

## Structural assignment of the trimethylsilyl-protected cyanohydrins of *R*-(-)-carvone.

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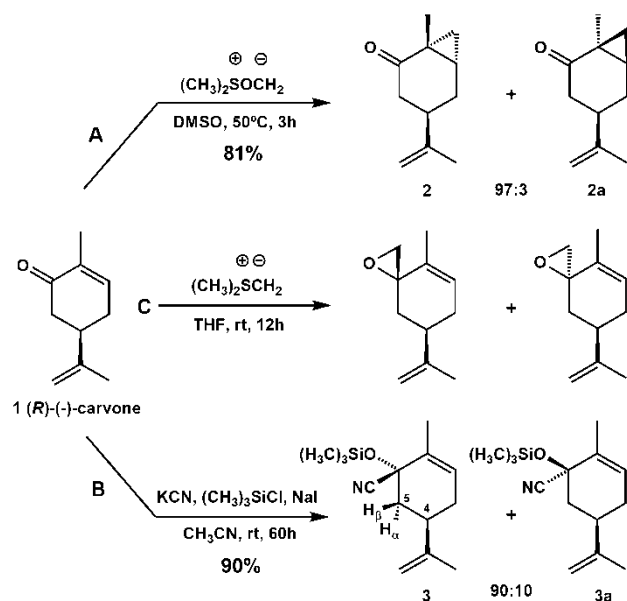
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### INTRODUCTION

In the course of our studies on the synthesis of perhydroazulene terpenes,<sup>1</sup> we have already determined the structures **2** and **2a**, and the (*dr*), of the cyclopropanation of *R*-(-)-carvone (**1**)<sup>2</sup> (Scheme 1, A). We now present a similar study of the 1,2 addition of cyanide (Scheme 1, B).

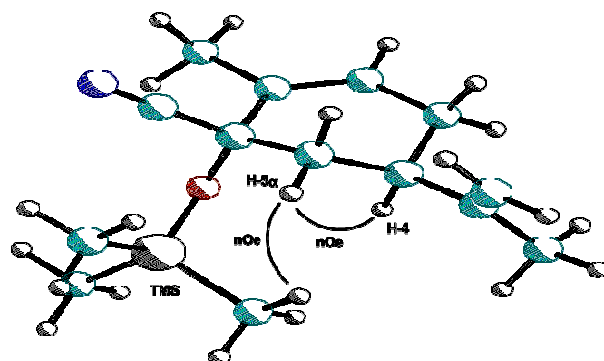
### RESULTS AND DISCUSSION

The formation of the TMS protected cyanohydrins of **1** furnished compounds **3** and **3a** in 90:10 ratio.



**Scheme 1.** A) cyclopropanation, B) cyanide addition, and C) epoxidation of *R*-(-)-carvone.

The proportion of the diastereomeric mixture was determined by gas chromatography of the non-purified product. The assignment of stereochemistry was deduced by several nOe irradiations, and complemented by conformational search (force field MMX) for comparison (Figure 1).



**Figure 1.** Minimized energy structure of the major diastereomer, and indication of observed nOe.

A strong nOe effect was observed between H-4 and H-5 $\alpha$ , as well as between the same H-5 $\alpha$  and the H of the TMS group, thus confirming that the cyanide group is *cis* with respect to the isopropenyl group in **3**. A complete assignment of this product was also performed by a 2D-NMR analysis, which is in agreement with this attribution.

### CONCLUSION

The *dr* of nucleophilic addition of cyanide to *R*-(-)-carvone was determined to be 90:10, the major isomer having the cyanide group *cis* to the isopropenyl group. Other studies, including the structural assignment of the diastereomers of 1,2 methylide epoxidation of **1**,<sup>3</sup> are being conducted (Scheme 1, C).

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