J. Org. Chem. 1980, 45, 2985-2995

Thermodynamic Rearrangements of Larger Polycyclic Hydrocarbons Derived from the 38.5 and 41.5 °C Melting Dimers of Cyclooctatetraene. Crystal and Molecular Structures of 5-Bromoheptacyclo[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}]hexadecane (5-Bromo-(C_2)-bisethanobisnordiamantane), 6,12-Dibromoheptacyclo[7.7.0.0^{2,6}.0^{3,15}.0^{4,12}.0^{5,10}.0^{11,16}]hexadecane, and Nonacyclo[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]docosane (Bastardane)[1,2]

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Received December 27, 1979

Hexahydrogenated cyclooctatetraene dimer **1** (mp 41.5 °C) isomerized with Lewis acid catalyst to give two isomeric ethanodiamantanes, **4** (C_1) and **5** (C_s). Compound **4** is favored thermodynamically over **5** by a factor of 13 at 28 °C. The tetrahydrogenated cyclooctatetraene dimer **2** (mp 38.5 °C) likewise isomerized into two novel heptacyclohexadecanes, (C_2)-bisethanobisnordiamantane (**6**) and a formal dimer of bicyclo[2.2.2]octadiene (**7**) with D_{2d} symmetry. Bromides from **6** and **7** were separated and their structures determined by X-ray analyses. Diels–Alder addition of 1,3-cyclohexadiene or methylcyclopentadiene to **2** followed by exhaustive hydrogenation gave $C_{22}H_{28}$ hydrocarbons, which were subjected to Lewis acid catalyzed rearrangement under strenuous conditions. The only product isolated was not one of the expected tetramantanes (**54–56**) but had a structure (**8**) with fused diamantane and 2,8-ethanonoradamantane units. Possible mechanisms of Lewis acid catalyzed interconversion between **4** and **5** and the most probable, shortest rearrangement pathway from tetrahydro **2** to **6** and **7** are described. Compounds **6**, **7**, and **8** are not the thermodynamically most stable isomers of their classes but represent local energy minima with great kinetic stability. This demonstrates the high possibility of falling into local energy minima before the stabilomers in multistep carbonium ion rearrangements of large polycyclic hydrocarbons are reached.

The aluminum halide catalyzed rearrangements of polycyclic hydrocarbons under thermodynamicly controlled conditions usually afford the most stable isomer (stabilomer)[5] and provide convenient synthesis of diamond molecules.[6,7] For tri-, tetra-, and pentacyclic C_8–C_{20} families, enumeration of possible isomers, force field calculations, and experimental rearrangement studies have revealed most of the stabilomers.[8] We wish to extend the search of stabilomers to larger polycyclic systems. The ultimate goal is the large-scale synthesis of the pentagonal dodecahedrane, which is probably the stabilomer of the undecacyclic $C_{20}H_{20}$ hydrocarbon family.[9,10]

Four major obstacles are anticipated. First, large polycyclic hydrocarbons suitable for use as rearrangement precursors are generally not readily available. Second, the danger of isomerizing molecules being trapped in local energy minima will increase as the complexity of the system increases. Third, disproportionation side reactions to give products of unwanted composition become more likely. Finally, the number of possible isomers increases exponentially with the number of component atoms and the exhaustive enumeration, and the estimation of relative stabilities of isomers, as has been successfully performed for smaller systems,[8] will become impracticable. For these reasons, the structure determinations of rearrangement products will have to rely heavily on diffraction analysis.

In the present work, we utilized the well-known cage dimers of cyclooctatetraene as the starting materials. Among six known dimers,[11,12] the 41.5 and 38.5 °C melting dimers (**1** and **2**)[13–17] provide convenient entries into the

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(3) (a) Hokkaido University. (b) Princeton University. (c) Gunma University. (d) Computer Center, Gakushuin University. (e) Department of Physics, Gakushuin University. (f) Friedrich-Alexander-Universität Erlangen-Nürnberg.

(4) Hokkaido University Postdoctoral Fellow.

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(15) Moore, H. W. *J. Am. Chem. Soc.* **1964**, *86*, 3398.

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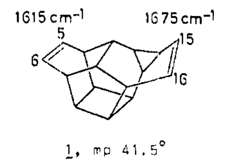
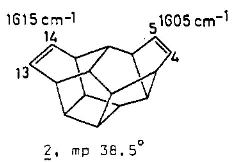
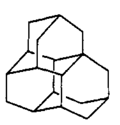


1, mp 41.5°



2, mp 38.5°



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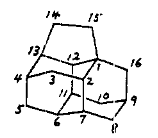
rare polycyclohexadecanes.[18] The reactive double bonds of **1** and **2** are an additional advantage and can be utilized to prepare even higher polycyclic precursors for rearrangement studies. **2** has been used as the starting material for the thermodynamically controlled rearrangement to triamantane (**3**) after elaboration with two extra carbon atoms.[19,20]

We now describe the preparation of three novel diamond hydrocarbons[7] and two new highly symmetric cage molecules by the rearrangement of precursors derived from **1** and **2**. These products are the isomeric ethanodiamantanes **4** and **5**, a doubly ethano-bridged bisnordiamantane (**6**), another bisethano-bridged molecule having a "bis(bicyclo[2.2.2]octadiene)" structure (**7**), and an ethano-bridged isomer of tetramantane (**8**). The structures of these molecules were determined by single-crystal X-ray analyses, except for that of **4** which was deduced by chemical methods. **6**, **7**, and **8** are not the stabilomers but are local energy minima as indicated by empirical force field calculations.



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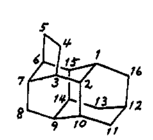

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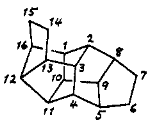

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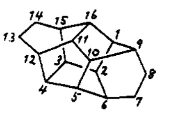

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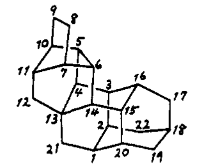
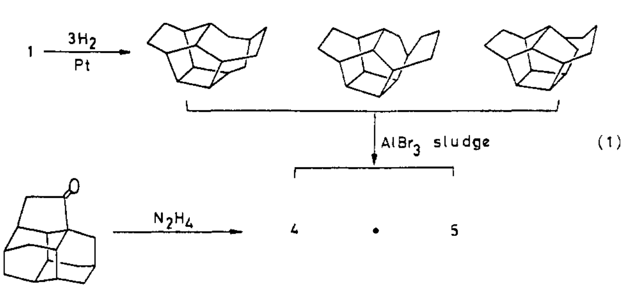


8

Results

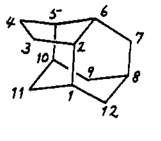
Rearrangements of the Hexahydrogenated 41.5 °C Melting Dimer of Cyclooctatetraene (1). Dimer **1** is known to absorb 3 mol of hydrogen.[15] Catalytic hydrogenation of **1** gave a three-component mixture of hexacyclic $C_{16}H_{22}$ isomers; treatment with aluminum sludge catalyst[21] without separation gave a waxy, solid product in high yield. This mixture was separated by preparative GLC into major (mp 206.5–208 °C, 85%) and minor (mp 110–111.5 °C, 15%) components (eq 1).

The main product was identified as hexacyclo$[7.6.1.0^{1,12}.0^{2,7}.0^{4,13}.0^{6,11}]$hexadecane or ($C_1$)-ethanodiamantane (**4**) by comparison with an authentic sample prepared by Wolff–Kishner reduction of the known ketone **9**.[20] The minor product was found to be an isomeric (C_s)-ethanodiamantane or hexacyclo$[10.3.1.0^{2,10}.0^{3,7}.0^{6,15}.0^{9,14}]$hexadecane (**5**) through X-ray analysis by Sundaralingam.[1b,22]



(1)

Treatment of **4** in refluxing liquid bromine gave a dibromide, mp 309–313 °C. On the basis of the higher reactivity of the 1-position ("belt") of diamantane[23] and the fact that ethanoadamantane (**10**) undergoes bromination most rapidly at C_6,[2b] the most likely positions of the bromine atoms in the product are at C_7 and C_{12} (**11**).[24]



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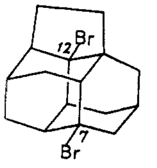

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Aluminum Bromide Catalyzed Equilibration between 4 and 5. During the rearrangement of hexahydrogenated **1** (eq 1), the ratio of **4** to **5** in the reaction mixture was about 4 in the first few hours but gradually increased to about 10 after 7 h of contact with the catalyst at room temperature (see Experimental Section). Equilibration with fresh aluminum bromide gave a ratio of 13.2 ± 1.5 at 28 °C in favor of **4**.

Molecular mechanics calculations[25] (Table I) using four popular force fields—Engler–Andose–Schleyer (EAS) version[26] and Allinger's 1971,[27] 1973 (MMI),[28] and 1977 (MM2)[29] version[30]—agree in finding **4** to be more stable than **5**. While the calculated equilibrium constants apply to the vapor phase, some of them agree very well with the experimental results in solution.[32]

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[22] Rao, S. T.; Sundaralingam, M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 694. The first five lines of this paper contain errors and should read as follows: "The ethano-bridged diamantane molecules I and II are prepared by aluminum halide rearrangement of an isomeric $C_{16}H_{22}$ hydrocarbon obtained by exhaustive hydrogenation of III. I was also obtained as a minor, disproportionation product of the rearrangement of $C_{16}H_{20}$ hydrocarbon prepared by hydrogenation of IV."

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[30] McKervey[31] calls Allinger's 1971 force field version "MM1". The QCPE program based on Allinger's 1973 version is named MMI[28c] and differs from "MM1".

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[32] Recent evaluation of these and other force field models regarding their capabilities of reproducing enthalpies of a number of diamond molecules[31] generally reveals the superiority of MM2 over the "first-generation force fields". Nevertheless, the agreement of the A71, MMI, and EAS results with experiment (Table I) are better.

Table I. Enthalpies and Strain Energies (kcal/mol, 25 °C, Gas) of Isomeric Ethanodiamantanes 4 and 5 as Calculated by Various Force Fields

	ΔH_f°				strain energy			
	EAS[a]	A71[b]	MMI[c]	MM2[d]	EAS	A71	MMI	MM2
4 (C_1)	−31.05	−32.77	−31.39	−27.16	22.44	21.08	16.02	30.54
5 (C_s)	−30.05	−31.00	−29.38	−26.62	22.33	21.69	16.06	30.10
$\Delta\Delta H_f$[f]	−1.00	−1.77	−2.01	−0.54				
K(28 °C)[e]	10.0	14.3	14.9	4.6				

[a] Engler-Andose-Schleyer force field.[26] [b] Allinger's 1971 force field.[27] [c] Allinger's 1973 force field.[28] [d] Allinger's 1977 force field.[29] [e] Entropy corrections include −1.38 eu (σ = 2) for 5 and 1.38 (DL) − 1.54 eu (group increment, see Table I of ref 2a) for 4. [f] In kcal/mol.

Table II. Calculated Enthalpies and Strain Energies (kcal/mol, 25 °C, Gas) of Selected Heptacyclohexadecanes and Nonacyclodocosanes

		ΔH_f°				strain energy			
no.		EAS[a]	A71[b]	MMI[c]	MM2[d]	EAS	A71	MMI	MM2
		heptacyclohexadecane							
6	[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}][f]	−4.35	−0.16	−0.06	−0.31	42.09	46.46	37.08	49.82
7	[7.7.0.0^{2,6}.0^{3,15}.0^{4,12}.0^{5,10}.0^{11,16}][f]	−8.14	−4.84	−5.33	−4.61	38.30	41.78	31.81	45.52
12	[7.7.0.0^{2,5}.0^{3,15}.0^{4,12}.0^{6,10}.0^{11,16}][f]	11.57	15.60	15.60	14.97	58.01	62.22	52.74	65.10
15	[8.6.0.0^{2,6}.0^{3,15}.0^{4,11}.0^{5,9}.0^{12,16}][f]	−0.74	4.12	3.76	3.67	45.70	50.74	40.90	53.80
38	[7.6.1.0^{3,8}.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}][f]	−9.42	−8.60	−8.50	−5.32	38.13	39.18	30.61	45.78
39	[7.7.0.0^{2,7}.0^{4,15}.0^{5,13}.0^{6,11}.0^{11,16}][f]	−4.44	−4.23	0.51	1.68	43.11	43.55	35.15	50.22
40	[7.6.1.0^{1,6}.0^{3,14}.0^{5,13}.0^{7,11}.0^{10,15}][f]	−4.20	−3.90	−3.60	−0.28	43.35	43.88	35.50	50.82
41	[7.7.0.0^{1,12}.0^{2,7}.0^{3,15}.0^{4,13}.0^{6,11}][f]	1.40	0.83	1.81	5.81	48.95	48.61	40.92	56.91
42	[10.3.1.0^{1,5}.0^{2,10}.0^{3,8}.0^{7,15}.0^{9,14}][f]	10.12	7.85	9.99	14.02	57.57	55.63	49.10	65.12
43	[8.6.0.0^{2,13}.0^{4,9}.0^{5,12}.0^{7,11}.0^{11,15}][f]	21.14	20.37	24.47	30.15	68.69	68.15	63.57	81.26
		nonacyclodocosanes[e]							
8	bastardane	−30.08	−29.90	−28.83	−23.94	36.37	36.88	27.18	48.52
54	isotetramantane	−53.52	−52.96	−52.08	−41.90	15.15	16.14	7.86	32.50
55	*anti*-tetramantane	−51.51	−51.01	−49.86	−42.47	16.06	16.93	8.12	30.95
56	skew-tetramantane	−46.59	−46.39	−44.86	−37.99	20.97	21.55	13.11	35.43

[a] Engler-Andose-Schleyer force field.[26] [b] Allinger's 1971 force field.[27] [c] Allinger's 1973 force field.[28] [d] Allinger's 1977 force field.[29] [e] EAS and A71 values taken from ref 8. [f] Cyclic designation for the heptacyclohexadecane.

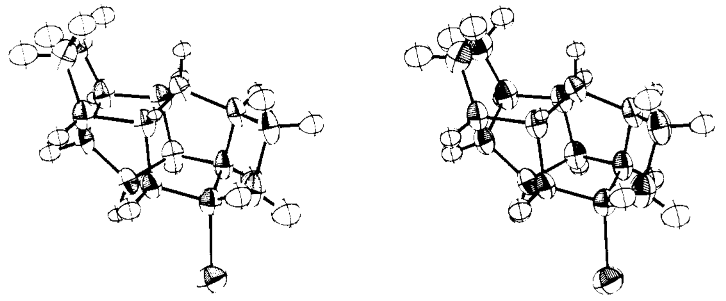
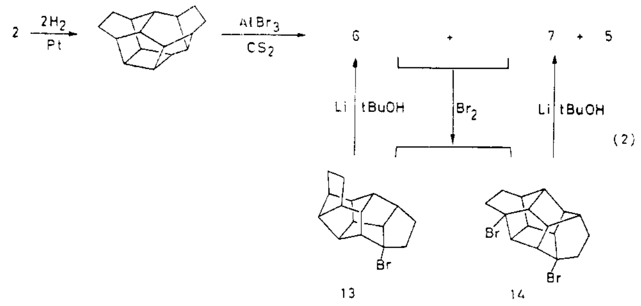


Figure 1. ORTEP stereodrawing of 5-bromoheptacyclo[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}]hexadecane (5-bromo-(C_2)-bisethanobisnordiamantane, 13).

Rearrangement of the Tetrahydrogenated 38.5 °C Melting Dimer (2) of Cyclooctatetraene. Hydrogenation of 2 gave a heptacyclohexadecane, mp 47 °C (12, eq 2). Treatment of 12 with aluminum bromide afforded a complex mixture, of which the two major products comprised 73 and 13% of the total yield. While attempted separation by preparative GLC was unsuccessful, these two major products could be separated by fractional crystallization of their bromides. Specifically, bromination of the rearrangement mixture with liquid bromine followed by crystallization of crude product from acetone–methanol first gave small, pillar-shaped crystals, mp 225–226 °C. When the mixture was allowed to stand, column-like crystals (mp 94 °C) separated from the filtrate. X-ray analyses of these crystals revealed the lower melting product to be 5-bromoheptacyclo[8.6.0.0^{2,8}.0^{3,13}.0^{4,11}.0^{5,9}.0^{12,16}]hexadecane (13)[1c] and the higher melting product to be 6,12-dibromoheptacyclo[7.7.0.0^{2,6}.0^{3,15}.0^{4,12}.0^{5,10}.0^{11,16}]hexadecane (14) (Figures 1 and 2).



Reductive debromination of the monobromide 13 with lithium/*tert*-butyl alcohol in tetrahydrofuran gave a low-melting (35 °C) hydrocarbon, whose GLC retention time and mass fragmentation pattern were identical with those of the most abundant rearrangement product. The new hydrocarbon 6 may be designated (C_2)-bisethanobisnor-

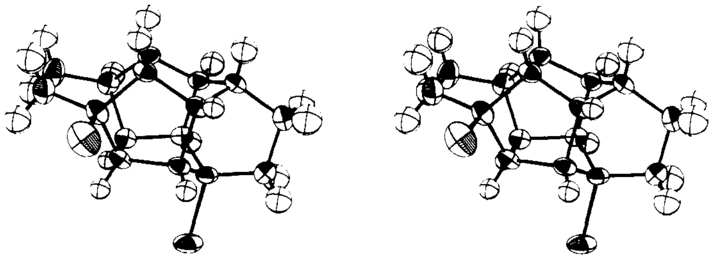
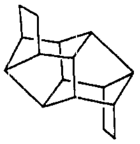


Figure 2. ORTEP stereodrawing of 6,12-dibromoheptacyclo[7.7.0.$0^{2,6}$.$0^{3,15}$.$0^{4,12}$.$0^{5,10}$.$0^{11,16}$]hexadecane (6,12-dibromobicyclooctadiene cage dimer, **14**).

diamantane.[33] The point group C_2 is included in order to differentiate **6** from the more symmetrical (point group C_{2h}) but less stable isomer **15** (Table II).



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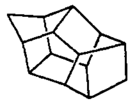


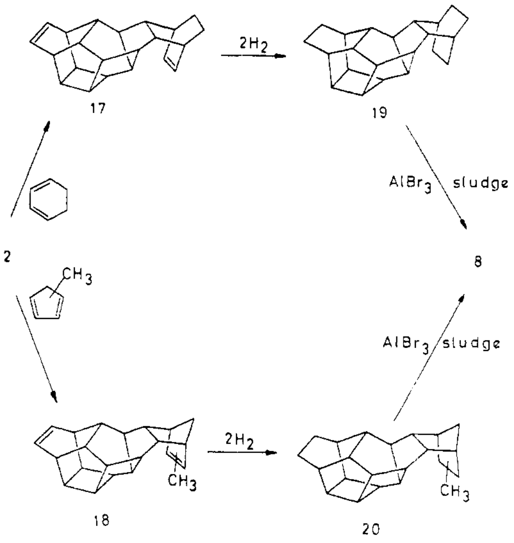
16

Likewise, dibromide **14** was reduced to a hydrocarbon (**7**, mp 68 °C) identical with the second most abundant product from the rearrangement of **12** (GC/MS analysis). **7** is a bishomologue of the well-known cage dimer of norbornadiene (**16**).[37] **6** and **7** represent the first examples of doubly ethano-bridged molecules resulting from "adamantane rearrangement" reactions.[8,38]

When aluminum bromide/*tert*-butyl bromide sludge catalyst[21] was used to effect the rearrangement, up to 20% of a disproportionation product ($C_{16}H_{22}$) formed[39] in addition to the isomerization products. The byproduct, separated by preparative GLC (mp 111.5 °C), was identified as (C_s)-ethanodiamantane (**5**).[40] Treatment of **12** under severer conditions (at 100 °C for 2 h) with aluminum-sludge catalyst neither brought about further rearrangement beyond **6** and **7** nor caused any increase in disproportionation. Apparently, both **6** and **7** are thermodynamically stable, and the disproportionation with aluminum sludge takes place only at earlier stages of successive carbonium ion rearrangement sequences starting from **12**.

We noticed that **16** also is thermodynamically stable.[41] Treatment of **16** with a large excess of aluminum bromide at 100 °C for 2 h did not lead to any noticeable change.

Attempted Synthesis of Tetramantane by Rearrangements of $C_{22}H_{28}$ Hydrocarbons. The 38.5 °C melting dimer of cyclooctatetraene (**2**) adds 1 mol of 1,3-cyclohexadiene or of methylcyclopentadiene (eq 3). The



(3)

addition takes place exclusively at the C_4–C_5 double bond on the basis of spectral evidence. Similar conclusions have been reached by Fray and Saxton.[17] The singlet C_4–C_5 olefinic proton peak of **2** at δ 5.82[42] disappeared upon adduct formation, and the complex multiplet at δ 6.4–5.7 intensified for the cyclohexadiene adduct **17**, or a broad singlet (1 H) appeared at δ 5.46[43] for the methylcyclopentadiene adduct **18**. The C=C stretch absorptions in **2** at 1615 (C_{13}–C_{14})[44] and at 1605 cm^{-1} (C_4–C_5)[45] are distinct but are combined into one sharp peak at 1609 cm^{-1} in **17**. In **18**, the frequencies are changed to 1628 and 1616 cm^{-1}. Two closely overlapping doublets centered at δ 1.65 (3 H,

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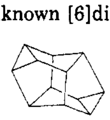
[33] We prefer the trivial name "bisnordiamantane" over "bisnordiadamantane" used by Hirao et al.[34] The latter should have included the number of carbon atoms common to the two adamantane-like units (see ref 35). The bisnordiamantane skeleton may also be regarded as a tetrahydro derivative of the unknown [6]ditriaxane:[36]



[34] Hirao, K.; Taniguchi, M.; Iwakuma, T.; Yonemitsu, O.; Flippen, J. L.; Karle, I. L.; Witkop, B. *J. Am. Chem. Soc.* **1975**, *97*, 3249.

[35] Graham, W. D.; Schleyer, P. v. R.; Hagaman, E. W.; Wenkert, E. *J. Am. Chem. Soc.* **1973**, *95*, 5785.

[36] (a) Nickon, A.; Pandit, G. *Tetrahedron Lett.* **1968**, 3663. (b) A dimethylditriaxane has been synthesized: Hirao, K.; Kajiwara, Y.; Ōuchi, H.; Yonemitsu, O. Proceedings of the 36th Symposium on the Synthetic Organic Chemistry, Nov 20, 1979, Tokyo, Abstr. 2-12.

[37] (a) Scharf, H.-D.; Weisgerber, G.; Höver, H. *Tetrahedron Lett.* **1967**, 4227. (b) Neely, S. C.; van der Helm, D.; Marchand, A. P.; Hayes, B. R. *Acta Crystallogr., Sect. B* **1976**, *B32*, 561.

[38] The third product remains unidentified.

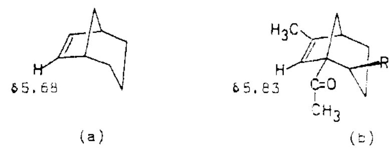
[39] The aluminum bromide sludge catalyst often produces larger amounts of disproportionation products compared to aluminum bromide alone or to the McKervey catalyst:[20] Ōsawa, E.; Slutsky, J. et al., unpublished results.

[40] Actually one of these crystals was used for the X-ray analysis which gave structure **5**. See Experimental Section.

[41] A sample of **16** was kindly donated by Professor H.-D. Scharf.

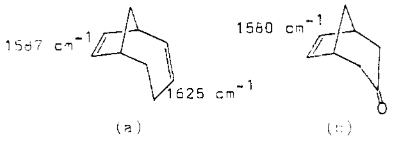
[42] (a) Krieger, H. *Suom. Kemistil. B* **1965**, *38*, 260. (b) Shudo, K.; Natsume, M.; Okamoto, T. *Chem. Pharm. Bull.* **1965**, *13*, 1019.

[43] Agrees with olefinic proton of 2-methylnorbornene at δ 5.42 (Finnegan, R. A.; McNees, R. S. *J. Org. Chem.* **1964**, *29*, 3234) but does not agree with that of 1-methylnorbornene at δ 5.82 (q).[42a]



[44] Cf. 1614 cm^{-1} for bicyclo[2.2.2]octene.[14]

[45] (a) Moore, W. R.; Moser, W. R.; LaPrade, J. E. *J. Org. Chem.* **1963**, *28*, 2200. (b) LeBel, N. A.; Liesemer, R. N. *J. Am. Chem. Soc.* **1965**, *87*, 4301.



Me) in **18**, in addition to the C=C frequencies mentioned above, indicate that the methyl group is attached to one of the sp^2 carbon atoms.

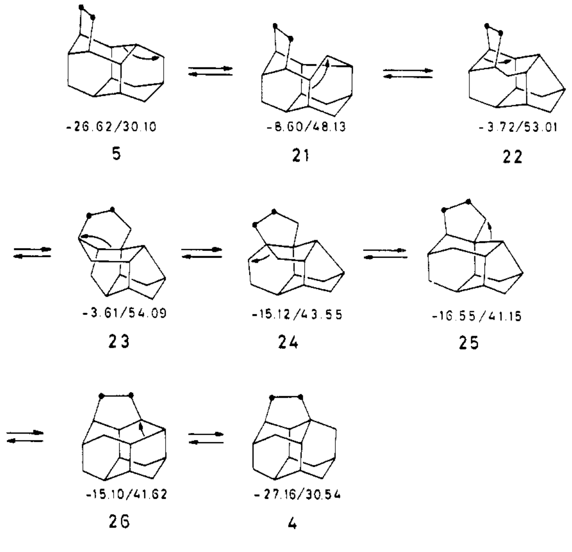
Hydrogenation of the adducts (**17** and **18**) gave nonacyclic $C_{22}H_{28}$ hydrocarbons **19** and **20**, respectively. These isomers of tetramantane are potential precursors for this higher adamantalogue.[1a,6] Treatment of **19** with aluminum-sludge catalyst in carbon disulfide solution at 100 °C for 2 h resulted in its complete disappearance; according to GLC analysis at least seven products formed. The most abundant of these products crystallized upon cooling the oily mixture at −78 °C for several days to give 5–8% of crude yield. The mass spectrum of the recrystallized product (mp 144.5–146.5 °C) indicated a high resistance to fragmentation: the molecular ion peak at m/e 292 is the parent peak and comprises 38% of the total fragmentation. X-ray analysis revealed that this major product was not one of the expected tetramantanes but was the "unwanted" nonacyclo-$[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]$docosane (**8**), or "bastardane", our proposed trivial name.[1a] This molecule provides another instance of an ethano-bridged product resulting from the thermodynamically controlled isomerization reaction.

The methyl-bearing isomer **20** required much longer reaction times than did **19** to rearrange into **8**. Under the same conditions for the rearrangement of **19**, **20** rearranged into a mixture of at least two stable intermediates still having methyl groups. Only half of the intermediates disappeared after heating with fresh sludge catalyst at 100 °C for 60 h. One of the rearranged products thus obtained was collected by preparative GLC and confirmed to be identical with **8**.

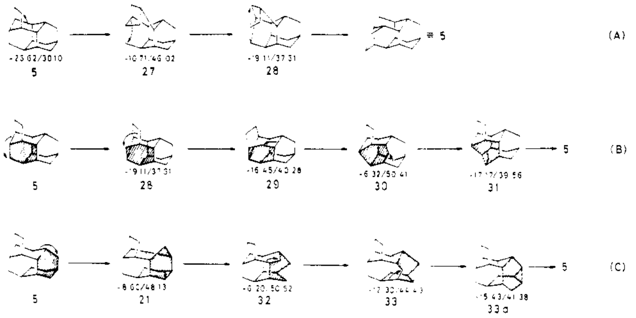
Discussion

Mechanism of Interconversion between Isomeric Ethanodiamantanes 4 and 5. A direct 1,3-shift of the ethano bridge in C_1^+-**5** would give C_3^+-**4** in one step but involves an impossible bond migration. While a sequence of 1,2 alkyl shifts is a much more likely mechanism for the interconversion,[46] the large size of the system precludes exhaustive mapping of all possible rearrangement pathways, as has been done for adamantane[47] and for methyladamantane.[48] Scheme I illustrates one possibility.[49] The first step from either starting material (**5** → **21** and **4** → **26**, the reverse of that shown) involves diamantane–protodiamantane transformations which are endothermic by 12–18 kcal/mol, as indicated by the MM2 calculations of heats of formation and strain energies of the intermediates given in Scheme I. This is in accordance with the observed slow rate of interconversion of **4** and **5**.[50]

Scheme I. ΔH_f°/Strain Energy (MM2) (kcal/mol)



Scheme II. ΔH_f°/Strain Energy (MM2) (kcal/mol)



According to Scheme I, the carbon atoms of the ethano bridges of **4** and **5** remain separate from the carbons of the diamantane skeleton during isomerization. Many other mechanisms can be conceived which should have low barriers and lead to more extensive carbon scrambling. For example, complete scrambling can be achieved by combinations of the three processes (A–C) depicted in Scheme II.[51] Process A can be analyzed by the extended Klemperer notation:[52]

$$\begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 \\ 10 & 9 & 8 & 7 & 3 & 4 & 5 & 6 & 15 & 14 & 13 & 12 & 16 & 1 & 2 & 11 \end{bmatrix} = \begin{bmatrix} 1 & 10 & 14 \\ 10 & 14 & 1 \end{bmatrix} \begin{bmatrix} 3 & 4 & 5 & 6 & 7 & 8 \\ 8 & 7 & 3 & 4 & 5 & 6 \end{bmatrix} \begin{bmatrix} 2 & 9 & 15 \\ 9 & 15 & 2 \end{bmatrix} \begin{bmatrix} 11 & 13 & 16 \\ 13 & 16 & 11 \end{bmatrix}$$

The atoms within the four groups scramble if process A is repeated. The important point is that the ethano-bridge carbons (C_4, C_5) exchange with those of the diamantane skeleton as a consequence. Similar analysis of processes B and C indicate that the carbon atoms in the shaded six-membered rings interchange by repeating these processes. Thus, combination of processes A, B, and C leads to complete scrambling of carbon atoms within the molecule. Like the pathway in Scheme I, the processes A, B,

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(46) Previous studies on the mechanism of multistep carbonium ion rearrangements in polycyclic hydrocarbons assumed the 1,2 alkyl shift as the only elementary step.[47,48]

(47) Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5769.

(48) Ōsawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361.

(49) IUPAC names of structures appearing in Scheme I: **21**, hexacyclo$[7.7.0.0^{2,6}.0^{5,14}.0^{8,13}.0^{11,15}]$hexadecane; **22**, hexacyclo$[8.6.0.0.^{2,7}.0^{4,16}.0^{6,15}.0^{9,14}]$hexadecane; **23**, hexacyclo$[7.6.1.0^{2,7}.0^{4,15}.0^{6,14}.0^{9,14}]$hexadecane; **24**, hexacyclo$[8.5.1.0^{2,7}.0^{4,15}.0^{6,14}.0^{10,14}]$hexadecane; **25**, hexacyclo$[7.6.1.0^{2,7}.0^{4,15}.0^{6,14}.0^{10,14}]$hexadecane; **26**, hexacyclo$[7.7.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{11,16}]$hexadecane.

(50) It should be mentioned that the isolated disproportionation product from **12** was not **4** but the less stable isomer **5**, indicating that this byproduct was formed under conditions of kinetic control.

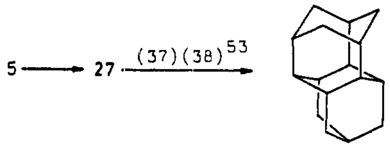
(51) IUPAC names of structures newly appearing in Scheme II: **27**, hexacyclo$[10.3.1.0^{2,10}.0^{3,7}.0^{5,15}.0^{9,14}]$hexadecane; **28**, hexacyclo$[10.3.1.0^{2,10}.0^{3,8}.0^{5,15}.0^{9,14}]$hexadecane; **29**, hexacyclo$[10.3.1.0^{2,10}.0^{3,7}.0^{4,15}.0^{9,14}]$hexadecane; **30**, hexacyclo$[9.4.1.0^{2,9}.0^{3,7}.0^{6,15}.0^{8,13}]$hexadecane; **31**, hexacyclo$[10.3.1.0^{2,10}.0^{3,7}.0^{6,15}.0^{8,14}]$hexadecane; **32**, hexacyclo$[9.4.1.0^{2,6}.0^{5,10}.0^{8,15}.0^{9,13}]$hexadecane; **33**, hexacyclo$[8.6.0.0^{3,7}.0^{4,15}.0^{8,14}.0^{12,16}]$hexadecane; **33a**, hexacyclo$[7.7.0.0^{2,6}.0^{3,14}.0^{4,10}.0^{11,15}]$hexadecane.

(52) Klemperer, G. in "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 2.

(53) Bond C_3–C_7 shifts to form a bond between C_3 and C_8.

and C should also have high barriers associated with the first steps.

(6)-Adamantane-iceane (hexacyclo$[9.3.1.1^{3,7}.0^{2,9}.0^{4,13}.0^{5,10}]$hexadecane, point group C_{3v}, **34**) can be generated after two 1,2 alkyl shifts from **5** (eq 4).

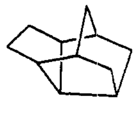


(4)

34

According to MM2[29] calculations, the highly symmetric molecule **34** is, however, 5 kcal/mol less stable ($\Delta H_f° = -21.62$, strain energy 35.11 kcal/mol) than ethanodiamantanes (**4** and **5**). We never observed any intermediate during isomerization of ethanodiamantanes.

Are the Isolated Products Stabilomers or Local Energy Minima? For such relatively large hydrocarbons, the systematic evaluation of relative stabilities of all possible isomers as developed previously[5,8,47,48] is practically impossible. Nevertheless, in view of the remarkable stability of the diamantane skeleton,[21] the ethanodiamantanes **4** and **5** are very probably the stabilomers. Two other cases are known where the attachment of an ethano bridge to a stabilomer of lower class produces a higher stabilomer: ethanonoradamantanes (**35** and **36**)[5,54] and ethanoadamantane (**10**)[2b,55] are the tetracycloundecane and tetracyclododecane stabilomers, respectively.



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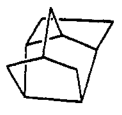
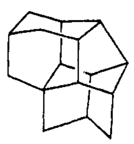


36

However, in the heptacyclohexadecane family, the bisethano-bridged products **6** and **7** are not the stabilomers. Although the true stabilomer of this class of hydrocarbons still has not been identified, a provisional search (Table II) indicates that one (**37**) of the six "bisnortriamantanes"



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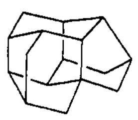

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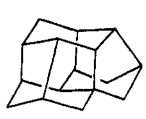

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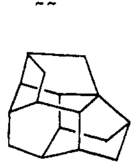

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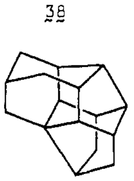

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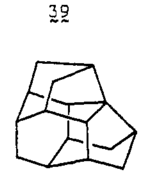
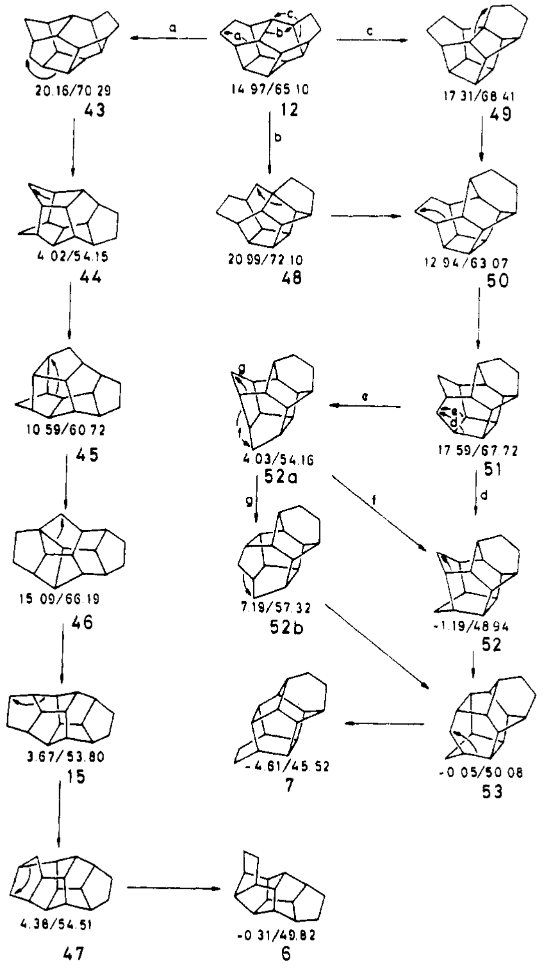


42

(**37**–**42**) is more stable than **6** or **7**. Table II includes calculated heats of formation for several other heptacyclohexadecanes (see also Scheme III). Interestingly, the four force fields employed here agree that (C_2)-bisethanobisnordiamantane (**6**) is 4 kcal/mol more stable than its C_{2h} counterpart (**15**). This difference in stabilities of **6** and **15** arises mainly from an angle strain term in the parent bisnordiamantane skeletons.[56]

Scheme III. $\Delta H_f°$/Strain Energy (MM2) (kcal/mol)



Clearly, the isolated hydrocarbons, **6** and **7**, must represent local energy minima, kinetically quite stable, along the pathway from **12** to the heptacyclohexadecane stabilomer. Graph-theoretical search of the rearrangement pathways by the "disource propagation method",[57a] modified slightly with the aid of energy calculations by the MM2 force field method,[57b] revealed that **6** and **7** can be reached after only seven 1,2 alkyl shifts (Scheme III).[58] Calculations also indicate that none of the intermediates

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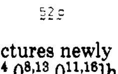
(54) The structures given in ref 5 are in error. For corrections, see: Kent, G. J.; Godleski, S. A.; Ōsawa, E.; Schleyer, P. v. R. *J. Org. Chem.* **1979**, *44*, 3739.

(55) Farcasiu, D.; Wiskott, E.; Ōsawa, E.; Thielecke, W.; Engler, E. M.; Slutsky, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 4669.

(56) Experimental as well as computational studies on the bisnordiamantanes are in progress and will be published elsewhere.

(57) (a) Tanaka, N.; Kan, T.; Iizuka, K. *J. Chem. Inf. Comput. Sci.* **1979**, *3*, 162. (b) The graph-theoretical search first suggested a pathway from **12** to **7** involving **52c** (heptacyclo$[7.7.0.0^{2,6}.0^{3,15}.0^{4,14}.0^{5,10}.0^{11,16}]$hexadecane) instead of **52**. However, **52c** is highly strained [$\Delta H_f^0 = 28.09$, strain energy 78.22 kcal/mol (MM2)], and the routes shown in Scheme III involving immediate opening of the cyclobutane ring of **51** (to **52** and **52a**) proved energetically much more favorable.

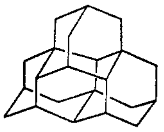


52c

(58) IUPAC names of structures newly appearing in Scheme III: **43**, heptacyclo$[7.7.0.0^{2,6}.0^{5,15}.0^{7,14}.0^{8,13}.0^{11,16}]$hexadecane; **44**, heptacyclo$[7.7.0.0^{2,14}.0^{3,7}.0^{6,13}.0^{8,12}.0^{11,15}]$hexadecane; **45**, heptacyclo$[8.6.0.0^{2,6}.0^{3,15}.0^{4,13}.0^{5,9}.0^{12,16}]$hexadecane; **46**, heptacyclo$[7.7.0.0^{2,6}.0^{3,15}.0^{4,11}.0^{5,9}.0^{12,16}]$hexadecane; **47**, heptacyclo$[8.6.0.0^{2,6}.0^{3,14}.0^{4,11}.0^{5,9}.0^{12,16}]$hexadecane; **48**, heptacyclo$[7.7.0.0^{2,6}.0^{3,16}.0^{4,14}.0^{5,11}.0^{11,15}]$hexadecane; **49**, heptacyclo$[7.7.0.0^{1,12}.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,10}]$hexadecane; **50**, heptacyclo$[7.7.0.0^{2,6}.0^{3,16}.0^{4,14}.0^{5,11}.0^{10,15}]$hexadecane; **51**, heptacyclo$[7.7.0.0^{2,7}.0^{3,16}.0^{5,14}.0^{8,13}.0^{10,15}]$hexadecane; **52**, heptacyclo$[7.7.0.0^{2,7}.0^{3,14}.0^{6,13}.0^{8,12}.0^{10}]$hexadecane; **52a**, heptacyclo$[7.7.0.0^{2,7}.0^{3,14}.0^{6,13}.0^{8,12}.0^{10,15}]$hexadecane; **52b**, heptacyclo$[8.5.1.0^{2,7}.0^{3,14}.0^{6,13}.0^{8,12}.0^{11,15}]$hexadecane; **53**, heptacyclo$[7.7.0.0^{2,6}.0^{3,15}.0^{4,13}.0^{5,10}.0^{11,16}]$hexadecane.

shown in Scheme III is excessively strained. The relatively strained compounds **46**, **48**, **49** (having quaternary carbon atoms), and **51** might be responsible for the disproportionation which took place in the presence of the sludge catalyst. Further rearrangements of **6** and **7** to more stable structures (e.g., to **37**) must involve intermediates too strained to survive under ordinary reaction conditions.

According to the calculations, bastardane (**8**) is much less stable than the three isomeric tetramantanes (**54–56**, Table II).[20,59,60] Again, further rearrangement of **8** is likely to involve quaternary carbon intermediates too unstable to overcome.



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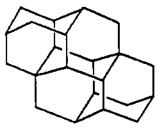

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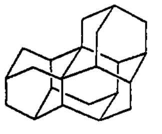

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Structural Consequences of Ethano Bridging in Cage Molecules. The X-ray structures of the rearrangement products provide a useful test of the ability of empirical force field calculations to reproduce the geometries of these molecules. Altona and Faber[61a] compared the observed bond lengths of **5** with those calculated by several force fields and found their own force field to reproduce the lengths with a standard deviation of 0.007 Å. For carbon atoms of **6**, **7**, and **8**, standard deviations of calculated (MM2) lengths and valence and dihedral angles from the observed values in compounds **13**, **14**, and **8** are about 0.01 Å and 1–2°, respectively.[61b] Agreement is good.

The ethano bridges of **4** to **8** are all eclipsed and "pinch" the cyclohexane ring across which the bridge is spun. The angles C_1–C_{12}–C_{13} of **4** and C_3–C_7–C_6 of **5** are reduced from the near tetrahedral value in diamantane to 100°,[22] and angle C_5–C_9–C_8 in **6** is reduced to 100° from the corresponding angles (102–108°) of noradamantane.[62] The distorsion of diamond molecules with a (C_2)-bisnordiamantane skeleton as noted here is in accord with our previous observations.[2]

Rao and Sundaralingam[22] regarded the length of the ethano-bridge C–C bond in **5** (1.552 ± 0.002 Å) to be significantly lengthened and suggested the interaction between the eclipsed hydrogen atoms on C_4 and C_5 as the primary cause of the bond lengthening.[63] Is such bond lengthening general? Table III[61b] summarizes experimental and calculated lengths of the eclipsed ethano bridges in several cage molecules. Calculations reproduce observed bridge lengths within the standard deviation of MM2 force field calculations, except for norbornane which is claimed to have an unusually long C–C bond of 1.56 Å. However, since this molecule is much more strained than the other molecules listed in Table III[26a] and since the various experimental bond length determinations disagree,[64] norbornane can be excluded from consideration. For **6**, **7**, and **8**, the ethano-bridge C–C bonds are of normal length. It is thus likely that the repulsion between eclipsed hydrogen atoms on the ethano bridge may not be the predominant contributior to the bond length; this term appears to be accounted for satisfactorily by molecular mechanics.

Table III. CH_2-CH_2 Bond Lengths (Å) of Eclipsed Ethano Bridges

compd	exptl	calcd[a]
norbornane	1.561 (av)[b,c]	1.541[c]
bicyclo[3.2.1]octane	1.55 (4) (ED)[d,e]	1.543[f]
ethanoadamantane (**10**)		1.546[g]
(C_1)-ethanodiamantane (**4**)		1.549[f]
(C_s)-ethanodiamantane (**5**)	1.552 (2) (X)[h,i]	1.547[f]
(C_2)-bisethanobisnordiamantane (**6**)	1.542 (4) (X)[j,f]	1.537[f]
bicyclo[2.2.2]octadiene dimer (**7**)	1.539 (5) (X)[k,f]	1.533[f]
bastardane (**8**)	1.535 (10) (X)[h,l]	1.539[f]

[a] Based on MM2 force field.[29] [b] The best composite based on electron-diffraction and X-ray analyses. [c] Reference 64. [d] Electron diffraction. [e] Osina, E. L. Dissertation, Moscow State University, 1976. [f] Present work. [g] Ōsawa, E.; Engler, E. M.; Godleski, S. A.; Inamoto, Y.; Kent, G. J.; Kausch, M.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 984. [h] X-ray analysis of hydrocarbon. [i] Reference 22. [j] X-ray analysis of 5-bromo derivative **13**. [k] X-ray analysis of 6,12-dibromo derivative **14**. [l] Reference 1a.

It is difficult to assess the origin of the small energy difference between **4** and **5**, which differ only in the attachment of the ethano bridge. **4** has less strain energy than **5** according to the A71 and MMI force fields but is more strained than **5** according to the EAS and MM2 force fields (Table I). If we consider only MM2 for discussion, the lower enthalpy of **4** compared to that of **5** is due to a subtle balance among the calculated enthalpy and the number of secondary, tertiary, and quaternary carbon atoms. Entropy contributes to shift the free-energy balance in favor of **4**.

Conclusions

Including the three known stabilomers, ethanoadamantane (**10**)[2,54] and the two ethanonoradamantanes **35** and **36**,[5] we have so far characterized eight cage hydrocarbons having one or two ethano bridges among the products of thermodynamically controlled, Lewis acid catalyzed rearrangements of polycyclic hydrocarbons. Such ethano-bridged cyclohexane arrangements are thus indicated to have high stability relative to alternative structures. The experience gained in these studies indicates that the thermodynamically controlled rearrangements of relatively *large* polycyclic systems tend to stop at local energy minima having ethano bridge(s). It thus appears advantageous to start from a precursor located as close as possible in the energy hypersurface to the target molecule.

The ethano-bridged products obtained in this study await further exploitation. Results with Engler's carbocation force field[47] were not consistent with the observed

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(59) It is likely that the diamantane portion of bastardane (**8**) comes from the right half of **19**, since several $C_{14}H_{20}$ isomers similar to this half are known to rearrange into diamantane: Gund, T. M.; Schleyer, P. v. R.; Gund, P. H.; Wipke, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 743. Likewise, the upper left half of **8** probably arises from the left half of **19**, in analogy with the pathway leading to **6** shown in Scheme III. Whereas the upper left half of **8** is 2,8-ethanonoradamantane (**36**) and is isomeric to 2,4-ethanonoradamantane (**35**) which consitutes the two halves of **6**, these ethanonoradamantanes can convert into each other quite readily.[5]

(60) The presently available algorithm of the "disource propagation method" does not allow the analysis of nonacyclodocosanes; hence, the rearrangement map involving precursor **19** and **20** cannot be examined.

(61) (a) Altona, C.; Faber, D. H. *Top. Curr. Chem.* **1974**, *45*, 1. (b) See paragraph at the end of the paper about supplementary material.

(62) Drew, M. G. B., unpublished results quoted in: Bingham, R. C.; Schleyer, P. v. R. *Top. Curr. Chem.* **1971**, *18*, 35.

(63) The elongation of a C–C bond by 0.01–0.02 Å corresponds to an increase of 6.5–13 kcal/mol in bond stretch energy in terms of the MM2 force field;[29] this alone would have accounted for the gauche–syn barrier of *n*-butane. Cf.: Ōsawa, E.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1979**, *101*, 4824.

(64) Newton, M. G.; Pantaleo, N. S.; Kirbawy, S.; Allinger, N. L. *J. Am. Chem. Soc.* **1978**, *100*, 2176.

selective formation of monobromide 13 from 6. Whereas the moderate bridgehead carbonium ion reactivity of bicyclo[2.2.2]octane with liquid bromine has long been known,[65] the isolation of dibromide 14 is quite unexpected.[66,67]

Experimental Section

General Methods. Melting points are corrected and boiling points uncorrected. Microanalyses were performed at the Combustion Analysis Center, Department of Pharmacy, Hokkaido University. Infrared spectra were determined on Perkin-Elmer 237B and JASCO IR-G spectrophotometers. Mass spectra were taken on AEI MS-9 and Hitachi RMU-6D spectrometers at 70 to 80 eV. Proton NMR spectra were recorded on Varian A-60 and Hitachi R-20B spectrometers.

Heptacyclo[7.5.2.$0^{2,14}$.$0^{3,8}$.$0^{4,12}$.$0^{7,11}$.$0^{10,13}$]hexadeca-5,15-diene (41.5 °C Melting Dimer of Cyclooctatetraene, 1). The dimer 1 was prepared according to the procedure of Lord and Walker.[14b] Freshly distilled cyclooctatetraene (bp 55–58 °C at 44 torr, 130 g) was heated in an oil bath at 160–170 °C for 24 h. Distillation gave 17.3 g of unreacted cyclooctatetraene (bp 34–52 °C, 35 torr) and 72.2 g of thick, colorless oil (bp 118–123 °C, 0.45 torr), leaving 40.1 g of liquid residue in the flask. The main fraction was dissolved in petroleum ether and cooled to −78 °C to give crystalline 1: mp 40–41 °C; NMR δ 6.60–5.30 (m, 4 H), 3.70–1.45 (m, 9 H), 1.34–0.60 (m, 3 H).

Contrary to the description of Jones,[13] heating cyclooctatetraene in refluxing *o*-dichlorobenzene resulted only in the formation of the 38.5 °C melting dimer (2) in good yield.

Exhaustive Hydrogenation of 1 to a $C_{16}H_{22}$ Mixture. The dimer 1 (18.4 g) was dissolved in 250 mL of 4:1 petroleum ether/ethanol mixture and hydrogenated over 0.3 g of platinum oxide in a Parr apparatus for 17 h at room temperature. The proton NMR spectrum of crude product indicated about half of the cyclopropyl protons still remained intact. The crude product was dissolved in 125 mL of 4:1 methylcyclohexane/acetic acid mixture and hydrogenated over 0.5 g of platinum oxide for 20 h at 50–70 °C in a Parr apparatus. Distillation afforded 15.4 g (81%) of an oil, bp 119–121 °C (1 torr). GLC analysis on a 3 mm × 2 m, 10% SE-30 column at 195 °C revealed three components in the following percentage (relative retention time): 12 (1.0), 74 (1.3), 14 (1.4); IR 2905, 1466, 1455, and 1437 cm^{-1}; NMR δ 3.1–1.0 (m with the most intense peak at 1.75); mass spectrum, *m/e* 214 (M*), 91. Anal. ($C_{16}H_{22}$) C, H.

Rearrangement of Hexahydrogenated 1 with $AlBr_3$-Sludge Catalyst. In a preliminary run, 0.5 mL of freshly prepared aluminum-sludge catalyst[8b] was added to a solution of 0.3 g of hexahydrogenated 1 in 10 mL of carbon disulfide under an atmosphere of hydrogen bromide gas at room temperature; the reaction course was followed by GLC analyses of aliquot samples. The starting mixture (relative GLC retention times (t_R) on a 0.02 in. × 300 ft, DC200 Golay column at 160 °C: 0.99, 1.00, 1.12) disappeared almost instantly, and two product peaks corresponding to 4 (t_R = 0.59) and 5 (t_R = 0.68) soon appeared in an initial ratio of 6:1. The ratio decreased to 4:1 after 2 h and then increased to about 15:1 after 7 h at the end of the reaction. An additional GLC peak (t_R = 0.46) indicated the presence of an intermediate in the rearrangement process. This intermediate comprised 17% of the total mixture 1 h after the start of reaction but decreased gradually and finally disappeared after 3 h. The decrease in the intermediate peak apparently corresponds to the temporary increase in the peak of product 5 after 2–3 h.

In a preparative run, 10 mL of sludge catalyst was added in two portions to a stirred solution of 9.3 g of hexahydrogenated 1 in 60 mL of carbon disulfide. A marked initial exothermic reaction caused boiling of the solvent. The mixture was stirred for 3 h and worked up to give 7 g of solid product (crude yield 75%). One recrystallization from acetone/petroleum ether gave a semisolid mixture consisting of the two products mentioned above in an 85:15 ratio. These were separated by preparative GLC on a $^3/_8$ in. × 25 ft Carbowax column at 215 °C. The main product (4) gave an analytical sample after one sublimation and three recrystallizations from acetone/cyclohexane: pillar-shaped crystals; mp 206.5–208 °C; IR 2963, 2913, 2870, 2847, 1473, 1452, 1363, 1336, 1050 cm^{-1}; NMR δ 2.1–1.0 (m with the most prominent peaks at 1.65 and 1.62); mass spectrum, *m/e* 214 (M*), 91. Anal. ($C_{16}H_{22}$) C, H.

The minor product (5), of 80% purity after GLC collection, was not purified futher. The GLC retention time and spectral characteristics were identical with those of the minor product isolated and purified from the rearrangement of 12 (see below).

1-Diamantanecarboxylic Acid. Koch–Haaf reaction on diamantane itself gave only a 25% yield of a low-melting carboxylic acid (201–202 °C).[68] With 1-bromodiamantane[68] as the starting material, the reaction proceeded smoothly. A suspension of well-pulverized 1-bromodiamantane (30 g, 0.112 mol) in 700 mL of concentrated sulfuric acid in a 2-L flask equipped with an efficient mechanical stirrer, dropping funnel, thermometer, and gas outlet was cooled to 10–17 °C. To this was slowly added 100 mL of 98–100% formic acid under vigorous stirring during 6 h. The reaction mixture foamed extensively especially at the outset. After further stirring for 1 h, the mixture was poured into 1 kg of ice through a glass wool filter. The precipitates were collected, washed, and recrystallized from 300 mL of acetone to give 20 g (77%) of colorless platelike crystals, mp 203.5–206 °C. Anal. ($C_{15}H_{20}O_2$) C, H.

(C_1)-Ethanodiamantan-15-one (9). The ketone 9 was prepared from 1-diamantanecarboxylic acid via the acid chloride (made with thionyl chloride; IR 1787 cm^{-1}) and diamant-1-yl diazomethyl ketone (prepared with diazomethane and the acid chloride: IR 2210, 1633, 1619 cm^{-1}):[20] IR 1737 cm^{-1}.

Wolff–Kishner Reduction of Ketone 9 to 4. Crude ketone 9 (2 g, 8.8 mmol) was mixed with 9.5 mL of 95% triethanolamine, 1.9 g of potassium hydroxide, and 1 mL of 85% hydrazine hydrate. The mixture was heated at reflux for 2.5 h, and water was distilled out. The mixture was heated at 200 °C (solution temperature) for 2 h. After the mixture cooled, 10 mL of concentrated HCl and 20 mL of water were added to the reaction flask. Organic substances were extracted three times with chloroform. The combined extracts were washed with water and dried with $CaCl_2$, and the solvent was removed. The resulting dark oil (1.7 g) was subjected to preparative GLC separation on a 6 mm × 9 m Apiezon L column at 300 °C. The combined fractions with the lowest retention times were purified by another preparative GLC separation followed by sublimation to give crystals, mp 204–206 °C. The NMR and mass spectra of these crystals were identical with those of the main product 4 from the rearrangement of hexahydrogenated 1.

Dibromo-(C_1)-ethanodiamantane (11). In 5 mL of liquid bromine was heated 0.73 g of 4 under reflux for 5 h. Workup gave 1.54 g of lightly colored solid product. Recrystallization from acetone and sublimation under high vacuum afforded 0.49 g (39%) of an analytical sample: mp 309–313 °C (sealed tube); NMR δ 3.0–1.0 (m with eminent peaks at 1.59, 1.75, 2.03, 2.42). Anal. ($C_{16}H_{20}Br_2$) C, H, Br.

Aluminum Bromide Catalyzed Equilibration of 4 and 5. About 100 mg of pure 4 was dissolved in 10 mL of carbon disulfide containing 200 mg of freshly sublimed aluminum bromide, and the solution was stirred under nitrogen at 28 ± 0.5 °C in a water bath for 5 days; aliquot samples were analyzed by GLC from time to time. The equilibrium ratio was 13.2 ± 1.5 (4/5, average of 11 determinations).

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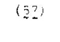
[65] Ōsawa, E. *Tetrahedron Lett.* **1974**, 115.

[66] One cannot expect the through-bond mechanism to operate to stabilize the 6,12-dication of 7, since the vacant orbitals at C_6 and C_{12} are orthogonal, in contrast to the situation in the diamantyl dications[23] and in the 1,4-bicyclo[2.2.2]octyl dication. See: Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829.

[67] The molecule 6 is rich in five-membered rings. Cleavage of the C_2–C_3 bond would lead to the unknown (C_2)-hexaquinane (57). See ref 10 for a known hexaquinane isomer.



(57)

[68] Gund, T. M.; Nomura, M.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2987.

Heptacyclo[8.6.0.0^{2,6}.0^{3,9}.0^{7,15}.0^{8,12}.0^{11,16}]hexadeca-4,13-diene (38.5 °C Melting Dimer of Cyclooctatetraene, 2). Precursor **2** was prepared according to the description of Jones.[13] Freshly distilled cyclooctatetraene (bp 93–94 °C at 185 torr, 366 g) was heated in 800 mL of *N*,*N*-diethylaniline at reflux temperature (220 °C) under a nitrogen atmosphere in the presence of hydroquinone for 64 h. The reaction mixture was distilled, and 204 g of a fraction boiling at 118–121 °C (0.5 torr) was collected. Redistillation gave 182 g of a fraction [bp 104 (0.25 torr)–114 °C (1.35 torr)] which solidified upon standing and showed 93% purity by GLC (50 ft × $^1/_{16}$ in., Carbowax, 135 °C; broad impurity peak immediately before that of **2**): NMR δ 6.55–5.55 (m with the strongest peak at 5.83, 4 H), 3.15–1.05 (m with the strongest peaks at 2.61, 12 H); IR 3042, 2900, 1615, 1605, 1365, 1250, 765, 732, 719, 692, 673 cm^{-1}. The melting point for the $AgNO_3$ 1:1 complex was 193.5–196 °C (from ethanol, lit.[13] mp 196 °C).

Heptacyclo[7.7.0.0^{2,5}.0^{3,15}.0^{4,12}.0^{6,10}.0^{11,16}]hexadecane (12). The 38.5 °C melting dimer of cyclooctatetraene (**2**, 20 g) was hydrogenated over 1 g of platinum oxide in 200 mL of a 1:1 petroleum ether/ethanol mixture in a Parr apparatus at room temperature. Hydrogen uptake was virtually complete after 3 min. After being shaken for 20 min more, the reaction mixture was filtered and the solvent evaporated. The semisolid residue was purified by distillation to give 18.9 g (95%) of a colorless fraction [bp 113–114 °C (1 torr)] which solidified in the receiver flask to give crystals: mp 44–47 °C (lit.[10] mp 44.5 °C); NMR δ 3.0–1.0 (m with the strongest peak at 1.79); mass spectrum, *m/e* 212 (M*), 91. Anal. ($C_{16}H_{20}$) C, H.

Rearrangement of 12. (a) With Aluminum Bromide Catalyst. Crystalline **12** (35 g) was heated with 50 g of sublimed, anhydrous aluminum bromide in 300 mL of carbon disulfide under reflux for 1.5 h with exclusion of moisture (calcium chloride tube). Workup of the reaction mixture gave 29 g (83%) of an oil. GLC analysis on a 3 mm × 2 m, Carbowax 20-M column at 150 °C showed a peak with short retention time [t_R (relative retention time) = 0.54, 8%] and a broad peak (t_R = 1.00, ~90%). A short-path distillation gave 2 g of a forerun, wherein the short retention time peak comprised one-third of the total area, and 26 g of a middle fraction, bp 97 °C (0.17 torr). GLC analysis of the latter with a Golay column (Apiezon L, 0.01 in. × 150 ft, 160 °C) revealed at least 14 peaks, of which three major components (relative retention times 0.54, 0.92, 1.00; relative areas 5, 14, 75) comprised 93% of the total peak area. GC/MS analyses of the two major components showed both predominent molecular ion peaks at *m/e* 212, but their fragmentation patterns were considerably different.

The distilled product mixture was subjected to bromination without further separation (see below).

(b) With Aluminum-Sludge Catalyst. In 5 mL of carbon disulfide was stirred 0.38 g of **12** with 0.4 mL of aluminum sludge at room temperature under an atmosphere of hydrogen bromide. GLC analyses of aliquot samples indicated that the starting material disappeared after 5 min. However, in addition to the product peaks mentioned above, a new peak with a longer relative retention time (t_R = 1.02, about 20%) appeared. After 1 h of reaction, the upper carbon disulfide layer was decanted, and the lower catalyst phase extracted with carbon disulfide. The combined carbon disulfide solutions were washed with water and dried over $CaCl_2$, and the solvent was evaporated to leave an oil. The crude products from several similar but larger runs were combined, and the new minor product having the highest retention time was collected by duplicate preparative GLC separations on a $^3/_8$ in. × 50 ft, 10% FFAP column at 245 °C, sublimed at 90 °C (4 torr), and recrystallized from acetone containing a small amount of petroleum ether to give pillar-shaped crystals: mp 110–111.5 °C; IR 2901, 2867, 1462, 1440 cm^{-1}; NMR δ 2.1–1.2 (m with the strongest peak at 1.71); mass spectrum, *m/e* 214 (M*), 91. Anal. ($C_{16}H_{22}$) C, H.

One of these crystals, subjected to X-ray analysis,[1b,22] revealed structure **5**.

Bromination of the Product Mixture from Rearrangement of 12. The distilled product mixture (11.8 g) was heated in 80 mL of liquid bromine under reflux for 18 h. Reducing the excess bromine with sodium bisulfite followed by extraction with dichloromethane gave 18 g of a mixture, which was subjected to column chromatography on alumina. Elution with hexane gave 13 g of a liquid fraction; elution with hexane–benzene then yielded 0.7 g of a crystalline fraction. The main liquid fraction was dissolved in acetone/methanol and cooled to give 11.5 g (71%) of colorless, needlelike crystals. One more recrystallization gave an analytical sample: mp 93.6–94.2 °C; NMR δ 3.1 (structured br s, 1 H), 2.84 (m, 2 H), 2.6–2.2 (m with prominent peaks at 2.46, 2.44, 7 H), 2.04 (m, 1 H), 1.96–1.40 (m with a prominent peak at 1.72, 8 H); mass spectrum, *m/e* 292, 290 (M*), 211 (M – Br). Anal. ($C_{16}H_{19}Br$) C, H, Br.

One of the monobromide crystals, subjected to X-ray diffraction analysis, gave structure **13** (see below).

The minor fraction was recrystallized from acetone/methanol to give cube-shaped crystals: mp 225–226 °C; NMR δ 3.2–1.5 (complex m); mass spectrum, *m/e* 291, 289 (M – Br), 210 (M – 2 Br), 209. Anal. ($C_{16}H_{18}Br_2$) C, H, Br.

One of the dibromide crystals, subjected to X-ray analysis, gave structure **14** (see below).

Reductive Debromination of 13 to Hydrocarbon 6. Winstein's dehalogenation method, lithium/*tert*-butyl alcohol in tetrahydrofuran,[69] proved effective. To a solution of 8.0 g of crystalline monobromide (**13**) in 160 mL of tetrahydrofuran containing 40 mL of dry *tert*-butyl alcohol was added 2 g of lithium wire cut in small pieces, and the mixture was heated under reflux and stirring for 2 h. The solution soon became turbid with inorganic precipitates, but some lithium metal remained undissolved at the end of reaction. The mixture was poured onto ice-water, this was extracted with ether, the combined extract was washed with brine and dried with sodium sulfate, and the solvent was evaporated. The residue was distilled to give 5.3 g (93%) of an oil [bp 95–98 °C (0.04 torr)] which solidified upon cooling to a mass: mp 35 °C; IR 2930, 2900, 1466, 1311 cm^{-1}; NMR δ 2.64 (br s, 2 H), 2.43 (br s, 6 H), 2.17 (s, 2 H), 2.07 (br s, 2 H), 1.73 (s, 8 H); mass spectrum, *m/e* (relative intensity) 212 (M*, 100), 130 (15.6), 117 (16.0), 91 (29.3), 80 (16.0), 79 (19.2), 77 (17.3). Anal. ($C_{16}H_{20}$) C, H.

Reductive Debromination of 14 to Hydrocarbon 7. On a smaller scale, debromination of 0.8 g of dibromide **14** was carried out under the same conditions as for that of **13**, except that 2 times as many equivalents of lithium were added. Workup afforded 0.35 g (79%) of crystalline hydrocarbon: mp 67–8 °C; NMR δ 2.05 (br s, 8 H), 1.51 (br s, 12 H); mass spectrum, *m/e* (relative intensity) 212 (M*, 100), 134 (15.0), 131 (15.0), 130 (18.2), 121 (25.7), 117 (21.9), 92 (16.9), 91 (36.9), 79 (18.2), 77 (17.5). Anal. ($C_{16}H_{20}$) C, H.

Diels–Alder Addition of 2 with 1,3-Cyclohexadiene. In a 100-mL pressure bottle were heated 22.2 g (0.10 mol) of **2** and 16.0 g (0.20 mol) of commercial 1,3-cyclohexadiene at 190 °C for 1 day under a nitrogen atmosphere in the presence of hydroquinone. Distillation of the reaction mixture gave 13.7 g (45%) of a fraction [bp 150–180 °C (0.1 torr)], which solidified upon standing. Recrystallization from ethanol/hexane afforded 7.1 g of needlelike crystals of **17**, mp 100–102 °C. An analytical sample (mp 104–105 °C) was obtained after three more recrystallizations: mass spectrum, *m/e* (relative intensity) 288 (22), 208 (100); NMR δ 6.3–5.8 (m, 4 H), 2.8–1.0 (m, 20 H); IR 3031, 2959, 2932, 2916, 2890, 2835, 1609, 708, 695, 680 cm^{-1}. Anal. ($C_{22}H_{24}$) C, H.

Hydrogenation of 17 to a $C_{22}H_{28}$ Precursor (19). Crude **17** (mp 97–103 °C, 28.4 g) was hydrogenated in a Parr apparatus with 1.4 g of platinum oxide in 250 mL of hexane and 100 mL of ethanol at room temperature for 1 h. At the end of the reaction, a white, solid mass had formed. After the solid was dissolved by the addition of 1 L of hexane and the catalyst removed by filtration, the solvent was distilled under vacuum to leave 27 g of crude product. Recrystallization from ethanol/hexane gave 18.6 g (65%) of plate-shaped crystals, mp 145.5–148.5 °C. An analytical sample (mp 147–149 °C) was obtained after four more recrystallizations from ethanol/hexane: mass spectrum, *m/e* 292 (base peak); NMR δ 9.0–7.0; IR 2949, 2919, 2905, 2858, 1467, 1253 cm^{-1}. Anal. ($C_{22}H_{28}$) C, H.

Rearrangement of 19 into Bastardane (8). Several test runs with a precursor hydrocarbon (**19**) to sludge catalyst ratio of 0.5 by weight gave the following results. After 2 h at room temperature, a new, intense NMR signal appeared at δ 8.2 in the

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(69) Howe, R. K.; Carter, P.; Winstein, S. *J. Org. Chem.* **1971**, *36*, 1316.

mixture after isolation (mp 90–100 °C), but the other features of the NMR remained unchanged. At 100 °C, the precursor disappeared completely after 2 h, and at least seven new GLC peaks appeared, all of which had shorter retention times than **19**. The product distribution did not change after 15 h of heating at 100 °C.

In a typical preparative run, 18 g of the precursor **19** (mp 145.5–148.5 °C) was dissolved in 50 mL of carbon disulfide. After the pressure bottle was purged with hydrogen bromide gas, 24 mL of freshly prepared aluminum bromide/*tert*-butyl bromide sludge catalyst was added. The bottle was tightly capped and the mixture stirred for 2 h at room temperature and then for 2 h at 100 °C. After the mixture cooled, the upper layer was decanted and the lower sludge catalyst layer washed with four 20-mL portions of carbon disulfide. The combined carbon disulfide solution was washed with water until neutral and dried with calcium chloride, and the solvent was evaporated to leave a dark oil. The crude product was dissolved in 10 mL of pentane and the solution cooled at −80 °C for 5 days. Crystals were collected and recrystallized from acetone/hexane to give 1.0 g (5.6%) of needlelike crystals, mp 100 °C.

In another run using the precursor melting at 142–145 °C, heating was continued at 100 °C for 9 h. The yield of crude product (mp 134 °C) was 8.5%.

An analytical sample of **8** was obtained after seven further recrystallizations and two vacuum sublimations at 140 °C (3 torr): fine pillar-shaped crystals; mp 144.5–146.5 °C; mass spectrum, *m/e* 292 (M* and base peak); IR 2944, 2925, 2896, 2876, 2860, 2835, 1458 cm^{-1}.[70] Anal. ($C_{22}H_{28}$) C, H.

Diels–Alder Addition of 2 with Methylcyclopentadiene to Give 19. Freshly prepared methylcyclopentadiene (9.6 g, 0.12 mol) and **2** (purity 92%, 22.4 g, 0.10 mol) were heated in a pressure bottle with a trace of hydroquinone under magnetic stirring for 20 h at 190–195 °C. Fractional distillation of the reaction mixture gave, after 1.4 g of a forerun, 30.9 g of a fraction with a boiling point of 135–188 °C (0.05 torr). The semisolid distillate was recrystallized from 1 L of ethanol containing 60 mL of hexane at −80 °C. The first crop, 15.0 g, was a sticky but analytically pure solid: mass spectrum, *m/e* (relative intensity) 288 (M*, 47.5), 273 (15.3), 209 (51.8), 208 (100), 167 (19.7), 165 (20.2), 141 (23.6), 129 (64.3), 128 (55.3), 115 (48.0), 91 (23.6), 80 (67.8); NMR δ 6.5–5.7 (octet, J = 7 Hz, 2 H), 5.46 (br s, 1 H), 3.0–0.95 (m, 21 H); IR 3036, 2937, 1628 (w), 1616, 1447, 1370, 698, 685 cm^{-1}. Anal. ($C_{22}H_{24}$) C, H.

Hydrogenation of 18 to a $C_{22}H_{28}$ Precursor (20). The adduct **18** (15.0 g, 0.052 mol) was hydrogenated over 0.7 g of platinum oxide in 70 mL of ethanol and 100 mL of hexane in a Parr apparatus at room temperature for 1 h. Workup of the mixture as described above and recrystallization of the crude product (13 g) gave 3.6 g of fine needles, mp 120–138 °C. Concentration of the mother liquor to two-thirds of its volume afforded a second crop of 1.4 g of ill-shaped cubic crystals, mp 75–100 °C (combined yield 33%). An analytical sample, mp 144–156 °C (the wide range reflecting a mixture of isomers), was obtained by recrystallization of a portion of the first crop: mass spectrum, *m/e* (relative intensity) 292 (M*, 100), 250 (23.0), 237 (38.5), 211 (34.6), 91 (26.0); NMR δ 2.9–0.9 (m); IR 2921, 2875, 1460, 1378, 1264 cm^{-1}. Anal. ($C_{22}H_{28}$) C, H.

Rearrangement of 20 into Bastardane (8). The procedure described for the rearrangement of **19** was followed. Treatment of **20** with aluminum-sludge catalyst at room temperature resulted in complete disappearance of **20** to produce a mixture of at least two intermediates having GLC retention times shorter than **20** and showing two methyl proton NMR signals at δ 1.06 and 0.88 as well as the strong "adamantanoid" proton signals at δ 1.70. Removal of components of short retention times by preparative GLC and cooling of the resulting mixture failed to give crystals. The oil was again dissolved in carbon disulfide, charged in a pressure bottle with fresh aluminum-sludge catalyst, and heated at 100 °C. After 16 h, **8** started to form as judged by GLC. However, even after 60 h of heating, only about half of the intermediates had isomerized. A small sample of the final mixture was separated by preparative GLC; one of the components was confirmed to be **8** by its NMR spectrum.

X-ray Crystallographic Analyses. The crystal data are as follows. compound **13**: $C_{16}H_{19}Br$; mol wt 291.2; monoclinic; a = 6.562 (2) Å, b = 8.102 (3) Å, c = 23.058 (6) Å, β = 95.58 (3)°, U = 1220.1 Å^3, d_c = 1.585 g/cm^3, z = 4, $F(000)$ = 600, μ(Cu Kα) = 43.7 cm^{-1}; systematic absences, $h0l$ for l odd, $0k0$ for k odd; space group $P2_1/c$.

Compound **14**: $C_{16}H_{18}Br_2$; mol wt 370.1; monoclinic; a = 11.899 (4) Å, b = 11.757 (4) Å, c = 9.577 (3) Å, β = 100.16 (5)°, U = 1318.8 Å^3, d_c = 1.864 g/cm^3, z = 4, $F(000)$ = 736, μ(Cu Kα) = 76.8 cm^{-1}; systematic absences, hkl for $h + k$ odd, $h0l$ for l odd; space group $C2/c$.

The sizes of crystals of **13** and **14** used for X-ray measurements were 0.4 × 0.3 × 0.3 and 0.3 × 0.3 × 0.3 mm^3, respectively. Cell dimensions and reflection intensities were measured on a Rigaku Denki four-circle diffractometer using LiF-monochromated Cu Kα radiation (λ = 1.5418 Å). Intensities of reflections with 2θ values up to 140° were collected by the θ–2θ continuous-scan method with a 2θ scan rate of 1°/min. Three standard reflections, measured at intervals of every 62 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors but not for the absorption or the extinction effect. A total of 2120 reflections of compound **13** above the $3\sigma(F)$ level and 1213 reflections of compound **14** above the $\sigma(F)$ level were used for the subsequent structure analyses.

The structure of compound **13** was elucidated by the heavy-atom method and that of compound **14** by the Monte Carlo direct method[71] using the ten strongest reflections as a starting set; the first random-phase set gave a correct solution. Approximate coordinates of nonhydrogen atoms were refined by the block-diagonal-matrix, least-squares method, at first with isotropic and then with anisotropic temperature factors. Difference Fourier maps revealed the locations of all hydrogen atoms. For each compound, the least-squares refinement was repeated with the inclusion of the hydrogen atoms and the anomalous dispersion effects of bromine atoms.[72] The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma(F)^2 \exp(AX^2 + BY^2 + CXY + DX + EY)]$, where $X = |F_o|$ and $Y = (\sin\theta)/\lambda$. The intensity data were grouped with constant intervals along two coordinates, X and Y. The coefficients, A, B, C, D, and E, were determined by the least-squares fit so as to give as equal values of $\langle w|\Delta F|^2\rangle$ for all the groups as possible. The final R values for compounds **13** and **14** are 4.3 and 3.5%, respectively.

Stereodrawings of molecular structures of **13** and **14** are given in Figures 1 and 2. Bond lengths, valence and dihedral angles, atomic coordinates, and structural factors are given as supplementary material.[61b]

Results of X-ray analysis of **5** have been published.[22] Preliminary results of the X-ray analysis of **8** have also been described.[1a] The crystal data for **8** are as follows: monoclinic, a = 6.328 Å, b = 22.544 Å, c = 12.656 Å, β = 122.56°, space group $P2_1/c$. Final structural parameters and atomic coordinates appear in the supplementary material.[61b,73]

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Registry No. **1**, 38445-87-3; **2**, 14339-83-4; **4**, 73635-82-2; **5**, 29571-69-5; **6**, 61214-74-2; **7**, 73635-83-3; **8**, 20497-81-8; **9**, 59078-40-9; **11**, 73635-84-4; **12**, 61349-54-0; **13**, 61173-84-0; **14**, 73635-85-5; **15**, 73635-86-6; **17**, 73635-87-7; **18**, 73635-58-2; **19**, 73635-88-8; **20**,

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73635-59-3; **38**, 73635-89-9; **39**, 73635-90-2; **40**, 73635-91-3; **41**, 73635-92-4; **42**, 73635-93-5; **43**, 73635-94-6; **54**, 73635-95-7; **55**, 27745-90-0; **56**, 73635-96-8; cyclooctatetraene, 629-20-9; 1-diamantanecarboxylic acid, 30545-18-7; 1-bromodiamantane, 30545-17-6; 1,3-cyclohexadiene, 592-57-4; methylcyclopentadiene, 26519-91-5; bicyclo[3.2.1]octane, 6221-55-2.

Supplementary Material Available: Bond lengths (Table IV); valence angles (Table V); dihedral angles (Table VI) of **13**, **14**, and **8**, including corresponding values calculated by the MM2 method for **6**, **7**, and **8**; standard deviations of the calculated structural parameters of **6**, **7**, and **8** from the observed values (Table VII); listings of final atomic coordinates of **13**, **14**, and **8** (Table VIII); thermal parameters (Tables IX and X) (17 pages). Ordering information is given on any current masthead page.

Novel Copper Complexes of Chiral Diphosphines: Preparation, Structure, and Use To Form Rhodium Complex Catalysts for Chiral Hydrogenations

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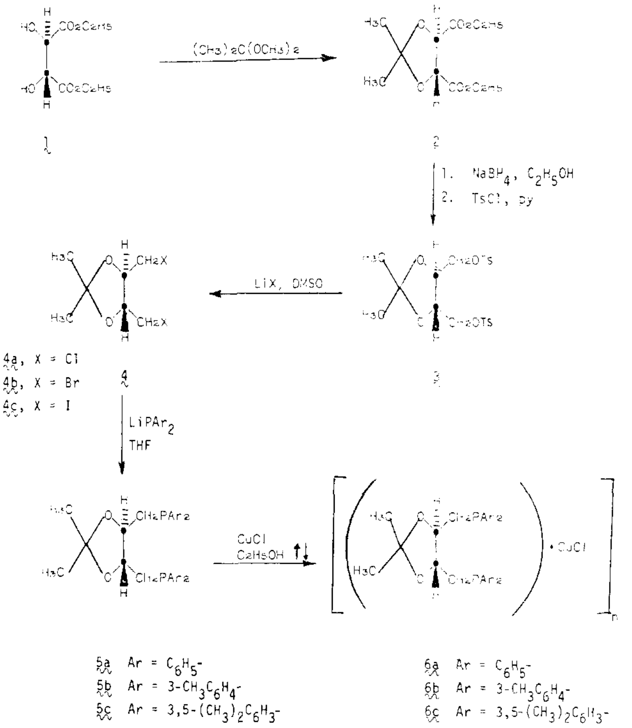
Treatment of chiral diphosphines **5a–c** and **13** ("DIOP", aryl derivatives and related substances) with CuCl in boiling ethanol gave complexes having the composition [Cu(diphosphine)(Cl)]$_n$, **6a–c** and **11**. Crystallizations of **6a–c** from crude 70–80% pure **5a–c** and decomposition of the complexes by ammonia gave the pure diphosphines. Ligand exchange between **6a–c** and [Rh(diolefin)(Cl)]$_2$ in methanol at 23 °C was rapid and complete. Treatment of the resulting solutions with H_2 gave active catalysts for asymmetric hydrogenations.

Homogeneous asymmetric hydrogenations catalyzed by rhodium complexes of chiral chelating diphosphines provide attractive syntheses of many enantiomeric substances.[2] A frequent problem, however, is obtention of the catalyst, especially preparation, isolation, and purification of the chiral phosphine ligand. We describe here a new method of preparing catalysts containing phosphines **5a–c** (DIOP derivatives)[3,4] bound to rhodium, which minimizes the need to isolate and purify the free phosphines. The method is based on the discovery that impure **5a–c**, such as are obtained as crude products of typical synthetic procedures, react with cuprous halides to form complexes which may be purified readily and which will transfer their diphosphine ligand quantitatively to rhodium under mild conditions.

The objective of our work was a practical synthesis of "DIOP" derivatives **5a–c**. The synthesis of **5a–c** outlined in Scheme I is essentially that first described by Kagan et al.[3,5] Synthesis of **3** was improved by replacing $LiAlH_4$[6] with $NaBH_4$ to reduce acetonide diester **2** to the corresponding diol (not shown). The diol was converted directly to **3** in 73% overall yield from **2**. The $NaBH_4$ reduction of the dimethyl ester analogue of **2** was unsatisfactory, probably because the methanol released catalyzes the decomposition of $NaBH_4$.[7] It was possible to condense **3** directly with alkali metal phosphides, but the several byproducts formed in these reactions made isolation of the noncrystalline **5b**[8] and **5c**[4] difficult. Cleaner reaction mixtures were obtained in condensations of lithium diaryl phosphides with dichloride **4a**,[3] which was easily obtained in high yield from **3**. Crude **5b** and **5c** obtained from **4a** could be purified by chromatography. A more attractive procedure, however, was to treat the crude diphosphine with cuprous chloride in hot ethanol solutions. Copper(I) complexes of the formula **6** precipitated from such solutions on cooling. Recrystallizations of **6** and decompositions with NH_3 gave the pure diphosphines **5** without chromatographic separations.[9]

Scheme I



It was also found that combination of **6** with [Rh(diolefin)(Cl)]$_2$[10] in methanol resulted in complete transfer of the diphosphine ligand from copper to rhodium. Thus,

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