phenylacetylene by a methyl or an ethyl group has little effect upon the rate. This suggests that acetylenic carbon C-2 has very little positive charge in the rate-determining transition state, consistent with an open-ion-like structure.

Such a conclusion is consistent with the rates of solvolysis of several α-bromostyrene derivatives. The effect of β-substituents on the formation of a phenyl-stabilized cation is small.[10] Further support for this explanation is found in the effect of substituents upon the rate of addition of 4-chlorobenzenesulfenyl chloride to phenylacetylenes.[11] In this reaction, substituting the acetylenic hydrogen of phenylacetylene by a methyl group causes a rate increase of 35.

It is found that the rate of bromination of diphenylacetylene is slower than phenylacetylene. This effect of a second phenyl group on the rates of electrophilic additions to alkenes and alkynes has been found in other studies.[11] This may be due to an inductive electron-withdrawing effect of the second phenyl group of tolan.

Summary

Systematic structure–reactivity data support the proposal that the rate-determining transitions states of bromine additions are different for alkyl- and phenyl-substituted acetylenes. An open vinyl-like rate-determining transition state is involved in the bromination of phenylacetylenes while a bridged-like rate-determining transition state is involved with alkyl-substituted acetylenes.

Experimental Section

Reagents. The alkynes are commercially available (Chemical Samples), and their purity was verified by GLC and NMR. Acetic acid was purified by refluxing for several hours with chromium trioxide and acetic anhydride and then was distilled through a column.[12] Di-*tert*-butyl peroxyoxalate was kindly provided by Professor T. T. Tidwell of this department. All other reagents are commercially available.

Kinetics. The kinetics were carried out as previously reported.[3]

Acknowledgment. Continued financial support by the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. **1**, 74-86-2; **2**, 74-99-7; **3**, 107-00-6; **4**, 598-23-2; **5**, 917-92-0; **6**, 627-19-0; **7**, 693-02-7; **8**, 503-17-3; **9**, 627-21-4; **10**, 21020-27-9; **11**, 999-78-0; **12**, 928-49-4; **13**, 17530-24-4; **16**, 622-76-4; **17**, 501-65-5; Br_2, 7726-95-6.

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Rearrangements of 1,6-Dihalotricyclo[4.2.2.0^{2,5}]decanes. Synthesis of Tricyclo[5.3.0.0^{4,8}]decane Derivatives[1,2]

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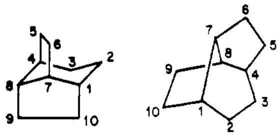
1,8-Diiodotricyclo[5.3.0.0^{4,8}]decane (**16**) was prepared by reaction of 1,6-dihalotricyclo[4.2.2.0^{2,5}]decanes **9a** and **9b** with aluminum triiodide. Reduction of **16** with di-*n*-butyltin dihydride produced the tricyclic hydrocarbon tricyclo[5.3.0.0^{4,8}]decane (**1**). Dichloride **9a** was prepared by a Diels–Alder reaction between 1,4-dichlorocyclohexa-1,3-diene (**10a**) and cyclobutene followed by catalytic hydrogenation of the adduct **12a**. The structure of **16** was determined by an X-ray diffraction study of a single crystal.

Adamantane (**2**) and its congeners have been the subject of numerous theoretical and experimental investigations.[3] The highly symmetrical diamondoid structure of adamantane, its striking physical properties, and the almost complete lack of strain have urged chemists to explore the interrelationships of its chemical and physical properties in exquisite detail. These researches have been encouraged by the discovery that adamantane can be prepared by Lewis acid isomerization[4-9] of a variety of less stable isomeric hydrocarbons, such as tetrahydrodicyclopentadiene,[4] twistane,[5] perhydroquinacene,[6] and protoadamantane.[7]



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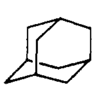

2

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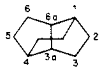
[1] Taken in part from the Ph.D. Dissertation of J.J.V., The University of Michigan, 1978.

[2] The von Baeyer system is used to name and to number the bridged ring systems in this paper. The *Chemical Abstracts* name for **1** is 1,4-ethano-1,2,3,3a,4,5,6,6a-octahydropentalene. Derivatives of **1** with double bonds in the ethano bridge (2,3-position using the von Baeyer numbering scheme) are indexed under 1,4-ethenopentalene.



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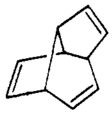
0022-3263/80/1945-0667$01.00/0

By contrast, the tricyclo[5.3.0.$0^{4,8}$]decane ring system has received only moderate attention and no general synthesis has been available to permit systematic chemical studies. The parent hydrocarbon 1 is shown in two perspective views.[2] Hydrocarbon 1 is isomeric with adamantane (2) and, like adamantane, has six methylene and four bridgehead methine carbon atoms. Unlike adamantane, hydrocarbon 1 is chiral since its only symmetry element is a twofold axis passing through the midpoints of carbon–carbon bonds 2–3 and 7–8. The carbon atoms of 1 occur in five symmetry-related pairs. Monosubstitution of 1 in any position creates a derivative devoid of any symmetry.

Only a small number of derivatives of 1 are known. The best studied derivative is tricyclo[5.3.0.$0^{4,8}$]deca-2,5,9-triene (3), known as lumibullvalene. Lumibullvalene has been identified[10b,d] as a member of the group of interconvertible $C_{10}H_{10}$ hydrocarbons related to bullvalene.[10] It has been synthesized elegantly by Katz and Cheung.[10e] The parent saturated hydrocarbon 1 has been synthesized in the course of the structure proof for lumibullvalene (5),[10d] but no properties are recorded for it. Commercial samples of the insecticide Chlordan have been shown[11] to contain small amounts of the chlorinated derivatives 4 and 5. Reaction of the sesquiterpene alcohol caratol with formic acid produced the formate ester **6a** whose structure was deduced by an X-ray crystallographic study of the corresponding *p*-iodobenzoate **6b**.[12]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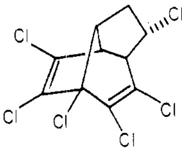

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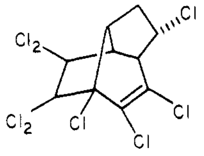

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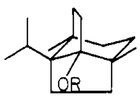
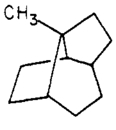


6a, R = CHO
b, R = p-IC_6H_4CO

Theoretical studies of the pathways for rearrangement of various $C_{10}H_{16}$ hydrocarbons into adamantane have led to the conclusion that tricyclic hydrocarbon 1 and derived carbocations are possible but unlikely intermediates in these reactions.[5,8,9] Engler, Androse, and Schleyer have calculated the heat of formation (−18.7 kcal/mol) and the strain energy (20.74 kcal/mol) of 1.[13] Thus, 1 is predicted to have greater thermodynamic stability than the majority of adamantane isomers. Also, graphical analyses of the rearrangements of $C_{10}H_{16}$ hydrocarbons into adamantane show hydrocarbon 1 at a dead end on the periphery of "Adamantaneland" and not on any of the favored rearrangement pathways. An analysis of rearrangements of tricyclic $C_{11}H_{18}$ hydrocarbons lists 7-methyltricyclo[5.3.0.$0^{4,8}$]decane 7 as a possible product which might result from ring contraction of 8.[14]



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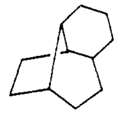
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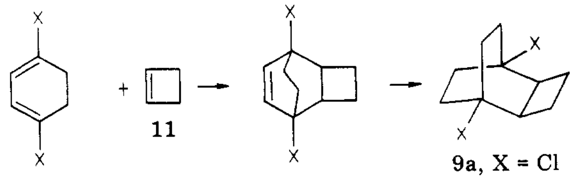
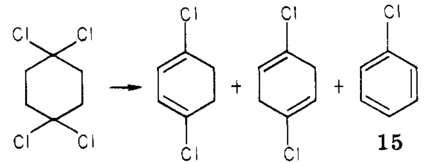
Results and Discussion

We have developed a simple synthesis of the tricyclo[5.3.0.$0^{4,8}$]decane ring system by rearrangement of 1,6-dihalotricyclo[4.2.2.$0^{2,5}$]decanes **9**. This method should be adaptable to the preparation of specifically substituted derivatives of the ring system. The most direct approach to the required 1,6-disubstituted tricyclo[4.2.2.$0^{2,5}$]decanes (**9**) involves the Diels–Alder reaction of 1,4-disubstituted cyclohexa-1,3-dienes (**10**) with cyclobutene (**11**). There is little precedential literature for Diels–Alder reactions involving cyclobutene,[15] but we have found that cyclobutene reacts with 1,4-diiodocyclohexa-1,3-diene (**10b**) at 100 °C over 30 days.[16]



10a, X = Cl
b, X = I
12a, X = Cl
b, X = I
9a, X = Cl
b, X = I

1,4-Dichlorocyclohexa-1,3-diene (**10a**) was prepared by dehydrochlorination of 1,1,4,4-tetrachlorocyclohexane (**13**).[17] A variety of methods, viz., potassium *tert*-butoxide in *tert*-butyl alcohol, sodium amide in liquid ammonia, sodium amide in tetrahydrofuran, and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in tetrahydrofuran, proved to be ineffective in inducing the desired elimination. However, diene **10a** was obtained in 95% yield at 45% conversion by treatment of **13** with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in tetrahydrofuran. Small amounts of 1,4-dichlorocyclohexa-1,4-diene (**14**) and chlorobenzene (**15**) were also produced. Diene **10a** could be readily separated from **13** but it was found to be more efficient and convenient to use the mixture in the next reaction.



13
10a
14
15

Cyclobutene (**11**) isomerized to 1,3-butadiene when the reaction of diene **10a** with cyclobutene was attempted in a sealed tube at 112 °C for 12 h. The desired Diels–Alder reaction was made to occur by employing an excess of cyclobutene and lowering the reaction temperature. Adduct **12a** was obtained in 69% yield from the reaction of diene **10a** with excess cyclobutene at 100 °C for 25 days. There is evidence for the formation of only one adduct

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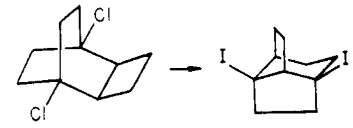
(VPC). Catalytic hydrogenation of adduct **12a** produced dichloride **9a**, mp 167–168 °C, in 64% yield. Dichloride **9a** exhibits five ^{13}C NMR resonances, in agreement with the symmetry of the assigned structure.

An attempt to convert dichloride **9a** into diiodide **9b**[16] using aluminum triiodide by the method of Pincock and Perkins[18,19] resulted in rearrangement as well as halogen exchange to produce 1,8-diiodotricyclo[5.3.0.0^{4,8}]decane (**16**), mp 82–83 °C, which was isolated in a pure state in 85% yield: ^{1}H NMR (CDCl$_3$) δ 3.10 (1 H, m), 2.70–0.85 (13 H, comp). The signal at δ 3.10 corresponds to the bridgehead hydrogen β to both iodines; there are no resonances attributable to protons α to iodine, so the iodine atoms must be on bridgehead carbons. The ^{13}C NMR spectrum shows ten resonances, in agreement with the lack of symmetry of **16**. Compound **16** is also formed by rearrangement of diiodide **9b**[16] catalyzed by aluminum triiodide. The structure of diiodide **16** was established conclusively by an X-ray diffraction study of a single crystal (see below).

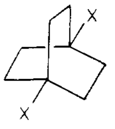


9a 16

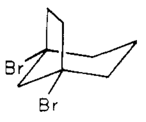
Reduction of diiodide **16** with di-*n*-butyltin dihydride produced the parent tricyclic hydrocarbon **1**.[10d] A small amount (6% by VPC) of an unidentified hydrocarbon of molecular formula $C_{10}H_{18}$ was also produced in this reduction. Reaction of **16** with tri-*n*-butyltin hydride also produced **1**, but the byproduct tri-*n*-butyltin iodide was difficult to separate from **1**. Hydrocarbon **1** is a volatile solid (mp 122–124 °C, sealed tube) with a penetrating camphoraceous odor. Its five ^{13}C NMR resonances are in agreement with the symmetry of the assigned structure.

Efforts to effect the halogen-exchange reaction without rearrangement were not successful. No reaction was observed at −24 °C. At 0 °C after 60 s, dichloride **9a** was completely destroyed and diiodide **16** was formed; no unrearranged diiodide **9b**[16] was found in the reaction. An additional minor product of molecular formula $C_{10}H_{14}ICl$ was detected by GC/MS analysis but could not be characterized further due to the small amount available. It is probably a reaction intermediate, possibly **21**, since it is not found after longer reaction times.

Significantly, the reaction of 1,4-dichlorobicyclo[2.2.2]octane (**17a**)[19] with aluminum triiodide requires 15 h at 25 °C to produce **17c**. Accordingly, the cyclobutane ring has an accelerating effect on the rearrangement of **9a**. Pincock, McKinley, and Scott[20] report that heating 1,4-dibromobicyclo[2.2.2]octane (**17b**) with aluminum tribromide at 80 °C produces a 2:1 mixture of dibromobicyclooctanes **18** and **17b**. This reaction is analogous to the rearrangement we have observed.



17a, X = Cl
b, X = Br
c, X = I



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Scheme I

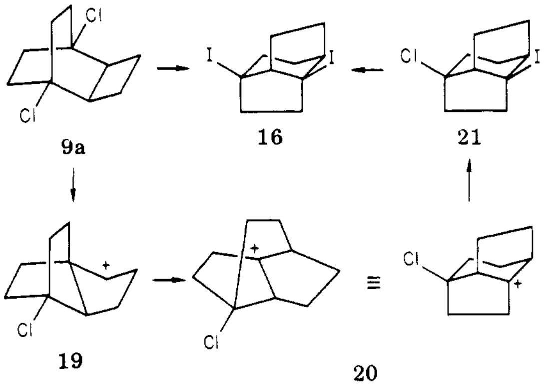

Table I. Summary of Crystal Data Conditions and Results

space group	$P\bar{1}$
a, Å	8.2255 (18)
b, Å	10.9466 (24)
c, Å	6.6518 (16)
α, deg	100.28 (2)
β, deg	100.27 (2)
γ, deg	78.80 (2)
V, Å^3	576.6 (2)
mol wt	338
Z	2
d(calcd), g/mL	2.25
crystal dimensions, mm	0.30
radiation	Mo Kα (graphite monochromator)
takeoff angle, deg	4.0
μ, cm^{-1}	52.6
scan speed, deg/min	2.0–12.0
scan range, deg	Mo Kα_1 − 0.8 to Mo Kα_2 + 0.8
bkgd time ratio	0.8
2θ limit, deg	55
reflections collected	2819
reflections with $F^2 \geq 3\sigma(F^2)$	1959

The probable mechanism for the rearrangement of **9a** (and **9b**) is shown in Scheme I. The aluminum triiodide assisted ionization of **9a** can proceed with anchimeric assistance from the strained cyclobutano bond to form cation **19**. The secondary cation **19** can undergo a 1,2-shift of the ethano bridge to generate tertiary cation **20** in a more stable ring system. Cation **20** possesses the tricyclo[5.3.0.0^{4,8}]decane ring system skeleton; it can capture iodide, giving **21** which can then undergo a second exchange without further rearrangement to produce **16**.

An approximation of the strain energy of the tricyclo[4.2.2.0^{2,5}]decane ring system is about 38 kcal/mol, the sum of the strain energies of cyclobutane (26.3 kcal/mol) and bicyclo[2.2.2]octane (ca. 12 kcal/mol).[13] The strain energy of **16**, the hydrocarbon derivative of chloro cation **14**, is calculated to be 29.65 kcal/mol,[13] and the strain energy of **1**, the dihydro analogue of **16**, is calculated to be 20.74 kcal/mol.[13] Thus, the individual steps are exothermic and the overall rearrangement is exothermic by about 18 kcal/mol.

Experimental Section

Crystallography. Single crystals of 1,8-diiodotricyclo[5.3.0.0^{4,8}]decane (**16**), $C_{10}H_{14}I_2$, were obtained by slowly cooling a solution in petroleum ether to 0 °C. The data crystal was mounted on a Syntex $P\bar{1}$ diffractometer and the space group determined. Table I contains a summary of data collection conditions and results.

Intensity data were collected by using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was perpendicular to the diffraction vector of the sample. Three

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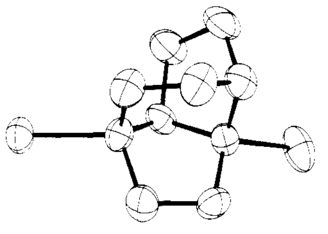

Figure 1. Crystallographically determined structure of 1,8-diiodotricyclo[5.3.0.0^{4,8}]decane (**16**), $C_{10}H_{14}I_2$. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted.

standard reflections were measured every 50 reflections. The data were reduced by procedures previously described.[21]

The structure was solved by Patterson and Fourier syntheses.[21] The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. In the least-squares refinement, the agreement indices $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ were used. The atomic scattering factors are from Cromer and Waber.[22] The average deviation in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of refinement parameters.

The position of the two iodine atoms obtained from the Patterson function gave $R_1 = 0.30$ and $R_2 = 0.38$. A difference Fourier map then revealed the 10 carbon atoms. Least-squares refinement using anisotropic thermal parameters for all nonhydrogen atoms and the anomalous dispersion correction[23] for the two iodine atoms converged to $R_1 = 0.048$ and $R_2 = 0.066$. Hydrogen positions were calculated and included as fixed contributions to give final values of $R_1 = 0.043$ and $R_2 = 0.054$. A view of the crystallographically determined structure of **16** showing thermal ellipsoids is shown in Figure 1. The final average deviation of an observation of unit weight was 1.82, using 1959 data and 109 least-squares variables. The largest noniodine residual was 0.43 e/Å^3. Final positional parameters with estimated standard deviations, anisotropic thermal parameters with estimated standard deviations, and the crystallographically determined bond distances and bond angles are available as supplementary material. A listing of observed and calculated structure factor amplitudes is available from the authors.

General Procedures. Nuclear magnetic resonance spectra at 60 MHz were recorded with Varian Associates T-60 and T-60A NMR spectrometers. Fourier transform proton (100 MHz) and carbon (25.03 MHz) magnetic resonance spectra were recorded with a JEOL JNM PS-100 spectrometer interfaced with a Texas Instruments 980B computer. Infrared spectra were recorded with Perkin-Elmer 457 and 727B spectrophotometers. Vapor phase chromatographic data were obtained with a Varian Aerograph Model 90-P gas chromatograph (helium flow rate 60 mL/min). Mass spectra were obtained on an Associated Electronics Instrument MS-902 mass spectrometer and a Du Pont Dimaspec 321 GC/MS mass spectrometer with a 10% OV-17 on Gas Chrom Q, 3 mm × 1.5 m column. Microanalyses were done by Spang Microanalytical Laboratory.

1,4-Dichlorocyclohexa-1,3-diene (10a). To 906 mg (4.12 mmol) of 1,1,4,4-tetrachlorocyclohexane (**13**)[17] dissolved in 40 mL of dry tetrahydrofuran under nitrogen at 25 °C was added a total of 5.5 g (44.0 mmol) of dry 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in the following amounts at the times given: 0.5 g, 0 h; 2.0 g, 4 h; 2.0 g, 72 h; 1.0 g, 125 h. After the initial DBN addition, a white precipitate formed. After 178 h, the reaction mixture was poured into 20 mL of water and extracted with petroleum ether (bp 35–60 °C) (3 × 50 mL). The petroleum ether extract was washed with water (3 × 10 mL) and dried (sodium sulfate). The solvent was distilled (110 °C, 760 torr), and the residue was placed on a rotary evaporator (25 °C, 10 torr) for 5 min to yield 751 mg of white crystalline residue. ^{1}H NMR integration indicated that this material contained 333 mg of **10a**, 407 mg of **13**, and trace amounts of 1,4-dichlorocyclohexa-1,4-diene (**14**) and chlorobenzene. Analytically pure samples of **10a** and **14** were obtained by preparative VPC (6 mm × 2.2 m column of 5% SE 30 on 60/80 Chromosorb G, 105 °C).

1,4-Dichlorocyclohexa-1,3-diene (**10a**): retention time 7.6 min; mp ca. 30 °C, white needles; ^{1}H NMR (CCl_4) δ 6.80 (2 H, s), 2.59 (4 H, s); IR (neat) $\tilde{\nu}$ 3060, 2972, 2890, 2834, 1641, 1475, 1360, 1025 cm^{-1}; MS m/e (relative intensity) 150 (70.5), 148 (100), 115 (84.0), 113 (91.0), 78 (68.5).

Anal. Calcd for $C_{10}H_6Cl_2$: C, 48.35; H, 4.02; Cl, 47.62. Found: C, 48.28; H, 3.88; Cl, 47.51.

1,4-Dichlorocyclohexa-1,4-diene (**14**): retention time 10.4 min; mp 59–61 °C, white needles; ^{1}H NMR (CCl_4) δ 5.67 (2 H, t, J = 1 Hz), 2.94 (4 H, d, J = 1 Hz); IR (CCl_4) $\tilde{\nu}$ 3059, 3033, 2895, 2832, 1649, 1460, 1362, 1020 cm^{-1}; MS m/e (relative intensity) 150 (54.5), 148 (100), 115 (99.0).

Anal. Calcd for $C_6H_6Cl_2$: C, 48.35; H, 4.02; Cl, 47.62. Found: C, 48.11; H, 4.07; Cl, 47.50.

Attempted Preparation of 1,6-Dichlorotricyclo[4.2.2.0^{2,5}]dec-7-ene (12a) at 112 °C. An NMR tube was charged with 75.1 mg (0.51 mmol) of 1,4-dichlorocyclohexa-1,3-diene (**10**), an excess amount of cyclobutene,[21] 0.5 mL of carbon tetrachloride, and 10 μL of benzene (internal standard). The tube was sealed under nitrogen at −77 °C and heated to 112 °C in an oven. After 16 h of heating, ^{1}H NMR revealed that 72% of the cyclobutene in the sample (δ 6.03) had isomerized to 1,3-butadiene (δ 5.11, 5.20).

1,6-Dichlorotricyclo[4.2.2.0^{2,5}]dec-7-ene (12a). A heavy-walled Pyrex tube was charged with 1.2 g (22.3 mmol) of cyclobutene[24] and 333 mg (2.23 mmol) of 1,4-dichlorocyclohexa-1,3-diene (**10a**) contaminated with 407 mg (1.83 mmol) of 1,1,4,4-tetrachlorocyclohexane (**13**) (amounts calculated by ^{1}H NMR integration) and sealed at −77 °C under nitrogen. The tube was heated for 25 days at 100 °C. The reaction mixture was homogeneous at 100 °C. The tube was cooled to −77 °C and broken open, and the yellow contents were washed out with dichloromethane. The volatile components were removed by distillation (70 °C, 10 torr). Analysis of the reaction mixture by ^{1}H NMR integration revealed that it contained 311 mg of **12a** contaminated with **13**, a 68.6% yield based on **10a**. An analytically pure sample of **12a** was prepared by preparative VPC (6 mm × 1.8 m column of 5% SE 30 on 60/80 Chromosorb G, 145 °C).

1,6-Dichlorotricyclo[4.2.2.0^{2,5}]dec-7-ene (**12a**): retention time 9.0 min; mp 76–81 °C, white needles; ^{1}H NMR (CCl_4) δ 6.23 (2 H, s), 2.90–2.49 (2 H, comp), 2.26–1.26 (8 H, comp); IR (CCl_4) $\tilde{\nu}$ 2970, 2933, 1601, 985, 910; MS m/e (relative intensity) 204 (10.0), 202 (15.0), 176 (27.5), 174 (43.5), 169 (30.0), 167 (85), 150 (40), 148 (100).

Anal. Calcd for $C_{10}H_{12}Cl_2$: C, 59.14; H, 5.78; Cl, 34.95. Found: C, 59.04; H, 5.78; Cl, 34.86.

1,6-Dichlorotricyclo[4.2.2.0^{2,5}]decane (9a). A mixture containing 94.0 mg (0.463 mmol) of 1,6-dichlorotricyclo[4.2.2.0^{2,5}]dec-7-ene (**12a**) contaminated with 84.1 mg (0.379 mmol) of 1,1,4,4-tetrachlorocyclohexane (**13**) (calculation based on ^{1}H NMR integration) was dissolved in 50 mL of ethyl acetate containing 48.4 mg of 5% palladium-on-carbon. The mixture was stirred under 1 atm of hydrogen for 12 h. VPC analysis (6 mm × 1.8 m column of 10% DEGS on Chromosorb W, 140 °C) revealed the complete disappearance of **12a**. The reaction mixture was filtered, the filter paper was washed with methylene chloride, and the combined filtrates were subjected to distillation (100 °C, 760 torr). The distillation residue was placed on a rotary evaporator (25 °C, 10 torr) for 10 min to remove residual ethyl acetate. The crude reaction mixture was separated by preparative thin-layer chromatography on silica gel with petroleum ether (bp 35–60 °C),

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[21] Computations were carried out on an Amdahl 470-V6 computer. Computer programs used during the structural analysis were SYNCOR (data reduction by W. Schmonsees), FORDAP (Fourier synthesis by A. Zalkin), ORFLS (full-matrix least-squares refinement by W. R. Busing, K. O. Martin, and H. A. Levy), ORFFE (distances, angles, and their esd's by W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), HATOMS (hydrogen atom positions by A. Zalkin), and PLANES (least-squares planes by D. M. Blow).

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developed two times. The band at R_f 0.11–0.28 contained **9a**, 60.7 mg, 64% yield. The band at R_f 0.39–0.50 contained **13**.

1,6-Dichlorotricyclo[4.2.2.0^{2,5}]decane (**9a**): mp 166–167 °C (petroleum ether), white needles; ^{1}H NMR (CDCl$_3$) δ 2.92 (2 H, t, J = 1 Hz), 2.55 (2 H, m), 2.17 (10 H, m); ^{13}C NMR (CDCl$_3$) (height %) δ 66.76 (20.00), 46.43 (72.17), 38.92 (>100), 33.80 (>100), 19.85 (97.55); IR (KBr) $\tilde{\nu}$ 2921, 1461, 974, 876 cm^{-1}; MS m/e (relative intensity) 206 (5.3), 204 (8.0), 171 (34.6), 169 (100).

Anal. Calcd for $C_{10}H_{14}Cl_2$: C, 58.54; H, 6.83; Cl, 34.63. Found: C, 58.51; H, 6.89; Cl, 34.76.

1,8-Diiodotricyclo[5.3.0.0^{4,8}]decane (16). Method A (25 °C). The procedure of Pincock and Perkins[18] was used. A mixture of 51.0 mg (1.89 mmol) of aluminum foil, cut into small pieces, and 92.8 mg (0.365 mmol) of iodine was heated at 65 °C until iodine vapor covered the aluminum (ca. 5 min). The mixture was charged with 10 mL of carbon disulfide and stirred under nitrogen at reflux for 1 h. The pink solution was cooled to room temperature, and 47.3 mg (0.231 mmol) of 1,6-dichlorobicyclo-[4.2.2.0^{2,5}]decane (**9a**) in 1 mL of carbon disulfide was added. The solution was stirred for 1 h at 25 °C and poured into 20 mL of saturated aqueous sodium sulfite solution. The pink color was discharged and the layers were separated. The aqueous layer was washed with dichloromethane (2 × 50 mL) and the combined organic extracts were dried (sodium sulfate). Removal of the solvents on a rotary evaporator (25 °C, 10 torr) yielded 89.8 mg of a yellow amorphous solid. Pure **16**, 76.0 mg (84.8% yield), was obtained by preparative thin-layer chromatography on silica gel with petroleum ether (bp 35–60 °C).

1,8-Diiodotricyclo[5.3.0.0^{4,8}]decane (**16**): mp 62–63 °C, white needles; ^{1}H NMR (CDCl$_3$) δ 3.10 (1 H, m), 2.70–0.85 (13 H, comp); ^{13}C NMR (CDCl$_3$) (height %) δ 68.62 (27.67), 51.89 (15.80), 50.92 (34.69), 45.79 (16.13), 45.11 (35.13), 40.72 (36.60), 39.41 (41.22), 30.97 (32.75), 30.09 (38.65), 21.65 (31.95); IR (CCl$_4$) $\tilde{\nu}$ 2950, 2865, 1465, 1400, 1305, 1235, 1210, 955 cm^{-1}; MS m/e (relative intensity) 388 (8.6), 261 (100), 134 (74.2), 133 (62.8).

Anal. Calcd for $C_{10}H_{14}I_2$: C, 30.94; H, 3.61; I, 65.45. Found: C, 30.95; H, 3.68; I, 65.33.

Method B (0 °C). The preparation of the aluminum triiodide reagent with 4.5 mg (0.17 mmol) of aluminum, 8.3 mg (0.033 mmol) of iodine, and 3 mL of carbon disulfide was identical with that described in method A. To a cooled solution (0 °C) of the reagent was added 2.2 mg (0.0011 mmol) of 1,6-dichlorotricyclo-[4.2.2.0^{2,5}]decane (**9a**) in 1 mL of carbon disulfide. The pink mixture was allowed to stir under nitrogen at 0 °C for 60 s, and then the reagent was quenched by the addition of 5 mL of saturated aqueous sodium sulfite solution. The pink color was immediately discharged. The layers were separated and the carbon disulfide layer was dried (sodium sulfate). The carbon disulfide was removed on a rotary evaporator (25 °C, 10 torr) to yield 4.2 mg of a semicrystalline residue. Analysis of the residue by VPC (6 mm × 1.8 m column of 10% DEGS on Chromosorb W, 180 °C) revealed the presence of two peaks. The first peak had a retention time (10 min) different from that of **9a** (3.8 min), and the second peak had the same retention time (19 min) as that of **16**. Analysis of the residue by mass spectrometry revealed it to be a mixture of at least two components: **16**, $C_{10}H_{14}I_2$, m/e 388, and $C_{10}H_{14}ClI$, possibly **21**, m/e 298 (33), 296 (100).

Method C. From 1,6-Diiodotricyclo[4.2.2.0^{2,5}]decane (9b). The preparation of the aluminum triiodide reagent with 72.3 mg (2.67 mmol) of aluminum, 110 mg (0.433 mmol) of iodine, and 20 mL of carbon disulfide was identical with that described in method A. To a solution of the reagent at 25 °C was added 117 mg (0.302 mmol) of 1,6-diiodotricyclo[4.2.2.0^{2,5}]decane (**9b**) in 2 mL of carbon disulfide. The pink solution was allowed to stir under nitrogen at 25 °C for 1 h. The workup procedure was identical with that described in method A. Preparative thin-layer chromatography on silica gel with petroleum ether (bp 35–60 °C) produced 106 mg, 90.4% yield, of **16**, identical in all respects with the material produced by methods A and B.

Tricyclo[5.3.0.0^{4,8}]decane (1). To 123.1 mg (0.317 mmol) of 1,8-diiodotricyclo[5.3.0.0^{4,8}]decane (**16**) dissolved in 5 mL of dry diethyl ether was added 0.10 mL (0.43 mmol) of di-n-butyltin dihydride.[25] The homogeneous colorless solution was allowed to stand for 20 min at room temperature under nitrogen. To the solution was added 2 mL of 5% aqueous sodium hydroxide solution. This resulted in the immediate formation of a milky white precipitate. The suspension was stirred for 12 h at room temperature. The layers were separated, and the aqueous portion was washed with diethyl ether (3 × 25 mL). The combined ether extracts formed a cloudy solution which was dried (sodium sulfate).

Filtration and distillation of the ether left a residue which showed **1** (94.7%) and an unknown hydrocarbon (6.3%) by VPC relative peak areas. Purified samples of **1** and the unknown hydrocarbon were obtained by preparative VPC (6 mm × 1.8 mm column of 10% DEGS on Chromosorb W, 65 °C). Compound **1** was obtained in 41.7% isolated yield.

Tricyclo[5.3.0.0^{4,8}]decane (**1**): retention time 9.0 min; mp (sealed tube) 122–124 °C, white needles; ^{1}H NMR (CDCl$_3$) δ 2.06 (2 H, m), 1.84 (2 H, m), 1.77–1.06 (12 H, comp); ^{13}C NMR (CDCl$_3$) (height %) δ 46.87 (18.7), 40.19 (19.3), 31.41 (24.7), 26.58 (25.2), 24.73 (24.7); IR (CDCl$_3$) $\tilde{\nu}$ 2920, 2860, 1465, 1340 cm^{-1}; MS m/e (relative intensity) 136 (75.4), 121 (37.7), 108 (51.4), 80 (100).

Anal. Calcd for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.34; H, 11.65.

Unknown compound: retention time 5.4 min; ^{1}H NMR (CDCl$_3$) δ 1.6–1.2 (comp); IR (CDCl$_3$) $\tilde{\nu}$ 2920, 2850, 1510 cm^{-1}; MS m/e (relative intensity) 138 (37.3), 109 (100), 67 (44.6). This compound was not further characterized.

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Registry No. 1, 19485-20-2; **9a**, 71786-17-9; **9b**, 68882-66-6; **10a**, 71786-18-0; **10b**, 68882-61-1; **11**, 822-35-5; **12a**, 71786-19-1; **13**, 60319-15-5; **14**, 71786-20-4; **16**, 71786-21-5; **21**, 71786-22-6; 1,3-butadiene, 106-99-0; aluminum triiodide, 7784-23-8.

Supplementary Material Available: Table II (final positional parameters), Table III (anisotropic thermal parameters), Table IV (bond distances and bond angles), and a figure showing the crystallographically determined structure for **16** (4 pages). Ordering information is given on any current masthead page.

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