Small-Ring Annulation and Ring Expansion of the Dodecahedrane Framework. Homododecahedranone and the 21-Homododecahedryl Cation

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Received February 24, 1989

Fusion of a cyclopropane ring to the dodecahedrane framework has been achieved in a two-step process from the parent hydrocarbon. Treatment with dichlorocarbene under phase-transfer conditions delivers (dichloromethyl)dodecahedrane (6), which undergoes rapid intramolecular C–H insertion when reacted with *tert*-butyllithium in ether at −100 °C. The action of excess methyl- or phenyllithium on 6 in ether solution at 0 °C gives rise to the methyl and phenyl analogues 8 and 9. X-ray crystallographic analysis of the latter hydrocarbon shows its three-membered ring to be free of distortion, while those pentagonal rings in the immediate vicinity are very meaningfully distorted. A ^{13}C NMR comparison with other cyclopropanated propellanes is made, and the probable path of the ring-closure process is discussed. Expansion of the dodecahedrane framework with incorporation of a ketonic carbon was efficiently realized by silver ion promoted rearrangement–hydrolysis of 6. The structural features of homododecahedranone (4), elucidated by X-ray crystallographic analysis, suggested that S_N1 solvolysis of a 21-homododecahedryl sulfonate ester should proceed at a rate comparable to that of the corresponding 2-adamantyl derivative. Acetolysis rates, determined conductometrically, fall nicely in line with these expectations. Furthermore, ionization to the 21-homododecahedryl cation (5) proceeds with retention of the intact polycyclic framework. The level of C–H scrambling in 5 was assessed by preparation of the monodeuterated mesylate and analysis of the d_1 acetate product mixture by ^{2}H NMR spectroscopy. The results point to predominant adoption of a nonstereospecific process involving a fully solvated carbocation and confirm the fact that 5 is indeed capable of degenerate rearrangement.

The molecular array embodied in dodecahedrane (1) is reknown for its exceptionally high symmetry and aesthetic allure.[3] It also may be considered the cornerstone of a family of unusual and theoretically fascinating structures that encompass a wide range of properties of multidisciplinary interest. With the availability of 1 in reasonable quantities,[4] there has developed in these laboratories a program directed toward the synthesis of select representatives of these desirable targets.

To date, dodecahedrene (2) has been observed only in the gas phase[5] and is not yet available as a viable laboratory intermediate. Consequently, any plan to prepare cyclopropadodecahedrane (3) cannot currently rely on 2 as a progenitor molecule. Although dichlorocarbene addition to a cycloalkene followed by dechlorination has served well as a synthetic entry to small propellane molecules containing a laterally fused cyclopropane ring,[6] this tactic is clearly not serviceable in the present context.

Our interest in 3 was motivated by knowledge that fusion of a three-membered ring across a key C–C bond of a bicyclic ring system universally results in the introduction of considerable structural distortion with concomitant enhancement of ground-strain.[7-9] In 1977, a detailed
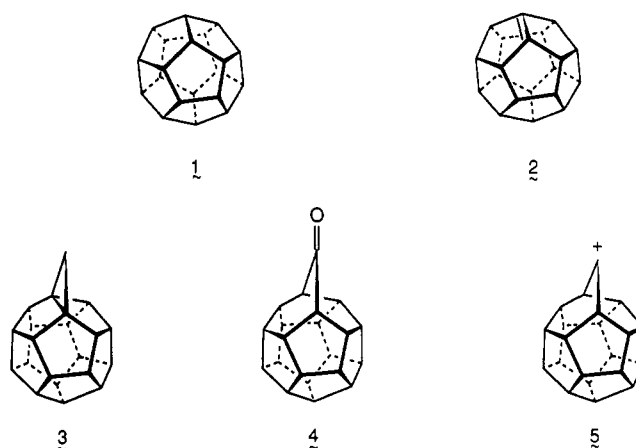
assessment of the energy costs associated with distorting the dodecahedrane framework from perfect I_h symmetry was reported by Ermer.[10] His principal conclusion was that any change in the angle deformation constants of 1 induces energy effects which are "absurdly large". The structural features of 3 or a derivative thereof would therefore provide considerable insight into the relative energetics of closely related spherical conformations.

Since neither 2 nor a 1,20-bridgehead difunctionalized homododecahedrane was available,[7-9] a new cyclopropanation procedure had to be developed. The features of this methodology are detailed herein.[11] Ideally, the route to 3 should proceed through an intermediate which would also be capable of ring expansion to homododecahedranone (4). This ketone was viewed as a key precursor to the 21-homododecahedryl cation (5), a most interesting electron-deficient species that has the latent potential to

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(6) 8,8-Dichlorotricyclo[3.2.1.0¹,⁵]octane is but one example. (a) Synthesis: Wiberg, K. B.; Lupton, E. C.; Burgmaier, G. J. *J. Am. Chem. Soc.* **1969**, *91*, 3372. (b) Structure: Wiberg, K. B.; Burgmaier, G. J.; Shen, K.; LaPlaca, S. J.; Hamilton, W. C.; Newton, M. D. *Ibid.* **1972**, *94*, 7402.

(7) 1,3-Dehydroadamantane. (a) Synthesis: Pincock, R. E.; Torupka, E. J. *J. Am. Chem. Soc.* **1969**, *91*, 4593. (b) Structure: Gibbons, C. S.; Trotter, J. *Can. J. Chem.* **1973**, *51*, 87.

(8) [2.1.1]Propellane: Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638.

(9) [1.1.1]Propellane. (a) Synthesis: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. (b) Structure: Honneger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *Ibid.* **1985**, *107*, 7172. (c) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *Ibid.* **1985**, *107*, 7247.

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be the record holder for all degenerate molecules.[12] Should its bonds interchange via consecutive 1,2-Wagner–Meerwein shifts, the same ionic entity would be reformed but with different connectivities. Complete carbon scrambling would involve 21!/2 or 2.56 × 10^{19} distinct isomers of **1**,[13] recognizable only in the presence of suitable isotopic labeling.

Our premise was that (dichloromethyl)dodecahedrane should serve both objectives admirably. A complete description of the preparation of ketone **4** and generation of cation **5** under short-lived conditions follows.[14] Herein, we also examine the detailed structural features of **4** by X-ray crystallography and compare its topography with those known for **1** and a pair of secododecahedranes.
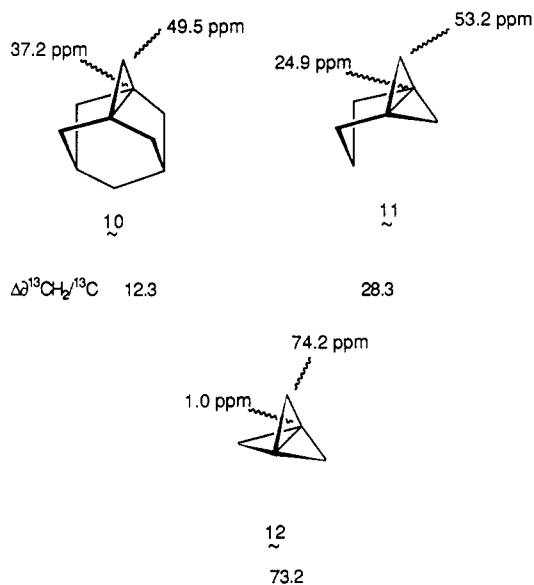
Synthesis of Cyclopropadodecahedranes. For reasons alluded to above, successful arrival at compounds such as **3** from dodecahedrane itself necessitated development of a direct annulation protocol not dependent on prior introduction of a double bond. We chose as the first of two steps the reaction of **1** with dichlorocarbene generated under phase-transfer conditions.[15–17] This procedure is known to be applicable to C–H bond insertion in those instances (benzylic, α-alkoxy, etc.) where reactivity is sufficiently elevated for ready capture of the electrophilic carbene. In addition, adamantane and diamantane are recognized to deliver dichloromethyl derivatives efficiently and selectively (at their bridgehead positions) under these conditions.[16] Regioselectivity is, of course, not a problem where dodecahedrane is concerned. Furthermore, **1** is responsive in general to electrophilic reagents.[4a,18] Not surprisingly, therefore, the addition proceeded relatively smoothly in hot benzene to deliver **6** in 59% yield.

This key intermediate features a pendant carbon atom properly functionalized for several exciting chemical undertakings. Existing precedent[19] enables us to assume that exposure of **6** to an organolithium reagent would proceed to generate DDH–C(Li)Cl$_2$. This intermediate was expected to serve as precursor to one or more reactive carbenoids whose insertion into one of the three equivalent flanking C–H bonds would deliver a product of type **7**. In the event, treatment of **6** with *tert*-butyllithium at –78 °C gave rise to an inseparable mixture of **7** and **8** (R = *t*-Bu) in a 3:1 ratio (capillary GC analysis). On lowering the temperature to –100 °C for 1 h, **7** (50%) and (chloromethyl)dodecahedrane (20%) were isolated in pure condition after chromatography.

Although **7** was obtained as a colorless solid, crystals of this hydrocarbon suitable for X-ray analysis could not be grown. The Δδ ^{13}CH$_2$/^{13}C for the three-membered ring in **7** happens to be 37.9. Comparison with the simpler
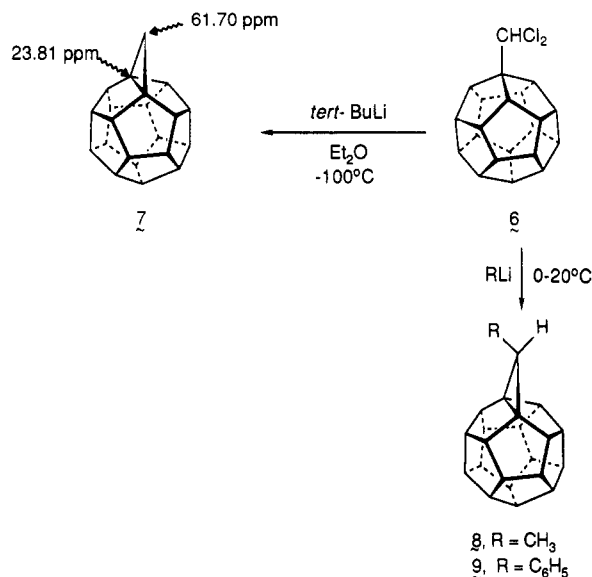
[3.3.1]propellane **10** shows the chemical shift difference in cyclopropadodecahedrane to be larger by a factor of approximately 3. The value does, however, reside between those determined earlier for **11** and **12**.[20] Thus, **7** may be comparably strained or, at least, possesses sufficient structural rigidity to enforce well-defined C–C bond alignments in the immediate vicinity of the cyclopropane ring.

The probable transient intervention of an α-chloro carbenoid intermediate during the **6** → **7** conversion was considered to offer the preparative advantage of incorporating RLi prior to three-membered ring formation. This phenomenon has been encountered in several structurally simpler carbenoids.[19b–f] In the present context, the action of excess methyllithium on **6** in ether solution at 0 °C gave rise to **8** in 67% yield. Similarly, phenyllithium acted on **6** to furnish **9** efficiently (81%).

A single-crystal X-ray analysis of **9** has been realized, and the results have been detailed elsewhere.[21] Most strikingly, the cyclopropane ring in **9** has all C–C bonds

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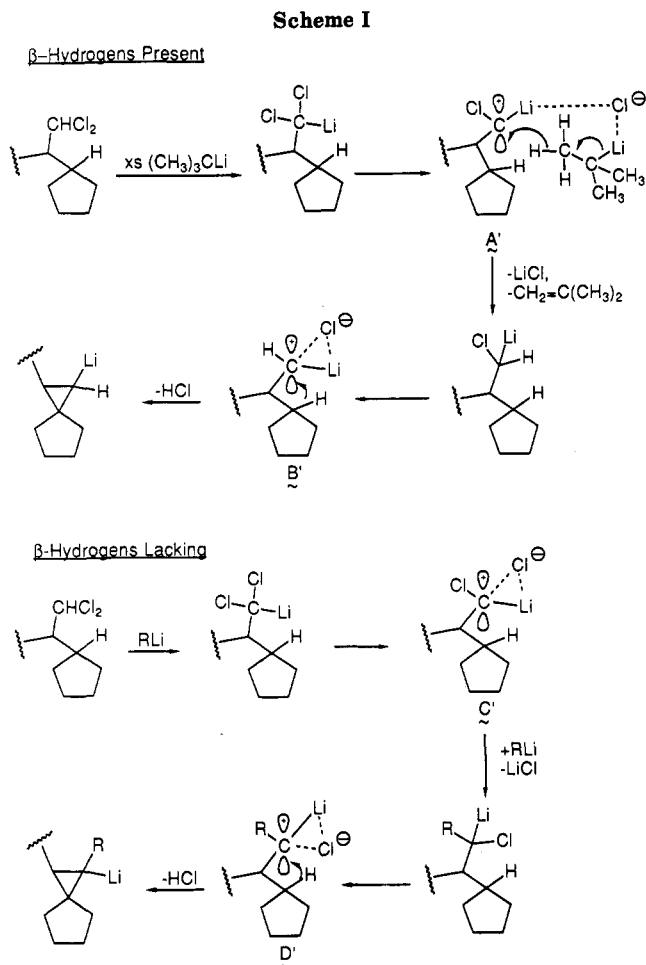
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Scheme I

With *tert*-butyllithium as coreagent, arrival at A' sets the stage for intermolecular delivery of a hydride ion. When the resulting chloro carbenoid experiences comparable ionization of the second chlorine atom as in B', the system responds by giving up a proton, but only when the relevant C–H bond is properly aligned (see below). When the lithium reagent is devoid of β-hydrogens, arrival at C' cannot be accompanied by intermolecular hydride abstraction and the lithium reagent behaves instead as a nucleophile. Once D' is produced, intramolecular collapse with loss of HCl delivers the functionalized cyclopropane. In this final carbenoid insertion, successful ring closure rests on the ability of the reaction center to eclipse the neighboring C–H bond. When this is not possible as in 1-(dichloromethyl)adamantane, reaction proceeds by insertion of a second equivalent of RLi to give the product where both chlorines are substituted by R.[11]

Homododecahedranone. When 6 was heated in 85% phosphoric acid at 120–150 °C as described for the adamantane derivatives,[16a] no reaction occurred. Therefore, attention was directed instead to silver nitrate in a solvent system composed of aqueous ethanol and benzene at the reflux temperature. Under these conditions, our expectation that 4 would result was realized (93% isolated).
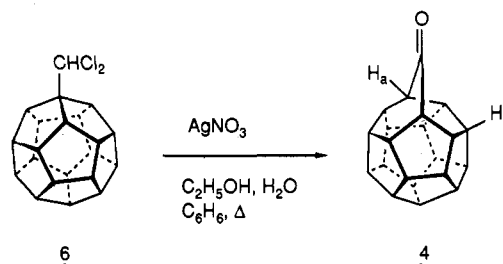
The ^1H NMR spectrum of 4 is characterized by two signals, each of area 2, at relatively high field. The triplet centered at δ 2.70 is due to H_a, and the quartet at δ 2.83 arises from H_b. All four protons are positioned within shielding cones emanating from the carbonyl group. As anticipated from the C_{2v} symmetry of 4, its ^{13}C NMR spectrum features 8 lines. Notably, the carbonyl carbon appears at 228.18 ppm. This chemical shift falls considerably to lower field than those commonly observed for ketone functional groups,[24] suggesting that reasonable strain and/or polarization may be concentrated at that site. In the infrared spectrum of 4, the carbonyl absorption is split into two bands observed at 1701 and 1679 cm^{-1} with relative absorbances of 55:45. This Fermi resonance[25] can be attributed to coupling between the carbonyl stretching mode and the overtone or combination band of another low-lying vibration mode. The weighted average band position of 1690 cm^{-1} is of additional interest in connection with the projected solvolysis rates of its alcohol derivatives (see below).

The clear, colorless crystals of 4 made possible its X-ray crystallographic analysis. Two ORTEP views of the molecule and the atomic numbering scheme are displayed in Figure 1. The crystallographic details, final positional parameters, and metrical parameters are summarized in Tables I–III. Additional relevant structural details have been deposited as supplementary material.

The point group symmetry of 4 (C_{2v}) is a consequence of the crystallographically imposed *mm* symmetry. One mirror plane contains atoms O, C21, C16, C6, C11', and C1' and bisects the C3'–C4 bond. The other mirror plane

and internal angles essentially equal. In comparison, those dodecahedrane bonds in the immediate vicinity of the fusion are extensively perturbed. From these data, it appears that the large C_{20} spherical framework is more able and willing to relieve strain by suitable distortion, much as encountered in secododecahedranes.[22]
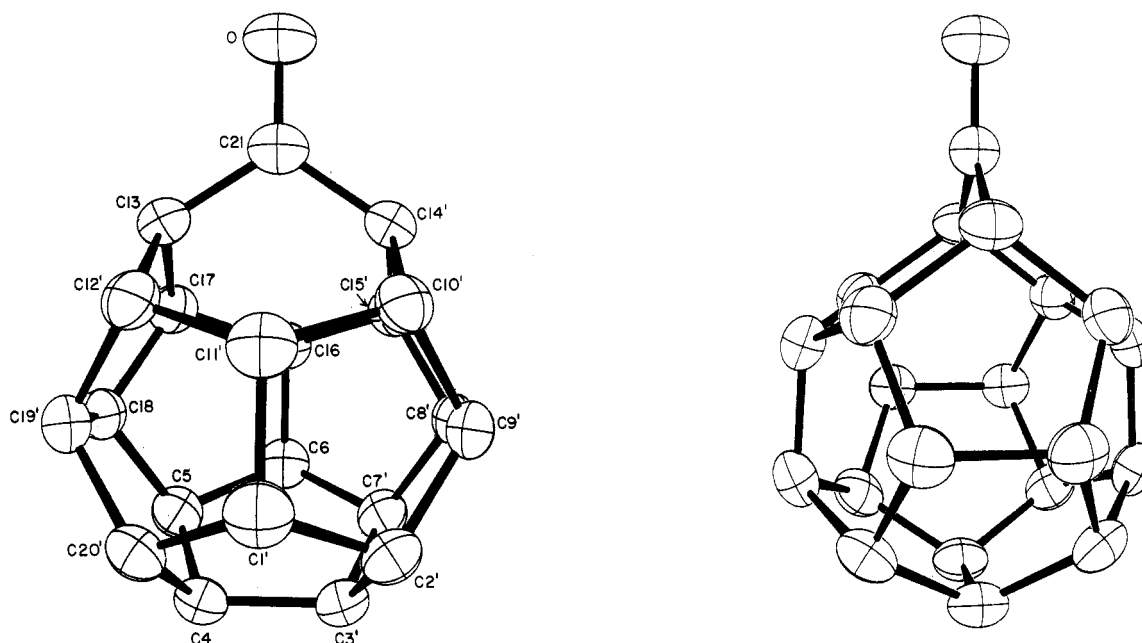
Although it is conceivable that the conversion of 6 to 8 and 9 may involve the addition of RLi to a chloro carbenoid intermediate, this mechanism does not account for the different products observed when using lithium reagents that do or do not have β-hydrogens. Furthermore, the need to postulate penultimate halogen–lithium exchange within a chlorocyclopropane by *tert*-butyllithium is highly unlikely. Chlorides that possess a proton on the halogen-bearing carbon only rarely undergo the halogen–lithium exchange process;[23a,b] instead, they are exceptionally prone to hydrogen–lithium exchange.[23c-h] Very recently, Walborsky and co-workers have provided evidence that the resulting carbenoids be best viewed as cationic intermediates.[23i-k] Accordingly, we interpret the observations made in the course of the present work as in Scheme I.

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(25) Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963.

Figure 1. ORTEP drawings of **4**. The left view shows the envelope conformation of two of the pentagonal rings. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

Table I. Crystallographic Details for 4

formula	$C_{21}H_{20}O_1$
formula wt	288.39
space group	*Cmcm* (no. 63)
a, Å	11.279 (2)
b, Å	10.293 (2)
c, Å	10.897 (1)
volume, Å³	1265
Z	4
density (calcd), g/cm³	1.51
crystal size	0.08 mm × 0.23 mm × 0.50 mm
radiation	Mo Kα with graphite monochromator
linear abs coeff, cm⁻¹	0.98
temperature, °C	ambient
2θ limits	4–60°
data collected	+*h*,+*k*,+*l*
unique data	1072
unique data, with F_o^2 > $1\sigma(F_o^2)$	629
final number of variables	84
$R(F)^a$	0.050
$R_w(F)^b$	0.053
error in observation of unit weight, e	1.68
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.045

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F) = [\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

incorporates atoms O, C21, C13, C14′, C4, and C3′ and bisects the C18–C19′ and C8′–C9′ bonds. The structure has one framework bond missing and a carbonyl group bridging the gap between atoms C13 and C14′. Hence, **4** is related to the monosecododecahedranes,[22] which also lack one framework bond and have been described in terms of approximate noncrystallographic C_{2v} point symmetry. For both molecular types, this lack of a framework bond imposes distortions on the dodecahedrane structure. For homododecahedranone, these distortions are less than those observed in the monoseco derivative. The extent of distortion results from the size of the gap between C13 and C14. In the monoseco derivatives, the C13–C14 distance is approximately 3.03 Å, chiefly as the result of an attempt on the part of the methylene carbons to minimize close contacts within the constraints of the spherical carbocyclic framework. In **4**, these two atoms are bonded to a common atom, viz. C21 of the carbonyl group, and the C13–C14′

distance is reduced to 2.48 Å. As reflected in Figure 1, the pentagonal ring containing C13 (along with the symmetry related ring containing C14′) is in an envelope conformation. Atoms C17, C18, C19′, and C12′ are required by symmetry to lie within one plane, and the flap of the envelope (C13) lies 0.37 Å away from this plane. The dihedral angle of this envelope at 23.9° is significantly less than the dihedral angles of 37.2° and 35.1° observed in the monoseco derivative.

Three other unique pentagonal rings exist. Two of these are found on that side of the molecule remote from the carbonyl group (C5, C4, C20′, C19′, C18 and C6, C5, C4, C3′, C7′) and are essentially planar. The third ring (composed of atoms C17, C16, C6, C5, and C18) is more proximal to the oxygenated site and is slightly distorted from planarity. The six-membered ring, which incorporates the ketonic center, has the approximate conformation of a half-chair. While C13, C12′, C10′, and C14′ are constrained by symmetry to reside in a plane, C11′ lies slightly (by 0.05 Å) out of this plane and C21 is significantly (by 0.66 Å) removed from it.

The transannular distances in Table IV show the same trend for **4** as observed for the monoseco derivatives. The ketone displays smaller deviations from an ideal intracavity distance of 4.314 Å (the average value determined for dodecahedrane itself[26]) than the monoseco derivatives. Not surprisingly, the largest distance, C3′–C13, involves an atom to which the framework bond has been broken.

All of the bond lengths within the pentagonal rings lie very close to the 1.546 Å value for cyclopentane.[27] The C—C and C=O bond lengths of the carbonyl group are normal. The bond angles of the five-membered rings display a slight distortion from the 108° value expected for a regular pentagon. In the pentagonal ring bonded to the carbonyl group, two angles are significantly smaller than 108°: C12′–C13–C17 at 106.5 (2)° and C13–C17–C18 at 106.1 (2)°. The remaining unique angle in this ring, C17–C18–C19′, is 107.7 (1)°. For all of the other pentag-

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Scheme II[a]
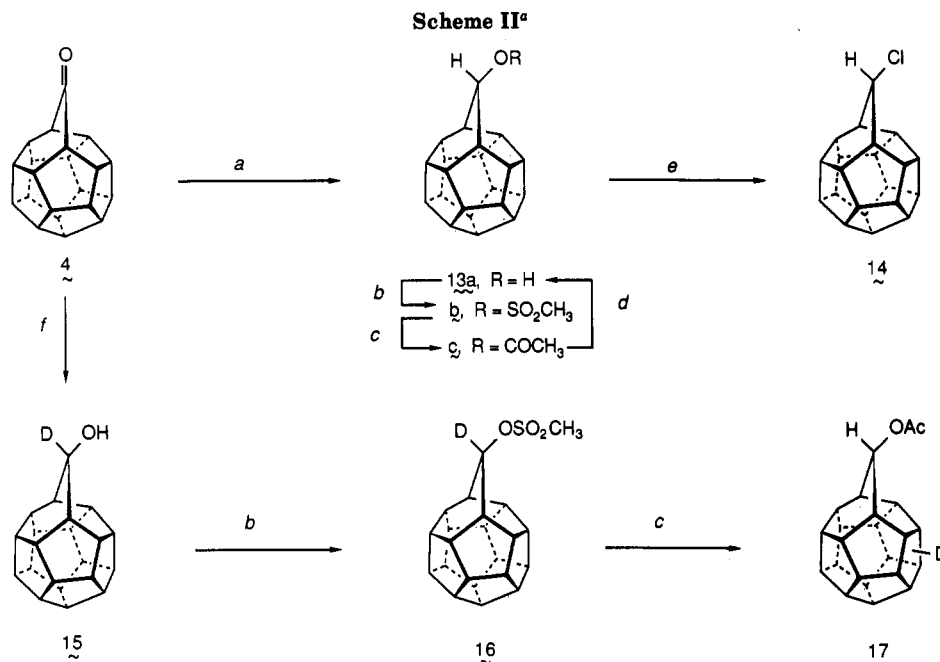
[a] (a) NaBH$_4$, CH$_3$OH, C$_6$H$_6$; (b) CH$_3$SO$_2$Cl, py; (c) HOAc, reflux; (d) KOH, C$_6$H$_6$, CH$_3$OH, H$_2$O, 70 °C; (e) SOCl$_2$, C$_6$H$_6$; (f) NaBD$_4$, CH$_3$OH, C$_6$H$_6$.

Table II. Final Positional Parameters for 4

atom	sym equiv	x	y	z	$B(eq)^a$ or B, Å^2
O		0.0	1.156 77 (28)	0.25	4.1 (1)
C21		0.0	1.038 41 (39)	0.25	3.0 (2)
C13	C14'	0.110 04 (25)	0.957 95 (25)	0.25	2.8 (1)
C17	C10', C12', C15'	0.118 31 (17)	0.868 57 (18)	0.363 61 (18)	2.77 (8)
C16	C11'	0.0	0.827 05 (28)	0.424 20 (27)	2.9 (1)
C6	C1'	0.0	0.677 28 (28)	0.432 20 (27)	3.0 (1)
C5	C2', C7', C20'	0.110 35 (18)	0.626 63 (18)	0.364 22 (19)	2.98 (8)
C18	C8', C9', C19'	0.182 71 (16)	0.744 82 (18)	0.320 65 (18)	2.85 (7)
C4	C3'	0.068 54 (24)	0.551 48 (27)	0.25	2.9 (1)
H13	H14'	0.1763 (28)	1.0194 (26)	0.25	3.7 (5)
H17	H10', H12', H15'	0.1666 (19)	0.9131 (19)	0.4239 (20)	3.8 (5)
H16	H11'	0.0	0.8651 (26)	0.5085 (28)	3.0 (6)
H6	H1'	0.0	0.6481 (29)	0.5212 (31)	4.1 (7)
H5	H2', H7', H20'	0.1572 (16)	0.5725 (17)	0.4166 (17)	2.7 (4)
H18	H8', H9', H19'	0.2635 (17)	0.7446 (17)	0.3497 (17)	2.7 (4)
H4	H3'	0.1008 (24)	0.4621 (25)	0.25	2.5 (6)

[a] The form of the equivalent isotropic thermal parameter is $B(eq)$

$$=(8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Table III. Final Metrical Parameters for 4

Bond Lengths, Å

O–C21	1.218 (5)	C6–C5	1.539 (3)
C13–C21	1.492 (3)	C5–C4	1.539 (3)
C13–C17	1.545 (2)	C5–C18	1.540 (3)
C17–C18	1.539 (3)	C18–C19'	1.540 (4)
C17–C16	1.549 (2)	C3'–C4	1.546 (5)
C6–C16	1.544 (4)		

Bond Angles, deg

C3'–C4–C5	107.8 (1)	C15'–C16–C17	119.0 (2)
C5–C4–C20'	107.9 (2)	C13–C17–C16	117.0 (2)
C4–C5–C6	108.2 (2)	C13–C17–C18	106.1 (2)
C4–C5–C18	108.1 (2)	C16–C17–C18	107.9 (2)
C6–C5–C18	108.0 (2)	C5–C18–C17	108.0 (2)
C5–C6–C7'	107.9 (2)	C5–C18–C19'	108.0 (1)
C5–C6–C16	108.1 (2)	C17–C18–C19'	107.7 (1)
C12'–C13–C17	106.5 (2)	C13–C21–C14'	112.6 (3)
C17–C13–C21	112.4 (2)	O–C21–C13	123.7 (2)
C6–C16–C17	107.4 (1)		

onal rings, the angles lie within the range 107.4–108.2°.

Acetolysis of 21-Homododecahedryl Mesylate. The Case for Degeneracy within the 21-Homododeca-

Table IV. Transannular Distances (Å) for 4 and Dimethylmonosecododecahedrane

atoms		4	seco compd
C1'–C16		4.178 (4)	4.125 (5)
C2'–C17		4.361 (3)	4.389 (5)
C3'–C13		4.643 (4)	4.761 (6)
C4–C14'	≡	C3'–C13	4.764 (7)
C5–C10'	≡	C2'–C17	4.385 (6)
C6–C11'	≡	C1'–C16	4.125 (5)
C7'–C12'	≡	C2'–C17	C2–C17'
C8'–C19'		4.400 (3)	4.429 (5)
C9'–C18	≡	C8'–C19'	C8–C19'
C15'–C20'	≡	C2'–C17	C5–C10'

hedryl Cation. With the availability of homododecahedranone (4), the opportunity to examine the nature and properties of the 21-homododecahedryl cation presented itself. Preliminary information about ionization within this structural type was gained by reduction of 4 to 13a and transformation of this alcohol into its mesylate (13b) (Scheme II). The tosylate was bypassed because the efficiency of its formation was significantly lower. Prep-

Scheme III

● = 100% deuterium label
⊘ = partial isotopic label

(time-averaged)

19

arative acetolysis of **13b** in hot, unbuffered acetic acid for 3 h provided acetate **13c** in 83% isolated yield. The structural assignment to **13c** was confirmed by ^{1}H NMR and capillary GC comparisons with an authentic sample acquired by the direct acetylation of **13a**. Additionally, saponification of the solvolysis product furnished homododecahedranol exclusively. Thus, the ready ionizability of **13b** with retention of the intact carbocyclic framework was demonstrated.

More elegant conceptually is the degeneracy that might be achieved within **18**. For the homododecahedrane system, only one type of rearrangement process—the 1,2-C,C shift—is necessary to achieve the peregrination that will eventually give rise to full equivalence among all constitutional hydrogen and carbon atoms. Detectability of this phenomenon rests, of course, on being able to identify uniquely the various C–H units in **18**. To this end, deuterated mesylate **16** was prepared from **12** and acetolyzed as before. Analysis of the recovered acetate (**17**) by ^{1}H and ^{2}H NMR showed that a reasonable level of deuterium migration around the sphere had indeed occurred under these short-lived conditions (Table V).

Since complete degeneracy had clearly not been achieved, the d_1-scrambled acetate was saponified and converted again to mesylate. A second acetolysis delivered **17** in which more deep-seated interchange of framework methine units had now materialized (Table V). Figure 2 illustrates the deuterium NMR spectra of **17** as recorded after the first and second acetolysis experiments. Also displayed is the proton NMR spectrum of the latter material in order to show the close correspondence of the ^{1}H and ^{2}H shifts that made possible the individual assignments.

Any discussion of the results should be preceded by consideration of the two mechanistic possibilities for deuterium scrambling. The first involves localized carbonium mesylate ion pairs for which backside stereospecificity would be anticipated if appreciable "leakage" was not occurring. A process having this restriction would in effect allow "rotation" of but one six-membered ring (viz. C1, C2, C6, C7, C20, and C21)[28] above a [5]peristylane base,

Table V. Deuterium-Labeling Results Based on ^{2}H NMR Analysis of 17

d_1

| chemical shift, δ	relative intensity, %	assignment	structure(s) responsible[a]
	First Acetolysis		
5.29	16	21	A
3.60–3.20	9	others	G
3.03	9	1, 20	B
2.84	31	14, 15, 19	C, E
2.59	35	2, 6, 7	D, F
	Second Acetolysis		
5.29	11	21	A
3.60–3.20	17	others	G
3.03	13	1, 20	B
2.84	30	14, 15, 19	C, E
2.59	29	2, 6, 7	D, F

[a] Consult Scheme III for structural illustrations.

while precluding migration of deuterium into the larger lower sector of the cation (see Scheme III). In essence, exchange would be relegated exclusively to those sites explicitly depicted as shaded circles in **19**.

The second option is a nonstereospecific one which would allow for eventual interchange of all sites.

The actual short-lived results (Table V) are in agreement with predominant adoption of the nonstereospecific process which is limited, however, by covalent capture of acetic

(28) The numbering scheme used here is that recommended by D. R. Eckroth [*J. Org. Chem.* **1987**, *32*, 3362]. A different atom chronology was used for the X-ray analysis and we apologize here for any inconvenience this may cause the reader.
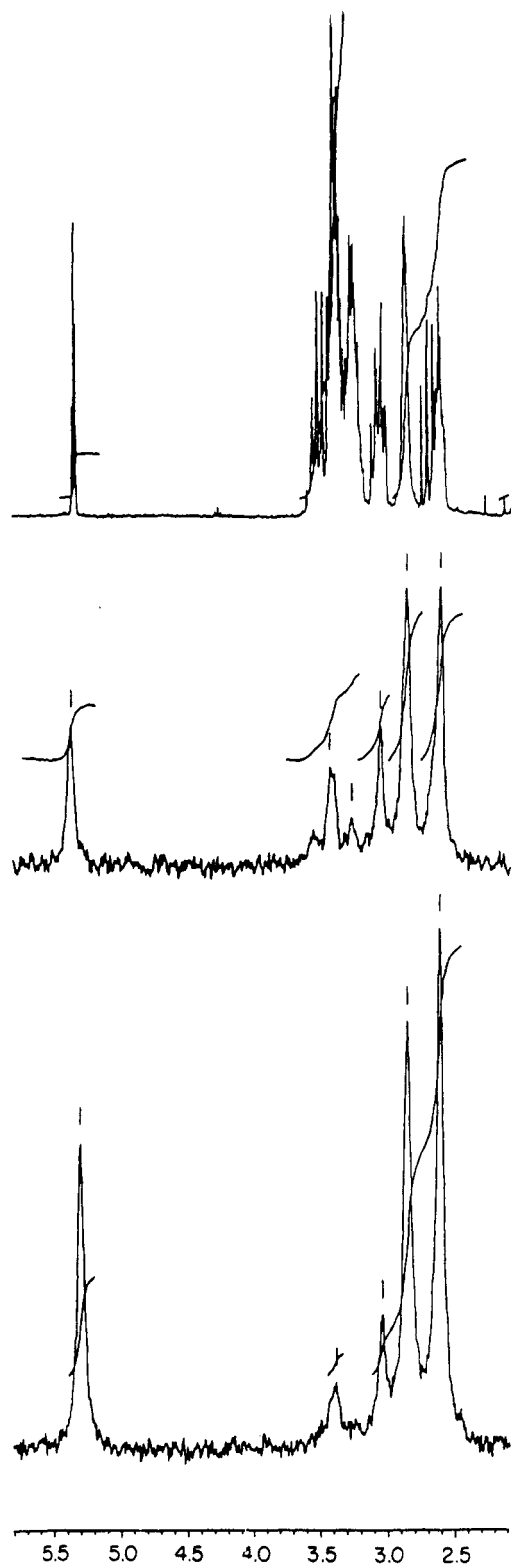
Figure 2. 76.8-MHz ^{2}H NMR spectra (CHCl$_3$ solution) of acetate 17, after the first (lower pane) and second (middle pane) acetolysis experiments. The upper pane is a 300-MHz ^{1}H NMR spectrum of the reacetolyzed product and therefore is the complement of the spectrum just below it.

acid after relatively few rearrangement steps have transpired. Thus, we see in Scheme IV that more than three Wagner–Meerwein shifts are necessary before the deuterium label finds it possible to exit the six-membered ring. On the other hand, formation of the freely solvated carbocation allows for passage to stereoisomeric pairs of acetates (i.e., C/D and E/F) and for the ultimate production of G.

Scheme IV
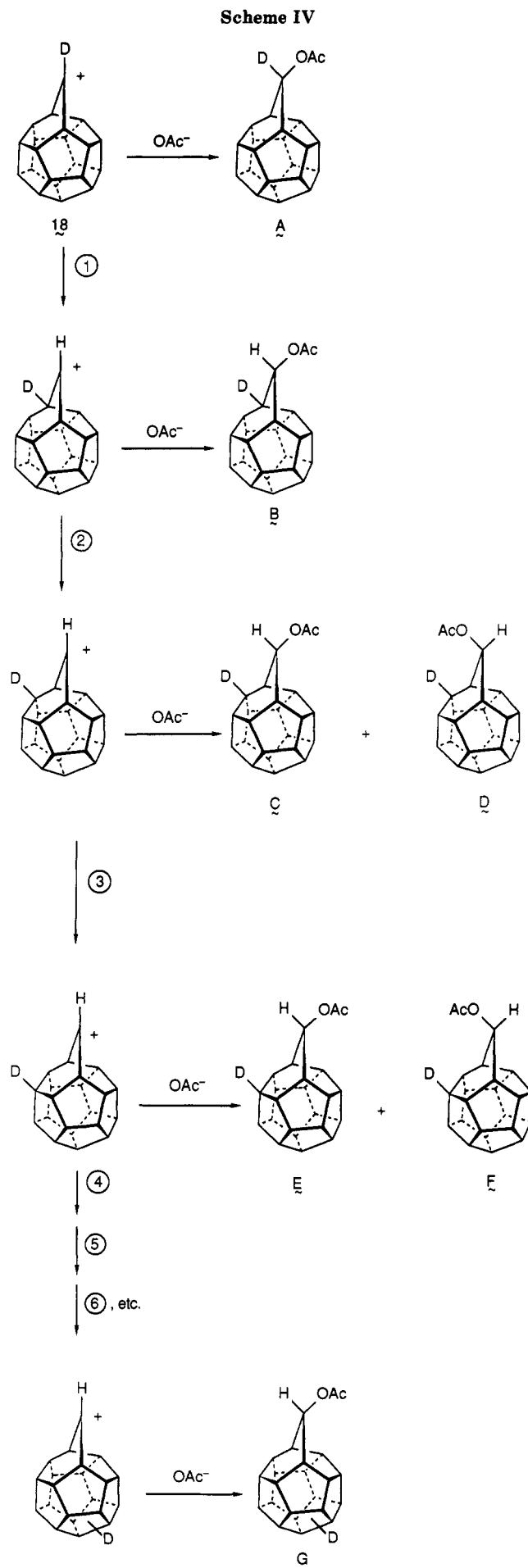
At this point, it becomes important to draw attention to the important contributions made by the magnetic anisotropy of the acetoxy group in **17** to the separation of certain key chemical shifts. As a direct consequence of its influence, protons and deuterons at C-2, 6, or 7, which find themselves syn to OAc (see Table V), are positioned approximately 0.25 ppm upfield from the 14, 15, 19 triad. The latter group of cyclohexyl substituents, like those at bridgehead sites 1 and 20, appear in regions of the spectrum also well separated from those absorptions arising for the H's or D's more remote to the homo bridge. In a fashion entirely characteristic of dodecahedryl systems, the distal protons/deuterons appear quite far downfield (δ 3.60–3.20).

The approximately equal integrals for the ^{2}H signals at δ 2.84 and 2.59 are consequently most logically interpretable in terms of mixtures of C/E and D/F, respectively (Scheme IV). The epimeric ratios of these isomer pairs are not definable. During one acetolysis, the deuterium label finds it possible to migrate into the [5]peristylane subunit to the extent of 9%. Repetition of this process essentially doubles this number (Table V), chiefly at the expense of the other nonbridgehead sites. Higher order degeneracy is not observed for two plausible reasons: (a) The short-lived conditions do not provide adequate lifetime to the homododecahedryl cation to allow complete isotopic scrambling; covalent capture of acetate should therefore occur in closer proximity to the deuterium label as it does. (b) Solvation effects could promote higher levels of reversibility somewhat related to tight ion pairing (Scheme III) that would enhance opportunities for retention of the label within the six-membered rings. Although **16** was never solvolyzed in unbuffered formic acid, this medium would likely have been more conducive to maximizing deuterium distribution throughout the subject cation.[29]

Instead, the decision was made to examine the possible generation of unlabeled **18** under long-lived conditions so as to allow for direct spectroscopic examination. Chloride **14** was therefore prepared and transmitted to Professor George Olah for study. Unfortunately, **14** does not serve as progenitor of the 21-homododecahedryl cation in magic acid solution at low temperatures. Instead, two different ionic species are formed. One of these appears to be the methyldodecahedryl cation; the other has not yet been identified. These results signal that the structural strain present in **18** can be and is alleviated under strongly acidic conditions through irreversible conversion to more stable entities.

Kinetic Studies. The homododecahedryl cation is also of unusual interest in connection with the Foote[30] and Schleyer[31] analyses, where secondary sulfonate ester acetolysis rates are shown to be correlatable to the carbonyl stretching frequencies and other geometric parameters associated with the respective ketone precursors. In particular, the location of a given carbonyl infrared absorption band is recognized to be quite sensitive to the internal C–CO–C bond angle,[32,33] a phenomenon that has been attributed to alterations in its sp hybridization status.[34] Since sulfonate ester ionization involves a change of carbon hybridization, the rates of such processes are

comparably influenced. In general terms, constriction of the C–C(OTs)–C angle to a value less than 109.5 inhibits ionization, while an angle greater than 109.5° is conducive to acceleration.[32,33]

2-Adamantanone serves as an informative comparison example. Its carbonyl stretching frequency of 1727 cm^{-1} is indicative of the fact that the C–CO–C bond angle in this system is 112.5°. Thus, the molecular rigidity of the adamantane framework precludes attainment of the optimum θ of 116°.[35] The log k (relative to cyclohexyl tosylate) of 2-adamantyl tosylate has been experimentally assessed as −1.18[30,31]

In the case of **4**, the X-ray determination denotes its C–CO–C angle to be 112.6°, entirely similar to that calculated for 2-adamantanone.[36] However, the similarity stops here. The weighted carbonyl band position for **4** is located at 1690 cm^{-1}. At 228.18 ppm, the ^{13}C shift of the carbonyl carbon in **4** appears considerably downfield of that in 2-adamantanone (216.0 ppm). Since eclipsed groupings do not exist around the reaction site in **13b**, torsional strain appears not to be of consequence. Since MNDO and AM1 calculations on the 2-adamantyl and 21-homododecahedryl cations provide no indication of any differences that would explain these spectroscopic anomalies,[37] tensor changes and Fermi resonance effects brought on by orbital interaction and vibrational mixing with other sectors of the molecule are thought to be operational in **4**.

Rate constants for the acetolysis of **13b** and 2-adamantyl mesylate were determined conductometrically[38] at 110.0 °C. Good first-order kinetics to 2 half-lives was observed in both instances. The respective k_1 values are 2.18 × 10^{-4} and 2.81 × 10^{-4} s^{-1}, in line with the Foote–Schleyer correlations based on internal dihedral angle considerations.[30,31]

Summary

The present results demonstrate that cyclopropadodecahedranes and homododecahedranes can be produced readily from the parent $C_{20}H_{20}$ hydrocarbon as starting material. The availability of the dichloromethyl derivative opens up efficient avenues to both classes of topologically interesting compounds. The cyclopropane-forming reactions appear to lend credence to Walborsky's earlier proposal that chloro carbenoids are capable of developing considerable levels of cationic character at the carbenoid carbon. Since the ground-state structure of a cyclopropadodecahedrane leaves the spherical segment of the molecule rather conformationally deformed from ideality, it would seem proper to consider the dodecahedrane framework to be capable of reasonable levels of deformation.

The 21-homododecahedryl cation evidently enjoys a greater facility for the degenerate Wagner–Meerwein than for vicinal hydride shift, at least under short-life solvolysis conditions. This behavior permits the onset of multiply degenerate rearrangement to an extent that requires formation of a fully solvated carbocation. No indication of

(29) See Bartlett, P. D. *Nonclassical Ions*; W. A. Benjamin, Inc.: New York, 1965.

(30) Foote, C. S. *J. Am. Chem. Soc.* **1964**, *86*, 1853.

(31) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1964**, *86*, 1854.

(32) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.

(33) Halford, J. O. *J. Chem. Phys.* **1956**, *24*, 830.

(34) (a) Coulson, C. A.; Moffitt, W. A. *Phil. Mag.* **1949**, *40*, 1. (b) Bartlett, P. D.; Stiles, M. *J. Am. Chem. Soc.* **1955**, *77*, 2806.

(35) The experimentally determined C–CO–C angle of acetone is 116.3°: Swalen, J. D.; Costain, C. C. *J. Chem. Phys.* **1959**, *31*, 1562.

(36) Calculated by means of the equation

$$\nu(\text{cm}^{-1}) = 1278 + 68k - 2.2\phi \quad (\text{see ref 33})$$

where ϕ is the C–CO–C angle in degrees and $k = 10.244$ to accommodate satisfactorily the fit for acetone.

(37) Schleyer, P. v. R.; Bremer, M., private communication.

(38) (a) Lancelot, C. J. Ph.D. Thesis, Princeton University, 1971. (b) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

conversion to isomeric tertiary cations is seen in acetic acid solution. In magic acid, the absence of comparable solvation features does not allow the 21-homododecahedryl cation to preserve its integrity even at low temperatures. This distinction holds interest and merits further detailed scrutiny.

Experimental Section

(Dichloromethyl)dodecahedrane (6). To a mixture of dodecahedrane (4.5 mg, 0.017 mmol), 50% aqueous sodium hydroxide solution (5 mL), and triethylbenzylammonium chloride (0.5 mg) in benzene (15 mL) heated at 50 °C was added chloroform (2 mL) over 6 h. The mixture was stirred at room temperature overnight, diluted with water, and extracted with benzene (3 × 10 mL). The combined organic extracts were washed with brine and dried. The residue obtained was purified by preparative TLC. Elution with hexane afforded 3.5 mg (59%) of 6 as a colorless solid: mp 209–210 °C (from hexane); IR (CHCl$_3$, cm^{-1}) 2950, 1300; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.71 (s, 1 H), 3.80–3.30 (m, 19 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 89.53, 82.32, 66.98, 66.61, 66.30 (2 C not observed); MS m/z (M + 2) calcd 342.0942, obsd 342.0914.

Cyclopropadodecahedrane (7). To a cold (−100 °C) solution of 6 (4.0 mg, 11.7 μmol) in ether (5 mL) was added dropwise a solution of *tert*-butyllithium in pentane (0.5 mL of 1.7 M). The mixture was stirred for 1 h at −100 °C before ethanol was slowly introduced to quench the lithiated compounds. Following warming to room temperature and dilution with benzene, the organic phase was separated, washed with water and brine, and dried. The products were separated by TLC (silica gel, hexane) to give pure 7 (1.6 mg, 50%) and (chloromethyl)dodecahedrane (0.7 mg, 20%).

For 7: colorless solid; mp >250 °C (from hexane); IR (CHCl$_3$, cm^{-1}) 2946, 1297, 1265, 917; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.42 (br s, 14 H), 2.96 (br s, 4 H), 1.00 (s, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 75.14, 67.58, 66.70, 66.56, 65.50, 64.79, 61.70, 23.81; MS m/z (M$^+$) calcd 272.1564, obsd 272.1556.

For DDH–CH$_2$Cl: colorless solid; mp 209–211 °C (from hexane); IR (CHCl$_3$, cm^{-1}) 2950, 1300; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.49 (s, 2 H), 3.39 (br s, 16 H), 3.19 (br s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 81.52, 70.41, 67.08, 66.62, 66.55, 55.78 (1 C not observed); MS m/z (M$^+$) calcd 308.1331, obsd 308.1333.

21-Methylcyclopropadodecahedrane (8). To a solution of 6 (5.0 mg, 14.6 μmol) in ether (5 mL) was added ethereal methyllithium (0.5 mL of 1.4 M) at 0 °C. The mixture was stirred at this temperature overnight. Water (15 mL) and benzene (15 mL) were added, and the separated organic phase was washed with water and brine prior to drying. The crude product was purified by TLC (silica gel, hexane) to give 8 (2.8 mg, 67%) as a colorless solid: mp 219–220 °C (from hexane); IR (CHCl$_3$, cm^{-1}) 2958, 1458, 1386, 1297; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.42 (br s, 14 H), 2.94 (m, 2 H), 2.87 (m, 2 H), 1.16 (q, J = 6.16 Hz, 1 H), 1.02 (d, J = 6.16 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 75.41, 67.52, 67.37, 67.16, 67.03, 66.53, 65.38, 65.35, 65.32, 65.03, 60.73, 26.43, 11.39 (1 C not observed); MS m/z (M$^+$) calcd 286.1721, obsd 286.1728.

21-Phenylcyclopropadodecahedrane (9). A solution of 6 (5.0 mg, 14.6 μmol) in anhydrous ether (3 mL) was treated with phenyllithium (0.5 mL of 2 M in ether–hexane, 1.0 mmol) at −10 °C. The mixture was stirred at this temperature for 6 h and at room temperature for 18 h. Water and benzene were added, and the organic phase was washed with water and brine prior to drying. Purification of the residue by TLC (silica gel, hexane) provided 4.1 mg (81%) of 9 as a colorless solid: mp 177–178 °C (from methanol); IR (CHCl$_3$, cm^{-1}) 3007, 2937, 1599, 1493, 1441, 1305, 1295; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.35–7.05 (m, 5 H), 3.46 (br s, 13 H), 3.17 (br s, 2 H), 2.91 (m, 3 H), 2.45 (s, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 138.90, 130.21, 127.82, 125.56, 75.68, 75.17, 67.46, 67.28, 67.14, 66.97, 66.52, 66.24, 65.34, 64.96, 61.35, 37.42, (1 C not observed); MS m/z (M$^+$) calcd 348.1878, obsd 348.1897.

Homododecahedranone (4). A solution of 6 (10 mg, 29 μmol) and silver nitrate (100 mg) in a mixture of ethanol (3 mL), benzene (1 mL), and water (1 mL) was heated at reflux for 20 h. The volatile solvents were evaporated in vacuo, and the residue was dissolved in benzene, washed with water (2×) and brine, and dried. Solvent evaporation followed by passage of the residue through

a short plug of silica gel (benzene as eluent) gave 7.8 mg (93%) of 4 as a colorless solid: mp >280 °C (from hexane–benzene, 3:1); IR (CHCl$_3$, cm^{-1}) 2945, 1701, 1679; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.80–3.50 (m, 16 H), 2.83 (q, J = 12.3 Hz, 2 H), 2.70 (t, J = 9.3 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 228.18, 68.70, 68.14, 67.84, 64.04, 62.32, 52.20, 46.35; MS m/z (M$^+$) calcd 288.1514, obsd 288.1493.

X-ray Crystallographic Analysis of 4. The morphology of several very large crystals of this clear, colorless compound seemed to indicate the presence of twinning. The single crystal used for data collection is best described as a wedge-shaped plate. Preliminary examination of the diffraction pattern on a Rigaku AFC5 diffractometer indicated an orthorhombic crystal system with systematic absences: hkl, $h + k = 2n + 1$ and $0kl$, $l = 2n + 1$, which limit the space group possibilities to $Ccm2_1$, $Cc2m$, and $Ccmm$, nonstandard settings of $Cmc2_1$, $Ama2$, and $Cmcm$, respectively. At room temperature the cell constants were determined from a least-squares refinement of the diffractometer setting angles for 25 reflections with 2θ values in the range 21–28° with Mo Kα radiation.

Intensities were measured by the $\omega - 2\theta$ scan method. The crystal was stable during the course of data collection as indicated by the six standard reflections, which were measured after every 150 reflections. On the assumption that the centrosymmetric space group is most likely correct, the reflection indices and unit cell constants were rearranged to correspond with the standard setting of Cmcm. Data reduction and all further calculations were done with the TEXSAN package of crystallographic programs.[39]

The structure was solved with the direct methods program MITHRIL[40] in space group $Cmcm$. With four molecules in the unit cell, this space group choice imposes crystallographic mm symmetry on the molecule. As a result there are only nine non-hydrogen atoms in the asymmetric unit; all these non-hydrogen atoms were located on the electron density map generated by MITHRIL. Full-matrix least-squares isotropic refinement of the model converged at an R value of 0.12 for the 580 intensities with $F_o^2 > 3\sigma(F_o^2)$. After a cycle of anisotropic refinement, all the hydrogen atoms were located on a difference electron density map. The hydrogen atoms were initially included in the model as fixed contributions, but in the final least-squares refinement cycles their positional and isotropic thermal parameters were refined. The final refinement cycle for the 629 intensities with $F_o^2 > 1\sigma(F_o^2)$ and the 84 variables yielded agreement indices of $R = 0.050$ and $R_w = 0.053$. A structure factor calculation for the subset of reflections with $F_o^2 > 3\sigma(F_o^2)$ gave an R value of 0.045. The final difference electron density map contains maximum and minimum peak heights of 0.26 and −0.24 e/Å^3. All refinements were based on F so that the function minimized in least-squares refinement was: $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Scattering factors were obtained from the usual sources.[41]

The numbering scheme used for this structure is that used for the dodecahedrane nucleus as previously defined.[26] Hydrogen atoms are labeled according to the attached carbon atom. Symmetry-related atoms are designated by primes in addition to their unique atom number.

Homododecahedranol (13a). A solution of 4 (9.0 mg, 0.031 mmol) and sodium borohydride (30 mg, 0.79 mmol) in methanol (3 mL) and benzene (1 mL) was stirred at room temperature for 20 h. The solution was concentrated, water was added, and the product was extracted into benzene (3 × 10 mL). The combined organic phases were dried and evaporated to leave a residue, which was purified by TLC (silica gel, chloroform). There was isolated 7.1 mg (78%) of 13a as a colorless solid: mp >280 °C (from benzene–hexane, 1:1); IR (CHCl$_3$, cm^{-1}) 3574, 2921; ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.19 (t, J = 3.98 Hz, 1 H), 3.65–3.20 (m, 12 H), 3.15–2.80 (m, 6 H), 2.77–2.50 (m, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$)

(39) TEXSAN, TEXRAY Structure Analysis package, version 2.1; Molecular Structure Corp.: College Station, TX, 1987.

(40) Gilmore, C. J., MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data; University of Glasgow: Scotland, 1983.

(41) Scattering factors for the carbon and oxygen atoms are from the *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

ppm 70.08, 68.79, 68.68, 67.44, 65.72, 65.46, 63.73, 63.14, 54.20, 48.35, 46.50, 46.31, 44.12; MS *m/z* (M⁺) calcd 290.1671, obsd 290.1632.

Homododecahedryl Methanesulfonate (13b). A solution of **13a** (3.2 mg, 11 μmol) and methanesulfonyl chloride (1 drop) in anhydrous pyridine (2 mL) was stirred at room temperature for 3 h. Pyridine was evaporated in vacuo, and benzene was added to the residue. The benzene solution was washed with aqueous sodium bicarbonate solution and dried. Solvent evaporation followed by purification of the residue by TLC (silica gel, elution with 10% ethyl acetate in petroleum ether) furnished 3.6 mg (87%) of **13b** as a colorless solid: mp 141–143 °C (from hexane); IR (CHCl₃, cm⁻¹) 2950, 1354, 1333, 1178, 912; ¹H NMR (300 MHz, CDCl₃) δ 5.28 (t, *J* = 4.1 Hz, 1 H), 3.63–3.15 (m, 12 H), 3.15–2.60 (m, 11 H), 3.02 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) ppm 83.98, 68.82, 68.57, 67.47, 65.73, 65.68, 63.77, 63.27, 54.51, 49.12, 46.38, 46.03, 41.59, 38.88; MS *m/z* (M⁺ − OSO₂CH₃) calcd 272.1565, obsd 272.1572.

Homododecahedryl Acetate (13c). A solution of **13a** (7.0 mg, 24 μmol) in a mixture of acetic anhydride (1 mL) and pyridine (2 mL) was stirred at room temperature for 17 h. The solvent was evaporated, and benzene was added to the residue. The organic phase was washed with aqueous sodium bicarbonate solution (3×) prior to drying. The concentrate was purified by passage through a short plug of silica gel (elution with benzene) to give 7.5 mg (94%) of **13c** as a colorless solid: mp 176–178 °C (from hexane); IR (CHCl₃, cm⁻¹) 2949, 1718, 1366, 1264, 1031; ¹H NMR (300 MHz, CDCl₃) δ 5.28 (t, *J* = 4.0 Hz, 1 H), 3.60–3.16 (m, 12 H), 3.10–2.95 (m, 2 H), 2.85 (br s, 3 H), 2.75–2.55 (m, 3 H), 2.04 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) ppm 171.13, 73.72, 68.74, 68.49, 67.45, 65.66, 65.55, 63.73, 63.27, 53.94, 49.25, 46.63, 43.36, 40.54, 21.60; MS *m/z* (M⁺ − OCOCH₃) calcd 272.1565, obsd 272.1565.

Homododecahedryl Chloride (14). A solution of **13a** (7.0 mg, 24 μmol) and thionyl chloride (1 mL) in benzene (5 mL) was stirred at room temperature for 24 h. The solvent was evaporated, and the residue was purified by TLC (silica gel, hexane) to give **14** (3.9 mg, 52%) as a colorless solid: mp >270 °C (from benzene-hexane, 1:5); IR (CHCl₃, cm⁻¹) 2942, 1310, 1299, 1279, 915; ¹H NMR (300 MHz, CDCl₃) δ 4.48 (t, *J* = 3.67 Hz, 1 H), 3.55–2.40 (m, 20 H); ¹³C NMR (75 MHz, CDCl₃) ppm 68.80, 68.40, 67.40, 66.07, 64.85, 63.80, 63.36, 62.38, 54.53, 49.36, 46.33, 45.87, 44.93; MS, *m/z* (M⁺) calcd 308.1332, obsd 308.1351.

Acetolysis of 13b. A solution of **13b** (2.0 mg, 5.4 μmol) in glacial acetic acid (2 mL) was heated at the reflux temperature for 3 h. The solvent was blown off with a stream of air, and benzene was added. The resulting solution was washed with sodium bicarbonate solution prior to drying and concentration. The product was purified by passage through a short silica gel plug (elution with benzene). There was isolated 1.5 mg (83%) of acetate **13c**.

Saponification of 13c. A total of 4.0 mg (12 μmol) of **13c** produced by acetolysis was heated at 70 °C together with potassium hydroxide (2 pellets) in a mixture of methanol (2 mL), water (0.5 mL), and benzene (0.5 mL) for 17 h. Benzene (10 mL) was added, and the organic phase was washed with water, dried, and evaporated. The residue was passed through a short plug of silica gel (elution with benzene) to provide 3.2 mg (92%) of alcohol **13a**.

Homododecahedranol-*21*-*d*₁ (15). A solution of **4** (6.0 mg, 20 μmol) and sodium borodeuteride (30 mg) in a mixture of

benzene (2 mL) and methanol (2 mL) was stirred at room temperature for 24 h. Solvent was evaporated, and the residue was taken up in benzene. This solution was washed with water, dried, and evaporated to give 4.7 mg (78%) of **15**. This substance lacks the triplet of area 1 centered at δ 4.19 that is featured in the ¹H NMR spectrum of **13a**.

Homododecahedryl-*21*-*d*₁ Methanesulfonate (16). Reaction of 17.0 mg of **15** with methanesulfonyl chloride as described above for **13a** furnished 16.6 mg (77%) of **16**. This substance lacks the triplet of area 1 centered at δ 5.28 that is featured in the ¹H NMR spectrum of **13b**.

Homododecahedryl-*21*-*d*₁ Acetate (17). Acetolysis of 16.6 mg of **16** in the predescribed manner provided 12.8 mg (87%) of **17**. The ²H NMR spectrum of this material is described in the text.

Saponification of this acetate as before led to 10.1 mg (97%) of deuterium scrambled homododecahedranol-*d*₁, which was transformed in turn into its mesylate (12.0 mg, 96%) and resubmitted to acetolysis. This treatment afforded 9.5 mg (88%) of **17**, the ²H NMR spectrum of which is described earlier.

Kinetic Studies. The acetic acid solutions used were 2.0 × 10⁻⁴ M in 2-adamantyl mesylate and 1.8 × 10⁻⁴ M in **13b**. The acetic acid used was freshly distilled from a solution containing ca. 10% acetic anhydride. Typically, the substrate was carefully weighed and introduced via a pipette, with assurance that the substrate was completely dissolved. After the cell was sealed with a rubber septum, it was placed in a constant temperature oil bath and allowed to equilibrate for 10–15 min. The background conductance was suppressed, and data were collected until a leveling-off occurred. Guggenheim treatment[42] of the first-order percent conductance versus time plot provided the rate data from which rate constants were determined by the method of least squares.

Supplementary Material Available: Tables of deviations from least-squares planes, final metrical parameters for the hydrogen atoms, selected torsion angles, anisotropic thermal parameters, as well as a unit cell drawing for **4** (Tables VI–IX, Figure 3) (5 pages); listings of observed and calculated structure factor amplitudes (Table X) (5 pages). Ordering information is given on any current masthead page.

(42) Laidler, K. J. *Chemical Kinetics*; McGraw-Hill: New York, 1965; p 14.