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총설

루테늄 카벤 촉매 복분해 상호교환 반응과 피리듐 염 광화학반응을 이용한 유기 합성

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Organic Synthesis Based on Ruthenium Carbene Catalyzed Metathesis Reactions and Pyridinium Salt Photochemistry

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요약. 이 총설 논문에서는 천연물 합성에서 새로운 합성전략으로 이용될 수 있는 세가지 합성방법에 대해 간단히 소개하고자 한다. 소개된 첫 번째 방법으로는 Grubbs에 의해 개발된 루테늄 카벤 촉매 고리 전이 복분해 반응을 이용한 합성방법으로 이 방법을 이용하여 알켄기로 치환된 사이클로알켄들을 열역학적으로 더 안정한 알켄기 치환 사이클로알켄으로 전환시킬 수 있어 새로운 유기합성과정으로 소개되었다. 두 번째 Grubbs에 의해 보고된 루테늄 카벤 촉매 다이엔아인 복분해 반응을 이용한 합성방법으로 이 합성방법을 이용한 과정들은 다이엔아인 화합물들을 접합 두고리 콘쥬게이트 다이엔 화합물들을 합성할 수 있게 한다. 마지막으로 새로 개발된 피리디늄 염의 광-전자고리화반응을 이용한 4-아미노사이클로팬텐-3,5-다이올 유도체 화합물들을 합성할 수 있는 방법을 소개하였다. 이 총설에서 루테늄 카벤 촉매 고리전이와 다이엔인 복분해 반응들을 함께 연결 이용하여 폴리하이드록시 인돌리지딘 알카로이드들과 레파디포르민과 실린드리신 알카로이드들을 피리듐 염 광화학 반응법을 통해 합성한 과정들을 상세히 소개하고 있다.

주제어: 고리전이 복분해 반응, 다이엔아인 복분해 반응, 광화학, 천연물 합성

ABSTRACT. In this account, three synthetic methodologies that serve as the basis for new strategies for the preparation of selected natural products are briefly introduced. One process, involving ruthenium carbene catalyzed ring rearrangement metathesis developed by Grubbs and his coworkers, transforms alkene-tethered cycloalkenes to thermodynamically more favored alkene-tethered cycloalkenes. Another ruthenium carbene promoted reaction, referred to as dienyne metathesis, was uncovered in early studies by Grubbs and his collaborators. This process converts dienynes to fused bicyclic conjugated dienes. Finally, a novel photo-electrocyclization reaction of pyridinium salts, which leads to the formation of 4-aminocyclopenten-3,5-diol derivatives, is discussed. Examples are provided to show the utility of these methodologies in natural product synthesis. Emphasis is given to studies in which pyridinium salt photochemistry is coupled with ring rearrangement and dienyne metathesis in routes for the synthesis of polyhydroxyalted indolizidine alkaloids and the construction of the tricyclic core of the lepadiformine and cylindricine alkaloids.

Keywords: Ring rearrangement metathesis, Dienyne metathesis, Photochemistry, Natural product synthesis

INTRODUCTION

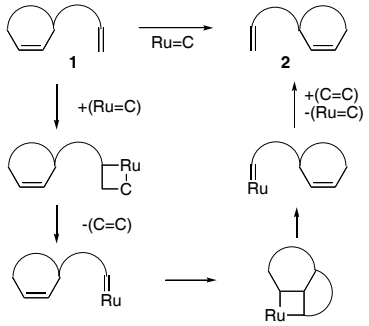
Since its advent in the mid 1900s, the flurry of activity centered on natural product synthesis has been driven in part by the desire to test new synthetic methodologies through their application to the construction of complex molecular structures. This feature, coupled with the development of mature procedures for designing approaches to targets, led to an enormous effort during the 1970-90 period aimed at the preparation of naturally occurring substances, especially those with interesting biological properties. The wave nature of interest in new methodologies that flowed through the organic synthesis community during this period is exemplified by related publications describing syntheses based on the same methodology. Reflecting this phenomenon are the grouped reports from numbers of research laboratories that

describe the use of methodologies, such as 2+2-photocycloaddition of enones and alkenes, intramolecular Diels-Alder reactions, in targeted synthesis.

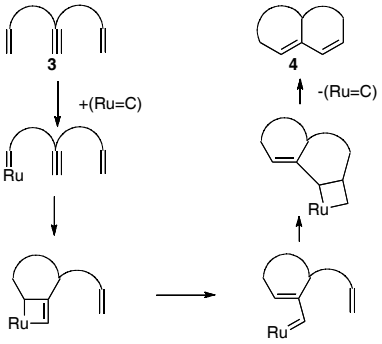
Albeit to a lesser degree, this trend has continued in recent years. Ruthenium carbene (Ru=C) catalyzed metathesis reactions exemplify newer methodologies that have attracted the wide interest of synthetic chemists.[1] As a consequence of the pioneering work of Grubbs and his coworkers, simple methods for performing incredibly versatile metathesis reactions were developed. In this "account," two interesting Ru=C promoted metathesis reactions will be discussed in the context of synthesis. One process, termed ring rearrangement metathesis (RRM),[2] transforms alkene tethered cycloalkenes **1** into new alkene tethered cycloalkenes **2** *via* the pathway shown in *Scheme* 1. Thermodynamic factors (*e.g.* release of ring strain) serve as driving forces for these processes. Another useful Ru=C induced reaction, referred to as dienyne metathesis (DYM),[3] takes place by a multi-stepped pathway in which a bis-alkene tethered alkyne **3** is transformed into a bicyclic conjugated diene **4** (*Scheme* 2).

Although much less spectacular and not as generally useful, photochemical reactions of pyridinium salts (PSP) represent a novel method for generating highly functionalized aminocyclopentenes from simple pyridine precursors in a highly stereocontrolled manner.[4] This process, outlined in *Scheme* 3, is initiated by excited state Nasarov-type cyclization of pyridinium salts **5** followed by stereocontrolled, exo-face nucleophilic addition to the intermediate bicyclic allylic cation **6** to form the bicyclic aziridine **7**. Owing to the inherent ring strain present in **7**, SN_2-type ring opening takes place either in a second synthetic step or under the photoreaction conditions to yield amino-cyclopentenes **8** with rigorously enforced trans, trans stereochemistry.

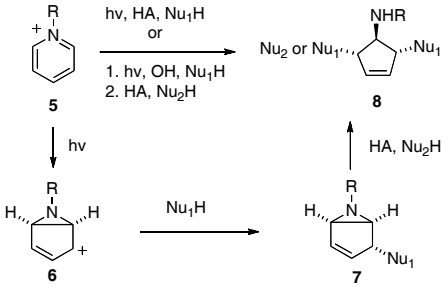
Two aims stimulated the preparation of this "account." Firstly, we wanted to summarize recent developments made in the applications of RRM, DYM and PSP methodologies in natural product synthesis. This is done below by describing selected examples in which these methods play key roles in routes for preparation of the targets. The second goal was to present the results of two studies carried out in our laboratory that focus on the combined use of PSP and Ru=C promoted metathesis processes in the construction of the structural backbones of two important natural product families. Although the results of most of the author's efforts described in this "account" have been published, some of the work has not yet been reported.



***Scheme* 1**



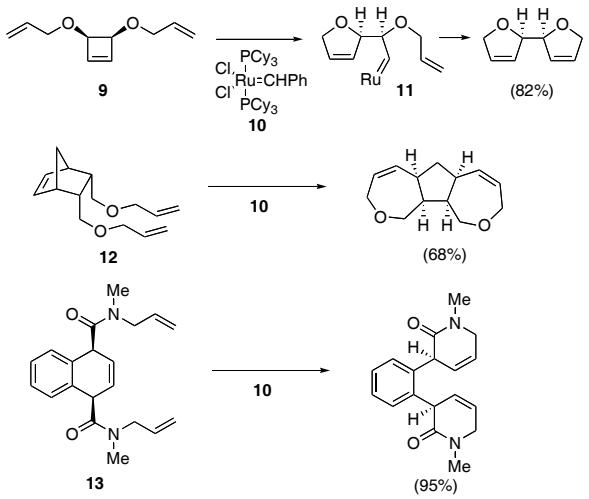
***Scheme* 2**



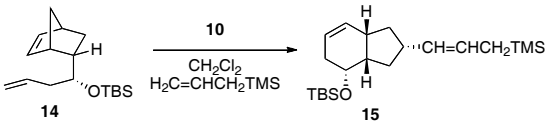
***Scheme* 3**

Ring Rearrangement Metathesis (RRM)

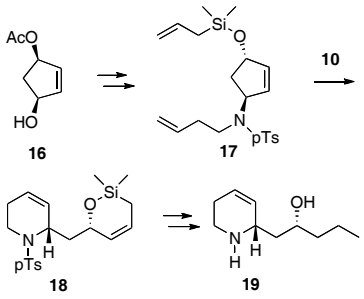
The seminal studies carried out by Zuecher, Hashimoto and Grubbs[5] on simple substrates demonstrated the high synthetic potential of Ru=C catalyzed RRM reactions. Selected examples from these earlier efforts are given in *Scheme* 4. For example, the symmetric bis-alkene tethered cycloalkenes **9**, **12** and **13** are efficiently converted to the corresponding rearranged products by treatment with 3 - 6 mol % of the first generation Grubbs catalyst **10**[6] under mild conditions (45 ^{o}C, C_6H_6). It should be noted the processes probed by Grubbs and his coworkers in this early effort represent special cases of RRM reactions in which initially formed Ru-alkylidene products (*e.g.* **11**, *Scheme* 4) undergo a final ring closing metathesis step.



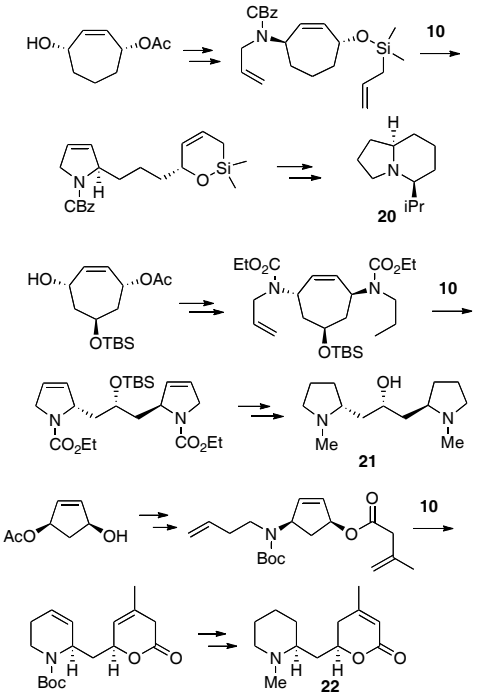
Scheme **4**



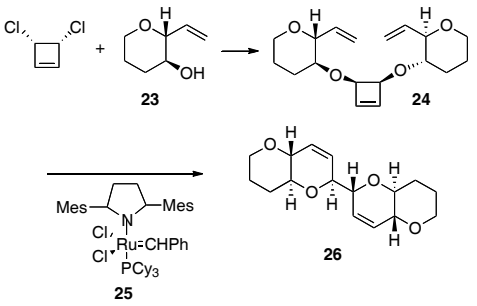
Scheme **5**



Scheme **6**



Scheme **7**



Scheme **8**

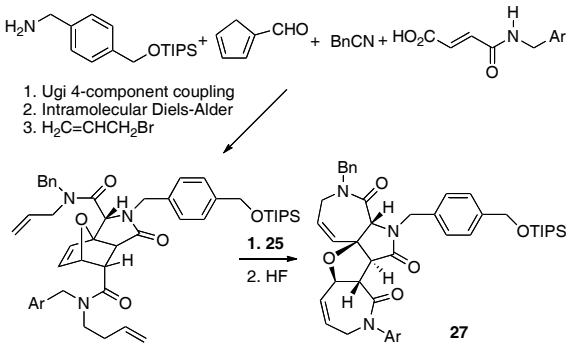
Additional examples of RRM reactions of simple substrates are found in studies by Stragies and Blechert, reported in 1998.[9] One example taken from this work (*Scheme* 5) involves the transformation of the alkene tethered norbornene **14** to the hydroindene **15**, catalyzed by using the ruthenium carbene **10**. This process is terminated by cross metathesis between the ruthenium alkylidene product and allytrimethylsilane.

Owing to the unique features of and mild conditions employed in these reactions, along with a high tolerance for diverse functional groups, RRM reactions have found wide application to the synthesis of natural and non-natural, biologically relevant substances. An early example was provided by Stragies and Blechert[10] in their synthesis of the piperidine alkaloid (-)-halosaline (**19**, *Scheme* 6). Two key features of this route are worth noting. Firstly, the sequence begins with the enantiomerically enriched cyclopentendiol mono-acetate **16**, generated by enzymatic desymmetrization of the corresponding meso bis-acetate. This substance is then converted to the aminocyclopentenol **17**, which undergoes RRM in a CH_2Cl_2 solution containing ruthenium carbene **10** to produce the tetrahydropyridine derivative **18**. This substance serves as a late stage intermediate in the synthesis of **19**.

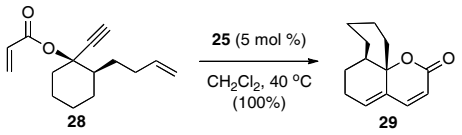
Other targeted synthesis applications of RRM processes developed by Blechert and his coworkers are outlined in *Scheme* 7. These include approaches to (-)-indolizidine 167B (**20**),[11] (+)-dihydrocuscohygrin (**21**)[12] and (+)-dumetorine (**22**),[13] all of which rely in the use of Grubbs' chemistry and exemplify highly concise routes for target preparation.

Another particularly interesting use of RRM chemistry comes from investigations by Nicolaou and his coworkers,[14] in which a novel strategy for construction of complex, cyclic polyethers was developed. In this effort, the bis-pyranyl cyclobutene **24** (*Scheme* 8), which serves as the substrate for the key RRM reaction, was generated by condensation of cis-3,4-dichlorocyclobutene with two equivalents of the sodium alkoxide derived from pyranyl alcohol **23**. Treatment of **24** with the second generation Grubbs ruthenium carbene catalyst **25**[15] promotes efficient conversion to the rearranged tetracyclic polyether **26**.

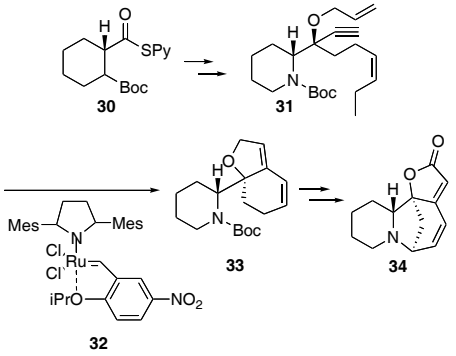
The final application of the RRM process that we will discuss comes from the work of Schreiber and his coworkers[16] aimed at the development of novel methods for diversity-oriented-organic-synthesis (DOOS). The key goal of DOOS is to prepare libraries of organic structures that can potentially govern (*e.g.* inhibit or activate) important biochemical pathways. Efforts in this area require the availability of techniques to produce a large array of different, structurally complex, yet related products in a concise manner. For this purpose, Schreiber and his coworkers designed a methodology that employs the tandem use of a group of well-known, complexity generating processes, including the Ugi-4 component condensation, Diels-Alder reaction, and RRM. The sequence, exemplified by the route shown in *Scheme* 9, enables rapid construction of a library of structurally complex tetracyclic bis-azepinanes **27**.



***Scheme* 9**



***Scheme* 10**



***Scheme* 11**

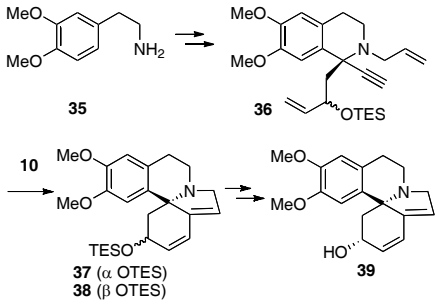
Dienyne Metathesis (DYM).

Many recent advances have been made in the application of DYM processes to the synthesis of natural and non-natural products. An excellent review of studies in the area prior to 2005 has been written by Lee.[17] As a result, the examples of DYM chemistry highlighted below have been selected on the basis of their relevance to recent studies carried out in our laboratory.

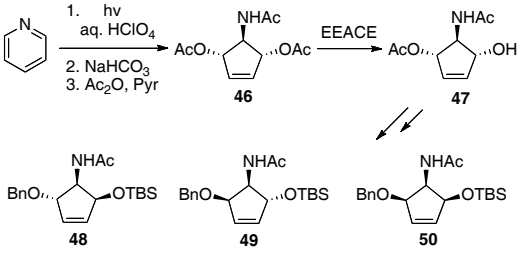
As can be seen by viewing the general pathway outlined in *Scheme* 2 above, DYM reactions transform bis-alkene tethered alkynes to bicyclic conjugated dienes. Grubbs and Choi[18] were the first to describe this reaction in studies using a simple set of substrates. One example, shown in *Scheme* 10, employs the 2nd generation Grubbs catalyst **25** to promote reaction of the cyclohexylacrylate derivative **28** that yields the tricyclic lactine **29**. In this process, a remarkable transformation occurs to convert a simply prepared substrate into a structurally complex product in a remarkably efficient manner.

Employment of the DYM process in target oriented synthesis is found in the approach to the tetracyclic alkaloid (-)-securinine (**34**, *Scheme* 11) developed by Honda and his coworkers.[19] The route begins with preparation of the N-Boc piperidine dienyne **31** from the α-pipecolic acid thioester **30**. The key DYM step in the sequence is catalyzed by the 3rd generation Grubbs[20] catalyst **32** and transforms **31** to the piperidine substituted bicyclic dihydrofuran **33**. Conversion of **33** to the target **34** consists of lactone formation, δ-bromination, and cyclization.

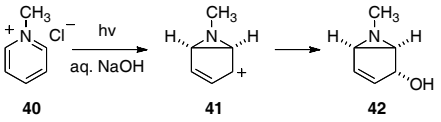
Hatakeyama and his coworkers[21] described a novel strategy for the synthesis of the erythrina alkaloid erythravine (**39**, *Scheme* 12) that is based on a design which incorporates DYM reaction of the bis-alkene substituted alkyne **36**. The route starts with conversion of the phenethyl amine derivative **35** to **36**. The tetracyclic diene **37** + **38** was then generated as a 3:2 mixture of diastereomers by **10** catalyzed reaction of **36**. The major isomer **37** was then converted to the racemic



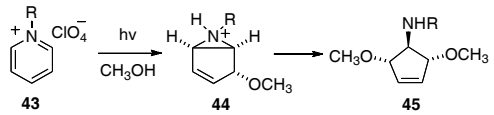
Scheme **12**



Scheme **15**



Scheme **13**



Scheme **14**

target **39**. It should be noted that Mori and his coworkers[22] accomplished a racemic synthesis of the closely related erythrina alkaloid erythrocarine that follows a plan that is closely related to the one employed by Hatakeyama.

Pyridinium Salt Photochemistry (PSP).

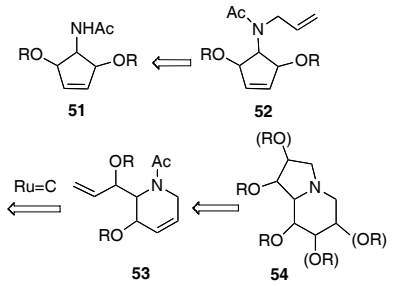
In an interesting report in 1972, Kaplan, Wilzbach and Pavlik[23] described the unusual photochemical reaction of N-methylpyridinium chloride (**40**) in aqueous base solution that produces the bicyclic allylic alcohol **42** (*Scheme* 13). These workers suggested a reasonable mechanism for this process that involves excited state electrocyclization to form the intermediate bicyclic allylic cation **41** followed by hydroxide addition to the least hindered exo-face. Over a decade later, Mariano, Yoon and their coworkers[24] observed that a similar excited state process is involved in the photochemical conversion of N-substituted pyridinium salts **43** to trans, trans-4-amino-cyclopentendyl ethers **45** (*Scheme* 14). In these cases, reactions are promoted by irradiation of methanol solutions that do not contain base and, consequently, N-protonated bicyclic aziridines **44** are generated and they undergo secondary SN_2 ring opening to form **45**. This observation led to efforts exploring a strategy for preparation of unsymmetrically substituted 4-aminocyclopentene derivatives that involves irradiation of pyridinium salts in basic solutions containing one nucleophile followed by acid promoted aziridine ring opening with a second nucleophile (see *Scheme* 3 above).[25]

The interesting discovery[25] that pyridine participates in a similar reaction sequence when irradiated in an aqueous acid solution led the way to novel methods for the preparation of stereochemically diverse 4-aminocyclopentendiol derivatives in enantioenriched forms. As shown in *Scheme* 15, irradiation of a pyridine solution in aqueous perchloric acid, followed by basic workup and peracetylation leads to efficient formation of the trans, trans-amino-cyclopentendiyl diacetate **46**. This substance can be desymmetrized by using enantioselective enzymatic hydrolysis with electric eel acetylcholinesterase (EEACE). This process generates the mono-diol **47** in *ca.* 80% ee.[26] Moreover, implementation of alcohol inversion procedures enables formation of a stereo diverse family of enantio-enriched, selectively protected 2-aminocyclopentendiol derivatives, exemplified by **48**-**50** (*Scheme* 15).

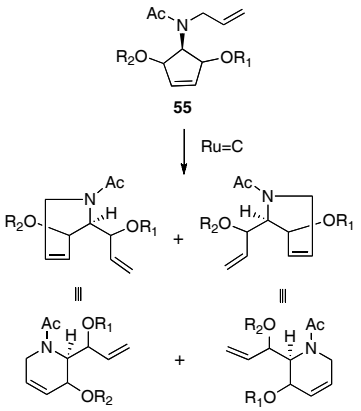
This interesting PSP based methodology has been applied to the synthesis of a variety of natural products, including (+)-mannostaten A,[26,27] the aminocyclitol of (-)-allosamizoline,[28] both enantiomers of trehazolamine,[29] (-)-cephalotaxine,[30] and non-natural products such as 3-amino-3-deoxy-aldopentoses.[31] The indolizidine alkaloids (-)-swainsonine and (+)-castanospermine have also been targets of efforts we carried out in which strategies based on PSP and RRM processes were used. The latter studies along with an investigation focused in the construction of the structural backbone of lepadiformine and cylindricine alkaloids are discussed in the remaining sections of this "account."

A Strategy for Preparation of the Polyhydroxylated Indolizidines (-)-Swainsonine and (+)-Castanospermine.

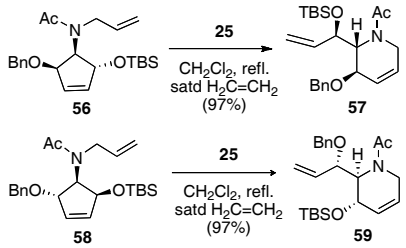
Recognizing the unique features of PSP processes and the broad generality of RRM chemistry, Song, Zhao and Mariano[32,33] embarked on an investigation of an application of these reactions to the synthesis of biologically active members of the polyhydroxylated indolizidine natural product



***Scheme* 16**



***Scheme* 17**



***Scheme* 18**

family. The general strategy employed for this purpose is outlined in *Scheme* 16. The starting materials for these preparative routes were 4-aminocyclopentene derivatives **51**, generated by using PSP methods (see above). We envisaged that RRM reactions would transform the corresponding N-allylamides **52** into the corresponding 2-allyl-1,2,3,6-tetrahydropyridines **53** that contain functionality needed to execute indolizidine ring formation and hydroxyl introduction to form the target indolizidines **54**.

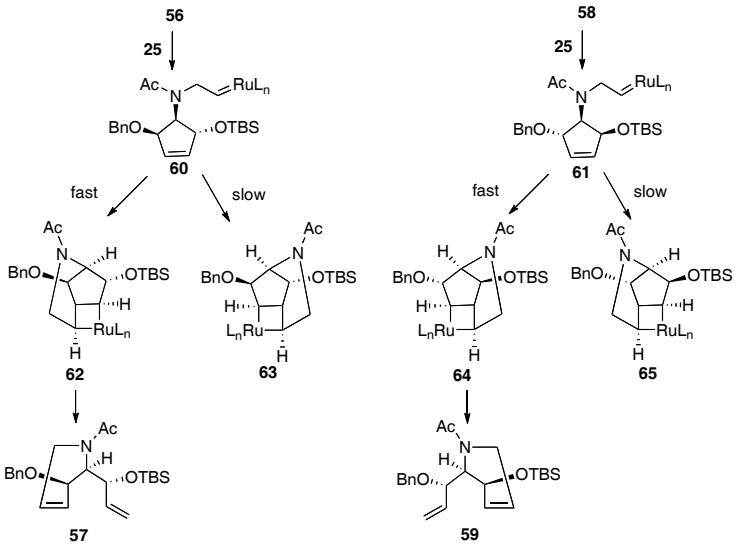
As part of this approach, interesting aspects regarding the control of the regiochemical outcomes of the RRM reactions of the N-allylacetamidocyclopentenes needed to be addressed. This is exemplified in *Scheme* 17, which portrays the two possible routes that could be followed in ruthenium carbene catalyzed reactions of the generalized N-acetamide derivative **55**. Obviously, regiochemical control is required for the strategy for polyhydroxylated indolizidine synthesis to be efficient. As a consequence of this question, a number of cyclopentene derivatives were prepared and subjected to RRM reactions. Two examples of the observations made in this effort are given in *Scheme* 18. It is clear from viewing these examples that an exceptionally high degree of regiocontrol, governed by stereochemistry attends these processes. In each case, reaction takes *via* formation and selective cycloaddition of the exocyclic ruthenium alkylidene (**60** and **61**, *Scheme* 19) across the endocyclic alkene moiety. It appears that the courses of these reactions are governed by formation of tricyclic ruthenocyclobutanes **62** and **64**, in which the bulky ligated ruthenium is bonded to the old cyclopentene moiety in an anti disposition relative to the OBn (in **64**) or OTBDMS (in **62**) groups. It should be noted that this preference exists despite the fact that formation of **62** and **64** encounters steric conjestion between the nitrogen containing two-atom bridge and the β-OTBS (in **64**) and OBn (in **62**) groups.

Molecular mechanics calculations on simple analogs were carried out to determine if the regiochemical preferences seen in these reactions are indeed the result of the dominance of two competing steric interactions. For this purpose, gem-dimethyl analogs of **62** and **64** (*i.e.* **66** and **67**, *Scheme* 20) were used. The results show that **66**, the analog of **64**, is of significantly lower energy than its regioisomer **67**, the analog of **65**. Thus, it appears that the regiochemical courses of RRM reactions of **60** and **61** are directed by steric interactions between the highly ligated ruthenium center and the syn OBn and OTBS groups.

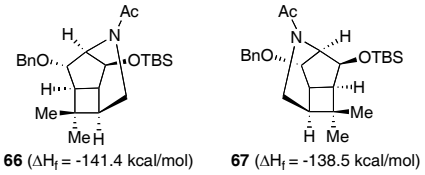
With these results in hand, efficient routes for the synthesis of two representative naturally occurring polyhydroxylated indolizidines were designed. In the approach to (-)-swainsinine (**69**, *Scheme* 21), the preference for exo *vs*. endo alkene, α-acetate guided dehydroxylation (→ **68**) was used advantageously to produce the late stage intermediate **68**. In contrast, the activation (directing effect of allylic hydroxyl groups on epoxidation reactions (→ **71**, *Scheme* 22) along with stereoelectronically mandated trans-diaxial epoxide ring opening (→**72**) were the cornerstones of late stage steps in the preparation of (+)-castanospermine (**73**).

Construction of the Tricyclic Structure of Members of the Lepadiformine and Cylindricine Alkaloid Families

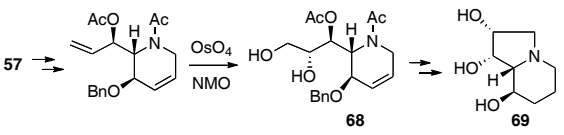
The results of studies in the area of PSP provided a foundation for a new strategy to construct the tricyclic backbone **74** of members of the lepadiformine and cylindricine alka-



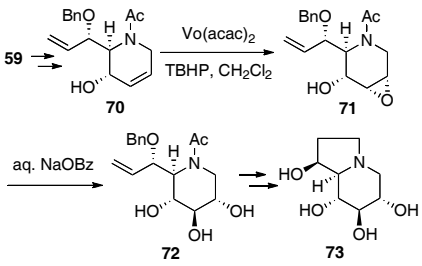
***Scheme* 19**



***Scheme* 20**

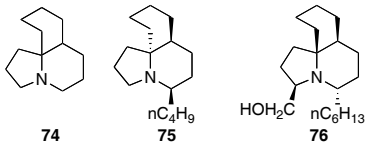


***Scheme* 21**

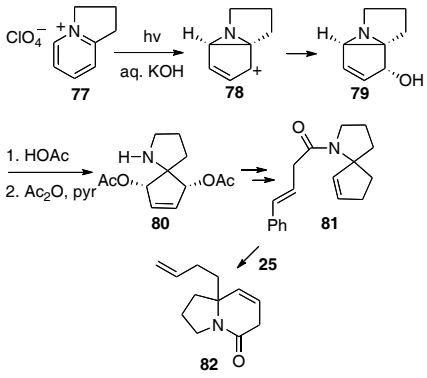


***Scheme* 22**

loids, exemplified by lepadiformine C (**75**) and cylindricine B (**76**) (*Scheme* 23). Earlier, we observed a remarkably high degree of regiocontrol in photocyclization reactions of the cyclopenta-fused pyridinium perchlorate **77** (*Scheme* 24).[34] Specifically, irradiation of **77** in an aqueous base solution leads to nearly exclusive formation of the tricyclic allylic

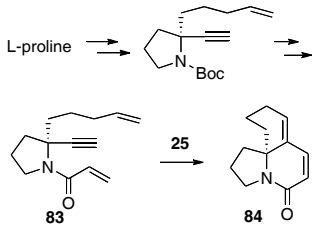


***Scheme* 23**



***Scheme* 24**

alcohol **79**, arising by selective addition of hydroxide to the intermediate allylic cation **78**. In addition, reaction of **79** with acetic acid followed by per-acetylation produces the spirocyclic triacetyl derivative **80**, which was converted to the corresponding butenamide **81** by using an unfortunately laborious sequence.[35] As anticipated, RRM reaction of **81**, promoted by the ruthenium carbene catalyst **25**, produces the indolizidine **82**. If it were not for the large effort required to prepare **81**, this sequence would represent a viable approach to synthesis of the tricyclic core of the lepadi-



***Scheme* 25**

formines and cylindricines since functionality is present in **82** to execute introduction of the final six-membered ring.

At this point, we recognized that a much more direct approach existed for preparation of the basic structure shared by these alkaloids. The strategy takes advantage of dienyne metathesis (DYM) reaction of the proline derived acrylamide **83** (*Scheme* 25). In order to test this proposal, **83** was prepared in enantiomerically pure form from L-proline by using the route outlined in *Scheme* 25. As anticipated, treatment of this dienyne with the 2nd generation Grubbs catalyst **25** in CH_2Cl_2 at reflux leads to exceptionally clean (*ca.* 100 %) conversion to the tricyclic dienamide **84**, which possess the alkaloid tricyclic structure. The results of this unpublished work[35] provide the framework of novel strategies for the preparation of members of the lepadiformine and cylindricine alkaloid families.

SUMMARY

The studies described above point out how remarkably efficient ruthenium carbene catalyzed metathesis reactions can be combined with pyridinium salt photochemistry in devising strategies for the preparation of biomedically relevant natural and non-natural products. It is hoped that this account will stimulate further interest in these areas.

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