**1-Homoadamantyl acetate** was prepared from a sample of 1-homoadamantanol kindly provided by S. Godleski and P. v. R. Schleyer.

**Registry No.**—1, 14504-81-5.

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(9) (a) The use of a single rate constant $k_2$ as the parameter characterizing the total rate of formation of **3** and **4** via six-centered reaction pathways is merely a convenience. This constant may actually be factored into two separate constants for the formation of **3** and **4**, respectively, whose rates varies little over the temperature range of study. (b) It is common to assume that the preference for the indicated mode (in Chart I) of cyclopropane ring opening, among a host of alternatives, is an expression of the stereoelectronic factors controlling the course of concerted rearrangements. (c) B. L. Adams, Ph.D. Dissertation, University of Wisconsin—Milwaukee, 1974. We are obliged for the opportunity to examine Dr. Adams' thesis during the course of preparing this manuscript for publication. The principal evidence supporting the preference expressed for the bridgehead olefin mechanism (Chart II) is the reported finding of 20% of **2**-$d_1$ arising from the Vycor tube thermolysis[1] of **1**-*d*. This, however, is unconvincing because (a) there is no clear indication given as to the location of the single deuterium in the purported **2**-$d_1$ structure, and (b) even the NMR spectrum[1] reported for the product **3** indicates that it is incompletely monodeuterated. The suspicion that surface-catalyzed (wall) reactions are significant in Vycor tube reactors[1] (packed or unpacked) may be inferred from the following results disclosed by the studies of Dr. Adams: (1) the presence of both **2**-$d_2$ and **2**-$d_1$ as well as **3**-$d_0$ in the Vycor tube reaction product, (2) the fact that **4** comprises only 2% of the product mixture from the Vycor tube compared with ten times (ca. 22% of **4**) as much from the gold-coil microreactor, and (3) the low (30–40%) total yield of the two major products realized from the Vycor tube, compared with the quantitative conversion to only three products from the noncatalytic microreactor.

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# Syntheses of the Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecyl (Trishomocubyl) and Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undeca-2,6-dienyl (Homohypostrophenyl) Systems[1]

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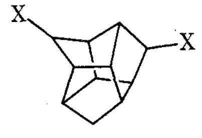
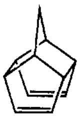
Acid-catalyzed rearrangement of the diol 6 obtained from the product of photocyclization of the *p*-benzoquinone–cyclopentadiene Diels–Alder adduct produces the $C_3$-symmetrical trishomocubane system. Diiodotrishomocubane (1c) produced either directly from 6 or by a sequence via bistosylate 1f provides a good source of the diene homohypostrophene (2) by reductive dehalogenation. The hydrocarbon trishomocubane (1a) can be obtained in high yield from the diiodide 1c by reduction with metallic zinc under acidic conditions.

Several reports in the recent literature have dealt with the syntheses of the closely related trishomocubyl (1) and homohypostrophenyl (2) systems. The unsubstituted hydrocarbon **1a** has been produced by reductive dehalogenation of dibromotrishomocubane **1b** as one of a mixture of products,[2a] by zinc–acetic acid reduction of the diiodide **1c**,[2b,c] and by Wolff–Kishner reduction of trishomocubanone (3).[3a] The monofunctional trishomocubanone (3) was obtained in a four-step sequence starting with the dione produced by ultraviolet irradiation of the *p*-benzoquinone–cyclopentadiene Diels–Alder adduct,[3a] as well as by decomposition of an organometallic intermediate derived from the photocyclization product of dicyclopentadiene.[3b] The diene **2**, which had been required for the synthesis of the first-reported[2a] trishomocubane structure, had been observed as a by-product in the attempted synthesis of homopentaprismane (**4**) from the dibromide **5**.[4] Homohypostrophene (**2**) was also obtained as a minor component of the



1a, X = H
b, X = Br
c, X = I
d, X = OAc
e, X = OH
f, X = OTs



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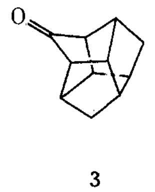

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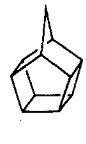

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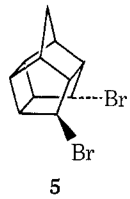

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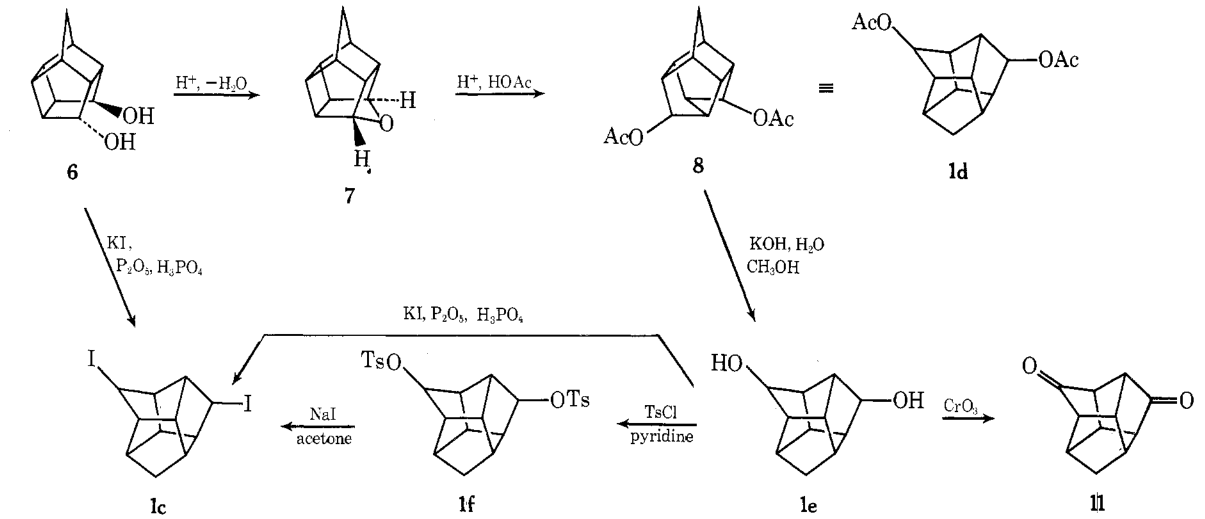
Scheme I



product mixture derived from treatment of the endo,endo ditosylate, prepared from the diol **6**, with NaI in hexamethylphosphoramide.[2c] As is often the case in initial syntheses of such polycyclic compounds, these approaches have usually been laborious or limited by high cost of reagents and low conversion to desired products.

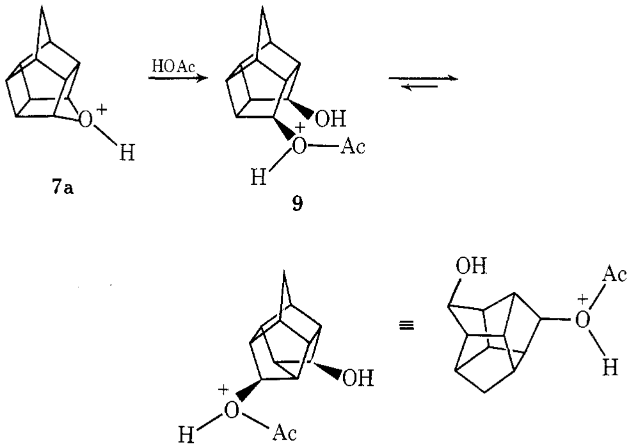
We report here syntheses of both title compounds by routes which are characterized by both convenience and reasonable yields, as well as by the fact that all starting materials are readily available. The precursor to the diene **2**, diiodotrishomocubane (**1c**), was obtained in two ways, the first by a directed synthesis via trishomocubanediol (**1e**) and the corresponding bistosylate **1f**, and the second which involves a single-step conversion of the diol **6** to **1c**.

The endo,endo diol **6** was readily synthesized from the corresponding dione by reduction with $LiAlH_4$ in tetrahydrofuran (THF), under conditions similar to published procedures.[5,6] Treatment of **6** with 48% aqueous HBr at elevated temperature resulted in good yields of cyclic ether **7**. This compound appeared to be identical in every respect but melting point[7] with an ether described by previous investigators as having been obtained simply by heating a sample of **6**.[4,6] Longer reaction times, at elevated temperature, gave products which apparently were the result of acid-catalyzed disruption of the ether linkage in **7**. The product appeared to be a mixture of compounds which presented serious separation problems, although one of these could be isolated as a crystalline solid of mp 128–130°, whose spectral properties were consistent with a structure which included both a bromine atom and a hydroxyl group. One interesting fact did emerge from this experiment, however. The NMR spectra of all cage intermediates prior to this step in the reaction sequence (e.g., the diol **6**, its dione precursor, and the ether **7**) exhibited a strongly characteristic AB-quartet pattern for the bridging methylene protons, indicating that the two protons are nonequivalent. After prolonged acid treatment of **6** (and hence **7**) the methylene protons in the NMR spectrum of products appeared as a narrow singlet absorption, suggesting equivalence. Obviously, skeletal reorganization had occurred, and it must have come about in such a way that the rearrangement product was symmetrical about an axis passing through the methylene in question.

Because aqueous HBr did not yield an easily workable set of products of rearrangement, other acidic media were investigated. Glacial acetic acid containing a catalytic amount of 98% sulfuric acid was found to be an efficient and mild medium by which to effect skeletal rearrangement (Scheme I). The diacetate produced in this way was identified as the trishomocubyl diacetate **8** (= **1d**) from its ir and NMR spectra, the latter of which exhibited the characteristic methylene singlet mentioned previously, as well as from the structures of the products of subsequent reactions. By examination of representation **8** of the diacetate in Scheme I, in which the diacetate is viewed as a derivative of bicyclo[2.2.1]heptane, the equivalence of the methylene protons is made more obvious, in the same way that structure **7** shows their nonequivalence.

The rearrangement presumably proceeds smoothly because the loss of a four-membered ring and its replacement with a five-membered ring serves as a driving force for the reaction. The protonated ether **7a** (Scheme II) is now vulnerable to nucleophilic attack by acetic acid, providing an intermediate **9** which includes a leaving group (HOAc) possessing the appropriate anti stereochemistry for opening of the four-membered ring, to produce a molecule which has the trishomocubane framework (**10**).[8] Such a mechanism predicts cis stereochemistry for the two substituents in structure **10**. We have not determined the stereochemistry of our disubstituted trishomocubanes; however, the high melting points of the diol **1e** and its tosylate **1f**, as well as the uniformity in shape of the tosylate crystals, suggests high stereochemical purity.

Scheme II



Hydrolysis of the diacetate in a mixture of KOH, methanol, and water resulted in formation of the corresponding diol **1e**, a crystalline solid of low solubility. The diol was assigned its structure on the basis of infrared data and on the basis of elemental analysis. Further support of the diol's structure was derived from its $CrO_3$–acetone conversion to trishomocubanedione **11**. The dione, mp 213–214°, exhibited the expected simple NMR spectrum consisting of only three absorptions in the ratio 1:2:2, and provided a correct elemental analysis.

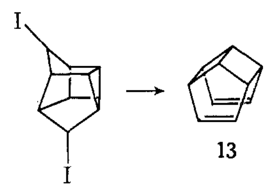
Treatment of the unpurified diol **1e** with *p*-toluenesulfonyl chloride in pyridine resulted in formation of the nicely crystalline bistosylate **1f**, whose NMR spectrum again was consistent with the assigned structure. The bistosylate, when solvolyzed in acetone in the presence of a large excess of NaI, gave the trishomocubyl diiodide **1c**. The structure of the diiodide, and hence of all preceding rearrangement molecules (**1d**, **1e**, **1f**, and **11**), followed from several pieces of data. Refluxing the diiodide with $LiAlH_4$ in THF produced only a single hydrocarbon product (albeit in low conversion) which we believe is trishomocubane (**1a**). Other reductive methods, among them sodium in liquid ammonia, sodium in THF-*tert*-butyl alcohol, and sodium–potassium alloy in tetrahydrofuran, produced varying amounts of two major components. One of these products was a saturated hydrocarbon identical with that obtained from the $LiAlH_4$–THF reduction, believed to be trishomocubane, and the other was the title compound tetracyclo[$6.3.0.0^{4,11}.0^{5,9}$]undeca-2,6-diene (**2**) (homohypostrophene). Trishomocubane **1a** could be prepared most conveniently, on a large scale and in excellent yields, simply by stirring diiodotrishomocubane (**1c**) with zinc dust in glacial acetic acid at elevated temperature.[2b] Another line of evidence supporting the structure of the diiodide is obtained from comparison of its NMR spectrum with that of the corresponding dibromide (**1b**) obtained from homohypostrophene (**2**) according to the procedure outlined by Underwood.[2a] The essential features of the two spectra are similar, the only significant differences being limited to those arising from the varying degree of deshielding experienced by the proton on the carbon bearing the halogen atom.

The 60-MHz $^1H$ NMR spectra of samples of trishomocubane (**1a**) obtained in the various reductions described above consisted of only two absorptions, broad singlets at $\delta$ 1.34 (6 H) and 1.97 (8 H), consistent with that expected based on consideration of the fact that the methinyl protons should appear at lower field than the methylene protons.[10] $^{13}C$ NMR spectra were identical with previously published results;[2b,3a] the proton-decoupled spectrum exhibited three singlets at $\delta$ 47.83 (6 C), 41.59 (2 C), and 33.27 (3 C). Undecoupled spectra showed the two lower field absorptions as doublets and the methylene carbon as a triplet, consistent with the symmetrical trishomocubane structure **1a**.

The diiodide **1c** could be most conveniently synthesized either by suitable manipulation of the rearranged diol **1e**, or in a single step from the endo,endo diol **6**. Treatment of **1e** with a mixture of $H_3PO_4$, $P_2O_5$, and KI[11] yielded **1c** in 85% yield as an epimeric mixture of diiodides. Since we were aware that **6** rearranged to the trishomocubyl skeleton under acidic conditions, it seemed reasonable that this diol would rearrange directly to **1c** in the $H_3PO_4$–$P_2O_5$–KI reaction medium; it was known that a diol mixture containing **6** in the presence of HI provided the diiodide **1c**.[2b]

At 105° in a mixture of $H_3PO_4$, $P_2O_5$, and KI, the diol **6** did in fact rearrange to a trishomocubane. After about 4 hr of reaction time rearrangement had taken place entirely, as evidenced by the disappearance of the methylene AB quartet in the NMR spectrum of **6** (and **7**) and replacement of this quartet by the methylene singlet discussed earlier. At this point, however, the NMR spectrum was quite complex, and showed evidence of the presence of some diiodide **1c** as well as hydroxyl absorptions, due presumably to the intermediacy of iodotrishomocubanol. After 12 hr of reaction time, the hydroxyl absorptions had disappeared and only diiodotrishomocubane (**1c**) was present. This approach has an obviously enormous time-saving advantage over the sequential approach described above.

The goal of these synthetic efforts, of course, was the conversion of the diiodide **1c** to homohypostrophene (**2**). We were encouraged by Underwood's report that treatment of dibromotrishomocubane (**1b**) under reductive conditions led to the formation of both the saturated hydrocarbon **1a** as well as the diene **2**,[2a] and especially by a report of a convenient synthesis of hypostrophene (**13**) by Paquette, in which reductive dehalogenation of diiodobishomocubane (**12**) resulted in diene formation.[12] It appeared that by a suitable choice of reducing conditions we could similarly obtain **2** in quantity.



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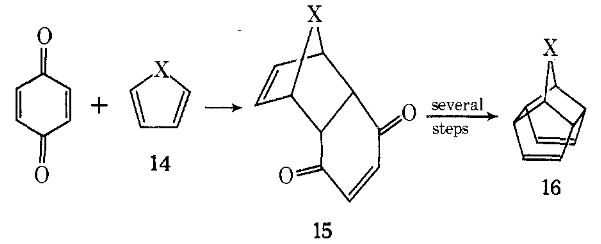
A variety of reduction methods was attempted, among them sodium in liquid ammonia, sodium–potassium alloy in tetrahydrofuran, *n*-butyllithium in anhydrous ether, and *tert*-butyllithium in anhydrous ether. As pointed out earlier, all procedures were complicated by the formation of the saturated hydrocarbon trishomocubane (**1a**), as well as, in most cases, small amounts of apparently higher molecular weight products, whose identities have not been established. NMR spectra of these materials are very similar in appearance to that of **1a**, suggesting that perhaps they incorporate the trishomocubyl skeleton.

Most successful for the production of homohypostrophene proved to be reduction of the diiodide **1c** with alkyllithium reagents. Apparently in this case **1c** suffered lithium–iodide exchange to provide an unstable anion from which lithium iodide could be eliminated with concomitant ring opening to the desired diene **2**. In the cases where *n*-butyllithium was employed, the reaction was further complicated by production of a hydrocarbon which appears to incorporate a *n*-butyl group. This complication could be averted by use of the less nucleophilic, more basic *tert*-butyllithium. Use of this reagent provided high yields of a hydrocarbon mixture which consisted of two compounds, about 25% of which was trishomocubane (**1a**) and 75% of which was homohypostrophene (**2**). The diene could be isolated as a pure compound by chromatography on a 20% $AgNO_3$–silica gel column. Final purification was accomplished by sublimation, and the product thus obtained was identical in its physical properties with those of the previously reported diene.[2a]

The synthetic approach to the diene **2** reported here should find general applicability to the synthesis of a variety of compounds bearing structural similarity to trishomocubane and homohypostrophene. Variation of structure would be made in the initial step of the sequence, the Diels–Alder reaction of *p*-benzoquinone with the appropriate diene **14**, to produce the adduct **15** which is subsequently transformed in several steps to the diene of generalized structure **16**. An appreciable number of adducts of structure **15** are now known. The generality of this approach to dienes of the structure **16**, and the chemistry of these compounds, are currently being investigated.



## Experimental Section

**Pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-8,11-diol (6).** A solution of 100 g of the dione obtained by irradiation of the *p*-benzoquinone–cyclopentadiene Diels–Alder adduct in 400 ml of anhydrous tetrahydrofuran was added under $N_2$ to a mechanically stirred mixture of 30 g of $LiAlH_4$ in 200 ml of anhydrous tetrahydrofuran. After addition had been completed, the reaction mixture was refluxed for 10 hr. The mixture was cooled in an ice bath and cautiously decomposed by addition of 45 ml of $H_2O$ followed by addition of sufficient 33% $H_2SO_4$ until inorganic salts had dissolved. The organic layer was separated, the aqueous portion extracted with chloroform, and the combined organic extracts washed with $H_2O$ and dried over $MgSO_4$. Removal of chloroform yielded 92 g (90%) of the diol, which was used without further purification.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undec-4,7-yl Diacetate (1d).** The diol 6[5,6] (1.1 g, 6.2 mmol) in 10 ml of glacial acetic acid containing 0.1 g of 98% $H_2SO_4$ was heated at 120° with stirring for 40 hr in a sealed reaction vessel. The reaction mixture was allowed to cool, then treated with 0.5 g of anhydrous NaOAc and subsequently with activated charcoal, and filtered, and most of the solvent was removed at diminished pressure with warming. Water was added to the residue, and the diacetate (**1d**) was extracted with $Et_2O$, the remaining acetic acid removed by extraction with aqueous $NaHCO_3$, the extracts dried over $MgSO_4$, and solvent removed at reduced pressure. The residue was chromatographed on a short silica gel column (13 × 2 cm) initially eluted with hexane. Elution with 20% $Et_2O$–hexane yielded 1.1 g (70%) of the diacetate **1d** as a colorless oil: NMR ($CDCl_3$) $\delta$ 1.42 (s, 2 H), 2.02 (6 H), 2.22 (br s, 6 H), 2.57 (br s, 2 H), 4.89 (2 H); ir (neat) 2988, 2884, 1737, 1367, 1248, 1050 and 737 cm$^{-1}$. For the usual applications, the diacetate was used without purification. The reaction may be scaled up without difficulty.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-4,7-diol (1e).** The diacetate **1d** (50 g) and 86 g of KOH were dissolved in 250 ml of 50% aqueous methanol and stirred for 30 hr at 60–65°. After cooling, the methanol was removed on a rotary evaporator, whereupon a light brown solid precipitated. This solid was filtered and washed with water and then with hexane to 32.5 g of the diol. Recrystallization from acetone afforded **1e** as colorless platelets: mp 203–205°; solubility difficulties precluded a suitable NMR spectrum; ir (KBr) 3280, 2960, 2895, 2875, 1350, 1274, 1190, 1100, 1077, 1066, and 778 cm$^{-1}$.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.40; H, 7.62.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-4,7-dione (11).** To a stirred solution of 1.0 g (5.6 mmol) of **1e** in 50% v/v aqueous acetone at 0° was added 1.51 g of $CrO_3$ in 2.8 ml of $H_2O$ and 1.35 ml of 98% $H_2SO_4$. After the addition was complete, the reaction mixture was stirred for 3.5 hr at room temperature. Water was added to dissolve the chromium salts and the mixture was extracted with $Et_2O$. Drying ($MgSO_4$), treatment with activated charcoal, and removal of solvent at reduced pressure gave 0.80 g of an oil which crystallized. Elution with 75% $Et_2O$–hexane on silica gel gave **11** as a white solid which was recrystallized from 66% $Et_2O$–heptane: mp 213–214°; NMR ($CDCl_3$) $\delta$ 1.79 (s, 2 H), 2.19 (br s, 4 H), 2.85 (br s, 4 H); ir ($CCl_4$) 3010, 2974, 1782, 1767, and 1152 cm$^{-1}$.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 76.13; H, 5.79.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undec-4,7-yl Bistosylate (1f).** A cold solution of 2.3 g (12.9 mmol) of the diol **1e** in 16 ml of dry pyridine was added to 7.39 g (38.9 mmol) of *p*-toluenesulfonyl chloride dissolved in 12 ml of cold, dry pyridine. After standing at 5° overnight, the reaction mixture was poured into 20 ml of ice water and extracted with $CHCl_3$. The organic phase was then washed once with 15 ml of $H_2O$ and with 4 × 15 ml of cold 4 *N* HCl. Treatment with $MgSO_4$ and activated charcoal and removal of solvent at reduced pressure gave an orange-yellow oil which crystallized by trituration with a small amount of $Et_2O$. Removal of the ether afforded 5.05 g (80%) of the bistosylate **1f** as white crystals which were recrystallized from aqueous acetone: mp 151.5–153°; NMR ($CDCl_3$) $\delta$ 1.33 (s, 2 H), 2.17 (8 H), 2.46 (s, 6 H), 4.70 (br s, 2 H), 7.60 (AB quartet, 8 H).

Anal. Calcd for $C_{25}H_{26}O_6S_2$: C, 61.71; H, 5.38. Found: C, 61.69; H, 5.33.

**4,7-Diiodopentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane (1c). A. From 1f.** Into a 200-ml pressure bottle were placed 14.3 g of bistosylate **1f**, 19.1 g of anhydrous NaI, and 100 ml of dry acetone. The flask was sealed and heated at 110–120° for 70 hr with magnetic stirring. The reaction mixture was cooled and poured into water, and the mixture carefully extracted with $CHCl_3$. The organic phase was washed with water, dried over $MgSO_4$, and treated with activated charcoal. Removal of solvent at reduced pressure yielded a white solid (10.2 g, 87%). Purification could be effected by recrystallization from $Et_2O$ or acetone. Presumably owing to the presence of stereoisomers, the diiodide was not well behaved with respect to a melting point: NMR ($CDCl_3$) $\delta$ 1.51 (s, 2 H), 2–3.4 (complex, 8 H), 3.96 (s, 2 H); ir ($CS_2$) 2988, 2880, 1304, 1279, 1275, 1250, 1188, 788, 778, 769, and 681 cm$^{-1}$.

**B. From Diol 6.** The procedure employed here closely followed one which appears in the literature.[11] To 7.8 g of 85% $H_3PO_4$ in a 100-ml round-bottom flask was added 5.9 g of $P_2O_5$. After the initial exothermic reaction had subsided, 11.2 g of KI and 2.0 g of endo,endo diol **6** were added. The flask was fitted with a reflux condenser and drying tube and stirred for 12 hr at 105–110°. The cooled, dark, viscous mass was transferred to a 125-ml separatory funnel using $Et_2O$ and water. After extracting with $Et_2O$, the organic phase was shaken with 2 × 10 ml of 10% aqueous $Na_2S_2O_3$ and twice with water (10 ml). The ethereal solution was dried and treated with activated charcoal. Removal of solvent in vacuo gave 4.06 g (91%) of the crude diiodide as an oil which partially crystallized. Material sufficiently pure for further reactions was obtained by trituration of the semisolid with acetone and cooling the mixture overnight. The NMR spectrum of this stereoisomeric mixture was identical with that of the diiodide described in part A.

**C. From Diol 1e.** Results similar to those described in part B were realized when the trishomocubyl diol **1e** was substituted, the yield of the crude diiodide being 85%.

**Pentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane (1a). A. From 1c Using $LiAlH_4$.** To a stirred suspension of 0.6 g of $LiAlH_4$ in 25 ml of freshly distilled tetrahydrofuran was added a solution of 1.1 g of diiodide **1c** in 30 ml of THF. The mixture was refluxed for 20 hr. Work-up involved decomposition of excess $LiAlH_4$ with 15% aqueous NaOH, filtration of residual solids, and washing with 30–60° petroleum ether. The filtrate was extracted with water in order to remove THF. The organic phase was dried and solvent was removed with a rotary evaporator at slightly reduced pressure. Sublimation of the residue (90°, 20 mm) yielded a white solid, the spectral properties of which were identical with those of trishomocubane **1a** prepared by the following method.

**B. From 1c with Zn–HOAc.** A mixture of the diiodide **1c** (2.0 g, 5.0 mmol), 4 g of zinc dust, and 40 ml of glacial acetic acid was stirred for 14 hr at 70°. The mixture was cooled and filtered, and the filtered solids washed carefully with petroleum ether. The combined filtrates were poured into water, layers separated, and the aqueous portion extracted twice with petroleum ether. The extracts were washed with water and saturated $NaHCO_3$ solution and dried ($MgSO_4$), and the solvent removed by distillation through a short Vigreux column. The residue was sublimed to provide 650 mg (90%) of trishomocubane (**1a**): mp 150.5–152° (lit. 147–149°);[2a] $^1$H NMR ($CDCl_3$) $\delta$ 1.34 (s, 6 H), 1.97 (br s, 8 H); $^{13}$C NMR ($CDCl_3$, undecoupled) $\delta$ 47.83 (d, 6 C), 41.59 (d, 2 C), 33.27 (t, 3 C) (proton decoupling resulted in collapse of all multiple absorptions to singlets); ir ($CCl_4$) 2970, 2883, 1465, 1301, 1280, and 967 cm$^{-1}$.

**Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undeca-2,6-diene (Homohypostrophene, 2). A. Reduction in Na–Liquid $NH_3$.** Sodium (5.0 g) was dissolved in 100 ml of $NH_3$ at −33° in a 250-ml round-bottom flask. A solution of 2.0 g of diiodide **1c** in 15 ml of freshly distilled ($CaH_2$) THF was added slowly, and the resulting mixture was stirred for 1 hr. The mixture was decomposed by careful addition of 15 g of $NH_4Cl$, petroleum ether was added, and the ammonia was allowed to evaporate. The mixture was then poured into water, layers separated, the aqueous portion extracted with petroleum ether, and the combined extracts dried over $MgSO_4$. Solvent was removed by distillation through a Vigreux column, and the residue sublimed (90°, 20 mm) to provide 380 mg of a mixture of **2** and trishomocubane (**1a**). The mixture was separated by chromatography on 20% $AgNO_3$–silica gel. Elution with hexane removed **1a**, while 50% $Et_2O$–hexane provided 285 mg (39% from **1c**) of homohypostrophene: mp 143–145° (lit. 143.5–144.5°);[2a] $^1H$ NMR ($CDCl_3$) $\delta$ 1.65 (br s, 2 H), 2.35 (br s, 4 H), 3.18 (unresolved multiplet, 2 H), 5.93 (s, 4 H); ir ($CCl_4$) 3066, 2956, 2872, 1332, and 848 $cm^{-1}$.

**B. Reduction with NaK Alloy in THF.** A solution of 10.4 g of **1c** in 30 ml of freshly distilled (from NaK alloy) THF was added under $N_2$ to a mixture of 21 g of NaK (50% by weight) and 200 ml of THF. Vigorous stirring was continued for 1.5 hr after addition had been completed. The reaction mixture was carefully filtered under a blanket of $N_2$, the residues washed thoroughly with petroleum ether, and the combined filtrates poured into water. Layers were separated and the aqueous layer extracted with petroleum ether. The combined extracts were washed with water and dried ($MgSO_4$), and solvent was removed by distillation through a Vigreux column. Sublimation of the residue as described previously yielded 2.24 g of a mixture of the hydrocarbons **1a** and **2**, from which 1.34 g of **2** could be isolated by chromatography on a 20% $AgNO_3$–silica gel column (36% from **1c**).

**C. Reaction with *tert*-Butyllithium in $Et_2O$.** To a mixture of 5.0 g of **1c** in 60 ml of anhydrous diethyl ether under $N_2$, 15 ml of *tert*-butyllithium (1.6 *M* in pentane) was added slowly. The reaction was exothermic. After addition had been completed, the reaction mixture was stirred for 10 min at room temperature. Water was added to decompose unreacted *tert*-butyllithium and to dissolve inorganic salts, the organic material separated, the aqueous portion extracted with $Et_2O$, and the combined extracts dried over $MgSO_4$. Solvent was removed by distillation through a Vigreux column, and the residue sublimed as before to provide 1.5 g of a hydrocarbon mixture consisting of 75% **2** and 25% **1a**, which could be separated (as described above) by chromatography on 20% $AgNO_3$–silica gel.

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**Registry No.**—**1a**, 30114-56-8; **1c**, 56061-35-9; **1d**, 57237-84-0; **1e**, 57237-85-1; **1f**, 57237-86-2; **2**, 30114-57-9; **6**, 56143-86-3; **6** diketone analogue, 2958-72-7; **11**, 57237-87-3; *tert*-butyllithium, 594-19-4.

## References and Notes

(1) This work was supported in part by a grant from the Research Council of the University of North Carolina at Greensboro.

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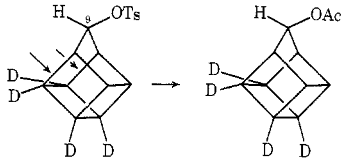
(7) We observed mp 228–230°, whereas two independent sources (ref 4 and 6) reported 190–191°. We have repeated their experiment by heating the diol **6** in vacuo and subsequently sublimed the decomposition product, and found its melting point (228–230°) to be identical with that of our acid-produced compound. NMR and ir spectral data for the compound from all sources are identical.

(8) In rearrangements of this sort, it appears that a leaving group anti to the migrating bond is a prerequisite to rearrangement. As one of a numerous set of examples of such a requirement, appropriately labeled homocubyl tosylate i undergoes solvolysis in acetic acid to produce acetate in which no deuterium appears at C-9, whereas the tosylate ii scrambles the deuterium label. Such a result requires that only the bonds indicated by arrows in the figure below are available for migration (ref 9).



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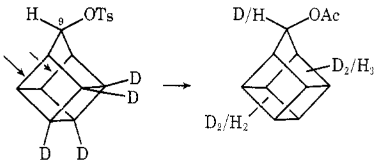

ii

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(10) In polycyclic hydrocarbons of this sort, the NMR spectra invariably exhibit absorptions for protons on relatively strained, more highly substituted carbons at lower fields than those attached to less strained carbons. See, for example, the NMR spectral data for the unsubstituted hydrocarbon whose carbon framework is identical with that of the diol **6** [R. J. Stedman, L. S. Miller, L. D. Davis, and J. R. E. Hoover, *J. Org. Chem.*, **35**, 4169 (1970)], for homocubane [W. J. Dauben and D. H. Whalen, *Tetrahedron Lett.*, 3743 (1966)], and for pentacyclo[$4.3.0.0^{2,4}.0^{3,8}.0^{5,7}$]nonane [H. Prinzbach and D. Hunkler, *Chem. Ber.*, **106**, 1804 (1973)].

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