Beta Lactams and Products

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Discovery and synthesis of penicillin and other beta-lactam antibiotics have received sustained attention. The use of *β*-lactam antibiotics is extensively documented in several thousand of publications. In modern times, microwave-induced reactions are also used extensively for the synthesis and stereochemical studies of diverse *β*-lactams. In this paper, the author describes a few crucial reactions that are performed toward the synthesis of *β*-lactams and products obtained from them under classical conditions as well as by domestic or automated microwave oven.

Beta Lactam | Synthesis | Microwave | Stereochemistry | Environmentally Benign

1. Introduction

Since the discovery and synthesis of penicillin, numerous *β*-lactam antibiotics have received attention. The use of *β*-lactam antibiotics is extensively documented in several books [1]. In modern times, microwave-induced reactions have been used extensively for the synthesis of diverse *β*-lactams. In this paper, the author describes some of the notable reactions that are performed toward the synthesis of *β*-lactams and products obtained from them under classical conditions as well as by domestic or automated microwave oven.

2. Results

We have been engaged in chemical and medicinal research on *β*-lactams for the past many years. This endeavor has become successful in the synthesis of diverse molecules. In particular, many of the products are prepared using domestic and automated microwave oven. A few reactions that are developed in our laboratory on *β*-lactams are mentioned in this perspective. To know these reactions in details, it is advised to go through the original references.

3. Synthesis of Racemic β-Lactams

Reaction of acid chloride (equivalent) with imine in the presence of a tertiary amine was performed. This method is called Staudinger cycloaddition reaction. A diverse range of acid chlorides and imines were studied for the preparation of β-lactams. In many instances, cycloaddition was successful and high yields of the products with defined stereochemistry were obtained [2].

These reactions were also conducted using chlorobenzene, DMF, dichloroethane or in the absence of any solvents in automated or domestic microwave oven. The temperature of the reaction was 50-90^{0}C. In some examples, *cis*

and *trans* β-lactams were formed [3].

A wide range of acid chlorides or activated acids were used successfully. Acetoxyacetyl chloride, benzyloxyacetyl chloride, phthalimidoacetyl chloride, phenoxyacetyl chloride, crotonyl chloride, phenylthio acetyl chloride, and butyryl chloride were employed for this purpose. The imines (Schiff bases) were prepared from aliphatic and aromatic primary amines by the reaction with carbonyl compounds (aldehydes and ketones) using a dehydrating agent. The stereochemistry of the β-lactams formed depended on many factors. The composition of the imine, acid chloride, conditions of the experiment and irradiation time was the crucial factors in determining the configuration of the β-lactams. The diastereoselectivity of the β-lactams was altered by changing the conditions of the experiments and adjusting the power of microwave [2][3].

4. Synthesis of Optically Active β-Lactams

Optically active β-lactams were synthesized following cycloaddition under classical and microwave irradiation method. It was also possible to control the product distribution by adjusting the conditions of the experiments. Some reactions were enantioselective. In some instances, an alteration of the absolute stereochemistry was not possible by changing the conditions of the experiments. The cycloaddition followed kinetically or thermodynamically-controlled pathway depending upon the structures of the starting materials and the conditions of the reaction [4].

5. Synthesis of Racemic and Optically Active Anticancer β-Lactams

Reaction of polyaromatic imines with acid chlorides produced *trans* β-lactams as the only products. However, conjugated polyaromatic imines preferred to form *cis* β-lactams. Microwave-induced reaction produced identical *trans* β-lactams. Trisubstituted polyaromatic imines produced a mixture of two isomeric products under microwave irradiation. A few *trans* β-lactams with angular ring system demonstrated anticancer activities *in vitro* against numerous cancer cell lines [5][6].

6. Synthesis of Glycosylated β-Lactams

The 3-hydroxy group of racemic and optically active β-lactams was reacted with a number of glycals in the presence of catalytic amounts of iodine. This reaction proceeded stereospecifically and separable glycosides were obtained. Finally, optically active β-lactams in enantiomeric forms were obtained [7]. Bismuth salts were also effective in catalyzing this process. Some of these methods were also investigated under automated microwave oven.

7. Synthesis of Amino β-Lactams

The preparation of amino β-lactams was performed by the reaction of phthalimido β-lactams with methyl hydrazine. The same compound was prepared using a domestic or an automated microwave oven. An extremely fast deprotection of the phthalimido group was observed [8]. No ring rupture of the β-lactam system was detected.

8. Synthesis of Pyrrole-Substituted β-Lactams

Iodine-catalyzed condensation of β-lactams with 2,5-hexane dione and 2,5-dimethoxytetrahydrofuran under microwave-assisted reaction produced pyrrole-substituted β-lactams. Bismuth salts were also used successfully for this reaction. This procedure was performed with racemic and chiral substrates. A microwave-induced reaction of racemic 3-keto β-lactam with optically active hydroxyl proline derivatives in the presence of mild acidic reagents afforded optically active *cis* and *trans* pyrrole-substutued β-lactams [9].

Hydrogenolysis and Hydrogenation of β-Lactams

Microwave-induced hydrogenolysis of the 3-benzyloxy group to the hydroxy group was performed by catalytic transfer hydrogenation. A number of hydrogen donors (ammonium formate, sodium formate and hydrazine) in the presence of Pd/C or Raney nickel were able to induce this transformation. The alkene group was hydrogenated smoothly by this condition. In some examples, a cleavage of the N-C4 bond was occurred. Non-cyclic amides were formed through this bond breakage reaction in some examples. The presence of multicyclic aromatic rings inhibited the cleavage of the bond [10].

9. β-Lactams as Synthons

Microwave-induced reaction of substituted β-lactams was used for molecular rearrangements to heterocyclic compounds [10]. A nucleophilic attack to the ring followed by the rearrangement was responsible for the overall success of this process. The ring rearrangement was the only route due to the strain present in the β-lactam system [10]. A few multicyclic β-lactams were prepared by radical-mediated and azide-alkyne cyclization methods [11].

10. Advantages of Microwave-Induced Reactions

Heating with a mantle or oil bath heats the walls of the vessels by convection or conduction. The reactants require longer time to be activated. On the other hand, microwave irradiation raises the temperature spontaneously. Our research had identified several advantages of microwave-induced reactions [3]. This includes fast reactions, mild method, useful selectivity, less solvent, high yield of the products and environmentally benign processes.

11. Conclusions

Synthesis of diverse β-lactams and products derived from them has become extremely useful. The results obtained as described herein by domestic and automated microwave oven remain identical. Microwave-mediate reactions are completed within minutes instead of hours that are required for reactions under conventional methods.

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