kcal/mol, as compared to just 12 kcal/mol for 1,2- and 1,6-$C_2B_4H_6$. In the optimized DTP-$B_6H_6^{2-}$ (C_s), the secondary apex, B_6, and two basal positions, B_1 and B_2, are especially favorable sites (Figure 3). The charges and overlap populations[11] imply that the DTP structure obtained above for $C_2B_4H_6$ should be the most stable of the several possible isomers. Hence, useful information concerning relative energies and favored rearrangement pathways in carboranes can be inferred from simpler computations on the parent boron hydride systems.

Further, a more electronegative substituent could invert the order of stability. Preliminary calculations on the hypothetical $N_2B_4H_4$ predict the 1,6-disubstituted DTP structure to lie 10 and 15 kcal/mol below 1,6- and 1,2-$N_2B_4H_4$, respectively. For $NB_5H_5^-$, however, the "octahedral" form is calculated as being the most stable, the 6-, 1-, 3-, and 5-substituted DTP structures lying higher in energy in the order expected from the $B_6H_6^{2-}$ atomic charges by 35, 48, ~90, and ~110 kcal/mol.[12] Finally, the attachment of electronegative substituents to carbon in the $C_2B_4H_6$ system may sufficiently stabilize the DTP structure to allow its experimental detection.

Acknowledgment. We thank the Office of Naval Research and the National Institutes of Health Grant GM 06920 for support.

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(7) See, e.g., S. Ehrenson, *J. Am. Chem. Soc.*, **96,** 3778 (1974).

(8) Carried out by restricting atoms 1–4 to a common plane, rather than as an orthogonal optimization.

(9) Computed as above with the constraint that the dihedral angle between planes (1,2,3) and (1,4,3), or (2,1,4) and (2,3,4), vary precisely linearly.

(10) The optimization of the LST_2 maximum employed the constraint that the angle between planes (1,2,3) and (1,4,3) remains unchanged.

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(12) Based on $B_6H_6^{2-}$ framework geometries, plus optimization of the nitrogen-atom position except in the 3- and 5-substituted DTP isomers.

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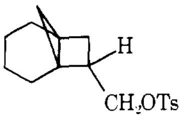
Conformationally Controlled Solvolysis. Ion Conformation as the Determining Factor in the Ring Expansion of Bicyclo[2.1.0]pentane Derivatives[1]

Sir:

Recently, we described the solvolytic behavior of the tosylates, **1** and **2**.[2] These epimeric compounds exhibited extremely diverse behavior on solvolysis in 90:10 v/v acetone-water buffered with 2,6-lutidine. Although product studies indicated that **1** and **2** gave dramatically different ions, the cause of this unique behavior was not established. In order to determine the mechanistic basis for our earlier observations, it was necessary to establish whether the tetramethylene bridges (and the associated tricyclic structures) of **1** and **2** were responsible for the presence of two divergent mechanistic paths or whether the observed behavior was a direct function of the stereochemical relationship between the cyclopropyl group and the carbinol moiety. In order to resolve this problem, we have prepared the tosylates **3** and **4**



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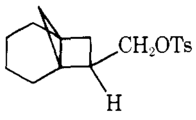

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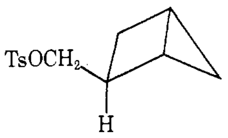

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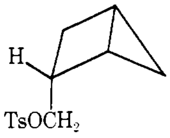

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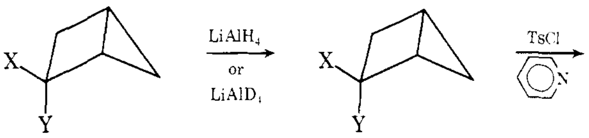
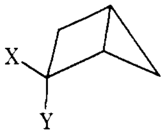
and studied their solvolyses. We now wish to report that our previously described results were not dependent on any interactions of the tetramethylene bridges of **1** and **2**. Furthermore, we wish to suggest that ion conformation is the determining factor in the diverse mechanistic paths followed by **3** and **4** (and through analogy by **1** and **2**).

Lithium aluminum hydride reduction of the known[3] esters **5** and **6** gave the carbinols **7** and **8**, while reduction with lithium aluminum deuteride gave the labeled carbinols **9** and **10** (>99% d_2 as determined by NMR spectroscopy). Treatment of **7**, **8**, **9**, and **10** with *p*-toluenesulfonyl chloride in pyridine gave the corresponding esters **3**, **4**, **11**, and **12**,



5, X = CO_2CH_3; Y = H
6, X = H; Y = CO_2CH_3

7, X = CH_2OH; Y = H
8, X = H; Y = CH_2OH
9, X = CD_2OH; Y = H
10, X = H; Y = CD_2OH

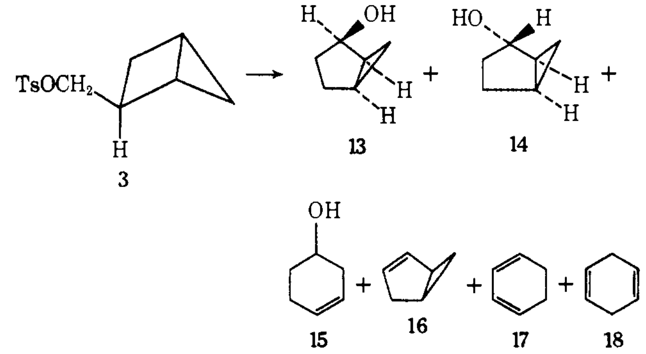


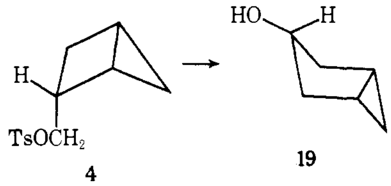
3, X = CH_2OTs; Y = H
4, X = H; Y = CH_2OTs
11, X = CD_2OTs; Y = H
12, X = H; Y = CD_2OTs

respectively. Solvolysis of **3** and **4** in 90:10 v/v acetone-water buffered with 2,6-lutidine gave excellent pseudo-first-order kinetics. However, little difference in the rates of ionization was observed: $k_3 = 3.17 \times 10^{-7}$ (25°) and $k_4 = 1.92 \times 10^{-7}$ (25°).

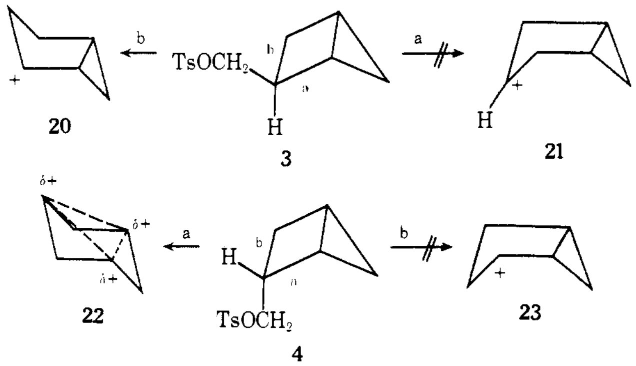
While kinetic studies failed to indicate any major differences between **3** and **4**, product studies established that **3** and **4** ionized to produce species which were very different. The solvolysis of **3** gave a mixture of **13** (5%), **14** (13%), **15** (55%), **16** (4%), **17** (7%), and **18** (7%).[4] In stark contrast to the complex mixture of products obtained from **3**, **4** gave **19** as the only product in 91% yield.

The very diverse nature of the products obtained from **3** and **4** indicated the formation of two distinct ions. Mechanistically, it appeared that **3** ionized with accompanying migration of the C_2–C_3 bond (b) to give the cyclopropyl carbinyl cation **20**. Shifting of the C_1–C_2 bond (a) of **3** would give the boat conformer **21**, in which the cyclopropyl ring

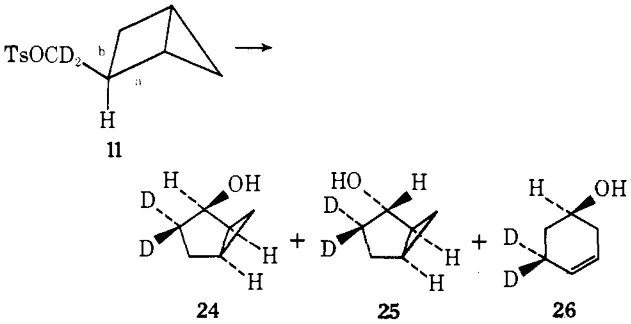




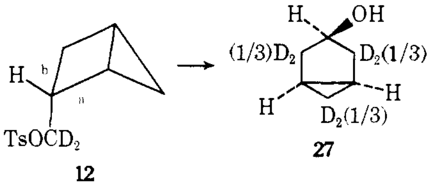
would not be able to lend any stabilizing influence to the incipient cation. The products obtained from **3** were similar to those obtained when the ion **20** was generated from other sources.[5] The isolation of only **19** from **4** was consistent with exclusive migration of the C_1-C_2 bond (a) to yield the trishomocyclopropenyl cation **22**. Migration of the C_2-C_3 bond (b) would produce the cyclopropyl carbinyl cation **23**, which should have significant nonbonded interactions of the C_3 and C_6 protons. The stereochemically clean formation of the syn alcohol from **4** was consistent with what would be expected from **22** based on the previous literature.[6]



Although the mechanistic picture presented above is plausible, it is not unequivocal. For instance, one could argue that the "a" bond was migrating in the rearrangement of both **3** and **4**, but that the ion **21**, derived from **3**, underwent a hydride shift and ring flip to produce **20**. In order to more rigorously define the total mechanistic scheme, the labeled *p*-toluenesulfonates, **11** and **12**, were solvolyzed. Under the solvolytic conditions **11** gave the alcohols **24**, **25**, and **26** with the deuterium labels as shown,[7] in addition to the three olefinic products. Since migration of bond "a" of **11** followed by deuteride shift and ring flip would have placed a deuterium α to the hydroxyl function, the presence of a proton at C_2 of **24** and **25** ruled out such a process.



Similar solvolysis of **12** gave **27** with the deuterium label equally distributed between the 2-, 4-, and 6-positions of **27**. No deuterium was found at the 1-, 3-, or 5-positions of **27** within the limits of analysis by NMR spectroscopy. This observation was consistent with the intermediacy of a trishomocyclopropenyl cation. The formation of **27** could only be reconciled with the initial migration (100 ± 5%) of bond "a" with the complete exclusion of any shifting of bond "b" in the ionization of **12**.



In summary, the solvolyses of **3** and **4** represent a special case of "conformationally controlled" solvolysis. Both **3** and **4** could have yielded a cyclopropyl carbinyl cation by migration of bond "b." However, only the ionization of **3** followed this path. Exclusive migration of bond "a" was the chosen path for the rearrangement of **4**. This indicates to us that the transition state leading to ion **22** was of considerably lower energy than that leading to ion **23**.[8] Similarly, it would appear that the transition state leading to ion **20** was far more accessible than that leading to **21**. We suggest that this difference in transition state energies reflects the relative stabilizing effects of neighboring group participation. This neighboring group participation should be a function of the conformation of the developing ion. Thus, it appears that ion conformation can be a critical factor in the solvolysis of compounds such as **3** and **4**. These observations indicate that the products derived from the solvolyses of **1** and **2** also were determined by ion conformation.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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(7) The labeling pattern was established on the basis of analysis by NMR spectroscopy. The details of this analysis will be presented in a full paper. Careful examination of the spectral data showed that **24** had 97 ± 5% of deuterium at the 3-position.

(8) Although the bicyclo[3.1.0]hexane skeleton is thought to prefer the boat conformation, little is known about the preferred conformations of the various cations derived from this system.

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