Synthesis of Tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene ("Homohypostrophene"), 10-Oxatetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene ("10-Oxahomohypostrophene"), and Hexacyclo[5.4.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$.$0^{8,10}$]undecane. Structure of *syn*-4,*syn*-7-Diiodopentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane. Synthesis and Rh(I)-Promoted Rearrangement of Hexacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]undecane ("Homopentaprismane")[1]

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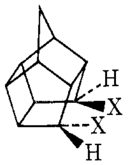
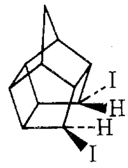
The reaction of ditosylate **1b** with sodium iodide in hexamethylphosphoramide affords five products: *exo*-8,*exo*-11-diiodopentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**2**), *syn*-4,*anti*-7-diiodopentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**3**), *syn*-4,*syn*-7-diiodopentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**4**), hexacyclo[5.4.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$.$0^{8,10}$]undecane (**5**), and homohypostrophene (**6a**). Confirmation of the structure and stereochemistry of diiodide **4** was obtained via single-crystal x-ray structural analysis. Control experiments revealed that products **3**–**6a** are formed from **2**; mechanisms for these conversions are suggested. A two-step synthesis of 10-oxahomohypostrophene (**6b**) from 11-oxa-3,4,5,*exo*-6-tetrachloropentacyclo[6.2.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]undecane-*endo*-3-carboxylic acid (**11**) is presented. Whereas **6a** could readily be photocyclized to homopentaprismane (**7a**), conditions whereby the corresponding photocyclization of **6b** to 4-oxahomopentaprismane (**7b**) might be effected could not be found. Homopentaprismane rearranged slowly to homohypostrophene upon treatment with either $(Ph_3P)_2Rh(CO)Cl$ ($CDCl_3$ solvent, 67 °C, 0.514 M in **7a**, 0.171 M in catalyst, $t_{1/2}$ = 9.8 h) or [Rh(norbornadiene)Cl]$_2$ (benzene-d_6, 40 °C, 0.456 M in **7a**, 0.0135 M in catalyst, $t_{1/2}$ = ca. 7.5 days). Compound **7a** did not undergo rearrangement when treated with Ag(I).

In a recent communication,[2] we reported some preliminary observations relating to the reaction of the ditosylate (**1b**) derived from *endo*-8,*endo*-11-dihydroxypentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**1a**) with sodium iodide in hexamethylphosphoramide (HMPA) solvent. This reaction was found to afford thre isomeric diiodides (**2**–**4**), a saturated $C_{11}H_{12}$ hydrocarbon (**5**), and homohypostrophene (**6a**). We now report full experimental details surrounding the synthesis, isolation, and characterization of **2**–**6a**. In addition, the synthesis of 10-oxatetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene ("10-oxahomohypostrophene", **6b**) is described. We also note the results of our attempts to photocyclize **6a** and **6b** to homopentaprismane (**7a**) and 4-oxahomopentaprismane (**7b**), respectively. Finally, the results of studies on the Rh(I)- and Ag(I)-promoted rearrangements of **7a** are discussed.



la, X = OH
b, X = OTs



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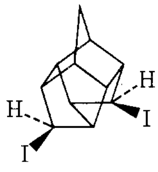

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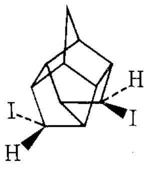

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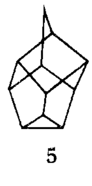

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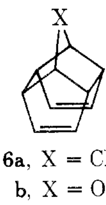
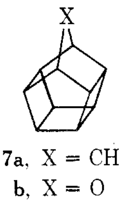


6a, X = CH_2
b, X = O

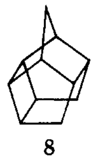


7a, X = CH_2
b, X = O

Results

A. Reaction of 1b with Sodium Iodide–HMPA. This reaction, when carried out as described in the Experimental Section, afforded two product fractions: a nonvolatile fraction consisting of the isomeric diiodides **2**–**4** and a volatile fraction consisting of the two $C_{11}H_{12}$ hydrocarbons (**5** and **6a**). Separation of the mixture of diiodides was effected via elution chromatography; the $C_{11}H_{12}$ hydrocarbons could be separated using preparative VPC techniques.

Proof of structure of each of the isomeric diiodides was accomplished via a combination of chemical[3–5] and NMR spectral[6] methods. These results are summarized in Table I. The carbon skeleton of **2** was assigned via its dehalogenation with tri-*n*-butyltin hydride. This procedure afforded the corresponding hydrocarbon, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**8**), which could be identified by comparison with an authentic sample.[3] The ^{13}C NMR spectral and chemical evidence are both consistent with **2** having the carbon–iodine bonds either endo,endo or exo,exo. We favor the latter on the basis of mechanistic considerations (i.e., **2** is most likely formed via S_N2 displacement of the endo tosylate groups in **1b** by iodide).



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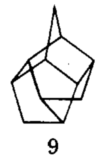


9

Dehalogenation of diiodides **3** and **4** with either zinc–acetic acid[4,5] or tri-*n*-butyltin hydride afforded trishomocubane (**9**). This fact, together with the ^{13}C NMR spectral evidence (Table I), requires that the carbon–iodine bonds in **3** have the syn,anti configuration. However, in the case of **4**, this same type of evidence is consistent with the carbon–iodine bonds being either syn,syn or anti,anti. The question of the configurations of these carbon–iodine bonds in **4** has been resolved via single-crystal x-ray structural analysis. The x-ray structure determination on **4** has shown these carbon–iodine bonds to be syn,syn (Figure 1).

Compound **4** contains a crystallographic twofold axis. Figure 2 shows the skeletal numbering, unique bond lengths, and unique bond angles. Symmetry-related pairs are I–I′, C(5)–C(3), C(6)–C(10), C(7)–C(11), C(8)–C(1), and C(9)–C(2). Carbon atom C(4) lies on the twofold axis.

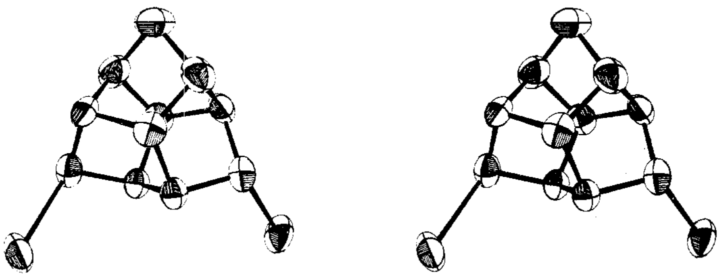


Figure 1. Stereoview of 4 generated by the ORTEP program.

One can recognize the presence of three norbornane systems in the carbon skeleton of 4: C(4)C(3)C(10)C(9)C(5)C(6)C(2), C(7)C(8)C(9)C(5)C(6)C(2)C(1), and C(11)C(1)C(2)C(3)C(10)C(9)C(8). In 4 (as in norbornane itself), one can differentiate between only three different types of carbon–carbon bond distances: types C(6)–C(7), C(5)–C(6), and C(5)–C(9). The distances in the first two types range between 1.51 and 1.53 Å, while the last, which is the only type possessing ethano-bridge character, ranges from 1.56 to 1.57 Å. These distances are in agreement with those observed in norbornane[7] and in a derivative of a cage dimer of norbornane.[8] On the other hand, the strain in the cage structure of 4 becomes apparent upon inspection of the bond angles, which are all smaller than 109.5°, and especially upon inspection of the conformations of the five-membered rings. The pseudorotation phase angles[9] are −1, −3, and 8° for the independent rings C(5)C(6)C(7)C(8)C(9), C(6)C(5)C(4)C(3)C(2), and C(6)C(7)C(8)C(1)C(2), respectively, indicating an approximate half-chair (*C*2) conformation. However, in norbornane, the five-membered rings are in the ideal envelope (*Cs*) conformation. There is one unusual feature in the molecular packing of the structure, i.e., there are short intermolecular I . . . I distances across the center of symmetry (¼, ¼, ½) of 3.80 Å, which are considerably shorter than the accepted van der Waals distance (3.95 Å[10]) but not as short as are the corresponding distances which occur in crystalline iodine (3.54 Å[11]).

Hydrocarbon 5 was identified via analysis of its proton noise decoupled and off-resonance decoupled ^{13}C NMR spectra (Table I, which indicate that 5 possesses *Cs* point symmetry) and by the fact that 5 reacts with a solution of bromine in chloroform to afford a ca. 1:2.5 mixture of isomeric dibromides ($C_{11}H_{12}Br_2$, **10a** and **10b**, which indicates that 5 contains one cyclopropane ring). The structure indi-

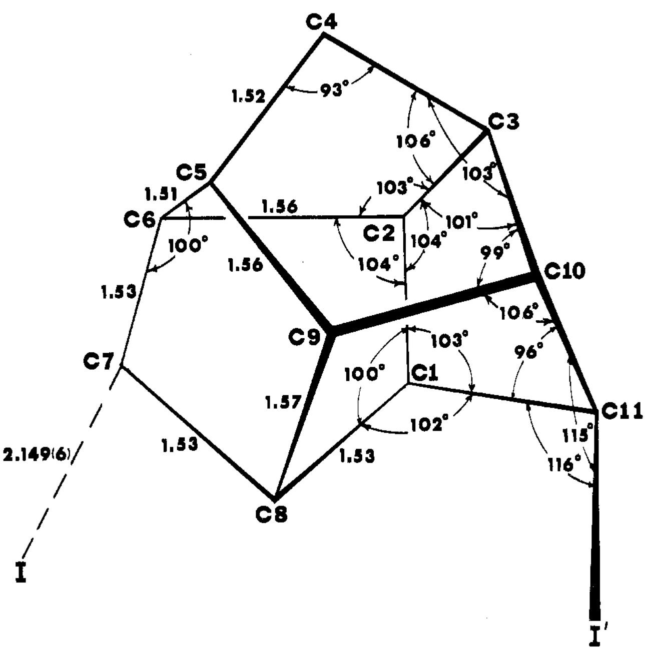
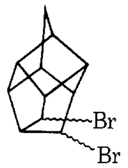
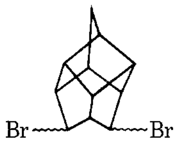


Figure 2. Atom numbering, bond lengths, and bond angles for 4. Standard deviations for bond lengths is 0.01 Å and for bond angles is 0.5°.



10a



10b

Table I. Structure Proof of Compounds 2–6a

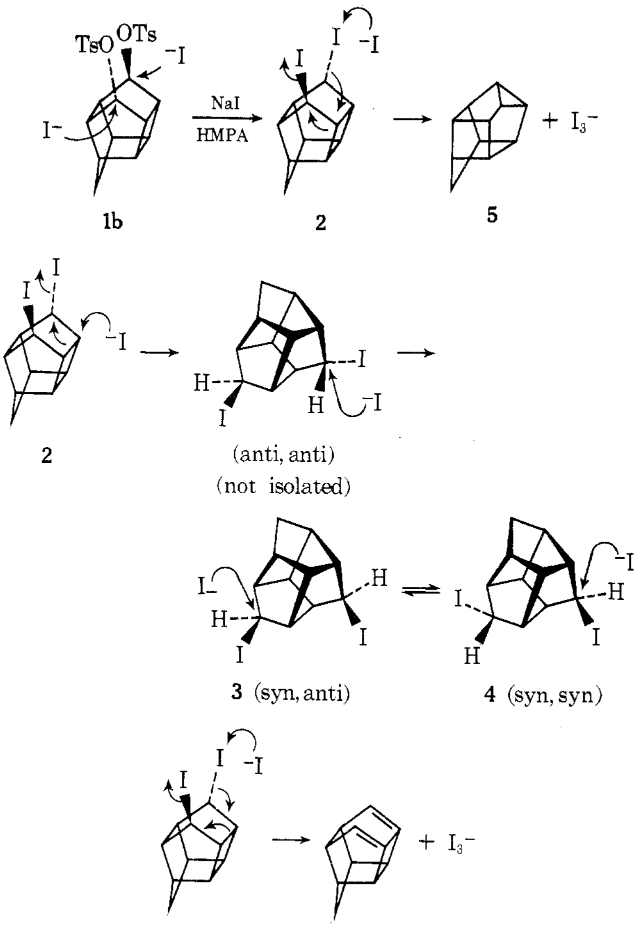
	^{13}C NMR spectrum[a]			
Compd	Proton noise decoupled[b]	Off-resonance decoupled[b]	Chemical method[c]	Ref
2	73.9 (2 C), 78.3 (2 C), 79.3 (2 C), 86.4 (2 C), 97.1 (2 C), 97.2 (1 C)	Five doublets and one triplet (97.2)	$2 \xrightarrow{(n\text{-Bu})_3\text{SnH}} 8$	3
3	69.2 (1 C), 70.7 (1 C), 71.8 (1 C), 75.1 (1 C), 79.1 (1 C), 79.9 (1 C), 87.2 (1 C), 88.0 (1 C), 95.9 (1 C), 98.1 (1 C), 98.6 (1 C)	Ten doublets and one triplet (95.9)	$3 \xrightarrow{\text{Zn, HOAc}} 9$ $3 \xrightarrow{(n\text{-Bu})_3\text{SnH}} 9$	4, 5 4, 5
4	68.9 (2 C), 72.2 (2 C), 81.9 (2 C), 87.7 (2 C), 94.3 (1 C), 99.2 (2 C)	Five doublets and one triplet (94.3)	$4 \xrightarrow{\text{Zn, HOAc}} 9$ $4 \xrightarrow{(n\text{-Bu})_3\text{SnH}} 9$	4, 5 4, 5
5	66.4 (1 C), 71.2 (2 C), 75.8 (2 C), 79.8 (1 C), 87.6 (1 C), 88.5 (2 C), 88.7 (1 C), 92.4 (1 C)	Seven doublets and one triplet (88.7)	$5 \xrightarrow[\text{CHCl}_3]{\text{Br}_2}$ **10a** + **10b**	
6a	96.8 (1 C), 79.5 (2 C), 63.6 (4 C), −8.6 (4 C)	Three doublets and one triplet (96.8)	$6a \xrightarrow[\text{xanthone}]{h\nu} 7a$	12

[a] Spectra of 2, 3, and 4 were measured at 25.2 MHz ($CDCl_3$ solvent, Me_4Si and benzene internal standards; spectra of 5 and 6a were measured at 22.63 MHz (CCl_4 solvent, CS_2 internal standard, benzene-d_6 lock). We thank Professor Michael Barfield, University of Arizona, for obtaining the ^{13}C NMR spectra of 5 and **6a**. [b] Shifts are in parts per million relative to internal benzene. Positive numbers indicate upfield shifts, negative numbers indicate downfield shifts relative to benzene. [c] See text.

cated for **5** appears to be the only reasonable structure corresponding to a saturated $C_{11}H_{12}$ hydrocarbon which contains only one cyclopropane ring and which possesses *Cs* point symmetry. Homohypostrophene (**6a**) was similarly identified via analysis of its ^{13}C NMR spectra[12] and by the fact that it could be converted photochemically to homopentaprismane (**7a**, see Experimental Section).

B. Mechanism of Formation of Products 2–6a. In order to gain information in this regard, diiodides **2–4** were each subjected in turn to the same experimental conditions under which ditosylate **1b** is converted to products **2–6a** (i.e., sodium iodide–HMPA, 125–130 °C, 45 h). Compound **2** when thus treated afforded all five products (**2–6a**). It was also demonstrated that **2** was stable to the VPC conditions under which the product analysis was performed. Either pure **3** or pure **4** when subjected to these reaction conditions afforded a *mixture* of **3** and **4** unaccompanied by **2**, **5**, or **6a**. The foregoing results suggest that hydrocarbons **5** and **6a** may be formed only from **2**. The trishomocubyl diiodides **3** and **4** simply equilibrate under the reaction conditions without proceeding to afford the hydrocarbon products (**5** and **6a**). A mechanistic scheme which is consistent with the foregoing observations is shown in Scheme I.

Scheme I



1b 2 5

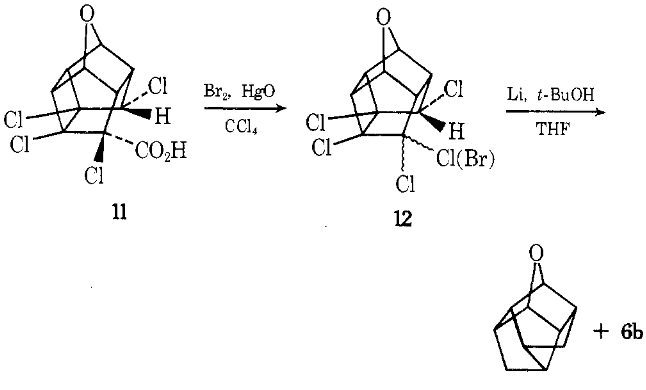
2 (anti, anti) (not isolated)

3 (syn, anti) 4 (syn, syn)

2 6a

C. Synthesis of 6b. Our synthesis of 10-oxahomohypostrophene (**6b**) is shown in Scheme II. Compound **11**, made available from another study,[13] was converted to **12** utilizing the Cristol–Firth modification[14] of the Hunsdiecker reaction. Dehalogenation of **12** with lithium-*tert*-butyl alcohol in tetrahydrofuran affords a mixture of **13** and **6b** which could be separated using preparative VPC techniques. Both compounds **13** and **6b** were identified via their ^1H NMR,[12] ir, and mass spectra, and by elemental microanalyses.

Scheme II



11 12

13

It was noted earlier that **6a** could be cyclized photochemically to afford **7a**. However, despite repeated attempts, we were unable to find a suitable set of conditions whereby **6b** might be cyclized photochemically to 4-oxahomopentaprismane (**7b**, see Experimental Section). The reasons for our failure to effect the photochemical conversion of **6b** to **7b** are not clear at present.

D. Transition Metal Catalyzed Rearrangements of 7a. The role of transition metals in catalyzing symmetry-forbidden processes is a subject of much current interest.[15–18] Accordingly, we have examined the reactions of **7a** with Rh(I) and with Ag(I). The reaction of **7a** with $(Ph_3P)_2Rh(CO)Cl$ in chloroform at 70–75 °C cleanly afforded diene **6a** within 20 h, as confirmed by NMR analysis of the product. A kinetic study of this rearrangement was performed at 67 °C. The disappearance of **7a** and the concomitant formation of **6a** could be followed using ^1H NMR spectroscopy (see Experimental Section). The reaction was found to be cleanly second order, first order in each of the reactants (**7a** and the Rh(I) catalyst). Least-squares treatment of a plot of log $[\mathbf{7a}]_0/[\mathbf{7a}]_t$ vs. time afforded a straight line having slope = 0.070 from which a rate constant $k_2 = 5.7 \times 10^{-5}\ M^{-1}\ s^{-1}$ could be calculated. The calculated rate constant corresponds to a half-life of ca. 9.8 h for this process (0.171 M in catalyst).

We have also examined the $[Rh(norbornadiene)Cl]_2$-catalyzed isomerization of **7a** to **6a**. The reaction at 40 °C in benzene-d_6 solvent was extremely slow: for a solution 0.456 M in **7a** and 0.0135 M in catalyst, the half-life was found to be ca. 7.5 days. The plot of log $[\mathbf{7a}]_0/[\mathbf{7a}]_t$ vs. time displayed considerable curvature. The rate data which we observed for this reaction can be compared directly with the corresponding rate data obtained for the $[Rh(norbornadiene)Cl]_2$-catalyzed isomerization of cubane (for which $k = 14\ M^{-1}\ s^{-1}$ in $CDCl_3$ solvent at 40 °C)![18] Additionally, it has been reported that the $[Rh(norbornadiene)Cl]_2$-catalyzed isomerization of 9,10-dicarbomethoxy-1,8-bishomocubane at 40 °C in dry benzene is complete in 40 h.[19]

Unexpectedly, compound **7a** was found to be inert toward $AgBF_4$ in chloroform solution (58–62 °C, 4 days) and toward $AgClO_4$ in benzene solution at 78 °C. Unreacted **7a** could be recovered essentially quantitatively after 10 days' exposure to silver perchlorate at this temperature. One might anticipate the product of Ag(I)-catalyzed rearrangement of **7a** to be **5** by analogy to the course of Ag(I)-catalyzed rearrangements of other strained cage systems.[16]

The driving force behind many transition metal catalyzed rearrangements of systems containing strained σ bonds is thought to be relief of steric strain.[16] In a recent review, Paquette[16] stated: "the lower limit of inherent ring strain required for rearrangement is yet to be established". Perhaps a better way to state this would be in terms of the minimum energy difference between reactants and products, ΔE, needed to promote these rearrangements. We can estimate the energy change for the transformation of **7a** to **5** in an approximate way by summing the strain energies of their composite fused rings.[20] Using published values of ring strain energies,[21] we arrive at ΔE = ca. 24 kcal/mol for the transformation of **7a** to **5**. Typical values for the relief of steric strain in transition metal catalyzed rearrangements of systems containing strained σ bonds usually fall in the range 35–50 kcal/mol.[16] We conclude that our failure to observe Ag(I)-catalyzed rearrangement of **7a** to **5** reflects the minimal driving force for this process.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were recorded on a Beckman IR-8 infrared spectrophotometer and were calibrated against the 1601-cm^{-1} band of polystyrene. ^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer (Me$_4$Si internal standard). ^{13}C NMR spectra were obtained using either a Brucker WH-90 FT NMR spectrometer operating at 22.63 MHz (University of Arizona) or a Varian XL-100-15 FT NMR spectrometer operating at 25.2 MHz (University of Oklahoma). Mass spectra were obtained at 70 eV (unless otherwise indicated) utilizing a Hitachi Perkin Elmer Model RMU-7E mass spectrometer. Values of m/e of each significant peak in the mass spectra are reported, followed parenthetically by the intensity of that peak (where the intensity of the base peak = 100). VPC studies were performed on a Varian Aerograph Model A90-P3 vapor phase chromatograph outfitted with a 0.25 in. × 5 ft column packed with 3% SE-30 on 45/60 mesh Chromosorb P. Column conditions (temperatures and He flow rates) are indicated in each case. Elemental microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. Unless otherwise noted, all reagents and solvents were reagent grade and were used without additional purification.

Reaction of 1b with Sodium Iodide in Hexamethylphosphoramide (HMPA). To a 500-ml three-neck round-bottom flask fitted with a nitrogen inlet and a side arm leading to a receiving flask was placed a mixture of **1b** (12.1 g, 0.025 mol) and sodium iodide (60 g, 0.4 mol) in freshly distilled HMPA (150 ml). The resulting mixture was heated under nitrogen with stirring at 125–130 °C for 45 h. During this period, the temperature of the receiving flask was maintained at −78 °C via external cooling (dry ice–acetone bath). At the conclusion of the reaction, the volatile products which had collected in the receiver were taken up in pentane, washed with water, and then dried (Na$_2$SO$_4$) and filtered. The filtrate was concentrated via distillation through a 12-in. Vigreux column. The oily residue was sublimed (80–90 °C, 1 atm), affording a colorless, waxy solid (415 mg, 11.6%). VPC analysis (column temperature 80 °C, He flow rate 120 ml/min) indicated the presence of two components (ca. 1:2.3) which could be separated via preparative VPC (column temperature 130 °C, He flow rate 120 ml/min). The major (less volatile) component was identified[2] as hexacyclo[5.4.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{8,10}]undecane (**5**): mp 132–134 °C (sealed tube); ir (CCl$_4$) 3040 (s), 2960 (s), 2850 (m), 1438 (w), 1301 (m), 1290 (m), 1198 (w), 1015 (w), 950 (w), and 930 cm^{-1} (w); ^{1}H NMR (CDCl$_3$) δ 1.43 (d, J = ca. 1 Hz, 2 H, 3-methylene protons), 1.83–2.48 (complex multiplet, 4 H), 2.48–3.17 (complex multiplet, 6 H); mass spectrum m/e 144 (molecular ion, 81), 129 (45), 128 (30), 116 (18), 115 (19), 79 (100), 78 (98), 77 (32), 66 (97), 51 (18), and 38 (30); ^{13}C NMR (see Table I).

Anal. Calcd for C$_{11}$H$_{12}$: C, 91.61; H, 8.39. Found: C, 91.78; H, 8.32.

The minor (more volatile) component of the mixture was identified as tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undeca-2,6-diene ("homohypostrophene", **6a**): mp 141.5–142.5 °C (sealed tube) (lit.[22] mp 143.5–144.5 °C); ir (CCl$_4$) 3055 (m), 2950 (s), 2806 (m), 1325 (m), 1018 (m), and 835 cm^{-1} (m); ^{1}H NMR (CDCl$_3$) δ 1.63 (br s, 2 H, 10-methylene protons), 2.33 (br s, 4 H, 1,4,5,8-methine protons), 3.17 (m, 2 H, 9,11-methine protons), and 5.93 (s, 4 H, vinyl protons); mass spectrum m/e 144 (molecular ion, 12), 129 (8), 115 (9), 79 (100), 78 (32), 77 (31), and 66 (15). The ^{13}C NMR spectrum of **6a** (Table I) was identical with that of authentic material.[12]

The dark mixture left in the reaction flask (nonvolatile products) was poured into water, and the products were extracted into hexane (4 × 100 ml). The combined extracts were washed with saturated aqueous sodium bicarbonate solution (2 × 100 ml) and water (3 × 100 ml), and then dried (Na$_2$SO$_4$), filtered, and concentrated. A colorless, oily material was thereby obtained which, upon recrystallization from hexane, afforded a mixture of isomeric diiodides (4.3 g, 43.4%). The ^{1}H NMR spectrum of this mixture displayed two broad singlets at δ 3.97 and 4.47 (intensity ratio 15:11) and complex multiplets at δ 1.2–3.6. Separation of this mixture was effected via column chromatography on Merck TLC grade silica gel (200 g, 1.5 in. o.d. column, hexane eluent). Repeated recrystallization of the first few fractions from hexane afforded pure *exo*-8,*exo*-11-diiodopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**2**) as colorless prisms: mp 132–133 °C; ir (CCl$_4$) 2990 (s), 2870 (m), 1292 (m), 1273 (m), 1165 (m), 1128 (s), 865 (m), and 692 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) AB pattern, δ_A 1.37, δ_B 1.78 (J_{AB} = 12 Hz, 2 H, 4-methylene protons), δ 2.57 (br s, 2 H, methine protons), 2.70–3.10 (m, 4 H, methine protons), 3.43 (m, 2 H, methine protons), and 4.47 (s, $W_{1/2}$ = ca. 2 Hz, 8,11 protons); mass spectrum m/e 398 (molecular ion, 0.2), 271 (37), 205 (15), 193 (18), 144 (41), 143 (18), 129 (12), 128 (12), 115 (10), 79 (100), 78 (29), 77 (23), and 66 (15); ^{13}C NMR (see Table I).

Anal. Calcd for C$_{11}$H$_{12}$I$_2$: C, 33.19; H, 3.04. Found: C, 33.17; H, 2.96.

Repeated recrystallization of the last few chromatography fractions (hexane) afforded pure *syn*-4,*anti*-7-diiodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**3**) as colorless needles: mp 122–123 °C; ir (CCl$_4$) 2985 (s), 2870 (m), 1298 (m), 1268 (s), 1172 (s), 1163 (s), and 670 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) δ 1.50 (d, J = ca. 1 Hz, 2 H, 11-methine protons), 1.93–2.80 (complex m, 6 H, methine protons), 2.80–3.30 (complex m, 2 H, methine protons), and 3.97 (br s, $W_{1/2}$ = ca. 5 Hz, 2 H, 4,7 protons); mass spectrum m/e 398 (molecular ion, 0.6), 271 (5), 205 (4), 193 (4), 144 (13), 143 (18), 129 (10), 128 (13), 115 (12), 79 (100), 77 (28), and 66 (23); ^{13}C NMR (see Table I).

Anal. Calcd for C$_{11}$H$_{12}$I$_2$: C, 33.19; H, 3.04. Found: C, 33.04; H, 2.99.

It was subsequently found that the middle chromatography fractions contained a mixture of **3** and a third diiodide. This mixture could be separated via additional, carefully executed column chromatography. In this way, *syn*-4,*syn*-7-diiodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**4**) was isolated. Recrystallization from hexane afforded pure **4** as colorless needles: mp 151–152 °C; ir (CCl$_4$) 2985 (s), 2870 (m), 1290 (s), 1280 (s), 1275 (s), 1238 (m), 1195 (m), 1175 (s), 1155 (s), and 670 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) δ 1.53 (s, $W_{1/2}$ = ca. 3 Hz, 2 H, 11-methylene protons), 2.20 (br s, 4 H, methine protons), 2.73 (br s, 2 H, methine protons), 3.03 (br s, 2 H, methine protons), and 3.97 (s, $W_{1/2}$ = ca. 3 Hz, 2 H, 4,7 protons); mass spectrum m/e 398 (molecular ion, 6), 271 (65), 205 (19), 193 (19), 144 (44), 143 (37), 79 (100), 78 (33), 77 (17), and 66 (15); ^{13}C NMR (see Table I).

Anal. Calcd for C$_{11}$H$_{12}$I$_2$: C, 33.19; H, 3.04. Found: C, 32.93; H, 3.07.

Dehalogenation of 2. A. Using Lithium–*tert*-Butyl Alcohol in Tetrahydrofuran. To a solution of **2** (635 mg, 1.6 mmol) in dry tetrahydrofuran (10 ml) were added *tert*-butyl alcohol (1 ml, 10.6 mmol) and lithium wire (140 mg, 20 mg-atoms). The reaction mixture was refluxed for 1 h and then poured into ice water. The product was extracted into pentane, and the pentane solution was washed with water and then dried (Na$_2$SO$_4$). The solution was then filtered, and the solvent was carefully removed via fractional distillation. The oily residue was sublimed (95 °C, 1 atm), affording a colorless, waxy solid (157 mg, 68.2%). VPC peak enhancement (column temperature 85 °C, He flow rate 120 ml/min) and analysis of the ^{1}H NMR spectrum of this product indicated it to be pure **6a**. No other product was found in this reaction.

B. Using Lithium Aluminum Hydride. A solution of **2** (520 mg, 1.3 mmol) in freshly distilled tetrahydrofuran (8 ml) was added dropwise over a 10-min period to a refluxing suspension of lithium aluminum hydride (0.38 g, 10 mmol) in tetrahydrofuran (5 ml) under nitrogen. Refluxing was continued for 1 h after the addition of **2** had been completed. The reaction mixture was then cooled to 0 °C (ice bath), and water was carefully added to destroy excess lithium aluminum hydride. The product (ca. 100 mg) was isolated and found to consist solely of diene **6a**.

C. Using Tri-*n*-butyltin Hydride. A solution of **2** (200 mg, 0.5 mmol) in anhydrous diethyl ether (10 ml) was heated to reflux under nitrogen. To the refluxing solution was added dropwise an excess of freshly distilled tri-*n*-butyltin hydride (0.5 ml, prepared via the reaction of tri-*n*-butyltin chloride with lithium aluminum hydride in diethyl ether[23]). After refluxing for 3 h, the reaction

Table II. Atomic Fractional Coordinates and Thermal Parameters of Unique Iodine and Carbon Atoms in 4[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
I	2018 (0)	5766 (1)	3562 (1)	34 (0)	224 (1)	161 (1)	−51 (1)	51 (1)	−59 (1)
C(5)	373 (5)	1153 (8)	1750 (8)	48 (3)	179 (11)	143 (9)	−87 (17)	59 (9)	14 (10)
C(8)	69 (4)	4294 (6)	1779 (5)	33 (2)	148 (9)	69 (5)	13 (11)	43 (6)	7 (7)
C(7)	1090 (4)	3861 (8)	2229 (6)	32 (2)	197 (11)	95 (6)	−39 (14)	50 (7)	−3 (8)
C(6)	1043 (4)	2158 (7)	2998 (6)	32 (2)	144 (9)	118 (7)	1 (13)	45 (6)	37 (7)
C(2)	407 (4)	2530 (7)	3862 (5)	40 (3)	173 (11)	86 (6)	43 (13)	40 (7)	14 (9)
C(4)	0 (0)	−205 (13)	2500 (0)	69 (6)	126 (14)	199 (17)	0 (0)	76 (16)	0 (0)

[a] The temperature factor is expressed as exp $[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$. All parameters are multiplied by 10^4. Standard deviations for last digits appear in parentheses.

Table III. Hydrogen Atom Parameters for 4[a]

	x	y	z	β, Å^2
H (5), H (3)	93 (8)	62 (10)	111 (10)	5.7 (28)
H (8), H (1)	0 (6)	536 (10)	117 (9)	3.6 (18)
H (7), H (11)	128 (6)	364 (13)	144 (9)	4.7 (20)
H (6), H (10)	173 (5)	169 (10)	347 (7)	2.4 (14)
H (2), H (9)	85 (7)	276 (12)	505 (10)	6.0 (24)
H (4), H (4)	− 56 (9)	−83 (9)	159 (11)	4.9 (23)

[a] The positional coordinates are multiplied by 10^3. Pairs of atoms are symmetry related by a twofold axis.

mixture was cooled, washed with 5% aqueous sodium hydroxide solution (5 ml) and water (5 ml), and then dried (Na_2SO_4). The solution was then filtered through silica gel (ca. 3 g), and the filtrate was concentrated via careful fractional distillation. The residue was sublimed to afford a solid material (ca. 40 mg) which was found by VPC to consist of two compounds. Separation was effected via preparative VPC (column temperature 150 °C, He flow rate 130 ml/min); the products were identified as **6a** and pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**8**) (ratio **6a**:**8** 9:7). Compound **8** was identified via comparison of its ir and ^1H NMR spectra with those of an authentic sample[3] and via VPC techniques (i.e., enhancement of a peak corresponding to authentic **8**[3]).

Dehalogenation of a Mixture of 3 and 4. A. Using Zinc–Acetic Acid. To a stirred solution of diiodides **3** and **4** (1.02 g, 26 mmol) in glacial acetic acid (5 ml) was added zinc dust (1 g). The resulting mixture was heated at 100 °C (oil bath) for 2 h and then poured into ice water (50 ml). The product was extracted into pentane (3 × 30 ml), and the combined extracts were washed with 5% aqueous sodium bicarbonate solution (3 × 30 ml) and water (2 × 30 ml), and then dried (Na_2SO_4). The solution was then filtered, and solvent was removed via careful fractional distillation. The oily residue was sublimed (100–110 °C, 1 atm), affording pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane ("trishomocubane", **9**) (0.300 g, 83.4%): mp 146–148 °C (sealed tube) (lit. 150–152,[4] 149–151,[5] 147–149 °C[22]); ir (CCl_4) 2960 (s), 2875 (s), 1455 (m), 1291 (s), and 1270 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.36 (br s, 6 H, methylene protons) and 1.97 (br s, 8 H, methine protons); mass spectrum *m/e* 146 (molecular ion) and 80 (100). The foregoing spectral data are in close agreement with the corresponding literature values for **9**.

B. Using Tri-*n*-butyltin Hydride. A mixture of diiodides **3** and **4** (590 mg, 1.5 mmol) in anhydrous diethyl ether (10 ml) was heated to reflux under nitrogen. An excess of freshly distilled tri-*n*-butyltin hydride (1.6 g) was added dropwise to this refluxing solution. The mixture was refluxed for 2.5 h after addition of the tri-*n*-butyltin hydride had been completed. The reaction mixture was then cooled, washed with 5% aqueous sodium hydroxide solution (5 ml) and water (5 ml), and then dried (Na_2SO_4). The dried solution was filtered through silica gel (ca. 4 g), and solvent was removed via careful fractional distillation. The residue was sublimed, affording a colorless solid (182 mg, 83.1%) which was identical in all respects with compound **9** prepared in part A above.

Single-Crystal X-Ray Structural Analysis of 4. The data crystal was obtained from an ethanol solution of **4**. It had ten faces with approximately an ellipsoidal shape having 0.3 and 0.6 mm as minimum and maximum dimensions. The mosaic spread was 1° measured at the peak base using an ω scan. The crystal data follow: $C_{11}H_{12}I_2$; mol wt 398.04; monoclinic; a = 15.650 (4), b = 7.698 (1), c = 9.951 (3) Å; β = 111.30 (2)°; V = 1123.6 Å^3; Z = 4; ρ_{calcd} = 2.368, ρ_{obsd} = 2.360 g cm^{-3} (aqueous thallous formate); $F(000)$ = 736; extinctions hkl ($h + k = 2n + 1$), $h0l$ ($h = 2n + 1$, $l = 2n + 1$), $0k0$ ($k = 2n + 1$), space group $C2/c$ as confirmed by structure determination; zirconium filtered Mo Kα radiation, λ(Mo Kα_1) = 0.70926 Å for 2θ data and $\bar{\lambda}$ (Mo Kα) = 0.71069 Å for intensity data.

The cell parameters were determined by a least-squares fit to the $+2\theta$ and -2θ values of 42 reflections distributed throughout all of reciprocal space. The 1348 data comprising all unique reflections with $\theta \leq 28°$ were measured using a θ–2θ scan technique. The scan widths were calculated as $\theta° = (1.2 + 0.12 \tan \theta)°$. The aperture was located 173 mm from the crystal; it had a horizontal width (mm) (= $4 + 0.4 \tan \theta$) and vertical width of 6 mm. Maximum scan time was 90 s, with ⅔ of the time spent on the peak scan and ⅙ of the time spent on each the left and right background. For 173 reflections the net intensity was indistinguishable from the background, i.e., less than 2σ(T); these reflections were assigned intensities equal to 1.41 σ(T). The weighting scheme used has been described.[24]

The structure was determined using the heavy-atom method. The least-squares refinement, using the block-diagonal method,[25] converged to a value for R (= $\Sigma||kF_o| - |F_c||/\Sigma|kF_o|$) of 0.050 for all 1348 data. Anisotropic temperature factors were given to the iodine and carbon atoms. Anomalous dispersion corrections were made for the iodine. All six independent hydrogen atoms were located and included in the refinement with isotropic temperature factors. In the last cycle of refinement all parameter shifts were less than 0.5 σ. A final difference Fourier map showed peaks around the iodine location of 1.4 e Å^{-3}.

The scattering factors used were from the International Tables for X-Ray Crystallography.[26] The least-squares calculations minimized the quantity $\Sigma w_F(kF_o - F_c)^2$. The mean values for $w_F\Delta F^2$ calculated for ranges of F_o were quite constant, validating the weighting scheme used. The final parameters are shown in Tables II and III. The observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

Brominolysis of 5. Bromine was added dropwise to a solution of **5** (57 mg, 0.4 mmol) in chloroform (3 ml) at 0 °C until the color of bromine persisted. The solution was allowed to stand at room temperature for 24 h, at which time the solution was washed sequentially with aqueous sodium thiosulfate solution and with water. The organic layer was dried (Na_2SO_4), filtered, and then concentrated, affording a mixture of isomeric $C_{11}H_{12}Br_2$ dibromides as an oil (ca. 100 mg). This oil displayed the following spectral characteristics: ir (film) 2970 (s), 2870 (m), 1380 (s), 1200 (s), 780 (s), and 710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.5 (br s) and 1.6 (center of an AB pattern, J_{AB} = ca. 1.5 Hz, total 2 H, methylene protons), 2.0–3.2 (complex m, 8 H, methine protons), and 4.2 (br s) and 4.35 (br s) (total 2 H, ratio ca. 2.5:1, CHBr); mass spectrum (10 eV) *m/e* 306 304 302 (molecular ion corresponding to $C_{11}H_{12}Br_2$, having the intensity profile characteristic of the Br_2 multiplet[27]), 224 (60), 223 (64), 145 (24), 144 (28), 143 (38), 79 (100), and 67 (38). Trituration of this oil with hexane afforded a solid which recrystallized from hexane to afford a colorless material, mp 89–105 °C. No further attempts were made to characterize this mixture.

Control Studies. A. Reaction of 2 with Sodium Iodide–HMPA. A mixture of **2** (718 mg, 2.36 mmol) and sodium iodide (4.1 g, 27.3 mmol) in freshly distilled HMPA (9 ml) was heated at 125–130 °C under nitrogen for 41 h. After this period, water (20 ml) and pentane (20 ml) were added and the layers were separated. The aqueous layer was extracted with pentane (3 × 20 ml), and the combined pentane extracts were washed with water (2 × 20 ml). The pentane solution was then dried (Na_2SO_4), filtered, and concentrated by careful distillation through a 6-in. Vigreux column. The residue (ca. 620 mg) was analyzed as follows: its ^1H NMR spectrum displayed signals at δ 4.47 (due to diiodide **2**) and 3.97 (due to diiodides **3** and **4**) having approximately equal areas; VPC analysis (column temperature 75 °C, He flow rate 120 ml/min) additionally indicated the presence of **6a** and **5** in the ratio ca. 9.5:1. In a separate experiment, **2** was shown to be stable to the VPC conditions employed in the analysis of the above reaction mixture.

B. Reaction of 3 with Sodium Iodide–HMPA. A mixture of **3** (571 mg, 1.88 mmol) and sodium iodide (3.3 g, 22 mmol) in freshly distilled HMPA (8 ml) was heated at 125–130 °C under nitrogen for 47 h. Work-up as described above afforded a crude product (ca. 540 mg) which was analyzed as follows: TLC displayed only one spot with R_f value equal to that of **3**; VPC analysis indicated the absence of any trace of hydrocarbons **5** or **6a**; the ^{1}H NMR spectrum displayed absorption signals corresponding to a mixture of diiodides **3** and **4**, no trace of **2** being detected by this method.

C. Reaction of 4 with Sodium Iodide–HMPA. A mixture of **4** (467 mg, 1.54 mmol) and sodium iodide (3 g, 0.02 mol) in freshly distilled HMPA (8 ml) was heated at 125–130 °C under nitrogen for 41 h. Work-up as described in part A above afforded a crude product (ca. 400 mg) which was analyzed as follows: TLC displayed only one spot whose R_f value was equal to that of **4**; VPC analysis (column temperature 75 °C, He flow rate 120 ml/min) indicated the absence of any trace of hydrocarbons **5** or **6a**; the ^{1}H NMR spectrum of the product exhibited absorption signals corresponding to **3** and **4**, no trace of **2** being detected by this method.

Tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undeca-2,6-diene (6a). To a stirred, refluxing suspension of sodium (0.75 g, 33 mg-atoms) in dry tetrahydrofuran (8 ml) was added dropwise a solution containing diiodides **2**, **3**, and **4** (2.0 g, 6.6 mmol) in tetrahydrofuran (10 ml); the entire reaction was conducted under a nitrogen atmosphere. After the addition was complete (ca. 20 min), the milky reaction mixture was refluxed for an additional 1.5 h. The reaction mixture was then filtered to remove insoluble material, and the filtrate was poured into ice water and extracted with pentane. The pentane solution was washed with water, dried (Na_2SO_4), and filtered, and the filtrate was concentrated via careful distillation through a 6-in. Vigreux column. The oily residue was sublimed (125 °C, 1 atm), affording diene **6a** (0.54 g, 74.7%) which was identical in all respects with the corresponding diene obtained from the reaction of **1b** with sodium iodide–HMPA.

Hexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane (7a). A solution of **6a** (1.45 g, 10.0 mmol) in pentane (350 ml) containing 9-xanthenone (4 g) as sensitizer was photolyzed under nitrogen with a Hanovia 200-W medium-pressure mercury lamp at 10–15 °C for 18 h. After this period, the reaction mixture was rapidly filtered through a short column of silica gel (20 g) to remove insoluble material. The solvent was removed via careful distillation through a 24-in. Vigreux column. The oily residue was sublimed (110 °C, 1 atm), affording a colorless solid (0.95 g). VPC analysis (column temperature 135 °C, He flow rate 120 ml/min) indicated the presence of an unidentified material (6.8%), unchanged **6a** (44.3%), and **7a** (48.9%); the retention times of these three products were ca. 10, 23, and 34 min, respectively. Pure **7a** was isolated via preparative VPC (column temperature 135 °C, flow rate 120 ml/min). An analytical sample of **7a** which was obtained via sublimation (90 °C, 1 atm) of the material thus obtained displayed mp 160–162 °C (sealed tube); ir (CCl_4) 2985 (s), 2870 (m), 1285 (m), 1245 (m), and 890 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.73 (t, J = ca. 1.5 Hz, 2 H, methylene protons), 2.67 (br s, 2 H, 3,5-bridgehead protons), and δ 3.03 (s, $W_{1/2}$ = ca. 3 Hz, 8 H, methine protons); mass spectrum m/e 144 (molecular ion, 3), 115 (11), 79 (100), 78 (41), 77 (46), 66 (23), 65 (12), 63 (10), 51 (17), and 39 (15). The foregoing ir and ^{1}H NMR spectra were essentially identical with the corresponding spectra obtained for authentic **7a**.[12]

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.66, 91.38; H, 8.37, 8.40.

Transition Metal Catalyzed Rearrangement of 7a. A. Using $(Ph_3P)_2Rh(CO)Cl$. A solution of **7a** (12 mg) in chloroform-d (ca. 0.5 ml) was placed in a standard 5-mm NMR sample tube. To this solution were added a few crystals of $(Ph_3P)_2Rh(CO)Cl$, and the mixture was degassed and sealed under vacuum. After 20 h at 70–75 °C, the ^{1}H NMR spectrum of this mixture was recorded; the resulting spectrum was found to be identical with that of diene **6a**. VPC analysis of the product revealed that **6a** was the only material formed in this reaction.

B. Using Silver Tetrafluoroborate. A mixture of **7a** (183 mg) and silver tetrafluoroborate (230 mg) in chloroform (7 ml) was sealed in a 20-ml test tube, and the mixture was heated at 58–62 °C for 4 days. After this period, the tube was opened and the chloroform solution was washed with brine. The organic layer was then dried (Na_2SO_4), filtered, and concentrated via careful distillation. A single volatile material could be separated from the oily residue via preparative VPC (Bentone 34, 5% SE-52 on 60/80 mesh Chromosorb W, 20 ft × 0.375 in. column, column temperature 130 °C, He flow rate 180 ml/min; under these conditions, the product isolated displayed a retention time of 44 min). The material thus collected (113 mg) exhibited a melting point (160–162 °C) and a ^{1}H NMR spectrum which were identical with those of the starting material (**7a**). No other volatile product could be isolated from this reaction.

C. Using Silver Perchlorate. A standard 5-mm NMR sample tube was washed first with dilute, aqueous ammonium hydroxide solution and then with distilled water. The tube was then dried (150 °C) and allowed to cool. A solution of **7a** (36 mg) in benzene-d_6 (0.5 ml) was placed in this tube; silver perchlorate (50 mg) was then added, and the NMR tube was flushed with nitrogen and then sealed. The tube and its contents were heated at 78 °C for 10 days. No change in the ^{1}H NMR spectrum of the reaction mixture was found to occur during (or at the conclusion of) this 10-day heating period. A similar lack of rearrangement of **7a** was observed when this mixture was further heated at 83–110 °C for 24 h.

Kinetic Measurements on the Rh(I)-Catalyzed Rearrangement of 7a. A. Using $(Ph_3P)_2Rh(CO)Cl$. A chloroform-d solution (0.5 ml) containing **7a** (37 mg, 0.514 M) and the Rh(I) complex (58.7 mg, 0.171 M) was placed in a standard 5-mm NMR sample tube, degassed (repetitive freeze–thaw method), and sealed under vacuum. The NMR tube was then thermostatted at 67 °C, and ^{1}H NMR spectra were obtained on the reaction mixture at measured intervals. Kinetic measurements were taken over a 24-h period (>2 half-lives). Integration of the signals corresponding to the olefinic protons of the diene (δ 6.0, 4 H, **6a**) and to the methylene protons [δ 1.65–1.75, 2 H (**6a** + **7a**)] permitted calculation of the homopentaprismane concentration at time t as

$$[\mathbf{7a}]_t = [\mathbf{7a}]_0 \times 1 - \left[\frac{(\text{integral of olefinic protons})/4}{(\text{integral of methylene protons})/2}\right]$$

B. Using Rhodium Norbornadiene Chloride Dimer. A benzene-d_6 solution (0.5 ml) of **7a** (32.8 mg, 0.456 M) and [Rh(norbornadiene)Cl]$_2$ (3.1 mg, 0.0135 M) was placed in a standard 5-mm NMR sample tube, and the NMR tube was sealed using the procedure described in part A above. Kinetic measurements were performed at 40 °C as described above for a period of 7.5 days (ca. 1 half-life).

Reaction of 11 with Bromine–Red Mercuric Oxide in Carbon Tetrachloride. A mixture of acid **11**[13] (4.4 g, 13.3 mmol) and red mercuric oxide (2.2 g, 10 mmol) in dry carbon tetrachloride (70 ml) was heated to reflux with stirring. A solution of bromine (3.0 g, 16.7 mmol) in carbon tetrachloride (25 ml) was added dropwise over a 1-h period to the refluxing mixture. Vigorous generation of carbon dioxide began in about 15 min, but the bromine color persisted throughout the entire addition period. After the addition of bromine had been completed, the reaction mixture was refluxed for an additional 100 min. The mixture was then cooled and filtered by suction through a Celite mat to remove mercury salts, and the residue was washed with carbon tetrachloride (25 ml). The clear filtrate was washed with 5% aqueous sodium hydroxide solution (30 ml), and the coagulated yellow material which formed during this process was removed via suction filtration. The organic layer was washed with water (2 × 30 ml) and then dried (Na_2SO_4), filtered, and concentrated to afford a colorless oil. Trituration of this oil with hexane afforded a solid which, upon recrystallization from hexane, afforded **12** as a colorless solid (3.95 g), mp 112–116 °C. Sublimation of this material (95 °C, 0.1 mm) followed by several recrystallizations of the sublimate from hexane raised its melting point to 117–120 °C: ir (KBr) 1200–1340 (complex absorption pattern, s) and 600–1090 cm^{-1} (complex absorption pattern, s); ^{1}H NMR ($CDCl_3$) δ 2.83–3.58 (complex m, 4 H, methine protons) and 5.3–5.73 (complex m, 3 H, containing a clearly defined doublet centered at δ 5.32, 1,6,8 protons); mass spectrum m/e (molecular ion not observable), 287 (23), 285 (49), 283 (37), 219 (35), 183 (36), 181 (37), 149 (58), 117 (30), 115 (100), 103 (30), and 69 (40). This product was judged to be a mixture of halogenated 11-oxapentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecanes (see structure **12**, Scheme II). Accordingly, this material was not further characterized; it was instead dehalogenated to afford a mixture of **6b** and **13** (vide infra).

Dehalogenation of 12 with Lithium–*tert*-Butyl Alcohol in Tetrahydrofuran. To a stirred solution of **12** (7.2 g) and *tert*-butyl alcohol (20 ml, 0.22 mol) in anhydrous tetrahydrofuran (125 ml) under nitrogen was added finely cut lithium wire (3.0 g, 0.40 g-atom). A vigorous exothermic reaction ensued after a few minutes which could be moderated by external cooling (ice bath) to maintain a gentle reflux. When the reaction subsided, the mixture was heated under reflux for an additional 3 h and then cooled. The mixture was then poured into crushed ice (300 ml), and the aqueous solution was extracted with pentane (3 × 100 ml). The pentane extracts were washed with water (3 × 100 ml), dried (Na_2SO_4), and then filtered. The solvent was removed from the filtrate by distillation through a 6-in. Vigreux column, and the oily residue was sublimed (80 °C, 20 mm) to afford a colorless, waxy material (2.23 g). VPC analysis (column temperature 95 °C, He flow rate 82 ml/min) indicated the presence of two major components (46 and 38%, respectively) and three minor components in this material. No further attempt was made to isolate and characterize the three minor components. However, the two major components could each be readily isolated from the product mixture via preparative VPC (column temperature 150 °C, He flow rate 144 ml/min). The predominant (more volatile, 46%) product was identified as 10-oxatetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene (**6b**): mp 168–169 °C (sealed tube); ir (KBr) 3050 (m), 2960 (s), 1575 (w), 1330 (s), 1250 (m), 1055 (s), 1010 (s), 995 (s), and 895 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.46 (br s, 4 H, 1,4,5,8-methine protons), 5.41 (quintet, J = ca. 3 Hz, 2 H, 9,11 protons), and 5.88 (s, $W_{1/2}$ = ca. 2 Hz, 4 H, vinyl protons); mass spectrum m/e 146 (molecular ion, 7), 118 (17), 117 (100), 115 (26), 91 (14), and 81 (32). The ^1H NMR spectrum of **6b** was identical with that of authentic material.[12]

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.26; H, 6.97.

The second (less volatile, 38%) of the two major products was identified as 4-oxapentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**13**): mp 235–236 °C (sealed tube); ir (KBr) 2970 (s), 2860 (m), 1330 (s), 1035 (s), 975 (s), and 895 cm^{-1} (s); ^1H NMR ($CDCl_3$) AB pattern, δ_A 1.13, δ_B 1.50 (J_{AB} = ca. 12 Hz, 4 H, 8,11-methylene protons; additional coupling is present in the pattern centered at δ 1.13), δ 2.35 (m, 2 H, methine protons), 2.60 (br s, 4 H, methine protons), and 4.73 (symmetrical m, 2 H, 3,5 protons); mass spectrum m/e 148 (molecular ion, 31), 92 (43), 91 (54), 82 (32), 80 (40), 79 (100), 77 (35), 70 (32), 69 (34), 66 (43), 41 (52), and 39 (57).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.07; H, 8.07.

Attempted Photocyclization of 6b to 7b. The light source was provided by the following lamps: (A) low-pressure "mercury pencil" lamp (quartz filter), Ultraviolet Products, Inc.; (B) Hanovia 200-W medium-pressure mercury lamp; (C) Hanovia 400-W high-pressure mercury lamp. Conditions for all VPC analysis were as follows: column temperature 80 °C, He flow rate 120 ml/min.

Photocyclization of **6b** to **7b** was attempted, without success, under the following conditions [solvent (sensitizer, if any), light source, temperature, irradiation time]: (a) acetone, lamp A, −78 to 25 °C, 15–20 h; (b) pentane (acetophenone sensitizer), lamp A, 0–25 °C, 10 h; (c) pentane (xanthone sensitizer), lamp A, 0–25 °C, 10 h; (d) pentane, lamp C, 10–15 °C, 20 h; (e) pentane (xanthone sensitizer), lamp C, 10–15 °C, 20 h; (f) pentane (xanthone sensitizer), lamp B, 10–15 °C, 63 h.

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Registry No.—**1b,** 58229-23-5; **2,** 58229-24-6; **3,** 56061-35-9; **4,** 58383-17-8; **5,** 58229-25-7; **6a,** 30114-57-9; **6b,** 58229-26-8; **7a,** 25107-14-6; **9,** 30114-56-8; **10a,** 58229-27-9; **10b,** 58229-28-0; **13,** 58229-29-1.

Supplementary Material Available. A listing of the structure factor amplitudes for compound 4 (6 pages). Ordering information is given on any current masthead page.

References and Notes

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