

Rearrangements

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

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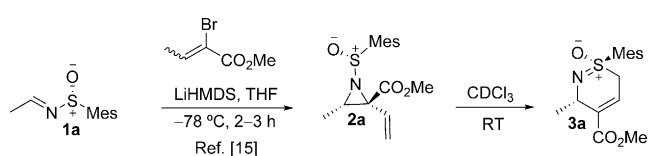
Abstract: A novel rearrangement of 2-vinyl aziridine 2-carboxylates to unusual chiral cyclic sulfoximines is described herein. The method allows the synthesis of substituted cyclic sulfoximines in high yields with complete stereocontrol, and tolerates a wide substrate scope. A one-pot process starting directly from sulfinimines provides 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 co-workers in 1950^[1] these sulfur-containing compounds have found applications in functional-group transformations and asymmetric synthesis,^[2] drug development,^[3] crop treatment,^[4] 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.^[3] Sulfoximines are three-dimensional motifs with three points of attachment in orthogonal vectors,^[6] and functionalisation at the nitrogen and carbon centers α to the sulfur atom is 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 sulfoximines^[10,11] and subsequent cyclizations.^[12] Furthermore, they generally describe benzofused 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, by cycloaddition with benzyne.^[13] Herein we describe

a simple and versatile method for the synthesis of nonfused six-membered cyclic sulfoximines with complete diastereocontrol and a wide substrate range.

Building on our prior work in the area of aza-Darzens-type aziridinations of chiral *tert*-butanesulfinimines^[14] 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 products, trisubstituted vinyl aziridine 2-carboxylates, would be potentially versatile intermediates for asymmetric synthesis.^[16] Thus, we investigated the aza-Darzens reaction of the acetaldehyde-derived *S*-mesitylsulfinimine **1a** using LiHMDS as base in THF at -78°C (Scheme 1). Pleasingly,



Scheme 1. Unprecedented rearrangement of aziridines leading to sulfoximines. HMDS = hexamethyldisilazide, Mes = 2,4,6-trimethylphenyl, THF = tetrahydrofuran.

we found excellent conversion into the vinyl aziridine **2a**. However, upon standing in deuteriochloroform, we observed that this vinyl aziridine underwent a rearrangement to afford a new compound. After purification and extensive characterization we found that the isolated product corresponds to the cyclic sulfoximine **3a** wherein chiral information is retained.

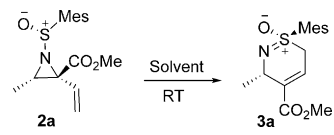
Herein, we present our findings on the substrate scope of this novel rearrangement and offer a mechanistic hypothesis for this interesting transformation.

Intrigued by the observed rearrangement, we wanted to explore the influence of solvent and temperature on the sulfoximine formation (Table 1). No clear correlation was found between the nature of solvent and the reaction performance, and best results obtained when CDCl_3 , $[\text{D}_6]\text{DMSO}$, MeOD, and C_6D_6 were used as a solvent. C_6D_6 was the selected solvent to study the influence of temperature on the described rearrangement. In a very straightforward manner we determined that an increase in temperature clearly improves the yield of the reaction, thus leading to the desired compound in 80 and 92 % yield when the solution was heated at 40 and 70°C , respectively.

Initially, reaction conditions performed at 40°C were chosen for the purpose of scope determination (Table 2). Several aziridines were synthesised following our previously reported method,^[15] and they were subsequently submitted to

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Table 1: Optimisation of reaction conditions.


Entry	Solvent	Yield [%] ^[a]	Entry	Solvent	Yield [%] ^[a]
1	CDCl ₃	50	6	[D ₇]DMF	12
2	[D ₆]DMSO	57	7	C ₆ D ₆	50
3	[D ₆]Et ₂ O	22	8	C ₆ D ₆	80 ^[b]
4	CD ₃ OD	50	9	C ₆ D ₆	92 ^[c]
5	CD ₃ CN	15	10	cyclohexene	60 ^[b,d]

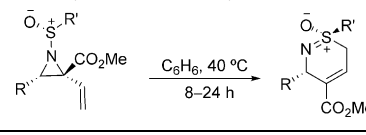
[a] Yield determined by NMR spectroscopy. [b] 40 °C. [c] 70 °C. [d] Yield of isolated product. DMF = *N,N*-dimethylformamide. DMSO = dimethylsulfoxide.

the rearrangement reaction conditions. 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 and 3). The reaction also performed well in the presence of saturated carbocycles (entries 4 and 5). Unsaturation and silyl ethers were also tolerated under the reaction conditions, thus affording sulfoximines in good yields (entries 6–8).

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

In the case of aziridine **2j** (Table 2, entry 10), we noted that the two diastereomeric aziridines formed from the corresponding sulfinimine rearranged to the same cyclic sulfoximine **3j**. We therefore decided to investigate whether the rate of rearrangement of these diastereomers was different. The rearrangement reactions of (*E*)-**2j** and (*Z*)-**2j** were monitored by ¹H NMR spectroscopy.^[17] The rearrangement of (*E*)-**2j** was found to be around three times faster than the corresponding *Z* isomer. Presuming a concerted rearrangement,^[18] we attribute this difference in rate to the increased steric bulk around the mesityl group for the *Z*-isomer (Scheme 2). As the reaction works in a wide range of solvents, including polar and nonpolar, as well as in nucleophilic solvents like methanol, this gives further evidence of a concerted rearrangement. De Kimpe and co-workers previously disclosed a related rearrangement wherein a 2-aryl, 2-vinyl aziridine heterolyses, thus yielding a transient allyl cation, and in that case the products formed are pyrrolines.^[19] Similarly Njardarson and co-workers have reported on the copper-catalyzed transformation of vinyl aziridines 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 the Supporting Information).

Although efficient for the preparation of mesityl sulfoximines, our procedure revealed low reactivity for *tert*-butylsulfoximines. In an effort to develop a more efficient process

Table 2: Sulfoximine synthesis from vinyl aziridines **2**.


Entry	2 ^[a]	3	Yield [%]
1			80
2			82
3			93
4			68
5			77
6			88
7			97
8			79
9			16 ^[b]
10			10 ^[b]
11			45 ^[b]

[a] Yield of product isolated after purification. Scale: 0.5 mmol. [b] 70 °C. [c] 1.2:1 *trans/cis*. TBS = *tert*-butyldimethylsilyl.

we envisaged a one-pot protocol. Thus, after the formation of aziridine was deemed complete, as determined 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

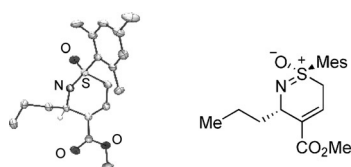
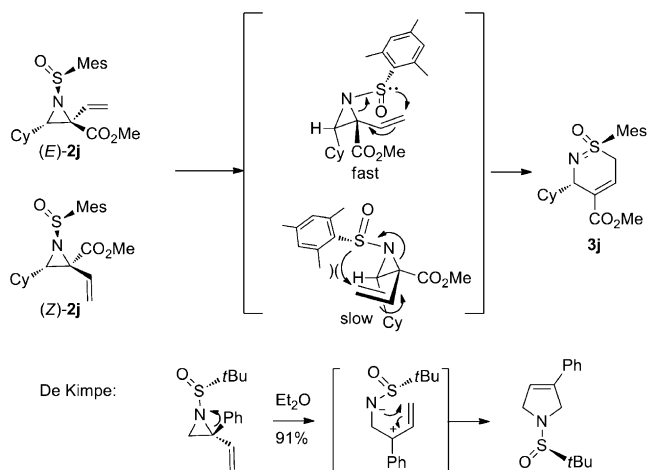


Figure 1. X-Ray structure of sulfoximine **3b** (CCDC 1484617). Thermal ellipsoids shown at 50% probability.



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

yields. In general they surpassed the yields of the two-step procedure^[21] (Table 3). The sulfoximine **3e** was isolated in 49% yield following the one-pot procedure compared to the 33% overall yield observed for the two-step method.^[22] Furthermore, the less reactive *tert*-butylsulfinimines (entries 3–7) were efficiently converted into the corresponding sulfoximines using this new protocol, although it was noted that these products were prone to thermal elimination of the *tert*-butyl group (this process was also noted by Hu and co-workers^[13] in their cyclic sulfoximines). We also found that the method is compatible with less common sulfinimines such as biphenyl- or 3,5-bistrifluoromethylphenyl sulfinimine, which can be conveniently synthesised in one step from the parent aldehyde^[14c] (entries 9 and 10). In all cases, the cyclic sulfoximines were isolated as single diastereomers.

Whilst exploring the reactivity of the new cyclic sulfoximines, we discovered that these compounds, themselves the product of a ring-expansion, upon treatment with camphor-sulfonic acid (CSA) and LiCl in 1,4-dioxane/MeOH at reflux, undergo ring contraction to yield pyrrolines. Reacting the sulfoximine **3f** under these reaction conditions yielded pyrroline **5** in 80% yield (Scheme 3).^[23] We believe this reaction proceeds by N-protonation, followed by an S_N2 ring opening of the sulfoximine^[24a] and ring closure onto the alkyl chloride and chloride-induced deprotection of the amine.^[24b]

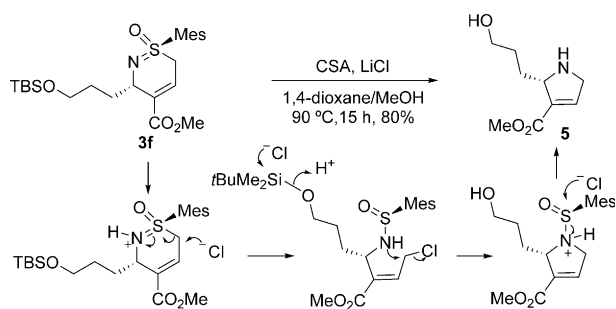
To exemplify the utility of these two novel ring transformations, we proceeded to carry out a formal synthesis of the pyrrolizidine alkaloid trachelanthamidine^[25] (Scheme 4). The synthesis started with a monoprotection of 1,4-butanediol (**6**) with TBSCl in an 85% yield, followed by Swern oxidation

Table 3: One-pot preparation of the sulfoximines **3**.

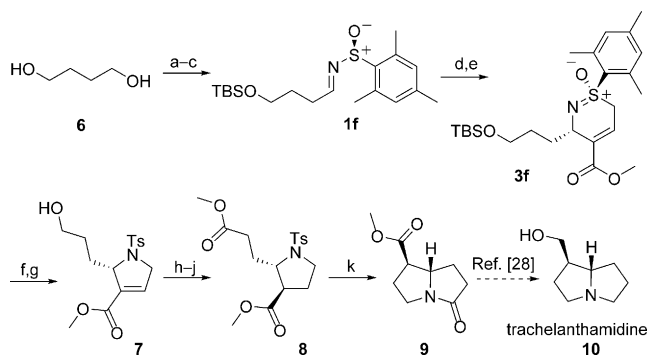
via		1. LiHMDS, THF, −78 °C, 2–3 h 2. benzene, 70 °C, 2–20 h		3		Yield [%]	
Entry	1 ^[a]			3			
1					3e	49	
2					3f	60	
3					3i	22 ^[b]	
4					3j	74	
5					3k	51 ^[b]	
6					3l	23	
7					3m	48	
8					3n	60	
9					3o	37	
10					3p	26	

[a] Yield of product isolated after purification. [b] Reaction in toluene for 7 days.

and condensation of the corresponding aldehyde with mesitylsulfonamide under Ellman's conditions to form the sulfin-



Scheme 3. Ring-contraction of sulfoximine to pyrroline.



Scheme 4. Formal synthesis of trachelanthamidine. Reagents and conditions: a) TBSCl, NaH, THF, RT, 19 h (93 %); b) DMSO, NEt₃, (COCl)₂, CH₂Cl₂, 19 h; c) (S)-mesitylsulfonamide, Ti(OEt)₄, THF, RT, 20 h (69 % over 2 steps); d) methyl 2-bromo-2-butenate, LiHMDS, THF, −78 °C, 3 h; e) H₂O, benzene, 40 °C to 70 °C, 19 h (60 % over two steps); f) CSA, LiCl, MeOH/1,4-dioxane 1:1, 90 °C, 18 h; g) NEt₃, TsCl, CH₂Cl₂, 0 °C to RT, 30 min. (44 % over two steps); h) Pd/C, H₂, MeOH, RT, 96 h (59 %); i) PDC, DMF, RT, 18 h; j) SOCl₂, MeOH, 0 °C to reflux, 18 h (78 % over two steps); k) Mg, MeOH, RT. to reflux, 7 h (65 %). PDC = pyridiniumdichromate, Ts = 4-toluenesulfonyl.

imine **1f** in 69 % yield over two steps.^[26] With **1f** in hand, **3f** was obtained by the previously described two-step, one-pot process. The aza-Darzens reaction with methyl 2-bromo-2-butenate generated the desired aziridine, which upon heating yields **3f** as a single enantiomer in a 60 % yield over two steps. Ring contraction of **3f** with CSA and lithium chloride yielded the desired pyrroline, which upon N-tosylation at 0 °C gave the pyrroline **7** in 44 % over two steps^[27] (Kamimura et al. had previously reported the synthesis of a *tert*-butyl ester in their synthesis of trachelanthamidine).^[28] Selective hydrogenation using the reaction conditions of Kamimura gave excellent selectivity, a 92:8 diastereomeric ratio as observed by ¹H NMR spectroscopy, however, the yield was moderate. To complete the formal synthesis of trachelanthamidine, the alcohol was exposed to PDC,^[29] thus producing the corresponding carboxylic acid followed by esterification with methanol to give the diester **8** in a 78 % yield over two steps: At this stage our synthesis intercepts that of Kamimura et al.^[28a] 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]

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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