



Stereoelectronic control in the solvolysis of spiroepoxidic 1-norbornyl triflates: unexpected reactivity in 3-bromomethyl derivatives

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ARTICLE INFO

Article history:

Received 27 December 2010

Revised 25 January 2011

Accepted 1 February 2011

Available online 17 February 2011

This article is dedicated to Professors Carlos Álvarez Ibarra and María Luz Quiroga Feijóo, our dear colleagues and friends, on the occasion of their retirement

Keywords:

1-Norbornyl cations
Stereolectronic effects
Domino reactions
Rearrangements

ABSTRACT

Interesting norbornane-fused tetrahydrofurans, with an additional synthetically-valuable vicinal dioxy-substitution in the norbornane skeleton, are enantiospecifically obtained in high yield from epimeric camphor-derived 3-*endo*-bromomethyl-substituted spiroepoxidic 1-norbornyl triflates. The process takes place via a domino reaction stereoelectronically controlled by the bromine atom. The described process has synthetic value, since it opens the way for a future enantiospecific preparation of 2,3-disubstituted tetrahydrofurans from camphor.

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1. Introduction

So far, the solvolysis of 1-norbornyl triflates **1** has attracted the attention of many organic chemists,¹ since it allows not only the easy generation of valuable 1-norbornyl derivatives (e.g., anti-Influenza 1-norbornyl amine **3** in Fig. 1),² but also the study of the interesting non-planar bridgehead 1-norbornyl cations **2**.³

We have demonstrated that the solvolytic reaction of several 1-norbornyl triflates can take place with a stereocontrolled rearrangement of the norbornane skeleton, allowing the interesting generation of new norbornanes, bicyclo[2.1.1]hexanes, cyclohexanes, cyclopentanes or, inclusive, cyclobutanes (Fig. 1).⁴ On the other hand, the easy enantiospecific access to several substituted 1-norbornyl triflates from commercial camphor or fenchone (reaction of 1-methylnorbornan-2-ones with buffered TiF_2O)⁵ expands the synthetic interest of the 1-norbornyl-triflate solvolysis reaction (Fig. 1).

Going in this line, some years ago we became interested in the solvolytic study of spirocyclopropanated 1-norbornyl triflate **4** (Fig. 2),⁶ due to the special structure of its corresponding

1-norbornyl cation intermediate (a cyclopropylcarbanyl cation). Fenchone-derived triflate **4** was then demonstrated to solvolyze without any rearrangement, giving place to the spirocyclopropanated 1-norbornanol **5** (Fig. 2), through the corresponding non-planar 1-norbornyl cation.⁶

After that, we discovered that the simple introduction of an oxygen atom in the cyclopropane moiety of **4**, makes analogues **6** to undergo solvolysis through a stereocontrolled C6–C1-to-C6–C2 pinacol-type Wagner–Meerwein rearrangement, leading to 1-hydroxymethyl 2-norbornanone **7** (Fig. 2).^{4a} Curiously, changing only the position of the *gem*-dimethyl substitution, from C7 in fenchone-derived **6**, to C3 in camphor-derived **8**, activates a stereocontrolled C3–C2-to-C3–C1 Wagner–Meerwein rearrangement, giving place to the interesting bicyclo[2.1.1]hexane-based α -hydroxyketone **9** (Fig. 2).^{7,4a}

Recently, we have also discovered that the introduction of an additional spiroxirane ring in the C7 norbornane position of **8**, makes the corresponding bis(spirocyclopropanated) 1-norbornyl triflate **10** undergo solvolysis under stereocontrolled C4–C7-to-C4–C1 Wagner–Meerwein rearrangement, to generate the synthetically-interesting eight-member cyclic ether **11** (Fig. 2).^{4e}

These seminal results show the rich chemistry of the spiroepoxidic 1-norbornyl triflates,^{4a,e,7} which, due to its stereocontrolled

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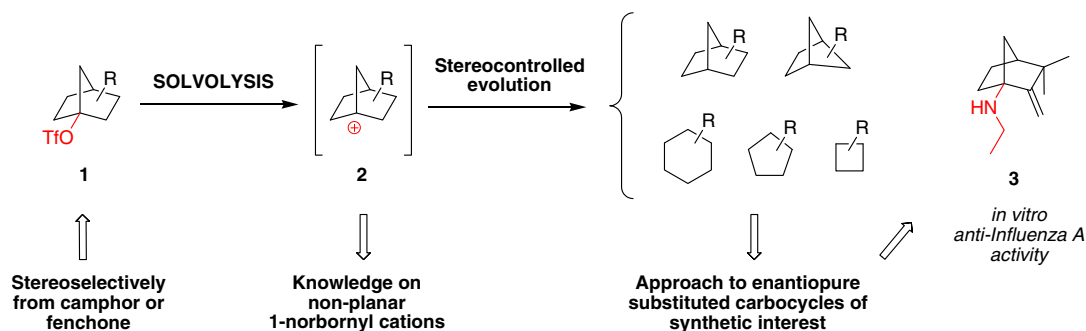


Figure 1. Utility of the 1-norbornyl-triflate solvolysis reaction.

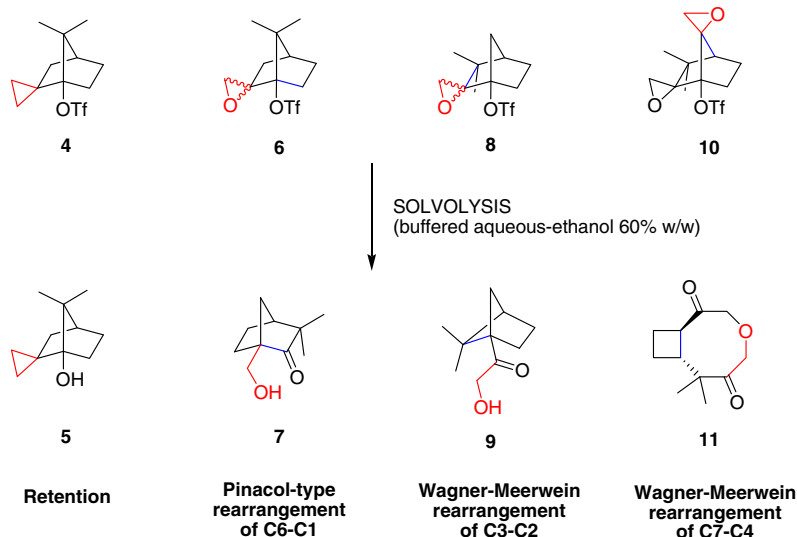
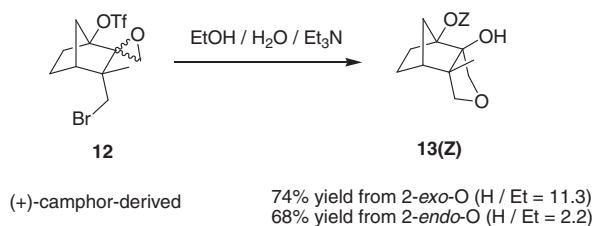


Figure 2. Different types of solvolysis of 1-norbornyl triflates (rearranging norbornane bond in blue).

character, could be a useful synthetic tool for the enantiospecific preparation of interesting substituted carbocyclic structures from terpenic camphor or fenchone.

2. Results and discussion

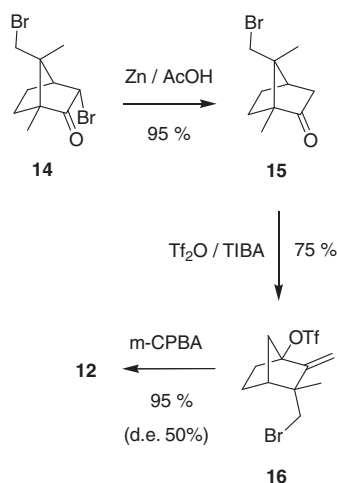
Continuing with the above-mentioned studies on the solvolytic behavior of spiroepoxidic 1-norbornyl triflates, we have now found that the attachment of a bromine atom at the *endo*-methyl group of **8**, makes the corresponding bromo analogues **12** to solvolyse without any norbornane rearrangement, leading to the interesting dioxy-substituted norbornane-fused tetrahydrofurans **13(Z)** (Scheme 1).^{8,9} The solvolysis was carried out individually for each epimer under the standard conditions used previously by us for the



Scheme 1. Unexpected solvolysis of epimeric triflates **12** (Z = Et and H).

reaction of related spiroepoxidic 1-norbornyl triflates (i.e., refluxing aqueous ethanol buffered with triethylamine).^{4a,e,7}

This new result has an important synthetic interest, since it constitutes the first example for the stereoselective construction



Scheme 2. Preparation of triflates **12**.

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