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Regiocontrolled Hydrogenolysis of Strained σ Bonds. Application to the Synthesis of *syn*- and *anti*-Tricyclo[4.2.1.1^{2,5}]decane and Two Elusive Cyclopentadiene Dimers

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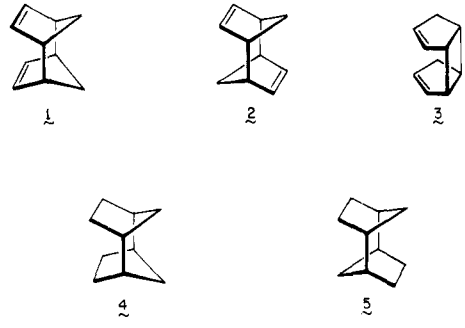
Abstract: Catalytic hydrogenation of hypostrophene over palladium on charcoal resulted in regiospecific σ bond hydrogenolysis to give *syn*-tricyclo[4.2.1.1^{2,5}]decane (**4**). Similar treatment of the *exo*-8-hydroxy derivative furnished *syn*-tricyclo[4.2.1.1^{2,5}]decan-*exo*-3-ol (**13a**). The latter compound served as precursor to both *syn*- and *anti*-tricyclo[4.2.1.1^{2,5}]-dec-3-enes. When pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-diol (**18**) was hydrogenated, the dihydro derivative **19a** resulted. By a sequence of reactions involving mesylation, displacement by iodide ion, and reductive deiodination, **19a** was transformed into *syn*-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (**1**). Warming of **1** to 55–80 °C promotes efficient Cope rearrangement to *cis,-syn,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (**3**). Lastly, the behavior of **4** under electrophilic and strongly acidic conditions is described. That neither the bromination of **4** nor its isomerization to adamantane can be effected readily is taken as an indication that this exceptionally highly strained molecule cannot ionize readily and transform itself into more thermodynamically stable cations capable of controlled Wagner–Meerwein shifts.

A thermally or photochemically excited polyolefinic molecule will almost invariably react with strict adherence to orbital symmetry control, because of the obvious energetic advantages to be gained by following such pathways. Cyclopentadiene is a case in point. While thermal association proceeds exclusively by [4 + 2]π cycloaddition to give *endo*-dicyclopentadiene, photochemical activation results only in intramolecular electronic reorganization and bicyclo[2.1.0]pentene formation.[1] Other possible dimerization reactions, such as those leading to the interesting tricyclic hydrocarbons **1–3,** are either disallowed on the basis of frontier orbital considerations or disfavored for entropic and steric reasons.



1 2 3 4 5

These molecules, and the related saturated hydrocarbons **4** and **5** as well, have attracted special interest for several reasons. As concerns **1–3,** knowledge of the relative levels of through-bond and through-space interaction would be revealing.[2,3] All three are considered to be reasonably rigid structures containing two π systems capable of effective through-bond interaction with resultant significant lengthening of these particular σ bonds on the molecular periphery. In contrast, while **1** and **3** might exhibit through-space coupling, **2** cannot possibly partake of this phenomenon because of obvious geometric constraints. At the same time, **1–3** are not anticipated to be capable of facile thermal fragmentation to cyclopentadiene. The energies required to achieve the necessary [4 + 4] and [2 + 2] cycloreversions could, on the other hand, provide quantitative indication of the "forbiddenness" of such reactions.

The $C_{10}H_{16}$ isomers **4** and **5** not only have comparable topological appeal, but also enjoy an isomeric relationship to adamantane. Molecular mechanics calculations have assessed **4** to be a highly strained substance, chiefly because the 1,3 fusion of two cyclopentane rings in "head-to-head" fashion leads to full eclipsing of all the endo hydrogens.[4] Steric strain is lowered in the "head-to-tail" orientation adopted by **5** as the direct result of the more staggered arrangement of the interior methylene hydrogens. Therefore, this pair of isomers could provide an estimate of the steric forces which gain importance as one five-membered ring is rotated by π/5 radians above a second while being maintained within bonding promixity. Also, the Lewis acid catalyzed isomerizations of **4** and **5** are anticipated to hold considerable mechanistic interest.[5] On the basis of molecular mechanics calculations, both **4** and **5** have been ignominiously relegated to mechanistic dead-end positions in "adamantaneland".

Clearly, the successful preparation of such molecules rests upon suitable improvisation of indirect synthetic methodology. In this paper, we report details of the relatively efficient preparation of **1** and **3–5.** Since the appearance of our preliminary communications on this subject,[7,8] Eaton and Ganter have published their independent work describing complementary alternative approaches to *syn*- and *anti*-tricyclo[4.2.1.1^{2,5}]decane (**4** and **5**).[9,10] Additionally, Turro and co-workers have recently gained access to **3** by suitable decomposition of an appropriate azo precursor molecule.[11]

***syn*-Tricyclo[4.2.1.1^{2,5}]decane (4).** The face-to-face juxtapositioning of two cyclopentane rings which forms the struc-

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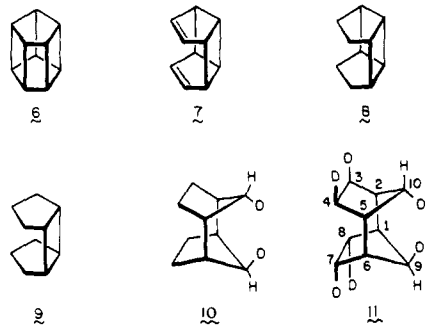
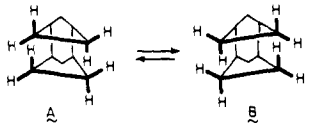
tural basis for **1**, **3**, and **4** reaches its pinnacle in pentaprismane (**6**), a substance which continues to defy synthesis. The removal of two contiguous interlayer bonds from **6** serves to release significant amounts of strain and, indeed, the successful preparation of hypostrophene (**7**) has been achieved by two



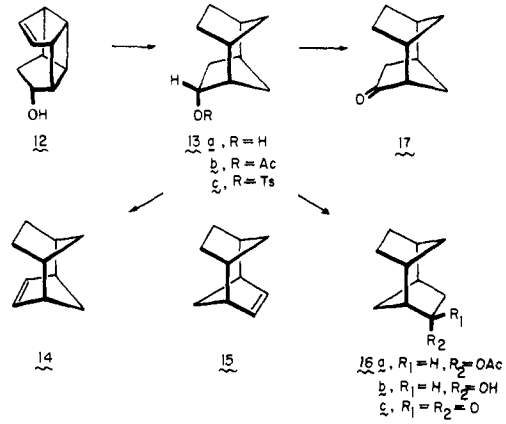
groups.[12,13] With the availability of this diene, our attention was drawn to recent reports emanating chiefly from Musso's laboratory[14] that strained cyclobutane rings are subject to hydrogenolysis under mild conditions.[15] Furthermore, the susceptibility to σ bond cleavage appears to parallel the level of stress being applied to a given C—C linkage. Although the pair of doubly allylic lateral σ bonds in **7** is known to be prone to relatively facile homolysis and [3.3]sigmatropic shift,[12] presumably because of their in-plane relationship to the $p\pi$ orbitals, strain energy is most certainly concentrated to the highest degree in the bond central to the bicyclo[2.2.0]hexane moiety. Support for this conclusion is available from the thermochemical behavior of numerous bicyclo[2.2.0]hexane derivatives[16-19] and photoelectron spectroscopy studies.[20]

In agreement with this precedent, catalytic hydrogenation of **7** over palladium on carbon at atmospheric pressure in hexane solution for several hours led quantitatively (75% isolated) to a crystalline hexahydro product which has been characterized as **4**. This substance differs unmistakably from **8** and **9** which are available by diimide reduction of **7** and Cu(I)-catalyzed photodimerization of cyclopentene,[21] respectively. The C_{2v} symmetry of **4** is particularly evident in its ^{13}C NMR spectrum which is comprised of only three signals. The ^1H NMR spectrum is characterized by five multiplets at δ 2.27 (4 H), 1.75 (2 H), 1.74-1.65 (4 H), 1.19 (4 H), and 0.45 (2 H). To assist in making appropriate assignments, use was made of Toyne's earlier observations[15d] that hydrogenolysis of strained σ bonds proceeds with retention of configuration. Accordingly, **8** was subjected to catalytic reduction in the presence of molecular deuterium. The sample of **10** so obtained was found to lack the two-proton signal centered at δ 1.75 and to have the normal upfield doublet at 0.45 supplanted by a broad singlet. The interior protons at C_9 and C_{10} are therefore substantially deshielded, in line with their highly compressed nature.[22] Hydrocarbon **11**, which was made available by comparable deuteration of **7**, shows only three singlets at δ 0.43 (2 H), 1.65 (4 H), and 2.26 (4 H) attributable to $H_{9,10exo}$, $H_{3,4,7,8endo}$, and $H_{1,2,5,6}$, respectively. Thus, compression effects in the ethano bridge are not reflected in equally dramatic chemical shift differences ($\Delta\delta$ = 0.46), as expected. This is thought to be a consequence of the fact that **4** adopts a twisted ground state conformation which rapidly flexes between forms A and B. Our attempts to scrutinize this presumed intercon-



version by NMR techniques at low temperatures proved fruitless. Nor were we hopeful of making direct observation of this dynamic interconversion in view of the very low barrier anticipated for the A $\rightleftarrows$ B process (<2.5 kcal/mol).

***anti*-Tricyclo[4.2.1.1^{2,5}]decane (5).** An obvious scheme for transforming the *syn*-tricyclo[4.2.1.1^{2,5}]decane framework into its anti counterpart involves Wagner-Meerwein shift of an interconnective bond. However, to avoid possible continued cascade to thermodynamically more stable isomeric structures, we initially considered it wise to avoid inducement of such 1,2 carbon migrations under carbocationic conditions. Therefore, our attention was first directed to development of a procedure which would be chemically controlled in this sense. To this end, the known alcohol **12**[13,23] was catalytically hydrogenated over 5% Pd/C on hexane to give **13a** in 98% yield. Flow pyrolysis of the derived acetate (**13b**) at 600 °C in the gas phase produced a mixture of the monoolefins **14** and **15** (ratio 1.4:1) in



addition to a minor unidentified substance. The conversion of **13b** to **15** may proceed by an ion-pair mechanism of the type proposed by others to account for charge effects observable in such acetate eliminations[23] or by the surface-catalyzed carbonium ion pathway advanced by Wertz and Allinger.[24] Irrespective of mechanistic detail, the driving force behind this rearrangement is undoubtedly steric strain relief since passage of a boat cyclohexane conformation to a chair form is also involved. The heats of formation and strain energies of **4** and **5** as calculated by using the Engler[4] and Allinger[26] force fields suggest **5** to be more stable by 8-11 kcal/mol.

In actuality, a more favorable product distribution (1:2) and improved yields were realized upon dehydration of **13a** with phosphorus oxychloride in pyridine.

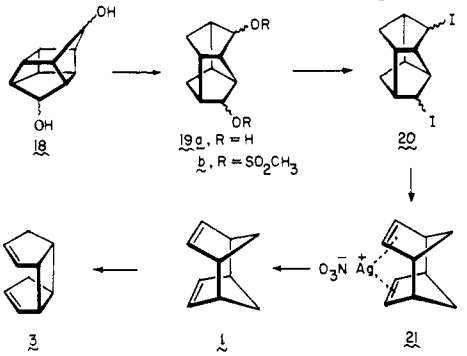
The preceding results ultimately led us to examine the buffered acetolysis of tosylate **13c**. This reaction proved to be remarkably clean and to give a 3:7 mixture of **15** and **16a** in high yield. No additional products could be detected! Structural assignment to the rearranged acetate is based on spectroscopic analysis and its sequential hydride reduction-Collins oxidation to **16c**. This ketone is seen to be the translocated isomer of **17** which was made available by comparable oxidation of **13a**.

Comparative analysis of the ^1H and ^{13}C NMR spectra of **14** and **15** is of some interest. The most characteristic features of the syn olefin are a narrow two-proton multiplet at δ 6.28 (in $CDCl_3$) and a well-defined doublet of triplets of area 2 at 0.90-0.75. Its remaining ten protons generate a continuum of multiplets in the 2.61-0.85 region. Because C_9 and C_{10} in the anti olefin find themselves in very different shielding environments, the exo protons at these sites become widely disparate in chemical shift (δ 0.80-0.67 and 1.27-1.07). Its olefinic protons are somewhat more shielded (δ 5.87) than those in **14** and a narrow two-proton multiplet centered at 2.40 appears well separated from the group of peaks at 1.99-1.57 (8 H). The three sets of methylene carbons in **14** appear consistently at higher field than those in **15**: 29.14 vs. 29.94; 33.88 vs. 35.61;

37.23 vs. 41.06 ppm. No comparable pattern materialized for the methine carbons: 36.77 and 40.36 vs. 32.70 and 43.97.

Catalytic hydrogenation of **15** gave **5** efficiently. Its ^{1}H NMR spectrum in $CDCl_3$ consists of a two-proton multiplet centered at δ 0.89 and companion multiplets at 1.58 (8 H), 1.78 (2 H), and 1.95 (4 H). The ^{13}C NMR spectrum clearly reveals the C_{2h} symmetry of the molecule: 29.28 (t), 33.69 (t), and 39.66 ppm (d).

***syn*-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (1).** Our strategy for the synthesis of **1** was founded entirely on the premise that suitable unmasking of the pair of double bonds in the final step would be most expeditious. To this end, the readily available bishomocubanediol **18**[13] was subjected to catalytic reduction over palladium on charcoal at 40–50 psig. In line with earlier results,[15d,e] regiospecific σ bond hydrogenolysis resulted to give **19a** exclusively. Conversion of **19a** to its dimesylate (**19b**) and subsequent elaboration of diiodide **20** through use of sodium



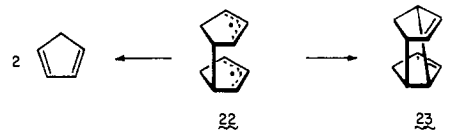
iodide in anhydrous hexamethylphosphoramide (135 °C, 3 days) proceeded essentially as planned. In the second step of this sequence, 10–15% of monoiodomonomesylate was invariably recovered, even when more extensive reaction times were utilized. Presumably this situation results from the low reactivity of one or more dimesylate epimers. Nonetheless, the ^{1}H NMR spectrum of purified **20** (in $CDCl_3$) unmistakably revealed the presence of three isomers on the basis of three methine signals at δ 3.95, 3.83, and 3.73. The dominant diiodide (50–70%) exhibited the peak at 3.83.

Reductive deiodination of **20** was effected most efficiently through use of sodium–potassium alloy, as developed earlier in our hypostrophene synthesis.[13] Overnight exposure to the liquid metal (1:1 w/w) in ether gave the desired pungent, volatile diene **1**. This hydrocarbon could not be successfully purified by preparative VPC due to its thermal lability (see below). Although **1** is easily sublimed, this procedure did not succeed in removing small amounts of equally volatile byproducts. Successful purification was achieved, however, by conversion to the stable, colorless, crystalline silver nitrate complex **21** and subsequent liberation of **1** by conventional treatment with concentrated ammonium hydroxide solution. The ease with which **21** can be reversibly transformed to **1** stands in striking contrast to the marked stability of its Rh(I) complex from which the diene cannot be freed.[27]

As with **4**, the transannular steric strain in **1** is easily detected spectroscopically. For example, the inner and outer methylene protons at C_9 and C_{10} appear in the ^{1}H NMR spectrum at δ 2.71 (d, J = 9.98 Hz) and 1.83 (br d, J = 9.98 Hz). Its three ^{13}C NMR signals reveal the symmetry of the molecule.

Characterized by a pair of low energy bands having IPs at 8.65 ± 0.1 and 8.90 ± 0.07 eV, the photoelectron spectrum of **1** attests to the existence of very intimate coupling of the σ and π orbitals.[28] The extreme broadness of the bands is particularly revealing in this regard. Similar effective through-bond coupling of exceptionally high lying σ levels has been observed previously in a few instances,[3a,29] although examples of preferred through-space overlaps also have been recognized.[30]

***cis,syn,cis*-Tricyclo[5.3.0.0^{2,6}]deca-3,9-diene (3).** Warming a C_6D_6 solution of **1** to 55–80 °C causes exceptionally clean [3,3]sigmatropic carbon shift to occur. The progress of this rearrangement could easily by monitored by ^{1}H NMR spectroscopy through integration of the signals of key protons in both **1** (disappearance) and **3** (appearance) relative to the area of the dioxane internal standard. First-order kinetic behavior was observed with rate constants $k_{58.5°C} = 1.64 \times 10^{-5}$ s^{-1}, $k_{68.5°C} = 5.68 \times 10^{-5}$, and $k_{79.5°C} = 18.41 \times 10^{-5}$. The corresponding activation parameters are $\Delta H^{\ddagger} = 26.1$ kcal/mol and $\Delta S^{\ddagger} = -1.98$ eu. When this skeletal isomerization was conducted through numerous half-lives, no spectroscopically detectable quantities of cyclopentadiene, *endo*-dicyclopentadiene, or *exo*-dicyclopentadiene (**23**) were detected. Apparently, the predescribed conditions are not conducive to the generation of biradical **22** which might be expected either to fragment or reclose with formation of **23**.



22 23

The structural assignment to **3** follows from its characteristic spectral properties: ^{1}H NMR (δ, C_6D_6) 5.83–5.77 (br m, 2 H), 5.44 (m, 2 H), 3.42 (m, 2 H), 2.89 (m, 2 H), and 2.25 (m, 4 H). In particular, double resonance studies involving independent saturation of the 5.44 and 2.89 multiplets caused the downfield olefinic peak to become a doublet (J = 5.1 Hz) and triplet (J = 4.0 Hz), respectively.

The overwhelming adherence by **1** to synchronous six-electron rearrangement rather than to a stepwise homolytic pathway involving the generation of **22** is mechanistically instructive. The observed reaction course delivers **3** in irreversible fashion; although this product is less strained than its precursor, it is clearly not strain-free. The exclusion of more thermodynamically favored products, e.g., **23**, is regarded as an exploitable benefit of orbital symmetry.

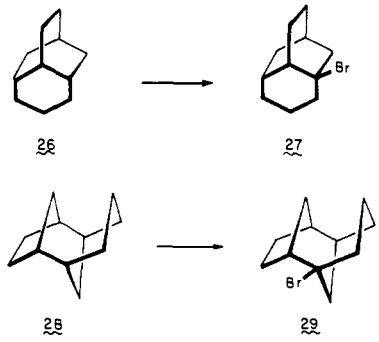
The level of through-bond interaction operative in **1** can be expected to result in significant extension of the C_1–C_2 and C_5–C_6 bonds. Although these lateral bonds are weakened, electrocyclic dissociation to two molecules of cyclopentadiene is disallowed. Therefore, only one of these bonds can experience fission and does so specifically by Cope rearrangement. Close analogy to this behavior has previously been observed with **24**[31] and predicted for *p,p'*-dibenzene (**25**).[3b]

24 25

Behavior of 1 under Electrophilic and Strongly Acidic Conditions. All previously known tricyclodecanes have been shown to rearrange to adamantane when treated with suitable Brönsted and/or Lewis acids.[5,32] The success of this chemistry rests on the high thermodynamic stability of adamantane relative to its isomers,[33] as well as the ability of the catalysts to produce cationic intermediates and to sustain their extensive and intricate isomerization through numerous intermediates until equilibrium is established. A serious limitation would obviously arise if cation formation were not initiated, although no limit of such a possible complication has been mentioned in the $C_{10}H_{16}$ rearrangements reported to date. However, none of these reactions has involved a substrate as strained as **4**.

Extreme variations in bridgehead reactivity are well known; for example, more than 12 powers of ten separate the solvolysis rates of 1-bicyclo[2.2.1]heptyl and 3-homoadamantyl derivatives.[34] This wide deviation has been satisfactorily accounted for in terms of the strain increase encountered in proceeding

from ground to transition state.[35] Principally as a result of Inamoto's efforts, we have also come to recognize that the relative reactivity of bridgehead sites in an *unstrained tricycloalkane* can be predicted from the nature of its bicyclic components. Thus, the brominations of 4-homoisotwistane (**26**) and tricyclo[4.3.1.1^{2,5}]undecane (**28**) proceed regiospecifically to deliver **27**[36] and **29**,[37] respectively. In both instances, rate-



26 **27**

28 **29**

determining hydride abstraction by Br^+ favors bicyclo[3.3.1]non-1-yl cation intervention over the other options. Solvolytic studies indeed show the bicyclo[3.3.1]non-1-yl cation to be $>10^5$ more stable than the bicyclo[3.2.1]- and bicyclo[2.2.2]oct-1-yl systems.[34]

Simple considerations of this type are not as directly applicable to **4** (calcd $\Delta H_f°$ 0.96)[4] which possesses substantially greater levels of strain than **24, 26,** or for that matter protoadamantane (calcd $\Delta H_f°$ −21.13) and bicyclo[3.3.1]nonane (calcd $\Delta H_f°$ −30.64) which also are prone to ready bridgehead bromination.[38,39] As expected, **4** proved to be strikingly recalcitrant to bromination. Our most forcing conditions (refluxing bromine as solvent with concomitant irradiation from a 275-W sunlamp for 24 h) have failed to give indication that more than a trace of a halogenated product had formed.

In view of the foregoing, it was not surprising to discover that heating solutions of **4** in dichloromethane with trifluoromethanesulfonic acid[40] or aluminum chloride for prolonged periods left the hydrocarbon unchanged. With $AlCl_3$ in refluxing hexane[41] for 57 h, **4** was found to be converted to a myriad of products, of which only three components were of formula $C_{10}H_{16}$ (VPC–mass spectral analysis). One of the latter could have been adamantane. No reaction was observed with $AlBr_3$ in carbon disulfide at 0 °C.[42] With aluminum bromide sludge[43] in cyclohexane at room temperature or at reflux, **4** is totally converted within 3 h to a mixture of products which does contain adamantane (6–8%), but is composed chiefly of compounds of higher molecular weight (*m/e* 138 and 166). These were not investigated.

Finally, alcohol **13a** was subjected to the action of fluorosulfonic acid in dichloromethane.[44] Although much decomposition resulted, an isomeric alcohol was isolated in 4% yield. This substance was not 1-adamantanol (^{1}H NMR analysis).

The inability of the *syn*-tricyclo[4.2.1.1^{2,5}]decane ring system to undergo facile skeletal isomerization to thermodynamically less strained isomers appears to be unprecedented in "adamantaneland". The suppression of Wagner–Meerwein rearrangements would seem to be attributable to the high strain embodied in this framework. This property seemingly precludes access to any of the carbonium ion intermediates which are believed to be capable of downhill cascade to the adamantane energy sink.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60, Varian HA-100, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C NMR spectra were also obtained with the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***syn*-Tricyclo[5.2.1.1^{2,5}]decane (4).** A solution of hypostrophene[13] (100 mg) in hexane (20 mL) was hydrogenated over 5% palladium on carbon (20 mg) at atmospheric pressure. Upon cessation of the uptake of hydrogen, the solution was filtered and the filtrate was carefully evaporated to leave 95 mg of a white solid. Sublimation of this material at 50 °C and 30 mm afforded 75 mg (75%) of **4**, mp 148–150 °C: $\nu_{max}^{CCl_4}$ 3025 (sh), 3000 (sh), and 2975 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27 (m, 4 H), 1.75 (m, 2 H), 1.75–1.65 (m, 4 H), 1.19 (m, 4 H), and 0.45 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 36.04 (4d, $^1J_{C-H}$ = 133 Hz), 29.57 (2t, J = 131 Hz), and 25.79 (4t, J = 132 Hz).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.11; H, 11.71.

Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]decane (8). To a magnetically stirred solution of hypostrophene (100 mg) and potassium azodicarboxylate (2.0 g) in 25 mL of methanol cooled to 0 °C under a nitrogen atmosphere was added dropwise 2.6 mL of acetic acid during 15 min. Stirring at 0 °C was maintained until the yellow color disappeared (3 h). After neutralization with sodium bicarbonate solution, 100 mL of water was added and this solution was extracted with pentane (3×). The combined organic layers were washed with brine, dried, and carefully evaporated to leave 60 mg of **8**: ^{1}H NMR ($CDCl_3$) δ 2.88 (m, 6 H) and 2.00–1.20 (m, 8 H); ^{13}C NMR ($CDCl_3$) 43.43 (2d), 40.41 (4d), and 27.84 ppm (4t).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.49; H, 10.35.

***syn*-Tricyclo[4.2.1.1^{2,5}]decane-*endo,endo*-9,10-d_2 (10).** A solution of **8** (60 mg) in hexane (15 mL) was reductively deuterated over 40 mg of 10% palladium on carbon by using 1 atm of pressure of deuterium gas. After 3 h, the solution was filtered and the filtrate evaporated to give 50 mg of **10** as a waxy solid: ^{1}H NMR ($CDCl_3$) δ 2.27 (m, 4 H), 1.69 (m, 4 H), 1.18 (m, 4 H), and 0.44 (m, 2 H); *m/e* calcd 138.1377, obsd 138.1380.

***syn*-Tricyclo[4.2.1.1^{2,5}]decane-*exo*-3,4,7,8-*endo*-9,10-d_6 (11).** A 55-mg sample of hypostrophene was deuterated as above to give 40 mg of **11** as a waxy solid: ^{1}H NMR ($CDCl_3$) δ 2.26 (m, 4 H), 1.66 (m, 4 H), and 0.43 (m, 2 H); *m/e* calcd 142.1629, obsd 142.1631.

***syn*-Tricyclo[4.2.1.1^{2,5}]decan-*exo*-3-ol (13a).** A solution of *exo*-tetracyclo[5.3.0.0^{2,6}.0^{3,10}]dec-4-en-8-ol (**12**) (1.2 g)[13,23] in hexane (50 mL) was subjected to atmospheric hydrogenation over 5% palladium on carbon for 24 h. The solvent was filtered and the filtrate evaporated to give 1.17 g (98%) of **13a** as a colorless crystalline solid, mp 137–138 °C: ^{1}H NMR ($CDCl_3$) δ 4.38 (m, 1 H), 2.65–1.0 (series of m, 14 H), and 0.54 (m, 1 H); ^{13}C NMR (ppm, $CDCl_3$) 73.38, 45.59, 38.51, 35.77, 35.07, 30.97, 25.79, and 25.20.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.62; H, 10.64.

***syn*- and *anti*-Tricyclo[4.2.1.1^{2,5}]dec-3-ene (14 and 15). A. Pyrolysis of Acetate 13b.** To a solution of **13a** (250 mg, 1.64 mmol) in pyridine (3 mL) was added 335 mg (3.28 mmol) of acetic anhydride. The flask was stoppered and left to stand at room temperature for 24 h. The reaction mixture was poured into ice–water and the product was extracted into pentane (3 × 40 mL). The combined organic extracts were washed successively with 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine (2 × 40 mL each). Drying and evaporation left 390 mg of crude acetate which was utilized without further purification.

A horizontal quartz pyrolysis tube (0.5 cm long, 1 cm diameter) packed with quartz chips was heated to 600 °C. The internal pressure was adjusted to 60 mm, while nitrogen was slowly swept through the system. The acetate (150 mg) was allowed to slowly evaporate into the heated tube and the products were collected in a cold (−80 °C) trap. The contents of the trap were taken up in ether and this solution was washed with sodium bicarbonate solution and brine prior to drying. Careful solvent removal left an oil (80 mg) which was analyzed by VPC (6 ft × 0.25 in. 1 PMPE-6 ring, 160 °C) and shown to be composed of three hydrocarbons in the ratio of 1.4:1:0.3.

The major component was collected and identified as **14**: colorless solid: ^{1}H NMR ($CDCl_3$) δ 6.28 (m, 2 H), 2.65–0.85 (m, 10 H), and 0.90–0.75 (dt, J = 11.4 and 2.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 141.52

(d, $J_{^{13}C-H}$ = 166 Hz, 2 C), 40.36 (d, 132 Hz, 2 C), 37.23 (t, 131 Hz, 1 C), 36.77 (d, 135 Hz, 2 C), 33.88 (t, 129 Hz, 1 C), and 29.14 ppm (t, 130 Hz, 2 C); *m/e* calcd 134.1095, obsd 134.1099.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.40; H, 10.66.

The second most dominant component was identified as **15**: colorless solid: ^{1}H NMR ($CDCl_3$) δ 5.88–5.85 (m, 2 H), 2.40 (m, 2 H), 1.99–1.57 (series of m, 8 H), 1.23–1.07 (m, 1 H), and 0.80–0.67 (m, 1 H); ^{13}C NMR ($CDCl_3$) 132.01 (d, $J_{^{13}C-H}$ = 162 Hz, 2 C), 43.97 (d, 130 Hz, 2 C), 41.06 (t, 120 Hz, 1 C), 35.61 (t, 114 Hz, 1 C), 32.70 (d, 130 Hz, 2 C), and 29.94 ppm (t, 129 Hz, 2 C); *m/e* calcd 134.1095, obsd 134.1098.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.19; H, 10.53.

The minor component was also isolated: ^{1}H NMR ($CDCl_3$) δ 5.72–5.48 (m, 2 H), 2.63–1.78 (m, 8 H), and 1.78–0.89 (m, 4 H). This hydrocarbon was not further characterized.

B. Dehydration of 13a with Phosphorus Oxychloride. A solution of **13a** (150 mg, 0.99 mmol) in dry pyridine (10 mL) was cooled in an ice bath and a solution of phosphorus oxychloride (2.5 mL) in pyridine was added dropwise with vigorous stirring. The reaction was allowed to warm to room temperature with stirring for 12 h and to stand unstirred for an additional 13 h. A few milliliters of cold water was introduced dropwise to the stirred mixture which had previously been cooled to −30 °C. The product was extracted into ether and the combined organic phases were washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine before drying. Careful solvent removal left a yellowish liquid consisting of three components which were separated by preparative VPC. There was isolated 17.1 mg (13%) of **15**, 10.4 mg (8%) of **14**, and 1.2 mg of an unknown liquid.

***syn*-Tricyclo[4.2.1.1^{2,5}]decan-*exo*-2-ol *p*-Toluenesulfonate (13c).** A solution of **13a** (500 mg) and *p*-toluenesulfonyl chloride (700 mg) in pyridine (7 mL) was kept in a refrigerator for 18 h, poured onto ice–water, and extracted with ether. The combined extracts were washed with cold dilute hydrochloric acid, saturated sodium bicarbonate solution, and brine before drying and solvent evaporation. The residual oil was dissolved in pentane and the solution was cooled to −20 °C where crystallization was induced. Repeated recrystallization gave pure **13c** as a colorless solid, mp 73–73.5 °C.

Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.62; H, 7.24. Found: C, 66.65; H, 7.30.

Buffered Acetolysis of 13c. A solution of **13c** (170 mg) and sodium carbonate (90 mg) in 6 mL of glacial acetic acid was heated at 71 °C for 110 h. After the usual workup, 90 mg of a mixture of **15** (30%) and **16a** (70%) was obtained. The acetate was purified by preparative VPC: ^{1}H NMR ($CDCl_3$) δ 5.08 (dt, *J* = 6.7 and 2.1 Hz, 1 H), 2.37–1.15 (series of m, 12 H), 1.99 (s, 3 H), and 1.02–0.87 (m, 2 H); *m/e* calcd 194.1307, obsd 194.1310.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.94; H, 9.18.

***anti*-Tricyclo[4.2.1.1^{2,5}]decan-*exo*-2-ol (16b).** To a stirred suspension of lithium aluminum hydride (220 mg, 4.67 mmol) in dry ether (20 mL) under an argon atmosphere was added dropwise a solution of **16a** (220 mg, 1.13 mmol) in ether (25 mL). The resultant mixture was stirred at room temperature for 2 h and treated sequentially with water (0.25 mL), 15% sodium hydroxide solution (0.25 mL), and water (0.75 mL). The organic layer was separated by decantation and the residual solids were leached with ether. The combined solutions were dried, filtered, and evaporated to give 180 mg of white solid. Chromatography of this material on silica gel (elution with 10% ether in pentane) followed by VPC purification gave the analytical sample of **16b**: ^{1}H NMR ($CDCl_3$) δ 4.26 (dt, *J* = 6.7 and 2.1 Hz, 1 H), 2.33–1.24 (series of m, 13 H), and 0.896 (m, 2 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.04; H, 10.70.

***anti*-Tricyclo[4.2.1.1^{2,5}]decan-2-one (16c).** Chromium trioxide (91 mg, 0.91 mmol) was added to a stirred solution of pyridine (143 mg, 1.81 mmol) in dichloromethane (5 mL). After 20 min, a solution of **16b** (22.7 mg, 0.149 mmol) in dichloromethane (5 mL) was introduced in one portion, and the resultant slurry was stirred at room temperature for 30 min. The organic layer was decanted off and the residue was leached with dichloromethane. The combined organic layers were washed with 5% sodium hydroxide solution, 5% hydrochloric acid, and brine before drying. Solvent removal left a colorless crystalline solid which was purified by VPC (12 ft × 0.25 in. 10% PMPE 6-ring, 95 °C). There was isolated 8 mg of **16c**: ^{1}H NMR ($CDCl_3$) δ 2.3–1.0 (series of m, 14 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.88; H, 9.66.

***syn*-Tricyclo[4.2.1.1^{2,5}]decan-2-one (17).** Oxidation of 400 mg (2.6 mmol) of **13a** in the predescribed manner followed by column chromatography on silica gel (gradient hexane–dichloromethane elution) afforded 330 mg (85%) of **17** as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 2.32 (br m, 2 H), 2.08 (br s, 2 H), and 1.59–1.21 (series of m, 10 H); *m/e* calcd 150.1045, obsd 150.1048.

Catalytic Hydrogenation of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-diol (18). A solution of **18**[13] (24.4 g, 0.149 mol) in absolute ethanol (125 mL) was admixed with 2.0 g of 10% palladium on charcoal and this mixture was hydrogenated on a Parr apparatus at 40–50 psig for 2 days. The catalyst was removed by filtration through Celite and the solvent was removed in vacuo. Recrystallization of the residue from ethyl acetate gave **19a** (20.2 g, 82%) as a colorless solid, mp 232–238.5 °C: ^{1}H NMR ($CDCl_3$) δ 3.91 (br s, 2 H), 3.65 (-OH), 3.61 (-OH), 2.86 (-OH), 2.49 (br s, 2 H), 2.10–2.01 (m, 4 H), 1.43 (d, *J* = 1.8 Hz, 2 H), and 1.02 (dd, *J* = 11.4 and 4.1 Hz, 2 H); *m/e* calcd 166.0994, obsd 166.0997.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.04; H, 8.62.

***syn*-Tetracyclo[4.2.1.1^{2,5}.0^{3,7}]decane-4,8-diol Dimethanesulfonate (19b).** A suspension of **19a** (11.0 g, 0.066 mol) in dichloromethane (2.5 L) was cooled to ~0 °C in an ice bath. Dry triethylamine (20.12 g, 0.199 mol) was added dropwise to the mechanically stirred suspension, followed by methanesulfonyl chloride (25.06 g, 0.219 mol). The diol slowly dissolved as reaction proceeded. After 90 min at 0 °C, the mixture was poured onto crushed ice (1000 g) and water (1.75 L). The organic layer was separated and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with 5 N hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying and evaporation left a colorless solid which was twice recrystallized from ethyl acetate: mp 134–136 °C: ^{1}H NMR ($CDCl_3$) δ 4.76 (br s, 2 H), 3.03 (s, 6 H), 2.84–2.69 (complex m, 2 H), 2.53–2.25 (complex m, 4 H), 1.67 (dd, *J* = 13.2 and 2.3 Hz, 2 H), and 1.20 (dd, *J* = 12.9 and 5.6 Hz, 2 H); *m/e* calcd 322.0545, obsd 322.0550.

Anal. Calcd for $C_{12}H_{18}O_6S_2$: C, 44.71; H, 5.63. Found: C, 44.76; H, 5.68.

4,8-Diiodo-*syn*-tetracyclo[4.2.1.1^{2,5}.0^{3,7}]decane (20). Dimesylate **19b** (32 g, 99.3 mmol) was dissolved in dry hexamethylphosphoramide (725 mL, freshly distilled from CaH_2) and finely powdered sodium iodide (310.9 g, 2.07 mol) was introduced into the mechanically stirred solution. The resulting suspension was heated in an oil bath maintained at 120–130 °C for 80 h, cooled, and diluted with 6 L of water. The product was repeatedly extracted into ether and the combined organic layers were washed with 5 N hydrochloric acid, saturated sodium bicarbonate solution, and brine. After drying and solvent removal, there was isolated a tan-colored semisolid which was chromatographed on Florisil (pentane elution). The diiodide containing fractions were combined to give 27.6 g (71%) of **20**. Recrystallization from pentane afforded a mixture of epimers, mp 60–123 °C: ^{1}H NMR ($CDCl_3$) δ 4.67 (m, 1 H), 3.97–3.91 (m, 1 H), 3.03 (s, 3 H), and 2.85–1.02 (series of m, 10 H). Column chromatography gave a single pure epimer, mp 134–135 °C: ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 2 H), 3.19–3.12 (m, 2 H), 2.83 (m, 2 H), 2.24 (m, 2 H), 1.62 (dd, *J* = 12.6 and 2.1 Hz, 2 H), and 1.05 (dd, *J* = 12.3 and 5.3 Hz, 2 H); *m/e* calcd 385.9032, obsd 385.9040.

Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13. Found: C, 31.19; H, 3.18.

From run to run, varying amounts of monoiodomonomesylate epimeric mixture were also isolated, mp 68–84 °C (from pentane); *m/e* calcd 353.9788, obsd 353.9795.

Anal. Calcd for $C_{11}H_{15}IO_3S$: C, 37.30; H, 4.27. Found: C, 37.73; H, 4.25.

Silver Nitrate Complex of *syn*-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (21). Small pieces of sodium (3.52 g) and potassium (3.52 g) were placed in a reaction flask which was then evacuated to 0.1 mmHg for 30 min. The metals were fused by gentle heating with a Bunsen burner. When the flask was cooled, dry argon was carefully introduced, a magnetic stirring bar was added, and the alloy was suspended in dry ether (100 mL). To the stirred suspension was added dropwise a solution of **20** (8.8 g, 22.8 mmol) in 200 mL of anhydrous ether and the mixture was stirred overnight at room temperature. The stirring was stopped and, after the solids had settled, the supernatant was carefully

transferred by syringe into a separatory funnel containing water (500 mL). The alloy was washed with ether (3 × 100 mL) and the combined organic phases were washed with water, dried, filtered, and carefully evaporated below 0 °C. The remaining yellow oil was taken up in hexane and a solution of silver nitrate (4 g) in water (10 mL) was added dropwise with shaking. A fine white precipitate formed immediately. This suspension was heated briefly on a steam bath and filtered. The solid was washed with ethanol–water (1:1), air-dried for 5 min, reslurried in a small amount of absolute ethanol, and again air-dried for 5 min. Final drying was accomplished at 30 mm for 2 h. The silver nitrate complex **24** was a white crystalline solid, mp 149–151 °C (dec).

***syn*-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (1).** The generally adapted procedure was as follows. The required amount of complex **21** was suspended in the solvent of choice and concentrated ammonium hydroxide was added dropwise with shaking until solid was no longer evident. The organic phase was pipetted from the aqueous layer, washed once with water, and dried. Diene **1** was liberated in essentially quantitative yield: ^{1}H NMR (C_6D_6) δ 6.08 (s, 4 H), 2.71 (d, J = 10 Hz, 2 H), 2.33 (s, 4 H), and 1.83 (d, J = 10 Hz, broadened by further coupling, 2 H); ^{13}C NMR (C_6D_6) 141.71 (4d, $^1J_{C-H}$ = 165 Hz), 45.59 (2t, J = 133 Hz), and 40.88 ppm (4d, J = 141 Hz); *m/e* calcd 132.0939, obsd 132.0942.

Cope Rearrangement of 1. A solution of **1** in C_6D_6 was sealed under vacuum in an NMR tube containing a small amount of Me_4Si. The tube was immersed in a constant-temperature oil bath (80 °C for the preparative run). Periodically the tube was removed (and immersed in an ice bath for kinetic runs) and the ^{1}H NMR spectrum recorded. After 421 min at 80 °C, no trace of **1** could be detected and diene **3** had been produced exclusively: ^{1}H NMR (C_6D_6) δ 5.83–5.77 (m, 2 H), 5.44 (m, 2 H), 3.42 (m, 2 H), 2.89 (m, 2 H), and 2.25 (br s, 4 H); ^{13}C NMR (C_6D_6) 134.04, 131.81, 50.98, 36.95, and 33.64 ppm; *m/e* calcd 132.0939, obsd 132.0942.

Acknowledgment. The authors thank the National Science Foundation for financial support, Dr. Charles Cottrell for the ^{13}C NMR spectra, and C. R. Weisenberger for the mass spectral data.

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