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Rearrangements of Spiropentyl Cation

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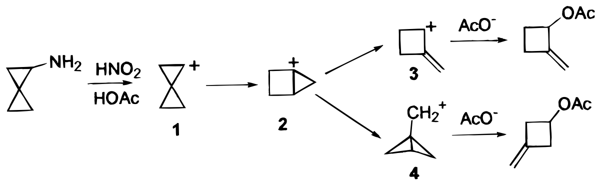
The structures of spiropentyl cation and its rearrangement products have been studied via ab initio geometry optimization at the MP2/6-31G* and B3LYP/6-311G* theoretical levels with additional calculations at the MP4/6-311G* level. The cation was calculated to be a transition state and underwent a cyclopropylcarbinyl to cyclobutyl cation rearrangement. This led to the products observed in the nitrous acid deamination of spiropentylamine. A closely related transition state, with the second cyclopropyl ring rotated 20° from the normal C_s geometry, was located. It led to a cyclopropyl cation type ring opening to an allyl cation, which formed the products observed in the solvolysis of spiropentyl chloride. The two transition states have essentially the same energy.

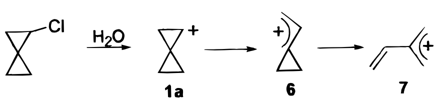
Introduction

The spiropentyl cation is an unusual species in that it is both a cyclopropylcarbinyl cation and a cyclopropyl cation. The first type of ion is relative stable and often leads to rearrangements giving cyclobutyl cations or different cyclopropylcarbinyl cations.[1] The second type of ion has a relatively high energy and leads to bond cleavage with the formation of an allyl cation.[2]

The reaction of spiropentylamine with nitrous acid in acetic acid has been reported to give 2-methylenecyclobutyl acetate and 3-methylenecyclobutyl acetate along with spiropentyl acetate in a 1:5:5 ratio.[3] These are the products that would be expected from a spiropentyl cation that behaved as a cyclopropylcarbinyl cation. Thus, initial rearrangement to bicyclo[2.1.0]pentyl-1 cation could be followed by conversion to 2-methylenecyclobutyl cation and bicyclo[1.1.0]butyl-1-carbinyl cation.[4] The latter is known to give 3-methylenecyclobutyl products.[5]



On the other hand, spiropentyl chloride undergoes solvolysis only slowly, as might be expected from a cyclopropyl halide.[6] The product is that expected from a cyclopropyl cation is a 2-vinylallyl alcohol. Why should the "spiropentyl cation" behave differently under these two conditions for its formation? To gain information on this question, we have carried out ab initio calculations for the ions **1**−**7** and for the transition states that connect them.



Calculations

Initial geometry optimizations were carried out at the MP2/6-31G* level, and MP4/6-311G* energies were obtained using these geometries. All electrons were included in the MP2 calculations, and the frozen core option was used for the MP4 calculations. In addition, B3LYP/6-311G* optimizations were carried out. The use of different theoretical treatments that include the effects of electron correlation should indicate whether there are problems with calculations for these compounds. The B3LYP[7] calculations also have the advantage that this theoretical level may be used for reaction field calculations of solvent effects on the energies and structures of the ions and transition states. The transition states were located by finding an approximate geometry, calculating the vibrational frequencies, and optimizing to a transition state. With both the MP2 and B3LYP calculations, the species were identified as minima or transition states by calculating the vibrational frequencies. IRC calculations[8] were carried out for the transition states to ensure that they connected the correct pair of minima.

Because the reactions are carried out in solution, it seemed important to examine the possible changes in structures and energies on going from the gas phase to solution. This was done using the SCIPCM reaction field model,[9] in which the solute is placed in a cavity in the solvent, which is taken as a dielectric continuum. The cavity is taken as the volume bounded by the 0.0004 e/au^3 electron density surface of the solute. It has been found to give good agreement with experimental molar volumes.

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10.1021/jo990655m CCC: $18.00

Table 1. Calculated Energies

						B3LYP/6-311G*			
cation	ZPE[a]	MP2/ 6-31G*[b]	ΔH_{rel}	MP4/6-311G*[c]	ΔH_{rel}	$\epsilon = 1$	ΔH_{rel}	$\epsilon = 80$	ΔH_{rel}
spiropentyl (**1**)	62.50	−193.67131	0.0	−193.77982	0.0	−194.36778	0.0	−194.45882	0.0
bicyclo[2.1.0]pentyl-1 (**2**)	63.66	−193.68637	−8.3	−193.79339	−7.4	−194.37490	−3.4	−194.46689	−4.0
TS23	62.94	−193.68278	−6.8	−193.79211	−7.3	−194.37444	−3.8	−194.46587	−4.0
2-methylenecyclobutyl(**3**)	61.77	−193.71269	−26.7	−193.82530	−29.2	−194.41727	−31.8	−194.50774	−31.4
TS24	63.26	−193.68545	−8.1	−193.79310	−7.6	−194.37446	−3.7	−194.46588	−3.7
bicyclo[1.1.0]butyl-1-carbinyl (**4**)	63.25	−193.71307	−25.5	−193.82195	−25.7	−194.40622	−23.4	−194.49703	−23.3
TS45	60.87	−193.67733	−5.3	−193.79221	−9.3	−194.38316	−11.2	−194.47898	−14.2
3-methylenecyclobutyl (**5**)	60.11	−193.67901	−7.1	−193.79424	−11.3	−194.38830	−15.2	−194.48347	−17.8
twist-spiropentyl (**1a**)	62.27	−193.67192	−0.6	−193.78014	−0.4	−194.36762	−0.1	−194.45837	0.1
1-vinylcyclopropyl (**6**)	62.40	−193.70543	−21.5	−193.81617	−22.9	−194.41042	−26.9	−194.49984	−25.8
TS67	62.20	−193.70447	−21.1	−193.81536	−23.6	−194.40867	−25.9	−194.49761	−24.6
2-vinylallyl (**7**)	62.30	−193.70690	−22.5	−193.82148	−26.3	−194.41343	−28.8	−194.50672	−30.2

[a] MP2/6-31G* scaled by 0.96. The ΔH_{rel} values include the differences in ZPE. [b] All electrons were included. [c] MP4(SDTQ) using the frozen core option and the MP2/6-31G* geometries.

Table 2. Structural Data

			B3LYP		bond
cation	bond	MP2	$\epsilon = 1$	$\epsilon = 80$	index
spiropentyl cation (**1**) C_s	C1−C2	1.483	1.480	1.480	1.041
	C1−C3	1.330	1.337	1.336	1.512
	C2−C3	1.511	1.516	1.512	0.957
	C3−C4	1.593	1.592	1.583	0.772
	C4−C5	1.434	1.442	1.444	1.100
cyclopropylcarbinyl	C1−C2	1.356	1.353	1.353	1.591
	C2−C3	1.646	1.663	1.655	0.714
	C3−C4	1.415	1.416	1.416	0.919
cyclopropyl	C1−C2	1.425	1.423	1.423	1.173
	C2−C3	1.532	1.535	1.533	0.955
bicyclo[2.1.0]pentyl (**2**)	C1−C2	1.534	1.550	1.540	0.914
	C1−C3	1.424	1.438	1.437	1.070
	C1−C4	1.543	1.524	1.507	0.968
	C2−C3	1.469	1.460	1.462	1.041
	C3−C4	1.720	1.793	1.765	0.407
	C3−C5	1.395	1.391	1.377	1.279
	C4−C5	1.760	1.830	1.899	0.638
TS23	C1−C2	1.641	1.602	1.608	0.843
	C1−C3	1.429	1.434	1.439	1.129
	C1−C4	1.519	1.530	1.528	0.977
	C2−C3	1.416	1.431	1.427	1.116
	C3−C4	1.896	1.881	1.886	0.302
	C3−C5	1.427	1.420	1.421	1.186
	C4−C5	1.668	1.709	1.698	0.754
2-methylenecyclobutyl (**3**)	C1−C2	2.499	2.503	2.497	0.262
	C1−C3	1.402	1.408	1.405	1.317
	C1−C4	1.479	1.478	1.478	1.092
	C2−C3	1.370	1.363	1.361	1.530
	C3−C5	1.523	1.531	1.528	0.985
	C4−C5	1.560	1.567	1.566	0.968
TS24	C1−C2	1.531	1.602	1.608	0.843
	C1−C3	1.450	1.434	1.431	1.128
	C1−C4	1.484	1.530	1.528	0.977
	C2−C3	1.467	1.431	1.427	1.116
	C3−C4	1.739	1.881	1.886	0.302
	C3−C5	1.372	1.400	1.421	1.187
	C4−C5	2.004	1.710	1.698	0.753
bicyclobutyl-1-carbinyl (**4**)	C1−C2	1.464	1.462	1.462	1.069
	C1−C3	1.621	1.644	1.641	0.561
	C2−C3	1.536	1.551	1.547	0.904
	C3−C5	1.358	1.349	1.347	1.617
3-methylenecyclobutyl (**5**)	C1−C2	1.456	1.462	1.460	1.138
	C2−C3	1.525	1.528	1.528	0.990
	C3−C5	1.327	1.321	1.320	1.822
twist-spiropentyl (**1a**) (C_1)	C1−C2	1.441	1.440	1.438	1.135
	C1−C3	1.338	1.339	1.339	1.519
	C2−C3	1.599	1.599	1.597	0.831
	C3−C4	1.580	1.590	1.577	0.862
	C3−C5	1.532	1.537	1.529	0.796
	C4−C5	1.451	1.455	1.459	1.067
vinylcyclopropyl (**6**)	C1−C2	1.371	1.366	1.366	1.558
	C1−C3	1.387	1.391	1.387	1.336
	C2−C3	2.357	2.378	2.368	0.264
	C3−C4	1.451	1.451	1.449	1.081
	C3−C5	1.442	1.442	1.441	1.097
	C4−C5	1.533	1.535	1.535	0.960
TS67	C1−C2	1.364	1.355	1.354	1.628
	C1−C3	1.399	1.411	1.408	1.246
	C3−C4	1.427	1.412	1.413	1.241
	C3−C5	1.419	1.406	1.407	1.252
	C4−C5	1.623	1.729	1.699	0.713
2-vinylallyl (**7**)	C1−C2	1.341	1.334	1.333	1.799
	C1−C3	1.465	1.470	1.475	1.080
	C3−C4	1.393	1.393	1.389	1.392
	C3−C5	1.391	1.392	1.388	1.398
	C4−C5	2.297	2.317	2.327	0.371

The effective charges at the surface are calculated, along with their interaction with the solvent, to give the free energy of solvation.

The calculated energies are summarized in Table 1. The zero-point energies were calculated at the MP2/6-31G* level and scaled by 0.96,[10] and the relative ΔH values include the effect of the zero-point energies. The structures of the compounds are summarized in Table 2. Because the bond lengths varied over a wide range suggesting a range of bond orders, the Fulton sharing indices[11] also were calculated and are recorded in Table 2. Unlike the Mulliken and similar bond orders, the sharing indices are obtained directly from the electron density distribution. The relationship between the sharing indices and the calculated bond lengths is shown in Figure 1. Despite the wide range of bond lengths, there is generally good agreement between the two quantities. One would not expect a perfect correlation because the bond length is in part determined by factors other than the sharing indices. These factors include distortions caused by intramolecular interactions such as steric effects, and the polarization of a bond that can lead to the shortening of a bond without increasing the sharing index.

The atomic charges were calculated using the AIM procedure.[12] As we have noted previously,[13] most of the

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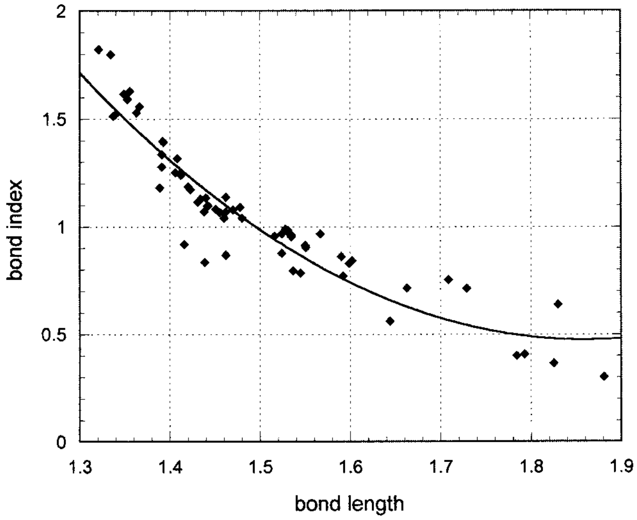


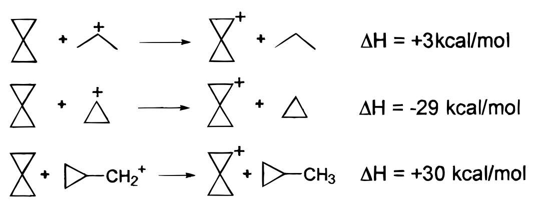
Figure 1. Relationship between the sharing indices and the bond lengths.

charge in the cations is located at the hydrogens. The full population analysis is available as Supporting Information, and the group charges are recorded in Table 3.

Spiropentyl Cation. Cyclopropylcarbinyl Cation Rearrangements

The spiropentyl cation was calculated to be a transition state at all theoretical levels including the effect of a polar solvent (i.e., one imaginary frequency). The structure is typical of a cyclopropylcarbinyl cation (Figure 2), with a short bond from the cationic center to the second three-membered ring and long C—C bonds adjacent to the first ring. Correspondingly, the C1—C3 sharing index is quite large (1.512). As a comparison, the index for the C—C bonds in benzene are 1.390, and for the C=C bond of ethylene it is 1.905.

To gain some information on the possible stabilization of this ion, the following isodesmic reactions were examined at the MP2/6-31G* level:



It can be seen that spiropentyl cation is only slightly less stable than a typical secondary cation, but it is considerably more stable than a cyclopropyl cation. On the other hand, it is considerably less stable than a cyclopropylcarbinyl cation.

The first product formed from **1** was located via the intrinsic reaction coordinate following method,[8] and it was the bicyclo[2.1.0]pentyl-1 cation (**2**). It had a considerably distorted structure in which the outside cyclobutyl C—C bond was quite long (1.76 Å) and one of the C—C bonds to the cationic center was quite short (1.39 Å). The long C_4—C_5 bond has a relatively low bond index (0.638), and there is a significant C_3—C_5 bond index (0.407).

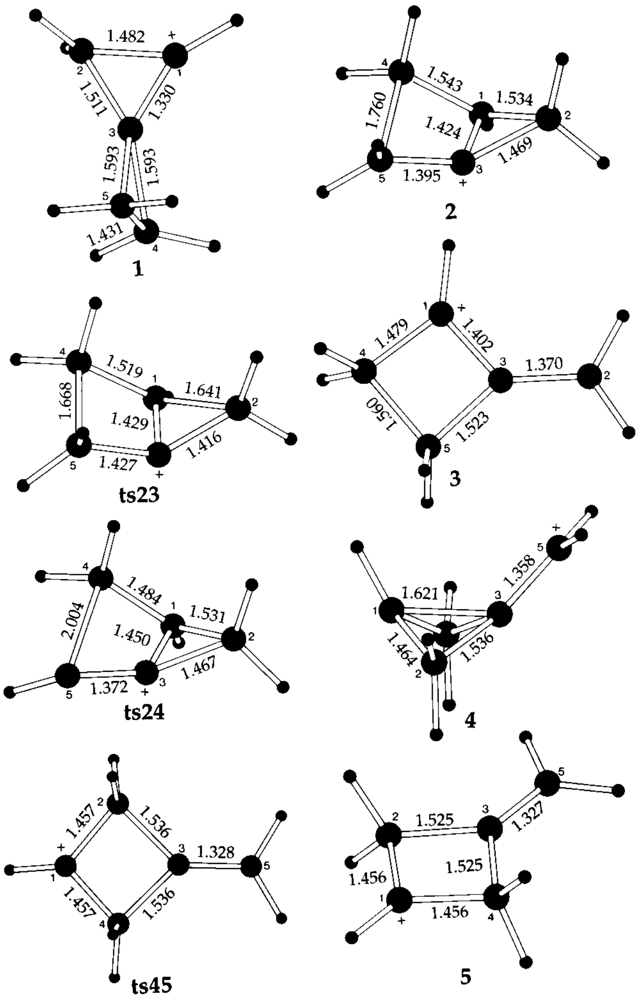


Figure 2. Structure of the *Cs* symmetric spiropentyl cation (**1**) and the ions derived from it. The structures to the left are transition states, and those at the right are minima on the potential energy surface.

Table 3. Group Charges

compound	C1H	$C2H_2$	C3	$C4H_2$	$C5H_2$
spiropentyl (**1**)	0.184	0.302	−0.083	0.300	0.300
bicyclo[2.1.0]pentyl (**2**)	0.140	0.295	−0.040	0.298	0.310
TS23	0.128	0.308	−0.002	0.288	0.279
2-methylenecyclobutyl (**3**)	0.181	0.335	0.043	0.246	0.196
TS24	0.129	0.308	−0.002	0.288	0.277
bicyclo[1.1.0]butyl (**4**)	0.201	0.264	−0.078	0.263	0.353
TS45	0.263	0.268	−0.049	0.268	0.251
3-methylenecyclobutyl (**5**)	0.232	0.285	−0.031	0.285	0.229
twist-spiropentyl (**1a**)	0.184	0.302	−0.083	0.300	0.300
vinylcyclopropyl (**6**)	0.214	0.336	−0.073	0.252	0.271
TS67	0.169	0.287	−0.037	0.283	0.293
vinylallyl (**7**)	0.066	0.176	0.060	0.351	0.349

Two transition states for the further reaction of **2** were located. The first (**TS23**) led to 2-methylenecyclobutyl cation (**3**) which is stabilized as an allyl cation. In the transition state, the long C—C bond in **2** becomes shorter, and the C—C bond from the cationic center in the three-membered ring becomes longer. These geometrical changes continue to form **3**, which is planar and has short C—C bonds for the allyl system. It is interesting that the C_2—C_3 bond is shorter and has a larger sharing index than the C_1—C_3 bond.

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The second (**TS24**) led to the bicyclo[1.1.0]butyl-1-carbinyl cation (**4**). In **TS24**, the C4−C5 bond has lengthened from 1.76 Å in **2** to 2.00 Å, and the sharing index has decreased to 0.37. This bond continues to lengthen as **TS24** moves toward **4**, in which it is completely broken.

The structure of **4** is again that of a typical cyclopropylcarbinyl cation, with a short bond length to the cationic center and long bond lengths in the ring adjacent to the cationic center. The 2-methylenecyclobutyl ion (**3**) is more stable than **4**, but the activation energy for the formation of **4** is smaller than that for **3** (Table 1). This fits well with the experimental observation that **3** and **4** are formed in a 1:5 ratio in the deamination of spiropentylamine. It is interesting to note that whereas **2** has a significantly lower total energy than **TS23** and **TS24**, the correction for the differences in zero-point energies makes all of them have similar energies.

The product derived from **4** is 3-methylenecyclobutyl acetate. As we have previously noted,[5] this product is probably not formed from a 3-methylenecyclobutyl cation (**5**) because this ion has a relatively high energy. A nucleophilic attack at C1 of **4** could lead to this type of product directly.

The calculations are in good accord with the results of the deamination reaction of spiropentylamine, provided that the spiropentyl acetate formed in the reaction is derived by direct nucleophilic attack by acetate ion on the spiropentyl diazonium ion before loss of nitrogen. Thus, the deamination should lead to the acetate having an inverted configuration. This has been tested experimentally and the reaction is found to give complete inversion of configuration.[14]

Cyclopropyl Cation Rearrangement

If the spiropentyl cation leads to ions **2**−**4**, how is the vinylallyl product formed in the solvolysis of spiropentyl chloride? It is presumably formed via a vinylcyclopropyl cation intermediate (**6**), which rearranges to the vinylallyl cation (**7**). The structures of these ions and of the transition state that connects them (**TS67**) were examined, giving the data in Tables 1−3. Then, a set of vinylcyclopropyl cations that were constrained to move toward the structure of a spiropentyl cation were studied, and a transition state (**1a**) was found. It had a structure and energy close to those of **1** (Figure 3), except that the two three-membered rings were twisted by 20° from the C_s structure. An IRC study showed that it was the transition state for the formation of **6**.

Solvent Effects

The effect of the solvent on the structures and energies of ions **1**−**7** was studied using the SCIPCM reaction field model with a dielectric constant of 80. In this model, any dielectric constant greater than ∼30 will give essentially the same result.[15] Although the energies of the ions decreased significantly, the relative energies were essentially unchanged, and except for the rather long and weak bonds, the structural changes were relatively small. This agrees with the general observation that the relative energies of carbocations are essentially phase-independent.[16]

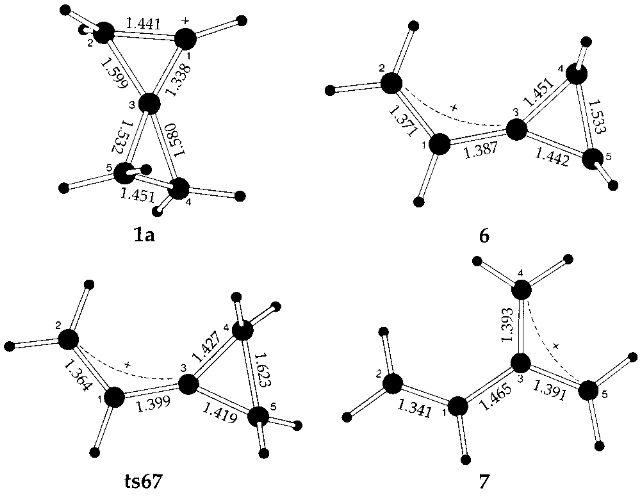
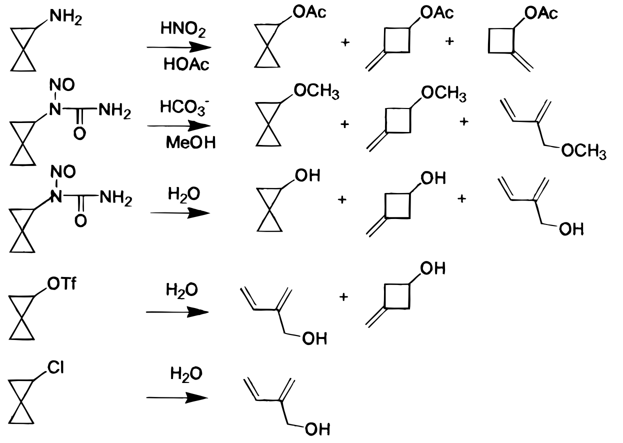


Figure 3. Structure of the *C*1 spiropentyl cation (**1a**) and the ions derived from it. The structures to the left are transition states, and those at the right are minima on the potential energy surface.

Discussion

Spiropentyl derivatives may undergo ionization via either one of two closely related transition states that lead to two different sets of products. The mode of reaction depends on the process; for example:[3,6,17,18]



As the leaving group becomes less effective, the course of the reaction changes from reaction via transition state **1** to reaction via **1a**. A plausible hypothesis is that as the leaving group becomes less effective and the reaction

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[15] The effect of the solvent is given by $(\epsilon - 1)/(2\epsilon + 2)$, It has the value 0.48 for $\epsilon = 30$ and 0.50 for an infinitely large value of ϵ.

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proceeds further toward products in the transition state, backside solvation becomes more important, leading to an unsymmetrical species such as **1a**.

Calculations. The ab initio calculations were carried out using Gaussian-95.[19] The AIM charges and the Fulton sharing indices were calculated using AIMALL.[20]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation.

Supporting Information Available: A table of AIM calculated charges for all of the ions and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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