Sigmatropic Rearrangement of Vinyl Aziridines: Expedient Synthesis of Cyclic Sulfoximines from Chiral Sulfinimines

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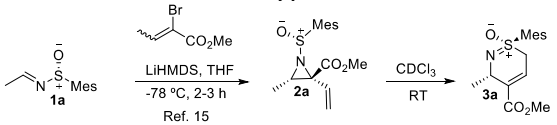
Abstract: A novel rearrangement of 2-vinyl aziridine 2-carboxylates to unusual chiral cyclic sulfoximines is described herein. The method allows the synthesis of substituted cyclic sulfoximines in high yields with complete stereocontrol, displaying a wide substrate scope under mild conditions. Further development of a one-pot process directly from sulfinimines shows the synthetic applicability of this protocol, providing access to complex chiral sulfoximines in only two steps from commercially available aldehydes. A mechanistic hypothesis and synthetic application in the formal synthesis of trachelanthamidine by transformation of a cyclic sulfoximine into a pyrroline is also disclosed.

Since the first isolation of sulfoximines by Bentley and coworkers in 19501 these sulfur containing compounds have found applications in functional group transformations and asymmetric synthesis,2 drug development,3 crop treatment4 and insect control.5 Largely ignored in medicinal chemistry for around 50 years, the sulfoximine group has recently been the object of significant new interest in this area.3 Sulfoximines are three-dimensional motifs with three points of attachment in orthogonal vectors,6 with functionalisation at nitrogen and carbon alpha to the sulfur both versatile and facile. 7-9

Despite the promising biological activity showed by the few previously synthesised cyclic sulfoximines,3 methods describing the synthesis of these compounds are scarce and mainly involve the multistep synthesis of linear sulfoximines10,11 and subsequent cyclisations.12 Furthermore, they generally describe benzo-fused cyclic sulfoximines. This limitation is found in the recent work reported by Hu et al where a very elegant one step synthesis of cyclic sulfoximines was achieved starting from enantiomerically pure sulfinimines through cycloaddition with benzynes.13 Herein we describe a simple and versatile method for the synthesis of non fused 6-membered cyclic sulfoximines with complete diastereocontrol and wide substrate range.

Building on our prior work in the area of aza-Darzens type aziridinations of chiral tert-butanesulfinimines14 and S-mesitylsulfinimines,15 we were drawn to the potential use of 2-bromobut-2-enoic acid methyl ester as a potential partner for an aza-Darzens type aziridination of chiral sulfinimines. The product trisubstituted vinyl aziridine 2-carboxylates would be potentially versatile intermediates for asymmetric synthesis.16 Thus, we investigated the aza-Darzens reaction of acetaldehyde derived S-mesitylsulfinimine 1a using LiHMDS as base in THF at -78 °C. Pleasingly, we found excellent conversion to the vinyl aziridine 2a. However, upon standing in deuterochloroform, we observed that this vinyl aziridine underwent a rearrangement to afford a new compound. After purification and extensive characterisation we found that the isolated product corresponds to the cyclic sulfoximine 3a wherein chiral information is retained (Scheme 1).

Herein, we present our findings on the substrate scope of this novel rearrangement and offer a mechanistic hypothesis for this interesting transformation.



Scheme 1. Unprecedented rearrangement of aziridines leading to sulfoximines

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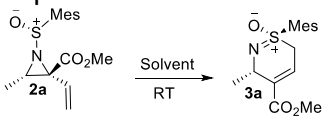
Intrigued by the observed rearrangement, we wanted to explore the influence of solvent and temperature on the sulfoximine formation reaction (Table 1). No clear correlation was found between the nature of solvent and the reaction performance, with best results obtained when CDCl3, DMSO-d6, MeOD and C6D6 were used as solvent. C6D6 was the selected solvent to study the influence of temperature in the described rearrangement. In a very straightforward manner we determined an increase in temperature clearly improves the yield of the reaction, obtaining the desired compound in 80% or 92% yield when the solution was heated at 40 or 70 ºC respectively. Initially, reaction conditions performed at 40 ºC were chosen for the purpose of scope determination (Table 2).

Table 1. Optimisation of reaction conditions

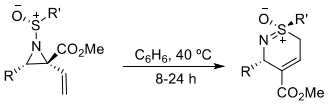


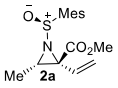
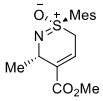
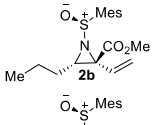
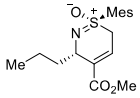
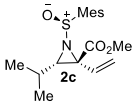
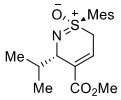
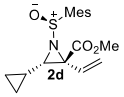
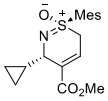
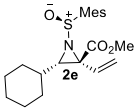
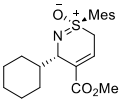
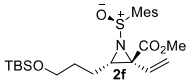
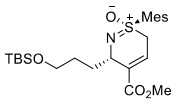
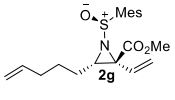
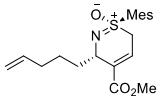
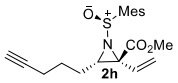
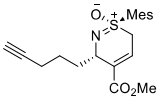
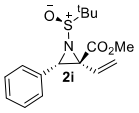
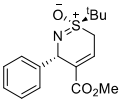
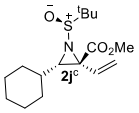
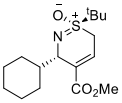
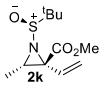
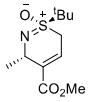
Entry	Solvent	Yield [%][a]	Entry	Solvent	Yield [%][a]
1	$CDCl_3$	50	6	DMF-d_7	12
2	DMSO-d_6	57	7	C_6D_6	50
3	Et_2O-d_6	22	8	C_6D_6	80[b]
4	CD_3OD	50	9	C_6D_6	92[c]
5	CD_3CN	15	10	cyclohexene	60[b,d]

[a] NMR yield. [b] 40 ºC. [c] 70 ºC. [d] Isolated yield.

Several aziridines were synthesised following our previously reported method,15 which were subsequently submitted to the rearrangement reaction conditions (Table 2). The rearrangement reaction showed broad scope for substitution at the 3 position of the vinylaziridine. The rearrangement seemed tolerant of sterically hindered alkylaziridines, which transformed into the corresponding sulfoximines in good yields (Entries 2, 3). The reaction also performed well in the presence of saturated carbocycles (Entries 4, 5). Unsaturation and silylethers were also tolerated under the reaction conditions affording sulfoximines in good yields. (Entries 6-8)

Table 2. Sulfoximine synthesis from vinyl aziridines 2.

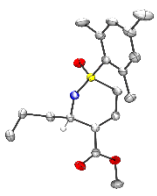


Entry	2[a]	3		Yield [%]
1			**3a**	80
2			**3b**	82
3			**3c**	93
4			**3d**	68
5			**3e**	77
6			**3f**	88
7			**3g**	97
8			**3h**	79
9			**3i**	16[b]
10			**3j**	10[b]
11			**3k**	45[b]

[a] Isolated yield after purification. Scale, 0.5 mmol. [b] 70ºC. [c] 1.2:1 trans/cis.

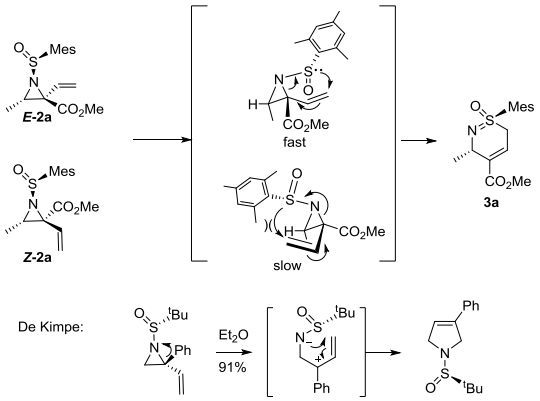
We were pleased to find that suitable crystals for X-Ray analysis were isolated from sulfoximine 3b [Figure 1], 3i and 3k from which unambiguous confirmation of the structure and configuration of the formed heterocycle was obtained (see supplementary information for further details).

Figure 1. X-Ray structure of sulfoximine 1b (CCDC 1484617). Thermal elipsoids shown at 50% probability.



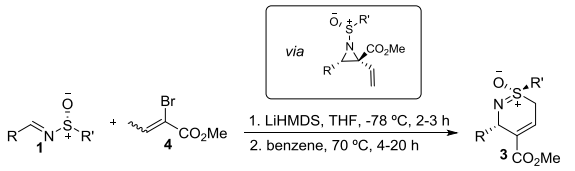
In the case of aziridine 2a (entry 10), we noted that both the two diastereomeric aziridines formed from the corresponding sulfinimine rearranged to the same cyclic sulfoximine 3a. We therefore decided to investigate whether the rate of rearrangement of these diastereomers was different. The rearrangement reaction of E and Z-aziridine 2a was monitored by 1H-NMR.17 The rearrangement of E-aziridine was found to be around 3 times faster than the corresponding Z isomer. Considering a concerted rearrangement,18 we attribute this difference in rate to the increased steric environment around the mesityl group for rearrangement to occur in the Z substrate (Scheme 2). As the reaction works in a wide range of solvents, including polar and non-polar, as well as in nucleophilic solvents like methanol, this gives further evidence of a concerted rearrangement. De Kimpe has previously disclosed a related rearrangement wherein a 2-aryl,2-vinyl aziridine heterolyses, yielding a transient allyl cation, and in that case the products formed are pyrrolines.19 Similarly Njardarson has reported on the copper-catalysed transformation of vinyl azidirines to pyrrolines.20 In our case it can be postulated that the ester functionality activates the alkene such that a sigmatropic rearrangement is possible. We believe that homolysis is not involved, as we saw no signs of radical trapping when carrying out reactions in the presence of radical traps or in cyclohexene as solvent (see supplementary information).

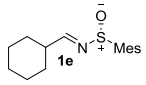
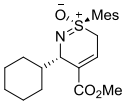
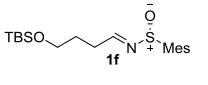
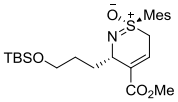
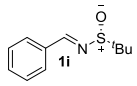
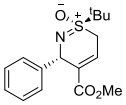
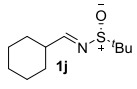
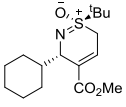
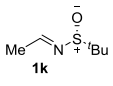
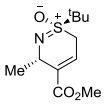
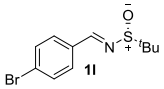
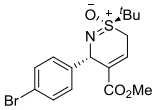
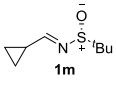
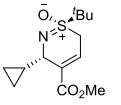
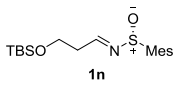
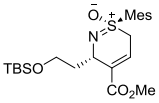
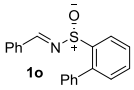
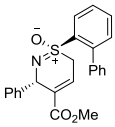
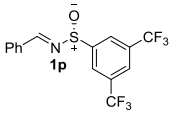
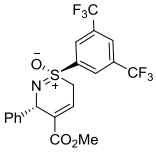
Scheme 2. Proposed mechanistic pathway, and comparison to De Kimpe's rearrangement.



Although efficient for the preparation of mesityl sulfoximines, our procedure revealed low reactivity for tert-butyl sulfoximines. In an effort to develop a more efficient process toward the synthesis we envisaged a one-pot protocol. Thus, after the formation of aziridine was deemed complete by TLC, excess base in the reaction was quenched by addition of water, and benzene was added to the reaction mixture, before heating. Pleasingly, the telescoped procedure resulted in good yields: in general surpassing the yields of the two-step procedure21 (Table 3). Sulfoximine 3e was isolated in 49% yield following the one-pot procedure compared to 33% overall yield observed for the two step method.22 Furthermore, the less reactive tert-butyl sulfinimines (entries 3-7) were efficiently converted into the corresponding sulfoximines following this new protocol, although it was noted that these products were prone to thermal de-tert-buylation by elimination (this process was also noted by Hu13 in their cyclic sulfoximines). We also found that the method is compatible with less common sulfinimines such as biphenyl or 3,5-bistrifluoromethyl phenyl sulfinimine, which can be convieniently synthesised in one step from the parent aldehyde14c (Entries 9 and 10). In all cases, the cyclic sulfoximines were isolated as single diastereomers.

Table 3. One-pot preparation of sulfoximines 3.



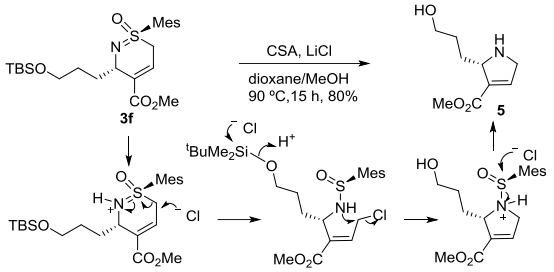
Entry	1[a]	3	Yield [%]
1		 **3e**	49
2		 **3f**	60
3		 **3i**	22[b]
4		 **3j**	74
5		 **3k**	51[b]
6		 **3l**	23
7		 **3m**	48
8		 **3n**	60[b]
9		 **3o**	37
10		 **3p**	26

[a] Isolated yield after purification. Scale, 0.5 mmol. [b] Reaction in toluene for 7 days

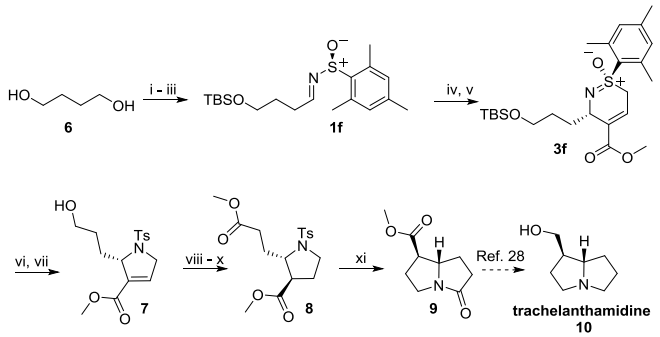
Whilst exploring the reactivity of the new cyclic sulfoximines, we discovered that these compounds, themselves the product of a ring-expansion, upon treatment with camphorsulfonic acid (CSA) and LiCl in dioxane/MeOH at reflux, undero a ring-contraction to yield pyrrolines. Reacting sulfoximine 3f under these conditions yielded pyrroline 5 in 80% yield.23 We believe this reaction proceeds by N-protonation, followed by an SN2 ring-

opening of the sulfoximine,24a followed by ring closure onto the alkyl chloride and chloride-induced deprotection of the amine.24b (Scheme 3)

Scheme 3. Ring-contraction of sulfoximine to pyrroline.



In order to exemplify the utility of these two novel ring transformations, we proceeded to carry out a formal synthesis of the pyrrolizidine alkaloid trachelanthamidine.25 (Scheme 4) The synthesis started with a mono-protection of 1,4-butanediol (6) with TBSCl in an 85% yield, followed by oxidation with PCC and condensation of the corresponding aldehyde with mesitylsulfinamide under Ellman's conditions to form sulfinimine 1f in 67% yield over two steps.26 With 1f in hand, sulfoximine 3f was obtained via the previously described two-step one pot process; the aza-Darzens reaction with methyl 2 bromo-2-butenoate generated the desired aziridine which upon heating yields sulfoximine 3f as a single enantiomer in a 60% yield over two steps. Ring-contraction of sulfoximine 3f with camphorsulfonic acid and lithium chloride yielded the desired pyrroline which upon N-tosylation at 0 °C gave pyrroline 7 in 44% over two steps27 (Kamimura had previously reported the synthesis of a tert-butyl ester in their synthesis of trachelanthamidine).28 Selective hydrogenation using the conditions of Kamimura gave excellent selectivity of 92:8 diastereomeric ratio as observed with the by 1H NMR, albeit with moderate yield. To complete the formal synthesis of trachelanthamidine, the alcohol was exposed to PDC producing the corresponding carboxylic acid followed by esterification with methanol to give diester 8 in a 78% yield over two steps at this point intercepting Kamimura's synthesis.28a,29 The N-tosyl protecting group of 8 was removed with Mg in MeOH,30 and subsequent cyclisation between the deprotected amine and the ester in the C2 side chain gave the desired pyrrolizidinone 9 in 65% yield.28a Several groups have previously converted 9 into trachelanthamidine, and thus this represents a formal synthesis.31



Reagents and conditions: i, TBSCl, NaH, THF, r. t., 19 h (93%); ii, DMSO, NEt3, (COCl)2, CH2Cl2, 19 h; iii, (S)-mesitylsulfinamide, Ti(OEt)4, THF, r. t., 20 h (69% over 2 steps); iv, methyl 2-bromo-2-butenoate, LiHMDS, THF, -78 °C, 3 h; v, H2O, benzene, 40 °C to 70 °C, 19 h (60% over two steps); vi, CSA, LiCl, MeOH:1,4 dioxane 1:1, 90 °C, 18 h; vii, NEt3, TsCl, CH2Cl2, 0 °C to r. t., 30 min. (44 % over two steps); viii, Pd/C, H2, MeOH, r. t., 96 h (59%); xi,

PDC, DMF, r. t., 18 h; x, SOCl2, MeOH, 0 °C to reflux, 18 h (78% over two steps); xi, Mg, MeOH, r. t. to reflux, 7 h (65%).

Scheme 4. Formal synthesis of trachelanthamidine.

In summary, we have developed a methodology for the synthesis of chiral cyclic sulfoximines starting from simple sulfinimines. The reaction can be either performed by isolation of the aziridine intermediate and subsequent thermal rearrangement (two step protocol) or in a one-pot fashion, the latter allowing for the isolation of the desired heterocycle without the need of manipulating otherwise relatively unstable aziridine intermediates. We have also demonstrated the formal synthesis of the biologically active natural product trachelanthamidine in an overall yield of 5%.

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Keywords: chiral sulfinimine • aziridine • sulfoximine • rearrangement • pyrroline

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