

Conjugate systems in the construction of heterocycles and quaternary stereocenters*

Carlos González-Romero, Pablo Bernal, Fabiola Jiménez, María del Carmen Cruz, Aydeé Fuentes-Benites, Adriana Benavides, Rafael Bautista, and Joaquín Tamariz[‡]

Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Prol. Carpio y Plan de Ayala, 11340 México, D.F. Mexico

Abstract: The synthetic application of 4,5-bis-alkylidene-1,3-oxazolidin-2-ones led to the efficient and regioselective synthesis of 2-(3*H*)-benzoxazolones and diarylamines with a short methodology. They were also valuable synthons in a total synthesis of naturally occurring carbazoles. New enantiopure 4-oxazoline-2-one and 4-methylene-2-oxazolidinone were prepared via a one-pot microwave (MW)-promoted condensation of α -ketols and an enantiopure isocyanate. These enamides were efficient nucleophiles when added to Michael acceptors to give a series of compounds with quaternary stereocenters in fairly good stereoisomeric ratios. The novel approach for the synthesis of benzofurans and indoles by intramolecular cyclization of enamminones has been applied in the preparation of furobenzofurans starting from benzo-bis-enaminones.

Keywords: 4,5-dimethylene-2-oxazolidinone dienes; carbazoles; 4-oxazolin-2-ones; enamminones; furobenzofurans.

INTRODUCTION

Among the conjugate π -systems, dienes, enones, enamines, and enamminones are some of the most useful building blocks in organic synthesis. Dienes are intimately related to the milestone Diels–Alder reaction for the preparation of the core of substituted cyclohexenyl derivatives [1]. Enones have also been involved in Diels–Alder additions as dienophiles [1] and heterodienes [2]. Moreover, they have proved to be conjugate acceptors in Michael nucleophilic additions [3]. Among these, enamminones are also privileged Michael acceptors in the addition of a large variety of nucleophiles, due to the activation of the conjugate π -system by the amino group [4]. In contrast, enamines and enamides are currently associated to nucleophilic species as neutral enolate equivalents [5].

Over the years, our interest in Diels–Alder reactions led to the design of a one-pot synthesis of novel dienes, the N-substituted 4,5-bis-alkylidene-1,3-oxazolidin-2-ones **1**, through tandem condensation of aliphatic α -diketones **2** with isocyanates **3** [6] (Scheme 1). These dienes proved to be highly reactive Diels–Alder substrates, and readily underwent stereoselective and regioselective cycloadditions, yielding the corresponding adducts **4**, which were useful starting materials for the synthesis of aryl-

*Paper based on a presentation at the 16th International Conference on Organic Synthesis (ICOS-16), 11–15 June 2006, Mérida, Yucatán, México. Other presentations are published in this issue, pp. 153–291.

[‡]Corresponding author: Fax: +5255-5729-6300/46211; E-mail: jtamariz@woodward.enqb.ipn.mx