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Cubylcarbinyl Cation: Fact or Fiction?

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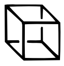
Ab initio molecular orbital calculations have been used to study the stability of the cubylcarbinyl cation (**21**). The secocubylcarbinyl cation (**25**) is the only minima found which resembles **21**. Conversion of **25** to the homocubyl cation requires 174.6 kJ/mol. A barrier of 303.7 kJ/mol is calculated for ring expansion of cubylmethanol (**7**) to 1-homocubanol (**13**). Protonation of **7** forms the corresponding oxonium ion (**30**) which has a C−O bond similar to that found in protonated methanol. The oxonium ion formed by protonation of cubylmethanol (**30**) undergoes ring expansion to the 1-homocubanoxonium ion (**32**) with a barrier of only 4.0 kJ/mol. Density functional calculations predict a barrier-free reaction. The presence of the hydroxyl function in **7** directs the reaction toward ring expansion rather than ring opening through formation of the oxonium ion **30**. A similar barrier reduction is observed in the methylene-transfer reaction in propanol (**33**) upon protonation.

Introduction

The chemistry of cubane (**1**) has unfolded nicely in the three decades following the first preparation of the cubane nucleus by Eaton and Cole in 1964.[1] In recent times excellent synthetic methodologies for the polyfunctionalization of the cubane nucleus have been developed, thereby providing access to a wide variety of polysubstituted cubane derivatives.[2] Indeed, much effort has been directed toward generating and understanding the properties of several cubane-derived reactive intermediates, including the cubyl cation (**2**),[3] cubyl radical (**3**),[4] the 1,4-diradical (**4**),[5] and cubene (**5**).[6] Recently, the chemistry of cubylmethyl radical (**6**) has been investigated in detail using a combination of experimental[7] and computational[8] techniques.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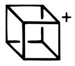
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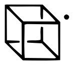
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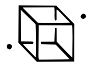
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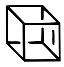
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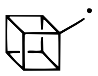
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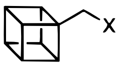
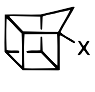
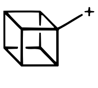
Cole was the first to observe the proclivity of cubylmethanol (**7**) toward Wagner−Meerwein ring expansion.[9] While attempting to prepare the tosylate **8** from **7** with *p*-toluenesulfonyl chloride in pyridine, Cole noted that the only product isolated was the tosylate **9**. The less solvolytically active *p*-nitrobenzoate (PNB) ester **10**, however, was prepared without difficulty. Solvolysis of **10** in glacial acetic acid at 100 °C furnished the homocubyl *p*-nitrobenzoate **11** as the major product. Indeed, **10** was found to undergo solvolysis 3 × 10^6 times faster than *tert*-butyl *p*-nitrobenzoate in aqueous acetone at room temperature.[10] The origin of this enhanced rate of solvolysis of **10**, relative to *tert*-butyl *p*-nitrobenzoate, was attributed to the release of strain in the transition state leading to ring expansion.[10,11] Attempts to prepare the carbinyl bromide **12** through exposure of **7** to aqueous HBr at room temperature produced a 2:1 mixture of **13** and the homocubyl bromide **14**.[9] Similar experiments with diphenylmethanols **15**[10] and **18**[12] under a variety of reaction conditions gave rise to analogous results (Scheme 1). Evidently, the two phenyl substituents have little effect on the course of these reactions.



7 X = OH
8 X = OTs
10 X = PNB
12 X = Br
20 X = I



9 X = OTs
11 X = PNB
13 X = OH
14 X = Br
19 X = I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(1) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962, 3157.

(2) (a) Tsanaktsidis, J. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1997; Vol. 6, in press. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421. (c) Griffin, G. W.; Marchand, A. P. *Chem Rev.* **1989**, *89*, 997.

(3) (a) Della, E. W.; Schiesser, C. H. *J. Chem. Soc., Chem. Commun.* **1994**, 417. (b) Eaton, P. E.; Yang, C.-X; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225. (c) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227. (d) Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228. (e) Kevill, D. N.; D'Souza, M. J.; Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Chem. Soc., Chem. Commun.* **1990**, 623.

(4) (a) Rhodes, C. J.; Walton, J. C.; Della, E. W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2125. (b) Della, E. W.; Elsey, G. M.; Head, N. J.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1589.

(5) (a) Eaton, P. E.; Li, J.; Upadhyaya, S. P. *J. Org. Chem.* **1995**, *60*, 966. (b) Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990**, *112*, 876. (c) Hassenruck, K.; Radzisewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873. (d) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112,* 875.

(6) (a) Lukin, K; Eaton, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 7652. (b) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

(7) Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10730.

(8) (a) Lee, M.-S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1995**, *117*, 10353. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6459.

(9) Cole, T. W., Jr. Ph.D. Dissertation, University of Chicago, 1966.

(10) Luh, T.-Y. Ph.D. Dissertation, University of Chicago, 1974.

(11) Dauben, W. G.; Chitwood, J. L.; Scherer, K. V., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1014.

(12) Hasegawa, T.; Nigo, T.; Kakita, T.; Toyoda, H.; Ueda, I. *Chem. Pharm. Bull.* **1993**, *41*, 1760.

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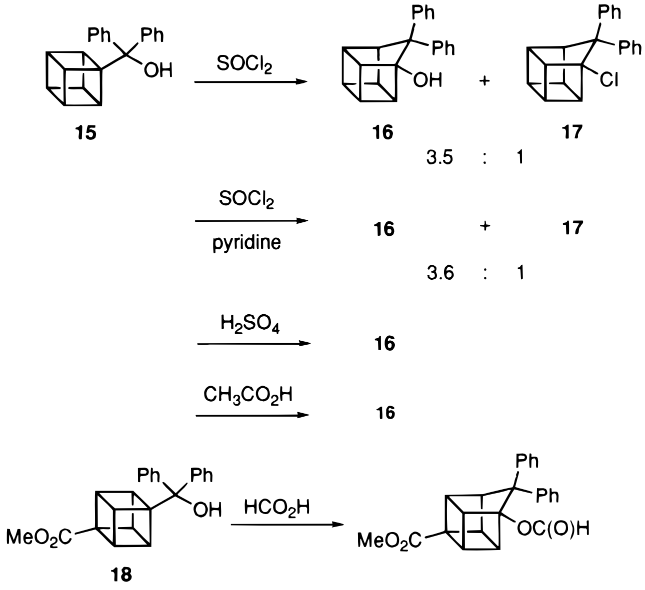
Scheme 1



Recently, Della and co-workers took advantage of this characteristic of the cubylcarbinyl system in their preparation of the homocubyl iodide **19** through the reaction of **7** with Ph_3P/I_2 in dichloromethane,[13] which presumably proceeds through the agency of the carbinyl iodide **20**, whereas Olah *et al.*[14] failed to detect any fluorine-containing products from the reaction of **7** with pyridine poly(hydrogen fluoride) with the rearranged alcohol **13** being the only product reported.

It would appear, based on the difficulty in isolating products which do not undergo rearrangement upon solvolysis of derivatives of **7**, that any carbonium ion formed in these reactions must be short-lived. In this paper, we disclose the results of detailed, high-level *ab initio* molecular orbital studies of cubylcarbinyl cation (**21**) and on the ring expansion of cubylmethanol (**7**). These studies indicate that **21** is not a discrete cationic intermediate on the $C_9H_9^+$ potential energy surface and that isomerization of the cube may be determined by the nature of the cation precursor.

Methods

Standard *ab initio* molecular orbital calculations[15] were performed using the GAUSSIAN 94[16] program. Geometries were optimized at the MP2(fc)/6-31G(d) level and improved relative energies obtained at these geometries at the MP2/6-311+G(2df,p) level. Unless otherwise noted, harmonic vibrational frequencies were evaluated at the HF/6-31G(d) level in order to characterize stationary points as minima or saddle points and to estimate zero-point vibrational and temperature corrections (to 298 K). Optimized geometries are supplied as Supporting Information. Calculated energies and thermal corrections are presented in Table 1. Energies in the text refer to MP2/6-311+G(2df,p) enthalpies at 298 K, and bond lengths are those obtained at the MP2(fc)/6-31G(d) level unless otherwise noted.

Table 1. Calculated Total Energies (hartrees), Zero-Point Vibrational Energies, and Temperature Corrections (millihartrees)

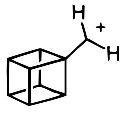
	MP2/ 6-311+G(2df,p)	B-LYP/ TZVP(A2)	ZPVE[a]	ΔH_{298-0}[a]
7	−423.075 82	−423.946 91	160.94	8.43
13	−423.155 41	−424.015 36	162.55	7.55
24	−347.063 37	−347.815 45	142.79[c]	7.24
25	−347.132 84	−347.882 47	146.16[c,d]	7.95[d]
26	−347.151 26	−345.912 12	144.26	7.78
27	−347.100 45	−347.854 09	145.98	6.58
28	−347.063 00	−347.828 42	144.07[c]	6.70
29	−422.955 52	−423.852 64	155.90[c]	8.85
30	−423.387 92	*b*	172.44	9.02
31	−423.383 27	*b*	168.80[c]	9.54
32	−423.465 59	−424.331 77	174.22	8.14
33	−193.933 06		104.16	6.59
34	−193.758 61		97.68[c]	7.46
35	−194.233 42		115.68	7.16
36	−194.209 46		109.50[c]	9.09
H_2O	−76.308 95	−76.443 03	20.52	3.78

[a] Harmonic frequecies scaled by 0.8929 unless otherwise noted. [b] No stationary point located. [c] Structure is a transition state with one imaginary frequency at the HF/6-31G(d) level. [d] Structure is a minima at the MP2/6-31G(d) level. Zero-point vibrational energy and temperature corrections calculated using MP2/6-31G(d) frequencies, scaled by 0.96.

Density functional (DFT) calculations were performed using the DGauss program.[17] This program includes implementations of the *nonlocal* or *gradient-corrected* correlation functionals due to Becke[18] (B) and to Lee, Yang, and Parr[19] (LYP). Energies reported here (Table 1) were calculated at the TZVP(A2) basis level upon geometries obtained using the DZVP(A1) basis.[17] The default choice of SCF and gradient convergence and integral accuracy were used for geometry optimizations, while high SCF convergence and integral accuracy were applied for calculations of energies for comparison purposes. Zero-point vibrational and temperature corrections (to 298 K) obtained at the HF/6-31G(d) level were applied to these energies.

Results

The cubylcarbinyl cation (**21**) can posses C_s symmetry with the methylene hydrogens constrained either in the symmetry plane, as depicted by structure **22**, or perpendicular to the symmetry plane, i.e., structure **23**. Optimization of these structures, with constrained C_s symmetry, leads to the ring-opened structures **24** and **25**, respectively. In **24** the separation between C_1-C_6 and C_1-C_8 is 1.85 Å, whereas the C_1-C_2 distance in **25** is 2.81 Å. Furthermore, the C_2-C_4 distance in **25** is considerably shorter (1.64 Å) than the analogous 1,3-separation in cubane (2.15 Å). Structure **25** is a first-order transition state at the HF/6-31G(d) level, which accesses the tetracyclic cation **26** (enantiomeric pair)



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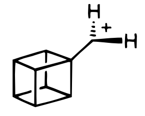

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(13) Della, E. W.; Head, N. J.; Janowski, W. K.; Schiesser, C. H. *J. Org. Chem.* **1993**, *58*, 7876.

(14) Head, N. J.; Rasul, G.; Mitra, A.; Bashir-Hashemi, A.; Prakask, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1995**, *117*, 12107.

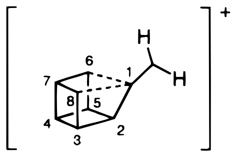
(15) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision C.3, Gaussian, Inc., Pittsburgh, PA, 1995.

(17) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.

(18) Becke, A. D. *Phys. Rev. B* **1988**, *38*, 3098.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.



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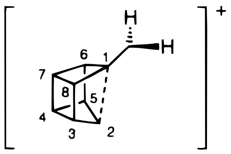

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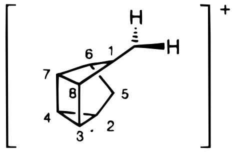
through migration of either the $C_3{-}C_4$ or $C_4{-}C_5$ bonds (i.e., interconverts structures **26** and **26′**).



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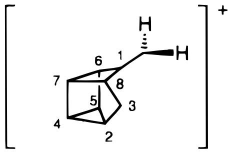
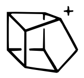


26′

The homocubyl cation **27**, the product of ring expansion, lies 81.0 and 134.8 kJ/mol higher in energy than structures **25** and **26**, respectively. The first-order transition state structure **28** was located 93.6 kJ/mol above **27** and was found to connect **27** with **25** along reaction coordinate which maintains C_s symmetry. At the HF level there must exist a branch point **26** (whose energy has not been determined) between **25** and **28**. The minimum energy path (MEP), however, will lead directly from **28** to **26**; there exists no barrier between **28** and **26**. At the MP2 level, however, **25** has all real frequencies. Thus the MEP from **28** leads to **25**, and there must exist a barrier between **25** and **26**. Conversion of **25** to **27**, through **28**, requires 174.6 kJ/mol. Structure **24** (lying 90.7 kJ/mol above **27** and 171.7 kJ/mol above **25**) is a first-order transition state at both HF and MP2 levels. Structure **24** appears to interconvert the related structures **25**, **25′**, and **25″**. Thus, there appears to exist three minima in this region of the potential energy surface, the homocubyl cation **27**, the tetracyclic cation **26**, and the secocubylcarbinyl cation **25**. Structure **24**, which resembles **21**, is a transition state species which connect various symmetry related structures **25**.



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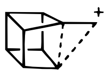

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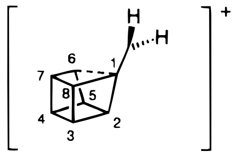
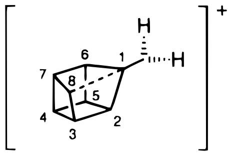


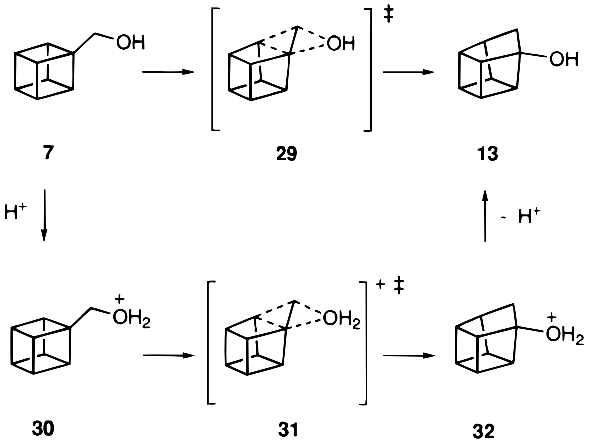
25′



25″

Protonation of **7** might be expected to form **21** through loss of a water molecule. However, protonation of **7** produces the oxonium ion **30**. Conversion of **30** through the transition structure **31** to the homocubyloxonium ion **32** requires just 4.0 kJ/mol. In comparison, direct conversion of **7** to **13** through the transition state **29** requires 303.7 kJ/mol (Scheme 2). Dissociation of the C−O bond in **32** requires 133.1 kJ/mol. A schematic potential energy profile describing the rearrangement of the cubylcarbinyl systems **7** and **30** to the homocubyl analogues **13** and **32**, respectively, is presented in Figure 1.

Scheme 2



Removal of H_2O from the cubylmethanol oxonium ion (**30**) will most likely yield the secocubycarbinyl cation **25**. The dissociated products (H_2O + **25**) lie 149.4 kJ/mol lower than **30**, but 52.1 kJ/mol higher than the homocubyloxonium ion **32**. However, any barrier to dissociation is likely to be significantly larger than the 4.0 kJ/mol required for ring expansion. Stretching the C−O bond in **30** leads to the transition structure **31** for ring expansion, and *not* to a transition structure for dissociation. Therefore, ring expansion is the most probable outcome following protonation of **7**.

We have shown that protonation of **7** forms **30**, not the cubylcarbinyl cation **21** in complex with a water molecule. The C−O bond length in **30** (1.578 Å) is only slightly longer than the corresponding distance in the methoxonium ion (1.517 Å) calculated at this level. The calculated proton affinity of **7** (yielding the oxonium ion **30**), 793.7 kJ/mol, is appreciably higher than the proton affinity for methanol calculated at this level, 747.5 kJ/mol (which is slightly lower than the experimental proton affinity[20] of methanol of 760 kJ/mol). The structural and energetic features of **30** appear typical for an oxonium ion. The proton affinity of **13**, 788.5 kJ/mol, is remarkably similar to that of **7**. The C−O bond length in **32** is found to be 1.541 Å.

The B-LYP method predicts a barrier to formation of **27** through **28** from **25** of only 133.1 kJ/mol, 41.5 kJ/mol lower than the MP2/6-311+G(2df,p) method. The energy of the barrier to ring expansion in **7** (via **29**) is 68 kJ/mol lower, and the energy difference between **7** and **13** is 29 kJ/mol less with B-LYP than with the conventional molecular orbital methods reported above. It has been shown previously[21] that the B-LYP method does tend to underestimate barrier heights, and reactions with low barriers can be predicted to be barrier-free. The small barrier to ring expansion in **30** (via **31**) found above is not found with B-LYP. The loss of H_2O from **32** is 57 kJ/mol less with B-LYP than the conventional molecular orbital results.

Discussion

The computational results from this study clearly show that the cubylcarbinyl cation (**21**) is not a stable discrete cationic species. Formation of this cation is predicted to result in collapse to the secocubylcarbinyl cation **25**.

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(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl. 1* **1988**, 17.

(21) Baker, J.; Muir, M.; Andzelm, J. *J. Chem. Phys.* **1995**, *102*, 2063.

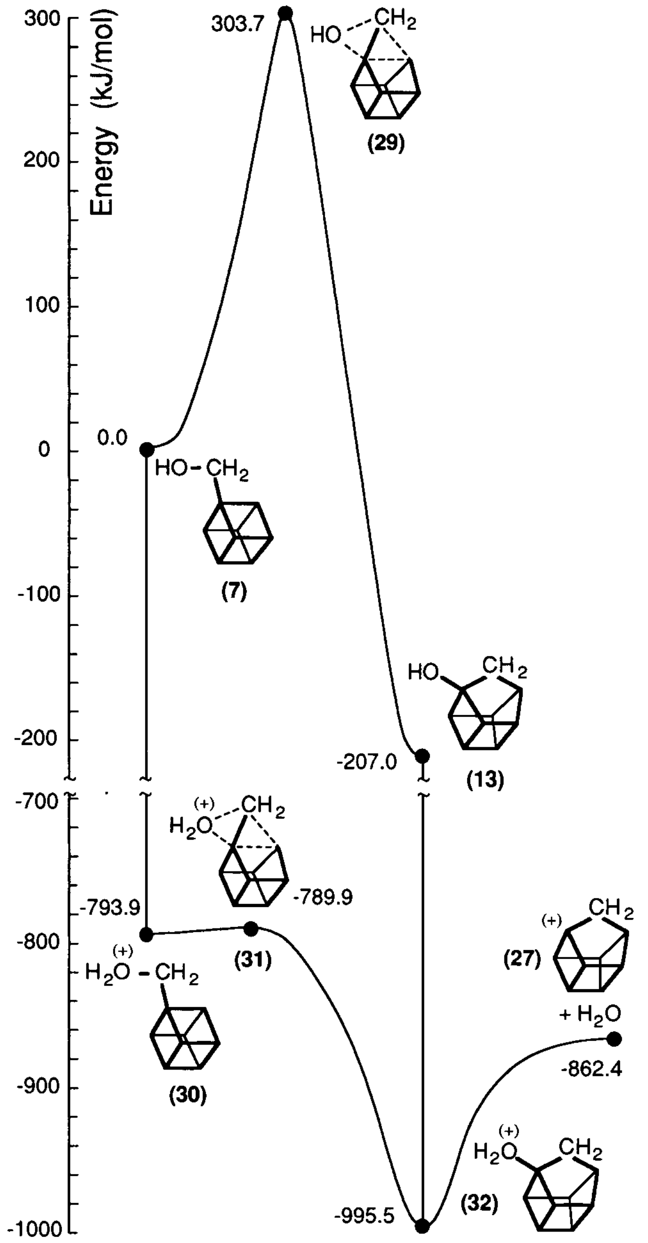
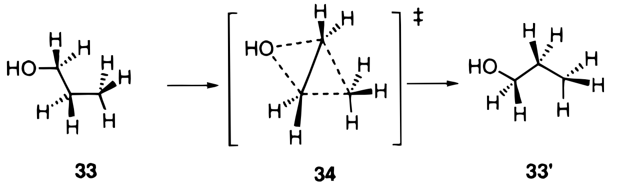


Figure 1. Schematic potential energy diagram for the ring expansion of the cubylcarbinyl system.

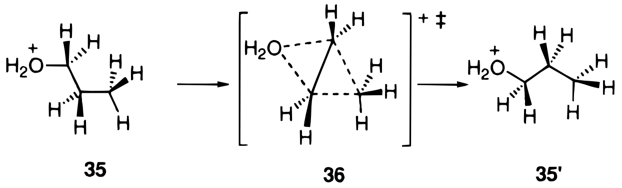
Conversion of **25** to the homocubyl cation is calculated to require 175 kJ/mol. Lower in energy than **25** is the tetracyclic cation **26**. There exists, however, no available experimental evidence for the formation of **25** or **26** from solvolysis of any cubylcarbinyl systems. There is a similarly high barrier for the formation of the homocubyl system from **7**.

Protonation of **7** yields a stable oxonium ion **30**. Protonation also significantly lowers the energy barrier to ring expansion. Indeed, only one path (ring expansion) has been established through experiment to date (i.e., via **31** on route to **13**). The presence of the hydroxyl function thus appears to direct the isomerization process toward ring expansion rather than ring opening through formation of the oxonium ion **30**.

Scheme 3



Scheme 4



Propanol (**33**) provides the simplest system in which methylene can undergo rearrangement similar to that found for **7**. The rearrangement of **33** via the transition structure **34** along a path in which C_s symmetry is constrained (Scheme 3) produces the tautomer of the reactant **33′**. Similarly, the propyloxonium ion (**35**) can undergo methylene rearrangement through the transition state **36** (Scheme 4).

The transition state **34** lies 443.3 kJ/mol above **33**. In contrast, **36** lies only 51.7 kJ/mol above **35**. For neopentanol and its cationic analogue,[22] the barriers are roughly 10–20 kJ/mol smaller. Thus, protonation is responsible for substantially reducing the methylene-transfer barrier. Presumably, release of strain is an additional influence responsible for the decrease in the barrier in the ring expansion of both **7** and **30**.

The 1-propyl cation provides the simplest example of methylene migration in a carbocation. While the 1-propyl cation is a stationary point on the $C_3H_9^+$ potential energy surface, it is not a minimum: it is a transition state.[23] Thus, while strain in the cubylcarbinyl cation (**21**) presumably causes elongation of C–C bonds of the transition states **24** and **25** (compared to the C–H bonds in the 1-propyl cation), it is not surprising that **21** is also not a minima.

Concluding Remarks

The critical outcomes from this study are as follows. (1) The carbinyl cation **21** is not a classical discrete cationic species. The secocubylcarbinyl cation (**25**) is the only minima found which resembles **21**. Conversion of **25** to the homocubyl cation requires 174.6 kJ/mol. (2) Protonation of cubylmethanol (**7**) significantly lowers the energy barrier to ring expansion. This is not a feature peculiar to the cubane system; the methylene-transfer energy barrier in propanol (**33**) is also significantly reduced upon protonation. (3) The presence of the hydroxyl function in **7** directs the reaction toward ring expansion rather than ring opening through formation of the oxonium ion **30**.

Supporting Information Available: Positional parameters for **7**, **13**, and **24**–**32** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[22] Smith, B. J. Unpublished results.

[23] Koch, W.; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 3479.