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

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INTRODUCTION

In the course of our studies on the synthesis of perhydroazulene terpenes,1 we have already determined the structures 2 and 2a, and the (dr), of the cyclopropanation of R-(-)-carvone (1)2 (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.

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-5α, as well as between the same H-5α 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 methylene epoxidation of 1,3 are being conducted (Scheme 1, C).

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