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Diastereoselective rhodium-catalyzed nitrene transfer starting from chiral sulfonimidamide-derived iminoiodanes

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Abstract—The dirhodium-catalyzed aziridination of olefins with chiral sulfonimidamides as iminoiodane precursors has been investigated under stoichiometric conditions. Diastereoisomeric excesses of up to 82% have been achieved using $[Rh_2\{(S)\text{-nttl}\}_4]$ as catalyst. Matching and mismatching effects were observed upon use of chiral rhodium(II) carboxylate catalysts.

1. Introduction

The transition metal-catalyzed aziridination of olefins is a powerful methodology for regioselective C–N bond formation. The reaction proceeds via intermediate metal complexed nitrene species, which are generated upon decomposition of iminoiodanes.[1] In conjunction with chiral copper, rhodium or ruthenium catalysts, these nitrene precursors may lead to asymmetric nitrene transfer reactions.[1b] It has recently been reported that iminoiodanes can be efficiently generated and decomposed to nitrenes in situ,[2,3] a process that greatly enhances the variety of nitrogenous compounds that can be used for this purpose. Based on this in situ methodology, rhodium- and copper-catalyzed nitrene transfers have been investigated in detail by our groups.[4] In order to broaden the scope of the stereoselective C–N bond formation, and with the objective of improving the stereoselectivity, we felt it was interesting to extend the in situ procedure to chiral iminoiodanes. To this end, we turned our attention to sulfonimidamides **1** ($R^1S(=O)(=NR^2)NH_2$)[5] as potential chiral hypervalent iodine(III) reagent precursors. These were initially found to give highly reactive nitrene species in the copper-catalyzed reactions, the use of **1a** ($R^1 = p$-Tol, $R^2 = Ts$) affording aziridines in very good yields and with diastereoselectivities up to 60%.[6,7] Since rhodium(II) catalysts are often complementary in scope to the copper species in various processes[1] and given the recent and increasing interest in the rhodium-catalyzed aziridination of olefins,[8] it therefore appeared to us interesting to determine and compare the efficiency of rhodium complexes in analogous diastereoselective nitrene transfers. Herein, we report the results of our first investigations with such rhodium(II) catalysts.

2. Results and discussion

Both enantiomers of sulfonimidamide **1a** (Ar = 4-MePh) were first prepared starting from *p*-toluenesulfinyl chloride **2** as described in the literature (Scheme 1).[9] Thus, after reaction with commercially available chloramine-T, the enantiomers of the resulting racemic chloride **3a** were separated via reaction with (*S*)-1-phenylethylamine and fractional recrystallization of the resulting sulfonimidamide **4a**. Cleavage of **4a** with trifluoroacetic acid afforded (*R*)- and (*S*)-**1a**. The procedure was adapted for **1b** ($R = 4\text{-}NO_2Ph$) by use of chloramine-N.[10] Single crystals of (−)-**1b** were obtained allowing us to determine the absolute configuration to be (*S*) by X-ray crystallography (Fig. 1).[11] By analogy and according to the literature,[9] the (*S*)-configuration was attributed to the (−)-enantiomer of **1a**.

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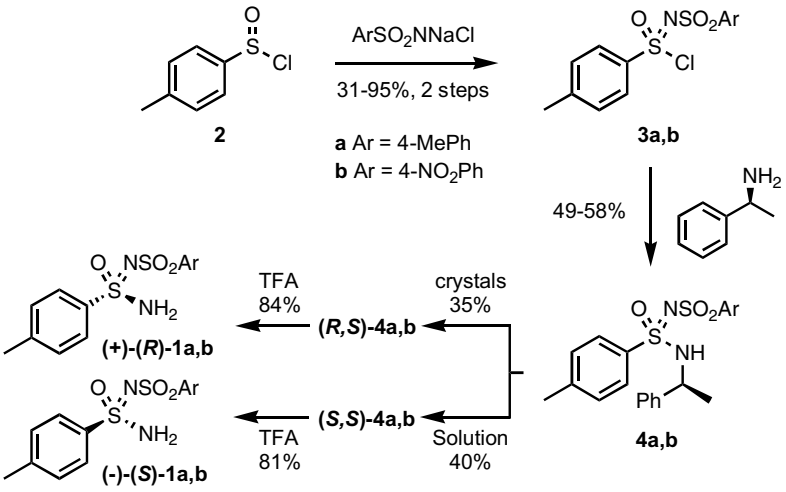


Scheme 1. Synthesis of sulfonimidamides.

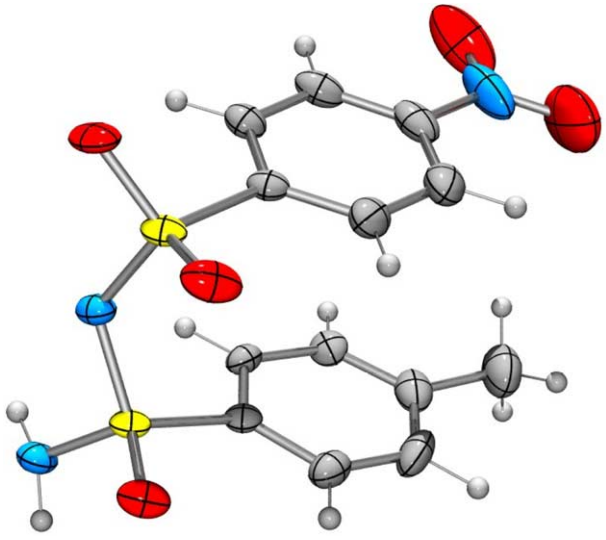
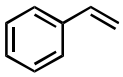
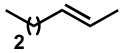
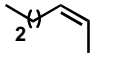
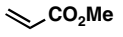


Figure 1. ORTEP view of the crystal structure of (−)-(*S*)-**1b**.

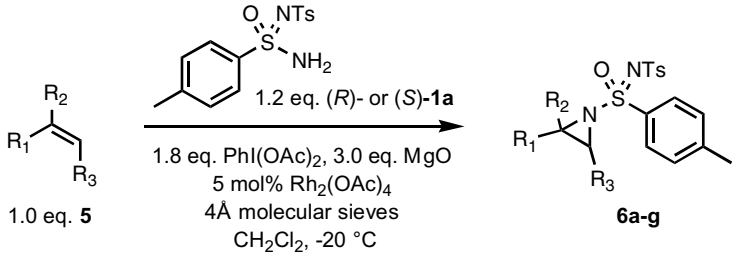
Sulfonimidamide **1a** was thus tested as the nitrene precursor in the rhodium-catalyzed aziridination of olefins (Scheme 2). A typical procedure involved, at −20 °C in dichloromethane, the use of alkenes **5** as the limiting component in the presence of a slight excess of **1a** (1.2 equiv), iodosylbenzene diacetate (1.8 equiv), magnesium oxide (3.0 equiv) and a catalytic quantity of [$Rh_2(OAc)_4$] (5 mol %).[12] Results are summarized in Table 1.

Table 1. Screening of olefins for diastereoselective $Rh_2(OAc)_4$-catalyzed aziridination

Entry	Olefin	Sulfonimidamide	Aziridine	Yield (%)[a]	de (%)[b]
1		(*S*)-**1a**	**6a**	42	20
2		(*R*)-**1a**	**6b**	34	<10
3		(*R*)-**1a**	**6c**	17[c]	<10
4		(*R*)-**1a**	**6d**	56[d]	<10
5		(*S*)-**1a**	**6e**	50	—
6		(*S*)-**1a**	**6f**	47	—
7		(*S*)-**1a**	**6g**	—	—

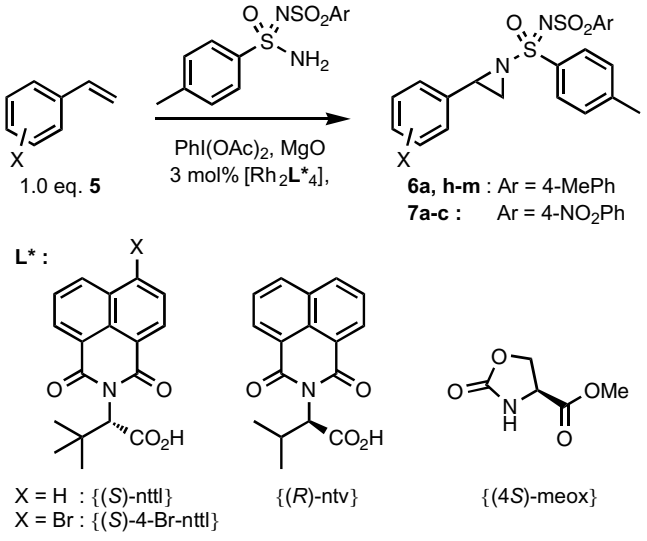
[a] Isolated yield after flash chromatography. Diastereoisomers could not be separated on silica gel.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] *trans*-Aziridine.
[d] *cis*-Aziridine.

Aziridination of styrene under these conditions was achieved in 42% yield with 20% de (entry 1). A terminal olefin such as 1-heptene was also reactive but afforded a lower yield than styrene (entry 2). More interestingly,



Scheme 2.

as shown for the reaction with *trans*- and *cis*-hex-2-ene, the aziridination was stereospecific with respect to the olefin geometry (entries 3 and 4). However, as often observed in Rh(II)-catalyzed cyclopropanations and aziridinations, the *trans*-isomer afforded a significantly lower yield than the *cis*-olefin.[13] It is noteworthy that in the case of cyclopentene and cyclohexene (entries 5 and 6), no insertion into an allylic C–H bond was observed. In both cases, only aziridines **6e** and **6f** were isolated in 50% and 47% yield, respectively. These results differ sharply from previous Rh(II)-catalyzed nitrene transfers with sulfonamide-derived iminoiodanes, for which allylic C–H insertion was the major pathway.[14] Finally, no reaction took place in the case of methyl acrylate (entry 7). This is in distinct contrast to the Cu-catalyzed aziridination with sulfonimidamides where acrylates gave very high yields.[6] This observation highlights the complementary role of rhodium and copper catalysts in nitrene transfers.



Scheme 3.

Chiral Rh(II) carboxylate and carboxamidate catalysts were then screened in conjunction with sulfonimidamides **1a**–**b** for the asymmetric aziridination of styrene and its *para*- or *meta*-substituted derivatives (Scheme 3).

Yields and diastereoselectivities were generally improved when the aziridination was carried out with the chiral rhodium carboxylate catalysts $[Rh_2\{(S)\text{-nttl}\}_4]$[15] or $[Rh_2\{(R)\text{-ntv}\}_4]$[16] (Table 2, entries 1, 3 and 4) while the chiral Rh(II) carboxamidate $[Rh_2\{(4S)\text{-meox}\}_4]$[17] gave the same low induction and modest yields (entry 5). More interestingly, matching and mismatching effects could be observed with the $[Rh_2\{(R)\text{-ntv}\}_4]$ catalyst (entries 3 and 4): a matched pair for double induction is formed with the sulfonimidamide (*R*)-**1a**. However, contrary to our expectations,[18] use of the *p*-nitro analogue **1b** did not give satisfactory results since both yields and diastereoselectivities were lower (entry 6 vs entry 1).

The effect of a substituent on the aromatic moiety of styrene was then studied using the preceding chiral dirhodium(II) carboxylate catalysts in combination with the matched sulfonamidamides. The best results in terms of yield and selectivity were obtained with *para*-halogenated styr- enes in the presence of sulfonimidamide **1a** (entries 7 and 9), *p*-bromostyrene, for example, affording aziridine **6h** in 59% yield and with 82% de. Once more, sulfonimidamide **1b** proved to be a less efficient nitrene precursor (entries 8 and 10). Electron-donor substituents, such as methoxy or methyl, resulted in lower yields and diastereo- selectivities (entries 12 and 13) while acceptor substituents, that is, *p*-trifluoromethyl- and *m*-nitrostyrene, afforded aziridines **6j** and **6m** with 60% and 55% de, respectively (entries 11 and 14).

3. Conclusion

In conclusion, we have shown that sulfonimidamide-derived iminoiodanes are efficient nitrene donors for the rhodium-catalyzed aziridinations of olefins. Under

Table 2. Aziridination of styrene and substituted styrenes with chiral Rh(II) catalysts

Entry	Sulfonimidamide	Chiral rhodium catalyst $[Rh_2L*_4]$	X	Aziridine	Yield (%)[a]	de (%)[b]
1	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	H	**6a**	63	80
2	(*S*)-**1a**	$[Rh_2\{(S)\text{-4-Br-nttl}\}_4]$[c]	H	**6a**	66	43
3	(*S*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	H	**6a**	54	20
4	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	H	**6a**	55	74
5	(*S*)-**1a**	$[Rh_2\{(S)\text{-meox}\}_4]$	H	**6a**	42	20
6	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	H	**7a**	29	61
7	(S)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Br	**6h**	59	82
8	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Br	**7b**	30	54
9	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	4-Cl	**6i**	52	70
10	(*S*)-**1b**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-Cl	**7c**	25	54
11	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-CF_3	**6j**	55	60
12	(*S*)-**1a**	$[Rh_2\{(S)\text{-nttl}\}_4]$	4-OMe	**6k**	17	49
13	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	4-Me	**6l**	33	36
14	(*R*)-**1a**	$[Rh_2\{(R)\text{-ntv}\}_4]$	3-NO_2	**6m**	18	55

[a] Isolated yield after flash chromatography. Diastereoisomers could not be separated on silica gel.
[b] Diastereoisomeric excess (de) was determined by NMR.
[c] With 2.3 mol % of catalyst.

stoichiometric conditions, aziridines could be obtained in modest to good yields (17–66%) with diastereoselectivities up to 82%. Matching and mismatching effects were also observed, indicating that selectivities could be optimized by carefully choosing the rhodium(II) carboxylate catalyst and the sulfonimidamide. A noteworthy feature is the complementarity between rhodium and copper complexes in terms of substrate: while copper salts give the best results with α,β-unsaturated carbonyl compounds,[6] rhodium catalysts are more suitable for styrene derivatives. Finally, the ability of rhodium(II) complexes to catalyze nitrene insertions into a C–H bond encourages us to evaluate the potential of sulfonimidamides in such diastereoselective processes since recent papers reflect the growing interest in developing efficient intermolecular C–H amination.[19] Work is currently in progress in this direction as is the preparation and the screening of a series of substituted sulfonimidamides.

Acknowledgements

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11. *X-ray crystallographic data* for ($C_{13}H_{13}N_3O_5S_2$), (−)-(*S*)-**1b**: $M_w = 355.4$, $\mu = 0.384\ mm^{-1}$, $D_x = 1.574\ g \cdot cm^{-3}$, monoclinic, $P2_1$, $Z = 2$, $a = 7.3572(6)$, $b = 6.9268(4)$, $c = 14.7339(13)$ Å, $\beta = 93.095(10)°$, $V = 749.77\ (11)$ Å^{-3}; pale yellow prism $0.40 \times 0.19 \times 0.0740$ mm. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 273222. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
12. *General procedure for aziridination of olefins*: CH_2Cl_2 (0.5–0.6 mL) ($c = 0.5$ M) was added by syringe to a flask containing the olefin (0.25–0.30 mmol), sulfonimidamide **1a** or **1b** (1.2 equiv), $PhI(OAc)_2$ (1.8 equiv), MgO (3 equiv), activated 4 Å molecular sieves and Rh(II) catalyst (2.3–5.0 mol %) under argon at −20 °C. The suspension was then stirred at −20 °C for 24 h. It was then diluted with CH_2Cl_2 (5 mL) and filtered through a pad of Celite. The filter cake was washed with CH_2Cl_2 and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (SiO_2, pentane/EtOAc 7:3) to afford the desired aziridine. Selected data for **6a** (values in italics refer to the minor diastereomer, where applicable): ^{1}H NMR (300 MHz, $CDCl_3$) *δ 2.38* (*s, 3H*), 2.39 (s, 3H), 2.42 (s, 6H), *2.44* (*d, J = 4.8 Hz, 1H*), 2.58 (d, $J = 4.8$ Hz, 1H), *3.12* (*d, J = 7.6 Hz, 1H*), 3.24 (d, $J = 7.6$ Hz, 1H), 3.84 (dd, $J = 7.6$ and 4.8 Hz, 1H), *3.98* (*dd, J = 7.6 and 4.8 Hz, 1H*), 7.20 (m, 18H), 7.82 (m, 8H); ^{13}C NMR (62.5 MHz, $CDCl_3$) *δ* 21.3, 21.5, 36.0, 37.6, 42.0, 43.4, 126.4, 126.5, 126.6, 127.7, 128.5, 129.0, 129.1, 129.8, 133.7, 134.1, 134.2, 140.4, 142.5, 142.6, 145.5; mass spectrum (ES) *m/z* 426 $(M)^+$. Anal. Calcd for $C_{22}H_{22}N_2O_3S_2$: C, 61.95; H, 5.20; N, 6.57; S, 15.03. Found: C, 61.74; H, 5.21; N, 6.36; S, 15.01.
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