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(33) **Note Added in Proof.** E. S. Lahaniatis, H. Parlar, S. Gäb, and F. Korte, *Synthesis*, 47 (1976), have recently reported a synthesis of several polychlorinated derivatives of **11** by a sensitized photocyclization process.

The Ethanonoradamantanes. An Experimental Evaluation of Empirical Force Field Predictions[1]

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2,4-Ethanonoradamantane (**6**) is the most stable of 2486 possible tetracyclic ring systems of empirical formula $C_{11}H_{16}$. While empirical force field calculations predicted **6** and 2,8-ethanonoradamantane (**7**) to be the most stable tetracycloundecanes and to have equal stability, $AlBr_3$-catalyzed isomerization of tetracyclo[6.3.0.0^{2,6}.0^{5,9}]undecane (**13**), noriceane (**9**), and methanotwistane (**14**) gave mixtures of **6** and **7** in a 97:3 (±1) ratio. The structures of **6** and **7** were established by syntheses based on the stereochemical control imposed on the C–H carbene insertion of *exo*- and *endo*-2-noradamantyl methyldiazo ketones (**19** and **20**). While **13** and **9** rearrange directly to **6** and **7** in high yield, **14** isomerized initially to **7**, which then underwent slow isomerization to the more stable **6**, accompanied by extensive disproportionation to 1-methyladamantane. Noriceane (**9**) was detected as an intermediate in the rearrangement of **14**. The mechanisms of these isomerizations are analyzed using a graph interconnecting 15 tetracycloundecanes. The overall results demonstrate the power of force field calculations, but indicate that there are still limitations in accuracy even when an isomerization between structurally related molecules is involved.

The $AlCl_3$-catalyzed rearrangement of tetrahydrodicyclopentadiene to adamantane demonstrated the synthetic potential of thermodynamically controlled polycyclic isomerizations.[3] Diamantane,[4] triamantane,[5] and many other cage molecules have now been prepared by this method.[6] A readily available precursor, generally with the same empirical formula and number of rings, is treated with a strong Lewis acid. Although exceptions are known,[7,8] rearrangement to the most stable isomer (the "stabilomer")[9] usually occurs.[6] Although it is rather obvious that adamantane should be the $C_{10}H_{16}$ stabilomer, predictions in other instances are much more difficult. For example, qualitative inspection of the structures of iceane (**1**) and of ethanoadamantane (**2**) does not provide a clear basis for understanding why the latter is the $C_{12}H_{18}$ stabilomer.[10]

Further progress in this area requires the development of a systematic method for the prediction of the stabilomer of any given saturated hydrocarbon set. We illustrate in this paper the procedure we have devised for the tetracyclic $C_{11}H_{16}$ series.

Prediction of the $C_{11}H_{16}$ Tetracyclic Stabilomer. In general, the prediction of a stabilomer will require three steps:

1. Determination and listing of all possible isomers. The number is likely to be prohibitively large.

2. Elimination of isomers expected qualitatively to be unstable on the basis of structural considerations.

3. Quantitative estimation of the free energies of formation of the remaining isomers. The isomer with the lowest free energy is predicted to be the stabilomer.

The computer program developed by Wipke for the elucidation of the number of polycyclic isomers[11] predicts that 2486 tetracyclic $C_{11}H_{16}$ ring systems are possible. This program further indicates the ring sizes present in each isomer. Since structures with three-membered rings tend to be highly strained (and do not, in any event, survive AlX_3 isomerization) these are unlikely stabilomer candidates. Elimination of such structures reduces the number of isomers to 812. Similarly, isomers with four-membered rings can also be rejected; this leaves only 68 possibilities. In order to check this latter assumption, we included the methano-bridged adamantane (**3**) in the set to be calculated, because it should be the most stable $C_{11}H_{16}$ tetracycle with a four-membered ring.[12,13]

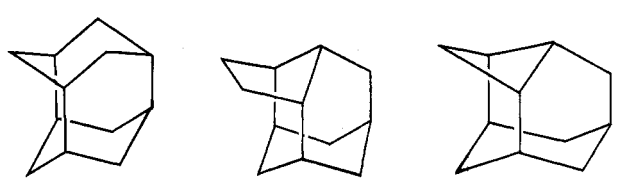
Inspection of the structures of the 68 theoretical $C_{11}H_{16}$ isomers with only five- and six-membered rings show that many have intertwined bridges or other obviously unfavorable features. While quite a manageable number of isomers remained, we chose to continue the screening process. If we had not had any access to experimental information, we would have at this point calculated the heats of formation of all viable $C_{11}H_{16}$ tetracyclic candidates by empirical force field calculations.[14,15] Estimation of the entropy and the free energies would have completed the process. Instead, we took

Table I. Structural Analysis of $C_{11}H_{16}$ Tetracyclic Ring Systems[a,b]

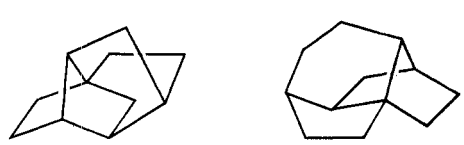
No. of unique C atoms	Total no. of $C_{11}H_{16}$ ring systems	No. of systems with n quaternary C atoms		
		$n = 0$	$n = 1$	$n = 2$
4	4	3	1	0
5	5	1	1	3
6	14	6	4	4
7	7	5	1	1
8	4	1	2	1
9	1	0	0	1
10	0	0	0	0
11	33	11	19	3

[a] Restricted to systems not containing three- or four-membered rings. [b] Based on the results of a computer program written by Professor T. Wipke.[11]

advantage of another feature of Wipke's program: its ability to give the number of unique carbon atoms in a given isomer, and the number of quaternary carbons in each structure (Table I). This information, in conjunction with ^{13}C NMR spectra of the $C_{11}H_{16}$ stabilomer (obtained by $AlBr_3$ isomerization, see below), further reduced the number of force field calculations required. The fully decoupled ^{13}C NMR spectum of the chief 97 ± 1% $AlBr_3$ rearrangement product exhibited six resonances, but the intensities suggested that there might be an accidental degeneracy, i.e., structures with seven unique carbons could not be excluded. Of the 14 structures with six unique carbons and seven with seven unique carbons (Table I), 13 can be eliminated from consideration because they possess highly strained intertwined bridges. The off-resonance decoupled ^{13}C NMR spectrum of the rearrangement product indicated that no quaternary carbons were present, eliminating two additional ring systems, tetracyclo[5.3.1.$0^{4,9}$.$0^{4,11}$]undecane (**4**) and tetracyclo[5.2.2.$0^{1,6}$.$0^{4,9}$]-undecane (**5**). In addition, these isomers contain elaborate norbornane structures which should be relatively high in strain.



1 **2** **3**



4 **5**

Empirical force field calculations[14,15] were carried out on the remaining six isomers, **6, 7, 9–12.** To these (Table II) were added 2,9-ethanonoradamantane (**8**) and methanoadamantane (**3**). Except for **10–12,** these choices could have been derived based on prior experience and calculations on related tricyclic and tetracyclic systems. Thus, ring contractions by elimination of a methylene group from various positions of ethanoadamantane (**2**), the $C_{12}H_{18}$ tetracyclic stabilomer,[10] gives **3** as well as **6–8.** These three ethanonoradamantanes (**6–8**) can also be arrived at by adding a $-CH_2CH_2-$ bridge to the C_9H_{14} tricyclic stabilomer, noradamantane.[16] Noriceane (**9**)[17] also seems intuitively to be a good stabilomer candidate, because it contains only five- and six-membered rings.

Both force fields [Engler,[14] designated (E); Allinger,[15] 1971, (A)] indicate 2,4-ethanonoradamantane (**6**) and 2,8-ethanonoradamantane (**7**) to have equal enthalpies of formation and both to be substantially more stable than any other isomers (Table II). Since both **6** and **7** have rigid structures, the same number of CH_2 and CH groups, and the same symmetry number (one), entropy differences are expected to be negligible.[18] Although the force field calculations pertain to the gas phase, relative energies of alkane isomers do not change much in the liquid phase.[18] Therefore, the calculations lead to the prediction that **6** and **7** should be formed in about equal amounts to the exclusion of any other $C_{11}H_{16}$ tetracyclic isomers at thermodynamic equilibrium at room temperature.[50]

Results

Three $C_{11}H_{16}$ isomers, tetracyclo[6.3.0.$0^{2,6}$.$0^{5,9}$]undecane (**13**), noriceane (**9**), and methanotwistane (**14**), were utilized as precursors for rearrangement into more stable tetracyclic undecane systems.

When (D_3)-trishomocubane (**15**) was prepared by $AlBr_3$ isomerization of a pentacyclic $C_{11}H_{14}$ precursor (**16**), two by-products (~5%, ~2%) both having *m/e* 148 ($C_{11}H_{16}$) formed.[19] Since the sample of **16** used in the rearrangement contained 6% of tetracyclic **13,** the latter seemed a logical precursor for the initial $C_{11}H_{16}$ isomerization studies.

Pure **13** was prepared by Wolff–Kishner reduction of the readily available tetracyclic diketone **17.**[20,21] Treatment of **13** with three times its weight of aluminum bromide in carbon disulfide at room temperature for 1.5 h gave in up to 84% yield a mixture of two *m/e* 148 isomers in a ratio 97:3. Small amounts of disproportionation products, adamantane (~1%) and 1-methyladamantane (~10%), were identified by characteristic GLC retention times and GC–MS. The amounts of the disproportionation products varied with the experiment, but tended to increase with longer reaction times. A small amount (~1%) of a *m/e* 146 isomer identified (GLC, GC–MS) as (D_3)-trishomocubane[19] was also observed. When the progress of the reaction was monitored by GLC no buildup of significant amounts of any additional intermediate rearrangement products was observed. The major component with *m/e* 148 was isolated by preparative GLC, mp 167–168 °C (designated as the solid isomer). Its ^{13}C NMR spectrum exhibited six resonances (one possible coincidence) and the chemical shifts were consistent with either **6** or **7.** 2,4-Ethanonoradamantane (**6**) and **7** are equally close mechanistically (Scheme I) to **13** in that both need involve only two 1,2-alkyl shifts.

Scheme I

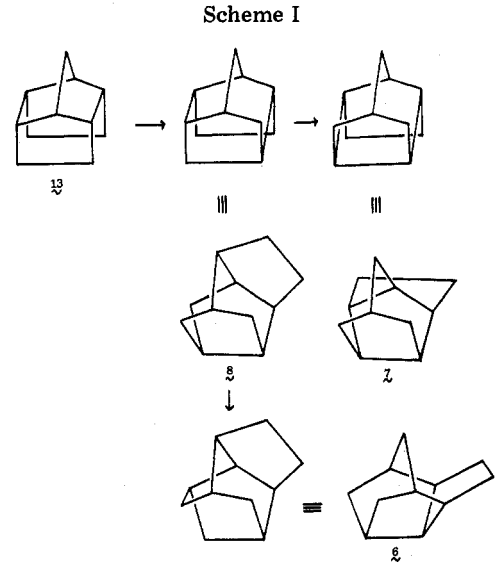
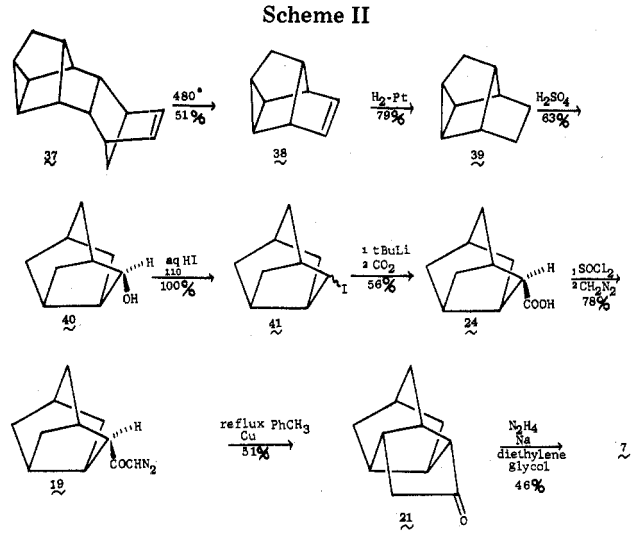


Table II. Molecular Mechanics Calculations of Selected $C_{11}H_{16}$ Hydrocarbons

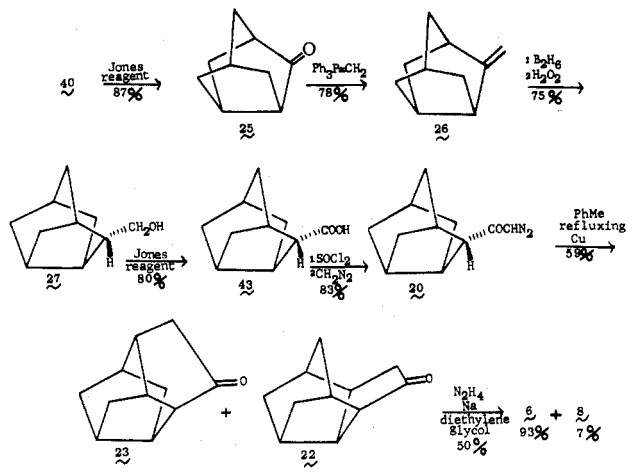
Compd		$\Delta H_f°$[a]
Tetracyclo[5.3.1.$0^{2,5}$.$0^{4,9}$]undecane	E[b]	7.61
(Methanoadamantane) (3)	A[c]	7.68
Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,9}$]undecane	E	−13.21
(2,4-Ethanonoradamantane) (6)	A	−13.16
Tetracyclo[6.2.1.$0^{2,6}$.$0^{5,10}$]undecane	E	−13.19
(2,8-Ethanonoradamantane) (7)	A	−13.17
Tetracyclo[6.2.1.$0^{2,9}$.$0^{5,9}$]undecane	E	−5.38
(2,9-Ethanonoradamantane) (8)	A	−7.16
Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane	E	−7.42
(Noriceane) (9)	A	−10.42
Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,11}$]undecane	E	7.34
(Trimethylenebisnoradamantane) (10)	A	10.58
Tetracyclo[5.4.0.$0^{3,10}$.$0^{5,9}$]undecane	E	−3.71
(11)	A	−3.91
Tetracyclo[6.2.1.$0^{2,6}$.$0^{4,9}$]undecane	E	14.23
(12)	A	8.13
Tetracyclo[6.3.0.$0^{2,6}$.$0^{5,9}$]undecane	E	−4.00
(13)	A	−2.22
Tetracyclo[6.2.1.$0^{2,7}$.$0^{4,9}$]undecane	E	0.17
(Methanotwistane) (14)	A	−4.86
Tetracyclo[5.4.0.$0^{2,9}$.$0^{4,8}$]undecane	E	−5.04
(Brexabrendane) (29)	A	−6.63
Tetracyclo[5.3.1.$0^{2,6}$.$0^{3,8}$]undecane	E	−2.54
(Brexatwistbrendane) (30)	A	−4.34
Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,8}$]undecane	E	−2.15
(31)	A	−3.45
Tetracyclo[6.2.1.$0^{2,6}$.$0^{4,10}$]undecane	E	−8.27
(Methanoprotoadamantane) (32)	A	−7.62
Tetracyclo[6.3.0.$0^{2,6}$.$0^{3,10}$]undecane	E	−10.11
(33)	A	−5.80
Tetracyclo[6.2.1.$0^{2,6}$.$0^{3,9}$]undecane	E	4.04
(34)	A	2.05

[a] Kcal/mol, gas phase, 25°C. Strain energies can be calculated by adding 38.61 (E) and 38.88 (A) to respective heats of formation. Ref 1. [b] Engler force field. Ref 14. [c] Allinger 1971 force field. Ref 15.

Scheme II

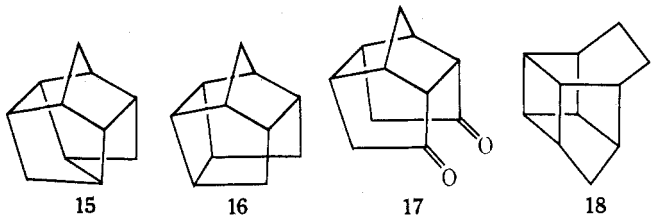


Scheme III



Noriceane[17] (**9**) reacted more smoothly (faster, less disproportionation) but gave essentially the same results as for **13**. Treatment of **9** with $AlBr_3$ under the same conditions as for **13** afforded after 1 h the same mixture of the two isomers (95 and 3%) as obtained above as well as 2% of 1-methyladamantane.

Methanotwistane (**14**), prepared by catalytic hydrogenolysis of the strained C–C bond of pentacyclo[6.2.1.$0^{2,7}$.$0^{4,9}$]undecane (**18**),[22] behaved somewhat differently from **13** and **9**. Upon contact with $AlBr_3$, **14** disappeared almost instantly and the same *m/e* 148 isomers were produced. However, the ratio of these isomers formed initially was quite different from that previously encountered, and thus afforded an opportunity to obtain the "other" (designated the liquid isomer) $C_{11}H_{16}$ rearrangement isomer. The new *m/e* 148 isomer, isolated by preparative GLC, was a liquid which showed seven resonances in the decoupled ^{13}C NMR spectrum; the structure therefore was compatible with either **6** or **7**. Prolonged treatment of the reaction mixture with $AlBr_3$ gradually reversed the ratio of the two isomeric products until the ratio of solid to liquid isomers approached 5:1. Extensive disproportionation to 1-methyladamantane (amounting to 93% of the mixture) did not allow accurate measurement of the equilibrium ratio. When the pure liquid isomer (synthetic sample, see below) was treated with $AlBr_3$, a 98:2 ratio of solid to liquid isomers was reached after 2 days at room temperature.



15 16 17 18

Two additional features of the methanotwistane (**14**) rearrangement merit special attention. During very early stages of rearrangement (up to 10 min), a small peak identified as noriceane (**9**) was detected by GLC and confirmed by GC–MS. Also, in very early stages of the rearrangement of **14**, use of a Golay capillary column revealed that substantial amounts of 2-methyladamantane had formed, but that only a small amount of 1-methyladamantane was present. 2-Methyladamantane no longer was present after 40 min of reaction at room temperature; rearrangement to 1-methyladamantane was nearly complete.[6b]

No structural assignment could be made to the two isomeric $C_{11}H_{16}$ rearrangement products, one a solid of mp 167–168 °C and the other a liquid, on the basis of ^{13}C NMR spectra. In addition, the amorphous nature of the crystals of the solid product discouraged submission for possible x-ray determination of the structure. We therefore chose to synthesize **6** and **7** independently.

Synthesis of 2,8-Ethanonoradamantane (7) and 2,4-Ethanonoradamantane (6). The stereochemical control imposed on the C–H insertions of the carbenes generated from the isomeric diazo ketones **19** and **20** under high-dilution conditions[23] forms the basis for the syntheses of **6** and **7** (Schemes II and III, respectively). The exo diazo ketone **19** gives ketone **21** while the endo diazo ketone **20** yields a mixture of ketones **22** and **23**. Wolff–Kishner reduction[24] of **21** yields **7**, while reduction of **22** and **23** gives **6** and **8**.

Diazo ketone **19** was prepared from *exo*-noradamantanecarboxylic acid (**24**) which was obtained stereochemically pure by carboxylation of 2-noradamantyllithium.[25] The stereochemistry was confirmed by ^{13}C NMR (see below). The stereoselectivity of carboxylation must be attributed to kinetic control, as a mixture of the methyl 2-noradamantanecarboxylates when epimerized in a methanol solution containing NaOMe gave an equilibrium containing only 75% of the exo ester. Model empirical force field calculations indicate *exo*-2-methylnoradamantane to be only 1.0 kcal/mol more stable than the endo isomer.

The 2,8-ethanonoradamantane (**7**) obtained by this route (Scheme II) was identical with the liquid *m/e* 148 isomer which predominated during the initial stages of the methanotwistane (**14**) rearrangement and was the minor product (3 ± 1%) from isomerization of **13** and **9**. When treated with $AlBr_3$, synthetically obtained **7** yielded a mixture of **6** and **7** in a 98:2 ratio after 48 h in CS_2 solution at room temperature. This result differs somewhat from that observed when **7** was produced as an intermediate during the rearrangement of **14**. This discrepancy may be due to variations in the activity of the $AlBr_3$ catalysts employed (the extent of disproportionation in these rearrangements is known[6b] to depend on the activity of the catalyst).

Synthesis and Rearrangement of 2,4-Ethanonoradamantane (6). The preparation of the diazo ketone precursor to **6** (Scheme III) depended on the known selectivity of attack of 2-noradamantane derivatives from the less hindered exo side.[26] The desired 2-noradamantane derivative was prepared as 2-noradamantanone (**25**) was converted by a Wittig reaction[27] to 2-methylenenoradamantane[28] (**26**).

Predominant attack of **26** from the less hindered exo face by diborane,[29] followed by hydrogen peroxide oxidation, gave ~95% of *endo*-noradamantylcarbinol (**27**) and only ~5% of *exo*-2-noradamantylcarbinol (**28**). No efficient means of

Table III. Comparison of Heats of Isomerization (Gas, kcal/mol) from Various Sources

Reaction	Exptl ΔH_{isom}		Calcd ΔH_{isom}	
	From direct isomerization data	From ΔH_f° differences	1971 Allinger force field	Engler force field
2-Methyladamantane → 1-methyladamantane	−2.77[a]	−4.91[b]	−3.85[c]	−3.88[c]
1-Methyldiamantane → 4-methyldiamantane	−2.14[a,d]	−3.68[b]	−2.78[c]	−3.26[c]
3-Methyldiamantane → 4-methyldiamantane	−2.70[a,d]	−5.93[b]	−3.86[c]	−3.91[c]
Protoadamantane → adamantane	(−11.0,[e] > 7.5[b])	−11.22[b]	−11.19[c]	−11.37[c]

[a] Reference 6b. This review summarizes the available data. [b] Reference 32a. [c] References 14, 15. [d] These values would be 0.3–0.5 kcal/mol larger if theoretical instead of experimental entropies are assumed (see ref 31c). [e] Indirectly estimated ΔG_{isom} from experimental data on derivatives in solution [D. Lenoir, D. J. Raber, and P.v.R. Schleyer, *J. Am. Chem. Soc.*, 96, 2149 (1974)]. [f] Lower limit (ΔG) from equilibration of acetates in solution [H. J. Storesund and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1452 (1975)].

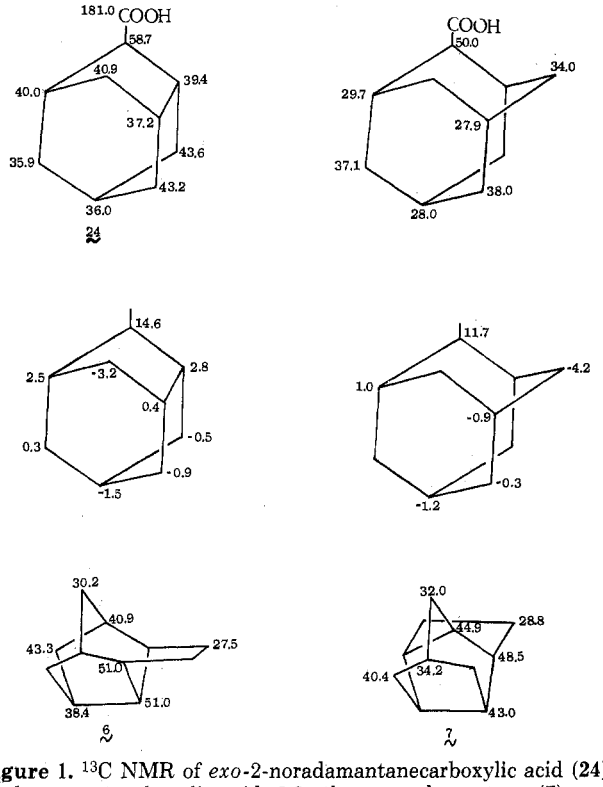


Figure 1. ^{13}C NMR of *exo*-2-noradamantanecarboxylic acid (**24**), 2-adamantanecarboxylic acid, 2,8-ethanonoradamantane (**7**), and 2,4-ethanonoradamantane (**6**). Chemical shifts for **6**, **7**, and acids indicated on molecule. Chemical shift differences for acids relative to the parent hydrocarbons are given on the noradamantane and adamantane structures.

physical separation of these isomers could be devised and **28** was carried throughout the subsequent reactions. A similar sequence as for the 2,8-ethanonoradamantane (**7**) synthesis was used (Scheme II) with comparable yields. Reduction of the mixture of ethanonoradamantanones obtained after C–H insertion (Scheme III) afforded a mixture of ~82% 2,4-ethanonoradamantane (**6**), ~11% 2,8-ethanonoradamantane (**7**), and ~7% 2,9-ethanonoradamantane (**8**).

2,4-Ethanonoradamantane, purified by preparative GLC, was identical with the solid *m/e* 148 rearrangement product, mp 167–168 °C, from **13**, **9**, and **14**. The hydrocarbon mixture of **6**, **7**, and **8** from the Wolff–Kishner reduction when treated with $AlBr_3$ in CS_2 gave an equilibrium ratio of **6**:**7** of 96:4.

^{13}C NMR. The ^{13}C NMR spectrum of *exo*-2-noradamantanecarboxylic acid (**24**) (Figure 1) provides further confirmation of its stereochemistry. In comparison with the chemical shifts for noradamantane, *one* CH_2 signal in **24** is found to be significantly shielded (syn-diaxial interaction) whereas two such shifted CH_2 signals (as in 2-adamantanecarboxylic acid) would have been expected[30] for the endo configuration.

Discussion

The rearrangement results establish 2,4-ethanonoradamantane (**6**) as the $C_{11}H_{16}$ stabilomer. The 97 (±1) to 3 (±1) equilibrium ratio of **6** to 2,8-ethanonoradamantane (**7**) observed from rearrangement of **7**, **9**, and **13** indicates a free-energy difference of approximately 2 kcal/mol. The symmetry numbers of **6** and **7** are the same and entropy differences should not be a significant factor in determining the equilibrium:[18,50] ΔH_{isom} should thus be ~2 kcal/mol. This contrasts with the prediction of both empirical force fields[14,15] that ΔH_f for **6** and **7** should be identical.[50] This discrepancy was a surprise to us. Although errors in absolute ΔH_f values calculated by empirical force field methods can be 2 kcal/mol or more, it is expected from experience (see Table III) that *energy differences* between such closely related isomers as **6** and **7** should be reproduced much more accurately.[31]

Nevertheless, empirical force field calculations have been extremely useful in directing the experiments outlined here; **6** and **7** were predicted to be the most stable isomers out of the 2486 possibilities.

In this context, it seems appropriate to point out that recent experimentally determined ΔH_f°'s of closely related isomers have relative errors on the order of 2 kcal/mol where compared with equilibration results[32] (Table III).

Isomerization Mechanisms. Several experimental observations are particularly pertinent:

1. Both **9** and **13** isomerize directly to the equilibrium mixture of **6** and **7** without the intervention of detectable intermediates.

2. Methanotwistane (**14**) rearranges to a mixture of **6** and **7** much richer in the latter than is found at equilibrium. Noriceane (**9**) is formed in the initial stages of the reaction, and may be an intermediate.

3. 2-Methyladamantane is formed rather than the more stable 1-methyl isomer from **14** by disproportionation.

4. The equilibration of **6** and **7** is slow compared to the isomerization of **9**, **13**, and **14**.

A rearrangement graph (Figure 2), similar to those for the tricyclodecanes[33] and the pentacyclotetradecanes,[31g] provides the best format for mechanistic discussions. This graph can be constructed starting from **9**, **13**, and **14** by taking all possible 1,2-alkyl shifts into account,[33] but disallowing isomers which result when they contain three- or four-membered rings or other highly strained structural features.[33] When all possibilities are examined, six additional tetracycloundecanes **29–34** appear as potential intermediates. These six isomers all have 11 unique carbon atoms, no quaternary carbons, and were present among the 68 structures generated by the Wipke program (Table I). The 15 ring systems **6–14** and **29–34** comprise a closed graph (Figure 2).

Calculations of ΔH_f° for the neutral possible intermediates **29–34** are included in Table II. From among these **32** and **33** emerge as stable ring systems which might be intermediates

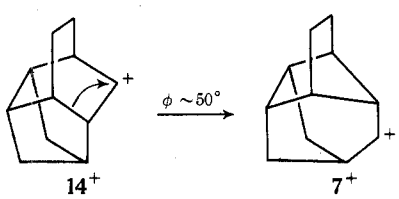
in the rearrangements. Figure 2 is constructed so that the ordinate is approximately proportional to the calculated $\Delta H_f°$'s; the most stable isomers are at the bottom. This presentation emphasizes that the tetracycloundecane energy surface has two distinct minima at **6** and **7**. Furthermore, the graph shows that any path involving **10**, **12**, or **34** is highly endothermic and can be excluded from further consideration.

The rates of 1,2-alkyl shifts in rigid polycyclic systems depend markedly on the dihedral angle between the migrating C–C bond and the "vacant" orbital of the adjacent carbenium ion.[31g,34] These dihedral angles, estimated from framework molecular models, are included in Figure 2 for each step. All possible steps involving dihedral angles >50° were omitted.

A complete treatment of the isomerization mechanism would also include calculation of the relative energies of all intermediate carbenium ions.[31f,35] In lieu of undertaking these extensive calculations, the individual rearrangement steps were examined to determine if any required energetically unfavorable bridgehead cations. This was not the case; secondary cations were found to account for all the isomerizations included in the graph.

In order to reach **6** and **7**, **13** must pass through 2,9-ethanonoradamantane (**8**) (Figure 2). The large calculated heats of reaction as well as the almost ideal dihedral angle for the paths **8** → **6** and **8** → **7** explain the rapid formation of **6** and **7** from **13**. No other intermediate other than **8** need be involved and even **8** could not be detected experimentally.

There are many possible routes from methanotwistane (**14**) to **6** and **7**. The direct pathway from **14** to **7** (eq 1) is not attractive because of the large dihedral angle required by the 1,2-alkyl shift. Therefore, the preferential formation of **7** from **14** during the early stages of the isomerization should involve at least one intermediate. Examination of the graph suggests **32** as this intermediate. The intermediacy of **32** can also account for the observation of **9** in the initial stages of the rearrangement. Since the direct route from **14** to **9** suffers from an unfavorable dihedral angle (45°), the transient appearance of **9** may best be explained as a side reaction of **32**. No good pathway from **14** to **6** is available except for mechanistically poor two-step routes involving **30** or **9**, or equally inferior three-step routes. This may explain the observed low percentage of **6** produced in the early stages of the rearrangement of **14**.



14^+ 7^+ (1)

The ready rearrangement of noriceane (**9**) to the stabilomer **6** is hard to understand. The direct path from **9** to **6** involves a rather large dihedral angle (45°) for the 1,2 shift.[36] Although this possibility cannot be ruled out, the similarity of product distribution and rate of isomerization of **9** and **13** suggests the intermediacy of **11** and **8**, despite the endothermicity calculated for the step **9** → **11**. We have no experimental evidence to support this possibility.

The slow equilibration of **7** to **6** may be due to the endothermicity involved in the most likely pathways via **8**, or via **32** and **9**, or via **32** and **33**.

The preferential appearance of 2-methyladamantane rather than 1-methyladamantane in the early stages of the rearrangement of **14** is not unprecedented in the tricycloundecane family.[37] A regioselective C–C bond rupture in **14** might account for the 2-methyladamantane. However, examination of all possible C–C bond cleavages in **14** failed to reveal any

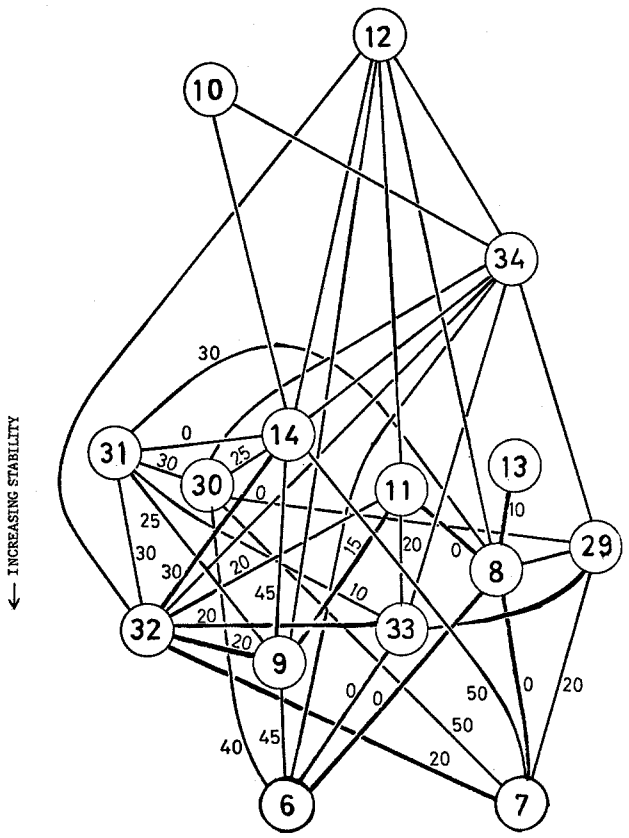
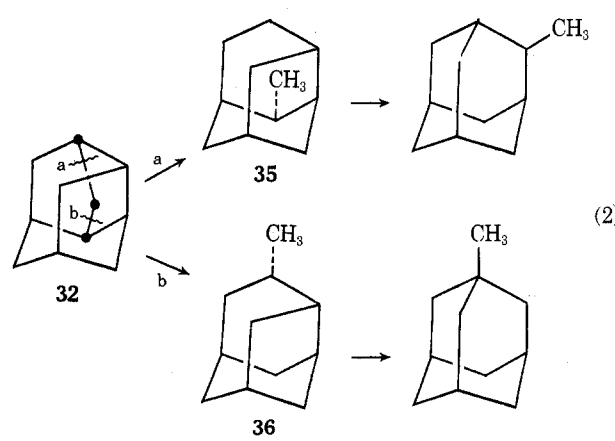


Figure 2. Tetracycloundecane graph. Numbers on each path are estimated dihedral angles between the migrating C–C bond and the empty orbital in the intermediate carbenium ion (shift proceeding to lower energy isomer). The ordinate is approximately proportional to calculated heats of formation (see text).

efficient route leading to the 2-methyl derivative. In addition, the calculated structure of **14** shows uniform strain distribution and **14** is therefore not likely to undergo C–C bond cleavage.[22,38] Examination of the structures closest to **14** in the graph indicates that of these **32** has a remarkably uneven strain distribution, e.g., in the variation of bond lengths. The calculations show that the strain is centered on the three central atoms (marked by filled circles, eq 2) of the norbornane-like moiety of **32**. Cleavage of one of these bridge bonds should result in a large amount of strain relief. Path a should predominate since it leads to 7-*exo*-methylprotoadamantane (**35**) which is 0.3 (A) and 2.0 (E) kcal/mol more stable than the product of b cleavage, 4-*exo*-methylprotoadamantane (**36**).[39] Furthermore, path a cleavage results in the placement of the positive charge at C-4 in **35**, exactly where required for subsequent rearrangement to the adamantane skeleton. The isomerization of **35** to 2-methyladamantane in the presence



32 **35** **36** (2)

of $AlBr_3$ is highly exothermic (calculated heat of reaction: 9.7 (E) and 12.4 (A) kcal/mol[39,40]) and therefore expected to be very rapid.

Experimental Section

General. Microanalyses were performed at the Combustion Analysis Center, Department of Pharmacy, Hokkaido University, and at Hoffmann-La Roche, Inc., Nutley, N.J. Infrared spectra were determined on a Perkin-Elmer 237B and a JASCO IR-G spectrophotometers. Mass spectra were taken on an AEI MS-9 spectrometer and Hitachi RMU-6D and -6E spectrometers at 70–80 eV. GC–MS analyses were performed on a Du Pont 21-490 instrument and JEOL JGC-20-KP gas chromatograph (0.01 in. × 150 ft column packed with Apiezon L or Silicone SE-30) connected to a JEOL JMS-D100 mass spectrometer. Preparative GLC was carried out on a Varian Aerograph 700 instrument. ^1H NMR spectra were recorded on a Varian A-60A and a Hitachi R-20B, while ^{13}C NMR spectra were measured on Varian XL-100 and JEOL FX-60 spectrometers.

Tetracyclo[6.3.0.0^{2,6}.0^{5,9}]undecane (13). Reduction of the known tetracyclic diketone (17)[20] by the Huang-Minlon modification of the Wolff–Kishner (using metallic sodium in place of KOH) gave camphorlike crystalline **13** in 75% yield: mp 153–4 °C; ^1H NMR (CCl_4) δ 2.05 (6 H, br s, methine), 1.56 (10 H, complex, methylene); MS *m/e* (rel intensity) 148 (M^+, 52), 119 (37), 91 (30), 81 (56), 80 (69), 79 (48), 67 (100), and 66 (99).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.84; H, 10.73.

Aluminum Bromide Catalyzed Rearrangement of 13. 1. Analytical Scale. In a 50-ml round-bottom flask were placed 90 mg of **13**, 300 mg of sublimed aluminum bromide, and 10 ml of carbon disulfide. With exclusion of moisture, the mixture was stirred at room temperature and the course of reaction followed by GLC analysis. Starting material disappeared completely after 1.5 h and a predominant product peak having shorter retention time appeared in addition to several minor peaks. The product distribution did not change significantly after heating the mixture for 24 h under reflux. The reaction mixture was then transferred to an aerosol tube, more aluminum bromide added, and heated at 100 °C for 1.5 h. GLC analysis revealed that about one-third of the main product disproportionated into 1-methyladamantane, but the remaining two-thirds survived. Relative GLC retention time on 3 mm × 3 m Silicone DC 550, 134 °C, N_2 21 psi: **13**, 1.79; **6**, 1.60; **7**, 1.38; 1-methyladamantane, 1.00.

2. Preparative Scale. In a 50-ml round-bottom flask, 1.22 g of **13** was dissolved in 20 ml of carbon disulfide. In the course of 1.5 h, 3.4 g of anhydrous aluminum bromide was added in three portions to the reaction flask while stirring at room temperature. The solution was decanted from the aluminum bromide sludge, which was further washed several times with carbon disulfide. The combined carbon disulfide solution was washed with water, dried over calcium chloride, and evaporated. The residue was sublimed at 100 °C (15 mmHg) to give 1.03 g (84%) of a colorless, camphorlike product. GLC analysis revealed 97% purity with 2.4, 0.2, and 0.4% minor products in decreasing order of retention time. An analytical sample of the main product, identified as **6** by comparison with an authentic sample (see below), was obtained by preparative GLC (6 mm × 9 m 5% FFAP at 119 °C, He 14 psi) followed by sublimation: mp 167–168 °C (cor, sealed tube); ^1H NMR (CCl_4) δ 2.6–2.0 (br, 6 H, methine) and 1.9–1.2 (complex with prominent peaks at 1.75 and 1.63, 10 H, methylene); ^{13}C NMR ($CDCl_3$) δ 51.1 (d, 2 C plus d, 1 C), 43.3 (t, 2 C), 41.0 (d, 2 C), 38.4 (d, 1 C), 30.1 (t, 1 C), and 27.4 (t, 2 C) (see Figure 1 for assignments); MS *m/e* (rel intensity) 148 (M^+, 84), 119 (33), 92 (37), 91 (39), 81 (43), 80 (100), 79 (91), 67 (47), and 66 (52).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.11; H, 10.88.

The main by-product (2.4%) was identified as 2,8-ethanonoradamantane (**7**) by comparison with an authentic sample (see below). The ratio of **6** to **7** obtained in a number of similar runs was 97 (±1):3 (±1). Two other side products (0.2 and 0.4%) were identified as (D_3)-trishomocubane (**15**, *m/e* 146)[19] and 1-methyladamantane (*m/e* 150), respectively, by GC–MS. In addition, GC–MS detected up to 1% of adamantane (*m/e* 136) in the reaction mixture. When the reaction was extended to 5 h at room temperature, the yield of 1-methyladamantane increased to 10%.

Aluminum Bromide Catalyzed Rearrangement of Noriceane (9). The rearrangement was performed under similar conditions as above using 90 mg of noriceane (**9**),[17] about 200 mg of sublimed aluminum bromide, and 5 ml of carbon disulfide. The reaction was followed by GLC; noriceane (rel retention time 2.09) disappeared completely after 50 min, giving a three-component mixture, **6**, **7**, and 1-methyladamantane, in the ratio 95:3:2. The usual workup gave 73 mg (81%) of this product mixture.

Table IV. Product Distribution (%) as a Function of Time in the Rearrangement of 14

Time	1-MeAd[a]	(D_3)-THC[b]	7	6	9
6 min	1	Trace	63[c]	34	2
10	5	Trace	61	33	1
20	13	1	55	32	0
40	19	1	48[d]	32	0
1 h	21	1	45	33	0
2	24	1	39	46	0
4	33	1	25	41	0
21	60	Trace	7	33	0
5 (reflux)	93	Trace	1	5	0

[a] 1-Methyladamantane. [b] (D_3)-Trishomocubane (**15**). [c] This peak contains about 25% of 2-methyladamantane (see text). [d] 2-Methyladamantane no longer is present.

Aluminum Bromide Catalyzed Rearrangement of Methanotwistane (14). In 15 ml of carbon disulfide, 0.1 g of methanotwistane (**14**)[22] and 0.49 g of sublimed aluminum bromide were stirred at room temperature. Methanotwistane (rel retention time 1.80) disappeared almost instantly. GC–MS analysis revealed the following change of product distribution with time (Table IV).

In a preparative run, 0.64 g of **14** was treated with 2 g of anhydrous aluminum bromide in 50 ml of carbon disulfide protected from moisture by a calcium chloride tube. After 6 min, a 10-ml aliquot was removed and quenched with water. The organic phase was worked up and subjected to GC–MS analysis. 1-Methyladamantane, (D_3)-trishomocubane (**15**), 2,8-ethanonoradamantane (**7**), 2,4-ethanonoradamantane (**6**), and noriceane (**9**) were identified by comparison of retention times and fragmentation patterns with those of authentic samples. The peak corresponding to 2,8-ethanonoradamantane (**7**) had a shoulder at a higher retention time which could be resolved only by the use of a Golay capillary column. The retention time of this shoulder was identical with that of 2-methyladamantane. Mass spectral analysis of the shoulder confirmed it to be 2-methyladamantane (M^+, *m/e* 150) mixed with 2,8-ethanonoradamantane.

The rest of the reaction mixture was quenched after 40 min of reaction at room temperature and worked up to give 0.45 g of colored oil, from which the main peak (2,8-ethanonoradamantane) was collected by preparative GLC to give about 100 mg of colorless liquid: ^1H NMR ($CDCl_3$) δ 2.2–0.8 (br m); ^{13}C NMR ($CDCl_3$) δ 48.6 (d, 2 C), 45.0 (d, 1 C), 43.1 (d, 2 C), 40.5 (t, 2 C), 34.2 (d, 1 C), 32.1 (t, 1 C), and 28.8 (t, 2 C); MS *m/e* (rel intensity) 148 (M^+, 100), 119 (71), 91 (53), 79 (75), 66 (78).

Hexacyclo[9.2.1.0^{2,10}.0^{3,7}.0^{4,9}.0^{6,8}]tetradecan-12-ene (Katz Dimer) (37). The [4 + 2] norbornadiene dimer was prepared essentially by the method of Mrowca and Katz.[41,42] Purification of the norbornadiene before introduction of the rhodium catalyst improved the yield of dimer significantly (from 15 to 50%).[43]

Typically, 1 kg of norbornadiene (Aldrich) was refluxed for 3 h with 80 g of maleic anhydride. The norbornadiene was then distilled directly into a predried, nitrogen-purged flask charged with 5 g of 5% rhodium on carbon catalyst (ROC–RIC). The suspension was then stirred and refluxed for 72–96 h. Additional 1-g portions of catalyst were added until no further change could be detected as determined by the NMR integration of the olefinic protons in norbornadiene and **37**. When the ratio of product to starting material reached 3:1, the mixture was diluted with 300 ml of pentane and filtered. The pentane and norbornadiene were distilled at atmospheric pressure and the dimers distilled at reduced pressure: bp 70–75 °C (0.4–0.5 mm) [lit.[41] bp 76–77 °C (0.8 mm)], yield about 50%.

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (Deltacyclene)[44] (38). The pyrolysis of **37** was carried out in a quartz tube (65 × 2.2 cm) heated to 480 °C.[44d] A nitrogen flow of 15 ml/min was maintained as **37** was added by means of an automatic syringe pump (100 ml added over 5-h period). Distillation of the pyrolysate gave deltacyclene (**38**, 51%) as a yellow liquid, bp 52–56 °C (25 mm) [lit.[44c] bp 55–58 °C (25 mm)].

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (Deltacyclane) (39). A solution of 50 g of deltacyclene (**38**) in 100 ml of ethyl acetate was hydrogenated over platinum oxide catalyst by shaking for 4 h in a Parr hydrogenator under 45 psi hydrogen pressure. The catalyst was filtered and solvent removed at reduced pressure; 40 g (79%) of **39** was obtained as a colorless liquid, bp 48–50 °C (17 mm) [lit.[45] bp 152–153 °C (760 mm)].

***exo*-Tricyclo[3.3.1.0^{3,7}]nonan-2-ol (*exo*-2-Noradamantanol) (40).** A solution of 25.0 g of deltacyclane (**39**) in 250 ml of pentane was cooled in an ice bath and then added rapidly with vigorous mechanical

stirring to 650 ml of 97% sulfuric acid at −5 °C. After 4.5 min the reaction was quenched by pouring onto 2.5 kg of ice. After separation of the layers, the aqueous phase was refluxed for 5 h to ensure hydrolysis of sulfate esters, and then extracted with methylene chloride. The organic layers were washed with water, saturated aqueous bicarbonate, and water and then dried over anhydrous magnesium sulfate. Removal of solvent gave 18 g (63%) of *exo*-2-noradamantanol (**40**) as a white solid: mp 221.9–223.6 °C (lit.[26] 221–222 °C); ir (CCl_4) ν 3360, 1105, 1040, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 1 H), 2.70 (s, 1 H), 2.35 (m, 3 H), 2.07 (m, 3 H), 1.58 (m, 6 H).

2-Iodotricyclo[3.3.1.0^{3,7}]nonane (2-Noradamantyl Iodide) (41). A solution of 2-noradamantanol (**40**, 10.0 g in 100 ml of 47% aqueous HI) in a Fischer-Porter bottle was heated to 110 °C and kept at this temperature for 4 h. During this time the iodide formed appeared as a second liquid phase at the bottom of the bottle. The mixture was allowed to cool, then extracted with ether (100 ml, three times). The ether extracts were combined and washed with aqueous sodium bisulfite, saturated aqueous sodium carbonate, and water. The ether solution was dried over anhydrous magnesium sulfate, and the solvent was removed at reduced pressure. Column chromatography (silica gel, pentane eluent) gave 18.0 g (100%) of **41** as a clear liquid: ir (CCl_4) ν 2925, 1468, 1320, 1300, 1290, 1180, 1160, 1050, 980, 900 cm^{-1}; ^1H NMR (neat) δ 4.48 (m, 1 H), 2.88 (m, 2 H), 2.62 (m, 2 H), 1.72 (m, 7 H).

Anal. Calcd for $C_9H_{13}I$: C, 43.57; H, 5.28; I, 51.15. Found: C, 43.86; H, 5.51; I, 50.86.

***exo*-Tricyclo[3.3.1.0^{3,7}]nonane-2-carboxylic Acid (*exo*-2-Noradamantanecarboxylic Acid) (24).** Ether (50 ml) was cooled to −60 to −78 °C in a 500-ml three-neck flask fitted with a dropping funnel and kept under a nitrogen atmosphere. *tert*-Butyllithium (Ventron, 0.75 M in pentane, 50 ml) was syringed into the ether at a rate such that the temperature of the solution was maintained at −50 °C. An ether solution of the iodide **41** (8.0 g in 15 ml of ether) was added slowly over a 45-min period (temperature kept at −40 to −45 °C).[25] The 2-noradamantyllithium solution was then transferred back into the dropping funnel and added rapidly to a flask containing dry solid CO_2 cooled to liquid nitrogen temperature. (Dry solid CO_2 was obtained by subliming dry ice through a tower of calcium chloride in a nitrogen flow, then recondensing the CO_2 in a flask cooled to liquid nitrogen temperature.) The CO_2–organolithium mixture was allowed to warm slowly to room temperature, then added to water made acidic with 3 N HCl. After the ether layer was separated, the aqueous phase was extracted with ether (100 ml, three times). The ether solutions were combined and extracted with aqueous sodium carbonate in order to separate the organic acid from coupling products (e.g., 2,2′-bisnoradamantane). The aqueous solution of the acid salt was then made strongly acidic with 6 N HCl, precipitating the organic acid. This heterogeneous mixture was extracted with ether (100 ml, three times) and the ether solution was washed with a small amount of dilute aqueous sodium bicarbonate (to remove any HCl). The ether solution was then dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure, yielding 3.0 g (56%) of **24** as a white solid. Recrystallization from pentane yielded an analytically pure sample: mp 94.0–96.2 °C; ir (CCl_4) ν 3350–2800, 1710, 1425, 1325, 1265, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.9 (s, 1 H), 2.87 (m, 1 H), 2.67 (m, 1 H), 2.57 (m, 2 H), 2.17 (m, 1 H), 1.67 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 181.0 (s, 1 C), 58.7 (d, 1 C), 39.4 (d, 1 C), 40.0 (d, 1 C), 40.9 (t, 1 C), 37.2 (d, 1 C), 43.6 (t, 1 C), 43.2 (t, 1 C), 35.9 (t, 1 C), 36.0 (d, 1 C) (see Figure 1 for assignments).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.24; H, 8.51. Found: C, 72.40; H, 8.28.

***exo*-Tricyclo[3.3.1.0^{3,7}]nonane-2-carboxylic Acid Chloride (*exo*-2-Noradamantanecarboxylic Acid Chloride) (42).** *exo*-2-Noradamantylcarboxylic acid (**24**, 9.8 g) in 15 ml of anhydrous ether was added dropwise to 11.5 g of $SOCl_2$ (distilled twice from quinoline and once from triphenyl phosphite)[46] in 20 ml of ether at ambient temperature. The mixture was then heated to 50 °C for 5 h. Ether and excess $SOCl_2$ were removed at reduced pressure. **42** distilled at 52.0 °C (0.15 mm) yielding 8.4 g (78%) of a colorless liquid: ir (CCl_4) ν 2940, 1800, 1480, 1430, 1315, 1165, 1100, 1070, 1040, 1010, 900 cm^{-1}; ^1H NMR (CCl_4) δ 3.03 (m, 1 H), 2.97–2.33 (m, 3 H), 2.22 (m, 1 H), 1.68 (m, 8 H).

Anal. Calcd for $C_{10}H_{14}OCl$: C, 65.04; H, 7.09; Cl, 19.20. Found: C, 64.93; H, 7.19; Cl, 18.90.

***exo*-2-Tricyclo[3.3.1.0^{3,7}]nonyl Methyl Diazoketone (*exo*-2-Noradamantyl Methyl Diazoketone) (19). Preparation of Water- and Ethanol-Free Diazomethane.** Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, Aldrich, 25 g) dissolved in 150 ml of ether was dropped into a solution of 7.3 g of KOH, 12 ml of ether, 40 ml of $C_2H_5O(CH_2CH_2O)_2H$, and 12 ml of water heated to 65 °C. A yellow solution of ether/diazomethane codistilled from this mixture and was trapped at 0 °C. An additional 50 ml of ether was added and the distillate eventually became colorless. The diazomethane–ether solution was dried over KOH, decanted, and fresh KOH was added. The solution was decanted again and sodium added. Throughout the drying process the solution was kept at 0 °C.

The diazomethane–ether solution was added to a 1-l. flask fitted with a thermometer, a dropping funnel, and a nitrogen inlet. The solution was cooled to 0 °C under a nitrogen blanket, and the acid chloride **42** (2.0 g in 25 ml of ether) was added dropwise over a 45-min period.[47] The reaction mixture was kept at 0 °C for 2 h, then allowed to warm to room temperature overnight. The ether was removed under reduced pressure leaving 2.1 g (100%) of **19** as a yellow, gummy solid. This compound must be stored at −5 °C to avoid thermal decomposition. Ir (CCl_4) ν 2920, 2100, 1650, 1360, 1340, 1320, 1260, 1150, 1100, 1060, 1030 cm^{-1}; ^1H NMR (CCl_4) δ 5.22 (s, 1 H), 2.77 (m, 1 H), 2.47–2.00 (m, 4 H), 1.6 (m, 8 H).

Tetracyclo[6.2.1.0^{2,6}.0^{5,10}]undec-3-one (21). Anhydrous $CuSO_4$ (18.0 g)[47,48] (pale brown when dried thoroughly over P_2O_5) was suspended in 300 ml of sodium-dried toluene, in a three-neck flask fitted with a high-dilution apparatus.[23] The solution was heated to reflux and 20 ml of toluene was distilled to remove any residual water as an azeotrope. Diazoketone **19** (2.0 g) in 500 ml of toluene was added via an addition funnel fitted with a cooling jacket. Addition via the high-dilution apparatus[23] continued for an 11-h period. The reaction mixture was refluxed for 12 h after the addition was complete, and then was allowed to cool to room temperature and the $CuSO_4$ filtered. The toluene solution was washed with 100 ml of water, 75 ml of 5 N NaOH (to remove any homologous acid, typically less than 10% of such acid was formed), and twice with 50 ml of water, and then dried over anhydrous magnesium sulfate. The solution was concentrated on a rotatory evaporator, and the light brown oil obtained was charged onto a silica gel column packed in hexane. The eluent was gradually changed to toluene. The initial fractions contained a clear oil. ^1H NMR of these fractions revealed the presence of olefinic protons; no further identification was attempted. The toluene fractions contained the desired ketone **21** obtained in 51% yield as a clear oil. Preparative GLC (20% Carbowax on 80/100 Chromosorb W, 0.25 in. × 1 m) was used to prepare the analytical sample.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.15; H, 8.73.

Tetracyclo[6.2.1.0^{2,6}.0^{5,10}]undecane (2,8-Ethanonoradamantane) (7). Diethylene glycol (20 ml) was heated to 80 °C and 1.0 g of sodium metal was added in small pieces. The ketone **21** (0.8 g) was then added, followed by 1 ml of anhydrous hydrazine.[24] The mixture was heated slowly to 180 °C in a Fischer-Porter bottle to avoid loss of the very volatile hydrocarbon product. The solution was allowed to cool to ambient temperature and water (50 ml) was added. The aqueous solution was extracted with pentane, and the combined extracts were washed with saturated aqueous NaCl and dried over anhydrous magnesium sulfate. The solution was concentrated on a rotatory evaporator and yielded 0.27 g (46%) of **7** as a clear oil. Preparative GLC (0.25 in. × 5 m, 10% SE-30 on 80/100 Gaspack W) gave an analytically pure sample: ir (CCl_4) ν 2900, 1470, 1450, 1320, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17–0.83 (br m); ^{13}C NMR ($CDCl_3$) δ 48.5 (d, 2 C), 44.9 (d, 1 C), 43.0 (d, 2 C), 40.4 (t, 2 C), 34.2 (d, 1 C), 32.0 (t, 1 C), 28.8 (t, 2 C) (see Figure 1 for assignments); MS *m/e* 148 (M^+), 119, 79, 66.

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.81; H, 10.73.

Aluminum Bromide Catalyzed Rearrangement of 2,8-Ethanonoradamantane (7). To a solution of 2,8-ethanonoradamantane (**7**, 100 mg) in 20 ml of carbon disulfide was added about 300 mg of $AlBr_3$. After 48 h at room temperature a mixture of *m/e* 148 isomers consisting of 98% 2,4-ethanonoradamantane (**6**) and 2% 2,8-ethanonoradamantane (**7**) was obtained. In addition, disproportionation products of *m/e* 136, 146, and 150 were identified as described for the rearrangement of **13**.

Tricyclo[3.3.1.0^{3,7}]nona-2-one (2-Noradamantanone) (25). 2-Noradamantanol (**40**, 13.8 g), oxidized using the Jones reagent,[49] afforded 12.0 g of **25** (87%): mp 208.0–211.9 °C (sublimed) (lit.[26] 214.5–215 °C); ir (CCl_4) ν 2925, 1750, 1450, 1170, 1070, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83–1.33 (br m).

2-Methylenetricyclo[3.3.1.0^{3,7}]nonane (2-Methylenenoradamantane) (26). 2-Noradamantanone (**25**, 3.2 g) was subjected to a Wittig reaction utilizing methyltriphenylphosphonium bromide, NaH, and Me_2SO.[27] Column chromatography yielded 2.5 g (78%) of **26** as a volatile solid: mp 43–44.5 °C (lit.[28] 46–47 °C); ^1H NMR ($CDCl_3$) δ 4.48 (d, 2 H), 2.77 (m, 1 H), 2.50 (m, 2 H), 2.22 (m, 1 H), 1.68 (m, 8 H).

***endo*-2-Tricyclo[3.3.1.0^{3,7}]nonanecarbinol (*endo*-2-Noradamantylcarbinol) (27).** 2-Methylenenoradamantane (**26**, 2.5 g) was converted to 2.1 g (75%) of a mixture of 95% **27** and 5% *exo*-2-norad-

amantylcarbinol (28) by a standard hydroboration–oxidation procedure.[29] The relative amounts of 27 and 28 were determined by ^{1}H NMR integration of the CH_2OH protons. An authentic sample of 28 was prepared by lithium aluminum hydride reduction of the corresponding acid (24). The mixture of alcohols was recrystallized from hexane: mp 56–59 °C; ir (CCl_4) ν 3600, 3500–3150, 1060, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (d, 2 H), 2.50 (s and m, 3 H), 2.03 (m, 3 H), 1.65 (br m, 8 H).

***endo*-Tricyclo[3.3.1.0^{3,7}]nonane-2-carboxylic Acid (*endo*-2-Noradamantanecarboxylic Acid) (43).** The 95:5 mixture of the alcohols 27 and 28 (2.56 g) in 50 ml of acetone was added dropwise to Jones reagent[49] cooled at 0 °C. Rapid mechanical stirring was maintained throughout the addition. After the addition was complete, the solution was allowed to warm to room temperature. Sodium bisulfite was then added until the oxidizing agent turned deep green and a second phase appeared. The upper layer was decanted from the dense green lower layer. The lower phase was extracted with pentane. The pentane extracts were combined with the original upper phase forming a second phase. The new lower phase was added to the dense green material and extracted with pentane. The pentane extracts were combined and washed with saturated aqueous NaCl, then saturated aqueous Na_2CO_3 to remove the organic acids (24 and 43) as their water-soluble salts. This aqueous phase when acidified with 3 N HCl yielded a white precipitate. The slurry of the organic acids in the aqueous phase was extracted with ether, and the ether extracts were washed with a small amount of dilute aqueous $NaHCO_3$ to remove any HCl and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, yielding 2.2 g (80%) of a white solid, mp 92–98 °C. Repeated recrystallization from pentane gave a white solid, mp 101.0–104.1 °C. The mixture of acids was not separable by TLC: ir (CCl_4) ν 3400–2200, 1700, 1420, 1299, 1060, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.45 (s, 1 H), 3.0–1.83 (br m, 7 H), 1.7 (m, 7 H). In addition, 0.4 g of a nonaqueous base soluble material was isolated from the pentane fraction but not identified.

***endo*-Tricyclo[3.3.1.0^{3,7}]nonane-2-carboxylic Acid Chloride (*endo*-2-Noradamantanecarboxylic Acid Chloride) (44).** The procedure described for 42 was followed giving the acid chlorides 42 and 44 (5:95) in 83% yield. No attempt was made to separate the acid chlorides: bp 72–73.5 °C (0.4 mm); ir (CCl_4) ν 3010, 1800, 1465, 1450, 1310, 1290, 1090, 1076, 1055, 1030, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.4–2.35 (m, 4 H), 2.20 (m, 1 H), 1.90 (m, 1 H), 1.70 (m, 8 H).

***endo*-2-Tricyclo[3.3.1.0^{3,7}]nonyl Methyl Diazoketone (*endo*-2-Noradamantyl Methyl Diazoketone) (20).** The procedure described for 19 was followed affording the mixture of diazoketones, 19 and 20, in 100% yield. No attempt was made to separate the diazoketones: ir (CCl_4) ν 2915, 2100, 1650, 1350, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 1 H), 2.78–1.70 (br m, 6 H), 1.53 (m, 7 H).

Tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undec-4-one (22) and Tetracyclo[6.2.1.0^{2,6}.0^{5,9}]undec-3-one (23). The ketones 22 and 23 were prepared from the mixture of diazoketones using the identical procedure as for 21. Column chromatography gave a white solid in 59% yield, mp 162–165 °C. The mixture of the ketones (21, 22, and 23) could not be separated by GLC: ir (CCl_4) ν 2910, 1740, 1400, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.95–1.97 (br m, 8 H), 1.96–1.48 (br m, 6 H); MS *m/e* 162 (M^+), 121, 120, 92, 79, 78.

Anal. Calcd for $C_{11}H_{14}$: C, 81.44; H, 8.70. Found: C, 81.69; H, 8.64.

Tetracyclo[5.3.1.0^{2,6}]undecane (2,4-Ethanonoradamantane) (6) and Tetracyclo[6.2.1.0^{2,6}.0^{5,9}]undecane (2,9-Ethanonoradamantane) (8). The modified Wolff–Kishner reduction[24] (identical as for 21) afforded a mixture of 82%, 2,4-ethanonoradamantane (6), 11% 2,8-ethanonoradamantane (7), and 7% 2,9-ethanonoradamantane (8) in 30% yield [0.125 in. × 16 ft Apeizon N on Chromosorb W 80/100, retention times at 150 °C: 2,8-ethanonoradamantane (7), 34 min; 2,4-ethanonoradamantane (6), 38–39 min; 2,9-ethanonoradamantane (8), 41 min]. The identification of 8 was made on the basis of GC–MS and mechanistic considerations: MS *m/e* 148 (M^+), 120, 119, 106, 105, 92, 91, 81, 80, 79, 78, 77. Preparative GLC (0.25 in. × 5 ft 10% SE-30, on 80/100 Gaspack W) afforded a pure sample of 6: mp 167–168 °C; ^{13}C NMR ($CDCl_3$) δ 51.0 (d, 3 C), 43.3 (t, 2 C), 40.9 (d, 2 C), 38.4 (d, 1 C), 30.2 (t, 1 C), and 27.5 (t, 2 C).

Equilibration of 2-Methylnoradamantanecarboxylates. An ether solution of 1.7 g of a 95:5 ratio of 24 and 43 was cooled to 0 °C under a nitrogen atmosphere. A diazomethane–ether solution prepared as described for 19 was added dropwise to the acids via an addition funnel fitted with a cooling jacket. The addition was continued until the yellow color of the added diazomethane persisted for 10 min. The solution was allowed to warm to room temperature overnight, then dried over anhydrous magnesium sulfate. The ether was removed at reduced pressure, yielding 1.8 g (100%) of a clear oil, bp 60–61 °C (0.01 mm). The methyl resonances of the two isomers were distinct, the endo isomer's methyl signal being 5 Hz downfield from the exo. The esters were added to a solution of 20 mg of sodium in 10 ml of anhydrous methanol. The endo isomer slowly epimerized to the exo ester and equilibrium was reached after 96 h at 70 °C: 75% exo:25% endo; ^{1}H NMR ($CDCl_3$) δ 3.65 (endo methyl), 3.57 (exo methyl) (s, 3 H), 2.98–1.16 (m, 13 H).

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Registry No.—3, 59014-95-8; 6, 59014-96-9; 7, 59014-97-0; 8, 59014-98-1; 9, 58008-54-1; 10, 59014-99-2; 11, 59015-00-8; 12, 59015-01-9; 13, 59015-02-0; 14, 59015-15-5; 15, 30114-56-8; 19, 59015-03-1; 20, 59042-76-1; 21, 59015-04-2; 22, 59015-05-3; 23, 59015-06-4; 24, 59015-07-5; 25, 17931-67-8; 26, 55795-14-7; 27, 59015-08-6; 28, 59042-77-2; 29, 59015-09-7; 30, 59015-10-0; 31, 59015-11-1; 32, 59015-00-8; 33, 59015-12-2; 34, 59015-13-3; 37, 7781-74-0; 39, 6567-11-9; 40, 18117-75-4; 41, 36280-29-2; 42, 59015-14-4; 43, 59042-78-3; 44, 59042-79-4; 1-methyladamantane, 700-56-1; norbornadiene, 328-34-7; Diazald, 80-11-5; 2-adamantanecarboxylic acid, 15897-81-1.

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Formation of a Novel Norcamphor upon Treatment of 2-Hydroxy-4-isopentyl-4-methylcyclopentanone with Acid

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Treatment of 2-hydroxy-4-isopentyl-4-methylcyclopentanone (1) with polyphosphoric acid or 85% phosphoric acid can lead to 1-isopropyl-4-methylnorcamphor (2), as well as the previously reported 1,4,4-trimethylbicyclo[3.2.1]-octan-6-one (3). An alternative preparation of 2 from 4-methylnorcamphor (4) is described, and formation of 2 from 1 is rationalized in terms of intermediates 14–18. The series of rearrangements suggested includes a 1,5-hydride shift, an intramolecular Prins reaction, and a pinacol rearrangement.

In this report we describe the acid-catalyzed dehydration and rearrangement of acyloin 1 to 1-isopropyl-4-methylnorcamphor (2). Some years ago we observed that treatment of 1 with polyphosphoric acid first at room temperature and then overnight at 100 °C led to 58% of 3 as the only volatile product.[1] In repeating this preparation we have confirmed the earlier observation but also found that treatment of 1 with polyphosphoric acid at room temperature only or at 100 °C for a shorter time yields 2 as well as 3. Both ketones are also formed from 1 in hot 85% phosphoric acid. Separate experiments have shown that 2 is destroyed much faster than 3 by hot acid and that the ketones are not interconvertible under the reaction conditions. Below we give evidence supporting structure 2, report an independent synthesis of this ketone, and comment on the mechanism of this exceptional transformation.

This new compound is isomeric with ketone 3, has an odor reminiscent of menthone, and has spectroscopic characteristics consistent with its formulation as an isopropyl- and methyl-substituted norcamphor. These included ir carbonyl absorption at 1744 cm^{-1}, a ^1H NMR spectrum containing a singlet methyl signal as well as absorption attributable to an isopropyl substituent with magnetically nonequivalent methyl groups, and a ^{13}C NMR spectrum compatible with the published spectra of methylnorcamphors,[2,3] particularly that of 4-methylnorcamphor (4).[3] There have been extensive investigations of the photochemistry of norcamphors,[4] and on previous occasions we have found that ultraviolet irradiation provided a convenient and informative degradation of novel bridged-ring ketones.[5] For these reasons we sought definitive structural information in photolysis of the new compound.