromatography on a 2 ft SE-30 column at 65 °C gave 18 mg (76%) of a colorless oil whose ^1H NMR spectrum was identical with that of **28b** prepared in part A.

***exo*-1,*syn*-8-Dihydroxy-*endo*-dicyclopentadiene (30).** Epoxide **26** (60 mg) was added to 5.0 mL of 10% perchloric acid. The flask was stoppered and the mixture shaken at room temperature for 3 h. Neutralization was effected with sodium bicarbonate solution. After dilution with brine (150 mL), the solution was continuously extracted with methylene chloride for 2 days. The extract was dried and concentrated to leave 50 mg (76%) of **30** which was directly acetylated (90%) to facilitate handling: NMR δ_{Me_4Si} ($CDCl_3$) 6.12–5.92 (m, 1), 5.92–5.73 (m, 2), 5.73–5.57 (m, 1), 4.98 (m, 1), 4.58 (m, 1), 3.57–3.18 (m, 2), 3.12–2.95 (m, 1), 2.65–2.47 (m, 1), 2.03 (s, 3), and 1.98 (s, 3). These compounds exhibited spectra identical with those of authentic samples.[35]

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