Acid-Catalyzed Rearrangement of Spiro[adamantane-2,1′-cyclobutane]. The Case for a Transannular Alkyl Shift

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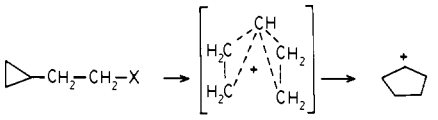
Abstract: The title compound, **5**, was prepared from 2-methyleneadamantane in three steps and subjected to carbocationic rearrangement catalyzed by aluminum bromide or by the milder catalyst trifluoromethanesulfonic acid. The final isomerization product was a mixture (3.5–4 to 96–96.5) of tetracyclo[7.3.1.$0^{3,8}$.$0^{4,11}$]tridecane (2,4-trimethyleneadamantane, **6**) and tetracyclo[6.3.1.$1^{3,10}$.$0^{4,8}$]tridecane (1,2-trimethyleneadamantane, **7**). At very short reaction times **6** was formed in a quantity higher than its equilibrium concentration: the ratio **6**/**7** extrapolated at time zero is about 2. The possible reaction pathways leading to **6** and to **7** were examined. The heat of formation of each intermediate and the bond alignment for each step in the reaction sequence were obtained by molecular mechanics calculations. It was found that a reaction pathway involving only 1,2 alkyl and hydride shifts could not account for the more rapid formation of **6**; this observation is well rationalized, however, by a transannular, 2,4 shift of the methylene bridge, resulting in the direct formation of **6**.

Even though 1,3 hydride shifts are much less common than their 1,2 counterparts, they are, nonetheless, well established in certain systems, for example, the 2-norbornyl cation,[2] the 2,4-dimethyl-2-pentyl cation,[3,4a] and the 1,3-dimethylcyclopentyl and 1,3-dimethylcyclohexyl cations.[4b]

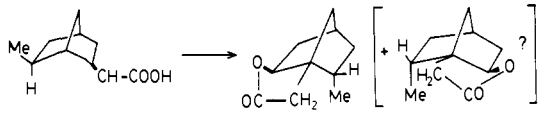
Evidence of 1,3 alkyl shifts, however, is meager. Solvolysis of various 2-cyclopropylethyl precursors (**1**) led to moderate pro-



1 **2**

portions of products with a five-membered ring, nominally resulting from a 1,3 alkyl shift; the special electronic nature of the cyclopropyl ring and unusually delocalized carbocationic intermediates (**2**) were invoked, however, to rationalize the products.[5] Similar arguments can be made concerning a solvolysis study of a 2-norbornyl substrates containing a spirocyclopropane moiety at C-6.[6]

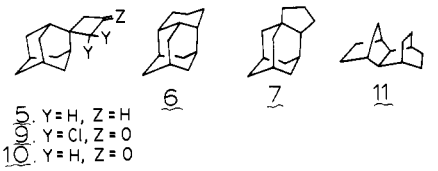
It was argued that a 6,2 methyl shift was involved in the acid-catalyzed rearrangement of optically active (6-*exo*-methyl-2-norbornylidene)ethanoic acid (**3**) to the lactone of (6-



3 **4**

endo-methyl-2-*exo*-hydroxy-1-norbornyl)ethanoic acid (**4**), because the product **4** had only a very low optical activity.[7] Optically pure **4**, however, was not prepared by an independent route, and the authors recognized the possibility that lactone **4** might have a very small specific rotation and that, in fact, no racemization had occurred in the rearrangement of **3**.[7] In the acetolysis of 6,6-dimethyl-2-*exo*-norbornyl tosylate,[8] no evidence was found for a 6,2 methyl shift, and recently it was observed that no ring expansion by a 6,2 methylene shift occurred in the solvolysis of a spiro[cyclobutane-1,6′-norbornyl-2] substrate.[9]

Herein we report on the acid-catalyzed rearrangement of the title compound, **5**. Our experiments strongly suggest that a 2,4 transannular alkyl shift has occurred in converting **5** to the known[10] tetracyclo[7.3.1.$0^{3,8}$.$0^{4,11}$]tridecane (2,4-trimethyleneadamantane, **6**).



5. Y = H, Z = H
9. Y = Cl, Z = O
10. Y = H, Z = O

6 **7** **11**

Spirane **5** was first synthesized as a precursor of substrates for a study of cyclobutylcarbinyl cations generated by solvolysis.[11] An intermediate in that synthesis was mentioned in a footnote of an earlier paper.[12] Aluminum bromide rearrangement of **5** to tetracyclo[6.3.1.$1^{3,10}$.$0^{4,8}$]tridecane (**7**, 1,2-trimethyleneadamantane) was later examined by one of us in connection with an extensive study of the formation and interconversion of tetracyclic C_{13} and C_{14} adamantanes.[10] Since attempts at separating **5** and **7** by gas–liquid chromatography were unsuccessful, the work on **5** was put aside. More recently, however, we were able to solve this separation problem (see the Experimental Section), and we reinitiated the project.

Results and Discussion

Synthesis of 5. The starting material was 2-methyleneadamantane (**8**), obtained from adamantanone, either by a Grignard reaction followed by dehydration[13] or in higher yields but using more expensive reagents by a Wittig reaction.[13b,14]

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(2) (a) Meerwein, H.; Montfort, F. *Liebigs Ann. Chem.* **1924**, *435*, 207. (b) Roberts, J. D.; Yancey, J. A. *J. Am. Chem. Soc.* **1953**, *75*, 3165, and references therein. (c) Doering, W. v. E.; Wolf, A. P. *Abstracts of Papers*; 12th International Congress on Pure and Applied Chemistry, New York, Sept 11, 1951; American Chemical Society: Washington, DC, 1951; p 437. (d) Waughan, W. R.; Perry, R., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 3168.

(3) Brouwer, D. M.; van Doorn, J. A. *Recl. Trav. Chim.* **1969**, *88*, 573.

(4) (a) Saunders, M.; Stofko, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 252. (b) Hewett, A. P. W. Thesis, Yale University, 1975.

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(6) Altmann-Schaffner, E.; Grob, C. A. *Helv. Chim. Acta* **1987**, *70*, 43.

(7) Vaughan, W. R.; Gross, B. A.; Burkle, S. E.; Langell, M. A.; Caple, R.; Oakes, D. *J. Org. Chem.* **1983**, *48*, 4792.

(8) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375.

(9) Kirmse, W., personal communication of unpublished results.

(10) Ōsawa, E.; Tahara, Y.; Togashi, A.; Iizuka, T.; Tanaka, N.; Kan, T.; Fărcaşiu, D.; Kent, G. J.; Engler, E. M.; Schleyer, P. v. R. *J. Org. Chem.* **1982**, *47*, 1923.

(11) Unpublished work from the laboratory of Professor P. v. R. Schleyer.

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

(13) (a) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182. (b) Kuthan, J.; Palecek, J.; Musil, L. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3491. (c) Fry, J. L.; Nicholas, R. D.; Schleyer, P. v. R. *Collect. Czech. Chem. Commun.* **1975**, *40*, 2173.

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Table I. Amounts and Ratio of **6** and **7** in the Isomerization of **5** and of **11**, as a Function of Conversion

		from **5**[a]			from **11**[b]		
no.	conversion,[c] %	%, **6**	% **7**	**6/7**	% **6**	% **7**	**6/7**
1	4.4				2.97	(0.02)[d]	(140)[d]
2	7.0[e]	3.25	2.87	1.13			
3	10.4[e]	3.91	4.86	0.80			
4	12.2				7.85	(0.08)[d]	(98.)[d]
5	24.7[f]	6.88	14.5	0.47			
6	26.0				16.7	0.91	18.4
7	40.7				22.2	4.53	4.90
8	42.0[f]	8.32	28.4	0.29			
9	50.7				25.4	6.93	3.67
10	51.2[f]	8.01	36.7	0.22			
11	60.4[e,g]	7.56	44.7	0.17			
12	63.2				28.5	13.7	2.08
13	77.2[e,g]	5.95	60.9	0.098			
14	86.4				23.3	33.5	0.70
15	88.8[f]	4.46	72.3	0.062			
16	100[e,g,h]	3.27	84.4	0.039			

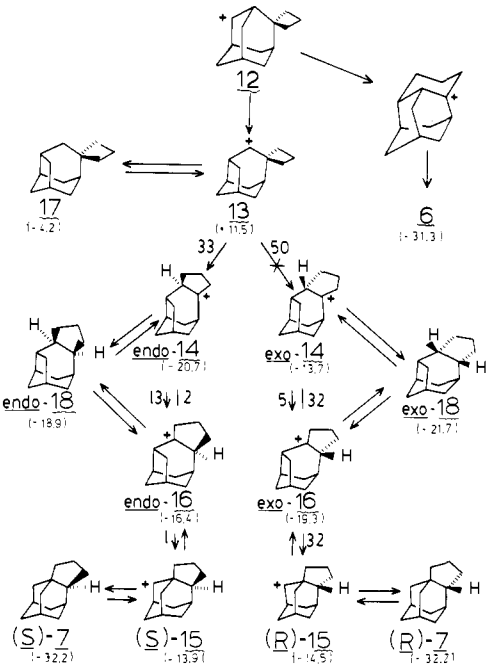
[a] In refluxing dichloromethane, with trifluoromethanesulfonic acid, GLC C. [b] $AlBr_3$–CS_2, 15 °C, GLC A. [c] 100 minus remaining starting material. [d] Large margin of error. [e] Batch I. [f] Batch II. [g] Fresh acid added after withdrawing the previous sample. [h] Equilibrium.

Cycloaddition of **8** with dichloroketene prepared in situ[15] gave the dichloroketone **9**, with 60% selectivity and 77% conversion. It should be noted that the alkene **8** obtained by dehydration of the tertiary alcohol always contained sizable amounts of saturated hydrocarbon product resulting from intermolecular hydride transfers.[13c] The material was used, however, as such in our experiments, since dichloroketone **9** was conveniently purified by column chromatography. Reductive dechlorination of **9** with zinc–copper couple[16] gave the saturated ketone **10**, and the Huang Minlon variant[17] of Kizhner–Wolff reduction converted **10** to **5**, completing the sequence.

Isomerization. Treatment of **5** with either aluminum bromide in carbon disulfide as described previously[18] or with the milder catalyst trifluoromethanesulfonic acid (TFMSA) in dichloromethane solution[19] led ultimately to the same equilibrium mixture of **6** and **7** (approximately 4:96) as did the experiments starting either with pure **6** or with tetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridecane (**11**).[10] The isomerization of **5**, however, was accompanied in all cases by the formation of a minor product with a shorter GLC retention time than **5**, **6**, or **7**, which contained two more hydrogen atoms in molecule than **5**, as established by GC–MS. The minor product was probably formed by the protonolysis of the four-membered ring, followed by a hydride abstraction from another molecule of starting material or product. At longer reaction times, at least two other short retention time products were formed at the expense of the first, in what probably is a trivial alkyladamantane isomerization. At the end of the reaction the dihydro products represented about 10% of their mixture with **6** and **7**. Two other materials, with much longer retention times, were also evidenced in the product by gas chromatography, but these were not investigated further.

The amount of **6** present in its equilibrium mixture with **7** (3.5–4%) did not change significantly between 25 and 45°.[20] In the early stages of the isomerization, however, the least stable of the two products was formed in quantities significantly exceeding its equilibrium value. The amounts of **6**, **7**, and the ratio **6/7** as a function of the total conversion of **5**, that is, including the disproportionation mentioned above, are shown in Table I, in columns 3–5, respectively. For comparison, the same quantities obtained for the rearrangement of **11** are shown in columns 6–8 of Table I. The large difference between the ratio **6/7** in the reaction mixtures at the very early stages of isomerization indicates that **6** cannot be formed from the two precursors, **5** and **11**, through the same key intermediate.

Scheme I



Reaction Mechanism. There is only one initiation reaction that can lead ultimately to the expansion of the four-membered ring of **5** by a mechanism involving only 1,2 alkyl and hydride shifts, and that is hydride abstraction from a secondary position two bonds removed from the quaternary carbon (C4, C8, C9, and C10) to form the ion **12** (Scheme I). The adamantyl–protoadamantyl rearrangement, first evidenced in the isomerization of 2-methyladamantane to 1-methyladamantane[21] and in the automerization of the adamantane ring,[22] converts **12** to **13**, which is a secondary cyclobutylcarbinyl cation; its ring expansion to a tertiary cyclopentyl cation, **14** (tetracyclo[6.3.1.1^{7,10}.0^{2,5}]tridecyl-2),

(14) Maercker, A. *Organic Reactions*, Wiley: New York, 1965; Vol. 14, pp 270, 395.
(15) Brady, W. T. *Synthesis* **1971**, 415. Ghosez, L.; Montaigne, R.; Roussel, A.; Vanherde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615.
(16) Smith, R. D.; Simmons, H. E. *Org. Synth.* **1961**, *41*, 72.
(17) (a) Huang Minlon *J. Am. Chem. Soc.* **1946**, *68*, 2487. (b) Whitlock, H. W., Jr.; Siefken, M. W. *Ibid.* **1968**, *90*, 4929.
(18) Fărcaşiu, D.; Bohm, H.; Schleyer, P. v. R. *J. Org. Chem.* **1977**, *42*, 96.
(19) (a) Takaishi, N.; Inamoto, Y.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 276. (b) Inamoto, Y.; Aigami, K.; Takaishi, N.; Fujikura, Y.; Tsuchihashi, K.; Ikeda, H. *Ibid.* **1977**, *42*, 3833.
(20) In the earlier paper, ref 10, an apparent value of 2.7 for the **7/6** ratio was determined from the gas chromatogram of the product of a rearrangement conducted with aluminum bromide sludge catalyst at 46 °C. In was indicated there that such a low ratio was probably an artifact.
(21) Majerski, Z.; Schleyer, P. v. R.; Wolf, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 5731.
(22) Majerski, Z.; Liggero, S. H.; Schleyer, P. v. R.; Wolf, A. P. *J. Chem. Soc., Chem. Commun.* **1970**, 1596.

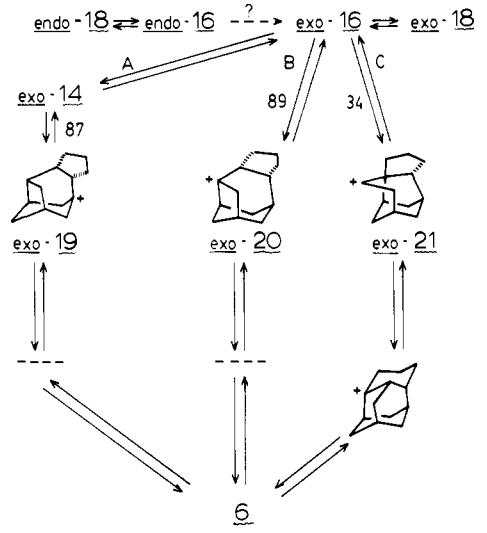
brings about a large relief of strain.

Two additional rearrangement steps, a hydride shift leading to the tetracyclo[6.3.1.1^{7,10}.0^{2,5}]tridecyl-5 cation (**16**), followed by a methylene bridge shift converting the 4-protoadamantyl-type ion **16** to the 2-adamantyl cation, **15**, separate **14** from the most stable isomer, **7**. We note that two stereoisomers, *exo*- and *endo*-**14** can be formed from **13**, resulting in two parallel pathways, which give ultimately two diastereoisomers of **7**.[23] Both pathways are shown in Scheme I, which also includes the hydrocarbons **17** and **18**, resulting from each of the intermediate carbocations by hydride transfer from a neutral molecule.

The rates of carbocationic rearrangements, particularly in rigid polycyclic systems, are governed by two factors: product ion stability and relative orientation of the migrating bond and empty orbital at the migration terminus.[21,22,24] Unless the shift is unusually endothermic, the second criterion ("bond alignment") appears to have the determining importance.[25] Both energy and geometry of hydrocarbons and carbocations can be estimated by molecular mechanics (empirical force field) calculations.[26] As a first approximation, the steric energies calculated for the starting material and product of each reaction step are compared.[10] A more rigorous approach, however, examines also the energies and geometries of the carbocations involved. Even though paucity of hard experimental data to be used in the parametrization of the force field makes the energies calculated for carbocations less accurate than those for hydrocarbons,[27b,28] the approach has afforded valuable insight into the rates and mechanism of reactions of various types of compounds.[27b,29] The bond alignment has to be examined for two mechanistic alternatives: 1,2-shift concerted with the ionization, for which the alignment of the migrating bond with the bond to the hydrogen atom abstracted as a hydride is sought (R–C–C–H dihedral angle is best at 180°), and nonconcerted shift, occurring from the preformed carbocation.[10] In the second case, bond alignments found in the geometries calculated for carbocations should be more accurate than the estimates based on the geometries calculated for the corresponding hydrocarbons. The most probable pathway of a complex rearrangement is found by comparing the energies of intermediates along all paths that connect the reactant with the product in the rearrangement graph.[30] The alignment for either type of 1,2-shift has to be favorable in each step.

In Scheme I, the relative energies (calculated heats of formation) are indicated in parantheses under each structure,[31] and the bond alignment (dihedral angle) for each migration is shown alongside the corresponding arrow.

Scheme II



The rearrangement graph of tetracyclotridecanes was discussed before in connection with the isomerization of **11** to **6** and **7**.[10] The pathway chosen as the most plausible had 4,5-*exo*-trimethyleneprotoadamantane (*exo*-**18**)[32] as the key intemediate. Examination of the geometry calculated for the neutral molecule suggested that the bond alignment is not proper for direct conversion to **7**.[10] The geometry calculated for the carbocation, however, indicates otherwise (Scheme I). It follows, then, that **11** must give **6** by a different route. Upon checking again the rearrangement graph, we found two alternative paths connecting **11** with **6**, even though we did not search all the possible pathways; the analysis is detailed in the supplementary material. The origin of the discrepancy lies in the rather flat energy surface of the rearrangement graph in the vicinity of **11**. The "tree method" of searching[10] required choices between structures differing in energy by quantities close to the uncertainty of the calculations.

Ostensibly, cation **16** can produce **6** as well, by the sequences depicted in Scheme II (paths A–C);[10] it can, indeed, under thermodynamic control, since **6** and **7** interconvert under the reaction conditions. We are studying, however, the course of the reaction under kinetic control, knowing that the initial rate of formation of **6** from **5** is twice that of **7**.[33] A careful examination reveals that the reaction sequences in Scheme II are less favorable and should be much slower than those illustrated in Scheme I.

Because of the very large energy difference between **13** and **14**, the ring enlargement of the former can be treated as irreversible. An examination of the bond alignments in Scheme I in light of the literature precedent[21,22,24,25] indicates that only the *endo*-methylene group of **13** should migrate. The same conclusion was reached based on MINDO/3 calculations on the hydride shift converting the 3-methyl-2-butyl cation (secondary) to the 2-methyl-2-butyl cation (tertiary), in which the shift occurred spontaneously for dihedral angles smaller than 35° but not for larger angles.[34] The concerted 1,2-shift mechanism is not expected to be available in this case, since the very strained ion **13** should rearrange before encounter with a hydride donor; anyway, the relevant dihedral angle for concerted shift of the *exo*-methylene in **17** is 82°.

It appears, nonetheless, that the bond alignment for *exo*-methylene migration in **13** can be improved by a distortion of the C4–C5 protoadamantane bridge. Molecular mechanics calcula-

(23) The absolute configurations indicated in Scheme I refer to the stereochemistry of C2. The barriers for the formation of the two diastereoisomers are unequal. As a matter of fact, cation **12** is chiral. There are, however, four equivalent positions in **5**, so that **7** formed is, naturally, racemic.

(24) (a) Brouwer, D. M.; Hogeveen, H. *Recl. Trav. Chim.* **1970**, *89*, 211. (b) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluck, H. W.; Schlatman, L. J. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246. (c) Vogel, P.; Saunders, M.; Thielecke, W.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971**, 1429. (d) Alford, J. R.; Cuddy, B. D.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2707.

(25) Nickon, A.; Weglein, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1271.

(26) (a) Review: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982. (b) Other reviews are listed in ref 10.

(27) (a) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582. (b) Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 3189.

(28) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Mislow, K. M.; Iverson, D. J.; Andose, J. D. BIGSTRAIN2. *QCPE* **1980**, *11*, 410. (c) A carbocation force field (Müller, P.; Mareda, J. *Tetrahedron Lett.* **1984**, *25*, 1703; *Helv. Chim. Acta* **1985**, *68*, 119) to be used with the MM2 force field for hydrocarbons (Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *11*, 395) was parametrized such as to reproduce the results of ref 28a, which means that it is not really a different force field.

(29) (a) Fărcaşiu, D. *J. Org. Chem.* **1981**, *47*, 453 and references therein. (b) Fărcaşiu, D. *J. Org. Chem.* **1978**, *43*, 3878 and references therein.

(30) Balaban, A. T.; Fărcaşiu, D.; Banica, R. *Rev. Roumaine Chim.* **1966**, *11*, 1205.

(31) The calculated energies for the secondary ions were increased by 12 kcal/mol for direct comparison with the tertiary cations: Engler, E. M.; Fărcaşiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5769. No correction for the β branching was deemed necessary in the present work.

(32) The standard convention by which the substituent on the side of the larger ring of the parent polycyclic system is assigned endo stereochemistry is employed throughout this paper.

(33) We have greatly benefited from the extensive comments of a reviewer of the manuscript.

(34) (a) Fărcaşiu, D. Presented at the International Symposium on Carbocations and Other Related Reactive Intermediates, Tübingen, Germany, Aug 18, 1988. (b) Fărcaşiu, D.; Rozeboom, M.; Houk, K. N., to be published.

tions on increasingly distorted conformations of **13** have shown that a reduction of the dihedral angle relevant for *exo*-methylene migration from 50° to 44° increases the energy of the ion by 0.25 kcal/mol, a reduction to 39° increases the energy by 0.68 kcal/mol, and for a further decrease in the dihedral angle the energy increases steeply. This extra strain energy represents a barrier to *exo*-methylene shift. Therefore, the endo pathway is clearly preferred for the rearrangement of **13**.

Now consider Scheme II. Starting with the exo isomer (for simplification the only one shown in the scheme), pathways A and B cannot occur directly, because the dihedral angles for the required hydride migrations are 87 and 89°, respectively. The indirect transformation, involving the parent hydrocarbon (*exo*-**18**) as intermediate can also be eliminated, because hydride loss from **18** to form the very strained[35] 6- and 3-protoadamantyl cations (*exo*-**19** and *exo*-**20**, respectively) cannot compete effectively with return to **16**, a tertiary 4-protoadamantyl cation.[36]

Migration of the C8–C3 bond of *exo*-**16** to C4, labeled as path C, shows a bond alignment about as good as the shift forming **15**. The competition, then, is between a 4-protoadamantyl to 4-protoadamantyl (**16** → **21**) rearrangement and a 4-protoadamantyl to 2-adamantyl (**16** → **15**) rearrangement. In both cases the product cation is secondary, but **15** is lower in energy.[35] We cannot expect, therefore, the shift to **21** to be the faster one. This competition was actually studied for the parent compound, protoadamantane, by ^{13}C labeling. Under kinetic control the shift to 2-adamantyl occurred exclusively.[37]

As discussed above, the sequence involving exo intermediates is disfavored relative to the endo sequence at the stage of ring enlargement of **13**. If we consider now the cation *endo*-**16** in Scheme II, the same objections as above hold for pathways A and B. Path C leads in this case to a highly strained secondary 4-protoadamantyl cation (*endo*-**21**), which contains a *trans*-bicyclo[3.3.0]octane moiety with a quaternary bridgehead. Therefore, this pathway can also be definitely ruled out.

It is possible, in principle, that *endo*-**14** is converted to *exo*-**16** via the $\Delta^{4,5}$-alkene, or the *trans*-(*endo*-4-) isomer of **18** (1.9 kcal/mol less stable than *endo*-**18** by MM2). This is a crossover route from the endo to the exo pathway in Scheme I.[33] It would then be needed that this crossover route be significantly faster than the direct conversion of *endo*-**14** to **15**, and, in addition, that conversion of *exo*-**16** to *exo*-**21** be faster than conversion of exo-**16** to **15**, but the latter requirement is not fulfilled, anyway.

Conclusion

Extrapolation of the data of Table I to time zero gives an initial ratio of approximately 2 for the rates of formation of **6** and **7**. Our analysis of the data indicates that such a ratio cannot be explained by a reaction pathway involving only 1,2-shifts of alkyl or hydride; instead, a direct transannular migration of the methylene bridge in **12** appears as the main source of **6**. The data also indicate that the transannular migration has an energy barrier similar to the energy difference between the 4-protoadamantyl cation **13** and the 2-adamantyl cation **12**.[36] We estimate, therefore, that this 1,3 alkyl shift driven by a large relief of strain has a barrier of about 10 kcal/mol.

Experimental Section

General Procedures. The NMR spectra were recorded in $CDCl_3$ with Me_4Si as internal standard, at 250 MHz for protium and 62.896 for carbon-13. Melting points are uncorrected. GLC analyses were run on one of the following columns: (A) 1% SP2100, 3 m × 3 mm o.d.; (B) 10% Carbowax 20M, 3 m × 3 mm o.d.; (C) capillary column coated with a 0.25-μm film of methyl/phenyl silicone 95:5 (DB-5), 30 m × 0.259 mm i.d. The carrier gas was dry nitrogen.

Dichloroketene Adduct of Methyleneadamantane (9). Methyleneadamantane[13a,c] used was of 60% purity, the rest being 2-methyladamantane and a dimer of **8**. This material (8.3 g, i.e., 5.0 g of pure **8**, 34 mmol) was dissolved in dry hexane (100 mL), and triethylamine (8.6 mL, 6.9 g, 62 mmol, distilled over sodium hydroxide pellets) was added. The solution was magnetically stirred vigorously under a nitrogen atmosphere, and dichloroacetyl chloride (4.5 mL, 6.9 g, 47 mmol) was added dropwise over a 2-h period. The resulting suspension was stirred for another 1 h, and then the solid was filtered and washed five times with ether. The combined ether/hexane solution was washed successively with 5% HCl, 5% Na_2CO_3, and water, dried ($MgSO_4$), and then concentrated under vacuum. The residue, an oil, was purified by column chromatography on silica gel (Woelm, 160 g). Elution with pentane gave 4.5 g of a hydrocarbon fraction containing about 2.15 g of **8** (GLC, column A, 120 °C). Elution with mixtures containing increasing amounts of ether in pentane afforded **9**, eluted with pentane/ether 93:7. Crystallization from pentane at −15 °C gave a yellow solid, mp 72–84 °C (4.1 g, 61% selectivity of conversion of **8**, 47% yield based on the total precursor used in the reaction). Repeated recrystallization from ether at low temperature gave analytically pure **8**, mp 91.8–92.8 °C, slightly yellow (analysis for $C_{13}H_{16}Cl_2O$: C, H, Cl). IR (Nujol mull): 1813 cm^{-1}. ^1H NMR (60 MHz): δ 3.03 (s, 2 H), 2.53–1.45 (br, 14 H).

Spiro[adamantane-2,1'-cyclobutan-3'-one] (10). Zinc–copper couple (15.6 g, 233 mmol)[16] was added to a solution of **9** (10 g, 38.8 mmol) in 250 mL of glacial acetic acid, with magnetic stirring, under nitrogen. A slightly exothermic effect was noticeable immediately. The resulting mixture was stirred until all the starting material had reacted (2.5 h). The reaction was monitored by TLC (silica gel plates from E. Merck, ether). The reaction mixture was then poured into ice–water and extracted with ether. The ether solution was washed with water, saturated $NaHCO_3$, and again water and then dried ($MgSO_4$). Solvent evaporation afforded 7.3 g of crude product. Recrystallization from pentane at low temperature yielded 7.1 g (96%) of pure **10**, mp 130–130.5 °C. (Analysis for $C_{13}H_{18}O$ by precise mass measurement, high-resolution MS.) IR (CCl_4): 1780 cm^{-1} (vs). ^{13}C NMR: δ 26.94 (C5, C7), 33.84 (C4, C8, C9, C10), 36.77 (C1, C3), 37.04 (C6), 37.24 (C2), 56.91 (C2', C4'), 209.12 (C3') (assignments made by the APT pulse sequence). ^1H NMR: δ 1.74 (C1, C3), 1.76 (C6), 1.78 (C4, C8, C9, C10), 1.89 (C5, C7), 2.81 (C2', C4') (determined by heteronuclear, C/H, 2D chemical shift correlation).

Spiro[adamantane-2,1'-cyclobutane] (5). Procedure a.[1a] The modified Kizhner–Wolff reduction[17] applied to **10** (2.3g, 12.1mmol) gave 2.0 g of an oil, which was purified by column chromatography on 60 g of silica gel in pentane, to give 1.5 g (70% yield) of pure (GLC columns A and C) **5**, mp 51–54 °C.

Procedure b.[1d] Benzene (50 mL) was added to a solution of **10** (5 g, 26.3 mmol), KOH (5 g, 85%, 75 mmol), and hydrazine hydrate (6 g, 92 mmol) in diethylene glycol (250 mL). The mixture was refluxed with an azeotropic distillation adapter until no more water distilled; then benzene was distilled off and the solution was heated under reflux at 200 °C for 4 h. The reaction mixture was cooled and poured into 100 mL of water. Extraction with pentane, washing with 5% HCl and then several times with water, drying ($MgSO_4$), and solvent evaporation gave a crude product, which was sublimed to afford 4.3 g (98%) of pure **5**, mp 58.5–59.5 °C. (Analysis for $C_{13}H_{20}$ by precise mass measurement, high-resolution MS.) ^{13}C NMR: δ 14.10 (C3'), 27.30 (C5, C7), 32.31 (C2', C4'), 32.83 (C4, C8, C9, C10) 37.35 (C6), 37.37 (C1, C3), and 45.74 (C2) (assignments made as indicated for **10**). ^1H NMR: δ 1.55 (C4, C8, C9, C10, cis to the four-membered ring), 1.68 (C6), 1.71 (C1, C3), 1.74 (C5, C7, C3'), 1.78 (C4, C8, C9, C10, trans to the four-membered ring), and 1.81 (C2', C4'), determined as indicated for **10**.

Rearrangement of 5 with TFMSA. In a typical experiment (batch I of Table I) a 15-mL 2-necked round-bottomed flask was fitted with a stopcock covered with a rubber septum and with a water-cooled reflux condenser carrying at the top an adapter with inlet and outlet tubes connected to a dry nitrogen line and to an oil bubbler, respectively. A stirring bar was placed in the flask. The installation was dried for 1 h at 125 °C and then assembled while hot and cooled in a stream of nitrogen. The reactant **5** (80 mg, 0.45 mmol), methylene chloride dried over $CaCl_2$ (5 mL), and redistilled TFMSA (150 mg, 1.32 mmol) were placed into the flask, and the mixture was brought quickly to boiling (time zero). A very slow stream of nitrogen was maintained throughout the experiment. Samples (0.5 mL each) were taken through the rubber septum with an oven-dried 2-mL syringe with long needle, opening the stopcock only for the time needed to withdraw the sample, which was then transferred to a small separatory funnel containg 2 mL of saturated $NaCO_3H$ solution and 1–2 mL of CH_2Cl_2. After swirling for neutralization, the lower layer was drained into a vial, dried over Na_2SO_4, and analyzed by GLC on column C at 110 °C (at the end of each analysis

(35) (a) Calculated (molecular mechanics) heats of formation for *exo*-**19**, *exo*-**20**, and *exo*-**21** are −2.3, −1.4, and −8.4 kcal/mol, respectively, to be compared with the values in Scheme I. (b) For the evaluation of relative reactivities of bridgehead positions in protoadamantane, see: Karim, A.; McKervey, M. A.; Engler, E. M.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971**, 3987.

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the column temperature was raised to 200 °C to elute the heavy byproducts). The first sample, taken after 2 h, showed a ratio of **5**/**6**/$C_{13}H_{22}$ of 96.8:2.4:0.7, but the peak for **7** was too small for accurate integration; therefore that data point was not included in Table I. The next sample (at 4 h) is entry 2 of Table I. To drive the reaction to equilibrium, fresh TFMSA was added after 10.5 h (150 mg), 23 h (200 mg), and 30.25 h (320 mg). The following sample (47 h) showed a **7**/**6** ratio of 25.8, which did not change to 71.5 h. **6**: M = 176 (GC-MS).

Batch II of Table I was conducted in the same way, except that 320 mg (2.81 mmol) of TFMSA was used. The first sample (entry 5) was taken after 1 h, and the last (entry 15), after 23 h.

Rearrangement of 5 with $AlBr_3$. The installation was the same as above, except that a 25-mL flask was used. **5** (0.57 g, 3.25 mmol), carbon disulfide (12 mL, reagent grade), and aluminum bromide (0.22 g, 0.825 mol, measured under nitrogen inside a drybox) were added, and then the tube to the nitrogen line was replaced with a connection to an HBr lecture bottle. The installation was flushed with HBr at the beginning of the run and occasionally thereafter. Sampling was done as described above. The first sample was taken after 20 min, and the highest concentration of **6** (checked on column B at 134 °C) was 7.9% after 50 min. The equilibrium ratio **7**/**6** (26.5) was reched after 9 h.

Rearrangement of 11 with $AlBr_3$.[10] In order to reduce the conversion rate, this reaction was run at 15 °C with more dilute catalyst. Aluminum bromide (0.5 g) was dissolved in CS_2 (25 mL) in the drybox; 5 mL of the resulting solution (0.37 mmol of $AlBr_3$) was brought to the reaction temperature and mixed with a solution of 0.35 g of **11** (2 mmol) in 5 mL of CS_2 at the same temperature. The installation and sampling technique were the same as above. Analysis was done mostly on column A at 120-250 °C; some samples were also checked on column C, as above. Samples taken at 0.25, 0.67, 2.0, 3.5, 5.0, 7.5, and 23 h are presented in Table I.

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Supplementary Material Available: An addition to the partial tricycloundecane rearrangement graph published previously[10] (Scheme III) with comments (3 pages). Ordering information is given on any current masthead page.

Mechanism of Solvolysis of Substituted Benzoyl Halides[1]

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Abstract: Most substituted benzoyl fluorides undergo hydrolysis in aqueous solution through an associative mechanism with ρ = 1.7, k_{HOH}/k_{DOD} = 2.3 ± 0.2, little dependence on the leaving group (k_{Cl}/k_F = 1.2), and general-base catalysis by fluoride ion. There is an abrupt change to a dissociative mechanism through an acylium ion intermediate for the hydrolysis of *p*-(dimethylamino)benzoyl and (in part) *p*-anisoyl fluorides, with $\rho^+ \leq -1.2$, $k_{Cl}/k_F = 10^6$-10^7, and k_{HOH}/k_{DOD} = 1.1 for *p*-$Me_2NPhCOF$. Common ion inhibition by fluoride ion traps the *p*-(dimethylamino)benzoyl acylium ion, which undergoes hydration with $k_h \sim 10^9$-10^{10} s^{-1}. The increase in the solvent isotope effect for hydrolysis of *p*-(dimethylamino)benzoyl fluoride to k_{HOH}/k_{DOD} = 1.9 in the presence of concentrated potassium fluoride is attributed to general-base-catalyzed hydration of the acylium ion intermediate. The large yield of trifluoroethyl ester from the solvolysis of *p*-anisoyl fluoride in TFE/EtOH/HOH suggests that the acylium ion reacts in a solvent-separated ion pair, with $k_h \sim 10^{12}$ s^{-1}; extrapolation predicts rate constants of $\geq 10^{13}$ s^{-1} for the hydration of less stable acylium ions. A change in sensitivity to solvent ionizing power from m = 1.4 in water to m = 0 in 60% ethanol for *p*-(dimethylamino)benzoyl fluoride suggests a change to an associative mechanism. Benzoyl fluorides and acylium ions show selectivity toward alcohols, with $\beta_{nuc} \sim 0.2$. The absence of common ion inhibition for the solvolysis of several benzoyl chlorides in water or 90% TFE/HOH is consistent with $k_h > 10^{11}$ s^{-1} for the acylium ions. Solvolysis occurs through the dissociative reaction channel, with $\rho^+ = -3.0$, even when the estimated lifetimes of the acylium ion species suggest that there is no chemical barrier for their hydration. However, there is a change to an associative mechanism for the solvolysis of *p*-nitrobenzoyl chloride in water.

In spite of intensive experimental examination of the mechanism of acyl-transfer reactions for many years, the mechanisms of most of these reactions are still not established.[2,3] Acyl-transfer reactions are commonly classified into three groups: (1) A dissociative mechanism, which may proceed through an acylium ion intermediate (S_N1)

$$\mathrm{RCOX} \longrightarrow \mathrm{RC^{+}(\cdot X^{-})=O} \xrightarrow{+Nu^-} \mathrm{RCONu} \qquad (1)$$

(2) A direct displacement mechanism (S_N2)

$$\mathrm{RCOX} \xrightarrow{+Nu^-} [\mathrm{TS}]^{\ddagger} \xrightarrow{-X^-} \mathrm{RCONu} \qquad (2)$$

(3) An associative addition-elimination mechanism, which may proceed through a tetrahedral intermediate (AE).

$$\mathrm{RCOX} \xrightarrow{+Nu} \mathrm{R-C(O^-)(Nu)-X} \xrightarrow{-X^-} \mathrm{RCONu} \qquad (3)$$

However, this classification of mechanisms is ambiguous because there is no clear distinction between the three mechanisms when they are concerted; all of them may be concerted displacements with added nucleophiles or solvent, which can have

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