Formation and Reactions of Bicyclo[1.1.1]pentyl-1 Cations

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Abstract: The ionization of 1-bicyclo[1.1.1]pentyl halides was shown to initially form the 1,3-bridged bicyclo[1.1.1]pentyl-1 cation. It appears to be a transition state that leads to the bicyclo[1.1.0]butyl-1-carbinyl cation which can be trapped with azide ion and can be directly observed by NMR in SO_2ClF. Although the major products of solvolysis of the halides are 3-methylenecyclobutyl derivatives, the corresponding cation was calculated to have a significantly higher energy than the bicyclobutylcarbinyl ion. Therefore, the products are probably formed by an attack of the nucleophile on the latter ion, accompanied by bond migration. The bridgehead iodide reacts under solvolytic conditions with azide ion to form bicyclo[1.1.0]butyl-1 azide as a product. It also reacts with potassium hydroxide to give [1.1.1]propellane, and the same reaction occurs on dissolving in acetonitrile or pyridine. The reaction of 1,3-diiodobicyclo[1.1.1]pentane with ethoxide ion also was found to give [1.1.1]propellane via a nucleophilic attack on one of the iodines. The propellane reacts with methyl hypoiodite to give 3-iodobicyclo[1.1.1]pentyl-1 cation, which can react with methanol to give 3-methoxybicyclo[1.1.1]pentyl-1 iodide and with azide ion to give 3-iodobicyclo[1.1.1]pentyl-1 azide. These data provide evidence for a discrete 3-iodobicyclo[1.1.1]pentyl-1 cation intermediate. The effect of substituents on the rate of solvolysis of bicyclo[1.1.1]pentyl-1 iodide was studied. With 3-aryl substituents, a value of $\varrho = -1.7$ was found, which is similar to that observed in the solvolysis of 3-arylcyclobutyl tosylates ($\varrho = -1.6$). The 3-substituted bicyclopentyl halides usually form the corresponding 3-methylenecyclobutyl cations rather than bicyclo[1.1.0]butyl-1-carbinyl ions, because most substituents will help stabilize the former type of ion.

1. Introduction

Bicyclo[1.1.1]pentane is unique among bicycloalkanes in having an exceptionally short C_1-C_3 nonbonded distance (1.87 Å).[1] This leads to a remarkably strong cross-ring interaction, as is seen in the 18 Hz NMR coupling constant between the bridgehead protons,[2] and other large long-range couplings across the bridgehead positions, such as 71 Hz for H••F,[3] 30−60 for H••P,[4,5] and 156−180 for H••Sn.[4] The bridgehead radical also has an unusually large hyperfine coupling constant.[6]

The short nonbonded distance should lead to a strong C_1-C_3 interaction in the bridgehead cation, similar to that found both theoretically[7] and experimentally[8] for the cyclobutyl cation. This leads to the relatively high solvolytic reactivity of cyclobutyl derivatives. The interaction should be even stronger in the bicyclopentane system because of the shorter nonbonded distance. In accord with this expectation, 1-halobicyclo[1.1.1]pentanes have been found to have a higher solvolytic reactivity than the corresponding *tert*-butyl derivatives,[9] despite the common observation that bridgehead halides are unreactive.[10]

In order to learn more about the interaction between the bridgehead carbons, we have carried out a detailed experimental and theoretical study of 1-bicyclo[1.1.1]pentyl cation (**1**) and its reactions. This report complements a recent study of 3-substituted bicyclo[1.1.1]pentyl-1 bromides by Della et al.,[11] and the relationship between the two studies will be discussed.

2. Theoretical Calculations

Theoretical calculations for the cyclobutyl cation at the MP2/6-31G* level have provided structural and energetic information[7] that has been confirmed by experimental results.[8] Therefore, this level of theory appeared reasonable for a study of the bicyclo[1.1.1]pentyl-1 cation and related bicyclo[1.1.1]pentanes. Most of the previous calculations for the ion and for substituted bicyclo[1.1.1]pentanes were carried out at the HF level.[12]

The results of the calculations are given in Table 1. We have reported some MP2/6-31G* results for the unsubstituted bicyclo[1.1.1]pentyl cation and found the cross-ring distance to be only 1.54 Å,[13] much smaller than that for the parent hydrocarbon (1.87 Å). The calculations also found the cation to be more stable with respect to bicyclo[1.1.1]pentane than is *tert*-butyl cation as compared to isobutane. This is in good accord with the observation that 1-chlorobicyclopentane[9a] and 1-bromobicyclopentane[9b] are more reactive in solvolysis than the cor-

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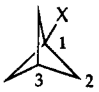
Table 1. Calculated (MP2/6-31G*) Energies and Geometries[a]



1-Substituted Bicyclo[1.1.1]pentanes[b]

X	energy (*H*)	r_{12}	r_{23}	r_{13}	ZPE
F	−293.612 86	1.535	1.550	1.826	66.2
Cl	−653.634 38	1.537	1.549	1.836	65.3
H	−194.582 33	1.547	1.547	1.872	70.7
Me	−233.762 12	1.552	1.545	1.878	87.2
SiH_3	−484.752 24	1.562	1.543	1.890	79.6
HO[c]	−269.622 07	1.535, 1.551	1.548, 1.546	1.849	73.3
H_2N[c]	−249.779 78	1.564, 1.544	1.543, 1.546	1.867	81.0
H_2P[c]	−535.994 34	1.533, 1.554	1.544, 1.545	1.876	75.6
F_3C[c]	−530.858 54	1.542	1.547	1.857	74.3

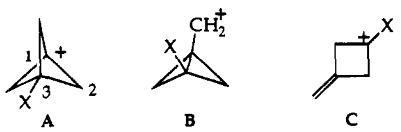
3-Substituted Bicyclo[1.1.1]pentyl-1 Cations

X	energy (*H*)	r_{23}	r_{12}	r_{13}	ν_L[f]	ZPE	product[g]
F	−292.661 82	1.607	1.467	1.550	331*i*	57.5	C
Cl	−652.711 25	1.603	1.465	1.543	113*i*	56.9	C
H	−193.702 07	1.592	1.467	1.526	110*i*[a]	61.6	B
Me	−232.885 81	1.597	1.463	1.539	113	79.6	A
SiH_3	−483.904 48	1.586	1.470	1.537	131	72.6	A
HO[d]	−268.702 21	1.500, 1.710 1.720	1.543, 1.425 1.426	1.558	491*i*	64.7	C
H_2N[e]	−248.879 25	1.645, 1.602	1.454, 1.462	1.546	417*i*	72.7	C
H_2P[e]	−535.126 78	1.571, 1.600	1.476, 1.464	1.541	134	68.3	A
F_3C	−529.951 68	1.589		1.530	66	66.3	A

Other Compounds

compound	MP2/6-31G*	ZPE	MP4/6-31G*	E_{rel}[h]
bicyclo[1.1.1]pentyl-1 (**1**)	−193.702 07	61.6	−193.743 80	0.0
bicyclo[1.1.0]butyl-1-carbinyl cation (**2**)	−193.713 07	62.0	−193.758 55	−9.7
TS (**2** → **3**)	−193.677 33	60.5	−193.727 97	8.9
3-methylenecyclobutyl cation (**3**)	−193.679 01	60.0	−193.730 27	6.9
1-chloro-3-methylene-cyclobutyl-1 cation	−652.743 23			

[a] Distances (*r*) are given in Å. The zero-point energies (ZPEs) were derived from HF/6-31G* calculations and were scaled by 0.893. The MP2 calculations correlated all electrons. [b] When two distances are given, the first is the unique value and the second is for the pair of C−C bonds. [c] The X−H bonds were staggered with respect to the C−C bonds. [d] The hydroxy-substituted cation was a transition state with no symmetry. [e] The NH_2- and PH_2-substituted cations were transition states with C_s symmetry. [f] Lowest calculated vibrational frequencies other than group rotations at the HF/6-31G* level. The corresponding MP2/6-31G* frequencies were X = H, 263*i*; X = Cl, 256*i*. [g] The products are as shown below:



[h] The relative energies include the difference in zero-point energies.

responding *tert*-butyl halides. The structure of the ion resembled that for [1.1.1]propellane,[13] and the ion appeared best described as having a proton attached to the nonbonded charge distribution[14] at one of the bridgehead carbons of the propellane.

A calculation of the vibrational frequencies for **1** at the MP2/6-31G* level found one degenerate imaginary frequency, indicating it to be a transition state. The imaginary mode was followed down to the first intermediate, which was found to be the bicyclo[1.1.0]butyl-1-carbinyl cation (**2**). This has also been found to be the case at the HF/6-31G* theoretical level.[15] The ion derives its stability from cyclopropylcarbinyl cation-type interactions. The energy of 3-methylenecyclobutyl cation (**3**), from which the product **4** appears to be derived, also was calculated, and at the MP2 level it was found to have an energy somewhat higher than that for **1** and considerably higher than that for **2** (Table 1). The HF calculation had led to the reverse order of energies.[15] The transition state for the conversion of **2** to **3** was located at the MP2/6-31G* level. Since the ions **1**, **2**, and **3** and the transition state are structurally quite different, the energies also were calculated at a somewhat higher theoretical level, MP4/6-31G*. The relative MP4 energies are summarized in Figure 1.

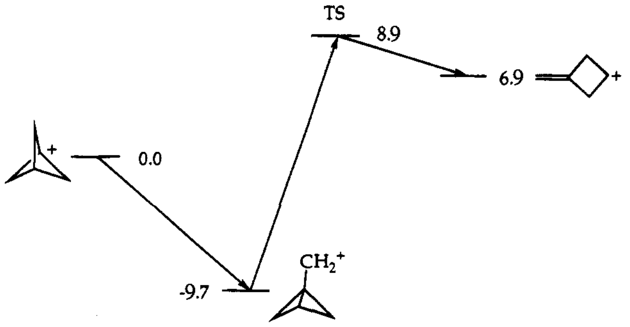
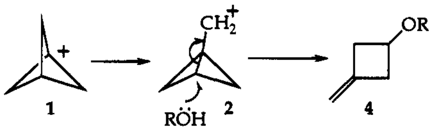


Figure 1. Relative energies of $C_5H_7^+$ ions (MP4/6-31G*), in kcal/mol.

The results of the calculations strongly suggests that the products are in fact derived from **2** via attack at C_3. This would



not be unreasonable in view of the high strain energy of the bicyclo[1.1.0]butane ring system (64 kcal/mol[16]) and the lower strain energy of the 3-methylenecyclobutane ring system (47 kcal/mol including the double bond). Relatively selective nucleophiles might then be expected to react so as to form the more stable product. This appears to be a fairly unique case, in which one structure is strongly favored as a carbocation and the other is strongly favored as the product.

A study of the charge distribution in **1** showed a large degree of charge transfer from C_3 and its hydrogen to C_1.[13] This suggested that large effects on solvolysis rates might be found when substituents are attached to C_3. In addition, substituents can affect the course of the reactions by stabilizing one of the ions that might be formed in the reaction. Therefore, a set of 3-substituted bicyclo[1.1.1]pentanes and their corresponding 1-cations were studied theoretically, giving the results shown in Table 1.

Substituents have a significant effect on the 1,3-nonbonded distance in the bicyclo[1.1.1]pentanes, and the distance is related to the electronegativity of the substituents (Figure 2). The first and second row substituents fall on different lines. The data suggest that the main effect of electronegative substituents is to decrease the charge density in the backside of the bridgehead carbon orbital, leading to a reduction in the nonbonded repulsion between the bridgehead carbons.[17] Evidence for this view is found in the observation that, despite the change in nonbonded

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(14) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

(15) Della, E. W.; Schiesser, C. H. *J. Chem. Res.* **1989**, 172.

(16) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

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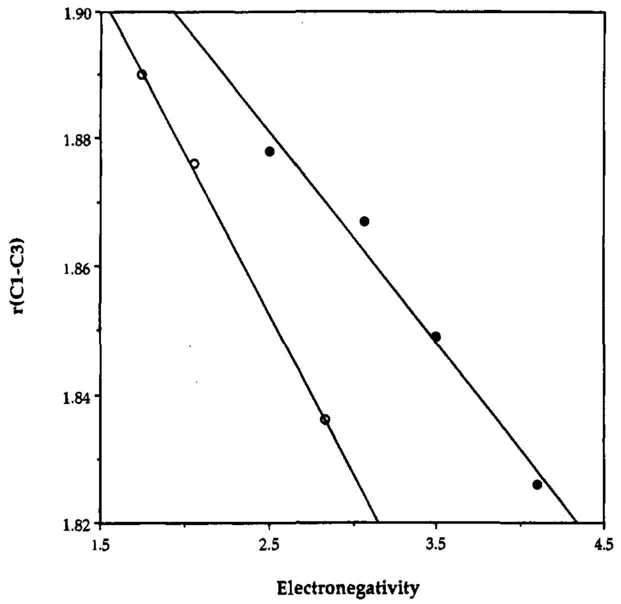
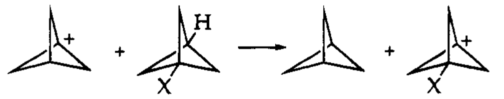


Figure 2. Relationship between the 1−3 nonbonded distance and electronegativity for 1-substituted bicyclo[1.1.1]pentanes (Table 1). The solid circles are for the first row substituents, and the open circles are for the second row substituents.

Table 2. Energies of Hydride Transfer Reactions (kcal/mol)

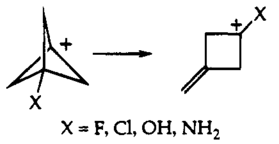


X	ΔE	X	ΔE
F	+44.8	H_2N	+13.5
Cl	+27.6	Me	−1.0
HO	+25.3	H_2P	−6.2
F_3C	+17.8	SiH_3	−18.3

distance, the charge density at the cage critical point[18] (the point of minimum charge density in all directions lying between the bridgehead carbons) is essentially constant.[19] Ordinarily, one would expect the charge density to increase with decreasing distance.

On going from the neutral compounds to the cations, r_{12} shortens somewhat, but r_{13} decreases by about 0.3 Å, reaching a value in the normal range for carbon−carbon single bonds. In contrast to the neutral precursors, in the cations r_{13} increases with increasing electronegativity of the substituents. The effect of the substituents might best be seen via the use of hydride transfer reactions, as shown in Table 2. It can be seen that electron-withdrawing substituents are expected to markedly retard ionization, whereas electron-releasing substituents should increase the solvolytic reactivity. Only the inductive effect of the substituents is important since the strong π donor, NH_2, is predicted to retard the reaction.

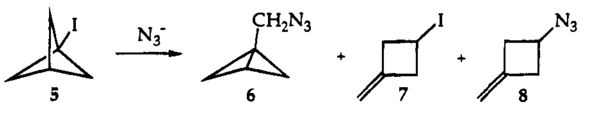
The vibrational frequencies of the substituted cations were calculated at the HF/6-31G* level, and the lowest calculated frequencies are listed in Table 1. With CH_3, SiH_3, CF_3, and PH_2 as the substituents, all of the frequencies were real, suggesting that these cations may have some lifetime before rearranging. The prediction for the SiH_3 substituent was checked at the MP2/6-31G* level, and again all of the calculated frequencies were real. In the other cases, the ion was calculated to be a transition state (an imaginary frequency), and in the case of the parent ion, this was confirmed at the MP2/6-31G* level. With F, Cl, OH, and NH_2 as substituents, following the imaginary mode down to the product led to 1-substituted 3-methylenecyclobutyl-1 cations. This ion is favored because the substituent is able to stabilize the positive charge, making use of one of its lone pairs.



In order to be sure that this conclusion is not an artifact of the use of the HF theoretical level, the energy of the 1-chloro-3-methylenecyclobutyl-1 cation was calculated at the MP2/6-31G* level (Table 1). There is a net change of 35 kcal/mol in the relative energies of the bicyclo[1.1.1]pentyl-1 and 3-methylenecyclobutyl-1 cations on chlorine substitution. Table 2 shows that 28 kcal/mol of the change is due to destabilization of the bicyclopentyl cation, and the remaining 7 kcal/mol represents stabilization of the methylenecyclobutyl cation.

3. Solvolytic and Related Studies for 1-Halobicyclo[1.1.1]-pentanes

The bicyclo[1.1.1]pentane derivatives were prepared as described in the Experimental Section. It is known that the solvolysis of the bridgehead halides gives only 3-methylenecyclobutyl products under ordinary conditions.[9] In order to see if evidence might be found for a bicyclobutylcarbinyl cation intermediate, reactions were carried out in the presence of azide ion, which is known to intercept most carbocations at every encounter and therefore is probably not very selective.[20] The reactions of bicyclopentyl iodide (**5**) were first carried out in a set of aprotic solvents: DMF, DMSO, methylene chloride, 1,2-dichloroethane, and nitrobenzene.[21] The iodide was used so that relatively mild conditions could be employed. The solvents contained sodium azide and 18-crown-6, and the reactions were carried out in the dark at room temperature. In each case, part of the products had distinctive NMR bands that were similar to those of bicyclo[1.1.0]butyl-1-carbinol,[22] suggesting that bicyclo[1.1.0]butyl-1-carbinyl azide (**6**) had been formed. The azide was independently prepared by the reaction of sodium azide with bicyclo[1.1.0]butyl-1-carbinyl 3,5-dinitrobenzoate, and it had the same NMR spectrum. The other major products were 3-methylenecyclobutyl iodide (**7**), which is probably formed by internal return from the initially formed ion pair, and 3-methylenecyclobutyl iodide (**8**).



When the reaction of the iodide **5** was carried out in acetonitrile or pyridine, the major product was [1.1.1]propellane. It is interesting that **5** reacts readily with mild bases to give the propellane. For example, the reaction with ethanolic KOH occurs in a few minutes at room temperature. 1-Bromobicyclo-

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[18] Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

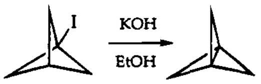
[19] The values for X = H, F, CF_3, NH_2, and PH_2 were 0.101±0.002 e/au³.

[20] Alonso, E. R.; Johnson, L. J.; Sciano, J. C.; Toscano, V. G. *J. Am. Chem. Soc.* **1990**, *112*, 1270.

[21] For a preliminary report, see: Wiberg, K. B.; McMurdie, N. D. *J. Org. Chem.* **1993**, *58*, 5603.

[22] Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.

[1.1.1]pentane has been reported to be converted to the propellane but required use of *tert*-butyllithium as the base.[23]



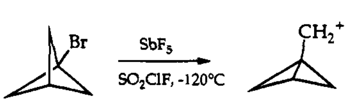
The reaction with pyridine was interesting in that an additional product was formed that had the characteristic ^{1}H NMR bands of bicyclo[1.1.0]butyl-1-carbinyl derivatives. The compound could also be formed by the reaction of [1.1.1]propellane with pyridinium iodide in pyridine and presumably corresponds to the azide **6**, with pyridine replacing the azide group.

There remained the question of whether the bicyclobutylcarbinyl ion was also involved in hydroxylic solvents. The solvolysis of **5** was carried out in ethanol in the presence of azide ion. In addition to the usual product, both **6** and **7** were found. Although the amount of **6** was small (5%), its formation clearly indicates that the bicyclo[1.1.0]butyl-1-carbinyl cation also is involved under these conditions.

Another way to study the reaction is via ^{13}C NMR spectroscopy. It is known that the calculated chemical shifts for carbocations are usually in good accord with the observed shifts,[24] and therefore it should prove possible to identify the ion formed in non-nucleophilic media. As a check on the calculations for the bicyclic systems, their NMR spectra were calculated via IGLO[25] using MP2/6-31G* geometries and basis sets I and II. The results are shown in Table 3 and are compared with the available experimental data. It can be seen that there is good agreement between the observed and calculated (basis set II) chemical shifts. It is interesting to note the large effect of a fluorine substituent on both C_1 and C_3. The calculated spectra for the 3-substituted bicyclo[1.1.1]pentyl-1 cations also are given in Table 3. The effect of substituents at the cationic center is quite remarkable, and the chemical shift decreases in the order of the substituent effects noted in Table 2. Large effects also are seen at C_3, where the shifts are often predicted to be upfield with respect to methane. This behavior has been noted for other bridged ions.[24]

The three ions that might possibly be observed are the bicyclo[1.1.1]pentyl cation (**1**), the 3-methylenecyclobutyl cation (**3**), and the bicyclo[1.1.0]butyl-1-carbinyl cation (**2**). Their spectra were calculated using the MP2/6-31G* geometries and basis set II, and the results are shown in Table 3. The differences in the chemical shifts were large enough that there should be no difficulty in identifying any ion that might be observed.

The reaction of bicyclo[1.1.1]pentyl-1 bromide with antimony pentafluoride in SO_2ClF was carried out using the "molecular beam" apparatus described by Saunders et al.[26] The solution



was kept at −120 °C and transferred to an NMR spectrometer. The ^{13}C spectrum had bands at δ 65.0, 46.4, 134.8, and 224.0, which agree very well with those expected for **2**. No olefinic carbon signals were found, indicating that **3** was not formed. It is worth noting that **2** is one of a small number of primary carbocations[27] that may be observed in solution.

Table 3. Calculated ^{13}C NMR Chemical Shifts Relative to Methane Using Basis Sets I and II

1-Substituted Bicyclo[1.1.1]pentanes

	C3		C2		C1	
X	I	II	I	II	I	II
F	13.7	17.5 (17.1)[a]	47.4	52.2 (55.5)[a]	67.8	73.6 (77.2)[a]
Cl	21.0	24.8	51.0	55.6	46.7	51.8
H	28.8	33.2 (35.9)[a]	46.2	49.8 (53.1)[a]	28.8	33.2 (35.9)[a]
Me	23.8	27.9	46.8	51.0	36.4	40.6
SiH_3	31.9	*b*	47.6	*b*	25.0	*b*

3-Substituted Bicyclo[1.1.1]pentyl-1 Cations

	C1		C2		C3	
X	I	II	I	II	I	II
F	262.9	266.4	75.3	79.3	60.5	65.0
Cl	278.2	281.6	83.0	88.3	−34.7	−34.4
H	138.9	141.2	76.5	79.4	−15.8	−14.4
Me	154.4	157.8	85.0	90.3	−2.0	0.9
SiH_3	102.3	103.9	79.9	83.3	−23.1	−23.4

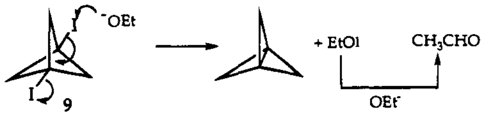
Other Cations Using Basis Set II

compound	atom	calcd	obsd
bicyclo[1.1.0]butyl-1-carbinyl	CH_2^+	229.4	224.0
	C1	129.9	134.8
	C2	57.3	46.4
	C3	67.9	65.0
3-methylenecyclobutyl	C1	397.1	
	C2	70.6	
	C3	134.7	
	CH_2=	137.3	

[a] Experimental chemical shifts. [b] This compound exceeded the internal limits in IGLO using this basis set.

4. 1,3-Diiodobicyclo[1.1.1]pentane

The calculations suggest that electron-withdrawing substituents such as the halogens should markedly reduce the rate of solvolysis. 1,3-Diiodobicyclo[1.1.1]pentane (**9**) is readily formed by the addition of iodine to [1.1.1]propellane.[4] The solvolysis of **9** in 80% ethanol was slow, but was subject to an acid-catalyzed process after some hydrogen iodide was formed.



9

In order to suppress this reaction, base was added to the reaction solution. Here, it was found·that the rate of reaction was markedly increased. Using sodium ethoxide as the base, the rate of reaction in dry ethanol at 25.0 °C was found to be first order in both **9** and ethoxide ion. The rate constant was (2.72 ± 0.08) × 10^{-3} L mol^{-1} s^{-1}. The product was [1.1.1]propellane. The reaction then appears to be a nucleophilic attack by EtO^- on one of the iodines, leading to central bond formation and the loss of iodide ion. This reaction appears to be unique to the bicyclo[1.1.1]pentane ring system. A similar reaction was attempted using other 1,3-diiodides, including 1,3-diiodocyclobutane, 1,3-diiodopropane, and 1,3-diiodobicyclo[2.1.1]-

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[23] Della, E. W.; Taylor, D. K.; Tsanaktsidis, J. *Tetrahedron Lett.* **1990**, *31*, 5219.

[24] Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1042.

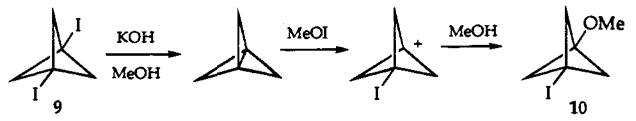
[25] Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919; *J. Am. Chem. Soc.* **1983**, *105*, 1360.

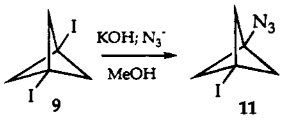
[26] Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6656.

[27] Olah, G. A.; Prakash, G. K. S.; Williams, R. E; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1977. Saunders, M.; Jimenez-Vazquez, H. H. *Chem. Rev.* **1991**, *91*, 375.

hexane, but in no case was there elimination of the iodines with the formation of a new carbon−carbon bond.

The reaction also was carried out in methanol, and here the product was 3-methoxybicyclo[1.1.1]pentyl-1 iodide (**10**). A careful examination of the reaction mixture during the reaction showed that [1.1.1]propellane was formed, and addition of methyl hypoiodite[28] to [1.1.1]propellane in methanol also gave **10**. The reaction then appears to have proceeded as shown above. This implies that the 3-iodo cation is relatively stable and does not readily rearrange. The addition of azide ion to the reaction mixture provides a test of the hypothesis since it should effectively compete with methanol for the capture of the carbocation. It was found that 3-iodobicyclo[1.1.1]pentyl-1 azide (**11**) was now the major product. The fluoro- and chloro-substituted cations were calculated to be transition states, but the much less electronegative iodine appears to give a somewhat stable cation. It is unfortunately not practical to calculate the energy and vibrational frequencies of 3-iodobicyclo[1.1.1]pentyl-1 cation at the level used for the other cations.





Our observations are nicely complemented by those of Adcock et al.[29] They found that the 1,3-diiodide reacts with tertiary amines and pyridine to give trapping products similar to **10** and **11**. They also provided an X-ray structure of 3-iodobicyclo[1.1.1]pentyl-1-pyridinium iodide, which has a C_1-C_3 distance of only 1.80 Å. This is in good accord with our structural calculations (Table 1), where 1-fluorobicyclopentane is predicted to have a distance of 1.826 Å. The strongly electron-withdrawing pyridinium ion substituent should reduce the distance even more.

5. Substituent Effects

One of the classical ways in which to probe changes in electron demand in a reaction is to carry out the reaction with a series of substituted phenyl derivatives and make use of the Hammett σ/ϱ treatment.[30] A study of this type has been carried out for 3-substituted cyclobutyl derivatives[31] in which a bridged intermediate is formed in the rate-determining step and will provide a useful point for comparison. A series of para-substituted 3-phenylbicyclo[1.1.1]pentyl iodides were prepared as shown in Scheme 1. The rates of solvolysis in 80% ethanol were determined at 45 °C, giving the data summarized in Table 4. A Hammett plot is shown in Figure 3, and gave $\varrho = -1.7$. This is essentially the same as that observed for the solvolysis of 3-aryl-substituted cyclobutyl tosylates ($\varrho = -1.54$).

Scheme 1

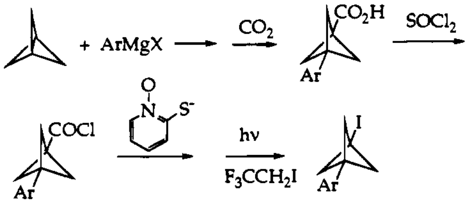


Table 4. Rates of Solvolysis in 80% (v/v) Ethanol

Phenyl Derivatives, 45 °C

X	$k \times 10^5$, s^{-1}
phenyl	4.10 ± 0.09
p-tolyl	8.13 ± 0.08
p-chlorophenyl	2.24 ± 0.02
p-anisyl	16.8 ± 1.5
p-nitrophenyl	0.23 ± 0.06

Other Compounds

compound	*T*, °C	$k \times 10^4$, s^{-1}
1-iodobicyclo[1.1.1]pentane	30.0	23.2 ± 0.3
	45.0	118
1-methyl-3-iodobicyclo[1.1.1]pentane	45.0	6.52 ± 0.12
1-ethyl-3-iodobicyclo[1.1.1]pentane	25.0	0.78 ± 0.01
	35.0	2.83 ± 0.02
	45.0	9.46 ± 0.03

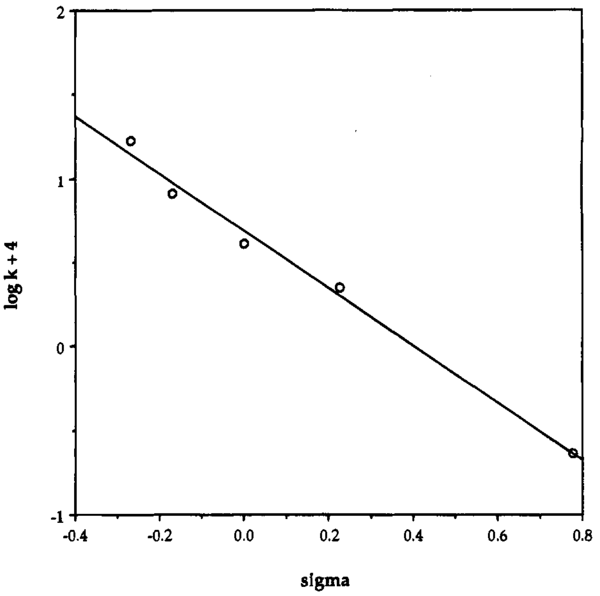


Figure 3. Relationship between the logarithms of the rate constants for the solvolysis of 3-aryl-substituted bicyclo[1.1.1]pentyl-1 iodides and σ. The slope (ϱ) is −1.7.

Della et al.[11] have examined the solvolysis of a number of 3-substituted bicyclo[1.1.1]pentyl-1 bromides and found the rates to be correlated with the inductive constant, σ_I, with a slope of −2.3. A value of $\varrho = -1.55$ may be derived from their data for 3-aryl-substituted bicyclo[1.1.1]pentyl-1 bromides, in good agreement with the value found for the iodides. Some additional data for the bicyclopentyl iodides are given in Table 4. A 3-methyl substituent retards the reaction by a factor of about 10, and an ethyl group also reduced the rate of solvolysis, but by a smaller amount. In the case of the bicyclopentyl bromides, a 3-methyl substituent retarded the reaction by a factor of 20.[11] It can be seen that the substituent effects are similar for the bromides and iodides.

We were interested in the effect of a trifluoromethyl substituent since the calculations (Table 2) suggest that it should

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[28] Methyl hypoiodite is more stable than ethyl hypoiodite, presumably because of the lesser stabilization of formaldehyde as compared to acetaldehyde (Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447).

[29] Adcock, J. L.; Gakh, A. A. *J. Org. Chem.* **1992**, *57*, 6206. Adcock, J. L.; Gakh, A. A.; Pollitte, J. L.; Woods, C. *J. Am. Chem. Soc.* **1992**, *114*, 3980.

[30] Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940.

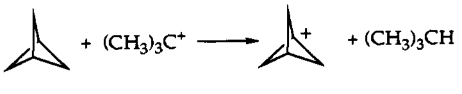
[31] Wiberg, K. B.; Shobe, D.; Nelson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 10645.

be strongly deactivating. 3-(Trifluoromethyl)bicyclo[1.1.1]pentyl-1 iodide (**12**)[29] was found to be unreactive under the solvolysis conditions, and even with silver acetate in 95% ethanol at 65 °C, no reaction was observed. We have found that the reaction of bromine with alkyl iodides leads to an intermediate which is remarkably reactive in ionization.[32] In methylene chloride, **12** is unreactive in the presence of excess bromine at -78 °C, but a reaction proceeds rapidly above -20 °C. Only polybrominated compounds were found, and no bicyclo[1.1.1]pentane derivatives were present in the reaction mixture. Therefore, the bridgehead ion is not sufficiently stable to be captured by bromine under these conditions. This is in contrast to the reaction of 1,3-diiodobicyclo[1.1.1]pentane with bromine, which leads to 1-bromo-3-iodobicyclopentane as one of the products.

An attempt was made to prepare 3-(trimethylsilyl)bicyclo[1.1.1]pentyl-1 iodide (**13**) by the thermal addition of trimethylsilyl iodide to [1.1.1]propellane. A mixture was obtained that appeared by NMR to contain **13** along with many other products, including 1,3-diiodobicyclo[1.1.1]pentane, 1-iodobicyclo[1.1.1]pentane, 1-(trimethylsilyl)bicyclo[1.1.1]pentane, and hexamethyldisilane. The compounds were sufficiently labile that chromatographic separation proved impossible. An attempt was made to solvolyze the crude mixture in ethanol, but the large number of products made it impractical to separate and identify them.

In their study of the bicyclopentyl bromides, Della et al. reported that the replacement of the hydrogen at the 3-position with deuterium reduced the rate of reaction by a factor of 1.3–1.4. We have calculated the MP2/6-31G* vibrational frequencies for the parent ion, and those for the 3d derivative are easily obtained from the force constants. 1-Chlorobicyclo[1.1.1]pentane was taken as the reactant, and the frequencies were calculated for it and its 3d isotopomer at the MP2/6-31G* level.[33] The isotope effect was then calculated using the statistical mechanics procedure of Bigeleisen and Wolfsberg,[34] giving $k_H/k_D = 1.65$. This is somewhat larger than the observed secondary isotope effect. The difference may be due to the effect of the solvent, or perhaps the cation is not fully formed in the solvolysis transition state.

Both studies agree that the bicyclo[1.1.1]pentyl-1 cation is formed in the transition state for the solvolysis of the bicyclopentyl halides. This is in accord with our observation that the



calculated energy change for the hydride transfer reaction[13] shown here is -1 kcal/mol, in agreement with the observation that the bicyclopentyl halides are slightly more reactive than the corresponding *tert*-butyl halides. There remains the question as to whether the cation is an intermediate or a transition state for rearrangement to another ion. This *cannot be answered* by studies of substituent effects for the structure of the ion, and its response to substituents will be essentially the same for either type of species.

We believe that the ion is best described as a transition state on the basis of the MP2/6-31G* calculation that finds it to have an imaginary vibrational mode and the observation that the ion cannot be trapped by azide ion. It is, of course, possible that it is an intermediate with such a small barrier to rearrangement that it cannot be trapped. But, the evidence presently available does suggest that it is a transition state.

Conclusions. The ionization of unsubstituted 1-bicyclo[1.1.1]pentyl halides has been shown to lead to the formation of bicyclo[1.1.1]pentyl-1 cation as a transition state, which then is converted to bicyclo[1.1.0]butyl-1-carbinyl cation. This ion reacts with solvent with bond migration to form 3-methylenecyclobutyl-1 derivatives. Evidence for this course of reaction has been obtained from solvolytic studies, NMR spectroscopic studies of the initially formed ion, and ab initio calculations. 1,3-Diiodobicyclo[1.1.1]pentane was found to be unreactive under solvolytic conditions, but it did react with ethoxide ion to give elimination of iodine, forming [1.1.1]propellane. The reaction with methoxide ion in methanol led to the addition of methyl hypoiodite to the initially formed propellane, via the 3-iodobicyclo[1.1.1]pentyl-1 cation. This cation can be captured by methanol or azide ion before rearrangement to another ion.

Solvolysis of 3-arylbicyclo[1.1.1]pentyl-1 iodides in 80% ethanol gave $\varrho = 1.7$, which is similar to that found for the solvolysis of 3-arylcyclobutyl tosylates.[31] In these cases, the bicyclopentyl cation is converted to a methylenecyclobutyl cation rather than a bicyclo[1.1.0]butyl-1-carbinyl cation. A 3-methyl or ethyl substituent gives a modest reduction in rate, and a trifluoromethyl substituent makes the iodide completely unreactive under solvolysis conditions. These data, along with the data of Della et al. for 3-substituted bicyclo[1.1.1]pentyl-1 bromides[11] and the calculations of the substituent effects, clearly indicate that the inductive effect of the substituent controls the rate of ionization.

The results obtained for the bicyclo[1.1.1]pentyl-1 derivatives closely parallel those for cyclobutyl derivatives.[31] With both the bicyclo[1.1.1]pentyl-1 cation and the cyclobutyl cation, the five-coordinate C_3 has relatively long C–C bonds and the three-coordinate C_1 has relatively short C–C bonds. In the parent ions, rearrangement occurs to give cyclopropylcarbinyl ions, and the 3-substituted ions rearrange to give homoallyl derivatives. Similar substituent effects are also found for the two cases. An important difference between the two systems is found in the C_1–C_3 distance, which is 2.2 Å in the cyclobutyl cation and 1.54 Å in the bicyclopentyl cation.

6. Experimental Section

General Information. Compounds obtained commercially were used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ ($\delta = 7.24$ for ^1H and 77.0 for ^{13}C) unless otherwise noted. Gas chromatographic analyses were carried out using a Hewlett Packard 5890 gas chromatograph with a 30 m bonded MeSi capillary column with a 2 mm i.d. Electron impact ionization mass spectra were obtained at 70 eV. GC/CI spectra were taken using isobutane as the reactant gas. Boiling points and melting points reported herein are uncorrected. Ab initio structures and energies were calculated using Gaussian 92.[35] Chemical shift calculations were carried out using the IGLO program.[25]

1-Iodobicyclo[1.1.1]pentane. Bicyclo[1.1.1]pentane-1-carbonyl chloride (1.31 g, 10 mmol) dissolved in 5 mL of 2-iodo-1,1,1-trifluoroethane was carefully added over 3 min to a stirred, refluxing suspension of 1.94 g (13 mmol) of the freshly dried sodium salt of 2-mercaptopyridine 1-oxide (Barton's reagent) and 60 mg of 4-(dimethylamino)pyridine in 35 mL of 2-iodo-1,1,1-trifluoroethane under an argon atmosphere. After the addition was complete, the reaction mixture was irradiated with a 300 W tungsten flood lamp to aid in decarboxylation. Carbon dioxide was immediately evolved. Heating continued for 1 h until no more gas was given off. The reaction flask was then cooled in an ice bath, and 50 mL of fluorotrichloromethane was added. The reaction

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[32] Wiberg, K. B.; Pratt, W. E.; Matturro, M. G. *J. Org. Chem.* **1982**, *47*, 2720.

[33] The calculated frequencies were scaled by 0.96.

[34] Bigeleisen, J.; Wolfsberg, M. *J. Chem Phys.* **1955**, *23*, 1535.

[35] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

mixture was washed three times with cold (0 °C) concentrated HCl, followed by two portions of cold saturated sodium bicarbonate solution. The organic layer was dried over sodium sulfate. After drying, the mixture was concentrated to approximately one-fifth of its original volume with a rotary evaporator. The remaining liquid was vacuum transferred to give a clear liquid. The distillate was concentrated on the rotary evaporator to give 1.2 g (62%) of 95% pure 1-iodobicyclo[1.1.1]pentane. The compound is a clear liquid which is acid, base, and heat sensitive. It decomposes rapidly above 70 °C and must be stored over potassium carbonate in the freezer in order to retain purity. ^{1}H NMR: δ 3.24 (s, 1H), 2.35 (s, 6H). ^{13}C NMR δ 60.21, 35.95, 10.34. EIMS: *m/z* (relative intensity) 194 (M^+, 0.5), 127 (36), 67 (100), 65 (41), 39 (47). HRMS: calcd for C_5H_8I (M + 1) 194.9672, found 194.9668.

Reaction of 1-Iodobicyclo[1.1.1]pentane with KOH. Formation of [1.1.1]Propellane. 1-Iodobicyclo[1.1.1]pentane (50 mg, 0.26 mmol) was added to an NMR tube which contained 29 mg (0.52 mmol) of KOH dissolved in 600 μL of ethanol-d_6. The progress of the reaction was followed by ^{1}H NMR. After 2 min, three-fourths of the starting material had been consumed. By 10 min, no iodide was visible in the NMR. The only signals that were present were those attributable to [1.1.1]propellane as compared with an authentic sample. ^{1}H NMR (EtOH-d_6): δ 2.06 (s, 6H). ^{13}C NMR (EtOH-d_6): δ 74.3, 1.0.

Bicyclo[1.1.0]butyl-1-carbinyl 3,5-Dinitrobenzoate. Bicyclo[1.1.0]butyl-1-carbinol[22] (0.301 g, 3.59 mmol, with 1% *tert*-butylcatechol as inhibitor) was added to 150 mL of dry ether under argon and cooled in an ice bath. To the magnetically stirred solution was slowly added 2.56 mL of a 1.4 M solution of MeLi (low salt) in ether. To this mixture was then added 0.827 g (3.59 mmol) of 3,5-dinitrobenzoyl chloride in one portion. The reaction mixture was stirred for an additional 3 h. It was then quickly flashed down a short plug of silica gel and washed with additional ether to remove all salts. The eluent was concentrated on a rotary evaporator to approximately one-fourth of its initial volume. The white crystals which had formed were filtered to give 750 mg (75%) of pure bicyclo[1.1.0]butyl-1-carbinyl 3,5 dinitrobenzoate, mp 91–92 °C. An analytical sample was obtained by an additional recrystallization from 1:1 ether/benzene. ^{1}H NMR: δ 9.22 (m, 3H), 4.88 (s, 2H), 1.75 (d, 2.9 Hz, 2H), 1.55 (br s, 1H), 0.929 (s, 2H). ^{13}C NMR: δ 162.58, 148.61, 134.12, 129.30, 122.15, 69.35, 34.79, 2.22. CIMS: *m/z* (relative intensity) 279 (M + 1, 15), 67 (100). HRMS: calcd for $C_{12}H_{11}N_2O_6$ (M + 1) 279.0617, found 279.0636. Anal. Calcd for $C_{12}H_{10}N_2O_6$: C, 51.81; H, 3.62. Found: C, 51.82; H, 3.62.

Bicyclo[1.1.0]butyl-1-carbinyl Azide. Bicyclo[1.1.0]butyl-1-carbinyl 3,5-dinitrobenzoate (50 mg, 0.17 mmol) and 65 mg (1.0 mmol) of sodium azide were added to 1.0 mL of DMF-d_7. This mixture was heated to 65 °C with stirring for 4 days. At the end of 4 days, the liquid was flash vacuum distilled. The only volatile compounds which transferred with the DMF were bicyclo[1.1.0]butyl-1-carbinyl azide and small traces of 3-methylenecyclobutyl-1 azide (see below). As long as the reaction temperature had been kept below 65 °C, the desired azide was produced in a better than a 95:5 ratio. Spectral analysis was carried out directly on the DMF solution. In order to quantify the yield, the DMF solution was added to 20 mL of ether. The ether solution was then washed five times with 0.5% NaOH solution to remove the DMF. The organic material was then dried with sodium sulfate and carefully concentrated on a rotary evaporator to give 9 mg (50%) of bicyclo[1.1.0]butyl-1-carbinyl azide as a clear liquid. ^{1}H NMR (DMF): δ 3.85 (s, 2H), 1.71 (d, J = 2.9 Hz, 2H), 1.48 (br s, 1H), 0.73 (s, 2H). ^{13}C NMR (DMF): δ 53.37, 34.10, 8.56, 0.64. FTIR: 2101 cm^{-1} (azide stretch). CIMS: *m/z* (relative intensity) 110 (M + 1, 3), 109 (M^+, 13), 81 (8), 80 (13), 69 (8), 67 (100). HRMS: calcd 109.0641, found 109.0638.

3-Methylenecyclobutyl-1 Azide. This compound was produced as a minor byproduct of the reaction to produce bicyclo[1.1.0]butyl-1-carbinyl azide as described above. When the S_N2 displacement was carried out in DMSO-d_6, larger quantities of the compound were produced. Because of the small amount of material and the inherent instability of azides, no attempt was made to completely isolate the compound. ^{1}H NMR (DMSO): δ 4.85 (m, 2H), 4.13 (dd, 1H), 3.10–2.63 (m, 4H). CIMS: *m/z* (relative intensity) 110 (M^+, 11), 85 (20), 82 (78), 67 (100).

Bicyclo[1.1.0]butyl-1-carbinyl Cation. Using the molecular beam apparatus of Saunders et al.,[23] 100 mg of 1-bromobicyclo[1.1.1]pentane was codeposited with 0.4 mL of SbF_5 (freshly distilled from KF) onto 1.6 mL of SO_2ClF (freshly distilled from SbF_5) at liquid nitrogen temperature under dynamic vacuum. The process required over 1.5 h and had to be done slowly in order to prevent localized heating, which caused violent decomposition of the material. Once deposition was complete, the cation chamber was removed from the vacuum line and allowed to warm to −120 °C in a 1:1 EtOH/MeOH liquid N_2 slush bath. Following the Saunders procedure, the now liquid cation solution was decanted into the attached NMR tubes and quickly frozen with liquid nitrogen. The NMR tubes were then sealed and cleaned of any attached, frozen alcohol. An NMR spinner was placed onto the NMR tube from the top. The tube was quickly placed into the NMR probe which had been precooled to −120 °C. The tube was allowed to thaw for 20 min before signal acquisition began. The ^{13}C NMR spectrum was then acquired over the next 2 h. The signals recorded were in good agreement with IGLO predictions. Predicted ^{13}C NMR shifts (relative to TMS): δ 67.9 (wing CH_2), 57.3 (bridgehead methine), 129.9 (quaternary bridgehead), 229.4 (methylene cation). Found: δ 65.0, 46.4, 134.8, 224.0.

Reaction of 1-Iodobicyclo[1.1.1]pentane in Polar Organic Solvents in the Presence of NaN_3. Bicyclo[1.1.0]butyl-1-carbinyl Azide. 1-Iodobicyclo[1.1.1]pentane (35 mg), 50 mg of 18-crown-6, and 100 mg of freshly dried sodium azide were placed in 1 mL of each of the following perdeuterated solvents: DMSO, DMF, pyridine, nitrobenzene, 1,2-dichloroethane, methylene chloride, acetonitrile, chloroform, THF, and nitromethane. Each of these mixtures was allowed to stir for 2–3 days at room temperature in the dark. At the end of this time, the solutions were analyzed by ^{1}H NMR and GC/MS. In all of the aprotic solvents where any reaction had occurred, the major products were 3-methylenecyclobutyl-1 azide (spectra described above) and 3-methylenecyclobutyl-1 iodide. However, in each of the following solvents, the proton peaks assignable to bicyclo[1.1.0]butyl-1-carbinyl azide as described above also appeared (in descending order of intensity): DMF, DMSO, methylene chloride, 1,2-dichloroethane, and nitrobenzene. The spectra from these solvents clearly show that the bicyclo[1.1.0]butyl-1-carbinyl cation had to be present and thus must be a true intermediate.

Acetonitrile and pyridine gave different results. In these solvents, [1.1.1]propellane was the initial product, presumably formed by deprotonation as described above for the KOH reaction. The pyridine reaction also proved interesting: in the ^{1}H NMR spectrum, there are strong signals which fit the pattern for the protons on the bicyclo[1.1.0]butyl-1-carbinyl skeleton but with different chemical shifts than those for azide trapping product. It is presumed that this is the pyridinium trapping product. This product could have been formed by direct solvolysis or by protonation of the [1.1.1]propellane followed by trapping. The ^{1}H NMR spectrum of this compound is as follows (pyridine-d_5): δ 0.85 (s, 2 H), 1.84 (br s, 1H), 2.07 (d, J = 2.9 Hz, 2H), 5.79 (s, 2H). Peaks from the perdeuterated pyridinium part of the molecule are obscured by solvent and of too low intensity to be visible. No attempt was made to isolate this compound because of the instability of this type of compound to heat and chromatographic conditions. In an independent experiment, 30 mg of [1.1.1]propellane was added to an excess of pyridinium iodide in pyridine-d_5. In this case, the same set of ^{1}H NMR signals attributable to the bicyclic compound was produced.

The reaction also was carried out in ethanol. To 1 mL of dry ethanol was added 35 mg of 1-iodobicyclo[1.1.1]pentane and 100 mg of tetra-*n*-butylammonium azide. The solution was stirred for 10 h at room temperature. The products were analyzed by GC/CI mass spectroscopy. In addition to 3-methylenecyclobutyl ethyl ether and azide, 5% of bicyclo[1.1.0]butyl-1-carbinyl azide was found.

Reaction of 1,3-Diiodobicyclo[1.1.1]pentane with Ethoxide Ion. To 1 mL of ethanol-d_6 which contained 5.6 mg (0.1 mmol) of potassium hydroxide and 10 mL of benzene as an internal standard was added 6.4 mg (0.02 mmol) of the diiodide. After 2 h, there was quantitative conversion to [1.1.1]propellane as shown by NMR spectroscopy. In a separate reaction, the stoichiometry of the reaction was determined by titrating the unreacted base, and it was found that 2.00 ± 0.01 equiv of base was used per equivalent of the diiodide.

Reaction of 1,3-Diiodibicyclo[1.1.1]pentane with Methoxide Ion. To a solution of 0.45 g (8 mmol) of sodium methoxide in 10 mL of dry methanol was added 1.0 g (3.1 mmol) of the diiodide. The solution was stirred for 4 days at room temperature, at which time all of the diiodide had dissolved. The reaction mixture was added to 150 mL of water and extracted with 30 mL of pentane. The organic layer was dried over sodium sulfate. After the solvent was evaporated, the resultant mixture was added to 25 mL of 95% methanol to precipitate unreacted diiodide. An additional 100 mL of water was added. The product was extracted with ether, and the ether solution was dried and concentrated to give 0.52 g (74%) of 1-iodo-3-methoxybicyclo[1.1.1]pentane. The compound is a liquid which is unstable at room temperature. An analytical sample was obtained by microdistillation at 50 °C and 18 mmHg. ^{1}H NMR: δ 3.27 (s, 3H), 2.32 (s, 6H). ^{13}C NMR: δ 71.6, 60.4, 54.5, −3.2. EIMS: *m/z* (relative intensity) 39 (58), 67 (40), 90 (100), 127 (20). HRMS: calcd for $C_6H_{10}IO$ (M + 1) 224.9777, found 224.9767.

The reaction also was carried out in the presence of azide ion. To a solution of 0.45 g (8 mmol) of sodium methoxide and 0.65 g (10 mmol) of sodium azide in 10 mL of 95% methanol was added 1.0 g of 1,3-diiodobicyclo[1.1.1]pentane. The reaction mixture was stirred at room temperature for 4 days, after which time all of the diiodide had dissolved. The reaction mixture was added to 150 mL of water and extracted three times with 30 mL of ether. The combined organic layers were dried over sodium sulfate and concentrated. The residue was chromatographed on a Florisil column using 1:1 hexane/ethyl acetate as the eluent. Evaporation of the solvent gave 0.58 g (79%) of 1-azido-3-iodobicyclo[1.1.1]pentane. It was a clear liquid which was unstable at room temperature. ^{1}H NMR: δ 2.43 (s, 6H). ^{13}C NMR: δ 61.3, 55.1, −3.1. FTIR: 2112 cm^{-1} (N_3). EIMS: *m/z* (relative intensity) 39 (33), 53 (100), 127 (70), 207 (1). HRMS: calcd for $C_5H_7IN_3$ (M + 1) 235.9687, found 235.9693. In the absence of methoxide ion, there was no significant reaction with azide ion.

Reaction of Bromine with 1,3-Diiodobicyclo[1.1.1]pentane. To a solution of 2.56 g (8 mmol) of 1,3-diiodobicyclo[1.1.1]pentane in 100 mL of carbon tetrachloride was added with stirring over 1 h 2.18 g (13.6 mmol) of bromine in 75 mL of carbon tetrachloride. After 6 h at 0 °C, the ice bath was removed, and the mixture was stirred overnight. It was added to 100 mL of water containing 4 g of sodium bisulfite. The layers were separated, and the aqueous layer was extracted three times with methylene chloride. The organic layers were combined, dried over sodium sulfate, and concentrated. The remaining solution was purified using a silica gel column with 10:1 pentane/ethyl acetate as the eluent. Evaporation of the solvent gave 0.31 g (14%) of 1-bromo-3-iodobicyclo[1.1.1]pentane. Sublimation at room temperature at 0.6 mmHg gave an analytical sample with mp 141−142 °C. ^{1}H NMR: δ 2.59 (s, 6H). ^{13}C NMR: δ 66.4, 32.5, −5.0. EIMS: *m/z* (relative intensity) 65 (100), 66 (61), 127 (34), 272 (16), 274 (16). HRMS: calcd for C_5H_6IBr 271.8698, 273.8678, found 271.8708, 273.8691. Anal. Calcd for C_5H_6IBr: C, 22.0; H, 2.2. Found: C, 22.0; H, 2.1.

Photochemical Addition of Alkyl Iodides to [1.1.1]Propellane.[36] Ethyl iodide (0.78 g, 5 mmol) was added to 400 mg (6 mmol) of [1.1.1]propellane in 21 mL of diethyl ether. After irradiation of the sample for 30 min at 0 °C with a medium pressure mercury lamp, the solvent was evaporated, giving 1.08 g (90%) of 95% pure (GC) 1-ethyl-3-iodobicyclo[1.1.1]pentane. It was a white solid that decomposed in air at room temperature. ^{1}H NMR: δ 2.15 (s, 6H), 1.50 (q, *J* = 7.5 Hz, 2H), 0.81 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR: δ 59.9, 49.3, 25.1, 10.7, 8.1. EIMS: *m/z* (relative intensity) 39 (32), 67 (70), 95 (100), 127 (15), 222 (0.5). FTIR: 459 cm^{-1} (C−I stretch). HRMS: calcd for $C_7H_{12}I$ (M + 1) 222.9989, found 222.9995.

The addition of methyl iodide to [1.1.1]propellane was effected in the same fashion, giving 68% of 96% pure (GC) 1-iodo-3-methylbicyclo[1.1.1]pentane as a clear liquid. ^{1}H NMR: δ 2.17 (s, 6H), 1.18 (s, 3H). ^{13}C NMR: δ 62.1,44.6, 18.3, 6.9. EIMS: *m/z* (relative intensity) 39 (5), 53 (4), 81 (100), 127 (1). CIMS: *m/z* (relative intensity) 81 (M − I, 100), 209 (M + 1, 0.5).

Addition of Grignard Reagents to [1.1.1]Propellane.[37] The [1.1.1]propellane derived from 74.0 g (0.25 mol) of 1,1-bis(chloromethyl)-2,2-dibromocyclopropane was transferred to a 3 L flask which contained 1.0 mol of the appropriate Grignard reagent in 700 mL of diethyl ether. The mixture was heated to reflux under argon for 24 h. The flask was cooled in an ice bath, and dry carbon dioxide was bubbled into the reaction mixture for at least 30 min. The mixture was slowly acidified with 500 mL of concentrated hydrochloric acid, and sufficient water was added to dissolve all of the salts. The layers were separated, and the aqueous layer was extracted three times with ether. The combined organic solutions was extracted four times with 300 mL of 5% aqueous potassium hydroxide. The basic solution was acidified and extracted with ether. The ether solution was dried and evaporated. The solid acid mixture was treated with excess thionyl chloride and heated to reflux for 2 h. The excess thionyl chloride was removed under reduced pressure, and the cooled product was treated with methanol to give a mixture of methyl esters.

Methyl 3-phenylbicyclo[1.1.1]pentyl-1-carboxylate was isolated by distillation, giving 3.1 g of the ester, bp 95−100 °C at 0.5 mmHg. It was a low melting solid. ^{1}H NMR: δ 2.32 (s, 6H), 3.71 (s, 3H), 7.21−7.25 (m, 3H), 7.29−7.33 (m, 2H). ^{13}C NMR: δ 36.9, 4.8, 51.3, 53.3, 126.9, 139.6, 170.7. EIMS: *m/z* (relative intensity) 65 (6), 77 (23), 128 (64), 143 (100), 187 (1). FTIR: 1722 cm^{-1} (C═O).

Methyl 3-(*p*-tolyl)bicyclo[1.1.1]pentyl-1-carboxylate was isolated by distillation, giving 9.8 g of the ester, bp 102−110 °C×b0 at 0.3 mmHg. It was a solid, mp 62−63 °C. ^{1}H NMR: δ 2.33 (s, 6H), 2.35 (s, 3H), 3.73 (s, 3H), 7.14 (m, 4H). ^{13}C NMR: δ 21.0, 36.8, 41.5, 51.3, 53.3, 125.9, 128.8, 136.4, 136.6, 170.6. EIMS: *m/z* (relative intensity) 39 (18), 65 (14), 91 (21), 115 (41), 142 (69), 157 (100), 201 (6), 216 (1). HRMS: calcd for $C_{14}H_{17}O_2$ (M + 1) 217.1229, found 217.1235. FTIR: 1728 cm^{-1} (C═O).

Methyl 3-(*p*-chlorophenyl)bicyclo[1.1.1]pentyl-1-carboxylate was isolated by distillation, giving 10.5 g of the ester, bp 135−145 °×b0C at 0.3 mmHg. It was further purified by recrystallization from methanol/water to give 10.1 g of pure ester, mp 98 °C. ^{1}H NMR: δ 2.29 (s, 6H), 3.69 (s, 3H), 7.12 (d, *J* = 7 Hz, 2H), 7.25 (d, *J* = 7 Hz, 2H). ^{13}C NMR: δ 36.9, 41.3, 51.7, 53.4, 127.5, 128.3, 132.7, 138.1, 170.4. EIMS: *m/z* (relative intensity) 39 (17), 75 (20), 115 (28), 142 (100), 177 (81), 179 (26), 236 (3), 238 (1). HRMS: calcd for $C_{13}H_{14}O_2Cl$ (M + 1) 237.0682, found, 237.0683. FTIR: 1724 cm^{-1} (C═O).

Methyl 3-(*p*-anisyl)bicyclo[1.1.1]pentyl-1-carboxylate was isolated by removing methyl anisate by distillation, followed by sublimation at 100−105 °×b0C at 0.3 mmHg. Recrystallization from methanol/water gave a 4.1 of the ester, bp 116−117 °C. ^{1}H NMR: δ 2.28 (s, 6H), 3.69 (s, 3H), 3.77 (s, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR: δ 36.8, 41.3, 51.6, 53.4, 55.3, 113.6, 127.1, 131.9, 158.6, 170.8. EIMS: *m/z* (relative intensity) 63 (8), 77 (15), 115 (15), 133 (43), 158 (47), 173 (100), 217 (4), 232 (7). HRMS: calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1112. FTIR: 1726 cm^{-1} (C═O).

Methyl 3-(*p*-Nitrophenyl)bicyclo[1.1.1]pentyl-1-carboxylate. Methyl 3-phenylbicyclo[1.1.1]pentyl-1-carboxylate (2.9 g, 14.4 mmol) was added to 6.0 g of the 2:1 complex of trifluoromethanesulfonic acid/fuming nitric acid in 100 mL of $CFCl_3$. After 1 h at 0 °C, the reaction mixture was slowly added to 100 g of ice. The organic layer was separated, dried with sodium sulfate, and concentrated with a rotary evaporator. The crude mixture was chromatographed through a short silica column using 2:1 hexanes/ethyl acetate to remove polynitrated material. The solvent was removed from the eluent, and the solid residue was dissolved in boiling heptane. The hot heptane solution was decanted from the insoluble material and allowed to cool. Evaporation of the heptane and recrystallization of the residue from methanol/water gave 1.45 g (41%) of methyl 3-(*p*-nitrophenyl)bicyclo-[1.1.1]pentyl-1-carboxylate as a light yellow solid with mp 109 °C. ^{1}H NMR: δ 2.39 (s, 6H), 3.73 (s, 3H), 7.35 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR: δ 37.2, 41.5, 51.8, 55.3, 123.6, 127.1, 146.8, 147.0, 170.0. EIMS: *m/z* (relative intensity) 40 (32), 77 (22), 128 (64), 143 (100). HRMS: calcd for $C_{13}H_{14}NO_4$ (M + 1) 248.0922, found 248.0919. FTIR: 1726 cm^{-1}.

Preparation of 3-Arylbicyclo[1.1.1]pentyl-1 Iodides. The esters were converted to the carboxylic acids by treatment with 1.5 equiv of potassium hydroxide in 200 mL of dry methanol at reflux for 2 h. The methanol was evaporated, and the salts were washed with three portions of pentane. Concentrated hydrochloric acid (50 mL) and 100 mL of water were added, and the solution was extracted four times with ether. The combined ether solutions were dried over sodium sulfate, and the solvent was evaporated. Thionyl chloride (120 mL) was added to the

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residue, and the mixture was heated to reflux for 2 h. The thionyl chloride was removed under reduced pressure. The acid chlorides thus formed were converted to the iodides using the procedure described above for 1-iodobicyclo[1.1.1]pentane.

1-Iodo-3-phenylbicyclo[1.1.1]pentane was obtained in 92% yield from the acid chloride as a white solid, mp 61 °C. It decomposes violently over 103 °C. ^{1}H NMR (benzene-d_6): δ 2.21 (s, 6H), 6.73 (m, 2H), 7.07 (m, 3H). ^{13}C NMR: δ 7.0, 50.4, 61.8, 126.2, 127.7, 128.5, 138.5. CIMS: *m/z* (relative intensity) 143 (M − I, 100), 199 (10).

1-Iodo-3-(*p*-tolyl)bicyclo[1.1.1]pentane was obtained in 96% yield as a solid, mp 95 °C. ^{1}H NMR (benzene-d_6): δ 2.07 (s, 3H), 2.23 (s, 6H), 6.71 (d, J = 8.1 Hz, 2H), 6.68 (d, J = 8.1 Hz, 2H). ^{13}C NMR: δ 7.1, 21.1, 50.3, 61.9, 126.2, 129.1, 135.7, 136.5. CIMS: *m/z* (relative intensity) 157 (M − I, 100), 213 (11).

1-Iodo-3-(*p*-chlorophenyl)bicyclo[1.1.1]pentane was obtained in 96% yield as a white solid, mp 106 °C dec. ^{1}H NMR (benzene-d_6): δ 2.10 (s, 6H), 6.40 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H). ^{13}C NMR: δ 6.2, 49.7, 53.4, 61.7, 127.6, 128.6, 133.0, 136.9. CIMS: *m/z* (relative intensity) 141 (33), 177 (M − I, 100), 233 (12).

1-Iodo-3-(*p*-anisyl)bicyclo[1.1.1]pentane was obtained in 87% yield as a solid that decomposes at 85 °C. ^{1}H NMR (benzene-d_6): δ 2.24 (s, 6H), 3.26 (s, 3H), 6.68 (AB quartet, 4H). ^{13}C NMR: δ 7.1, 50.1, 54.8, 62.0, 114.0, 127.3, 128.3, 130.8, 159.2. CIMS: *m/z* (relative intensity) 173 (M − I, 100), 229 (13).

1-Iodo-2-(*p*-nitrophenyl)bicyclo[1.1.1]pentane was obtained in 96% yield as a solid that decomposed violently at 116 °C before melting. ^{1}H NMR (benzene-d_6): δ 2.04 (s, 6H), 6.30 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H). ^{13}C NMR: δ 5.5, 49.6, 61.4, 123.5, 126.7, 144.6, 147.1. CIMS: *m/z* (relative intensity) 141 (6), 188 (M − I, 100), 228 (1).

Solvolytic Studies. The solvolyses were carried out in 80% (v/v) ethanol−water, and the reaction temperature was maintained ±0.03 °C. The solvent (50 mL) was allowed to equilibrate in a constant temperature bath for 45 min. To the solvent was added 0.7 mmol of the iodide in one portion, producing a 0.014 M solution. A 3 mL portion was withdrawn and added to 20 mL of dry ethanol at 0 °C, and the timer was started. The aliquot was titrated to a methyl red endpoint using 0.01 N sodium hydroxide. Aliquots were removed at appropriate time intervals over the first two half-lives of the reaction. The final infinity titer was determined after at least 10 half-lives. At least three runs were carried out at each temperature.

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