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MICROWAVE-INDUCED BISMUTH NITRATE-CATALYZED INTRAMOLECULAR DIELS-ALDER REACTION

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Abstract: Microwave-induced bismuth nitrate-catalyzed intramolecular Diels Alder reaction has been perfomed with a diene derived from optically active citranellal toward a tricyclic system.

Keywords: Microwave, Diels-Alder Reaction, Citranellal

Introduction:

Tricyclic nitrogen-containing systems are important fragments of natural product. Bismuth nitrate-catalyzed microwave-induced reaction has been used to prepare these types of compounds.

Results and Discussion:

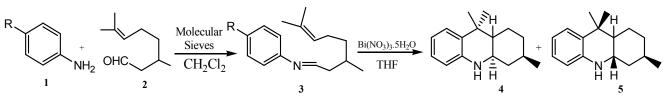
Diels-Alder reaction is perhaps the most important reaction for the construction of the polycarbocyclic and polyheterocyclic compounds. Acidic reagents have been used to accelerate this cyclization reaction extensively. In previous publications, we reported a few bismuth nitrate-catalyzed reactions.¹ In some cases, microwave irradiation method was very helpful to accelerate the process and to obtain better yield of the products.² In this paper, we report microwave-assisted intramolecular Diels-Alder reaction of diene to the corresponding tricyclic system.

The diene was prepared by reacting with citranellal (2) and aromatic amine (1) using molecular sieves. After filtration, the crude diene (3) was treated with bismuth nitrate and irradiated in a CEM microwave for 10 minutes (power levels 300 watts and temperature 50°C) using THF as the solvent. This reaction produced tricyclic system (Scheme 1). The NMR analysis indicated the presence of two isomers (*cis* and *trans*) in a ratio of 20:80.

This method is simple and mild compared to the other available methods for the synthesis of these types of compounds. This reaction produced product without microwave irradiation. However, more time (2h) was needed for complete consumption of starting compound. No reaction took place in absence of bismuth nitrate. An excess use of bismuth nitrate was found to be problematic since the starting imine is not very stable under acidic conditions. For success of the reaction, appropriate concentration of the catalyst and substrate in THF was necessary. From

a few experiments, 10 mol% catalyst was found to be ideal for this reaction when reaction was conducted with 1 mmol of the substrate in 10 mL of THF.

Scheme 1:



Conclusion:

An excellent bismuth nitrate-catalyzed microwave-assisted intramolecular Diels Alder reaction for the preparation of tricyclic nitrogen-containing system has been demonstrated using appropriately substituted starting compounds.

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