



# $^1\text{H}$ NMR-based kinetic and theoretical studies of the simultaneous formation of two discrete rotameric systems of a novel difenchyl sulfite ester



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## ABSTRACT

Attempted repetition of a reported synthesis of fenchene from fenchol has afforded, in high overall yield, a mixture shown by spectroscopic and elemental analysis to comprise a pair of discrete rotameric systems of a novel 2-endo-2'-endo-difenchyl sulfite ester. The kinetics of the formation of these dimeric rotameric systems (**I** and **II**) has been explored experimentally, using  $^1\text{H}$  NMR spectroscopic analysis, and theoretically at molecular and quantum mechanical levels. Construction of a theoretical model has permitted calculation of rate constants for each of the steps, while modelling of the transition state complexes corresponding to the rate-determining steps for the formation of the rotameric systems **I** and **II** has revealed their independent access to further sets of interconverting rotamers.

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## 1. Introduction

Norbornyl and substituted norbornyl systems often react in unexpected ways. When carbocation intermediates are involved, many mechanistic pathways may be possible and a range of products may be observed.<sup>1</sup> As part of an ongoing mechanistic study of the racemization of a bornyl-derived tosylate,<sup>2</sup> the  $^{13}\text{C}$ -labeled L-camphor **3** was required to distinguish possible racemization pathways. The synthesis of L-camphor **3** from fenchol **1** was proposed to involve oxidative cleavage of the double bond in the intermediate fenchene **2** and subsequent alkylation of a bridgehead carbon with  $^{13}\text{C}$ -labeled methyl iodide (Scheme 1).

Access to the intermediate fenchene **2** was expected to involve reaction of fenchol **1** with thionyl chloride, followed by dehydrohalogenation and concomitant Wagner-Meerwein rearrangement of the chlorinated intermediate **5** as outlined in Scheme 2 (Path A). In the event, this reaction followed a very different course and, in this paper, we report on the characterization of the products, which were actually isolated, and on kinetic and theoretical studies undertaken to elucidate their formation.

## 2. Results and discussion

### 2.1. Attempted synthesis of fenchene **2** and formation of isolable rotamers of difenchyl sulfite ester **6**

Literature procedures for the synthesis of fenchene **2**,<sup>3,4</sup> were followed but the white crystalline material obtained in high yield was shown to comprise a mixture of two products.  $^1\text{H}$  NMR spectroscopic analysis indicated the presence of a major product **6a**, characterized by a pair of doublets with a small coupling constant (2 Hz) at 3.94 and 4.10 ppm, and a minor product **6b** exhibiting a pair of overlapping doublets at 4.02 ppm. A correlated spectroscopy experiment confirmed that the protons responsible for each pair of doublets were coupled with each other via long-range coupling. After purification using column chromatography,  $^1\text{H}$  NMR analysis of each of the isolated products indicated the presence of six methyl singlets (this was confirmed using multiplicity-edited HSQC), compared with three methyl singlets for the starting material, fenchol **1**, indicating that both “products” (**6a** and **6b**; Scheme 2; Path B) were dimeric. These “products” were later identified as discrete rotameric systems (**I** and **II**) of 2-endo-2'-endo-difenchyl sulfite. Due to slow interconversion between these two “products” (as discussed later) it was not possible to obtain either in absolutely pure form; their formation, however, was reproducible under several variations of the reaction conditions (A–E: Table 1) in which

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