The Mechanisms of Carbonium Ion Rearrangements of Tricycloundecanes Elucidated by Empirical Force Field Calculations

Eiji Ōsawa,*[1a,2] Koji Aigami,[1b] Naotake Takaishi,[1b] Yoshiaki Inamoto,[1b] Yoshiaki Fujikura,[1b] Zdenko Majerski,[1c] Paul von R. Schleyer,[1d,e] Edward M. Engler,[1d] and Malvina Farcasiu[1d]

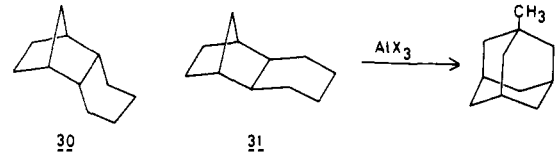
Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan, Industrial Research Laboratories, Kao Soap Company, Ltd., Wakayama 64091, Japan, Ruder Boskovic Institute, 41001 Zagreb, Croatia, Yugoslavia, Department of Chemistry, Princeton University, Princeton, New Jersey 08540, and Institut für Organische Chemie, Universität Erlagnen-Nürnberg, 8520 Erlangen, West Germany. *Received February 14, 1977*

Abstract: All possible 69 isomers of tricycloundecane not containing alkyl groups and three- and four-membered rings are generated and their enthalpies calculated using Engler and 1971 Allinger force fields. All possible paths of interconversion among these isomers through 1,2-alkyl shifts involving favorable bond alignments are examined. The most promising pathways in the rearrangement of 2,3-tetramethylenenorbornanes (**30, 31**) to 1-methyladamantane are illustrated graphically. The most favorable pathway is suggested to be **30, 31** → 1,7-trimethylenenorbornane (**60**) → 1,2-*exo*-tetramethylenenorbornane (**49**) → 1,2-*endo*-trimethylenebicyclo[3.2.1]octane (**47**) → 1,2-trimethylenebicyclo[2.2.2]octane (**63**) → 1,7-*exo*-trimethylenebicyclo[3.2.1]octane (**51**) → 4-homoisotwistane (**40**) → tricyclo[4.4.1.$0^{3,8}$]undecane (**45**) → homoadamantane (**18**) and/or methylprotoadamantanes → methyladamantane. A general mechanism for the ring contraction step is discussed.

The acid-catalyzed isomerization of polycyclic hydrocarbons into thermodynamically more stable, diamond-lattice structures (adamantane rearrangements) has aroused great interest in recent years.[3] The intriguing problem of predicting the "stabilomer" (the most stable isomer)[4] for each polycyclic C_nH_m family has consequently been probed to considerable depth.[3,4] The mechanism of skeletal transformation of tetrahydrodicyclopentadiene to adamantane has been studied extensively. This fascinating riddle was finally solved by the combination of graph theory[5] with empirical force field (molecular mechanics) calculations.[6] The rearrangement graph for tricyclic $C_{10}H_{16}$ isomers,[5] involving only 1,2-alkyl shifts and excluding highly strained structures and primary cation intermediates, defines the pathways available. The energy surface involving the hydrocarbon ground state and the intermediate carbocation stabilities, and estimates of the barrier heights of interconversion, can be obtained most conveniently by molecular mechanics.[6] Application of the same tactics to the elucidation of the mechanisms of rearrangement of various pentacyclotetradecanes, which lead to the next higher adamantalog, diamantane, would be an enormous task involving tens of thousands of possible intermediates and countless interconversion pathways. Consequently, the analysis was limited to the determination of the optimum pathway.[7]

The tricyclic $C_{11}H_{18}$ rearrangement energy surface, the subject of the present paper, involves at least two new features. First, extensive investigations in recent years have led to the isolation and identification of a number of intermediates formed during the isomerization of various tricycloundecane precursors.[8-13] In contrast, in the rearrangement of tetrahydrodicyclopentadiene to adamantane, no intermediate has ever been identified.[3] During the interconversion of a hydrogenated dimer of norbornadiene (Binor-S) to diamantane, only two intermediates are reported to appear, and these are formed at early stages along the reaction path.[7] Second, the $C_{11}H_{18}$ rearrangements are the simplest cases where alkyl-substituted adamantanes are produced. Many examples are known where the stabilomer is an alkyl-substituted diamondoid structure,[3] but the mechanism of the ring contraction giving rise to such alkyl group is not well understood.[11-16]

A total of 434 $C_{11}H_{18}$ tricyclic isomers are possible in which all carbon atoms are incorporated into the rings.[17] If isomers containing methyl (but not other alkyl) groups are included, the number rises to 2889.[17] However, a complete analysis of all rearrangement possibilities involving so many isomers—a horrendous task!—is not necessary.[6,7] Leaving out the methyltricyclodecanes for the moment, and excluding isomers with three- or four-membered rings and other exceedingly strained skeletons, reduces the possibilities to 69, certainly a manageable number. In fact, these 69 structures (Table I, **1–69**) have been known to us for some time and have already supplied the valuable stability and symmetry information which assisted the structure determination of intermediates which have been isolated from their ^{13}C NMR spectra.[8-13,14b,c] In this paper, we first describe generation of a simplified tricycloundecane rearrangement graph including enthalpies of isomers and their interconversion paths. Then we deduce the most favorable pathway to 1-methyladamantane (the $C_{11}H_{18}$ stabilomer) from the readily available tricycloundecanes, the 2,3-tetramethylenebicyclo[2.2.1]heptanes, **30** and **31** (eq 1). The former was the original starting material used for the first synthesis of 1-methyladamantane by rearrangement.[15]



30 31 (1)

Favorable carbonium ion rearrangement pathways of other tricycloundecanes, including homoadamantane (**18**),[14,16] 2,3-trimethylenebicyclo[2.2.2]octane (**25**),[8a,9] 4-homoisotwistane (**40**),[9,10] 6.7-trimethylenebicyclo[3.2.1]octanes (**27** and **29**),[10] and 2,4-ethanobicyclo[3.3.1]nonane (**20**),[11,12] are also analyzed.

Results and Discussion

Wipke's program CISGEN[4b,17] gave 43 constitutional tricycloundecane isomers which met the strain criteria described above. At this stage, structures with a methyl group were not considered. For each constitutional isomer, all relatively unstrained configurational (and conformational) isomers were

generated by using framework models; this raised the total number of structures to 69. Molecular mechanics calculations using the Engler[18] and the 1971 Allinger[19,20] force fields gave the heats of formation summarized in Table I.[21-23]

The much greater stabilities of 1-methyladamantane ($\Delta H_f°$(obsd)[25] = −40.57 ± 0.34, (calcd)[18] −41.92 (E), −42.89 (A) kcal/mol) and 2-methyladamantane ($\Delta H_f°$(obsd)[25] −35.66 ± 0.62, (calcd)[18] −37.94 (E), −39.04 (A) kcal/mol) relative to the other tricycloundecanes are quite evident. Thus, the overall heat of isomerization of **30** and **31** to 1-methyladamantane is calculated to be nearly −20 kcal/mol. Since the rearrangement is found experimentally to proceed readily,[3,15] any structure having an enthalpy much higher than that of **30** and **31** (−21.7 kcal/mol) is unlikely to play a significant role in the rearrangement course. (No large entropy gain can be expected.) From the standpoint of thermodynamic stability, the following tricyclic $C_{11}H_{18}$ isomers appear to be particularly attractive: a homo(acs)triquinane (**10**),[26,27] [3.3.3]propellane (**13**),[28] **18**,[3,13,14] **27**,[11,12] **40**,[8,9,14b] 1,7-*exo*-trimethylenebicyclo[3.2.1]octane (**51**),[12] and 1,2-*exo*-trimethylene-*cis*-bicyclo[3.3.0]octane (**67**).[12,29-31] All these isomers are predicted to have heats of formation lower than −27 kcal/mol and have been identified as intermediates in acid-catalyzed rearrangements of tricycloundecanes.[8-12]

All possible interconversions among isomers **1–69** by 1,2-alkyl shifts were then studied by examination of framework models in order to assess the bond alignment factors.[32,33] Wagner–Meerwein shifts involving interorbital dihedral angles of zero or 180° are considered to be ideal while those involving angles between 60 and 120° are excluded since they are highly unfavorable energetically.[34,35]

Products of all possible 1,2-skeletal shifts from each of the isomers are shown in Table II. Tables I and II can be combined into a rearrangement graph consisting of 69 isomers and 251 paths among them, similar to that of the tricyclodecanes.[5,6] This graph actually was derived (by three of us independently!), but is unduly cumbersome and not reproduced here since it is complicated by a large number of unrealistic pathways. The partial graph described below (Figure 1), although still formidable, is more convenient for the search for favorable rearrangement pathways from **30** and **31** to 1-methyladamantane.

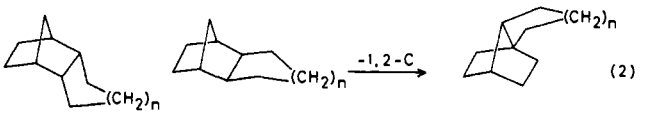
We adopted the following three working principles in our study of the tricycloundecane rearrangements:

1. Hydride abstraction is assumed[6,7] to be rather indiscriminate, with the familiar positional selectivity differences tertiary > secondary > primary significantly reduced in magnitude relative to that of typical carbonium ion reactions.[3] This means that carbocations can be generated at any skeletal position.

2. In the favorable rearrangement pathway, as many reaction steps as possible should be exothermic. The heat of each isomerization step is estimated by comparing the calculated enthalpies of neutral molecules before and after the skeletal shift. A tolerance of ±2 kcal/mol was assumed due to the inherent uncertainty in the energy-predicting abilities of the force field employed.[4a,18] Entropy differences between ground state isomers should be small[4] and have been neglected. Any errors introduced by this assumption should be within the tolerance range adopted.

3. The transition state energy of a given 1,2-skeletal shifts is influenced by the bond alignment factor.[32-34] Since there is no quantitative measure of this factor on activation energy, we took into account only those pathways which involve bond alignments in the ranges 0 ± 60° and 180 ± 60°.[34,35] Furthermore, we took full advantage of the well-known ease of bond migration in 2-norbornyl, 2-bicyclo[2.2.2]octyl, and 2-bicyclo[3.2.1]octyl cations (for either concerted or stepwise mechanisms).[10,38] Paths which contain these structural features were given preference over other, otherwise equally favorable paths after applying the three criteria.

Favorable Pathways of the Rearrangement of 2,3-Tetramethylenenorbornane (30, 31) to Homoadamantane. Figure 1 illustrates the partial graph prepared according to the working principles mentioned above. All possible 1,2-skeletal shifts of **30** and **31** are shown. Among the ten possibilities, that leading to **60** (eq 2) appears most favorable in view of the 4 kcal/mol



n=1 70 n=1 71 n=1 72
n=2 30 n=2 31 n=2 60

of calculated exothermicity, and the 2-norbornyl cation type bridging. The path **31** → **33** is also as exothermic as **31** → **60**, but lacks the assistance from 2-norbornyl bridging. The isomerization **30, 31** → **60** is formally analogous to the proposed first step in the rearrangement of tetrahydrodicyclopentadiene to adamantane (**70, 71** → **72**, eq 2).[6] While this step is endothermic and rate determining in the tricyclodecane series,[6] we predict that the exothermic reactions **30, 31** → **60** should proceed smoothly. Among nine possible isomerization paths from **60** (Figure 1), those leading to **16, 26, 32,** and **43** are less likely thermodynamically. Steps leading to **25, 37,** and **63** involve unfavorable bond alignments, but the steps leading to **48** and **49** may be assisted by 2-norbornyl cation type bridging. Thus, the paths **60** → **48, 49** seem the most likely candidates for the second step in the rearrangement sequence.

In order to avoid excessive complexity in the graph, all possible paths and products are not further reproduced, but only the most relevant ones (Table II gives additional possibilities). Only one path from **48** involves 2-norbornyl bridging. This leads to **49.** Despite as many as ten possible 1,2-skeletal shifts of **49** (Table II), only that leading to **47** appears acceptable. This step satisfies the anti-periplanar requirements for the concerted mechanism, but it is less favorable if a free carbocation is involved (dihedral angle ca. 30°). In contrast to the preceding steps, there cannot be any assistance from bridging. Among ten possible interconversion possibilities of **47,** two paths, both leading to **63,** can involve assistance due to 2-bicyclo[3.2.1]octyl cation type bridging. These two paths can be initiated by exo-hydride abstraction at tertiary C_5 and secondary C_7, respectively (see **47,** Table I, for numbering).

As this selection process is continued, the graph inevitably becomes more and more complex. The screening of possible interconversion paths based on the working principles adopted is continued for all the new isomers which appear along favorable pathways until circuits of the most probable rearrangement routes are identified. These are shown in Figure 1 by darkened lines. These circuits include our provisional goal, homoadamantane (**18**), which is known to isomerize to the methyladamantanes.[3,14,16] If the ring contraction of homoadamantane giving rise to the methyladamantanes is slow compared to the interconversions of other tricycloundecanes, a steady state will be reached whereby a number of tricycloundecane intermediates are equilibrated with the two most stable isomers in the circuits, [3.3.3]propellane (**13**) and 4-homoisotwistane (**40**). **40** is surely more important than **13,** since the main reaction route leading to homoadamantane passes through **40,** while **13** with a structure far removed from the methyladamantanes appears to be a mechanistic dead end. The same is true of **10** and **44,** unless ring contraction steps proceed from these isomers (see below).

Roles of Observed Intermediates in Favorable Pathways. Fourteen tricycloundecane intermediates have been isolated

Table I. Calculated Enthalpies of Tricycloundecane Isomers (kcal/mol, 25°C, Gas)

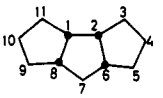
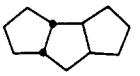
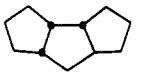
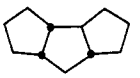
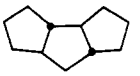
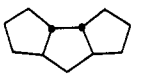
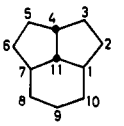
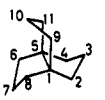
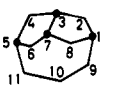
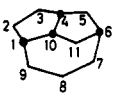
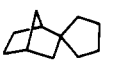
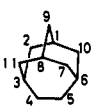
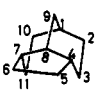
No.	C[a]	Name[b]	Structure	Calcd $\Delta H_f°$[c,d] E[d]	Calcd $\Delta H_f°$[c,d] A[e]
1	6	(1*S*, 2*R*, 6*R*, 8*S*)-[6.3.0.0^{2,6}][f]		−23.24	−19.28
2	6	(1*S*, 2*S*, 6*S*, 8*S*)-[6.3.0.0^{2,6}][f]		−24.96	−20.45
3	11	(1*S*, 2*R*, 6*S*, 8*S*)-[6.3.0.0^{2,6}][f]		−19.53	−17.71
4	11	(1*S*, 2*S*, 6*R*, 8*S*)-[6.3.0.0^{2,6}][f]		−20.95	−18.92
5	6	(1*S*, 2*S*, 6*R*, 8*R*)-[6.3.0.0^{2,6}][f]		−10.23	−9.16
6	6	(1*S*, 2*R*, 6*S*, 8*R*)-[6.3.0.0^{2,6}][f]		−3.07	−2.15
7	7	(1*R*, 4*R*, 7*S*, 11*S*)-[5.3.1.0^{4,11}]		−19.64	−19.21
8	11	(1*S*, 4*R*, 7*S*, 11*S*)-[5.3.1.0^{4,11}]		−24.72	−23.46
9	11	(1*S*, 4*S*, 7*S*, 11*R*)-[5.3.1.0^{4,11}]		−11.68	−12.27
10	7	(1*S*, 4*S*, 7*R*, 11*R*)-[5.3.1.0^{4,11}]		−29.52	−25.89
11	7	(1*S*, 4*R*, 7*R*, 11*R*)-[5.3.1.0^{4,11}]		−22.02	−20.59
12	7	(1*R*, 4*S*, 7*S*, 11*S*)-[5.3.1.0^{4,11}]		−19.63	−19.15
13	3	[3.3.3.0] ([3.3.3]Propellane)[g]		−30.28	−28.98
14	5	*cis*-[3.3.3.0^{3,7}]		−20.01	−14.41
15	11	(1*R*, 4*R*, 6*S*, 10*R*)-[4.3.2.0^{4,10}]		−23.41	−19.42
16	5	Spiro[cyclopentane-1-7′-norbornane]		−17.51	−19.39
17	11	Spiro[cyclopentane-1-2′-norbornane]		−19.44	−19.74
18	5	[4.3.1.1^{3,8}] (Homoadamantane)[h] eclipsed		−29.96[i]	−27.39[i]
		twisted		−29.84[j]	−27.77[j]
19	7	(4*R*, 7*S*)-[5.2.2.0^{4,8}] chair–chair		−26.20	−26.12
		boat–boat		−20.01	−21.19

Table I (*Continued*)

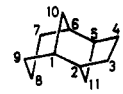
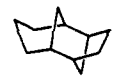
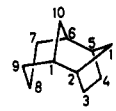
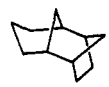
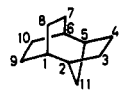
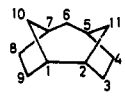
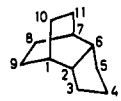
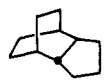
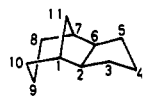
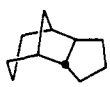
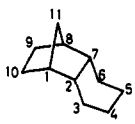
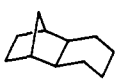
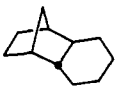
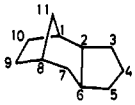
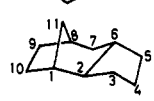
No.	C[a]	Name[b]	Structure	Calcd $\Delta H_f°$[c,d] E[d]	Calcd $\Delta H_f°$[c,d] A[e]
20	7	(1*R*, 2*R*, 5*S*, 6*S*)-[4.3.1.1^{2,5}][k] chair		−18.47	−20.66
		boat		−17.97	−20.66
21	7	(1*R*, 2*S*, 5*R*, 6*S*)-[4.3.1.1^{2,5}][k] chair		−10.78	−12.92
		boat		−1.75	−3.35
22	6	(2*R*, 5*S*)-[4.2.2.1^{2,5}]		−10.01	−12.66
23	6	(1*R*, 2*S*, 5*S*, 7*R*)-[5.2.1.1^{2,5}]		−12.56	−11.43
24	6	(1*R*, 2*R*, 5*R*, 7*R*)-[5.2.1.1^{2,5}]		−18.81	−17.98
25	6	*cis*-[5.2.2.0^{2,6}][l]		−24.30	−26.77
26	5	*trans*-[5.2.2.0^{2,6}]		−13.61	−18.37
27	7	*cis,exo*-[5.3.1.0^{2,6}][m]		−27.79	−27.57
28	11	*trans*-[5.3.1.0^{2,6}]		−9.41	−9.73
29	7	*cis,endo*-[5.3.1.0^{2,6}][n]		−21.94	−20.91
30	6	*cis,endo*-[6.2.1.0^{2,7}][o]		−21.67	−21.79
31	6	*cis,exo*-[6.2.1.0^{2,7}][p]		−21.71	−21.87
32	11	*trans*-[6.2.1.0^{2,7}][q]		−16.88	−17.73
33	11	(1*S*, 2*S*, 6*S*, 8*S*)-[6.2.1.0^{2,6}][q]		−24.91	−25.54
34	11	(1*R*, 2*S*, 6*S*, 8*R*)-[6.2.1.0^{2,6}]		−22.50	−21.86
35	11	(1*R*, 2*R*, 6*S*, 8*R*)-[6.2.1.0^{2,6}]		−17.83	−18.25

Table I (*Continued*)

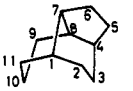
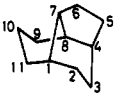
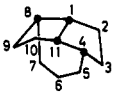
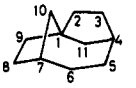
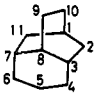
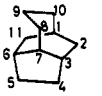
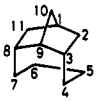
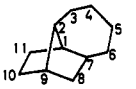
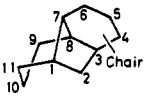
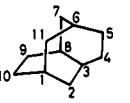
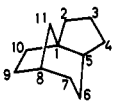
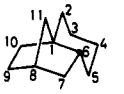
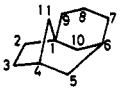
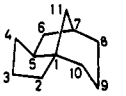
No.	C[a]	Name[b]	Structure	Calcd ΔH_f°[c,d] E[d]	A[e]
36	11	(1*S*, 2*R*, 6*S*, 8*S*)-[6.2.1.0^{2,6}]		−22.73	−23.54
37	11	[5.4.0.0^{4,8}] chair		−25.67	−25.81
		boat		−22.64	−23.70
38	6	[6.3.0.0^{4,11}]		−16.82	−14.33
39	6	[5.2.1.1^{1,4}]		2.10	−4.66
40	8	[5.3.1.0^{3,8}] (4-Homoisotwistane)[r]		−28.60	−30.34
41	8	[4.4.1.0^{3,7}]		−19.82	−20.29
42	7	[6.2.1.0^{3,9}] chair		−15.27	−14.39
		boat		−16.24	−16.27
43	11	[5.4.0.0^{2,9}]		−13.06	−14.05
44	6	[5.4.0.0^{3,8}]		−25.48	−26.78
45	6	[4.4.1.0^{3,8}] [s]		−24.97	−26.10
46	11	(1*S*, 5*S*, 8*R*)-[6.2.1.0^{1,5}]		−26.05	−26.72
47	11	(1*S*, 5*R*, 8*R*)-[6.2.1.0^{1,5}]		−26.02	−27.32
48	11	(1*S*, 6*R*, 8*S*)-[6.2.1.0^{1,6}] [t]		−25.05	−25.82
49	11	(1*S*, 6*S*, 8*S*)-[6.2.1.0^{1,6}] [t]		−27.39	−27.45
50	11	[4.3.1.1^{1,4}]		0.87	−7.82
51	11	(1*R*, 5*S*, 7*S*)-[5.3.1.0^{1,5}] [t]		−28.32	−28.39

Table I (*Continued*)

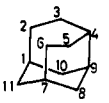
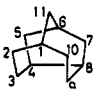
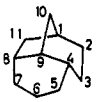
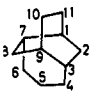
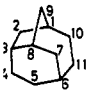
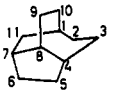
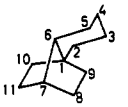
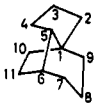
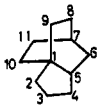
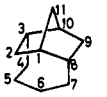
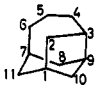
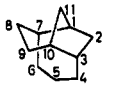
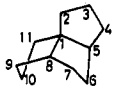
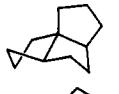
No.	C[a]	Name[b]	Structure	Calcd $\Delta H_f°$[c,d] E[d]	A[e]
52	11	(1*R*, 5*R*, 7*S*)-[5.3.1.$0^{1,5}$]		−17.03	−18.96
53	6	[5.4.0.$0^{4,9}$]		−16.83	−20.85
54	7	[5.3.1.$0^{4,9}$] (Dihydronoriceane)[u]		−24.50	−24.74
55	7	[4.4.1.$0^{4,8}$]		−22.61	−20.98
56	11	[6.2.1.$0^{4,9}$]		−26.36	−25.93
57	6	[5.4.0.$0^{3,9}$] (4-Homotwistane)		−18.18	−23.04
58	11	[4.3.2.$0^{3,8}$]		−15.97	−20.94
59	11	[5.3.1.$0^{4,8}$]		−23.23	−23.31
60	11	[5.2.2.$0^{1,6}$]		−24.95	−25.94
61	11	(1*R*, 5*S*, 6*R*)-[4.3.2.$0^{1,5}$]		−25.28	−26.16
62	11	(1*R*, 5*R*, 6*R*)-[4.3.2.$0^{1,5}$]		−19.34	−21.03
63	11	[5.2.2.$0^{1,5}$] [t,v]		−24.77	−27.54
64	6	[6.3.0.$0^{3,10}$]		−11.04	−10.66
65	11	[5.3.1.$0^{3,9}$] (4-Homoprotoadamantane)[q]		−21.61	−20.35
66	11	[5.4.0.$0^{3,10}$]		−12.91	−14.36
67	6	*cis,cis*-(5*S*, 8*S*)-[6.3.0.$0^{1,5}$] [r]		−28.24	−25.23
68	11	*cis,trans*-(5*S*, 8*R*)-[6.3.0.$0^{1,5}$]		−16.46	−16.64
69	6	*trans,trans*-(5*R*, 8*R*)-[6.3.0.$0^{1,5}$]		10.70	7.55

Table I (*Continued*)

[a] Number of unique carbon atoms. [b] Repetition of "tricyclo...undecane" is avoided for simplicity. Examples of full IUPAC nomenclature: (1*S*, 2*R*, 6*R*, 8*S*)-tricyclo[6.3.0.0^{2,6}]undecane for 1, and *cis,endo*-tricyclo[6.2.1.0^{2,7}]undecane for 30. [c] Strain energies of the molecules shown, as defined by P. v. R. Schleyer and K. R. Blanchard, *J. Am. Chem. Soc.*, 92, 2377 (1970), can be obtained by simply subtracting the following ΔH_f° (kcal/mol) value of strain-free tricycloundecane $C_k(CH)_m(CH_2)_n$ from the calculated ΔH_f° (kcal/mol) of the molecule: −46.77 (E), −47.27 (A) for $k = 2$, $m = 0$, $n = 9$; −45.66 (E), −46.11 (A) for $k = 1$, $m = 2$, $n = 8$; −44.55 (E), −44.96 (A) for $k = 0$, $m = 4$, $n = 7$. [d] Calculations based on Engler force field described in ref 18. [e] Calculations based on the Allinger 1971 force field described in ref 19. [f] Configurational isomers of a triquinane. See ref 26. [g] References 13 and 28. [h] For conformational ambiguity of this molecule, see E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2525 (1972). [i] Taken from ref 18. [j] Taken from ref *h*. [k] Reference 11. [l] References 8a and 41. [m] Reference 9. [n] Reference 10. [o] J. A. Bone, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 2644 (1972). See also ref 10 and 13. [p] References 10, 13, and 15. [q] The energy values refer to trimethylene bridge in endo conformation. [r] References 8–10. [s] C. A. Cupas, W. E. Heyd, and M. S. Kong, *J. Am. Chem. Soc.*, 93, 4623 (1971). [t] Reference 13. [u] Reference 42a. [v] A. Krantz and C. Y. Lin, *J. Am. Chem. Soc.*, 95, 5662 (1973).

Table II. Products of 1,2-Skeletal Shifts[a] from Each Tricycloundecane Isomer (Numbers Refer to Table I)

Starting	Products	Starting	Products
1	29, 34, 52	36	3, 6, 17, 26, 28, 30, 35, 49, 51, 63
2	27, 33, 51	37	38, 40, 41, 43, 44, 46, 53, 56, 59, 60, 61, 62, 66, 67
3	28, 36, 51	38	15, 37, 59, 62, 66
4	28, 35, 52	39	46, 50, 58, 59
5	None	40	37, 43, 44, 45, 49, 50, 51, 56, 57, 59, 63, 65
6	35, 36	41	37, 43, 44, 45, 50, 51, 52, 57, 59, 65
7	46, 67	42	43, 48, 49, 56, 64, 65
8	9, 46, 47, 68, 69	43	37, 40, 41, 42, 49, 57, 60, 64
9	8, 68, 69	44	37, 40, 41, 51, 57, 61
10	15, 19, 47, 56, 68	45	18, 40, 41, 50, 53, 54, 55, 57, 58, 59
11	67	46	7, 8, 37, 39, 47, 48, 50, 51, 56, 59, 63, 67
12	68	47	8, 10, 19, 46, 49, 52, 56, 63, 68, 69
13	61, 62	48	17, 34, 35, 42, 46, 49, 56, 60
14	15, 58, 65	49	17, 33, 36, 40, 42, 43, 47, 48, 50, 60
15	10, 14, 19, 38, 52, 56, 58, 59, 65, 66	50	24, 33, 39, 40, 41, 45, 46, 49, 51, 65
16	17, 25, 60	51	2, 3, 33, 36, 40, 41, 44, 46, 50, 52, 61, 63, 67
17	16, 30, 31, 32, 33, 34, 35, 36, 48, 49	52	1, 4, 15, 34, 35, 41, 47, 51, 56, 62, 63, 68
18	45, 54, 55, 58, 65	53	37, 45, 54, 55, 57, 59, 66
19	10, 15, 47, 54, 56, 58, 59	54	18, 19, 45, 53, 56, 58, 59, 65, 66
20	21, 22, 24, 27, 31, 33	55	18, 45, 53, 58, 59, 65, 66
21	20, 22, 23, 29, 30, 34	56	10, 15, 19, 37, 40, 42, 46, 47, 48, 52, 54, 58, 63, 65, 66
22	20, 21, 23, 24, 25	57	40, 41, 43, 44, 45, 53, 65, 66
23	21, 22, 24, 34	58	14, 15, 18, 19, 39, 45, 54, 55, 56, 59, 65
24	20, 22, 23, 33, 50	59	15, 19, 37, 38, 39, 40, 41, 45, 46, 53, 54, 55, 58, 63
25	16, 22, 26, 27, 29, 33, 34, 60, 61, 62	60	16, 25, 26, 30, 31, 32, 37, 43, 48, 49, 63
26	25, 28, 35, 36, 60, 61	61	13, 25, 26, 27, 37, 44, 51, 62, 63, 67, 68
27	2, 20, 25, 33, 61	62	13, 25, 28, 29, 37, 38, 52, 61, 63, 67, 68
28	3, 4, 26, 35, 36, 62	63	33, 34, 35, 36, 40, 46, 47, 51, 52, 56, 59, 60, 61, 62
29	1, 21, 25, 34, 62	64	42, 43, 65, 66
30	17, 21, 31, 36, 60	65	14, 15, 18, 40, 41, 42, 50, 54, 55, 56, 57, 58, 64, 66
31	17, 20, 30, 33, 35, 60	66	15, 37, 38, 53, 54, 55, 56, 57, 64, 65
32	17, 33, 34, 60	67	7, 11, 37, 46, 51, 61, 62
33	2, 17, 20, 24, 25, 27, 31, 32, 34, 49, 50, 51, 63	68	8, 9, 10, 12, 47, 52, 61, 62
34	1, 17, 21, 23, 25, 29, 32, 33, 48, 52, 63	69	8, 9, 47
35	4, 6, 17, 26, 28, 31, 36, 48, 52, 63		

[a] Paths involving bond alignment factor between approximately 60 and 120° are excluded. See text and footnote 34.

from the rearrangements of various starting materials. Twelve of them have been identified: **10**,[39] **13**,[12] **18**,[12] **27**,[9] 2,3-*cis,exo*-trimethylenebicyclo[3.2.1]octane (**33**),[40] **37**,[39] 4-homoisotwistane (**40**),[8,9,14b] 1,2-*endo*-tetramethylenenorbornane (**48**),[12] 1,2-*exo*-tetramethylenenorbornane (**49**),[12] **51**,[12] 1,2-trimethylenebicyclo[2.2.2]octane (**63**),[12] and **67**.[12] These isomers, as well as **30** and **31**, are indicated by darkened circles in Figure 1. Furthermore, six additional tricycloundecanes have been synthesized: a 2,4-ethanobicyclo[3.3.1]nonane (**20**),[12] 2,3-trimethylenebicyclo[2.2.2]octane (**25**),[41] 6,7-*endo*-trimethylenebicyclo[3.2.1]octane (**29**),[10] 2,3-*trans*-tetramethylenenorbornane (**32**),[40] a dihydronoriceane (**54**),[42a,43] and 3,6-*endo,endo*-trimethylenebicyclo[3.2.1]-octane (**65**),[40,43] indicated in Figure 1 by broken circles. Thus, including **30** and **31**, we have 20 experimental clues out of the 44 structures of Fig. 1 which can be used to help elucidate the favorable rearrangement pathway.

Note that *all* of the identified intermediates isolated from the reaction mixture are included in the independently derived favorable circuits of Figure 1. This provides some confidence in our procedures. The six synthetic tricycloundecane isomers have been checked by GLC against various reaction mixtures, but none of them corresponds in retention time to the peaks observed.[11,40] However, the favorable pathway circuits contain two of these isomers, **25** and **54**. The nondetection of **25** is not easy to rationalize within our scheme, but **18** is much more stable than **54** and its rapid isomerization may preclude observation. A similar explanation may also apply to **25**, which is known to disappear quite rapidly on contact with acid catalyst (see below).[10]

Monitoring the course of rearrangements under various conditions by the GLC–MS technique indicates that **48**, **49**,

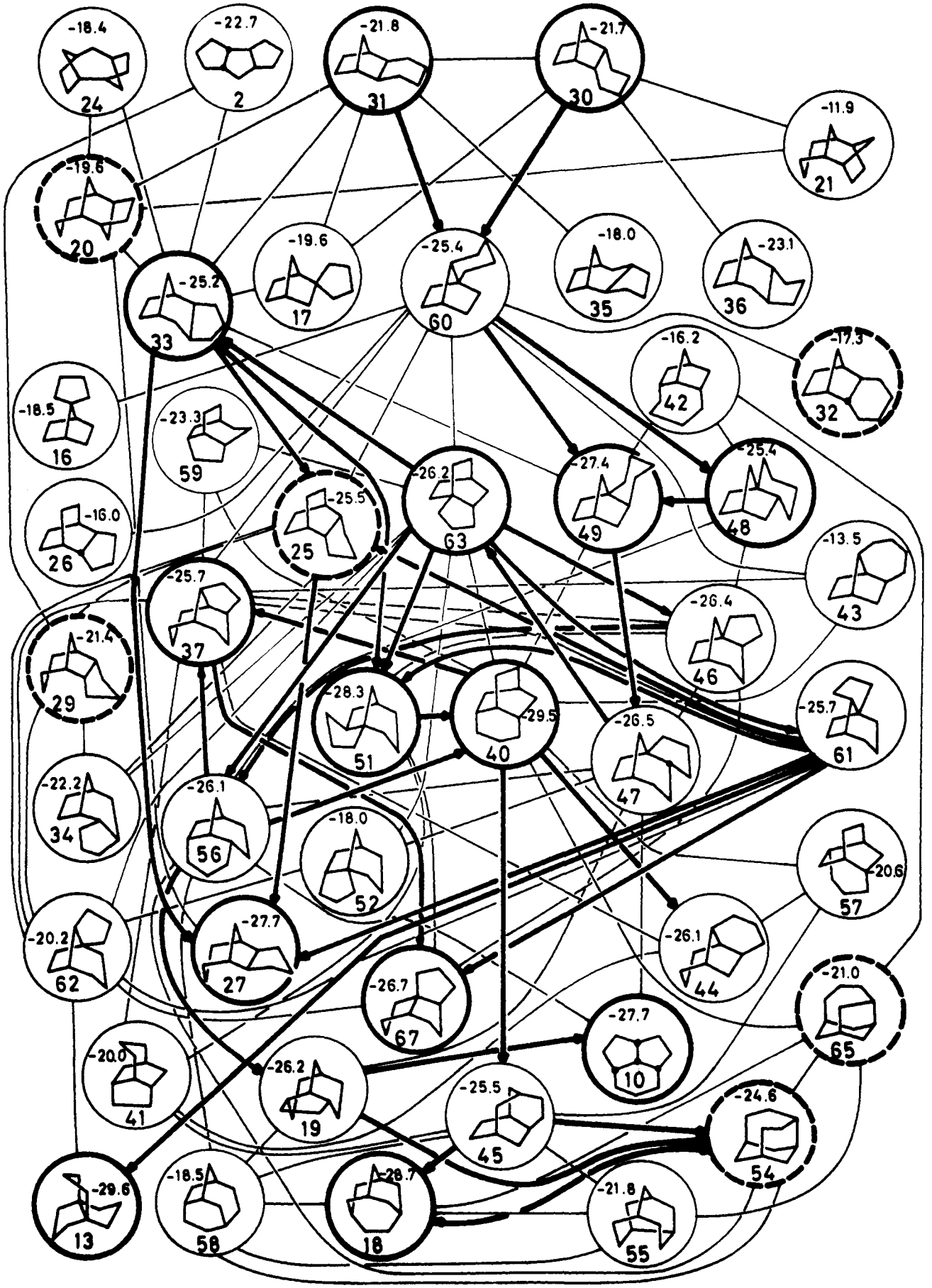
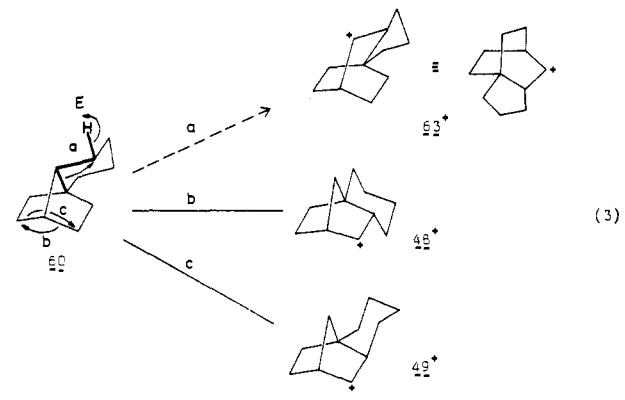


Figure 1. Main portion of tricycloundecane graph. Structure numbers refer to Table I. Negative numbers are average $\Delta H_f°$ values (kcal/mol, 25 °C, gas) calculated from Table I. Darkened lines, likely pathways; darkened circles; intermediates identified; broken circles, compounds confirmed not to be intermediates.

63, and at least one additional unidentified intermediate (designated as C_2) should be located between **30** (**31**) and **40** in the favorable pathway.[12] Furthermore, by using **40** as the starting material, equilibration with **49** and **63**, together with several other intermediates including **13**, **18**, **27**, **51**, and **67**, could be demonstrated.[10,12] These results are in good agreement with the scheme presented in Figure 1.

In a previous paper,[12] it was suggested that **63** may be formed directly from **60** by a single 1,2-skeletal shift. While a concerted mechanism is certainly feasible for this transformation (eq 3, path a), the alternate three-step mechanism via



(3)

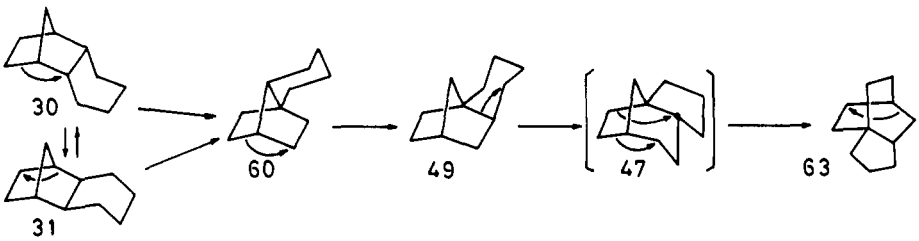
48 and **49**, assisted by 2-norbornyl cation type bridging, and then **47**, may be more favorable.

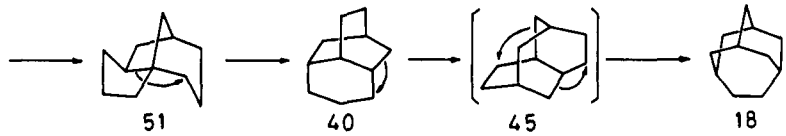
We can now assign structures to C_2 and still another unknown intermediate, C_1, presumed to be located between **30** (**31**) and **40** by our previous experiments.[12] Upon treatment of **40** with an acid catalyst, **49**, but neither C_2 nor **48**, is formed along with several other tricycloundecanes.[12] That is, by starting from **40** and allowing the reaction to reverse toward **30** (**31**), **49** but not other isomers further removed can be formed under the reaction conditions employed.[12] Only two potential intermediates exist between **49** and **30** (**31**) in the proposed pathway of Figure 1: **60** and the already identified **48**. Consequently, C_2 is, by elimination, most likely to be 1,7-tetramethylenenorbornane (**60**). This structure is consistent with the ^{13}C NMR spectrum of C_2, which indicates the presence of one quaternary carbon atom.[12,42b]

Only three possibilities exist for C_1: **46**, **47**, or **61**. C_1 also contains a quaternary carbon atom according to its ^{13}C NMR spectrum,[12] and all other quaternary isomers included in the favorable circuits have already been identified. According to the GLC monitoring of the reaction course,[12] C_1 never appears during earlier, but only in later stages of the rearrangements. **47** is located in the circuits between **49** and **63**, both of which are detected by GLC monitoring from the very beginning of the rearrangement of **30** (**31**).[12] Thus, if **47** were the structure of C_1, it should also have been detected at the same time. Consequently, **47** can be eliminated as a candidate for C_1. On the other hand, **46** and **61** are both located in the later part of the suggested circuits. **61**, as opposed to **46**, can be converted directly into the identified intermediates **13**, **27**, and **67** in the most favorable circuits of Figure 1. Therefore, C_1 probably is 1,8-trimethylenebicyclo[3.2.1]octane (**61**).[44]

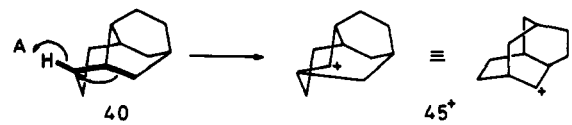
The shortest pathway from **30** (**31**) to homoadamantane is summarized in eq 4. This pathway involves only two undetected structures, **45** and **47**. Perhaps the steps preceding the formation of **45** and **47** are slow compared to their further reaction. This appears to be the case. The transformation **49** → **47** is the only step in the part of the suggested pathway leading from **30** (**31**) to **40** which has no possibility of being assisted by bridged ion type stabilization in the transition state. **49** tends to accumulate in the reaction mixture; it is the second most abundant intermediate (next only to **40**) in earlier stages of the rearrangements of **30**.[12] On the other hand, the step **40** → **45** probably is endothermic. Our calculations predict the heat of reaction to be +4 kcal/mol (Table I). Experimentally, **40** always accumulates very rapidly and then slowly decreases as the methyladamantanes are formed.[10,12]

After **40**, no assistance from bridged ion type stabilization in the most probable pathways can be expected, because bridged ion forming bicyclic partial structures are no longer present. However, favorable bond alignments for concerted 1,2-skeletal shifts **40** → **45** → **18** are available as shown in eq 5 and 6.

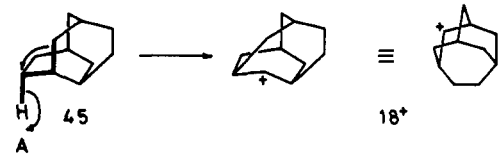




(4)

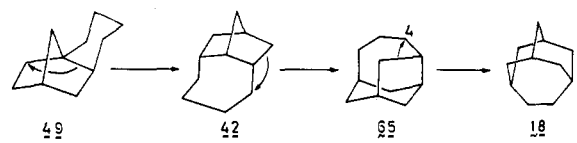


(5)



(6)

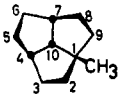
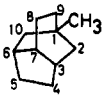
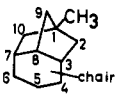
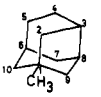
A potential alternative route from **49** to **18** is shown in eq 7. The first step seems favorable (yielding a tertiary cation)



(7)

compared to the step **49** → **47** (eq 4). **42** can be converted to **65**, and then to **18**. This route is three steps shorter than eq 4 and similar to the adamantane pathway from tetrahydrodicyclopentadiene (**70** or **71**).[6] However, we reject this route for two reasons. First, the calculated enthalpy of **42** is too high (Table I). Second, the 1,2-skeletal shift of 4-**65**$^+$ to 2-**18**$^+$ in-

Table III. Calculated Enthalpies and Strain Energies of Selected Methyltricyclodecanes (kcal/mol, 25°C, Gas)

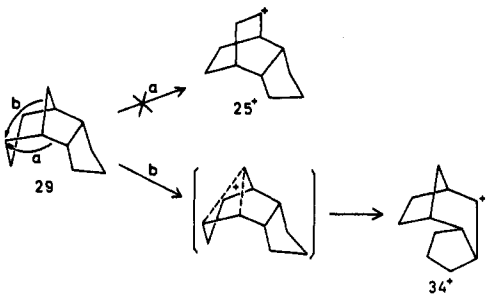
No.	Name	Structure	ΔH_f° E[a]	ΔH_f° A[b]	Strain E[a]	Strain A[b]
73	1-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−32.60	−28.38	15.01	19.49
74	10-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−32.97	−26.58	14.64	21.29
75	2-*exo*-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−30.88	−26.45	15.62	20.26
	2-*endo*-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−30.59	−26.42	15.91	20.29
	3-*exo*-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−31.68	−26.89	14.82	19.82
	3-*endo*-Methyltricyclo[5.2.1.0^{4,10}]decane[c]		−26.35	−20.84	20.15	25.87
80	1-Methyltricyclo[4.3.1.0^{3,7}]decane		−28.05	−28.41	19.56	19.46
	7-Methyltricyclo[4.3.1.0^{3,7}]decane		−26.36	−26.67	22.25	21.20
78	1-Methyltricyclo[5.2.1.0^{3,8}]decane		−29.82	−29.03	17.79	18.84
	8-Methyltricyclo[5.2.1.0^{3,8}]decane		−29.18	−28.77	18.43	19.10
76	1-Methylprotoadamantane		−30.54[d]	−31.88	17.03[d]	15.99
	2-*exo*-Methylprotoadamantane		−27.43[d]	−28.71[d]	19.07[d]	18.00[d]
	2-*endo*-Methylprotoadamantane		−24.66[d]	−25.58[d]	21.84[d]	21.13[d]
	3-Methylprotoadamantane		−30.15[d]	−31.39	17.46[d]	16.48
	8-Methylprotoadamantane		−30.64[d]	−31.76	16.97[d]	16.11
	9-*endo*-Methylprotoadamantane		−25.67[d]	−27.04[d]	20.83[d]	19.67[d]

[a] Calculated based on Engler force field described in ref 18. [b] Calculated based on 1971 Allinger force field described in ref 19. [c] According to empirical force field calculations, perhydrotriquinacene is about 10 kcal/mol more stable in the twisted (C_3) than in the eclipsed conformation (C_{3v}): (a) R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 93, 3189 (1971); (b) E. Ōsawa and I. T. Jacobson, unpublished results. Values presented in the table refer to more stable twist conformation. Mean dihedral angles $C_1C_2C_3C_4$, $C_4C_5C_6C_7$, $C_7C_8C_9C_1$ are −34.3° (73), −34.5° (74), −34.6° (2-*exo*-methyl), −35.8° (2-*endo*-methyl), −34.8° (3-*exo*-methyl), −30.4° (3-*endo*-methyl). [d] Reference 51.

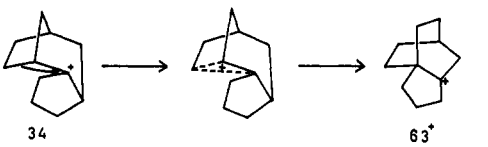
volves an unfavorable bond alignment factor and, in fact, could not be observed to occur experimentally by treatment of **65** with an acid catalyst.[43]

In a previous paper,[10] we reasoned that the 10^4 times faster disappearance rate of **30** compared to **31** arose either from the 2-norbornyl cation type bridging stabilization of the transition state from **30**, induced by 2-exo-hydride abstraction, or from the ground state strain difference between **30** and **31**.[10] Our calculations (Table I) predict essentially the same enthalpy for **30** and **31**. Therefore, the observed rate difference may be due to the more favorable abstraction of the 5-exo-tertiary hydrogen of **30**.

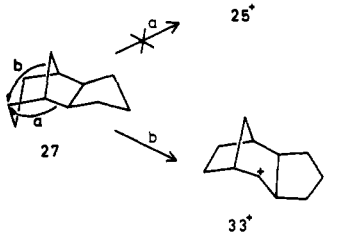
Favorable Pathways of Rearrangements of Other Starting Materials to the Methyladamantanes. Similarly, we can construct the most likely rearrangement pathways of other starting materials. The rearrangement of 4-homoisotwistane (**40**) has already been described above. Four of the five possible steps in the first rearrangement stage of 6,7-*endo*-trimethylenebicyclo[3.2.1]octane (**29**)[10] are included in Figure 1.[45] Among them, the one leading to **25** seems to be favorable because of the possibility of bicyclo[3.2.1]octyl cation type bridging and the higher exothermicity. However, the product distribution from **29** and that from **25** are quite different;[10,40] this seems to exclude step **29** → **25** (path a, eq 8). During the isomerization of **29** to **34** (path b, eq 8), bicyclo[3.2.1]octyl cation type assistance[40,46] may also be expected. From **34**, the path leading to **63** should be particularly favorable because of its exothermicity (eq 9). **63** is included in the circuit of favored intermediates (Figure 1) and the favorable routes should be followed afterwards.



(8)



(9)



(10)

27, the cis,exo isomer of **29**, has also been studied as a starting material.[10] Substantially the same arguments apply. Despite the possibility of 2-bicyclo[3.2.1]octyl cation type bridging leading to **25**, **27** appears to isomerize to **33** (eq 10),[40]

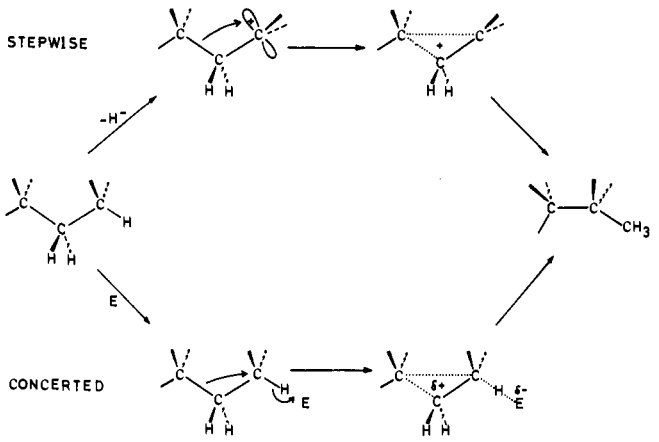


Figure 2. Schematic illustration of ring contraction processes.

which is in one of the circuits of favored intermediates and should equilibrate with **40**. In accord with this analysis,[37] the observed product distributions in the rearrangements of **27** and **29** are virtually the same as that of **40**.[10]

2,4-Ethanobicyclo[3.3.1]nonane (**20**) was also studied.[11] Five out of the six possible initial 1,2-skeletal shifts of **20** (Table II) are shown in Figure 1.[47a] None of these appear to be as favorable as those indicated by darkened lines in Figure 1 for other isomers. Based mostly on energetic grounds, the paths leading to **27** and **33** appear likely to occur. The observed products from **20** include **27** as well as **40**, among other intermediates, and again demonstrate the usefulness of Figure 1.

25 is very interesting; this seemingly important intermediate has never been detected in the reaction mixtures resulting from all other starting materials examined. Rearrangements of isotopically labeled **25** are under investigation and will be reported elsewhere.[47b]

Finally, the acid-catalyzed isomerization of homoadamantane (**18**) and closely related systems have been extensively studied.[3,13-16] Irrespective of the conditions employed, rearrangement predominantly into 1- and 2-methyladamantane is rapid. (This will be discussed in the next section.) Figure 1 indicates that there should be a possibility of observing **40** under conditions of thermodynamic control. Treatment of **18** with trifluoromethanesulfonic acid[16] as well as 4-**18**-ol with H_2SO_4-pentane[13c,14b] did indeed produce **40** along with **27**, **51**, **67**, and the methyladamantanes.[43]

Ring Contraction. Homoadamantane (**18**) appears to be a key intermediate through which other tricycloundecane isomers can be transformed into the more stable methyladamantanes.[3,13-16] However, **18** is *not* the only tricycloundecane which may undergo ring contraction and methyl group generation. Recently, we have isolated two (acs)methyltriquinane isomers,[26] **73** and **74** (Table III), from the reaction mixtures resulting from **25**, **27**, **29**, **30**, **31**, and **40**.[10,12,48] Neither **73** nor **74** can arise directly from homoadamantane. These methyltricyclodecane isomers probably represent important clues to the ring contraction mechanism.[49]

Theoretically, the ring contraction that gives rise to methyl expulsion can occur at any place in the tricycloundecane energy surface; stepwise and concerted processes are illustrated in Figure 2. Favorable bond alignments are parallel disposition between migrating and vacant orbital for the stepwise mechanism, and anti-periplanar arrangement of three involved bonds for the concerted mechanism. Since primary carbenium ions are unstable, bridged protonated cyclopropane type intermediates or transition states are assumed to be involved and have been implicated for solvolytic 3-homoadamantyl to 1-adamantyl carbinyl ring contractions.[13a,36] This particular isomerization is reversible because of offsetting carbonium ion stability and ring strain factors. In principle, any ring contraction under acid catalysis is reversible, but it may be possible in fact that the methyltricyclodecanes, once formed, do not revert back to tricycloundecanes, but rearrange more rapidly to the methyladamantane end products.[32] The further steps may follow the tricyclodecane graph[6] with necessary modifications due to the presence of the methyl group.

GLC monitoring of the reaction mixtures revealed that the methyltriquinanes, **73** and **74** (Table III), appeared irrespective of the starting material, but only in the later stages of rearrangement.[10,12] When **30** is used as the starting material, a number of intermediates, including **27**, **37**, **40**, **67**, and probably **61**, have already appeared while **73** and **74** still could not be detected by GLC. We thus assume that the ring contraction takes place from one or more intermediates located *after* **40** in the favored sequence of Figure 1.

The possibilities of methyl expulsion from the 11 favored tricycloundecane intermediates appearing after **40** were studied in terms of heats of reaction and bond alignments. Since the number of possible methyltricyclodecanes is too large

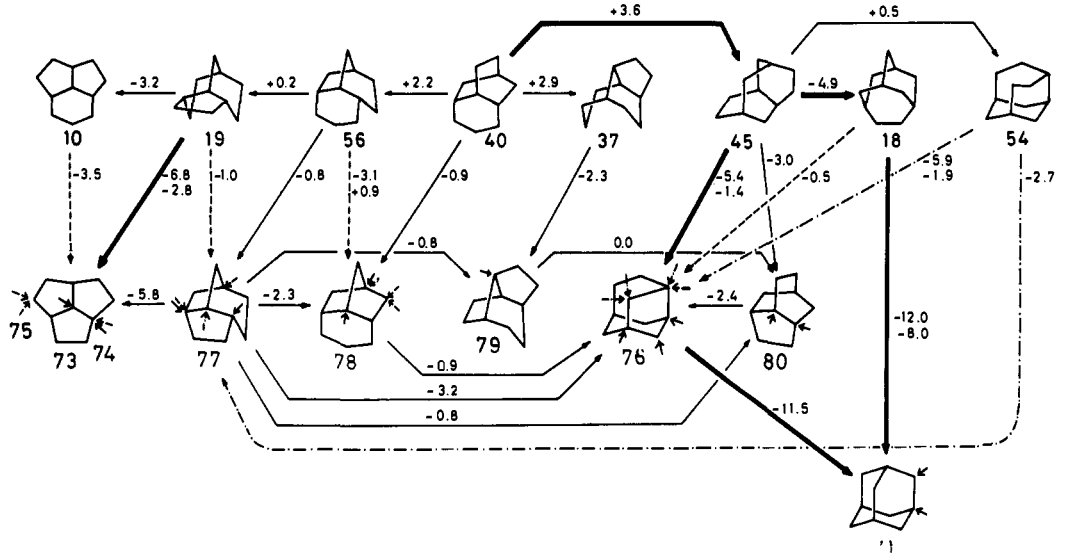
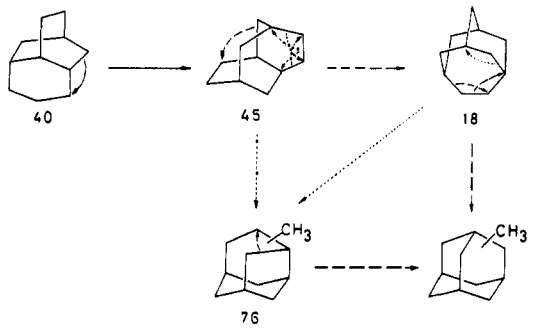


Figure 3. Favored ring contraction and further steps in tricycloundecane to methyltricyclodecane rearrangements. Positions of methyl group are indicated by small arrows. Structure numbers of tricycloundecanes refer to Table I, while those of methyltricyclodecanes refer to Table III. Figures on the reaction paths are the heats of reaction along the direction indicated, calculated based on Engler force field of ref 18. Darkened lines show likely pathways.

to calculate, we chose to use a group increment additivity scheme (−8.4 kcal/mol for substitution of a methyl at a bridgehead position and −6.9 kcal/mol at a bridge position)[50] to predict the heats of formation for the methyltricyclodecanes. As usual, strongly endothermic paths were eliminated.

Figure 3 summarizes the remaining possibilities, all of which involve favorable bond alignment factors. Vertical changes represent ring contraction processes while the horizontal interconversions correspond to tricycloundecane isomerizations (upper) and methyltricyclodecane isomerizations (lower). Numbers on the reaction paths are estimated heats of reaction; two numbers, where present, correspond to the maximum and minimum heats of reaction for the various methylated products as given by the two force fields employed. From a thermodynamic standpoint, the most favorable routes from the prominent intermediate **40** to the methyladamantanes are shown in eq 11. Of these, only step **40** → **45** is endothermic and perhaps



(11)

rate determining. When **45** is reached, the two indicated paths that follow appear to be almost equally plausible. Some of the methylprotoadamantanes (**76**)[51] are predicted to be remarkably stable (Table III), and their probable role in the ring contraction step has already been suggested.[8b,43] Furthermore, the significance of a seemingly trivial by-path, **18** → **76**, has been demonstrated recently.[16,43]

The methyltriquinanes, **73** and **74**, must have arisen directly from **10** or **19**, or from **19** via **56** and **77**. **73** and **74** probably are local minima, since bridgehead methylated (acs)triquinanes are second only to methyladamantanes among all the methyltricyclodecanes in their stability (Table III). In addition, the only path available for further isomerization to methyladamantane, **73**, **74** → **77**, is quite endothermic.[52] Thus, **73** and **74** tend to accumulate and are observed to be converted only slowly to the stabilomer.[12]

The direct path from **40** to **78** is clearly unfavorable because it involves a 1-bicyclo[2.2.2]octyl-type carbocation. We have at present no reason to reject other possible rearrangement paths depicted in Figure 3. In addition to the most probable ring contraction routes shown in eq 11, we are of the opinion that several alternative routes probably exist.

Conclusion

Tricycloundecane rearrangements are extremely complex. Identification of several intermediates and determination of relative rates do not provide definitive mechanistic information. A graphical analysis coupled with calculations of thermodynamic stabilities of $C_{11}H_{18}$ isomers and an assessment of dihedral angle requirements of each possible 1,2 shift are powerful aids for the solution of such problems. The explicit calculation of the energies of the vast number of potential carbocation intermediates was circumvented by making simplifying assumptions based on the favorable rearrangement routes observed experimentally.

Acknowledgments. We thank Professor W. T. Wipke for computer generation of isomer structures. A part of this work was done during E.O.'s temporary stay at Universität Karlsruhe under the financial support provided by the Alexander von Humboldt-Stiftung. This work was also supported by a grants from the Research Council of the Republic of Croatia (Yugoslavia) and by the National Science Foundation and the National Institutes of Health (at Princeton). Computations were carried out at the Hokkaido University Computing Center (FACOM 230-75), Kao Soap Co. (UNIVAC 1110), Rechenzentrum der Universität Karlsruhe (UNIVAC 1108), and the Princeton University Computing Center (IBM 360-91).

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(1) (a) Hokkaido University; (b) Kao Soap Co.; (c) "Ruder Boskovic" Institute; (d) Princeton University; (e) Universität Erlangen-Nürnberg.
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(35) These assumptions imply that both sp^2 and sp^3 alignment factors[33] are considered, since both stepwise and concerted mechanisms are likely to occur for the 1,2-skeletal shift. While concerted mechanisms often prevail in solvolytic reactions,[36] 1,2 shifts initiated by hydride abstraction with strong acids have been traditionally considered to involve free carbonium ions.[3,6,7] However, we have recently presented some kinetic, albeit indirect, evidence indicating the operation of concerted mechanism in hydride abstraction with trifluoromethanesulfonic acid.[10,37] Since we have no firm grounds to reject either of these two mechanisms, and our present goal is to consider all possible Wagner–Meerwein shifts among 69 isomers of $C_{11}H_{18}$, we tentatively follow the dual policy.
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(49) Taking a single, reverse step from each of **73** and **74** to suggest **10** and/or **19** as their progenitors, as has been done in the previous paper,[12] may be oversimplification. Other undetected methyltricyclodecane intermediates may be involved.
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Structural Effects in Solvolytic Reactions. 22. Effect of Ring Size on the Stabilization of Developing Carbocations as Revealed by the Tool of Increasing Electron Demand

Herbert C. Brown,* M. Ravindranathan,[1a] Edward N. Peters,[1b] C. Gundu Rao,[1a] and Morris M. Rho[1c]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received February 7, 1977*

Abstract: Representative aryldialkylcarbinyl (RR'ArCOPNB) and 1-aryl-1-cycloalkyl ($(\overbrace{CH_2)_{n-1}}C$ArOPNB) *p*-nitrobenzoates were synthesized and their rates of solvolysis in 80% aqueous acetone determined in order to examine the electron deficiency in the developing carbocationic center as measured by the tool of increasing electron demand. A rough parallelism exists between the observed rates and the ρ^+ values: *tert*-cumyl (R, R' = Me), −4.72; 2,3-dimethyl-2-butyl (R = *i*-Pr; R' = Me), −4.76; 3-pentyl (R, R' = Et), −4.52; 1-cyclopropyl ($n = 3$), −5.15; 1-cyclobutyl ($n = 4$), −4.91; 1-cyclopentyl ($n = 5$), −3.82; 1-cyclohexyl ($n = 6$), −4.60; 1-cycloheptyl ($n = 7$), −3.87; and 1-cyclooctyl ($n = 8$), −3.83. The similarity in the ρ^+ values for the *tert*-cumyl, 2,3-dimethyl-2-butyl, and 3-pentyl derivatives indicates that the stabilizing effect of the alkyl groups (methyl, ethyl, and isopropyl) on the developing cationic center must be nearly the same. The high negative values observed for the cyclopropyl and cyclobutyl derivatives are attributed to the effect of I-strain in destabilizing the cationic center, resulting in an increased demand on the aryl system for electronic contributions to stabilize the electron deficiency. The marked difference in the relatively high (−) value in ρ^+ for cyclohexyl as compared to the other ring systems (five, seven, and eight) is attributed to the resistance of the conformationally stable cyclohexyl system to the introduction of an sp^2 cationic center in contrast to the ready accommodation of such a center in the more crowded five-, seven-, and eight-ring systems (I-strain). The 1-methyl-1-cycloalkyl *p*-nitrobenzoates were also synthesized and solvolyzed. In these systems the tool of increasing electron demand yields results entirely consistent with earlier studies based primarily upon direct comparison of rates.

For many years solvolysis rates have been utilized to arrive at an understanding of the factors influencing the stability of carbonium ions.[2,3] A remarkably consistent body of knowledge has been built up in this way.[4,5]

One possible difficulty has been the necessity of comparing the rate with a suitable model system.[6,7] Occasionally this can lead to ambiguities.[8] The tool of increasing electron demand appears to minimize such ambiguities.[8]