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Fused and Bridged Tetracyclic C_{13} and C_{14} Adamantanes. Synthesis of Methyl-2,4-ethano-, 1,2-Trimethylene-, 2,4-Trimethylene-, and 1,2-Tetramethyleneadamantane

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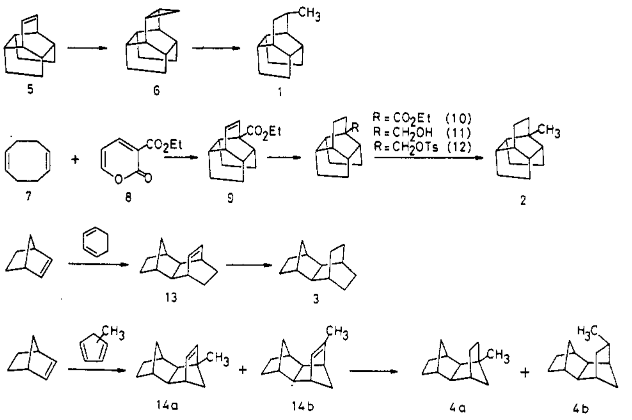
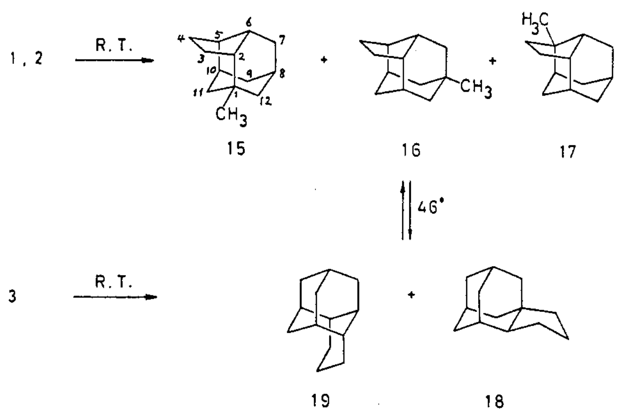
Carbocation isomerization of methyltetracyclododecanes **1** and **2** gives an equilibrium mixture (5:3:2) of 1-, 2-, and 8-methylethanoadamantanes **15**–**17**. By contrast, a tetracyclotridecane (**3**) which does not contain a methyl group rearranges under mild conditions to a mixture (97:3) of 1,2- and 2,4-trimethyleneadamantane (**18** and **19**). Under more vigorous conditions, the two sets of products interconvert, but determination of an equilibrium composition is hampered by extensive fragmentation with the formation of alkyladamantanes. Isomerization of a tetracyclotetradecane precursor (**34**) leads to 1,2-tetramethyleneadamantane (**36**) as the sole product. The products of rearrangement (**15**–**19** and **36**) are consistent with the results of empirical force field calculations. It is suggested that such calculations might be relied upon to predict the most stable isomers when kinetic barriers or extensive side reactions prevent an accurate experimental determination of the equilibrium composition. Possible rearrangement mechanisms for the conversions **3** → **18**/**19** and **34** → **36** were analyzed by means of the isomerization graph composed of all isomers connected by 1,2 alkyl shifts. Plausible pathways involving eleven steps for isomerization of **3** into **18** and eight steps for the isomerization of **34** into **36** are identified.

Since the discovery of the adamantane rearrangement,[3] a large number of diamond hydrocarbons[4] have been prepared by thermodynamically controlled isomerization of appropriate polycyclic precursors.[5] It is of synthetic and theoretical importance to extend such rearrangement studies to additional polycyclic C_nH_m hydrocarbons.[6] Among tetracycloalkanes, $C_{11}H_{16}$[7] and $C_{12}H_{18}$[8] isomers have already been examined. We now report the behavior of $C_{13}H_{20}$ and $C_{14}H_{22}$ tetracyclic systems.[9]

Scheme I



Scheme II



Not every hydrocarbon can be converted to the corresponding "stabilomer"[6] by carbocationic isomerization.[8,9a] For some structures, rearrangement pathways avoiding prohibitively high energy barriers are not available. It is therefore desirable to investigate several isomeric hydro-

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[2] Part 12 of "Application of Potential Energy Calculations to Organic Chemistry" (formerly "Application of Force Field Calculations to Organic Chemistry") from Hokkaido. Part 11: Ōsawa, E.; Furusaki, A.; Hashiba, N.; Matsumoto, T.; Singh, V.; Tahara, Y.; Wiskott, E.; Farcasiu, M.; Iizuka, T.; Tanaka, N.; Kan, T.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 2985. Part 10: Ōsawa, E.; Engler, E. M.; Godleski, S. A.; Inamoto, Y.; Kent, G. J.; Kausch, M.; Schleyer, P. v. R. *Ibid.* **1980**, *45*, 984. Part 9: Ōsawa, E. *J. Am. Chem. Soc.* **1979**, *101*, 5523.

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[7] (a) Godleski, S. A.; Schleyer, P. v. R.; Ōsawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 38. (b) Godleski, S. A.; Schleyer, P. v. R.; Ōsawa, E.; Inamoto, Y.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 2596.

[8] (a) Farcasiu, D.; Wiskott, E.; Ōsawa, E.; Thielecke, W.; Engler, E. M.; Slutsky, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 4669. (b) Ōsawa, E.; Engler, E. M.; Godleski, S. A.; Schleyer, P. v. R.; Inamoto, Y.; Kent, G. J. *J. Org. Chem.* **1980**, *45*, 984. (c) Berman, S. S.; Denisov, Y. V.; Murakhovskaya, A. S.; Stepanyants, G. V.; Petrov, A. A. *Neftekhimiya* **1974**, *14*, 3.

[9] Preliminary accounts: (a) Gund, T. M.; Ōsawa, E.; Williams, V. Z., Jr.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2979. (b) Ōsawa, E. *Tetrahedron Lett.* **1975**, 4403.

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Table I. Relative Free Energies of Tetracyclotridecane Isomers as Calculated by Use of the MM2 Force Field

compd	ΔH_f°(calcd), kcal/mol	$\Delta\Delta H_f$,[a] kcal/mol	entropy correction, eu		$-T\Delta\Delta S$,[d,e] kcal/mol		$\Delta\Delta G$(calcd),[e] kcal/mol		$\Delta\Delta G$(obsd),[f] kcal/mol	
			A[b]	B[c]	25 °C	46 °C	25 °C	46 °C	25 °C	46 °C
15	−32.25	−0.01	1.38 (*dl*)	−2.68	0.79	0.85	0.78	0.84	0.00[g]	−0.78
16	−33.01	−0.77	−1.38 ($\sigma = 2$)	−2.68	1.62	1.73	0.85	0.96	0.30	−0.50
17	−31.53	0.71	1.38 (*dl*)	−2.68	0.79	0.85	1.50	1.56	0.54	−0.27
6-MeEA[h]	−30.28	1.96	−1.38 ($\sigma = 2$)	−2.68	1.67	1.73	3.63	3.69		
18	−32.24	0.00	1.38 (*dl*)	0.00	0.00	0.00	0.00	0.00	0.00[i]	0.00
19[j]	−31.25	0.99	−1.38 ($\sigma = 2$)	1.54	−0.36	−0.38	0.63	0.61	1.96	0.06

[a] Relative to an arbitrary standard of 18. [b] Symmetry and heat of enantiomer corrections. [c] Group increment entropy corrections based on Benson's gas phase values: $2CH_2 \rightarrow CH + CH_3$, −0.50, Me correction −2.18, net correction −2.68; $2CH \rightarrow C + CH_2$, −1.54; $CH_2 + CH \rightarrow CH_3 + C$, −2.04, net correction −4.22. [d] $S = A + B$. [e] Relative to 18. [f] Based on the composition of a long-reaction mixture with extensive side reactions taking place (see text). [g] Standard for methylated series. [h] 6-Methyl-2,4-ethanoadamantane (6-methyltetracyclo[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecane).[8b] [i] Standard for the non-methylated series. [j] The contribution from the boat conformation (10%) is taken into account (see Table II).

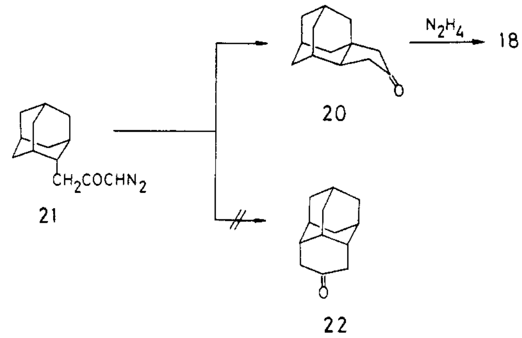
carbons as starting materials. If at least two of these give the same products, it is likely that thermodynamically the most stable isomer is at hand. As in earlier works,[7,8ab] empirical force field calculations[10] were used as an auxiliary tool for steric interpretations.

Results and Discussion

Tetracyclotridecanes. Four nondiamondoid $C_{13}H_{20}$ hydrocarbons (**1**–**4**) were employed in this study. Scheme I outlines the syntheses of these precursors. Rearrangements conducted at room temperature, either with $AlBr_3$ catalyst or its "sludge" with *tert*-butyl bromide,[9a] did not lead to the same products from all the precursors. As shown in Scheme II, starting materials containing methyl groups (**1** and **2**) gave an equilibrium mixture of three isomeric methylethanoadamantanes (**15**–**17**), which were separated by preparative GLC and identified by comparison with authentic materials (**15** and **17**)[8b] or by agreement between measured and calculated ^{13}C NMR chemical shifts (**16**).[8b] Apparent equilibrium (5:3:2 **15**/**16**/**17**) was reached in 1 h at room temperature.

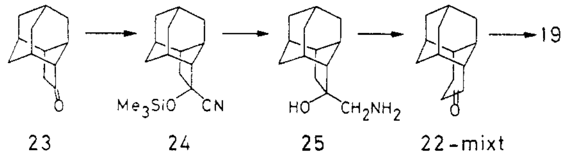
Treatment of **3** with either catalyst gave 1,2-trimethyleneadamantane (**18**) as the main product. With aluminum bromide at room temperature, virtually no fragmentation to alkyladamantane occurred. Three peaks due to intermediates were observed in GLC during the reaction; the most rapidly formed intermediate, identified as 2,4-trimethyleneadamantane (**19**), could be isolated by preparative GLC. At a longer reaction time, the concentration of **19** in the mixture decreased to about 3%. Treatment of pure (synthetic) **18** with aluminum bromide led to a 96:4 mixture of **18** and **19**.

The structures of **18** and **19** were confirmed by independent syntheses. For **18**, the corresponding ketone, **20**, has been described previously.[11] We obtained **20** by decomposition[12] of 2-adamantylmethyl diazomethyl ketone (**21**). The possible alternative product, the six-membered-ring ketone **22**, could not be positively identified in the reaction mixture. This is consistent with previous observations of preference for five-membered- over six-membered-ring formation in such carbenoid diazo ketone cyclization.[13] Wolff–Kishner reduction of **20** gave **18** (eq 1).



(1)

The other trimethyleneadamantane, **19**, was prepared by starting from the known[8a] 2,4-ethanoadamantanone (**23**). The adduct (**24**) of the ketone with trimethylsilyl cyanide[14,15] was reduced with lithium aluminum hydride to give an amino alcohol (**25**), which gave by Demjanov ring enlargement a mixture of six-membered ketones (**22-mixt**) in similar quantities (1:0.6). Wolff-Kishner reduction of the ketone mixture led to the desired hydrocarbon **19** (eq 2).[16] The new bridged adamantane fortuitously exhibits



(2)

a single ^1H NMR signal at δ 1.73. Bicyclo[3.3.1]nonane and diamantane behave similarly in this respect.[5]

Interconversion between the two groups of products (**15**–**17**, **18**, and **19**) occurred upon refluxing **1**, **2**, or **3** with the sludge catalyst in carbon disulfide. After 30 h, the composition of the mixture **15**/**16**/**17**/**18**/**19** was determined to be 42:27:19:8:3.[18] However, extensive side re-

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(10) (a) Reviews: Hursthouse, M. R.; Moss, G. P.; Sales, K. D. *Ann. Rep. Prog. Chem., Sect. B* **1978**, *75*, 23. Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. Kitaigorodsky, A. I. *Chem. Soc. Rev.* **1978**, *7*, 133. Ōsawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117. Ermer, O. "Aspekte von Kraftfeldrechnungen"; Wolfgang Baur Verlag: München, 1981. (b) MM2 force field: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *11*, 395.

(11) Chakrabarti, J. K.; Szinai, S. S.; Todd, A. *J. Chem. Soc. C* **1970**, 1303.

(12) Wenkert, E.; Mylari, B. L.; Davis, L. C. *J. Am. Chem. Soc.* **1968**, *90*, 3870.

(13) Farcasiu, D.; Bohm, H.; Schleyer, P. v. R. *J. Org. Chem.* **1977**, *42*, 96.

(14) Ernst, B.; Ganter, C. *Helv. Chim. Acta* **1978**, *61*, 1775.

(15) In view of the stereoselectivity in the reaction of **23**,[13] the attack of cyanide is assumed to take place from the exo side.

(16) Ring enlargement of **23** by a Wittig reaction followed by thallium(III) oxidation was found unsuitable as the method of preparing **19**.[17]

(17) Farcasiu, D.; Schleyer, P. v. R.; Ledlie, D. B. *J. Org. Chem.* **1973**, *38*, 3455.

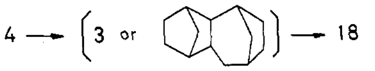
(18) The ratio **18**/**19** in the reaction mixture after long hours at 46 °C (3:1 compared with 24:1 in the steady-state mixture at 25 °C) appears abnormally low. The very small GLC peak of **19** in the 46 °C sample is severely influenced by the tailing from the large peaks of methylethanoadamantanes and thus gives an inaccurate analysis.

actions occurred under these conditions (alkyladamantanes account for about one-third of the reaction mixture), and the rates of destruction of **15–19** probably are different. Hence, the observed composition may not represent the equilibrium ratios accurately. The free energies deduced from the isomerization results are compared with values calculated by use of the MM2 force field[10b] in Table I. We chose MM2 because of its superior performance for adamantanoid hydrocarbons to other force fields.[19] The observed free energies of isomerization at room temperature, where side reactions are unimportant, agree reasonably well within the methylated (**15–17**) and nonmethylated (**18, 19**) series. Nevertheless, the calculated relative stabilities of isomers do not agree with the product distribution observed at 46 °C. In view of the reasonable agreement of calculations with experiments within each series at 25 °C, the calculated stabilities of **15–17** relative to that of **18** can be considered more reliable than the values observed under conditions where extensive side reactions are taking place.[20]

Treatment of the mixture of **4a** and **4b** with sludge catalyst at room temperature led to the isomerization of **4b** into **4a** as the only product observed. Representation **4a** is the most stable structure deduced by empirical force field calculations.[21]

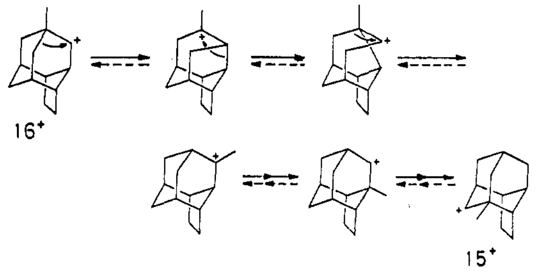
A number of mechanistic features of the rearrangement of these $C_{13}H_{20}$ hydrocarbons deserve comment. The difficult interconversion among methylethanoadamantanes (**15–17**) and trimethyleneadamantanes (**18, 19**) indicates that changes in the degree of branching of a polycyclic system (like the extrusion of a methyl group from a ring or the incorporation of a methyl carbon into a ring) are steps requiring higher activation energies.

Precursor 4 did not rearrange into **15–17** under our standard conditions. Two reasons appear responsible: the difficulty of methyl incorporation as mentioned above and the inability of the parent system of 4, with no methyls, to rearrange. The latter effect has already been recognized experimentally and analyzed theoretically.[8a,22] It is reported that, under more vigorous conditions, the material isolated from 4 was 18 (eq 3).[8c]

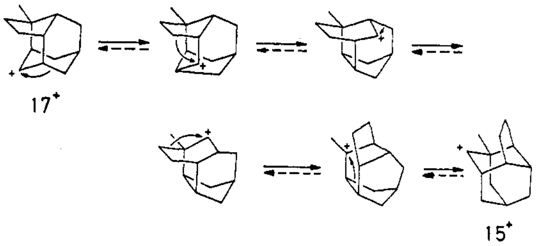


(3)

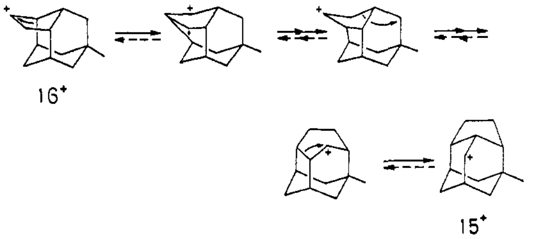
The mechanism of isomerization of the tetracyclic parent skeleton of **1** and **2** into 2,4-ethanoadamantane has been rationalized.[8a] The presence of a methyl group should not alter this basic pathway. The migration of methyl group in the products ($15 \rightleftarrows 16 \rightleftarrows 17$) could involve interconversion between adamantyl and protoadamantyl cations as in the 1-methyl- and 2-methyladamantane isomerization[23] (eq 4) or could proceed by more extensive skeletal rearrangements (e.g., eq 5 and 6).[24]



(4)



(5)



(6)

The "tree method"[25a] of searching for the most plausible rearrangement pathway was applied to the rearrangement of **3** into **18** and **19**. In this method, all possible products expected to result from 1,2 alkyl shifts from a given intermediate are examined in terms of two factors: relative stabilities of products and bond alignments in the alkyl shifts. The product indicated to be most favorable is taken as the next intermediate, and the procedure is repeated until **18** is reached. As in the studies of tricycloundecane rearrangement mechanisms,[25c,d] evaluation of the stabilities of transient carbocations was omitted for simplification. This implies the assumption that all necessary carbocation intermediates are energetically accessible under thermodynamically controlled conditions.

Figure 1 gives some of the results obtained by this method. Given under each structure is its heat of formation calculated by using the MM2 force field.[10b] Another criterion, the bond alignment angle for each 1,2 alkyl shift, is given on the lines connecting the structures. For nonconcerted mechanisms involving a carbocation intermediate,[25c] the bond alignment angle is considered to be the dihedral angle, R–C–C^+–p, in which R represents the migrating group and C^+–p the axis of the unoccupied p orbital. This dihedral angle was estimated from the minimum-energy structure of the neutral intermediate

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[19] Clark, T.; Knox, T. M.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404.

[20] Members of each group of $C_{13}H_{20}$ adamantanoid hydrocarbons, **15–19**, have apparently been isolated from petroleum: Weidenhoffer, Z.; Hala, S. *Sb. Vys. Sk. Chem.-Tekhnol. Praze, Tecknol. Paliv.* 1971, *D22*, 5. See also ref 8.

[21] See the microfilm edition of this article for supplementary material.

[22] Dr. D. Lenoir has made these observations independently; private communication. See also: Engel, P.; Nowacki, W.; Slutsky, J.; Grubmüller, P.; Schleyer, P. v. R. *Chem. Ber.* **1979**, *112*, 3566.

[23] Majerski, Z.; Schleyer, P. v. R.; Wolf, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 5731. Majerski, Z.; Liggero, S. H.; Schleyer, P. v. R.; Wolf, A. P. *J. Chem. Soc., Chem. Commun.* **1970**, 1596.

[24] In eq 4 and 5, the carbon atoms of the ethano bridge and of the adamantane skeleton do not interchange during the methyl migration. In eq 6, the ethano bridge and the adamantane skeleton scramble their carbon atoms. Differentiation between these possibilities is amenable to experimental examination.

[25] (a) Gund, T. M.; Schleyer, P. v. R.; Gund, P.; Wipke, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 743. (b) Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 5769. (c) Ōsawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *Ibid.* **1977**, *99*, 5361. (d) Takaishi, N.; Inamoto, Y.; Aigami, K.; Fujikura, Y.; Ōsawa, E.; Kawanisi, M.; Katsushima, T. *J. Org. Chem.* **1977**, *42*, 2041.

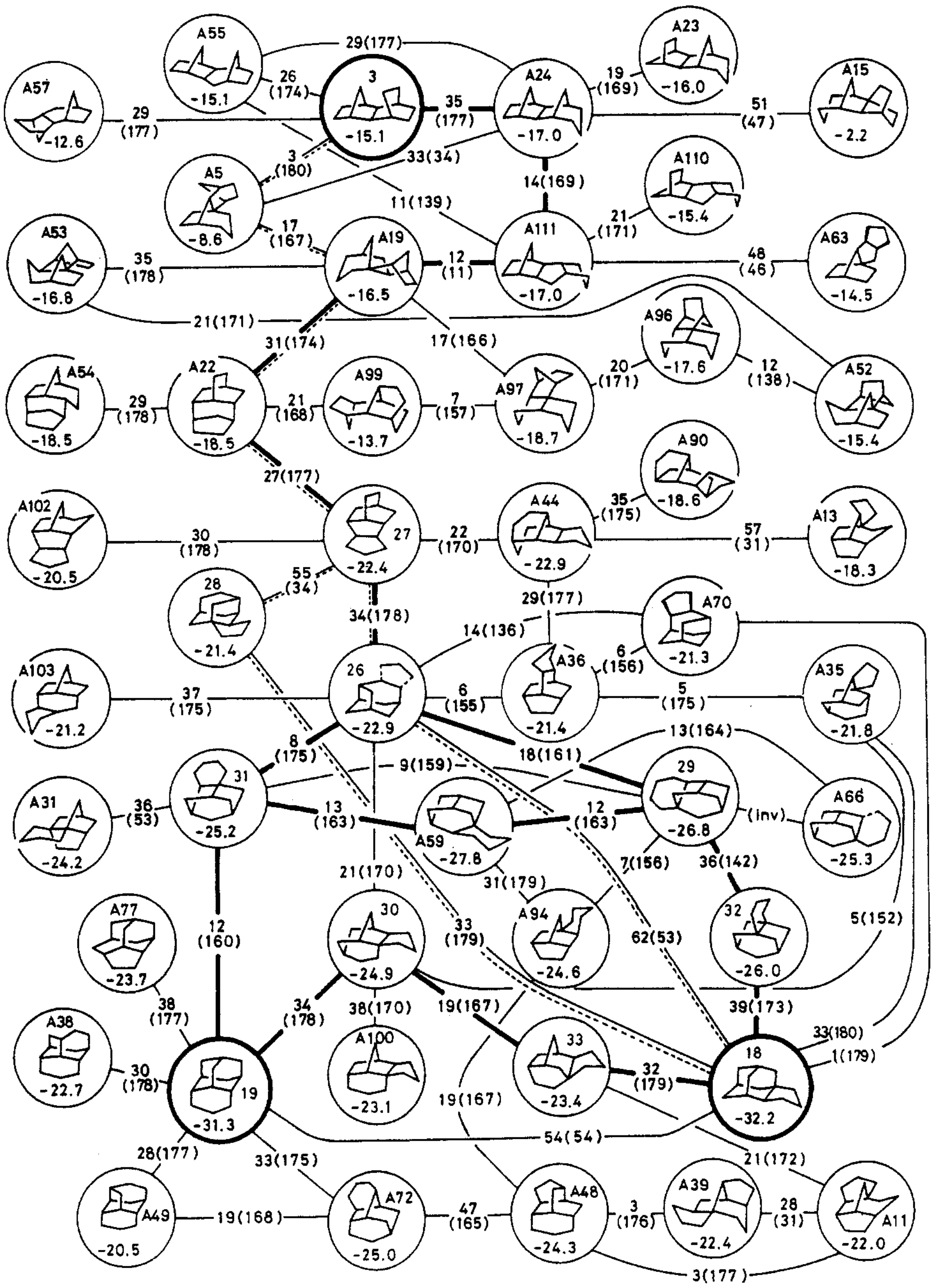

Figure 1. Simplified rearrangement graph of tetracyclotridecane (**3** → **18**, **19**) based on the "tree search" method. Structure numbers refer to Tables I and IV. Values under each structure are the MM2-calculated heats of formation in kcal/mol. Values on each reaction arrow are the estimated dihedral angle involved in the 1,2 alkyl shift. The unparenthesized angle value refers to the stepwise mechanism and the parenthesized value to the concerted mechanism of bond migration. A thick line indicates the most plausible pathway, and a dotted line corresponds to the pathway predicted by the graph-theoretical disource propagation method.

(unparenthesized number in Figure 1).[26] For a concerted 1,2 shift[25c] to be most favorable, the dihedral angle R–C–C–H should be close to 180°. This angle was estimated directly from the calculated minimum-energy structures (parenthesized number).[21]

Analysis leads to *exo*,*exo*-4,5-trimethyleneprotoadamantane (**26**) as a key intermediate. The selection of **26** from its immediate precursor **27** illustrates our procedure. The two most favorable rearrangements from **27** are those leading to **26** and **28**; both of these can then give **18** in a few steps (Figure 1). In addition to the slightly greater calculated stability of **26** ($\Delta H_f = -22.9$ kcal/mol) relative to **28** (−21.4 kcal), the bond alignment definitely favors **27** → **26** (34° for a nonconcerted and 178° for a concerted mechanism) over **27** → **28** (55° and 34°, respectively).

It appears unlikely that **26** leads directly to **18** in view of the unfavorable bond alignments predicted (62° and 53°). Instead, three pathways leading to **29**–**31**, respectively, should be most favorable. Whereas both **29** and **30** lead to **18** in two steps, these pathways involve either large dihedral angles (**29** → **32** → **18**) or unstable intermediates (**30** → **33** → **18**). One-step formation of **19** from **31** should be more favorable. This explains the observed preferential formation of **19** prior to **18**. Direct conversion of **19** into

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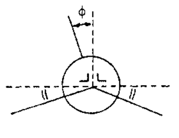
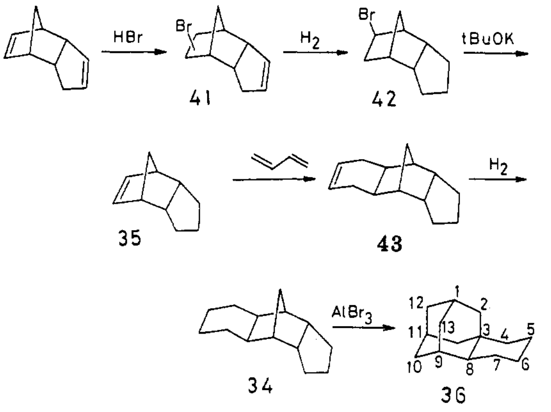
[26] This approximation was necessitated by the lack of carbonium ion parameters in the MM2 force field. The angle (ϕ) was estimated from the two alkyl bonds in the neutral molecule, rather than from the C–H bond to be broken.



18 is prohibited by the large bond shift angle (54°). Our failure to detect any intermediate in the conversion of **18** to **19** is in accord with the calculations (Figure 1) which indicate that there are no intermediates having stabilities comparable (±2 kcal) to those of **18** and **19**.

Alternatively, the shortest possible pathway from **3** to **18** can be obtained by straightforward application of the graph-theoretical "disource propagation method" wherein no energy factors are taken into account.[27] This pathway is given in Figure 1 by broken lines but only partly overlaps with the most plausible pathway mentioned above.

Tetracyclotetradecane. In the $C_{14}H_{22}$ series, only one precursor, tetracyclo[6.5.1.$0^{2,7}$.$0^{9,13}$]tetradecane (**34**), was examined. This hydrocarbon was prepared by a Diels–Alder addition of butadiene to dihydrodicyclopentadiene **35**[28-30] followed by hydrogenation (eq 7).



(7)

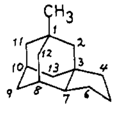
The precursor **34** rearranged smoothly on treatment with aluminum bromide in carbon disulfide to 1,2-tetramethyleneadamantane (**36**).[31] Neither fragmentation nor disproportionation product was detected in any significant quantity, but at least four intermediates were observed in the course of rearrangement. The most abundant one, isolated by preparative GLC as a liquid, exhibited 14 signals in the ^{13}C NMR spectrum (one quaternary, four tertiary, and nine secondary carbon atoms), but the structure was not established.

Table II. MM2 Calculations of 2,4-Trimethyleneadamantane (**19**) and Related Hydrocarbons

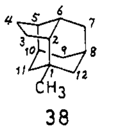
	$\Delta H_f°$, kcal/mol	strain energy, kcal/mol
bicyclo[3.3.1]nonane, CC[a]	−30.48	12.33
BC[a]	−28.16	14.66
19, chair	−31.24	31.41
boat	−29.94	22.71
chair/boat transition state[b]	−27.0	25.6
12-*endo*-Me-**19**, chair	c	c
boat	−30.50	29.56

[a] CC, chair–chair; BC, boat–chair; taken from ref 34a. [b] Based on the simultaneous drive calculations of two dihedral angles, ϕ(3-4-5-6) and ϕ(2-3-4-5). The transition state was estimated from intrapolation of the energy vs. dihedral angle curve, wherein endocyclic dihedral angles along the flipping six-membered ring are 64.2°, −27.2°, −10.0°, 10.0°, 27.2°, and −64.2°. [c] No energy-minimum chair conformation could be located.

The product **36** has been expected as the stabilomer among $C_{14}H_{22}$ isomers[6] and has previously been obtained as a disproportionation product in rearrangements of several $C_{14}H_{20}$ hydrocarbons containing strained rings.[9a,13,32,33] The structure of **36** has been established by an independent synthesis starting with ketone **20**.[17] Other low-energy $C_{14}H_{22}$ isomers are the methyl-1,2-trimethyleneadamantanes and the dimethyl-2,4-ethanoadamantanes. MM2 calculations of all possible substitutional isomers of these species[21] predict that none of them is more stable than **36**. According to the calculations, **37** and **38** are the most stable representatives of the two methylated and fused adamantane families mentioned above, but their calculated heats of formation are both nearly 3 kcal/mol higher than that of **36** ($\Delta H_f = -43.79$ kcal/mol). It is thus reasonable that neither **37** nor **38** was found in the rearrangement mixture from **34**.

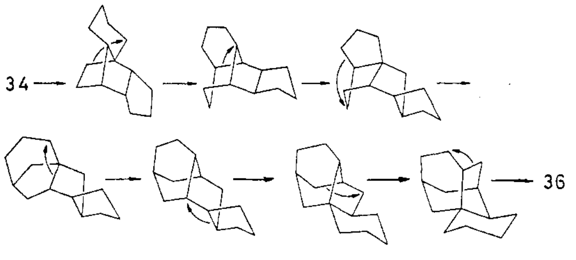


37



38

A search for the most plausible rearrangement pathway of the isomerization of **34** into **36** by the "tree method" revealed a rather flat energy hypersurface near **36**. Several almost equally favorable pathways emerged. One of these is given in eq 8.[21] Once again, the shortest possible pathway generated by the purely graph-theoretical algorithm[27] involved high-energy intermediates; there was little correspondence with the pathway deduced by "tree search".



(8)

Structural Features of Tetracyclotridecane and Tetracyclotetradecane Stabilomers. 2,4-Trimethyleneadamantane (**19**) may be regarded as a bicyclo[3.3.1]nonane half-locked into a fixed conformation by fusion with the adamantane unit.[34] The constraint should

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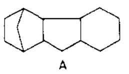
(27) Tanaka, N.; Kan, T.; Iizuka, T. *J. Chem. Inf. Comput. Sci.* **1979**, *3*, 162.

(28) de Koch, R. J.; Veermans, A. *Makromol. Chem.* **1966**, *95*, 179. As claimed by these authors, the endo configuration was written for the HBr adduct to dicyclopentadiene and also for subsequent products (eq 7). We did not check these assignments, however. Cf.: Foster, R. G.; McIvor, M. C. *J. Chem. Soc. B* **1969**, 188.

(29) The dehydrobromination of **42** with alcoholic KOH as mentioned (Youngblood, G. T.; Wilder, P., Jr. *J. Org. Chem.* **1956**, *21*, 1436) was in our hands less successful than the one described in the Experimental Section.

(30) Alternative methods claimed for the preparation of **34**: Cristol, S. J.; Seifert, W. K.; Soloway, S. B. *J. Am. Chem. Soc.* **1960**, *82*, 2351. Neff, J. R.; Nordlander, J. E. *J. Org. Chem.* **1976**, *41*, 2590. Nicholas, K. M. *J. Am. Chem. Soc.* **1975**, *97*, 3254. Bruson, H. A.; Riener, T. W. *Ibid.* **1945**, *67*, 723, 1178. Wilder, P., Jr.; Culberson, C. F.; Youngblood, G. T. *Ibid.* **1959**, *81*, 656.

(31) Professor M. Farina (Milan) prepared a $C_{14}H_{20}$ hydrocarbon (A) by Diels–Alder addition of cyclopentadiene to indene followed by hydrogenation of the adduct. Thermodynamically controlled rearrangement of A also gave **36** (private communication).

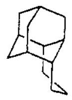


A

(32) Hala, S.; Novak, J.; Landa, S. *Sb. Vys. Sk. Chem.-Tekhnol. Praze, Tekhnol. Paliv* **1969**, *D19*, 31.

(33) 12-*endo*-(Methoxycarbonyl)- and 3,12-*endo*,*endo*-bis(methoxycarbonyl)-substituted **36** also are known: Peters, J. A.; van der Toorn, J. M.; van Bekkum, H. *Tetrahedron* **1975**, *31*, 2273.

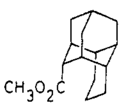
destabilize the chair conformer relative to boat **19**. MM2



boat 19

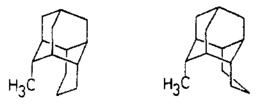
calculations confirmed this expectation (Table II) and predict a conformational boat–chair energy difference of 1.2 kcal/mol, significantly lower than that in the parent bicyclo[3.3.1]nonane (2.3 kcal/mol).[34a] The barrier of chair/boat interconversion in **19** was also calculated to be very low (4.2 kcal/mol, Table II). Hence, the boat conformer should populate to the extent of 10% at room temperature. The formation of two isomeric ketones by ring enlargement upon deamination of **25** is consistent with calculations;[35] an exo aminomethyl group in **25** should generate 3-oxo-substituted **19** in the boat conformation and 4-oxo-substituted **19** in the chair conformation.

The high strain in chair **19** leads us to cast some doubt on the chair conformation proposed for 12-*endo*-(methoxycarbonyl)-substituted **19** on the basis of the ^{1}H NMR spectrum.[33] Attempted MM2 minimization of chair 12-*endo*-Me-**19**, as a model, failed to reveal an energy minimum, but continued iteration led spontaneously to the boat conformation (Table II).



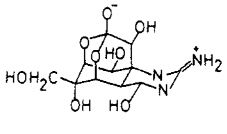
chair

12-endo-CO_2CH_3-19

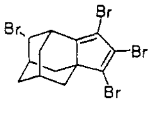


chair boat

12-endo-CH_3-19



39



40

Both calculations and experiments establish 1,2-tetramethyleneadamantane (**36**) as the stabilomer of $C_{14}H_{22}$ isomers. MM2 calculations of **36** indicate little strain in this skeleton. Hence it is not surprising to find a heteroatom-containing skeleton of **36** in a natural product, tetrodotoxin (**39**).[36] In contrast, the fusion of the cyclopentane ring at the 1,2-position of adamantane to give 1,2-trimethyleneadamantane (**18**) introduces considerable strain at the ring junction (Table I). This molecule may be regarded as involving both *cis*- and *trans*-hydrindanes. The calculated strain energy of **18** (21.38 kcal/mol by MM2) is comparable to the sum of strain energies of *cis*- and *trans*-hydrindane (23.57 kcal). The strain in **18** is responsible for the lower stabilities of methyl-substituted **18** isomers, e.g., **37**, compared to that of **36**.

Conclusions

The availability of variously fused and bridged tetracyclic adamantanes by simple rearrangement routes expands the spectrum of adamantane cage molecules significantly. However, the chemistry of tetracyclotridecane and tetracyclotetradecane stabilomers has scarcely been exploited. The only reaction of the now readily available 1,2-cyclopentanoadamantane (**18**) that has been studied is the bromination with liquid bromine.[9b] This gave a novel tetrabromide (**40**). Compared to **18**, the availability of 2,4-trimethyleneadamantane (**19**) is limited. The best way to obtain **19** by a rearrangement route in some quantity is to stop the isomerization of **3** after a short contact time with Lewis acid and collect this transient intermediate by preparative GLC. The chemical behavior of **36** has not yet been investigated.

Molecular mechanics calculations proved useful in interpreting the relative thermodynamic stabilities of adamantanoid structures (especially when extensive fragmentation hinders the determination of reliable equilibrium constants experimentally), in analyzing the most plausible multistep rearrangement pathways, and in predicting structural features of the stabilomers obtained.

Experimental Section

General Methods. Melting points are corrected, and boiling points are uncorrected. GLC/mass spectra were recorded at 70 eV on JEOL JMS-D300 and du Pont 21-491 instruments. ^{1}H NMR spectra were measured in $CDCl_3$ with Me_4Si as a standard at 60 MHz on Varian A-60A and Hitachi R-20B instruments and at 100 MHz on a JEOL JNM PS-100 spectrometer. IR spectra were obtained on a JASCO IR-G spectrometer. Elemental analyses were performed through the courtesy of Hoffmann-La Roche, Inc., Nutley, NJ. Commercial diethylzinc was purchased from Mathieson Co.

Pentacyclo[6.5.0.0^{4,13}.0^{5,9}.0^{10,12}]tridecane (6). Tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene (**5**)[37] was cyclopropanated by a modified Simmons–Smith procedure.[38] To a solution of **5** (6.19 g, 41.8 mmol) and diethylzinc (5.23 g, 42.4 mmol) in 20 mL of benzene was added methylene iodide (25 g, 96 mmol) slowly (7 h) under static nitrogen pressure. White precipitates began to form after 6 h of reaction. The reaction mixture was then heated at 50 °C overnight. The precipitates were dissolved by addition of 8 mL of 1% HCl, and the benzene layer was separated, washed with sodium bicarbonate solution and then water, and dried with calcium chloride. Evaporation of the solvent left an oil, which contained unreacted methylene iodide. For removal of the iodide, a solution of sodium ethoxide from 2 g of sodium in 20 mL of ethanol was added and the mixture stirred at room temperature overnight. Ethanol was evaporated, water added, and the mixture extracted with petroleum ether. The combined extracts were washed with water, dried, and evaporated to leave 5.45 g (81%) of almost pure **6** as an oil. An analytical sample was obtained by preparative GLC on a $^3/_8$ in. × 50 ft FFAP column at 245 °C followed by microdistillation of the collected material: bp 187 °C; IR 3085, 2927, 1457, 1017, 817 cm^{-1}; mass spectrum, *m/e* 174 (M*, base peak); ^{1}H NMR δ 2.2–1.1 (m, 14 H), 1.1–0.8 (m, 2 H), 0.5–0.18 (m, 2 H).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C,89.72; H, 10.56.

10-Methyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecane (1). A solution of 5.34 g (30.6 mmol) of **6** in 50 mL of acetic acid was hydrogenated in the presence of 1 g of platinum oxide at 75 °C for 25 h. The workup gave 4.03 g (75%) of pure **1**: bp 72–74.5 °C (2 mm); IR 2900, 1457 cm^{-1}; mass spectrum *m/e* 176 (M*, 100), 161 (50), 147 (43), 134 (59), 93 (92), 79 (90); ^{1}H NMR δ 2.5–0.8 (m, 17 H), 1.98 (d, *J* = 12 Hz, 3 H).

Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.61; H, 11.57.

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(34) For the conformation of bicyclo[3.3.1]nonane, see: (a) Ōsawa, E.; Aigami, K.; Inamoto, Y. *J. Chem. Soc., Perkin Trans. II* **1979**, 172. (b) Mastryukov, V. S.; Osina, E. L.; Dorofeeva, O. V.; Popik, M. V.; Vilkov, L. V.; Belikova, N. A. *J. Mol. Struct.* **1979**, *52*, 211. (c) Peters, J. A.; Baas, J. M. A.; van de Graaf, B.; van der Toorn, J. M.; van Bekkum, H. *Tetrahedron* **1978**, *34*, 3313. (d) Bovill, M. J.; Cox, P. J.; Flitman, H. P.; Guy, M. H. P.; Hardy, A. D. U.; McCabe, P. H.; Macdonald, M. A.; Sim, G. A.; White, D. N. J. *Acta Crystallogr., Sect. B* **1979**, *B35*, 669.

(35) Farcasiu, M.; Farcasiu, D.; Slutsky, J.; Schleyer, P. v. R. *Tetrahedron Lett.* **1974**, 4059.

(36) (a) Goto, T.; Kishi, Y.; Takahashi, S.; Hirata, Y. *Tetrahedron Lett.* **1964**, 779. (b) Woodward, R. B.; Gougoutas, J. Z. *J. Am. Chem. Soc.* **1964**, *86*, 5030. (c) Also see: Nourse, J. G.; Smith, D. H.; Carhart, R. E.; Djerassi, C. *J. Am. Chem. Soc.* **1980**, *102*, 6289.

(37) Akhtar, I. A.; Fray, G. I.; Yarrow, J. M. *J. Chem. Soc. C* **1968**, 812.

(38) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1968**, *24*, 53.

9-(Ethoxycarbonyl)tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene (9). A mixture of ethyl α-pyrone-3-carboxylate (8; 20.0 g, 0.119 mol)[39] and 1,5-cyclooctadiene (7, 160 mL) was heated under reflux for 24 h. The excess of cyclooctadiene was removed on a rotary evaporator at a bath temperature of 90–100 °C, and the residue was distilled under vacuum to give 27.6 g (99%) of pure **9**, bp 106 °C (0.05 mm).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.49; H, 8.79.

9-(Ethoxycarbonyl)tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecane (10). In a 500-mL pressure bottle were placed 12.0 g (50 mmol) of tetracyclic ester **9**, 200 mL of absolute alcohol, and 400 mg of palladium black. Hydrogenation was carried out in a Parr shaker overnight. The catalyst was filtered, the solvent evaporated, and the product distilled in vacuum to give 10.15 g (84%) of pure **10**, bp 102–104 °C (0.05 mm).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.59; H, 9.69.

9-Tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecylcarbinol (11). A solution of the hydrogenated ester **10** (20.0 g, 86 mmol) in dry ether (100 mL) was added during 90 min to lithium aluminum hydride (3.6 g, 95 mmol) and ether (200 mL) in a flask provided with a stirring device, a reflux condenser, and a drying tube. The mixture was refluxed for 2 h and then stirred at room temperature overnight. A cold, saturated solution of sodium dihydrogen phosphate was added to the cold reaction mixture. After the mixture was filtered, the ether solution was washed twice with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and evaporated in vacuo. The crude product was recrystallized from hexane to give 9.9 g (60%) of pure alcohol **11**, mp 142 °C.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.26; H, 10.67.

9-Tetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecylcarbinyl Tosylate (12). The carbinol (**11**) from the above reaction (9.9 g, 52 mmol) was dissolved in 27 mL of pyridine, freshly distilled over barium oxide. The solution was cooled to 0 °C, and 10.8 g (57 mmol) of *p*-toluenesulfonyl chloride was added. After being kept at 0 °C for 2 days, the mixture was poured onto ice and extracted three times with ether. The combined ether solution was washed three times with 1.5 N hydrochloric acid and three times with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed under vacuum. Recrystallization from benzene gave 15.4 g (86%) of pure tosylate **12**, mp 117 °C.

Anal. Calcd for $C_{20}H_{26}O_3S$: C, 69.36; H, 7.57; S, 9.26. Found: C, 69.37; H, 7.66; S, 9.53.

9-Methyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecane (2). The tosylate **12** (15.0 g, 43.5 mmol), dissolved in 600 mL of dry ether, was added over a period of 2 h to 8.63 g (228 mmol) of lithium aluminum hydride in 300 mL of ether with stirring. The mixture was boiled under reflux for 36 h, cooled in ice, and treated with saturated aqueous sodium dihydrogen phosphate. The filtered ether solution was washed three times with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed under vacuum. The residue was chromatographed on neutral alumina (65 g) with hexane (500 mL) as the eluent. The residue from the hexane solution (6.7 g, 88%) was pure **2**: mp 131–133.5 °C; ^{1}H NMR δ 2.4–1.0 (m, 17 H, with a prominent peak at 1.66), 0.75 (s, 3 H).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.69; H, 11.34.

Tetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridec-9-ene (13).[40] Freshly distilled norbornene (400 g, 4.25 mol) and 1,3-cyclohexadiene[41] (203 g, 2.53 mol) were heated at 200 °C in an autoclave for 20 h. Distillation afforded 142 g of crude product [bp 87–95° (6 mm)] which is, according to GLC analysis, a roughly 1:1 mixture of cyclohexadiene dimer (two components)[42] with **13**. Spinning-band distillation of the mixture gave 51.3 g (25%) of the cyclohexadiene dimer [bp 94–100 °C (11 mm)], 8.5 g of an intermediate fraction, and 60.8 g of **13**, bp 104–106 °C (7 mm). The intermediate fraction was subjected to preparative GLC ($^3/_8$ in. × 50 ft FFAP column at 215 °C): combined yield of **13** was 63.2 g (14.5%); IR 3035, 3025 (sh),[43] 2935, 2856, 1477, 1458, 1446, 710 cm^{-1}; ^{1}H NMR δ 5.90 (q, 2 H), 2.45 (br s, H1 and H8), 2.15 (dt, *exo*-H13), 1.81 (br s, H3 and H6),[44] 1.57 (br s, H2 and H7),[45] 1.5–0.8 (m, 8 H), 0.58 (d, *endo*-H13), *J*(13-endo, 13-exo) = 9.5 Hz, *J*(2,13-endo) = 2 Hz, *J*(1,10) = 4.6 Hz, *J*(2,10) = 3.2 Hz, *J*(10,11-endo) = 3.2 Hz.

Table III

temp, °C	time	rel amt of 15 + 16 + 17 in the total GLC peak area, %
ambient	10 min	98.2
46	2 h	85.7
100^a	1.25 h	66.3
100^a	20 h	0.0

^{a} In a glass pressure tube.

Tetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridecane (3). The olefin (**13**) from the above reaction was hydrogenated over palladium in a Parr apparatus at room temperature. A portion of the crude product was purified by preparative GLC ($^3/_8$ in. × 50 ft FFAP column at 235 °C) to give an analytical sample of **3**: mp 50.5–51.0 °C (lit.[40] mp 43 °C); IR 3022,[43] 2900, 1493, 1460, 1300 cm^{-1}; mass spectrum, *m/e* (relative intensity) 176 (M*, 48), 135 (100); ^{1}H NMR δ 2.2–0.9 (m with the most intense peak at 1.45).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.65; H, 11.27.

8- and 9-Methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (14a,b). In a 1-L autoclave were heated 240 g (2.55 mol) of norbornene and 150 g (0.94 mol) of freshly distilled methylcyclopentadiene dimer at 200 °C for 17 h. Excess norbornene was removed by distillation at 50 °C (120 mm) and the residue was subjected to vacuum distillation to give **14**: 225 g (69%); bp 50–60 °C (1.5 mm). The product is a three-component mixture (28:11:61 in the order of increasing GLC retention time on Carbowax 20M at 165 °C). Portions of the two major components were collected by preparative GLC ($^3/_8$ in. × 20 ft SE-30 column at 135 °C) and further purified by short-path distillation [bp ca. 80 °C (1.5 mm)].

The component with the shorter retention time was shown to be 8-methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (**14a**) on the basis of spectral data:[45] IR 3083, 1653, 1477, 1356, 1314, 752 cm^{-1}; mass spectrum, *m/e* (relative intensity) 174 (M*, 23), 160 (9), 91 (16), 80 (100), 66 (73); ^{1}H NMR δ 5.9–5.5 (m, 2 H), 2.71 (br s, H1), 2.2–1.8 (m, H2, H3, H6, H7), 1.7–0.8 (m, H4, H5, H11, H12a), 1.28 (s, Me), 0.51 (d, *J* = 9 Hz, H12s).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 90.02; H, 9.98.

The component with longer retention time was similarly identified as 9-methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene (**14b**): IR 3033, 1664, 1482, 1456, 1293, 871 cm^{-1}; ^{1}H NMR δ 4.33 (br s, H10),[45] 2.9–2.4 (2 br s, H1, H8), 2.2–1.8 (m, H2, H3, H6, H7), 1.71 (d, *J* = 2 Hz, Me), 1.6–0.8 (m, H4, H5, H11, H12a), 0.60 (d, *J* = 10 Hz, H12s).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.69; H, 10.32.

8- and 9-Methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (4a,b). The 1:2 mixture of **14a** and **14b** (4.0 g, 23 mmol) was hydrogenated over palladium on charcoal in a Brown hydrogenator.[46] Hydrogen uptake was complete in 0.5 h at room temperature. Distillation of the crude product gave a colorless oil: 3.7 g (91%); bp 71–76

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[39] Windholz, T. B.; Peterson, L. H.; Kent, G. J. *J. Org. Chem.* **1963**, *28*, 1443.

[40] Scharf, H.-D. *Tetrahedron* **1967**, *23*, 3057.

[41] 1,3-Cyclohexadiene was prepared by quinoline dehydrobromination of 3-bromocyclohexene, which in turn was obtained from cyclohexene and *N*-bromosuccinimide: Bailey, W. J.; Lawson, W. B. *J. Am. Chem. Soc.* **1957**, *79*, 1444. For an alternative method: Schaefer, J. P.; Enders, L. *Org. Synth.* **1967**, *47*, 31.

[42] Valentine, D.; Turro, N. J., Jr.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202.

[43] Congested hydrogen atom. See: Kivelson, D.; Winstein, S.; Bruck, P.; Hansen, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 2938.

[44] The relative order of bridgehead protons H2(H7) vs. H3(H6) is inferred from the decoupling experiments of tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-ene, a Diels–Alder adduct of norbornene with cyclopentadiene: Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3274.

[45] Finnegan, R. A.; McNees, R. S. *J. Org. Chem.* **1971**, *36*, 1316.

[46] Brown, H. C.; Brown, C. A. *J. Org. Chem.* **1966**, *31*, 3989.

[47] Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.

[48] (a) Huang-Minlon, *J. Am. Chem. Soc.* **1946**, *68*, 2487. (b) Whitlock, H. W., Jr.; Siefken, M. W. *Ibid.* **1968**, *90*, 4929.

°C (4 mm); about a 1:2 mixture of the two components by GLC; ^{1}H NMR δ 2.5–0.8 (m).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.32; H, 11.43.

Treatment of 1 with Aluminum Sludge Catalyst. (1) Preliminary Runs. The precursor 1 (0.1 g) was treated with 0.3 mL of freshly prepared aluminum sludge catalyst[9a] in 10 mL of carbon disulfide under a stream of hydrogen bromide gas at room temperature. The extent of the reaction was monitored by GLC (0.01 in. × 150 ft Apiezon L column, 190 °C). The reaction was continued for 24 h at room temperature. The starting material (relative retention time 1.00) disappeared almost instantly upon contact with the catalyst. An intermediate peak (t_R = 0.93) was visible for 30 min but disappeared thereafter. The relative abundance of three major isomerization products, **15** (t_R = 0.75), **16** (t_R = 0.74), and **17** (t_R = 0.79), reached a steady state (5:3:2) in 1 h. After 5 h, **19** (t_R = 0.87) started to appear and reached about 4% of the total GLC peak area after 24 h.

Similar small-scale runs were repeated at various temperatures with the results shown in Table III. The sludge catalyst clearly promotes disproportionation of the substrate at higher temperatures. The products of disproportionation consist of at least eight alkyladamantanes (t_R = 0.4–0.6).

(2) Preparative Runs. In an atmosphere of hydrogen bromide gas, 1 (3.11 g) was dissolved in 15 mL of carbon disulfide containing 5 mL of sludge catalyst. After 10 min, the isomerization was discontinued. The usual workup of the reaction mixture gave a quantitative yield of product mixture, which was then subjected to preparative GLC separation on a $^3/_8$ in. × 50 ft FFAP column at 170 °C.

The most abundant, solid fraction was sublimed at 60–70 °C (3 mm) and recrystallized from methanol–acetone to give needles (mp 127–129 °C) identical in every respect with the 1-methylethanoadamantane **15** obtained previously.[8b]

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.33; H, 11.37.

The second most abundant fraction was subjected to further preparative GLC purification (6 mm × 6 m, Carbowax 20M, 120 °C); the pure material was a liquid. The ^{13}C NMR spectrum of this material has been described in detail elsewhere:[8b] the structure of 8-methylethanoadamantane **16** was assigned mainly on the basis of this spectrum: IR 2930, 2890, 2830, 1492, 1456 cm^{-1}; mass spectrum, *m/e* (relative intensity) 176 (M*, 29), 151 (100), 133 (21), 119 (19), 105 (36), 93 (20), 91 (24), 81 (18), 79 (23); ^{1}H NMR δ 2.0–1.3 (m, outstanding peaks at 1.80, 1.54, and 1.42, 16 H), 1.12 (d, *J* = 12 Hz, 1 H), 0.80 (s, 3 H).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.42; H, 11.19.

The third most abundant fraction was recrystallized from methanol–acetone to give a crystalline solid (mp 126–131 °C) which was identical in every respect with an authentic sample of 2-methylethanoadamantane **17** obtained previously.[8b]

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.29; H, 11.40.

Another preparative run was carried out to obtain the nonmethylated and disproportionation products. In a pressure glass bottle was mixed 1.47 g of 1 with 2 mL of aluminum sludge catalyst and 5 mL of carbon disulfide. After the atmosphere was purged with hydrogen bromide gas, the bottle was capped tightly and heated under magnetic stirring at 100 °C for 2.25 h. The workup of the reaction mixture gave 1.31 g (89% recovery) of a lightly colored oil, which was then separated by preparative GLC on a $^3/_8$ in. × 50 ft FFAP column at 175 °C. From among at least eight peaks with low retention times (disproportionation products) the two most abundant (t_R = 0.57 and 0.35) were collected. They were both colorless liquids and were identified by ^{1}H NMR spectra as 1,3,5-trimethyladamantane and 1-ethyl-3-methyladamantane, respectively.[49] Of the two peaks with longer retention times (which were not formed in the first preparative run), enough of the more abundant one could be collected to obtain an ^{1}H NMR spectrum. It was identified as 1,2-trimethyleneadamantane (**18**) as described below. The other peak was too small to allow collection of a sample, but the GLC retention time (t_R = 1.00 min) agreed with that of synthetic 2,4-trimethyleneadamantane (**19**).

Treatment of 2 with Sludge Catalyst. The results were essentially the same as those described above with 1, except that an intermediate was the most abundant product after 10 min of contact with the catalyst at room temperature. An attempt to collect this intermediate by preparative GLC was frustrated by the observation that this intermediate actually gave two closely overlapping GLC peaks on a $^3/_8$ in. × 50 ft FFAP column at 175 °C (retention time 200 min).

Equilibration of $C_{13}H_{20}$ Rearranged Products under Drastic Conditions. 1, 2, 16, and 18 gave the same equilibrium mixture under more drastic conditions. The equilibrium experiment with 18 is described here. A mixture of 0.1 g of 18, 0.5 mL of aluminum sludge catalyst, and 5 mL of carbon disulfide was stirred for 1 day at room temperature in a flask equipped with a calcium chloride tube. At the end of this period, about one-third of the material had rearranged into 15–17, one-third had disproportionated, and the remaining one-third was unchanged. After 0.5 mL of fresh sludge catalyst was added, the mixture was heated under reflux for 30 h. At the end of this time, about two-thirds of the material had disproportionated to low retention time products. Two GLC analyses of the rearranged mixture gave the following composition of 15/16/17/18/19: (a) 42.0:27.4:19.3:8.5:2.8, (b) 42.5:27.6:19.1:7.9:2.9. The low ratio of 18/19 is probably an artifact (see below).

Disproportionation was more extensive when methylated materials (1, 2, and 16) were treated under such drastic conditions.

Rearrangement of 3. (a) With Aluminum Bromide. The catalyst (0.40 g, 1.5 mmol) was added to a solution of 3 (1.00 g, 98% pure, 5.7 mmol) in 15 mL of carbon disulfide, and the solution was stirred magnetically at room temperature. Occasionally the flask and condenser (with calcium chloride drying tube) were flushed with hydrogen bromide gas while the progress of reaction was monitored by GLC.[21] After 24 h, the remaining solution was neutralized with saturated sodium bicarbonate solution, washed with water, and dried with sodium sulfate. Evaporation of solvent gave 0.6 g of an almost colorless solid, mp 40–45 °C.

(b) With Sludge Catalyst. A solution of 0.5 g of 3 in 100 mL of carbon disulfide was added to 50 mL of sludge catalyst in 50 mL of carbon disulfide under ice cooling during 1 h. After further stirring overnight, the reaction mixture was worked up as described above. The crude product was distilled through a heated 10-cm fractionating packed column. A fraction boiling between 87 and 92 °C (3 mm) was collected to give 42.0 g (46%) of a solid, mp 46–50 °C. GLC analysis of this fraction showed it to be 1,2-trimethyleneadamantane (**18**) of 82% purity. Both the yield and purity were lower than those found with aluminum bromide as catalyst.

An analytical sample of **18** was obtained by preparative GLC on a 0.25 in. × 20 ft Carbowax 20M column at 210 °C. Collected material was sublimed at 40 °C (7 mm) to give a waxy solid: mp 54–57 °C; IR 2908, 2853, 1460, 1356, 1096 cm^{-1}; ^{1}H NMR δ 2.0–1.0 (m, with the most intense peak at 1.57); ^{13}C NMR δ 50.4 (single intensity, C7), 44.1 (s, C2 or C13), 39.0 (s, C11), 38.5 (s, C4) [38.5 (s, C3)], 37.7 (s, C9 or C12), 36.5 (s, C2 or C13), 30.3 (s, C9 or C12), 30.0 (s, C8), 29.3 (s, C1 or C10), 28.5 (s, C1 or C10), 25.8 (s, C6), 20.0 (s, C5); mass spectrum, *m/e* (relative intensity) 176 (M*, 100), 148 (22.5), 135 (5), 133 (11).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.90; H, 11.01.

A small sample of **19** was also collected and sublimed at 80 °C (7 mm) to give crystals, mp 118–122 °C. Spectral properties of this material were identical with those of synthetic 2,4-trimethyleneadamantane (see below).

Equilibration of 18 and 19. A solution of 0.13 g of synthetic 18 and 0.2 g of aluminum bromide in carbon disulfide was stirred at room temperature for 3 days. GLC analysis ($^1/_8$ in. × 13 ft, 15% Carbowax 20M, 165 °C) indicated, in addition to **18** (t_R = 1.00), a small new peak (t_R = 1.44). GC/MS analysis of the new peak ($^1/_8$ in. × 8 ft, Carbowax 20M, 140 °C) revealed a mass fragmentation pattern identical with that of authentic 2,4-trimethyleneadamantane (**19**). The peak area ratio (18/19) was 95.6:4.4.

Tetracyclo[6.3.1.1^{1,5}.0^{6,10}]tridecan-3-one (20). (2-Adamantyl)acetic acid[50] was converted to (2-adamantyl)methyl

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[49] (a) Fort, R. C., Jr.; Schleyer, P. v. R. *J. Org. Chem.* **1965**, *30*, 789. (b) Schneider, A.; Warren, R. W.; Janoski, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5365.

diazomethyl ketone (21) by the standard procedure.[13] The diazo ketone (21) obtained from 20.6 mmol of the acid chloride was treated[11,12] with 2.5 g (15.6 mmol) of anhydroud copper sulfate in boiling toluene (total volume 580 mL) as described,[13] but without high dilution. The crude product was purified by column chromatography on silica gel (benzene eluent) to give **20**: 2.26 g; white solid; mp 83–87 °C. Sublimation of a less pure fraction obtained from the column at 90 °C (12 mm) gave 0.31 g of pure product: combined yield 66.8% (better than that from the reaction of (1-adamantyl)methyl diazomethyl ketone);[11,12] IR 1745 cm^{-1}; ^{1}H NMR δ 2.4–1.3 (m, with sharp peaks at 2.22 and 1.93).

1,2-Trimethyleneadamantane (18, Tetracyclo[6.3.1.1^{3,10}.0^{3,7}]tridecane). The modified Wolff–Kishner reduction[48] of **20** (0.50 g) gave 0.47 g of an oil, which was chromatographed on 30 g of silica gel (pentane eluent). The purified product (0.38 g, 82% yield; mp 45–51 °C) had spectral properties identical with those of the material obtained by rearrangement.

Tetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecan-3-one (23) was prepared according to the published procedure.[13] The material obtained had the following: mp 175–180 °C; mass spectrum, *m/e* (relative intensity) 176 (M*, 100), 148 (17.6), 92 (26.6), 91 (15.0), 80 (17.5), 79 (34.9).

Anal. Calcd for $C_{12}H_{14}O$: C, 81.77; H, 9.15. Found: C, 81.66; H, 9.23.

2,4-Dinitrophenylhydrazone: yellow crystals; mp 211–211.5 °C; IR 3300, 1618, 1588 cm^{-1}; ^{1}H NMR δ 10.85 (s, 1 H), 9.08 (d, J = 9 Hz, 1 H), 8.47 (dd, J = 2, 9 Hz, 1 H), 7.91 (d, J = 9 Hz), 2.8–1.6 (m, prominent peaks at 2.48 and 1.85, 15 H), 1.45 (d, J = 14 Hz); mass spectrum, *m/e* (relative intensity) 356 (M*, 100), 177 (10.5), 174 (19.0), 133 (21.7), 91 (17.4), 79 (18.3).

Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.48; H, 5.53; N, 15.97. Found: C, 60.57; H, 5.66; N, 15.72.

3-*exo*-Cyano-3-*endo*-[(trimethylsilyl)oxy]tetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecane (24). Ethanoadamantanone **23** (663 mg, 3.77 mmol) and the 18-crown-6 ether complex of potassium cyanide (124 mg, 0.377 mmol) were placed in a flask under an atmosphere of argon. Dry benzene (5 mL) was injected through a serum cap; only **23** dissolved. Thereupon, 685 μL (562 mg, 5.67 mmol) of trimethylsilyl cyanide (bp 114–117 °C)[51] was injected with stirring into the flask during 1.5 h. The mixture was stirred for another hour at room temperature. It was then diluted with ether, and the undissolved solid was removed by filtration. The solid collected on the filter was washed with ether, and the combined washings and filtrate were evaporated to leave lightly colored oily crystals. The crude product was purified by passing its solution through an alumina column to give 825 mg (79%) of colorless crystals, mp 87–90 °C. An analytical sample was obtained after two recrystallizations from ether and pentane: mp 91–92.5 °C; IR 2200 cm^{-1}; mass spectrum, *m/e* (relative intensity) 275 (M*, 6.7), 260 (100), 247 (56.5), 23 (14.7); ^{1}H NMR δ 2.68, 2.54 (q, J = 7 Hz, 2 H), 2.4–1.6 (m, 13 H), 1.33 (br d, J = 12 Hz, 1 H).

Anal. Calcd for $C_{16}H_{25}NOSi$: C, 69.76; H, 9.15; N, 5.09. Found: C, 68.92; H, 9.03; N, 4.87.

3-*exo*-(Aminomethyl)tetracyclo[6.3.1.0^{2,6}.0^{5,10}]dodecan-3-*endo*-ol (25). A solution of 223 mg (1 mmol) of α-silyloxy nitrile **24** in 2 mL of dry ether was added to a suspension of 76 mg (2 mmol) of lithium aluminum hydride in 3 mL of dry ether by syringe during 1 h with ice cooling under argon.[52] After the addition was complete, the ice bath was removed, and the mixture was allowed to warm to room temperature under stirring for 1 h. Excess lithium aluminum hydride was slowly decomposed by addition of water, 3 N NaOH, and water in this order.[53] After further stirring for 1 h, the mixture was poured into ice–water and extracted with ether. The combined extracts were washed, dried, and evaporated to give 123 mg (74%) of white solid, mp 99–103 °C. An analytical sample was obtained by two recrystallizations from ether–pentane (1:1): mp 114.5–116 °C; IR 3500–3150 cm^{-1}; mass spectrum, *m/e* (relative intensity) 207 (M*, 4.7), 190 (3.9), 177 (100), 176 (79.2); ^{1}H NMR δ 2.9–1.1 (m).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.05; H, 10.32; N, 6.49.

Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridecan-3- and -4-one (22-mixt).[54] In a flask equipped with a gas outlet connected to a liquid paraffin seal to detect gas evolution was dissolved 165.5 mg (0.80 mmol) of amino alcohol **25** in 50 μL of acetic acid and 1 mL of water, and the mixture was cooled at −5 °C. A solution of 110.2 mg (1.60 mmol) of sodium nitrite in 1 mL of water was added during 1 h, and the stirring was continued for an additional hour at −5 °C. The mixture was heated at 90–100 °C for 3 h to complete the reaction and again cooled in ice to neutralize the solution with sodium bicarbonate. The reaction mixture was extracted with ether, and the combined extracts were evaporated to give 105 mg of low-melting, lightly colored solid. The crude product was purified by column chromatography through alumina to give 74 mg (49%) of pasty solid which showed two close GLC peaks (intensity ratio 1:0.7): IR 1725–1690 (maximum 1709) cm^{-1}; mass spectrum, *m/e* 190 (M*); ^{1}H NMR δ 2.6–1.0 (m).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 81.90; H, 9.58.

Tetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridecane (19, 2,4-Trimethyleneadamantane). Modified Wolff–Kishner reduction[48] of the mixed ketone (**22**-mixt, 74 mg) gave 54 mg (79%) of a white solid, mp 65–70 °C. An analytical sample was obtained by column chromatography through alumina followed by recrystallization from pentane: mp 102–105 °C; mass spectrum, *m/e* (relative intensity) 176 (M*, 100), 135 (13.4), 134 (12.7), 133 (35.3), 91 (15.3); ^{1}H NMR δ 1.73 (br s).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.40; H, 11.59.

Treatment of 4 with Aluminum Bromide Sludge Catalyst. The rearrangement reaction was carried out at 0 °C as described above. According to GLC analysis, an intermediate peak was dominant during the first 10 min but disappeared in 4 h. After 5 h, the mixture contained virtually only **4a**; stirring overnight at 0 °C produced no further transformation. The reaction mixture was quenched in ice, and **4a** was separated by preparative GLC on Apiezon L grease (6 mm × 9 m column) at 160 °C. The identity of the collected liquid with **4a** was established by mixture injection on two different GLC columns: IR 3025, 2940, 1477, 1458, 1378 cm^{-1}; ^{1}H NMR δ 2.08 (br s, 3 H), 1.95–0.60 (m, 14 H), 1.10 (s, 3 H); mass spectrum, *m/e* (relative intensity) 176 (M*, 6), 161 (10), 147 (37), 81 (100).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.54; H, 11.27.

The above run was repeated at reflux temperature for 5 h. At the end of this period, the GLC peak of **4a** had virtually disappeared, and a complex mixture of low-retention components (retention times relative to **4**: 0.62, 0.54, 0.40, 0.35, 0.31) resulted. The two most abundant components (t_R = 0.40 and 0.62) were collected by preparative GLC and identified as 1,3,5-trimethyladamantane and 1-methyl-3-ethyladamantane, respectively, by ^{1}H NMR spectra.[49]

8- and 9-Bromotricyclo[5.2.1.0^{2,6}]dec-3-ene (41). Addition of dry hydrogen bromide to 50 g (0.38 mol) of freshly distilled dicyclopentadiene [bp 58–59 °C (112 mm)] as described[28] gave 52.2 g (65%) of an oil, bp 67–68 °C (1 mm) [lit.[28] bp 114.5–115.5 °C (10 mm)]. GLC analysis on a 2 mm × 2 m SE-30 column at 90 °C revealed two closely spaced peaks of almost equal intensities: IR 3050, 2960, 1613, 740, 695, 678 cm^{-1}; ^{1}H NMR δ 5.5 (s, 2 H), 4.1–3.7 (m, 1 H), 3.3–1.3 (m, 10 H); mass spectrum, *m/e* 214, 212 (M*).

Anal. Calcd for $C_{10}H_{13}Br$: C, 56.35; H, 6.15; Br, 37.50. Found: C, 56.45; H, 6.21; Br, 37.74.

8-Bromotricyclo[5.2.1.0^{2,6}]decane (42). Hydrogenation[46] of 49.5 g (0.232 mol) of **41** was carried out over palladium/charcoal catalyst in 50 mL of hexane and 50 mL of ethanol. Distillation of the crude product gave 41.9 g (84%) of an oil: bp 75–77 °C (0.5 mm); IR 2955, 1450, 938 cm^{-1}; ^{1}H NMR δ 4.3–4.0 (m, 1 H), 2.7–1.2 (m, prominent peak at 1.52, 14 H); mass spectrum, *m/e* 216, 214 (M*).

Anal. Calcd for $C_{10}H_{15}Br$: Br, 37.14. Found: Br, 37.05.

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***endo*-Tricyclo[5.2.1.0^{2,6}]dec-8-ene (35).** In 350 mL of *tert*-butyl alcohol, freshly distilled from lithium aluminum hydride, was dissolved 17 g (0.43 atom) of potassium with heating under reflux for 1 day. A solution of 41.8 g (0.194 mol) of **42** in dry tetrahydrofuran (also freshly distilled from lithium aluminum hydride) was added, and the mixture heated under stirring and reflux for 1 day under an atmosphere of nitrogen. The reaction mixture was diluted with 200 mL of *n*-pentane and washed with water to remove *tert*-butyl alcohol. The pentane layer was dried with sodium sulfate and evaporated, and the residue was distilled under vacuum to give 25 g (97%) of an oil: bp 86–87 °C (39 mm) [lit.[30c] bp 92–94 °C (40 mm)]; IR 3060, 1646, 1570, 1347, 1253, 1236, 1142, 736 cm^{-1} (lit.[30a] 1645, 1575, 1348, 1241, 1144 cm^{-1}); ^{1}H NMR δ 6.06 (s, 2 H), 2.70 (m, 4 H), 2.0–0.7 (m, 8 H).

Anal. Calcd for $C_{10}H_{14}$: C, 89.48; H, 10.52. Found: C, 89.21; H, 10.42.

Tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradec-4-ene (43). Liquid butadiene (20 g, 370 mmol) was mixed with 8.8 g (66 mmol) of **35** and 100 mL of toluene containing a trace of hydroquinone. The mixture was heated in an autoclave at 180 °C for 1 day. The solvent was removed under vacuum and the residue subjected to fractional distillation to afford 2.3 g of unreacted **35** and 4.7 g (51% based on reacted **35**) of an oil [bp 81–89 °C (0.08 mm)] which solidified in the receiver to a mass: mp 44.5–45.3 °C; IR 3030, 1637 cm^{-1}; ^{1}H NMR δ 5.8 (m, 2 H), 2.6–1.1 (m, prominent peak at 1.56, 18 H); mass spectrum, *m/e* 188 (M*, 9.8), 120 (17.7), 91 (7.5), 79 (9.1), 66 (100).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.21; H, 10.42.

Tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradecane (34). Hydrogenation[46] of 4.5 g (24 mmol) of the above product (**43**) was carried out over palladium/charcoal in 25 mL of *n*-hexane and 20 mL of ethanol. Evaporation of the solvent left 3.0 g (66%) of an oil [bp 99 °C (0.7 mm)] which crystallized upon refrigeration to plates melting at room temperature: IR 2918, 1471, 1442 cm^{-1}; ^{1}H NMR δ 2.36 (m, 2 H), 1.9–0.8 (m, prominent peak at 1.56, 20 H); mass spectrum, *m/e* (relative intensity) 190 (M*, 30), 122 (59), 121 (100), 120 (22), 108 (48), 107 (23), 95 (26), 94 (45), 93 (38), 91 (25), 81 (29), 80 (54), 79 (67), 67 (49), 55 (24), 41 (30).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.41; H, 11.58.

Tetracyclo[7.3.1.1^{3,11}.0^{3,8}]tetradecane[55] (36, 1,2-Tetramethyleneadamantane). To a solution of 2 g (10.5 mmol) of **34** in 50 mL of carbon disulfide was added 2 g of aluminum bromide, and the mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with water and extracted with carbon disulfide; the combined extract was dried over sodium sulfate, and the solvent was evaporated. The residue was passed through a short alumina column and further purified by preparative GLC (3 mm × 6 m, 10% Carbowax 20M, 250 °C). The collected oil was finally subjected to molecular distillation to give 0.78 g (44%) of pure **36**: IR 2900, 1447 cm^{-1}; ^{1}H NMR δ 2.23, 2.10, 1.93, 1.78, 1.46, 1.17, 0.98 (m); mass spectrum, *m/e* (relative intensity) 190 (M*, 100), 148 (45), 135 (44), 133 (42), 91 (57).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.41; H, 11.58.

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Registry No. **1**, 81012-51-3; **2**, 81012-52-4; **3**, 81012-53-5; **4a**, 81012-54-6; **4b**, 52353-10-3; **5**, 18326-53-9; **6**, 81012-55-7; **7**, 111-78-4; 8, 1008-44-2; **9**, 81012-56-8; **10**, 81012-57-9; 11, 81012-58-0; 12, 81012-59-1; **13**, 81012-60-4; **14a**, 81012-61-5; **14b**, 81012-62-6; **15**, 72708-45-3; **16**, 81012-63-7; **17**, 72708-46-4; **18**, 52353-12-5; **19**, 74475-01-7; **20**, 27174-68-1; **21**, 81012-64-8; **22a**, 81012-65-9; **22b**, 81012-66-0; **23**, 41171-93-1; **23** hydrazone, 81012-67-1; **24**, 81012-68-2; **25**, 81012-69-3; **34**, 52353-11-4; **35**, 2826-19-9; **36**, 41171-94-2; **40a**, 6936-52-3; **40b**, 81012-70-6; **41**, 81012-71-7; **42**, 81012-72-8; norbornene, 498-66-8; 1,3-cyclohexadiene, 592-57-4; cyclohexadiene dimer, 6143-79-9; methylcyclopentadiene dimer, 59444-91-6; 1,3,5-trimethyladamantane, 707-35-7; 1-methyl-3-ethyladamantane, 1687-34-9; (2-adamantyl)acetic acid, 26082-22-4.

Supplementary Material Available: A graph of configurational isomers of **4** which interconvert by 1,2 alkyl shifts with MM2 calculated enthalpies (Figure 2); MM2 heats of formation and strain energies of four methyl-1,2-trimethyleneadamantane isomers (**18**-Me) and nine dimethyl-2,4-ethanoadamantane isomers (Table III); IUPAC names, MM2 heats of formation, and strain energies of 128 tetracyclotridecane isomers examined in the "tree search" of the most plausible pathways of rearrangements of **3** into **18** (Table IV); listing of products of 1,2 alkyl shifts in each branch of the "tree search" of the tetracyclotridecane rearrangement graph (Table V); GLC analyses of rearrangement courses starting from **3** (Table VI); a simplified tetracyclotetradecane rearrangement (**34** → **36**) graph based on the "tree search" method (Figure 3) (12 pages). Ordering information is given on any current masthead page.

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[55] The IUPAC name given earlier (Takaishi, N.; Inamoto, Y.; Aigami, K.; Ōsawa, E. *J. Org. Chem.* **1975**, *40*, 1483) for **36** is incorrect.