



Michael type reactions mediated by NbCl₅.

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INTRODUCTION

Over the years researchers have been increasingly interested in the Michael addition [1], because this is one of the most useful reactions for the construction of carbon-carbon bonds, particularly in the synthesis of naturally occurring products and compounds with biological and pharmacological activity [2].

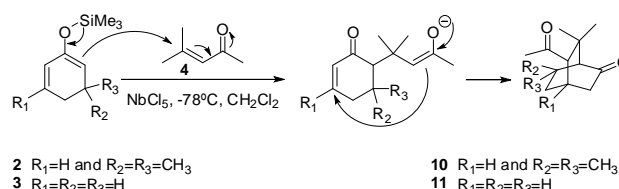
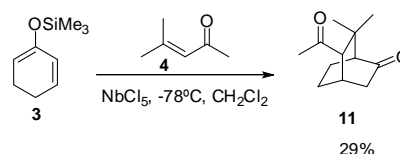
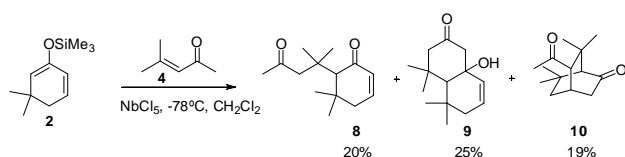
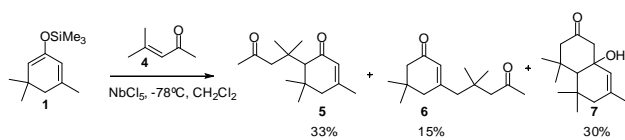
We report here some experimental results involving NbCl₅ mediated Michael addition followed by cyclization to bicyclic systems. Bicyclic compounds are traditionally synthesized through Diels Alder reactions. In this work, bicyclo[2.2.2]octan-2-ones have been synthesized using cross-conjugate dienes derived from cyclohexenones [3].

RESULTS AND DISCUSSION

In the course of our studies on the synthesis of natural products we directed our attention to the reaction between dienol silyl ethers (**1-3**) with mesityl oxide (**4**) mediated by NbCl₅.

In these reactions we obtained Michael adducts (**5, 6** and **8**) in 15 - 33 % yield, together with bicyclic products (**7, 9, 10** and **11**) (Schemes 1 - 3).

Compounds **7, 9, 10** and **11** are formed by further Robinson type condensation or a second Michael addition (Scheme 4) on the intermediates.



The bicyclic product analogous to **10** and **11** is not formed in the reaction with **1**, possibly due to the sterical hindrance [4] produced by the extra methyl group (R₁ ≠ H).

CONCLUSION

In these studies we obtained interesting compounds through Michael type reactions. The double Michael addition is a convenient alternative to Diels-Alder reactions for the preparation of bicyclo[2.2.2]octan-2-ones.

Products of the Robinson type condensation were also obtained.

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Capes, CNPq, FAPESP.

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