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Ring-closing metathesis on deactivated allyl-phosphonates and –phosphoramidates: access to dihydrophosphinine oxides bearing an ester group.

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ABSTRACT

The preparation of new allylphosphonates and allylphosphoramidates bearing alkoxycarbonyl substituents is described. Both P-based precursors were subjected to RCM. In this context, several Ru-based catalysts were tested and compared in order to prepare new oxa- and aza-dihydrophosphinine oxides. P-heterocycles and homodimers have been obtained depending on the nature of the catalyst and the reaction conditions. In addition, homodimers were converted into six-membered cyclic phosphonates and phosphoramidates under Ru-promoted conditions.

Introduction

Phosphinine oxide derivatives belong to the large family of P-heterocycles that continuously attracted the attention of the scientific community over the last two decades. One phosphorus atom linked to second heteroatom such as oxygen or nitrogen within the cyclic unit was of especial interest during this time frame by three main aspects: (i) such six-membered heterocycles displayed a wide array of biological activities. (ii) the modulation of these activities was closely related to the presence of various and valuable substituents. (iii) the selective construction of such heterocyclic targets remained a synthetic challenge.

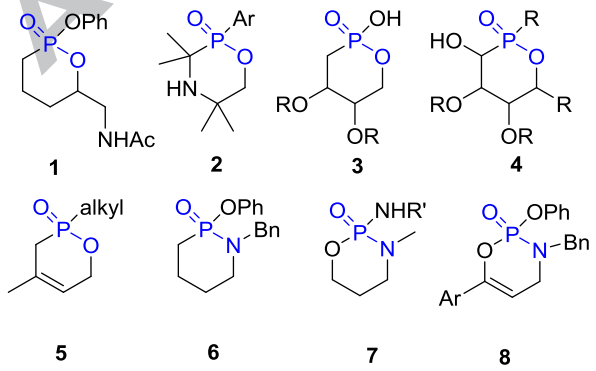

Figure 1. Biologically active phosphinine oxide derivatives.

As examples, phosphinine oxide **1** efficiently prevents antibody-catalyzed formation of lactones,[1] azoxaphosphinine oxide **2** is a close structural analogue of antidepressive hydroxybupropion,[2] polyoxygenated heterocycles **3** and **4** display anti-proliferative properties and are considered as P-sugar or (lyso)phosphatidic acid analogues.[3] More complex and fused phosphinine oxides can be further found in functionalized hydroxyvitamin D_2 analogues.[4] Azaphosphinine oxides **6** and **7** are potent biodegradable insecticides and renowned examples of anti-tumor alkylating agents respectively.[5] Dihydro-phosphinine oxides such as **5** and **8** are considered as a key precursors in sequences leading to phosphinine oxide targets. Indeed, most of such building blocks allowed a selective introduction of valuable substituents towards derivatives that exhibit potential biological activities.

In this context, the construction of dihydro-P-heterocycles continues to receive widespread attention of the scientific community and the popular ring closure metathesis (RCM) rapidly emerged as a powerful tool that led to appealing synthetic advances in this area. The synthesis of dihydro-phosphinine oxides as well as diverse phosphorus heterocycles using metathesis has been thoroughly reviewed.[6] Despite recent reports,[7] only a few studies have reported the RCM of bisallylphosphonates and bisallylphosphoramidates (Scheme 1).[3b,3d,8]

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