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Mechanism of the Solvolysis of Bicyclo[1.1.1]pentyl-1 Derivatives

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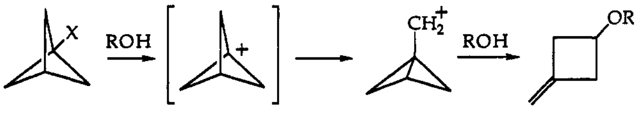
Summary: The ionization of bicyclo[1.1.1]pentyl-1 derivatives is shown to involve rearrangement to the bicyclo[1.1.0]butyl-1-carbinyl cation rather than the 3-methylenecyclobutyl cation. This is in good accord with MP2-6-31G* theoretical predictions and is in contrast to the products of solvolysis which are 3-methylenecyclobutyl derivatives.

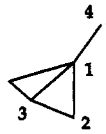
Despite the usual low reactivity of bridgehead halides,[1] the solvolysis of bicyclo[1.1.1]pentyl-1 derivatives occurs more rapidly than that of the corresponding *tert*-butyl derivatives and leads to 3-methylenecyclobutyl products.[2] Although the formation of the 3-methylenecyclobutyl cation from the bicyclopentyl-1 cation would require only the breaking of one bond, computational studies at the MP2/6-31G* theoretical level have suggested that the initial reaction leads to the bicyclo[1.1.0]butyl-1-carbinyl cation.[3] We now present two sets of experimental data that confirm the results of the calculations.



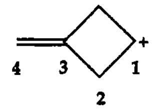
It seemed possible that if a very good nucleophile such as azide ion[4] were present it might trap the carbocation in the unrearranged form. Bicyclo[1.1.1]pentyl-1 iodide (1) was used in these experiments since it is considerably more reactive than the chloride, allowing the solvolyses to be carried out under relatively mild conditions. The iodide was dissolved in a set of aprotic solvents (DMF, DMSO, methylene chloride, 1,2-dichloroethene, or nitrobenzene) containing excess sodium azide and 18-crown-6 and allowed to react at room temperature. In each case, part of the product had NMR bands (δ 3.85 (s, 2H), 1.71 (d, 2H), 1.48 (br s, 1H) and 0.73 (s, 2H)) that were similar to those of bicyclo[1.1.0]butyl-1-carbinol,[5] suggesting that bicyclo[1.1.0]butyl-1-carbinyl azide (2) had been formed. The other major products were 1-iodo-3-methylenecyclobutane which is presumably formed by internal return from the initially formed ion pair and 1-azido-3-methylenecyclobutane.

An authentic sample of 2 was prepared by the reaction of sodium azide with bicyclo[1.1.0]butyl-1-carbinyl 3,5-dinitrobenzoate in dimethylformamide at 65 °C. It had ^{1}H NMR bands which corresponded to those found in the solvolysis reaction.

Table I. IGLO Calculations for ^{13}C Chemical Shifts[a]



carbon no.	3	2	1	4
calcd shift	67.9	57.3	129.9	229.4
expl	65.0	46.4	134.8	224.0



carbon no.	4	3	2	1
calcd shift	137.3	134.7	70.6	397.1
expl		not observed		

[a] Calculated using the MP2/6-31G* geometries and referenced to TMS.

When the reaction of the iodide (1) was carried out in acetonitrile or pyridine, the major product was [1.1.1]propellane. It is interesting that 1 reacts readily with mild bases to give the propellane. For example, the reaction with ethanolic KOH occurs in a few min at room temperature. 1-Bromobicyclo[1.1.1]pentane has been reported to be converted to the propellane, but required using *tert*-butyllithium as the base.[6]

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 (2) with pyridine replacing the azide group.

Another way to study the reaction is via ^{13}C NMR spectroscopy. The NMR spectra of 3-methylenecyclobutyl cation (3) and of bicyclo[1.1.0]butyl-1-carbinyl cation (4) were calculated via IGLO[7] using MP2/6-31G* geometries and basis set II. The results are shown in Table I. The reaction of bicyclo[1.1.1]pentyl-1 bromide with antimony pentafluoride was carried out using the "molecular beam" apparatus described by Saunders, et al.[8] The solution in SO_2ClF 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 4. No olefinic carbon signals were found, indicating that 3 was not formed. It is worth noting that 4 is one of

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[7] Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919; *J. Am. Chem. Soc.* **1983**, *105*, 1360. It should be noted that IGLO calculations and experimental ^{13}C chemical shifts have been used to establish the structures of a number of carbocations. Cf. 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.

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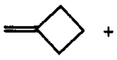
Table II. Results of ab Initio Calculations[a]

		 4	 TS	 3
MP2	−193.702 07	−193.713 07	−193.677 33	−193.679 01
MP3	−193.708 07	−193.721 21	−193.693 86	−193.696 03
ZPE	61.7	62.0	60.5	60.0
E_{rel} (MP3)	0.0	−8.0	+7.6	+5.8

[a] The total energies are given in hartrees, and the zero-point and relative energies are given in kcal/mol. The energies were calculated at the MP2/6-31G* geometries, and the zero-point energies were derived from HF/6-31G* frequencies scaled by 0.893.

a small number of primary carbocations[9] that may be observed in solution.

The formation of 3-methylenecyclobutyl derivatives in the solvolysis of bicyclopentyl halides, despite the relatively high energy of the corresponding cation, probably results from the lower energy of the methylenecyclobutyl products as compared to the bicyclobutylcarbinyl products. The strain energy of the bicyclobutane ring is 64 kcal/mol[10] whereas the strain energy of methylenecyclobutane is only 47 kcal/mol (including the double bond). This would allow the nucleophile to attack C3 of the bicyclobutylcarbinyl ion so as to give the more stable product. The stability of 4 presumably results from the same interactions that stabilize cyclopropylcarbinyl cations,[11] and would result in significant positive charge at C3.

It might be noted that the bicyclo[1.1.1]pentyl-1-cation has been calculated to be a transition state.[2] Some 3-substituted bicyclo[1.1.1]pentyl derivatives have been calculated to behave differently than the parent. With R = methyl, silyl, CF_3, or PH_2, the corresponding bicyclo[1.1.1]pentyl cation is calculated to be a minimum on the potential surface. The results of the solvolysis of a set of 3-substituted bicyclo[1.1.1]pentyl-1 iodides will be reported at a later time.

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Supplementary Material Available: Full experimental details for the preparation of new compounds and for the reactions of the bicyclo[1.1.1]pentyl-1 derivative (5 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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