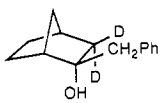
Ring Expansion of the 2-Benzyl-2-norbornyl Cation

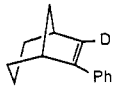
Summary: Reaction of 2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol with HSO_3F at −78 °C results in quantitative formation of the 6-phenylbicyclo[3.2.1]octan-6-yl cation via a mechanism which has been unambiguously elucidated by deuterium-labeling experiments.

Sir: As part of a detailed study of the reactions of benzylcarbinols with fluorosulfonic acid we examined the reaction of 2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol (**1**) with HSO_3F at −78 °C. This resulted (Scheme I) in smooth conversion of **1** to the 6-phenylbicyclo[3.2.1]octan-6-yl cation (**2**), the identity of which was confirmed by comparison of the ^{13}C NMR spectrum with that previously reported[1] for **2** and supported by the observation that quenching of the acid solution gave alkene **3**.[2] This therefore represents a more convenient method of preparation of this well-studied cation[1,3,4] than that previously reported[1] from the less readily available phenyl alcohol **4**.

Several mechanisms are possible for the conversion of **1** to **2**. These can be subdivided according to whether the key ring expansion step occurs by migration of C3 (methylene migration) or C1 (bridgehead migration), both of which have ample precedent in the literature.[5] These two possibilities were distinguished by means of deuterium labeling in the 3-position of alcohol **1**. Thus reaction of 3,3-dideuterio-2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol (**5**) with HSO_3F followed by quenching resulted in quantitative formation of 7-deuterio-6-phenylbicyclo[3.2.1]-oct-6-ene (**6**).[6,7] This result is consistent only with C3 (methylene) migration since mechanisms involving C1 (bridgehead) migration would have resulted in deuterium incorporation in the 8-position of the product alkene.[8]



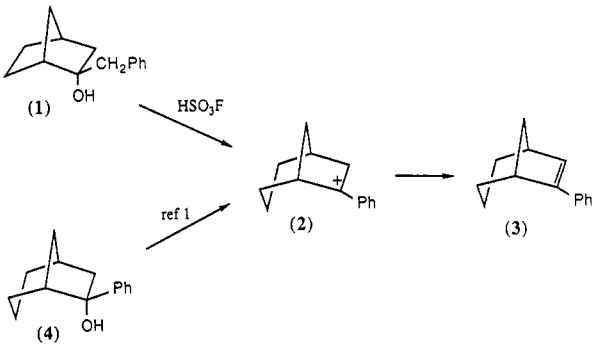
(5)



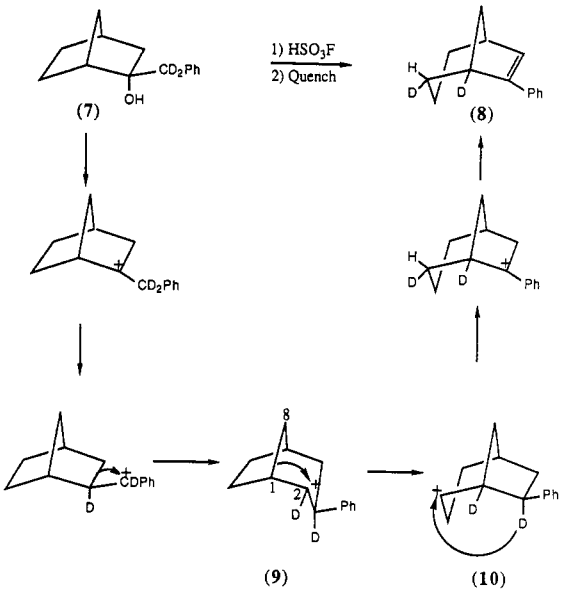
(6)

Unambiguous determination of the specific rearrangement mechanism was achieved by means of deuterium labeling of the benzylic protons. Thus reaction of α,α-dideuterio-2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol (**7**) as above gave 4,5-dideuterio-6-phenylbicyclo[3.2.1]oct-6-ene (**8**).[6] The mechanism consistent with these results is shown in Scheme II. Notable is the fact that both deuteride migration steps occur without loss of the deuterium label, thereby excluding the intermediacy of olefin or cyclopropyl intermediates[4,9] (i.e., deprotonation followed by reprotonation). Also of interest is the migration of the methano, rather than ethano, bridge of **9** to give **10**. While Wagner–Meerwein rearrangement involving ethano bridge migration is greatly preferred over methano bridge migration in bicyclo[2.2.1]heptan-2-yl (2-norbornyl) cations, for the bicyclo[3.2.1]octan-2-yl system overlap of the C1–C8 bond with the vacant p orbital at C2 is increased, thereby facilitating methano bridge migration.

Scheme I



Scheme II



(1) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847.
(2) All new compounds gave satisfactory spectra and elemental analyses in accord with the proposed structures.
(3) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089.
(4) Wolf, A. D.; Farnum, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 5175.
(5) Krow, G. R. *Tetrahedron* **1987**, *43*, 3.
(6) Location of the label in the product was established by a combination of ^1H, ^2H, and ^{13}C NMR spectroscopy.
(7) Separate experiments using 3-exo and 3-endo monodeuterio alcohols showed that the loss of deuteron was nonstereospecific.
(8) Bridgehead migration would result in formation of the 2-phenylbicyclo[3.2.1]octan-2-yl cation, derivatives of which have been shown[4] to rearrange to derivatives of **2**. However, by this mechanism **5** would produce the 4,4-dideuterio-2-phenylbicyclo[3.2.1]octan-2-yl cation which would then rearrange[4] to the 8,8-dideuterio-6-phenylbicyclo[3.2.1]octan-6-yl cation.
(9) Coxon, J. M.; Steel, P. J. *Aust. J. Chem.* **1979**, *32*, 2441.

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