

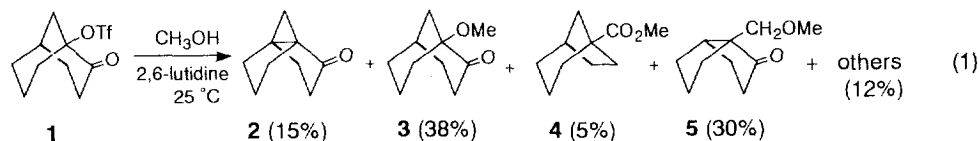
## Formation of a Propellanone in the Solvolysis of a 2-Oxo Bicyclic Bridgehead Compound

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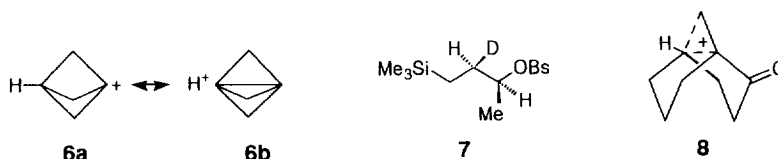
**Abstract:** Methanolysis of 2-oxobicyclo[3.3.1]non-1-yl triflate gives the corresponding [3.3.1]-propellanone **2** in 15% yield. Primary factors involved in the reaction would be the marked electrophilicity of the destabilized 2-oxo bridgehead carbocation and stabilization of the cyclopropane ring of **2** by the  $\pi$  acceptor carbonyl group. Copyright © 1996 Elsevier Science Ltd

The solvolysis of bridgehead compounds has been an actively studied subject in physical organic chemistry.<sup>1,2</sup> We herein report that the methanolysis of 2-oxobicyclo[3.3.1]non-1-yl trifluoromethanesulfonate (triflate) (**1**) gives [3.3.1]propellanone **2** (2,3,5,6-tetrahydro-3a,6a-methano-1*H*,4*H*-pentalen-1-one) besides the three methoxylated products **3** – **5** that we previously described (eq. 1).<sup>3</sup> To our knowledge, this finding provides the first example of the  $\sigma$  bond formation between a bridgehead cationic carbon and another bridgehead carbon in solvolysis.<sup>4</sup>



In a previous communication, we reported that the methanolysis of **1** (0.02 mol l<sup>-1</sup>) in the presence of excess 2,6-lutidine (0.025 mol l<sup>-1</sup>) at 25 °C for 140 h (11 half-lives) yielded **3** – **5** and a mixture of unidentified products (27%).<sup>3</sup> By careful investigation of the unidentified products, we found that **2** was formed in 15% yield and succeeded in its isolation by liquid chromatography. The identification of **2** rests upon the exact mass and perfect agreement of the <sup>13</sup>C NMR and IR data with those reported for **2** that was derived by cyclopropanation of a ketal of 2,3,5,6-tetrahydro-1*H*,4*H*-pentalen-1-one.<sup>5-7</sup> The formation of **2** is highly dependent on solvent: in 2,2,2-trifluoroethanol or acetic acid buffered with 2,6-lutidine or sodium acetate, respectively, **2** was not detected to the limit of detection (1%) by <sup>13</sup>C NMR and GLC.

The mechanism for the formation of **2** is not necessarily clear. A possible mechanism involves the homohyperconjugative interaction of the bridgehead cationic p orbital with the sp<sup>3</sup> back lobe on the other bridgehead carbon. For example, resonance stabilization **6a** ↔ **6b** has been postulated to explain the unexpectedly facile formation of the bicyclo[1.1.1]pent-1-yl cation in solvolysis.<sup>8,9</sup> Promotion of the homohyperconjugative interaction by a silyl substituent has been demonstrated in the solvolysis of an open-chain system **7**.<sup>10</sup> Alternatively, a  $\sigma$ -bridged ion **8** might be formed and deprotonated to give **2**. The intermediacy of **8** can also account for the formation of **5**.



Whatever the precursor to **2** may be, we assume that **1** gives an unbridged carbocation as the first intermediate. Concerted processes, in which the  $\sigma$  bond is formed between the bridgehead carbons simultaneously with departure of the nucleofuge ( $\text{TfO}^-$ ) and deprotonation, or **8** is formed synchronously with ionization, may be less probable. The complex product pattern of eq. 1 would preclude the possibility of concerted processes and the solvolysis of **1** does not appear to be accelerated by neighboring group participation.<sup>3</sup>

It seems to us that the propellane formation is characteristic of highly destabilized bridgehead carbocations. In fact, the conjugatively stabilized 2-methylenebicyclo[3.3.1]non-1-yl cation gave only the bridgehead substitution product in methanol.<sup>3,11</sup> For the moment, we postulate that two factors are principally responsible for the formation of **2**. First, 2-oxo carbenium ions are highly electrophilic.<sup>12</sup> Secondly, the carbonyl group stabilizes **2** by working as a  $\pi$  acceptor to the cyclopropane ring.<sup>13</sup> Studies on structural requirements of bridgehead carbocations that give propellanes and the mechanism for their formation are in progress in this laboratory.

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