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# Study of the Highly Strained Bicyclo[1.1.1]pentyl Cations under Stable Ion Conditions[1]

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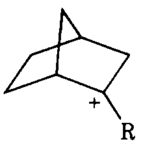
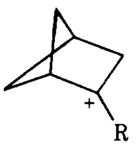
**Abstract:** 2-Chlorobicyclo[1.1.1]pentane in $SbF_5/SO_2ClF$ solution, even at −140 °C, upon ionization, immediately rearranges to the 3-cyclopentenyl cation. The parent 2-bicyclo[1.1.1]pentyl cation, thus, could not be directly observed. In contrast, 2-phenyl-2-bicyclo[1.1.1]pentanol, under similar conditions, gives the stable 2-phenyl-2-bicyclo[1.1.1]pentyl cation, which is observed together with the 3-phenyl-3-cyclopentenyl cation, formed in the rearrangement reaction. The structures of these ions were studied by $^1H$ and $^{13}C$ NMR spectroscopy.

## Introduction

2-Bicyclo[2.2.1]heptyl and 2-bicyclo[2.1.1]hexyl cations **1** and **2** are well studied and characterized.[2,3] The degree of charge delocalization into the neighboring C–C bonds in these ions depends on the nature of the substituent (R) and geometric arrangements. The considerably more strained 2-bicyclo[1.1.1]pentyl cations, **3**, have not yet been directly observed in solution. Interested in the effect of strain on carbocations, we report now the study of 2-bicyclo[1.1.1]pentyl cations in superacidic solutions.



**1**



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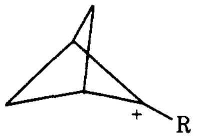
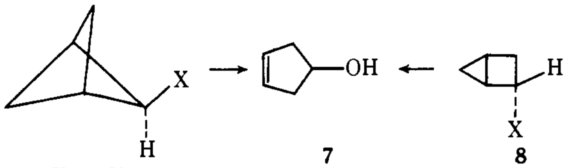


**3**

## Results and Discussion

Wiberg and Williams[4] first prepared 2-chlorobicyclo[1.1.1]pentane (**4**) and 2-bicyclo[1.1.1]pentanol (**5**). Subsequently, the solvolysis of the dinitrobenzoate (ODNB) **6** in 60% aqueous acetone was studied.[5] The sole product **7**[6] derived from **6** had also been observed starting with 2-bicyclo[2.1.0]pentyl derivatives.[5]

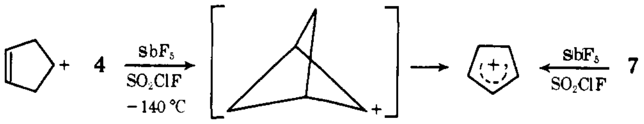


**4**, X = Cl
**5**, X = OH
**6**, X = OPNB

**7**

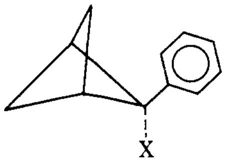
**8**

When chloride **4** was ionized in $SbF_5/SO_2ClF$ solution at −140 °C (cooled with liquid $N_2$-pentane slush), the $^1H$ and $^{13}C$ NMR spectrum of the solution, thus obtained, showed the exclusive presence of only the allylic 3-cyclopentyl cation **10**.[7] Ion **10** has been previously prepared by ionization of **7**. There was no observation of any of the secondary 2-bicyclo[1.1.1]pentyl cation **9**. The results obtained from both the solvolysis and stable ion studies agree with each other, indicating the extreme instability of the very strained 2-bicyclo[1.1.1]pentyl cation. The expected rearrangement of the ion **9** to **10** apparently involves the 4-cyclopentenyl ion **11** as the transient species, as the latter was quenched under solvolytic conditions.

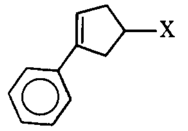


**11** **9** **10**

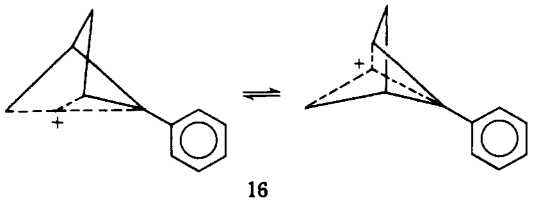
Padwa has extended the study of the bicyclo[1.1.1]pentyl system to the preparation of 2-phenyl-2-bicyclo[1.1.1]pentanol (**12**)[8,9] and the solvolysis of its *p*-nitrobenzoate derivative **13**.[10] The alcohol **12** was found to be extremely labile to acidic conditions and rearranged readily to 3-phenyl-3-cyclopenten-1-ol (**14**) through an assumed bicyclo[2.1.0]pentyl cation intermediate. Kinetic evidence obtained from the solvolysis of the *p*-nitrobenzoate ester **13** suggested that the ionization proceeded with participation of the one-carbon bridge adjacent to the departing *p*-nitrobenzoate group (**16**). These results lead



**12**, X = OH
**13**, X = OPNB



**14**, X = OH
**15**, X = OPNB



**16**

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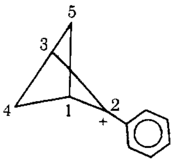
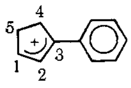
**Table I.** $^1$H and $^{13}$C NMR Parameters[a] of 2-Phenyl-2-bicyclo[1.1.1]pentyl Cation and 3-Phenylcyclopentenium Ion in $FSO_3H/SO_2ClF$

| ion | temp, °C | | 1 | 2 | 3 | 4 | 5 | others |
|---|---|---|---|---|---|---|---|---|
|  | −90 | $\delta^{13}C$ | 90.00<br>($J_{CH}$ = 166.8 Hz) | 256.10 | 90.00<br>($J_{CH}$ = 166.8 Hz) | 42.40 | 42.40 | aromatic:<br>$C_p$ = 158.00<br>$C_o$ = 144.03<br>$C_m$ = 132.80<br>$C_i$ = 136.70 |
| | −80 | $\delta^1H$ | 6.10<br>(broad) | | 6.10<br>(broad) | 4.42<br>(anti)<br>4.65<br>(syn) | 4.42<br>(anti)<br>4.65<br>(syn) | aromatic:<br>multiplet<br>~8.4-8.8 |
|  | −90 | $\delta^{13}C$ | 229.30 | 140.23 | 209.10 | 40.51 | 42.43 | aromatic:<br>$C_p$ = 146.08<br>$C_o$, $C_o{}^1$ = 137.80<br>136.53<br>$C_{m,m^1}$ = 131.64,<br>130.93<br>$C_i$ = 124.83 |
| | −80 | $\delta^1H$ | 9.70<br>(broad) | 8.55<br>(m) | | 4.2<br>(broad) | 3.7<br>(broad) | aromatic:<br>multiplet<br>7.9-8.8 |

[a] Chemical shifts are from external capillary $Me_4Si$.

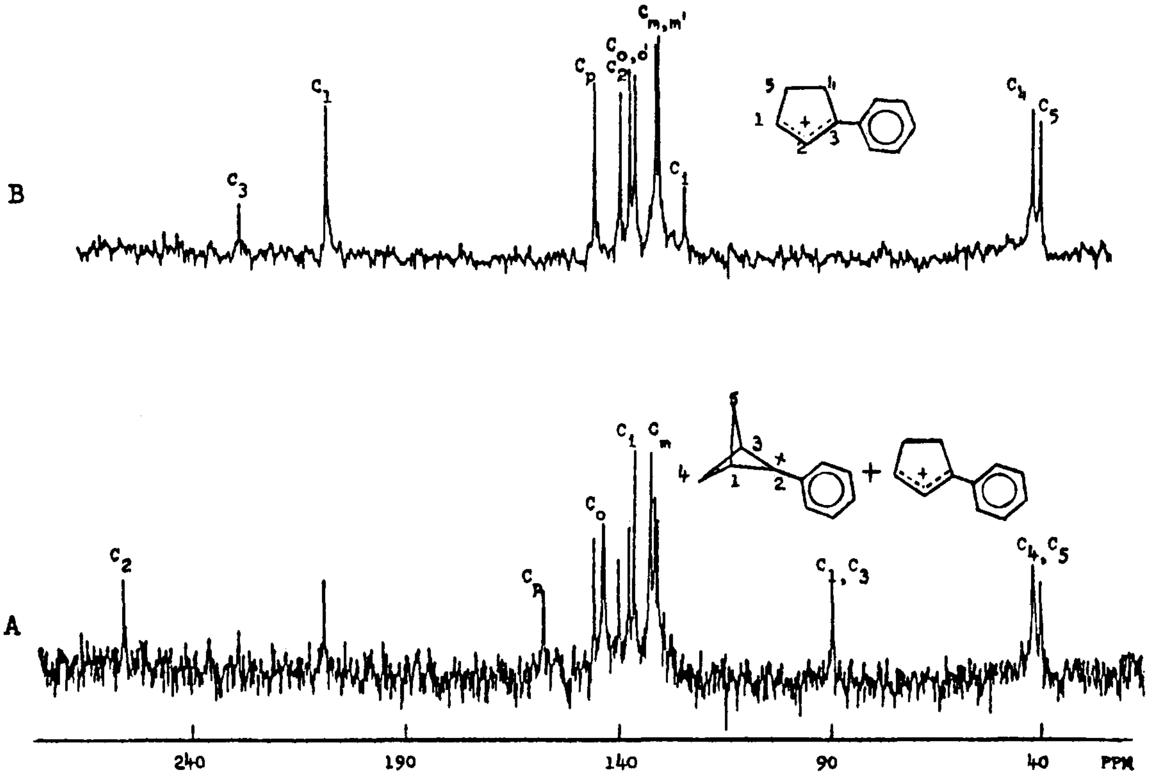
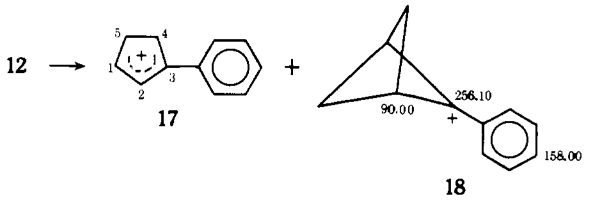


**Figure 1.** 20-MHz proton-decoupled $^{13}$C NMR spectrum of (A) a mixture of 2-phenyl-2-bicyclo[1.1.1]pentyl cation and 3-phenylcyclopentenium ion in $FSO_3H/SO_2ClF$ at −90 °C; (B) pure 3-phenylcyclopentenium ion in $FSO_3H/SO_2ClF$ at −90 °C.

Padwa to suggest that the phenyl group was not sufficient enough to overcome the neighboring C–C $\sigma$-bond participation in the bicyclo[1.1.1]pentyl system.

Hoping that phenyl substitution would sufficiently stabilize the incipient tertiary bicyclo[1.1.1]pentyl cation under stable ion conditions, we ionized alcohol **12** with $FSO_3H/SO_2ClF$ at −140 °C. Besides the expected allylic ion **17**, the tertiary 2-phenyl-2-bicyclo[1.1.1]pentyl cation **18** was, indeed, observed. It quantitatively rearranged to the allylic ion **17** upon heating to −30 °C. The ionization of **12** in $SbF_5/SO_2ClF$ gave the same result. Under no conditions were we able to completely eliminate the obviously facile rearrangement of **18** to **17** to obtain ion **18** free of **17**.



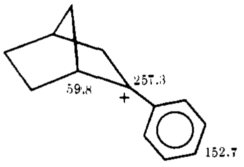
**17** **18**

The 60-MHz $^1$H NMR and 20-MHz $^{13}$C NMR spectral data are summarized in Table I. The $^{13}$C NMR spectra of ions **18** and **17** are shown in Figure 1. In the $^1$H NMR spectrum, the three broad absorptions for **18** in the aliphatic region at $\delta$ 4.42, 4.65, and 6.10 are assigned to $H_4$, anti ($H_5$ anti), $H_4$syn

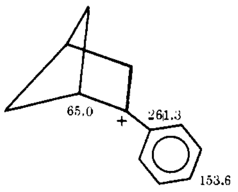
($H_5$ anti), and the bridgehead protons ($H_1$ and $H_3$), respectively. The phenyl group of **18** was observed as a broad multiplet at $\delta$ 8.4–8.8. In the $^{13}C$ NMR spectrum, the carbenium center was observed at $\delta$ 256.10, followed by the phenyl ring absorptions ($C_p = 158.00$, $C_o = 144.03$, $C_i = 136.70$, and $C_m = 132.80$). The bridgehead $C_1$, $C_3$ carbons and methylene $C_4$, $C_5$ carbons absorbed at $\delta$ 90.00 ($J_{C-H} = 166.8$ Hz) and 42.40, respectively.

It is interesting to compare the $^{13}C$ NMR chemical shifts of **18** with those of the bicyclo[2.2.1]heptyl and bicyclo[2.2.1]hexyl analogues **19** and **20** (recorded at −80 °C).

The carbenium center in all the three bicyclic ions, **18, 19,** and **20,** absorbs around $\delta$ 255–261, which indicates the similar nature of these ions. The bridgehead carbons are substantially deshielded in **18** as compared to those in **19** and **20.** The C–H coupling constant of the bridgehead carbon in **18** is similar to the one observed for the parent hydrocarbon bicyclo[1.1.1]pentane ($J_{C-H} = 164.0$ Hz).[4] These observations are indicative of little or no C–C $\sigma$-bond delocalization in **18.** The positive charge at $C_2$ is, however, dispersed into the phenyl ring as indicated by the significant deshielding of the *p*-phenyl carbon. The $^1H$ and $^{13}C$ NMR shifts observed for ion **17** are, thus, typical of a phenylsubstituted allylic ion.[11]



**19**



**20**

The present work supports the conclusions drawn from the solvolytic study of bicyclo[1.1.1]pentyl derivatives[5] that the very strained neighboring C–C $\sigma$ bonds strongly interact with the electron-deficient carbocation center to cause rearrangement to the related allylic ions. This tendency, however, is diminished by phenyl substitution, allowing ion **18** to be observed at low temperature.

## Experimental Section

2-Bicyclo[1.1.1]pentanol (**5**), 2-chlorobicyclo[1.1.1]pentane (**4**), and 2-phenyl-2-bicyclo[1.1.1]pentanol (**12**) were prepared by the previously published procedures.[4,8,9]

**Preparation of Carbocations.** Freshly distilled $FSO_3H$ or $SbF_5$ was dissolved in a threefold amount of $SO_2ClF$ at −140 °C (in pentane/liquid $N_2$ slush). To this solution was slowly added a precooled slurry of the precursor in $SO_2ClF$ with vigorous stirring to obtain approximately 15–20% solution of the ion.

**Proton Magnetic Resonance Spectra.** $^1H$ NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer, equipped with a variable temperature probe. External (capillary) $Me_4Si$ was used as the reference.

**Carbon-13 Magnetic Resonance Spectra.** The spectrometer used was a Varian Associates Model FT-80 equipped with broad band variable temperature probe, broad band $^1H$ decoupler, and a 24K computer. Chemical shifts were measured from (external) $Me_4Si$.

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## References and Notes

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