The [1, 3] O-to-C rearrangement: opportunities for stereoselective synthesis

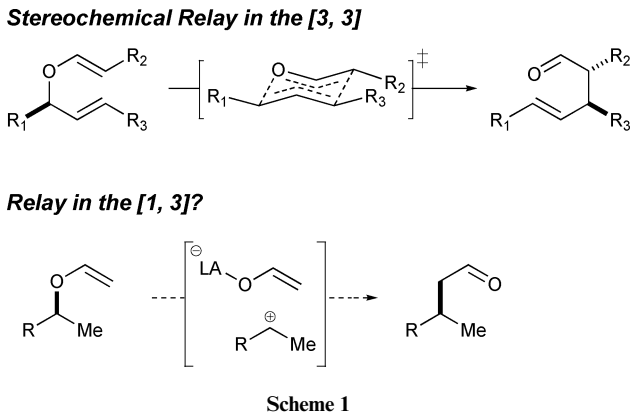
Christopher G. Nasveschuk and Tomislav Rovis*

Received 27th September 2007
First published as an Advance Article on the web 4th December 2007
DOI: 10.1039/b714881j

The relay of stereochemistry of a breaking C–O bond into a forming C–C bond is well-known in the context of [3, 3] sigmatropic shifts; however, this useful strategy is less well-known in other types of molecular rearrangements. Though the first successful example of a [1, 3] O-to-C rearrangement was reported more than 100 years ago, this class of reactions has received less attention than its [3, 3] counterpart. This perspective analyzes the various methods used for the activation and [1, 3] rearrangement of vinyl ethers with an emphasis on mechanism and applications to stereoselective synthesis. We also highlight our own contributions to this area.

1 Introduction

Central to the synthesis of complex molecular targets are methodologies to construct carbon–carbon bonds. One such strategy is the Claisen rearrangement, which constructs a new C–C bond by way of a [3, 3] sigmatropic shift. The utility of this reaction lies in its power to translate stereochemistry from the breaking C–O bond to the forming C–C bond (Scheme 1).[1] This strategy takes advantage of our ability to control C–O bond stereochemistry to relay it to generate C–C bond-based stereocenters. On the other hand, [1, 3] O-to-C rearrangements are less well-known, and while thermal [1, 3] sigmatropic shifts that relay stereochemical information have been reported, there are a dearth of examples and the transformation lacks generality. It is not surprising then to find that in a field where novelty and creativity reign supreme, chemists



Scheme 1

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA; Fax: +1 (970) 491-1801; Tel: +1 (970) 491-7208. E-mail: rovis@lamar.colostate.edu

Christopher G. Nasveschuk

Christopher G. Nasveschuk received his B.A. degree from Middlebury College in 2001 where he conducted undergraduate research under the direction of Professor Jeffrey Byers. He subsequently began his graduate studies under the direction of Tomislav Rovis at Colorado State University. He received his Ph.D. in 2007 and is a currently a postdoctoral fellow with Andrew Phillips at CU Boulder.

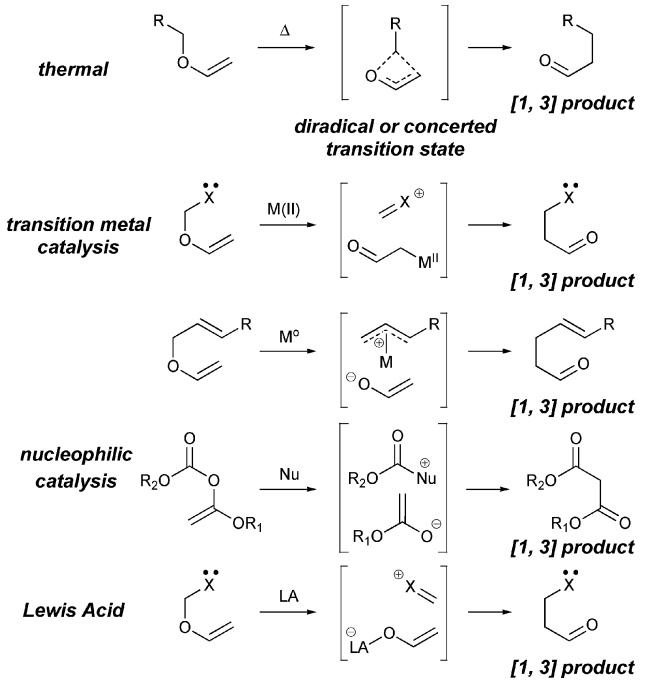
Tomislav Rovis

Tomislav Rovis was born in Zagreb in the former Yugoslavia but was largely raised in Southern Ontario, Canada. Following his undergraduate studies at the University of Toronto, he earned his Ph.D. degree at the same institution in 1998 under the direction of Professor Mark Lautens. From 1998–2000, he was an NSERC postdoctoral fellow at Harvard University with Professor David A. Evans. In 2000, he began his independent career at Colorado State University and was promoted in 2005. His group's accomplishments have been recognized by a number of awards including an NSF CAREER award. He has been named a GlaxoSmithKline Scholar, Amgen Young Investigator, Eli Lilly Grantee, Alfred P. Sloan Fellow and most recently a Monfort Professor at Colorado State University.

 This journal is © The Royal Society of Chemistry 2008

have discovered a plethora of other methods to promote [1, 3] O-to-C rearrangements. In 2000, we initiated a program aimed at providing a general solution to this problem. Herein we provide a critical analysis of the potential mechanisms involved, and a summary of the major advances in this field, with an outlook to the future.

There are four general methods for the activation and [1, 3] rearrangement of vinyl ethers (Scheme 2). The oldest method, thermal activation, can furnish [1, 3] products through two different mechanisms: 1) a diradical, or 2) a concerted shift. [1, 3] Rearrangement by transition metal catalysis proceeds by electrophilic or nucleophilic activation of the substrate. Nucleophilic catalysis may also be mediated by an organocatalyst. Lastly and most intensely studied are Lewis acid-mediated processes. The unifying theme among these diverse methods of activation is that an intermediate pair is formed, whether it be radical or ionic in nature, and control of these species leads to the formation of the desired products.[2]



Scheme 2

2 Orbital symmetry of [1, 3] rearrangements

[1, 3] Sigmatropic shifts can be rationalized by frontier molecular orbital theory.[3] For a reaction to occur there must be symmetry within the system to allow for HOMO–LUMO orbital overlap between the reacting ends of the molecule. For a thermal [1, 3] sigmatropic rearrangement to be symmetry-allowed, it must occur by an antarafacial rather than a suprafacial approach (**A** *vs.* **B**, Fig. 1).[4] If the migrating group possesses a p-orbital, the suprafacial [1, 3] shift is symmetry-allowed and proceeds with inversion of stereochemistry at the migrating carbon (**C** to **D**, Fig 1).[5] The majority of migrating groups in O-to-C [1, 3] shifts are sp^3-hybridized, which places additional geometric constraints on the system.

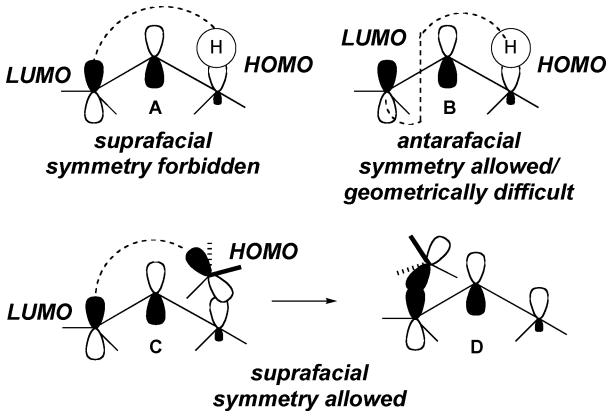
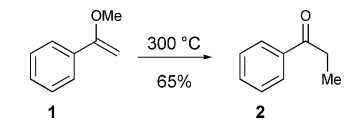


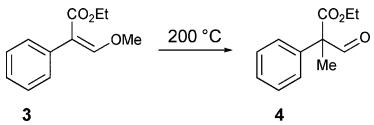
Fig. 1

3 Early examples

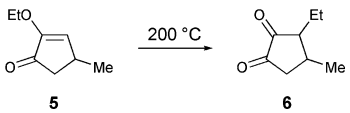
The seminal report of a thermal [1, 3] rearrangement was presented by Claisen in 1896,[6] prior to his discovery that *O*-allyl acetoacetate undergoes a [3, 3] sigmatropic rearrangement.[7] He stated that, "on short superheating such as boiling for a few hours under two atmospheres' pressure" α-methoxystyrene provides propiophenone, the product of formal [1, 3] shift. A qualitative enhancement in reaction efficiency for [1, 3] alkyl shifts was reported to follow the general trend *n*-propyl > ethyl > methyl (eqn 1). Wislecenus and Schrotter (1921) illustrated that this methodology could be used to generate quaternary stereocenters (eqn 2).[8] The thermal [1, 3] shift also proceeds efficiently with cyclic systems to provide substituted cyclopentanediones (eqn 3).[9]



(1)



(2)



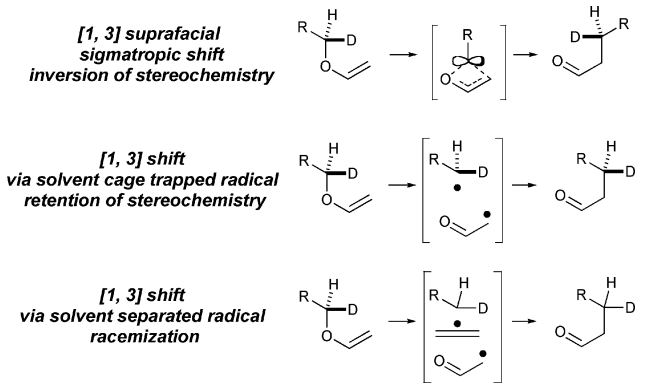
(3)

4 Thermal reactions

4.1 Thermal reactions: mechanism and stereochemistry

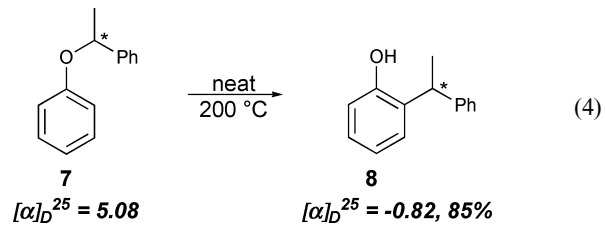
Early studies of the [1, 3] O-to-C rearrangement were primarily focused on identification and expansion of the substrate scope, and the mechanism was not addressed until 1933, when Spielman[10] suggested that the thermally initiated [1, 3] rearrangements proceed by way of a radical process.[11] However, consideration of stereochemistry in the context of thermal [1, 3] O-to-C rearrangements is a more sensitive probe of mechanism. In the event that rearrangement proceeds with inversion of configuration at the migrating center, a concerted [1, 3]-sigmatropic shift is the operative mechanism.[12] On the other hand, if the rearrangement proceeds with retention of configuration at the migrating center, a

fast intra-solvent-cage radical–radical trapping mechanism can be invoked.[13] If racemization predominates, dissociation or rotation of a radical pair[14] can be invoked (Scheme 3).

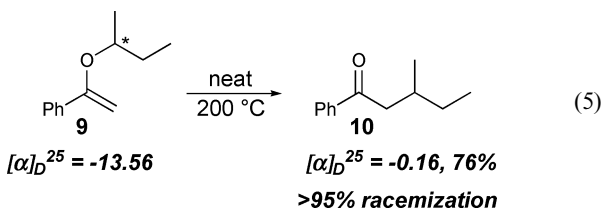


Scheme 3

In 1954, a report by Hart and Eleuterio described the rearrangement of optically active phenethyl phenyl ether, which proceeds with approximately 20% retention of optical purity (eqn 4).[15] The argument was advanced that there is an intramolecular component to the reaction. This type of stereochemical test was shown to be substrate dependent by Wiberg and Rowland, in a process in which optically active α-2-butoxystyrene was racemized upon heating, thus suggesting radical pair dissociation (eqn 5).[16]

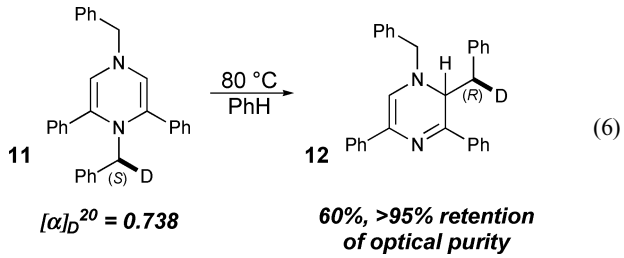


(4)



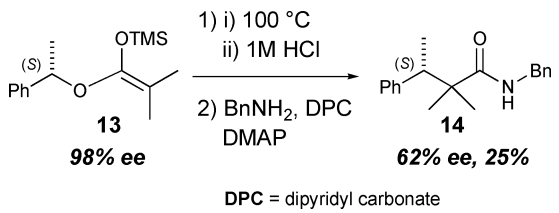
(5)

A [1, 3]-sigmatropic N to C rearrangement has been accomplished by Lown, Akhtar, and McDaniel (eqn 7). Deuterium-labeled 1,4-dibenzyl-1,4-dihydropyrazine **11** was thermally rearranged in the presence of radical inhibitor butane thiol[17] to provide **12** with >95% retention of optical purity and inversion at the migrating benzyl carbon. The reaction follows first-order kinetics, which implies that it proceeds through a concerted process and not a radical mechanism.[18]



(6)

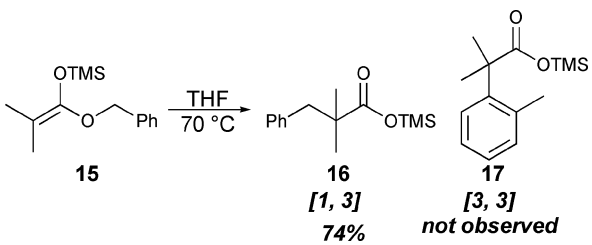
In an interesting report by Shiina and Nagasue a "[1, 3] sigmatropic rearrangement" proceeding with *retention* of configuration at the migrating phenethyl group was described (eqn 7).[19] In light of the above mechanistic discussion, it seems more likely that this particular example proceeds *via* the radical pair mechanism.



(7)

4.2 Thermal rearrangements: examples

The concept of [1, 3] rearrangement *via* migration of an alkyl group, specifically -CH_2Ar, found broad success under the thermal reaction manifold. Presumably, this functionality could stabilize either radical intermediates or charge build-up in the transition state for the concerted mechanism. Arnold and Kulenovic showed that silyl enol ethers derived from benzyl acetate would rearrange upon heating to provide [1, 3] adducts in good chemical yield (eqn 8). In all cases, no [3, 3] product was observed.[20]



(8)

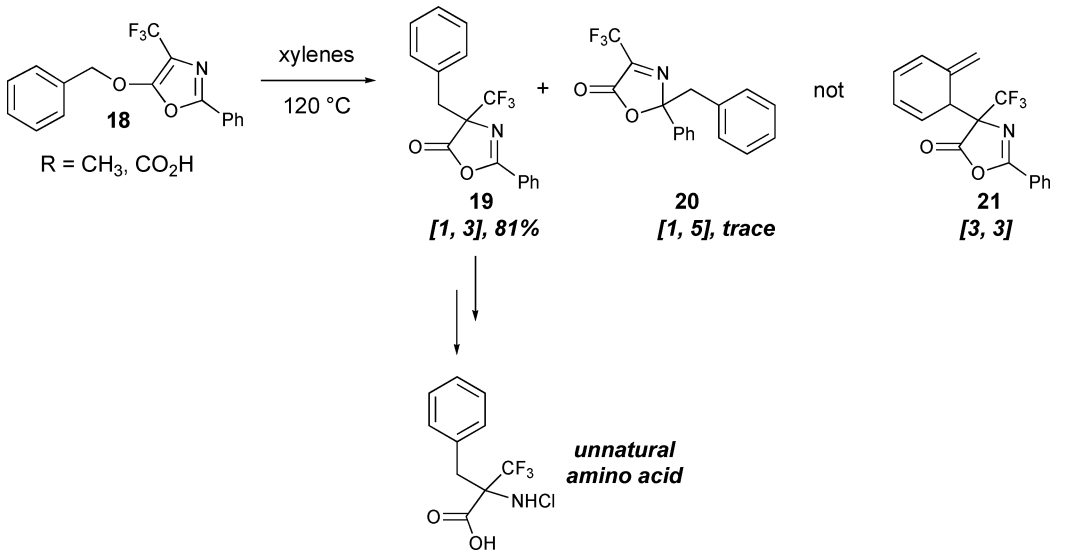
Heteroaromatics also participate as the vinyl ether component *en route* to unnatural amino acids (Scheme 4)[21] and functionalized butenolides (eqn 9).[22] It is important to note that the major competing process in this system is not the [3, 3] rearrangement which would provide **21**, but rather the corresponding [1, 5] shift to generate **20**.

During their studies of aminomercuration of alkynes, Barluenga and coworkers found that with furanyl substitution, β-oxy enamine products would undergo a subsequent [1, 3] rearrangement in 60% yield (eqn 10).[23] Deuterium labeling experiments revealed a secondary kinetic isotope effect of 1.83, which suggests complete C–O bond cleavage in the transition state and that the reaction may proceed by a radical pair mechanism. The thermally initiated [1, 3] O-to-C rearrangement can also be used to synthesize spirocyclic systems as described by Swenton (eqn 11).[24]

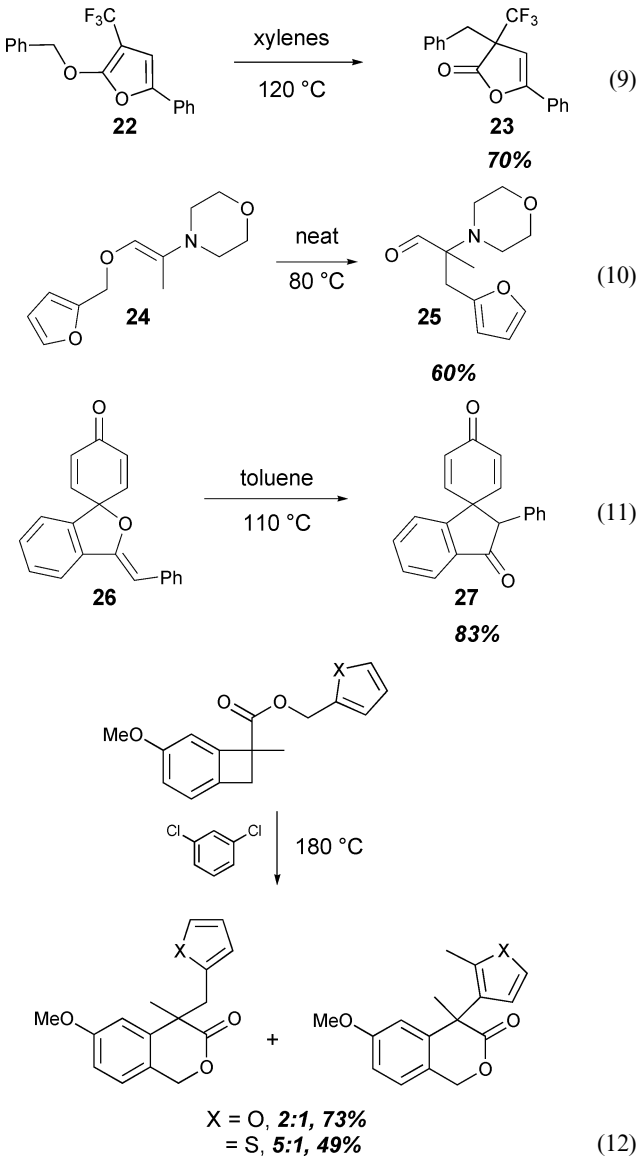
[1, 3] Benzyl group migrations have been used as the termination step in a domino reaction (Scheme 5).[25] Benzocyclobutane **28** rearranges *via* a 4π electrocyclic ring opening followed by a 6π electrocyclic ring closing and [1, 3] benzyl shift, to provide isochromene **29**. However, when heteroaromatics such as furyl or thiophenyl are employed the [3, 3] termination process is competitive (eqn 12).

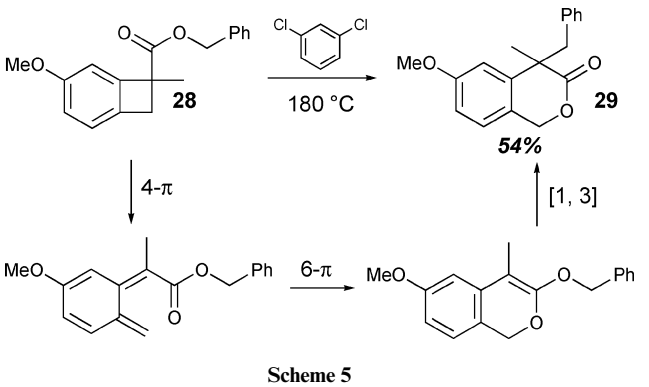
A thermal [1, 3] rearrangement of allyl vinyl ethers has been noted in two instances. In both cases the [3, 3] process is inhibited by a significant kinetic barrier due to strain in the transition state, and thus the [1, 3] rearrangement predominates. Danishefsky

 This journal is © The Royal Society of Chemistry 2008



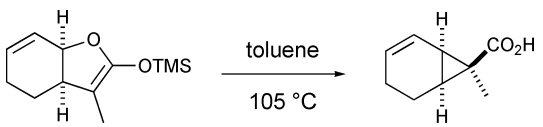
Scheme 4





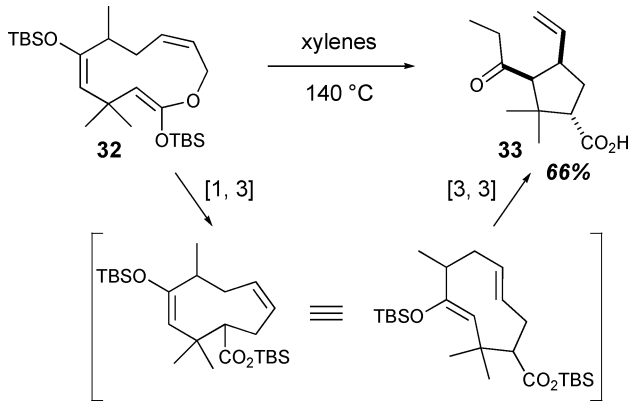
Scheme 5

reported an unusual ring contraction of lactone enolates of type **30** (eqn 13).[26]

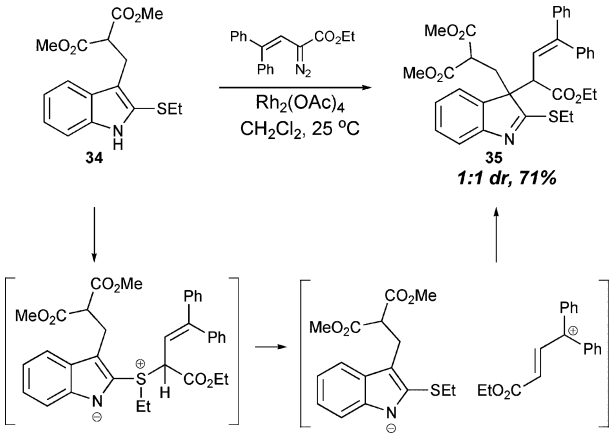


Knight showed that silyl enol ether **32** resists rearrangement until it is heated in refluxing xylenes (Scheme 6).[27] The structure of cyclopentane **33** was confirmed by X-ray analysis and is proposed to arise from initial [1, 3] shift followed by a Cope rearrangement.

Rainier and coworkers reported an interesting [1, 3] rearrangement of an allyl vinyl thioether (Scheme 7).[28] The reaction initiates *via* rhodium-mediated coupling of a thioether and a vinyl diazoacetate to provide an ylide, which typically rearranges in a [3, 3] manner. However, if the allyl moiety is sufficiently sterically encumbered, ionization predominates and [1, 3] products are formed. Although the ionization is proposed to be spontaneous in this mechanism, the possibility of rhodium assistance has not been ruled out.



Scheme 6



Scheme 7

5 [1, 3] Rearrangements proceeding through an ion pair

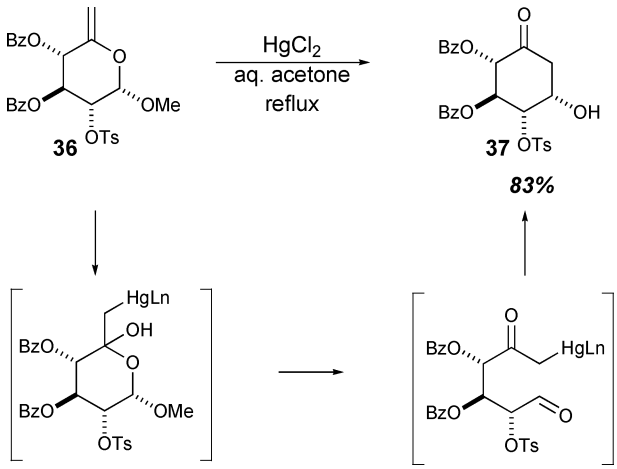
5.1 Transition metal(II)-mediated reactions

In 1979, Ferrier reported that $HgCl_2$ mediates a [1, 3] rearrangement of hexose **36** to cyclohexanone **37**, in a reaction that now bears his name.[29,30] The transformation is thought to proceed *via* oxymercuration of the olefin, followed by fragmentation and subsequent aldehyde alkylation with the mercury enolate (Scheme 8). Palladium(II) also catalyzes a similar carbocyclization, presumably through electrophilic-Pd(II) activation of the vinyl ether (eqn 14).[31,32]

5.2 Transition metal(0)-mediated reactions

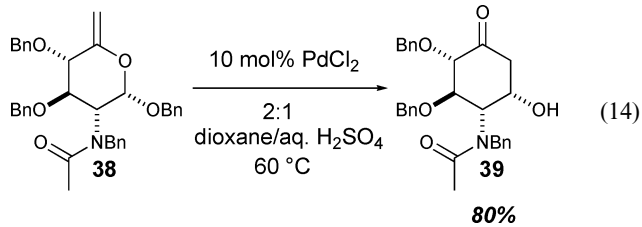
Alkylidenetetrahydrofurans of type **40** are known to undergo a thermal [3, 3] rearrangement to produce cycloheptanones (eqn15).[33] In 1980, Trost and coworkers described a Pd(0) catalyst system that rearranges **42** in a [1, 3] sense to produce cyclopentanone **43** (eqn 16).[34] It was later found that a complementary Pd–ligand combination would provide the cycloheptanone product (eqn 17).[35]

Formation of cyclopentanone **48** presumably proceeds by coordination of Pd(0) to the 1,1-disubstituted olefin of **46** followed by an S_N2' attack to create the zwitterionic intermediate **47**,

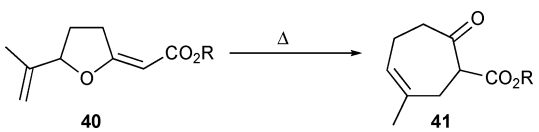


Scheme 8

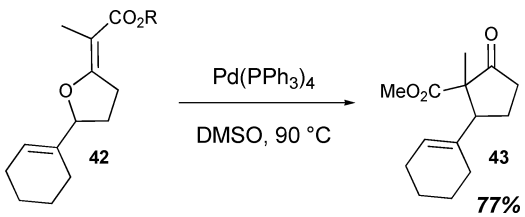
which subsequently collapses in regioselective fashion.[36] The reaction proceeds with overall retention of configuration by double inversion (Scheme 9).[37]



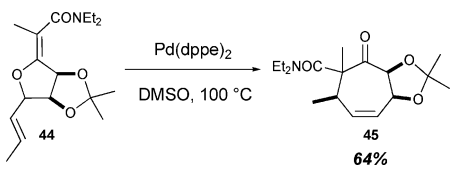
(14)



(15)



(16)

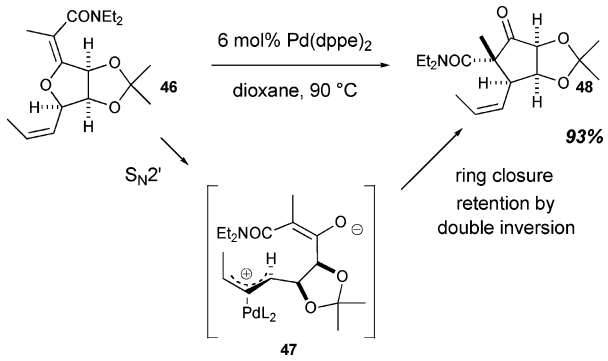


(17)

5.3 Other nucleophilic catalyst-mediated reactions

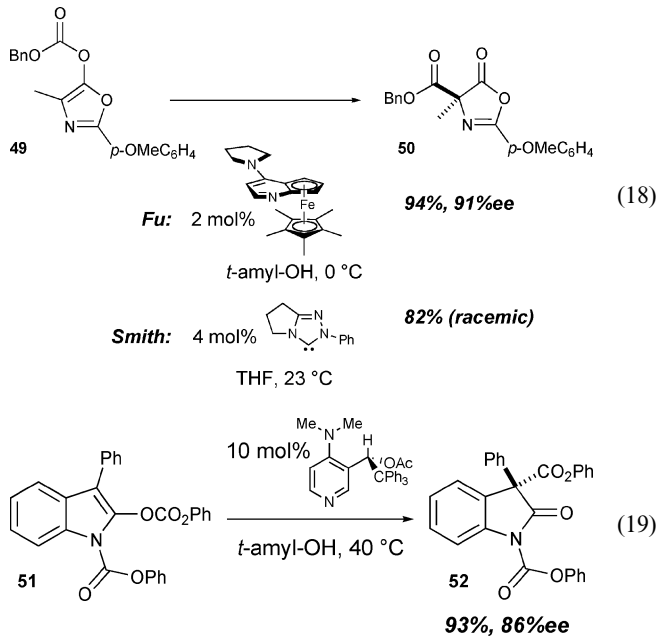
[1, 3] Rearrangements of enol esters may also be catalyzed by nucleophilic small molecules or organocatalysts, as first demonstrated by Höfle and Steglich in 1970.[38] The reaction proceeds by nucleophilic addition of the catalyst to the carbonyl, which then fragments to create an ion pair intermediate, followed by C-alkylation and formation of the product. Elegant work by Fu (eqn 18) and Vedejs (eqn 19) showed that chiral enantioenriched DMAP-type catalysts may render the reaction asymmetric.[39] The

This journal is © The Royal Society of Chemistry 2008



Scheme 9

reaction will also proceed in the presence of an N-heterocyclic carbene (eqn 18).[40]

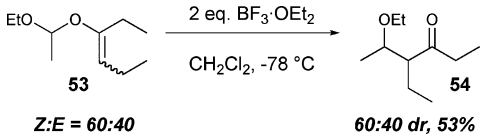


(18)

(19)

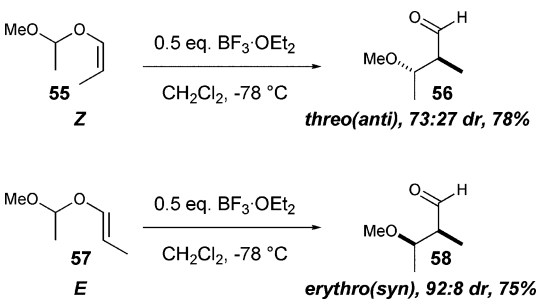
5.4 Lewis acid-mediated reactions

5.4.1 Lewis acid-mediated [1, 3] rearrangement of acyclic systems. Potentially the most general way to access ion pair intermediates that facilitate [1, 3] rearrangement is treatment of a suitably functionalized substrate with a Lewis acid. The overall process is of considerable utility owing to the often convergent and rapid assembly of starting materials and the ability to control the stereochemical course of the reaction through judicious choice of rearrangement parameters. Originally developed as a route to cross-aldol products, β-hydroxy ketones,[41] Lewis acid-mediated [1, 3] rearrangement of vinyl acetals showed early promise. Vinyl acetal **53**, bearing a trisubstituted alkene as a 60 : 40 mixture of geometrical isomers, rearranges in the presence of superstoichiometric amounts of Lewis acid to produce protected β-hydroxy ketone **54** as a 60 : 40 mixture of diastereomers (eqn 20).[42]



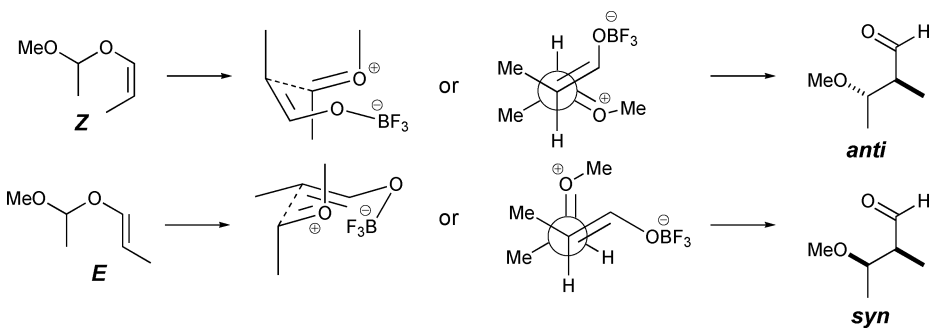
(20)

It was later shown that the [1, 3] O-to-C alkyl group migration could be rendered diastereoselective if a single alkene isomer was employed in the starting material (Scheme 10).[43] The authors rationalized the stereochemical outcome of the rearrangement as an "electrostatically stabilized chair transition state" in a Zimmerman–Traxler model (Scheme 11). A presumed electrostatic attraction between the boronate and the oxocarbenium ion holds the ion pair in the ordered transition state; however it may be more prudent to rationalize stereochemistry using a simple Newman projection viewed down the axis of the forming bond.

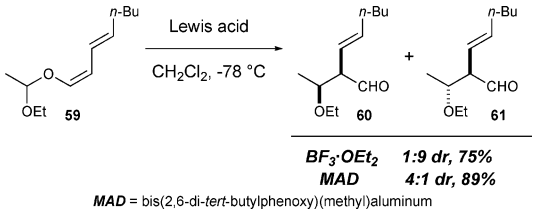


Scheme 10

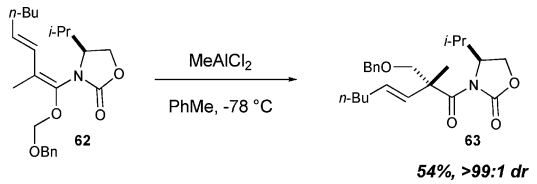
More recently, dienes have been shown to undergo a regio- and diastereoselective rearrangement (eqn 21).[44] These results are consistent with the rearrangement of vinyl acetals shown in Scheme 10 and most likely proceed *via* a similar transition state. In the presence of a chiral auxiliary, the [1, 3] rearrangement can be rendered highly diastereoselective to produce all-carbon quaternary stereocenters (eqn 22).[45]



Scheme 11



(21)

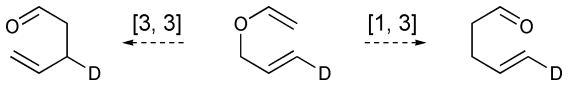


(22)

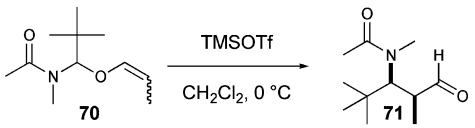
Okahara and coworkers provided early mechanistic insight for the [1, 3] rearrangement of vinyl acetals in a crossover study that was seminal to our own work in this area. At −78 °C the ratio of expected products to crossover products was 0.96 : 1.00 : 0.41 : 0.49, while at 0 °C the amount of crossover products decreased (Scheme 12).[46] The dependence of the degree of crossover on temperature suggests that the reaction proceeds through a contact *vs.* solvent-separated ion pair.[47] We have taken advantage of this insight to establish ion pairing as a control element for the [1, 3] rearrangement of pyranyl vinyl acetals, which will be discussed in depth in the following section.

N,*O*-Vinyl acetals undergo facile Lewis acid-induced O-to-C migration, in which the corresponding ion pair consists of an *N*-acyliminium ion and a metalloenolate. The Lewis basicity of the amine functionality necessitates its attenuation *via* a carbonyl or some π-withdrawing substituent for adequate reactivity. Frauenrath and coworkers were the first to report this reactivity and showed that sterics will override the stereochemical influence of enolate geometry (eqn 23).[48]

The allyl group also provides sufficient electron donation to fragment allyl vinyl ethers in the presence of a Lewis acid. The corresponding ion pair allows access to the [1, 3] product in the face of a possible [3, 3] rearrangement. The [1, 3] product is accessed under kinetic conditions, where product selectivity is governed by approach of the metalloenolate to the more exposed terminus of the corresponding allyl cation (Scheme 13).

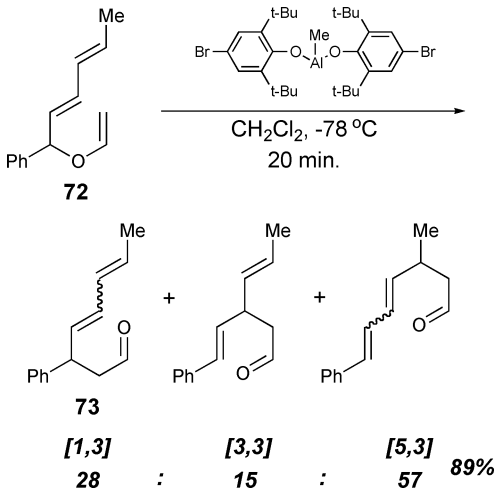


Scheme 13



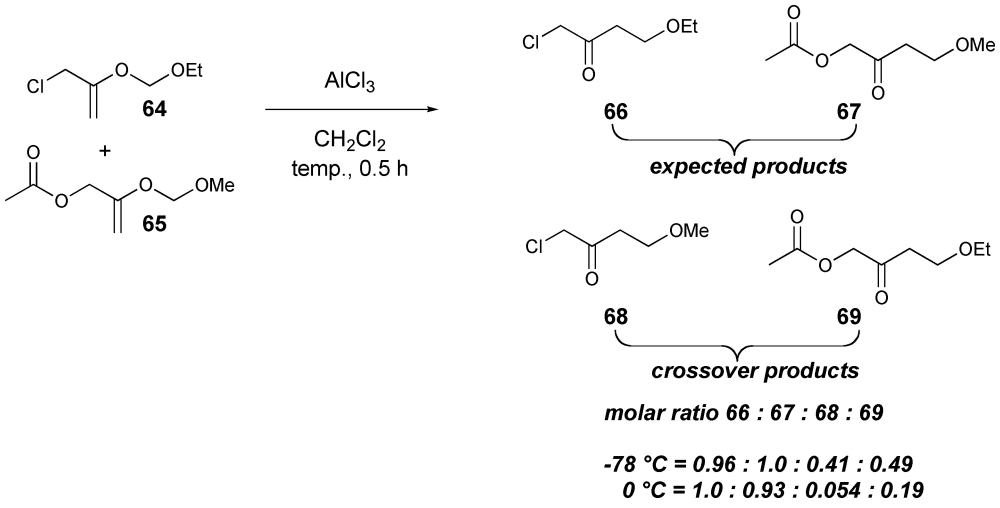
(23)

An early example by Yamamoto and coworkers showed that, under ionizing conditions, the [1, 3] product is accessible in acyclic systems (eqn 24).[49] Rearrangement of pentadienyl vinyl ether **72** provides a mixture of products in which the [1, 3] product **73** is a significant portion of the isolated material.



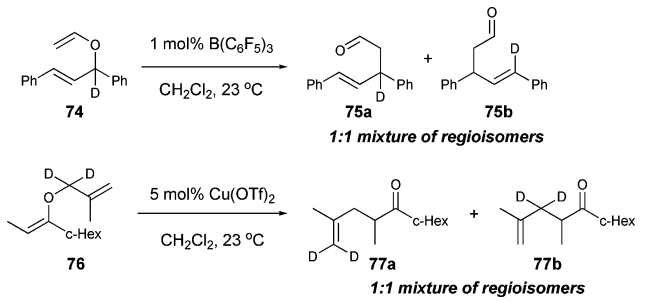
(24)

Gansauer showed that labeled symmetrical allyl vinyl ethers rearrange in the presence of catalytic Lewis acid to a 1 : 1 mixture of regioisomeric aldehydes through an unselective trapping of the symmetrical cation intermediate (Scheme 14).[50] A mixture of vinyl



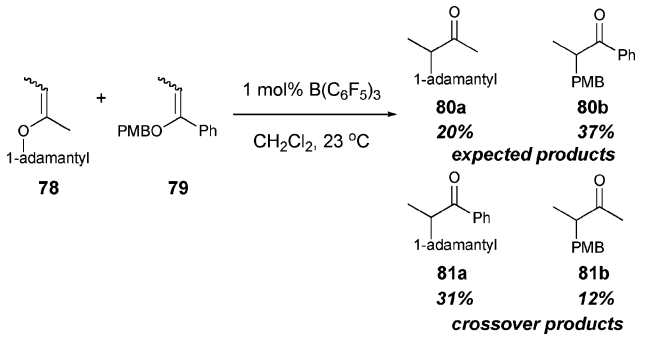
Scheme 12

 This journal is © The Royal Society of Chemistry 2008



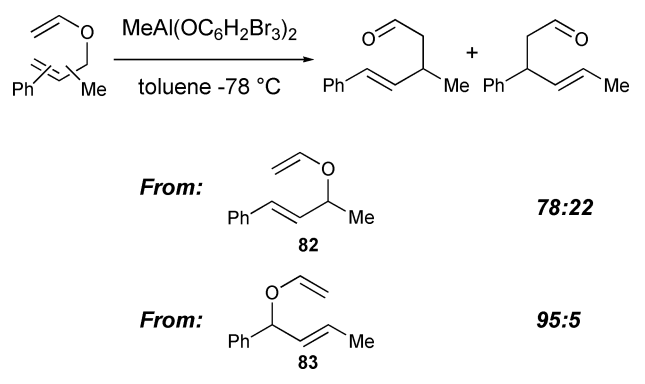
Scheme 14

ethers **78** and **79** produce a significant quantity of ion-exchanged products (Scheme 15).

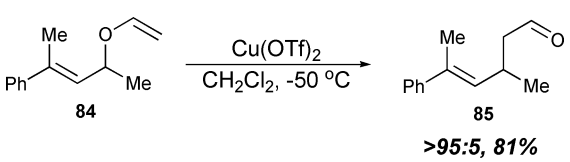


Scheme 15

In our own studies, we have established that a regioselective rearrangement of allyl vinyl ethers is possible through electronic differentiation of the two ends of the corresponding allyl cation (Scheme 16). Ultimately, the system could be controlled by installation of an additional methyl or alkyl group on the allyl portion of the allyl vinyl ether. This creates a situation where reaction at the more substituted carbon, in a formal [3, 3] rearrangement, would produce a quaternary carbon center. The steric congestion in the TS leads to selective kinetic trapping to produce the [1, 3] adduct (eqn 25).[51]

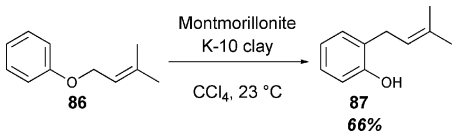


Scheme 16



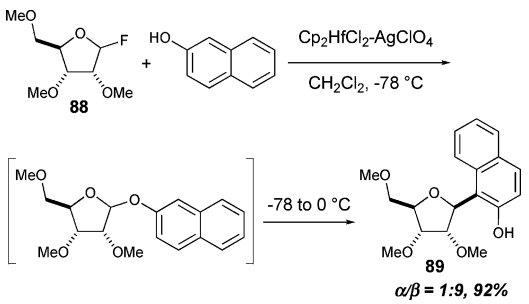
(25)

O-Allyl phenols undergo a [1, 3] rearrangement catalyzed by montmorillonite K-10 clay as originally reported by Dauben.[52] This reaction was later optimized by Dintzner and coworkers to produce the product of [1, 3] rearrangement (eqn 26). It was noted that the activity of the catalyst diminished significantly in successive runs.[53]



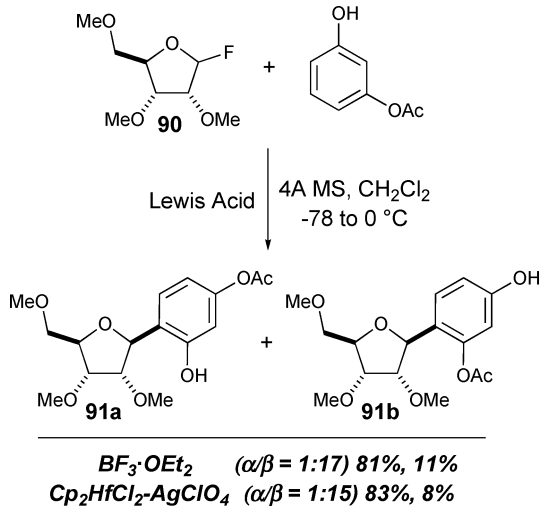
(26)

5.4.2 Lewis acid-mediated [1, 3] rearrangement of pendant aryl and vinyl ethers. Development of the [1, 3] rearrangement of pendant aryl and vinyl ethers illustrates both the utility and convergence of this reaction manifold. At the heart of the stereochemical issues associated with this rearrangement are ion pairing and molecular conformation. A variety of models can be used to rationalize the observed product ratios; however, the steric influence of substituents primarily dictates product stereochemistry. An early example of a [1, 3] O-to-C rearrangement was disclosed by Suzuki and coworkers. A mixture of anomeric fluorides and a phenol first forms an O-glycosidic linkage, which upon warming rearranges to its C-congener. Tin and boron Lewis acids are effective for the formation of the α-product, while the Cp_2HfCl_2–$AgClO_4$ mixed Lewis acid provides the β-product (eqn 27).[54]



(27)

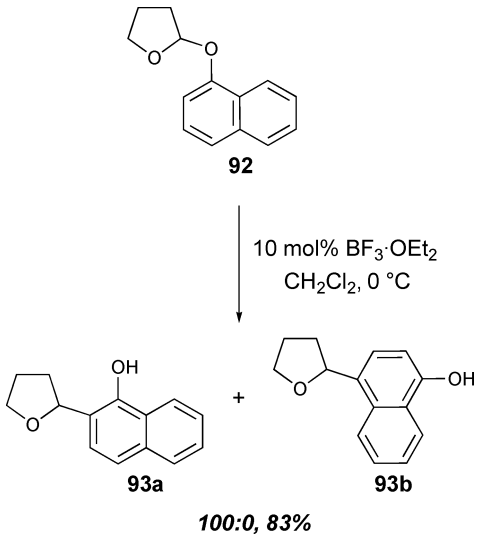
Resorcinol derivatives also perform well under these reaction conditions, favoring the β-product with good regioselectivity (eqn 28).[55] This method has been expanded to incorporate *O*-acetyl glycosides as efficient glycoside donors[56] and as an approach



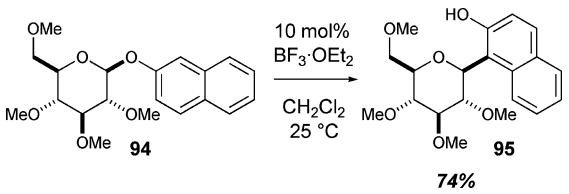
(28)

toward the vineomycin skeleton.[57] Suzuki proposes that these reactions proceed through ion pairs.

Preformed tetrahydrofuranyl *O*-aryl glycosides rearrange efficiently in the presence of catalytic Lewis acid, as shown by Kometani and coworkers (eqn 29).[58] In more complex sugar-derived systems the β-anomer is the favored product (eqn 30).[59]

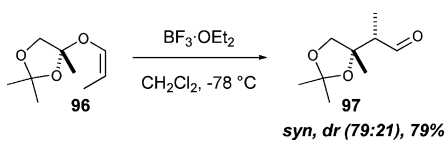


(29)

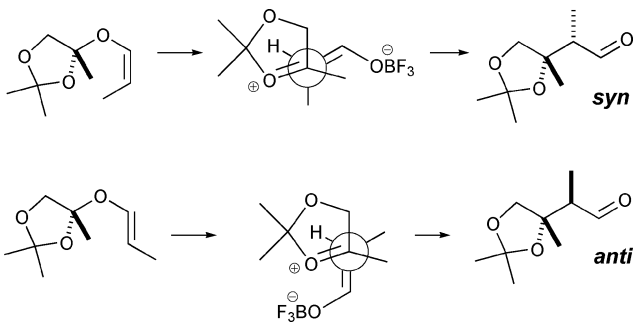


(30)

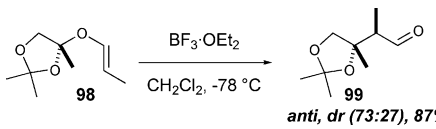
Frauenrath and Runsink described the stereoselective rearrangement of dioxolanylpropenyl ethers **96** and **98** to the corresponding aldehydes (eqns 31 and 32).[60] Once again, double bond geometry affects the stereochemistry of the product: a *Z* olefin configuration provides the *syn* product (dioxolane oxygen *syn* to methyl) and an *E* olefin configuration gives the *anti* product, although neither proceeds with high selectivity (Scheme 17).



(31)

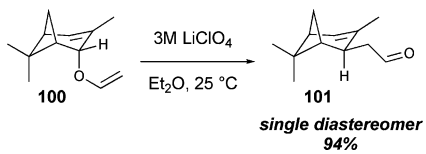


Scheme 17



(32)

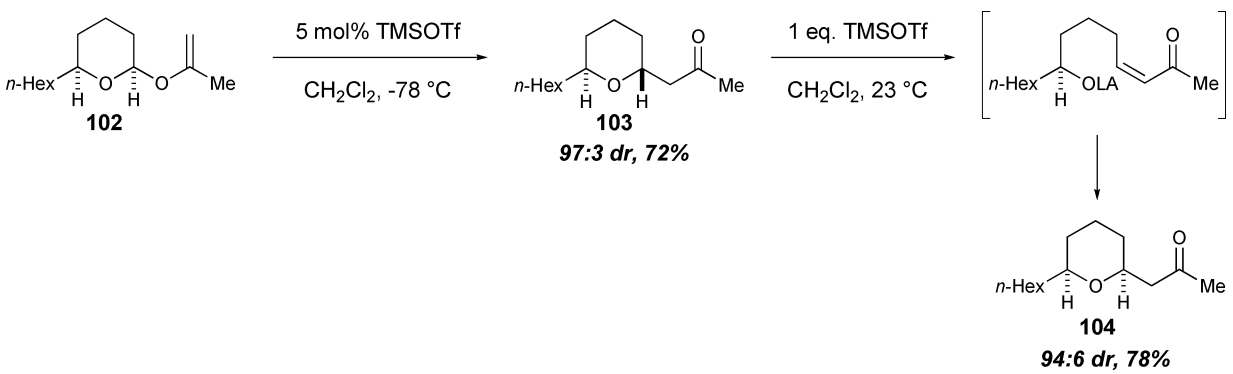
The steric environment about the allyl cation can also control facial selectivity in the recombination event. Grieco and coworkers developed a $LiClO_4$–Et_2O protocol for the [1, 3] rearrangement of aliphatic allyl vinyl ethers. In a particularly nice example, a verbenol-derived allyl vinyl ether **100** rearranges with complete inversion (eqn 33). A crossover experiment revealed that these conditions were enabling the reaction to proceed through a dissociated ion pair, which mandates that product selectivity arises from recombination from the less hindered face of the ring system.[61]



(33)

A sequence of papers by Ley and coworkers described the rearrangement of pyranyl vinyl acetals and related anomerically linked nucleophiles.[62,63] Typically, products of 2,6-*trans* stereochemistry about the pyran ring are isolated. The *trans* products are essentially identical to those that can be accessed by intermolecular oxocarbenium ion alkylations. However, by simply increasing the amount of Lewis acid and the reaction temperature, the *trans* product could be equilibrated to the *cis* stereochemistry, presumably through ring-opening of the pyran (Scheme 18).[64]

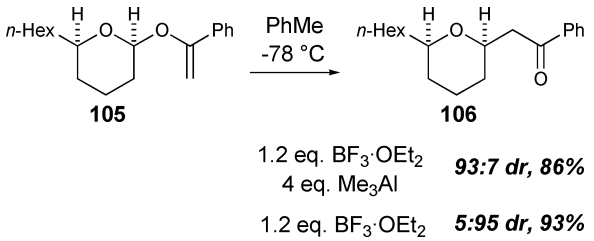
Using Okahara's insight into the nature of the ion pair intermediates formed by Lewis acid-mediated cleavage of vinyl acetals,



Scheme 18

 This journal is © The Royal Society of Chemistry 2008

our laboratory has developed a stereoretentive rearrangement of pyranyl vinyl acetals. A mixture of Lewis acids (Me_3Al and $BF_3{\cdot}OEt_2$ in a 4 : 1 ratio) produces a tight ion pair from the cleavage of vinyl acetal **105**, which leads to the formation of the 2,6-*cis* pyran **106** (eqn 36).[65] The reaction of **105** in presence of $BF_3{\cdot}OEt_2$ provides *trans*-**106** in 95 : 5 dr and 93% yield.

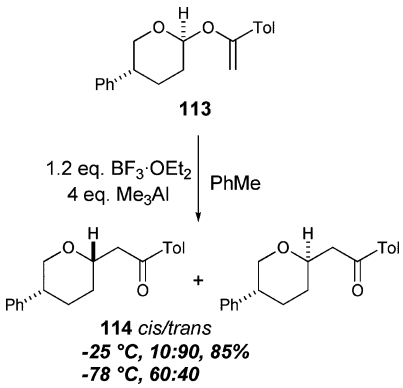


(34)

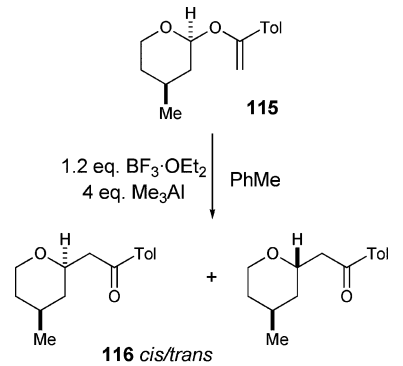
It was hypothesized that a tight contact ion pair was responsible for the *cis* product stereochemistry. Indeed, a crossover experiment revealed minimal amounts of products arising from ion scrambling, while providing *cis* stereochemistry (Scheme 19). The crossover experiment, when performed in the presence of $BF_3{\cdot}OEt_2$, provides primarily the *trans* products with modest but significant amounts of crossover. This suggests that two different ionic species are involved: 1) a tight ion pair that provides the *cis* product ($Me_3Al/BF_3{\cdot}OEt_2$) and 2) a solvent-equilibrated ion pair ($BF_3{\cdot}OEt_2$) that emulates an intermolecular nucleophilic addition to an oxocarbenium ion, but presumably does not fully dissociate in the low polarity medium.

Another interesting observation that evolved from this report is an example of an isoinversion[66] effect: lower temperatures provide lower selectivity, while higher temperatures provide greater selectivity (eqns 35 and 36), a situation easily explained when one considers the entropic factors involved in solvating two distinct ions.[46] This method also provides stereoselective access to 2,7-disubstituted oxepanes and 2,5-disubstituted tetrahydrofurans.

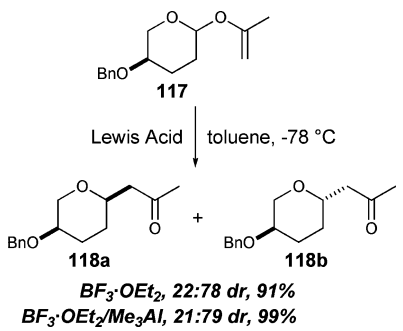
Woerpel and Shenoy showed that 5-(benzyloxy)pyranyl vinyl acetal **117** rearranges under the Rovis conditions for generating contact ion pairs and $BF_3{\cdot}OEt_2$ to provide the *trans* product stereochemistry in nearly identical yield and selectivity (eqn 37).[67] They suggest that the reaction proceeds under both conditions *via* a solvent-equilibrated ion pair. In this case ion pairing does not explain their results, which remain consistent with their inside-attack model.[68]



(35)

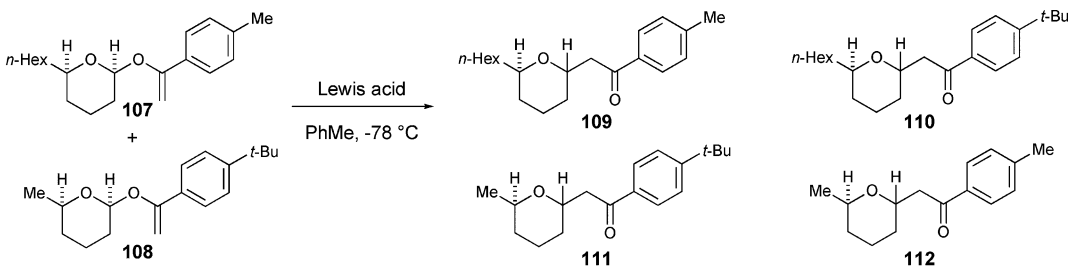


(36)



(37)

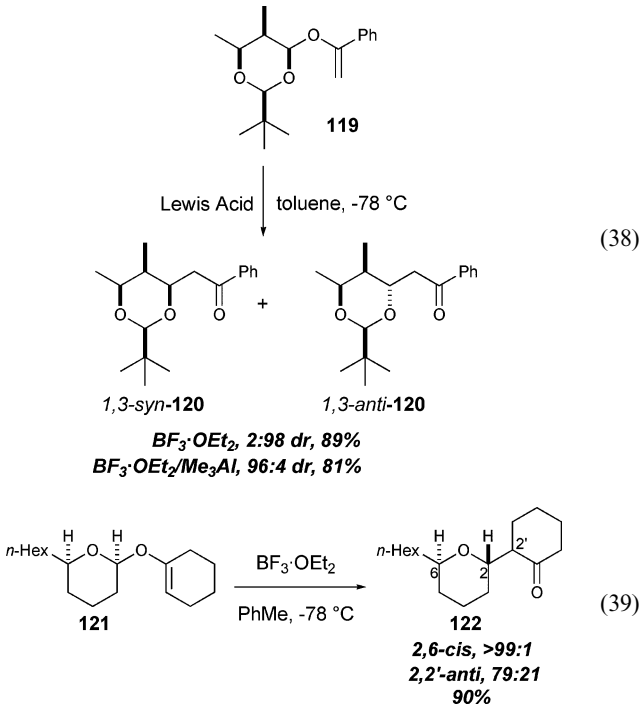
We have also shown that this rearrangement could be applied to more complex systems. Rearrangement of vinyl acetal **119** can provide access to 1,3-polyol arrays through a stereoretentive



	non-crossover products				crossover products			
Lewis Acid	*cis*-**109**	*trans*-**109**	*cis*-**111**	*trans*-**111**	*cis*-**110**	*trans*-**110**	*cis*-**112**	*trans*-**112**
$BF_3{\cdot}OEt_2$	0.5	23.0	0.3	36.0	0.6	20.8	0.1	15.3
$Me_3Al/BF_3{\cdot}OEt_2$	48.8	1.4	42.8	6.8	0	0.3	0	<0.2

Scheme 19

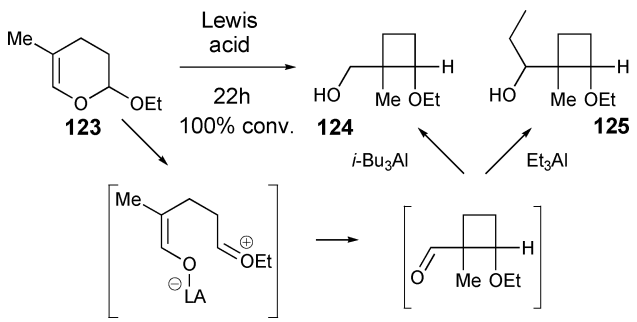
process that provides *syn*-**120** or a solvent-equilibrated ion pair that provides *anti*-**120** (eqn 38).[69] The rearrangement of pendant cyclic vinyl ethers also works well under the solvent-equilibrated ion pair conditions to provide **122** with the simultaneous formation of two new contiguous stereocenters (eqn 39).[70]



(38)

(39)

5.4.3 Lewis acid-mediated [1, 3] rearrangement to make heterocycles and carbocycles. Lewis acid-mediated rearrangement of cyclic vinyl ethers to form either heterocycles or carbocycles is fundamentally different from the rearrangement of pendant vinyl ethers because they lack a cyclic oxocarbenium ion that can be used as a control element. As a result the selectivity in these reactions is strongly influenced by both the size of the Lewis acid employed and the nature of the substituents on the substrate in question. In an early report, Menicagli and coworkers showed that dihydro-2*H*-pyrans would undergo ring contraction to form the corresponding cyclobutanes (Scheme 20).[71]



Scheme 20

They later confirmed the stereochemistry about the cyclobutane ring to be *cis* (hydroxy methylene *cis* to ethoxy group). Interestingly, employment of an Al–etherate complex provides the product of alkyl group transfer (secondary OH) in preference to reduction (Scheme 21).[72]

Seven-membered rings may be converted into their five-membered ring counterparts *via* Lewis acid activation. Frauenrath and coworkers described a ring-contraction of 2,4-disubstituted dioxepins; however, a surprising effect was noted. The *cis*-2,4-disubstituted dioxepin provides a mixture of the four possible diastereomeric tetrahydrofurans, while the *trans*-disubstituted dioxepin provides only two tetrahydrofuran products with good selectivity for **137** (Scheme 22).[73]

Takano and coworkers illustrated a diastereoselective ring contraction to produce a 2,3,4-trisubstituted tetrahydrofuran *en route* to (±)-asarinin (Scheme 23). They showed that two different Lewis acids would provide complementary diastereomeric tetrahydrofurans with good selectivity.[74]

We chose to expand on these isolated examples of 1,3-dioxepin ring contractions and hypothesized that the stability of the oxocarbenium ion intermediate was key in controlling the relative stereochemistry of the tetrahydrofuran. The Frauenrath and Takano conditions were ineffective for the rearrangement of **141** (Table 1). However, when MeCN was used as the solvent, the ring contraction proved selective for one of the four diastereomeric tetrahydrofurans. This allowed for vast expansion of the substrate scope.[75]

The relative configuration in the 2,3,4-trisubstituted tetrahydrofuran products can be rationalized with our proposed stereochemical model (Fig. 2). Both R_1 and R_2 prefer to be in the equatorial positions (**A** *vs.* **B**). We also believe that there is an interplay of energy minimization brought about by the potential relief of $A_{1,3}$ strain between R_2 and the metalloenolate (**A** *vs.* **C**).

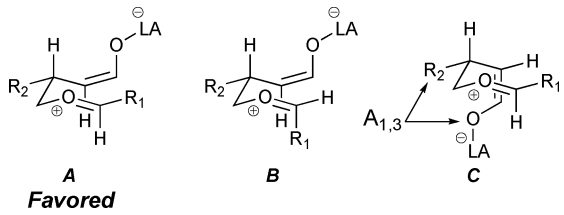
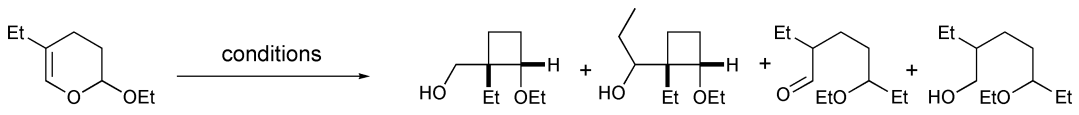


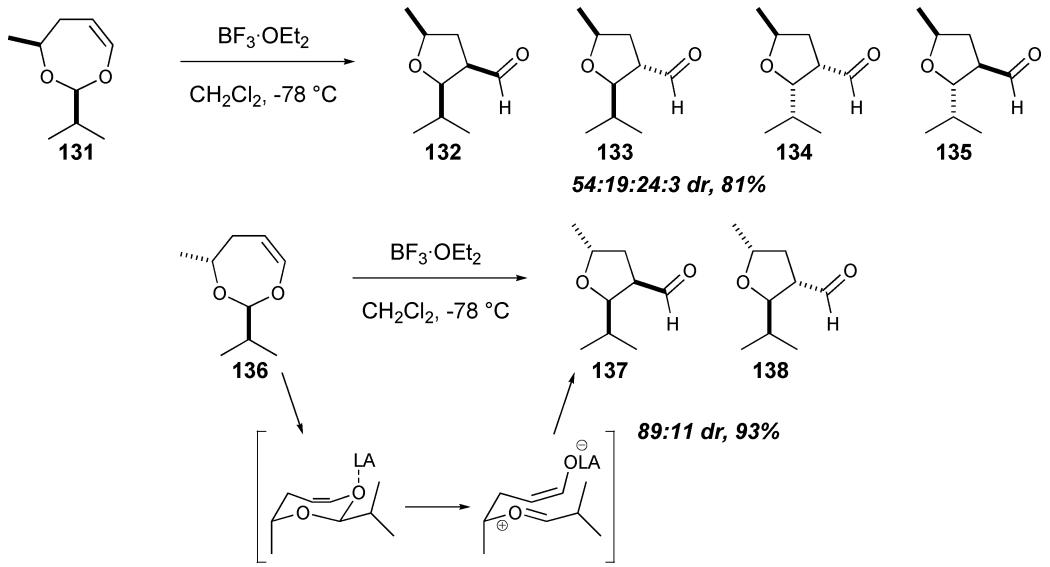
Fig. 2



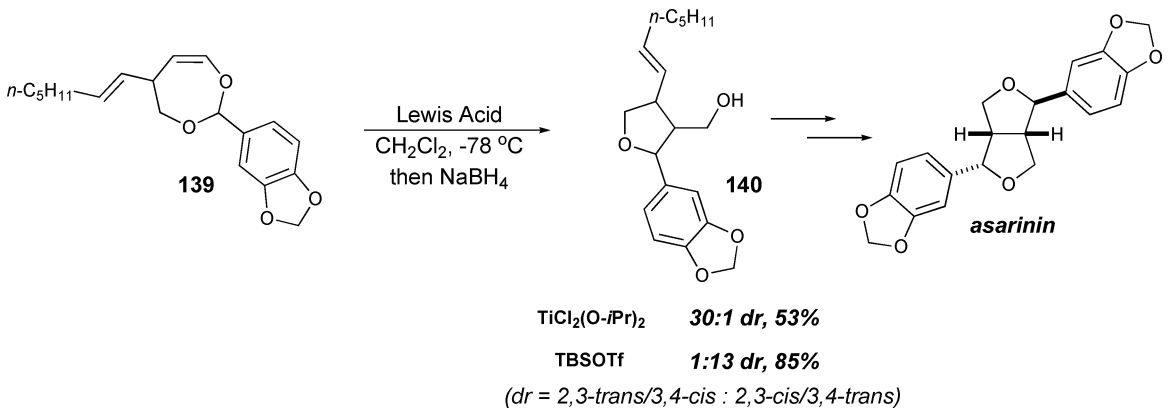
	127	:	128	:	129	:	130
0.5 eq. Et_3Al, 98 °C, 4.5h, (100% conv.)	34	:	51	:	15	:	0
0.5 eq. $Et_3Al{\cdot}OEt_2$, 98 °C, 20.5h, (100% conv.)	9	:	91	:	0	:	0

Scheme 21

 This journal is © The Royal Society of Chemistry 2008

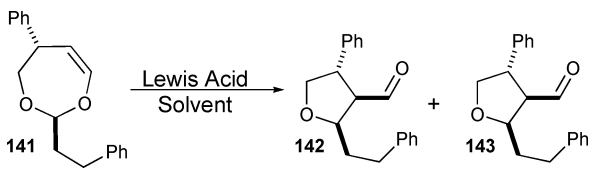


Scheme 22



Scheme 23

Table 1 Optimization of [1, 3] ring contraction of 1,3-dioxepins



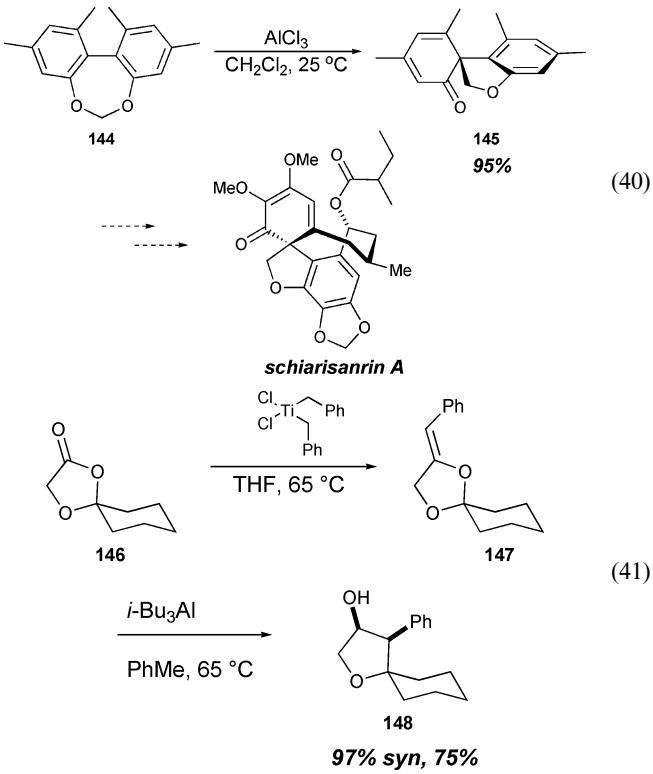
Entry	Lewis acid	Eq.	Solvent	T/°C	dr (**142**:**143**:minor products)	Yield (%)
1	$BF_3{\cdot}OEt_2$	0.1	CH_2Cl_2	−78	62 : 24 : 3 : 11	93
2	$Cl_2Ti(O\textit{i}\text{-}Pr)_2$	1.1	CH_2Cl_2	−78	19 : 66 : 11 : 4	92
3	TMSOTf	0.1	CH_2Cl_2	−78	55 : 33 : 6 : 8	80
4	TMSOTf	0.1	MeCN	−40	91 : 5 : 4 : <1	85

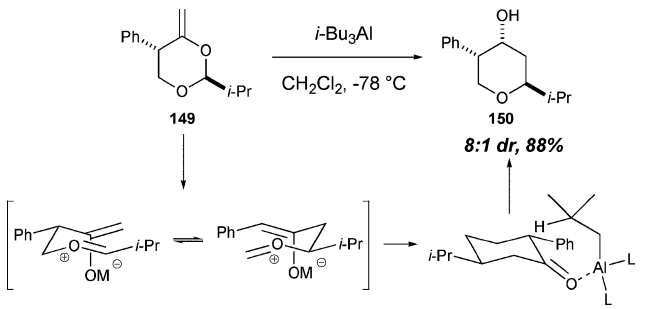
Coleman and coworkers described a similar ring contraction of dibenzodioxepins, as an approach to the spirobicyclic ring system of the schiarisanrin class of natural products (eqn 40).[76]

Another effective and convergent oxacycle synthesis emerged from the labs of Petasis.[77] Condensation between a hydroxy acid and a ketone provides spirocycles of type **146**. Carbonyl olefination with the Petasis reagent provides the desired vinyl acetal, and when treated with i-Bu_3Al, rearrangement followed by ketone reduction furnishes **148** with excellent *cis* diastereoselectivity (eqn 41). Tertiary alcohols may be accessed using this method through the use of Me_3Al or Et_3Al as the Lewis acid/alkylating reagent.

Pyrans may also be constructed using this method, for which the reduction to the secondary alcohol proceeds with good diastereoselectivity (Scheme 24).[78] In spite of the potential for an oxonia-Cope rearrangement, the reaction still proceeds with excellent diastereoselectivity between the phenyl and isopropyl substituents in product **150**.

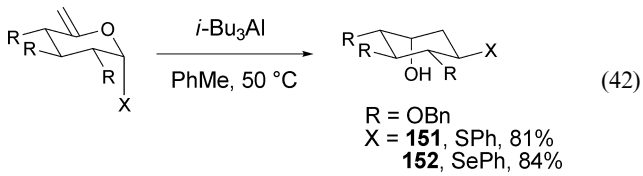
Electron-donating groups other than the ether functionality will sufficiently activate a vinyl ether towards [1, 3] rearrangement.





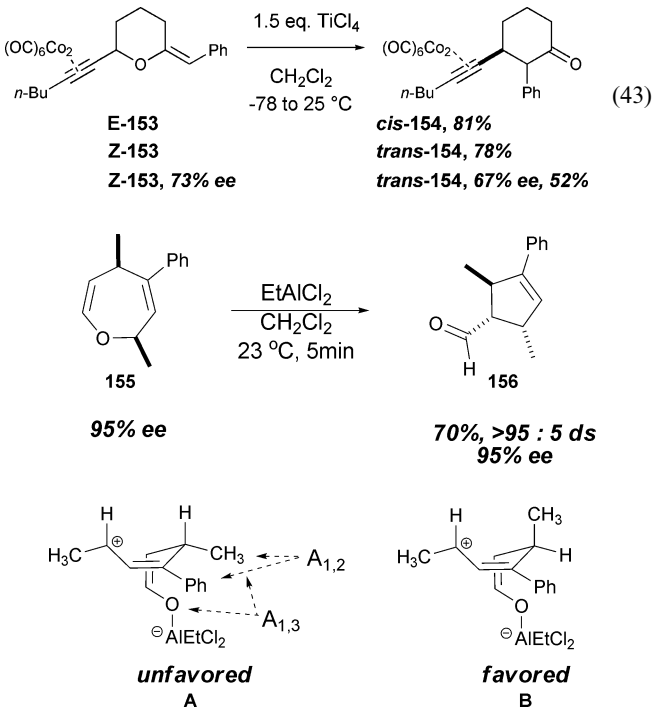
Scheme 24

Sinay and coworkers reported a Lewis acid-mediated Ferrier reaction for a variety of functionalized C-glycosides (eqn 42).[79,80] The ketone intermediates, formed after the rearrangement, are further reduced by *i*-Bu_3Al as per the work of Petasis.

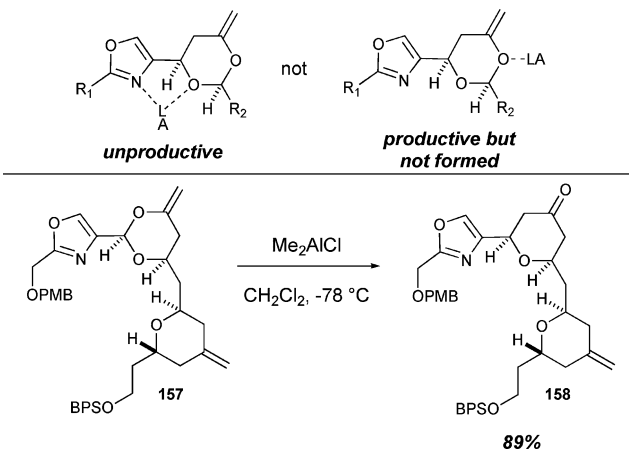


Dicobalt hexacarbonyl complexes of alkynes are known to stabilize propargylic cations[81] and thus have been used in the context of [1, 3] rearrangement of pyrans.[82,83] In contrast to the example by Smith (*vide supra*), Harrity and coworkers have illustrated that *E* and *Z* olefin isomers lead to different diastereomers (eqn 43). Enantioenriched pyran *Z*-**153** rearranges efficiently in the presence of $TiCl_4$ with minimal racemization.

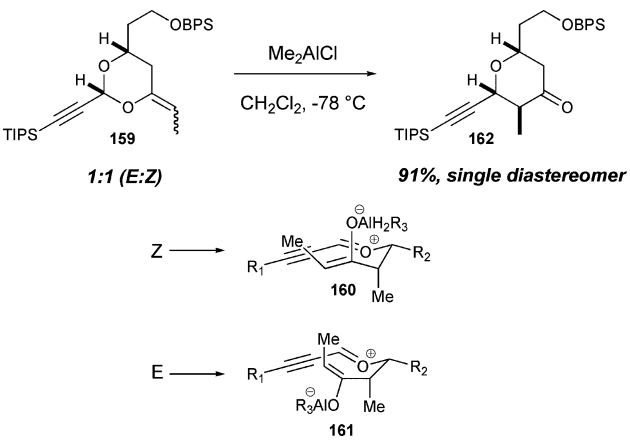
We have shown that allylic stabilization of the carbocation will allow for [1, 3] rearrangement of cyclic allyl vinyl ethers (2,5-dihydrooxepins) in a modular route to densely functionalized cyclopentenes (Scheme 25).[84] A pre-existing stereocenter that is



Scheme 25

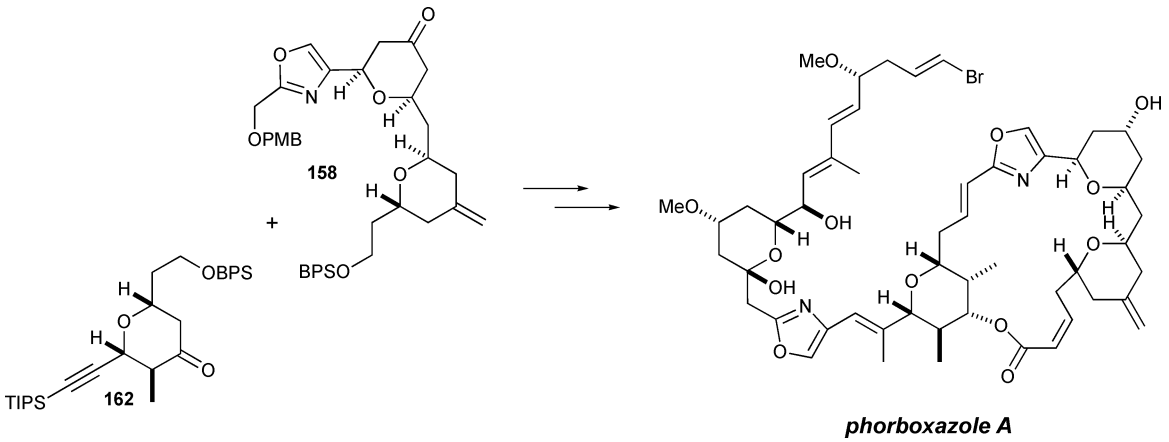


Scheme 26



Scheme 27

This journal is © The Royal Society of Chemistry 2008



Scheme 28

not epimerizable under the reaction conditions leads to enhanced levels of diastereoselection through minimization of $A_{1,2}$ and $A_{1,3}$ strain (**A** *vs.* **B**).

In the arena of natural product synthesis, the most spectacular examples of this type of transformation were accomplished by Smith and coworkers *en route* to (+)-phorboxazole A.[85,86] A first-generation approach to the key dioxane revealed that the oxazole and ether oxygen could form a chelate with the Lewis acid, suppressing reactivity (Scheme 26). This problem was overcome through the synthesis of a regioisomeric dioxane, which rearranges in the presence of Me_2AlCl.

Stereoconvergent rearrangement of a 1 : 1 mixture of *E* and *Z* trisubstituted alkene isomers **159** provides **162** as a single diastereomer in good yield (Scheme 27). This surprising result was rationalized as follows: the *Z* isomer reacts *via* a preferred chair transition state **160** while the *E* isomer rearranges through a boat conformation **161**.

Both **158** and **162** were carried on to complete the total synthesis of (+)-phorboxazole A (Scheme 28). This carbocyclization has also been effectively used by Smith and coworkers *en route* to (−)-kendomycin and the EF fragment of (+)-spongistatin 1.[87,88]

6 Conclusion

This review has attempted to comprehensively survey advances in the development of [1, 3] rearrangements. Although significant progress has been made in this area, there is room for improvement of existing methods and their application to more complex scenarios. In particular, the incorporation of nitrogen into rearrangement precursors would undoubtedly expand the utility of this class of reactions. Certainly, future research with an eye towards substituent effects and ion pairing will have a large impact on the general understanding and development of new [1, 3] rearrangements.

References and notes

1 (*a*) R. P. Lutz, *Chem. Rev.*, 1984, **84**, 223–247; (*b*) P. Wipf, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, Oxford, 1991, vol. 5, pp. 827–873; (*c*) S. Blechert, *Synthesis*, 1989, 71–82; (*d*) H. Ito and T. Taguchi, *Chem. Soc. Rev.*, 1999, **28**, 43–50; (*e*) N. Udo, *Synthesis*, 2003, 961–1008; (*f*) A. M. Martin Castro, *Chem. Rev.*, 2004, **104**, 2939–3002.

2 There are other [1, 3] rearrangements that do not fall into any of these categories such as Fries-type processes and related transformations. However, these reactions lie outside of the scope of this review, which is focused on the potential for stereoselective synthesis, and in particular that involving carbon sp^3 stereocenters.

3 (*a*) R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970; (*b*) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley-Interscience, New York, 1976.

4 There are few examples of [1, 3] antarafacial shifts. For an example see: J. E. Baldwin and R. H. Flemming, *J. Am. Chem. Soc.*, 1972, **94**, 2140–2142.

5 J. A. Berson, *Acc. Chem. Res.*, 1972, **5**, 406–414.

6 L. Claisen, *Chem. Ber.*, 1896, **29**, 2931–2932.

7 L. Claisen, *Chem. Ber.*, 1912, **45**, 3157–3166.

8 W. Wislicenus and R. Schrotter, *Ann. Chem.*, 1921, **424**, 215–232.

9 H. Staudinger and L. Ružicka, L., *Helv. Chim. Acta*, 1924, **7**, 377–390.

10 W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1933, **55**, 4923–4930.

11 (*a*) S. G. Powell and R. Adams, *J. Am. Chem. Soc.*, 1920, **36**, 646–658; (*b*) W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1920, **36**, 1572–1574; (*c*) M. A. Spielman and C. W. Mortenson, *J. Am. Chem. Soc.*, 1939, **55**, 666–667; (*d*) K. B. Wiberg, T. M. Shryne and R. R. Kintner, *J. Am. Chem. Soc.*, 1957, **79**, 3160–3164; (*e*) F. H. MacDougall, W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1933, **55**, 4089–4097; (*f*) K. B. Wiberg, R. R. Kintner and E. L. Motell, *J. Am. Chem. Soc.*, 1963, **85**, 450–454.

12 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, New York, 1970.

13 F. D. Greene, M. A. Berwick and J. C. Stowell, *J. Am. Chem. Soc.*, 1970, **92**, 867–874.

14 [1, 3] O-to-C rearrangements that proceed *via* an ion pair will be discussed in Section 5.

15 H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, 1954, **76**, 519–522.

16 K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.*, 1955, **77**, 1159–1163.

17 Used as a radical trap for dissociated radicals produced under thermal rearrangement conditions; approximately 12% of the butane thiol adduct was isolated.

18 J. W. Lown, M. H. Akhtar and R. S. McDaniel, *J. Org. Chem.*, 1974, **39**, 1998–2006.

19 I. Shiina and H. Nagasue, *Tetrahedron Lett.*, 2002, **43**, 5837–5840.

20 R. T. Arnold and S. T. Kulenovic, *J. Org. Chem.*, 1980, **45**, 891–894.

21 K. Burger, K. Gaa, K. Geith and C. Schierlinger, *Synthesis*, 1989, 850–855.

22 K. Burger, A. Fuchs, L. Hennig, B. Helmreich and D. Greif, *Monatsh. Chem.*, 2001, **132**, 929–945.

23 (*a*) J. Barluenga, F. Aznar, R. Liz and M. Bayod, *J. Chem. Soc., Chem. Commun.*, 1984, 1427–1428; (*b*) J. Barluenga, F. Aznar, R. Liz and M. Bayod, *J. Org. Chem.*, 1987, **52**, 5190–5194.

24 (*a*) G. W. Morrow, S. Wang and J. S. Swenton, *Tetrahedron Lett.*, 1988, **29**, 3441–3444; (*b*) S. Wang, G. W. Morrow and J. S. Swenton, *J. Org. Chem.*, 1989, **54**, 5364–5371.

25 K. Shishido, E. Shitara and K. Fukumoto, *J. Am. Chem. Soc.*, 1985, **107**, 5810–5812.

26 S. Danishefsky, R. L. Funk and J. F. Kerwin, Jr., *J. Am. Chem. Soc.*, 1980, **102**, 6891–6893.
27 K. M. Kahn and D. W. Knight, *J. Chem. Soc., Chem. Commun.*, 1991, 1699–1701.
28 V. Novikov, A. R. Kennedy and J. D. Rainier, *J. Org. Chem.*, 2003, **68**, 993–996.
29 (*a*) R. J. Ferrier, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1455–1458; (*b*) R. Blattner, R. J. Ferrier and S. R. Haines, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2413–2416.
30 (*a*) Other examples of Hg(II)-mediated carbocyclization: D. H. R. Barton, J. Camara, P. Dalko, S. D. Gero, B. Quiclet-Sire and P. Stutz, *J. Org. Chem.*, 1989, **54**, 3764–3766; (*b*) D. H. R. Barton, S. Augy-Dorey, J. Camara, P. Dalko, J. M. Delaumeny, S. D. Gero, B. Quiclet-Sire and P. Stutz, *Tetrahedron*, 1990, **46**, 215–230.
31 S. Adam, *Tetrahedron Lett.*, 1988, **29**, 6589–6592.
32 Other examples of Pd(II) catalysis: P. Laszlo and A. Dudon, *J. Carbohydr. Chem.*, 1992, **11**, 587–593.
33 (*a*) S. J. Rhoads and J. M. Watson, *J. Am. Chem. Soc.*, 1971, **93**, 5813–5815; (*b*) E. Demole and P. Enggish, *J. Chem. Soc., Chem. Commun.*, 1969, 264–265.
34 (*a*) B. M. Trost, T. A. Runge and L. N. Jungheim, *J. Am. Chem. Soc.*, 1980, **102**, 2840–2841; (*b*) B. M. Trost and T. A. Runge, T., *J. Am. Chem. Soc.*, 1981, **103**, 7550–7559.
35 B. M. Trost and T. A. Runge, *J. Am. Chem. Soc.*, 1981, **103**, 2485–2487.
36 B. M. Trost and T. A. Runge, *J. Am. Chem. Soc.*, 1981, **103**, 7559–7572.
37 (*a*) B. M. Trost, *Tetrahedron*, 1977, **33**, 2615–2649; (*b*) B. M. Trost, *Acc. Chem. Res.*, 1980, **12**, 385–393.
38 W. Steglich and G. Höfle, *Tetrahedron Lett.*, 1970, **11**, 4727–4730.
39 (*a*) J. C. Ruble and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 11532–11533; (*b*) S. A. Shaw, P. Aleman and E. Vedejs, *J. Am. Chem. Soc.*, 2003, **125**, 13368–13369; (*c*) S. A. Shaw, P. Aleman, J. Christy, J. W. Kampf, P. Va and E. Vedejs, *J. Am. Chem. Soc.*, 2006, **128**, 925–934.
40 J. E. Thomson, K. Rix and A. D. Smith, *Org. Lett.*, 2006, **8**, 3785–3788.
41 M. Takahashi, H. Suzuki, Y. Moro-oka and T. Ikawa, *Chem. Lett.*, 1981, 1435–1438.
42 M. Takahashi, H. Suzuki, Y. Moro-oka and T. Ikawa, *Tetrahedron Lett.*, 1982, **23**, 1079–1082.
43 M. Takahashi, H. Suzuki, Y. Moro-oka and T. Ikawa, *Tetrahedron Lett.*, 1982, **23**, 4031–4039.
44 E. Tayama and W. Isaka, *Org. Lett.*, 2006, **8**, 5437–5439.
45 T. Suzuki, M. Inui, S. Hosokawa and S. Kobayashi, *Tetrahedron Lett.*, 2003, **44**, 3713–3716.
46 X. P. Gu, I. Ikeda and M. Okahara, *J. Org. Chem.*, 1988, **53**, 2737–2740.
47 For further reading about contact ion pairs, see: (*a*) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 1965, **87**, 669–670; (*b*) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 1966, **88**, 307–318; (*c*) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 1966, **88**, 318–324.
48 H. Frauenrath, T. Arenz, G. Raabe and M. Zorn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 83–85.
49 K. Nonoshita, H. Banno, K. Maruoka and H. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 316–322.
50 (*a*) A. Gansäuer, D. Fielenbach and C. Stock, *Adv. Synth. Catal.*, 2002, **344**, 845–848; (*b*) A. Gansäuer, D. Fielenbach, C. Stock and D. Geich-Gimbel, *Adv. Synth. Catal.*, 2003, **345**, 1017–1030.
51 C. G. Nasveschuk and T. Rovis, *Org. Lett.*, 2005, **7**, 2173–2176.
52 W. G. Dauaben, J. M. Cogen and V. Behar, *Tetrahedron Lett.*, 1990, **31**, 3241–3244.
53 M. R. Dintzner, K. M. Morse, K. M. McClelland and D. M. Coligado, *Tetrahedron Lett.*, 2004, **45**, 79–81.
54 T. Matsumoto, M. Katsuki and K. Suzuki, *Tetrahedron Lett.*, 1988, **29**, 6935–6938.
55 T. Matsumoto, T. Hosoya and K. Suzuki, *Synlett*, 1991, 709–711.
56 T. Matsumoto, T. Hosoya and K. Suzuki, *Tetrahedron Lett.*, 1990, **31**, 4629–4632.
57 (*a*) T. Matsumoto, M. Katsuki, H. Jona and K. Suzuki, *Tetrahedron Lett.*, 1989, **30**, 6185–6188; (*b*) K. Suzuki, *Pure Appl. Chem.*, 1994, **66**, 2175–2178.
58 T. Kometani, H. Kondo and Y. Fujimori, *Synthesis*, 1988, 1005–1007.
59 A similar rearrangement in the presence of stoichiometric Lewis acid was reported: N. G. Ramesh and K. K. Balasubramanian, *Tetrahedron Lett.*, 1992, **33**, 3061–3064.
60 H. Frauenrath and J. Runsink, *J. Org. Chem.*, 1988, **53**, 1860–1862.
61 P. A. Grieco, J. D. Clark and C. T. Jagoe, *J. Am. Chem. Soc.*, 1991, **113**, 5488–5489.
62 (*a*) M. F. Buffet, D. J. Dixon, S. V. Ley and E. W. Tate, *Synlett*, 1998, 1091–1092; (*b*) D. J. Dixon, S. V. Ley and E. W. Tate, *Synlett*, 1998, 1093–1095; (*c*) D. J. Dixon, S. V. Ley and E. W. Tate, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3125–3126; (*d*) D. J. Dixon, S. V. Ley and D. J. Reynolds, *Angew. Chem., Int. Ed.*, 2000, **39**, 3622–3626; (*e*) M. F. Buffet, D. J. Dixon, G. L. Edwards, S. V. Ley and E. W. Tate, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1815–1827; (*f*) M. F. Buffet, D. J. Dixon, S. V. Ley, D. J. Reynolds and R. I. Storer, *Org. Biomol. Chem.*, 2004, **2**, 1145–1154.
63 For a related, seminal reference, see: K. Mikami and H. Kishino, *Tetrahedron Lett.*, 1996, **37**, 3705–3708.
64 D. J. Dixon, S. V. Ley and E. W. Tate, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2385–2394.
65 Y. Zhang, N. T. Reynolds, K. Manju and T. Rovis, *J. Am. Chem. Soc.*, 2002, **124**, 9720–9721.
66 For a review on this concept, see: H. Bushmann, H.-D. Scharf, N. Hoffmann and P. Esser, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 477–515.
67 S. R. Shenoy and K. A. Woerpel, *Org. Lett.*, 2005, **7**, 1157–1160.
68 (*a*) J. A. C. Romero, S. A. Tabacco and K. A. Woerpel, *J. Am. Chem. Soc.*, 2000, **122**, 168–169; (*b*) L. Ayala, C. G. Lucero, J. A. C. Romero, S. A. Tabacco and K. A. Woerpel, *J. Am. Chem. Soc.*, 2003, **125**, 15521–15528.
69 Y. Zhang and T. Rovis, *Tetrahedron*, 2003, **59**, 8979–8987.
70 J. D. Frein and T. Rovis, *Tetrahedron*, 2006, **62**, 4573–4583.
71 R. Menicagli, C. Malanga, L. Lardicci and L. Tinucci, *Tetrahedron Lett.*, 1980, **21**, 4525–4528.
72 R. Menicagli, C. Malanga and L. Lardicci, *J. Org. Chem.*, 1982, **47**, 2288–2291.
73 (*a*) H. Frauenrath, J. Runsink and H.-D. Scharf, *Chem. Ber.*, 1982, **115**, 2728–2729; (*b*) H. Frauenrath and J. Runsink, *J. Org. Chem.*, 1987, **52**, 2707–2712.
74 S. Takano, K. Samizu and K. Ogasawara, *Synlett*, 1993, 785–787.
75 C. G. Nasveschuk, N. T. Jui and T. Rovis, *Chem. Commun.*, 2006, 3119–3121.
76 R. S. Coleman, J. M. Guernon and J. T. Roland, *Org. Lett.*, 2000, **2**, 277–280.
77 N. A. Petasis and S.-P. Lu, *J. Am. Chem. Soc.*, 1995, **117**, 6394–6395.
78 N. A. Petasis and S.-P. Lu, *Tetrahedron Lett.*, 1996, **37**, 141–144.
79 M. Sollogoub, J.-M. Mallet and P. Sinaÿ, *Angew. Chem., Int. Ed.*, 2000, **39**, 362–364.
80 For more varied examples, see: (*a*) S. K. Das, J.-M. Mallet and P. Sinaÿ, *Angew. Chem., Int. Ed. Engl.*, 1997, **109**, 493–496; (*b*) P. Sinaÿ and P. Dalko, *Angew. Chem., Int. Ed.*, 1999, **111**, 819–823; (*c*) A. J. Pearce, M. Sollogoub, J.-M. Mallet and P. Sinaÿ, *Eur. J. Org. Chem.*, 1999, 2103–2117.
81 A. M. Nicholas, *Acc. Chem. Res.*, 1987, **20**, 207–214.
82 (*a*) S. J. Meek, F. Pradaux, D. R. Carbery, E. H. Demont and J. P. A. Harrity, *J. Org. Chem.*, 2005, **70**, 10046–10056; (*b*) D. R. Carbery, S. Reignier, N. D. Miller, H. Adams and J. P. A. Harrity, *J. Org. Chem.*, 2003, **68**, 4392–4399; (*c*) D. R. Carbery, S. Reignier, J. W. Myatt, N. D. Miller and J. P. A. Harrity, *Angew. Chem., Int. Ed.*, 2002, **41**, 2584–2587.
83 This method may also be used in the diastereoselective ring contraction of dihydro-2*H*-pyrans to provide cyclobutanes: S. J. Meek, F. Pradaux, E. H. Demont and J. P. A. Harrity, *Org. Lett.*, 2006, **8**, 5597–5600.
84 C. G. Nasveschuk and T. Rovis, *Angew. Chem., Int. Ed.*, 2005, **44**, 3264–3267.
85 (*a*) A. B. Smith, P. R. Verhoest, K. P. Minbiole and J. J. Lim, *Org. Lett.*, 1999, **1**, 909–912; (*b*) A. B. Smith, K. P. Minbiole, P. R. Verhoest and T. J. Beauchamp, *Org. Lett.*, 1999, **1**, 913–916; (*c*) A. B. Smith, K. P. Minbiole, P. R. Verhoest and M. Schelhaas, *J. Am. Chem. Soc.*, 2001, **123**, 4834–4836.
86 A. B. Smith, C. Sfouggatakis, D. B. Gotchev, S. Shirakami, D. Bauer, W. Zhu and V. A. Doughty, *Org. Lett.*, 2004, **6**, 3637–3640.
87 (*a*) A. B. Smith, C. Sfouggatakis, D. B. Gotchev, S. Shirakami, D. Bauer, W. Zhu and V. A. Doughty, *Org. Lett.*, 2004, **6**, 3637–3640; (*b*) A. B. Smith, E. F. Mesaros and E. A. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 6948–6949; (*c*) A. B. Smith, E. F. Mesaros and E. A. Meyer, *J. Am. Chem. Soc.*, 2006, **128**, 5292–5299.
88 After submission of this manuscript, Magnus and coworkers reported an example of a [1, 3] rearrangement in a formal total synthesis of diazonamide A; see: C.-M. Cheung, F. W. Goldberg, P. Magnus, C. J. Russell, R. Turnbull and V. Lynch, *J. Am. Chem. Soc.*, 2007, **129**, 12320–12327.

 This journal is © The Royal Society of Chemistry 2008