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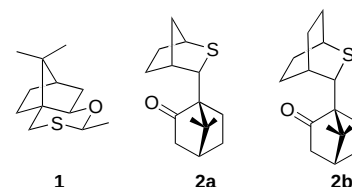
Application of Chiral Sulfides to Catalytic Asymmetric Aziridination and Cyclopropanation with In Situ Generation of the Diazo Compound**

Varinder K. Aggarwal,* Emma Alonso, Guangyu Fang, Marco Ferrara, George Hynd, and Marina Porcelloni

In the preceding paper we described a highly efficient catalytic process for converting carbonyl compounds into

epoxides with high enantioselectivity. Herein we describe the extension of this work to the asymmetric aziridination of imines^[1] and to the asymmetric cyclopropanation of electron-deficient alkenes.^[2]

We previously reported that 1,3-oxathiane **1** gave good yields and high enantioselectivity in aziridination^[3] and cyclopropanation^[4] reactions. However, these processes are



potentially hazardous, cannot be easily scaled up, and the sulfide cannot be fully recovered. We successfully solved these problems in the epoxidation reaction by generating the diazo compound in situ and by developing a new class of chiral sulfides **2**,^[5] which were completely stable to the reaction conditions. We were keen to examine whether these new conditions and new sulfides were compatible with the aziridination and cyclopropanation processes.

Optimization of the conditions for aziridination of the *N*-SES-activated imine derived from benzaldehyde^[6] (this imine is easily prepared and provides a readily cleavable group) with sulfide **2a** revealed that 1,4-dioxane was the best solvent. A broad study of different activating groups on the nitrogen atom showed that sulfonylimines^[7] led to aziridines in good yield, high enantioselectivities, but low diastereoselectivities (Table 1, entries 1–3). A notable example is the naphthylsulfonylimine, which gave excellent results and this group is considerably easier to deprotect^[8] than the toluene-4-sulfonyl (tosyl) group. Improved diastereoselectivity was observed

Table 1. Effect of the nitrogen substituent on the yield, diastereoselectivity, and enantioselectivity.^[a]

$\text{Ph}-\text{C}(=\text{O})-\text{N}(\text{R})-\text{N}(\text{Ts})-\text{N}(\text{Na}^+)+\text{Ph}-\text{C}(=\text{O})-\text{N}(\text{R})-\text{N}(\text{Ts})-\text{N}(\text{Na}^+)+\text{Rh}_2(\text{OAc})_4(1\text{ mol}\%) + \text{BnEt}_3\text{N}^+\text{Cl}^-(10\text{ mol}\%) \xrightarrow[1,4\text{-dioxane, } 40^\circ\text{C}]{\text{sulfide } \mathbf{2a} (20\text{ mol}\%)}$				
Entry	R	Yield [%] ^[b]	d.r. ^[c] (<i>trans</i> : <i>cis</i>)	ee [%] ^[d]
1	SES	75	2.5:1	94
2	Ts	68	2.5:1	98
3	SO ₂ C ₁₀ H ₇	70	3:1	97
4	Boc	33 ^[e,f]	8:1	89
5	TcBoc	71	6:1	90
6 ^[g]	SES	66	2.5:1	95

[a] Tosylhydrazone salt (1.5 equiv), imine (1.0 equiv), phase-transfer catalyst (PTC, 0.1 equiv), Rh₂(OAc)₄ (0.01 equiv), 1,4-dioxane (0.33 M), chiral sulfide **2a** (0.2 equiv), 40 °C. [b] Yield of isolated product. [c] The *trans*:*cis* ratio was determined by ¹H NMR spectroscopy. [d] Enantiomeric excess values were determined on a Chiralcel OD column; the absolute configuration was 1*R*,2*R*. [e] 0.05 equiv of PTC were used. [f] *trans*-stilbene oxide was obtained as the main side product. [g] 5 mol % of sulfide was used. Ts = tosyl = toluene-sulfonyl.

[*] Prof. V. K. Aggarwal,^[+] Dr. E. Alonso, G. Fang, M. Ferrara, Dr. G. Hynd, M. Porcelloni
Department of Chemistry
University of Sheffield
Brook Hill, Sheffield, S3 7HF (UK)

[+] Current address:
School of Chemistry
Bristol University
Cantock's Close, Bristol, BS8 1TS (UK)
Fax: (+44)117-9298611
E-mail: V.Aggarwal@bristol.ac.uk

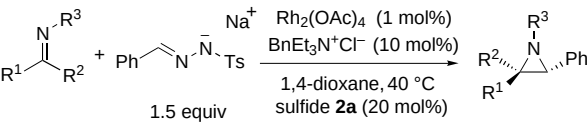
[**] We thank Avecia (M.P.), the EPSRC (M.F.), the EU for a Marie Curie Fellowship (E.A.); HPMF-CT-1999-00076, Lu'an Teacher's College and the Education Minister of The Peoples Republic of China (G.F.), and Sheffield University for financial support. We thank Dr. J. Blacker (Avecia), Dr. R. V. H. Jones (Zeneca Agrochemicals), and Dr. R. Fieldhouse (Zeneca Agrochemicals) for their interest and support of this work.

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with carbamoylimines (entries 4 and 5),^[9] and of the two tested the TcBoc-protected^[9] imine gave the higher yield (the Boc-protected imine partially hydrolyzed during the course of the reaction). The sulfide loading could be reduced to just 5 mol % without a significant reduction in the yield, and the aziridine was obtained with the same enantioselectivity (entry 6).

This study of activating groups on the nitrogen atom revealed that sulfonyl- or TcBoc-activated imines provided the best combination of yield, enantioselectivity, and diastereoselectivity to date in a practical, user-friendly catalytic process.^[10] These groups were therefore tested with a range of imines derived from aromatic, heteroaromatic, unsaturated, and even aliphatic aldehydes and ketones^[11] (Table 2). As sulfonyl-substituted imines were easier to prepare than

Table 2. Asymmetric aziridination of a range of imines.^[a]

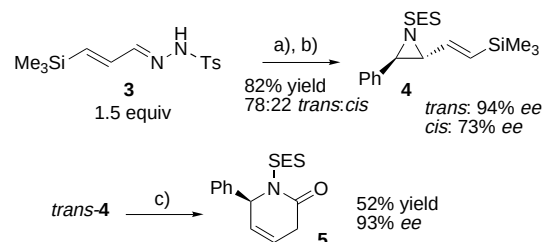
						
Entry	R ¹	R ²	R ³	Yield [%] ^[b]	d.r. ^[c]	ee [%] (<i>trans</i> : <i>cis</i>) ^[d]
1	<i>p</i> -ClC ₆ H ₄	H	TcBoc	56	6:1	94:90
2	<i>p</i> -ClC ₆ H ₄	H	SES	82	2:1	98:81
3	C ₆ H ₁₁	H	SES	50	2.5:1	98:89
4	<i>t</i> Bu	H	Ts	53	2:1	73:95
5	<i>trans</i> -PhCH=CH	H	SES	59	8:1	94
6	<i>p</i> -MeOC ₆ H ₄	H	SES	60	2.5:1	92:78
7	3-furfuryl	H	Ts	72	8:1	95
8	Ph	Ph	SO ₂ C ₈ H ₇	50	–	84

[a] Tosylhydrazone salt (1.5 equiv), imine (1.0 equiv), PTC (0.1 equiv), Rh₂(OAc)₄ (0.01 equiv), 1,4-dioxane (0.33 M), chiral sulfide **2a** (0.2 equiv), 40 °C. Bn = benzyl. [b] Yield of isolated product. [c] Determined by ¹H NMR spectroscopy. [d] Enantiomeric excess values were determined on a Chiralcel OD column. See the Supporting Information.

TcBoc-substituted ones, most studies were conducted with the former group. In all cases good yields and high enantioselectivities were observed, although the diastereoselectivity was found to be dependent on both the nature of the nitrogen activating group and on the imine substituent. Most encouragingly was the observation that good diastereoselectivity could be achieved with sulfonyl activating groups on the imines derived from cinnamaldehyde (Table 2, entry 5) and 3-furfural (Table 2, entry 7). High enantioselectivity was obtained from imines derived from aliphatic aldehydes (Table 2, entry 3), although curiously the *tert*-butyl imine only gave high enantioselectivity in the formation of the *cis*-aziridine (Table 2, entry 4). The origin of this unusual selectivity is not known at present and is currently under investigation. The imine derived from benzophenone could also be employed and allowed access to trisubstituted aziridines (Table 2, entry 8).

The process could also be extended to alkenyldiazomethanes and again good yields, high enantioselectivities, and good diastereoselectivities were obtained with the *N*-SES-activated imine derived from benzaldehyde (Scheme 1). The

synthetic utility of the process was demonstrated by further manipulation of the unsaturated aziridine. Unsaturated aziridines are very useful intermediates which are known to undergo ring expansion under a variety of conditions to give



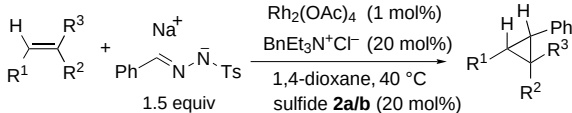
Scheme 1. Reagents and conditions: a) LiHMDS (1.5 equiv), THF, –78 °C, 1 h; b) PhCHNSES (1 equiv), Rh₂(OAc)₄ (1 mol %), phase-transfer catalyst (PTC, 10 mol %), sulfide **2a** (20 mol %), 1,4-dioxane, 40 °C, 12 h; c) [Pd₂(dba)₃·CHCl₃] (15 mol %), PPh₃ (1.3 equiv), PhH, CO (1 atm), 50 °C, 12 h. HMDS = 1,1,1,3,3,3-hexamethyldisilazane, SES = 2-(trimethylsilyl)ethanesulfonyl, dba = *trans,trans*-dibenzylideneacetone.

either β -^[12] or δ -lactams.^[13] Treatment of *trans*-aziridine **4** with Pd and CO led cleanly to the δ -lactam **5** in good yield and with the same high enantiomeric excess. This selectivity for the formation of the δ -lactam must be a consequence of a directing effect of the silyl group since a similar compound without the silyl group gave the β -lactam under the same conditions.^[12b] The origin of this selectivity is the subject of further investigations.

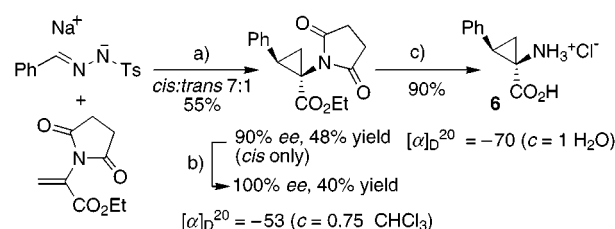
Having developed a highly efficient, practical process for asymmetric aziridination, we focused our attention to the cyclopropanation of electron-deficient alkenes. The reaction of chalcone with sulfide **2a** was initially chosen, and once again 1,4-dioxane emerged as the optimal solvent (Table 3, entry 1). However, although high enantioselectivity was obtained, the yield was rather poor. Since six membered ring sulfides were found to be superior to five membered ring sulfides in cyclopropanation reactions,^[4] we decided to test the novel [2.2.2] bicyclic sulfide **2b**. Sulfide **2b** did indeed give improved yields in the cyclopropanation of chalcone (Table 3, entry 2)^[14] and so studies were extended to a range of Michael acceptors. It was found that phenyl ketones were excellent substrates (Table 3, entries 2 and 3), whilst methyl ketones were less good (Table 3, entries 4 and 5). Although unsubstituted acrylates (Table 3, entry 6) were not very effective substrates, we found that α -amino-substituted acrylates performed extremely well to give cyclopropanes in high yields, high enantioselectivities, and high diastereoselectivities (Table 3, entries 7 and 8). In all cases, high enantioselectivity was obtained and the sulfide could be recovered in quantitative yield.

The cyclopropanes derived from the amino acrylates could be converted in one step into the corresponding amino acids (Scheme 2) or the Boc-protected amino esters (Scheme 3). Furthermore, a single recrystallization either before or after deprotection led to enantiomerically pure material (Schemes 2 and 3). The acrylates are made in one step^[15, 16] and thus provides the most efficient route to this important class of conformationally locked amino acids. This cyclo-

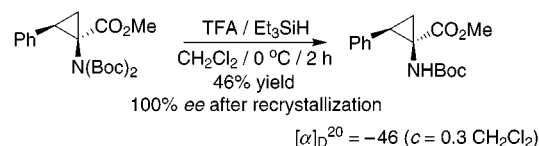
Table 3. Catalytic asymmetric cyclopropanation of electron-deficient alkenes.^[a]

								
Entry	R ¹	R ²	R ³	Sulfide	Yield [%] ^[b]	d.r. (<i>trans</i> : <i>cis</i>)	ee [%] ^[d]	Absolute config.
1	Ph	H	COPh	2a	30 ^[e]	5:1 ^[c]	89	1 <i>R</i> ,1 <i>R</i>
2	Ph	H	COPh	2b	73	4:1 ^[c]	91	1 <i>R</i> ,1 <i>R</i>
3	CH ₃	H	COPh	2b	50	4:1 ^[c]	90	1 <i>R</i> ,1 <i>R</i>
4	Ph	H	COCH ₃	2b	5	—	—	—
5	CH ₃	H	COCH ₃	2b	12	1:1:1 ^[f]	—	—
6	H	H	CO ₂ Et	2b	10	7:1 ^[c]	—	—
7	H	<i>N</i> -succinimide	CO ₂ Et	2b	55	1:7 ^[c]	91	1 <i>S</i> ,1 <i>S</i>
8	H	N(Boc) ₂	CO ₂ Me	2b	72	1:6 ^[c]	92	1 <i>S</i> ,1 <i>S</i>

[a] Tosylhydrazone salt (1.5 equiv), alkene (1.0 equiv), sulfide **2a/2b** (0.2 equiv), PTC (0.2 equiv), Rh₂(OAc)₄ (0.01 equiv), in dioxane (0.13 M) at 40 °C. Bn = benzyl. [b] Combined yield of all isomers. These can be separated except in those cases indicated. [c] Ratio of *trans*:*cis* isomers was determined by ¹H NMR spectroscopy. [d] Enantiomeric excess values were determined on a Chiralcel OD column. See the Supporting Information. [e] 50 % of enone was recovered.

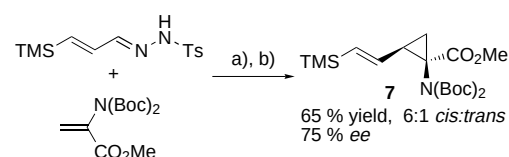


Scheme 2. Reagents and conditions: a) Sulfide **2b** (20 mol %), Rh₂(OAc)₄ (1 mol %), PTC (20 mol %), 1,4-dioxane, 40 °C, 24 h; b) Recrystallization. c) 6 N HCl, reflux, 4 h. Ts = tosyl = toluene-4-sulfonyl.



Scheme 3. Partial hydrolysis of the protected amino acid. TFA = tri-fluoroacetic acid, Boc = *tert*-butoxycarbonyl.

propanation methodology was further illustrated in the synthesis of protected vinylcyclopropyl amino acid **7** (Scheme 4). In this scheme an unsaturated diazocompound was prepared in situ using our modified Bamford–Stevens reaction.^[5] The vinylsilane moiety provides a very useful handle for the incorporation of alternative functional groups^[17] onto the cyclopropane ring and so will allow access to a much broader range of conformationally locked amino acids.



Scheme 4. Reagents and conditions: a) LiHMDS (1.2 equiv), THF, -78 °C; b) Rh₂(OAc)₄ (1 mol %), sulfide **2b** (100 mol %), BnEt₃N⁺Cl⁻ (20 mol %), 1,4-dioxane, 40 °C, 16 h. Ts = toluene-4-sulfonyl.

The absolute stereochemistries of the cyclopropanes derived from chalcone^[4b] and α-succinimide acrylate^[18] were determined by comparison of the [α]_D values with those reported in the literature. All other absolute stereochemistries are given by analogy with the above and are in keeping with the absolute stereochemistries obtained in the related epoxidation and aziridination reactions.

The high enantioselectivity in the aziridination and cyclopropanation reactions can be readily accounted for by using the same model as described for epoxidation.^[5] Further work is needed to understand the diastereoselectivity, and studies in this area are ongoing.^[19]

In summary, we have developed a highly effective, user-friendly, catalytic asymmetric process for the aziridination of imines and the cyclopropanation of electron-deficient alkenes. The process is general and can be applied to a broad range of electrophiles and diazo precursors. Further applications of these new processes in asymmetric synthesis are ongoing.

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- [19] We have found from crossover experiments relating to aziridination that betaine formation is irreversible. Thus, the diastereoselectivity is controlled by nonbonding interactions that lead to the betaine.

Oxoammonium Resins as Metal-Free, Highly Reactive, Versatile Polymeric Oxidation Reagents**

Steffen Weik, Graeme Nicholson, Günther Jung, and Jörg Rademann*

Complex organic molecules can be constructed either in solution or attached to an insoluble polymeric support. Polymer-assisted solution-phase (PASP) synthesis^[1–3] offers a highly attractive supplement to these concepts by exploiting the virtues of both traditional approaches. Polymeric reagents^[4, 5] can be used in high excess and are removed by filtration, the products can be easily analyzed and further transformed in solution. They are especially suitable for parallel combinatorial synthesis.^[6, 7] They allow preparation of complex libraries by multistep syntheses in solution, they can be utilized in automated and in flow-through systems, and finally they can be employed—as will be demonstrated herein—to transform single compounds as well as complex mixtures.^[8]

The oxidation of alcohols to carbonyl compounds is one of the most relevant transformations in organic synthesis, owing to the large diversity of products that can be obtained from aldehyde and ketone precursors.^[9] Common oxidative agents for this transformation include dimethyl sulfoxide (DMSO),^[10] periodinanes^[11] as well as various heavy-metal reagents, the latter usually based on either chromium^[12] or ruthenium oxides.^[13] There are several examples of polymer-supported oxidation reagents,^[14] including heavy-metal oxides bound to ion-exchange resins.^[15, 16] One resin of this type has been recently employed in a reaction sequence leading to heterocyclic compounds.^[17] However, low reactivity with non-benzylic alcohols, potential persistence of highly toxic heavy metals in the products as well as overoxidation of aldehydes limits the use of solid-supported metal oxides in parallel syntheses.

Herein we report on the generation of oxoammonium halides as oxidizing reactive species on a solid support and on the use of this reagent in the oxidation of single alcohols and of complex compound collections. Oxoammonium salts have been postulated as reactive intermediates in oxidations employing the 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO), which is commonly employed under phase-transfer conditions with, for example, sodium hypochlorite as activating oxidant in the aqueous phase.^[18, 19] Recently TEMPO has been used in solution together with a polymer-attached oxidizing agent^[20] and as a catalyst on silica.^[21] No reports were found about using oxoammonium salts on insoluble, crosslinked polymers, which would allow the

[*] Dr. J. Rademann, Dipl.-Chem. S. Weik, G. Nicholson, Prof. Dr. G. Jung
Institut für Organische Chemie, Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
Fax: (+49) 7071-295560
E-mail: joerg.rademann@uni-tuebingen.de

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