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Rhodium-Catalyzed Asymmetric Arylation of Allyl Sulfones under the Conditions of Isomerization into Alkenyl Sulfones

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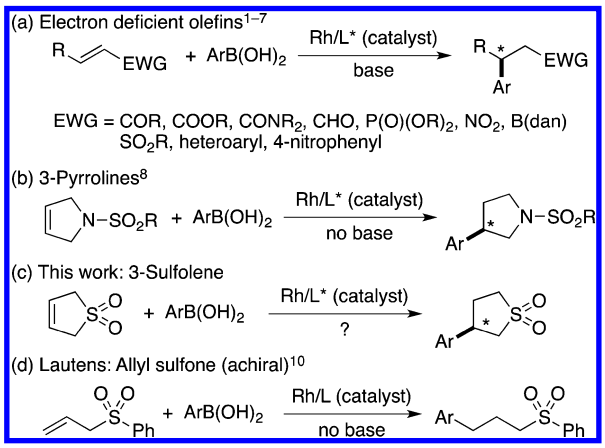
Supporting Information

ABSTRACT: The reaction of 3-sulfolene with arylboronic acids in the presence of a chiral diene-rhodium catalyst under highly basic conditions (10 equiv of KOH) gave high yields of 3-arylsulfolanes with high enantioselectivity, where 3-sulfolene is in equilibration with 2-sulfolene by base-catalyzed isomerization and the more reactive 2-sulfolene undergoes the rhodium-catalyzed asymmetric arylation.

It has been well documented that the rhodium-catalyzed asymmetric arylation of olefins with arylboronic acids is one of the most convenient and reliable methods of creating benzylic stereocenters with high enantioselectivity.[1] The olefinic substrates successfully applied for the asymmetric arylation are mostly electron-deficient olefins including α,β-unsaturated carbonyl compounds,[2] alkenylphosphonates,[3] nitroalkenes,[4] borylalkenes,[5] alkenyl sulfones,[6] and some alkenylarenes[7] (Scheme 1a). The reactions are usually carried out in the presence of a substoichiometric amount (10–100 mol %) of inorganic bases, typically KOH.[1] Recently, we reported a 3-pyrroline as a new type of substrate whose asymmetric arylation is catalyzed by a bisphosphine-rhodium complex under nonbasic conditions[8] (Scheme 1b). As a cyclic olefin substrate analogous to 3-pyrroline, we have focused our attention on 3-sulfolene, which is industrially manufactured and is therefore abundant and inexpensive,[9] for the rhodium-catalyzed asymmetric arylation (Scheme 1c). As structurally relevant compounds with 3-sulfolene, linear allyl sulfones have been used by Lautens[10] for the rhodium-catalyzed arylation (Scheme 1d), in addition to the alkenyl sulfone substrates for the asymmetric conjugate arylation.[6,11−13]

Scheme 1. Rhodium-Catalyzed Asymmetric Hydroarylation of Alkenes



To simply summarize the results obtained for asymmetric arylation of **1** and **2** with boronic acid **3a** catalyzed by rhodium complexes coordinated with binap and diene ligands under a neutral condition (entries 1−6 in Table 1), 3-sulfolene (**1**) is less reactive than 2-sulfolene (**2**), and the enantioselectivity is much higher for 2-sulfolene (**2**) than for 3-sulfolene (**1**). On the other hand, it has been reported that the isomerization between allyl sulfone **1** and alkenyl sulfone **2** takes place in the presence of a transition metal[20] or base catalyst[21] and the equilibrated ratio of **1**:**2** is 60/40−50/50 (Scheme 2). Because the arylation of 2-sulfolene (**2**) is faster than that of 3-sulfolene (**1**) ($k_2 \gg k_1$ in Scheme 2) particularly with diene ligands, if the isomerization of **1** into **2** is much faster than the arylation of **1** ($k_i \gg k_1$) and the reaction condition for the isomerization is

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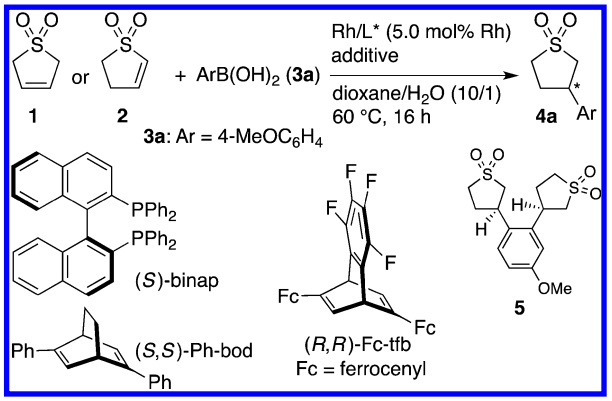
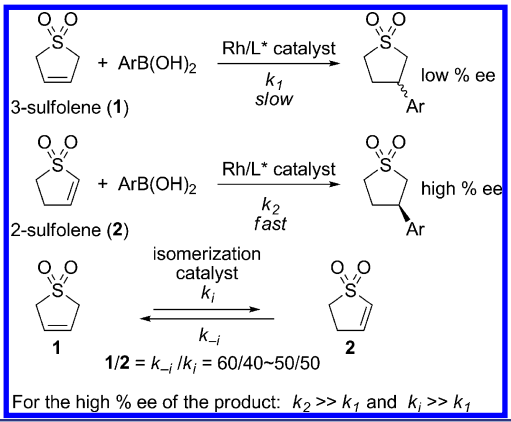
Table 1. Rhodium-Catalyzed Asymmetric Arylation of 3-Sulfolene (1) and 2-Sulfolene (2)[a]



entry	1 or 2	ligand on Rh	additive (equiv)[b]	ratio of 1:2:4a[c]	yield (%)[d] 4a	% ee 4a
1	1	(*S*)-binap[e]	—	92:0:8	8	37 (*S*)
2	2	(*S*)-binap[e]	—	0:60:40	38	91 (*R*)
3	1	cod[f]	—	94:0: 6	—	—
4	2	cod[f]	—	0:0: 100	90	—
5	1	(*R*,*R*)-Fc-tfb[g]	—	89:0:11	10	10 (*R*)
6	2	(*R*,*R*)-Fc-tfb[g]	—	0:0:100	66[h]	99 (*R*)
7	1	(*R*,*R*)-Fc-tfb[i]	KOH (1.0)	85:1:14	14	40 (*R*)
8	1	(*R*,*R*)-Fc-tfb[i]	KOH (3.0)	77:8:15	13	66 (*R*)
9	1	(*R*,*R*)-Fc-tfb[i]	KOH (5.0)	4:4:92	87	94 (*R*)
10	1	(*R*,*R*)-Fc-tfb[i]	KOH (10.0)	0:0:100	91	98 (*R*)
11[j]	1	(*R*,*R*)-Fc-tfb[i]	KOH (10.0)	0:0:100	90	98 (*R*)
12[j]	2	(*R*,*R*)-Fc-tfb[i]	KOH (10.0)	0:0:100	79[h]	99 (*R*)
13[j]	1	(*S*,*S*)-Ph-bod[k]	KOH (10.0)	—[l]	39	23 (*R*)
14[j]	1	(*S*)-binap[m]	KOH (10.0)	—[l]	30	67 (*R*)

[a]Reaction conditions: 3- or 2-sulfolene (0.15 mmol), $ArB(OH)_2$ (0.45 mmol unless otherwise noted), Rh catalyst (5 mol % of Rh), dioxane/H_2O (1.0/0.1 mL). [b]Equivalents to sulfolene. [c]Determined by ^1H NMR of the reaction mixture. [d]Isolated yield. [e]$[Rh(OH)(coe)_2]_2$/(*S*)-binap. [f]$[Rh(OH)(cod)]_2$. [g]$[Rh(OH)((R,R)\text{-Fc-tfb})]_2$. [h]As a side product, the formation of 3,3′-(4-methoxy-1,2-phenylene)-bis(tetrahydrothiophene 1,1-dioxide) (**5**) was observed. [i]$[RhCl((R,R)\text{-Fc-tfb})]_2$. [j]$ArB(OH)_2$ (0.23 mmol). [k]$[RhCl(coe)_2]_2$/(*S*,*S*)-Ph-bod. [l]Not determined. [m]$[RhCl(coe)_2]_2$/(*S*)-binap.

Scheme 2. Rhodium-Catalyzed Asymmetric Arylation of 3- and 2-Sulfolenes



compatible with the rhodium-catalyzed asymmetric arylation of **2**, we have a chance to obtain a high yield of the arylation product **4a** with high enantioselectivity.

Several basic conditions were examined by changing the amount of KOH (entries 7−10 in Table 1). With 1.0 equiv (to **1**) of KOH, which is one of the standard conditions for asymmetric hydroarylation of α,β-unsaturated ketones,[1,2] the product (*R*)-**4a** of 40% ee was formed in a slightly higher yield (14%) (entry 7), and with 3.0 equiv of KOH the % ee of (*R*)-**4a** was increased to 66% ee (entry 8). The higher % ee (40% and 66% ee vs 10% ee in entry 5) indicates that a part of **4a** is produced by the asymmetric arylation of **2** under these conditions, but the isomerization of **1** into **2** is not fast enough to supply **2** for the catalytic arylation to produce a high yield of **4a**. The recovery of unreacted sulfolene as 3-sulfolene (**1**) is consistent with this slow isomerization. The addition of 5.0 equiv of KOH greatly improved the result (entry 9). The reaction gave (*R*)-**4a** of 94% ee in 87% yield. Finally, with 10 equiv of KOH, (*R*)-**4a** of 98% ee was produced in 91% yield (entry 10). The amount of boronic acid **3a** was decreased from 3.0 to 1.5 equiv (to **1**) without loss of yield or selectivity (entry 11). The high enantiomeric purity (98% ee) of **4a** produced with 10 equiv of KOH for the reaction starting with 3-sulfolene (**1**) (entries 10 and 11) is almost the same as 99% ee observed for the reaction starting with 2-sulfolene (**2**) (entry 6). Interestingly, the yield of **4a** is higher in the reaction of 3-sulfolene (**1**) under the basic conditions than that in the reaction of 2-sulfolene (**2**) (entries 6 and 12) where the formation of side product **5**[19] is accompanied. It should be noted that the yield and % ee of **4a** are low with other ligands, for example, Ph-bod[22] and binap (entries 13 and 14). It is likely that the Rh-catalyzed arylation of 2-sulfolene (**2**) is not fast enough with other chiral ligands to produce a high yield of **4a**.

Under the optimized conditions found for the reaction of 3-sulfolene (**1**) with $4\text{-MeOC}_6H_4B(OH)_2$ (**3a**) (entry 11 in Table 1), the Rh/(*R*,*R*)-Fc-tfb catalyst was examined for its scope in the asymmetric hydroarylation of **1** with several other arylboronic acids **3**. The results summarized in Table 2 show that the reaction in the presence of 10 equiv of KOH is applicable to a variety of arylboronic acids. Thus, the phenylboronic acids substituted with methyl and alkoxy groups at para, meta, and ortho positions all gave the corresponding products with high % ee ranging between 98% and 99% ee except for 2-MeC_6H_4 (entries 3−8). The enantioselectivity was higher (>99% ee) in the arylation with boronic acids bearing electron-withdrawing groups, halides and trifluoromethyl, on the para position (entries 9−12). The asymmetric introduction of 3-cyclopentyloxy-4-methoxyphenyl group provided us with one step synthesis of enantiomerically enriched (*S*)-**4o** which is of pharmaceutical interest[23] (entry 15).

The absolute configuration of the product **4k** (Ar = 4-Br-C_6H_4) was determined to be (*R*) by its X-ray crystallographic analysis.[24] The *R* configuration obtained with (*R*,*R*)-Fc-tfb is rationalized by the coordination of 2-sulfolene to an aryl−rhodium intermediate with its *si* face. The coordination with the other face is much less favorable due to the steric repulsions between the cyclic alkyl chain of 2-sulfolene and one of the ferrocenyl groups on the diene ligand[25] (Scheme 3). All the products under the present conditions with (*R*,*R*)-Fc-tfb ligand are predicted to have the same absolute configuration (*R*).

For six-membered ring sulfone, the Rh-catalyzed asymmetric arylation under the isomerization condition is more difficult and challenging, because equilibration of the isomerization between allyl sulfone **6** and alkenyl sulfone **7** is heavily on the allyl sulfone side.[26] In our experiments with DBU as a base in THF at 25 °C, the equilibrated ratio was 97/3 for **6**/**7**.[27] Under the standard conditions (1.5 equiv $ArB(OH)_2$, 10 equiv KOH,

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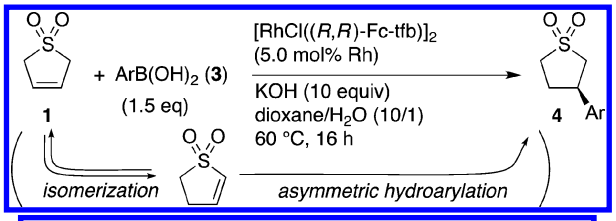
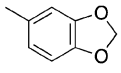
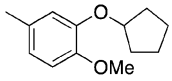
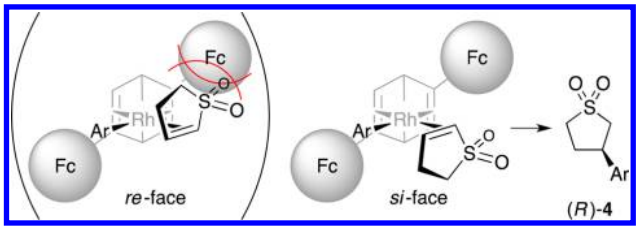
Table 2. Rhodium-Catalyzed Asymmetric Hydroarylation of 3-Sulfolene (1) with Arylboronic Acids 3[a]



entry	ArB(OH)$_2$ (**3**): Ar	product **4**	yield (%)[b]	ee (%)[c]
1	**3a**: 4-MeOC$_6$H$_4$	**4a**	90	98 (*R*)
2	**3b**: C$_6$H$_5$	**4b**	80[d]	97 (*R*)
3	**3c**: 4-MeC$_6$H$_4$	**4c**	67[d]	>99 (*R*)
4	**3d**: 3-MeC$_6$H$_4$	**4d**	89	98 (*R*)
5	**3e**: 2-MeC$_6$H$_4$	**4e**	97	93 (*R*)
6	**3f**: 4-PhOC$_6$H$_4$	**4f**	87	99 (*R*)
7[e]	**3g**: 3-MeOC$_6$H$_4$	**4g**	95	98 (*R*)
8	**3h**: 2-MeOC$_6$H$_4$	**4h**	84	>99 (*R*)
9	**3i**: 4-FC$_6$H$_4$	**4i**	89	>99 (*R*)
10	**3j**: 4-ClC$_6$H$_4$	**4j**	90	>99 (*R*)
11	**3k**: 4-BrC$_6$H$_4$	**4k**	94	>99 (*R*)
12	**3l**: 4-CF$_3$C$_6$H$_4$	**4l**	87	>99 (*R*)
13	**3m**: 2-naphthyl	**4m**	97	97 (*R*)
14[f]	**3n**: 	**4n**	93	95 (*S*)[g]
15	**3o**: 	**4o**	61	91 (*S*)[g]

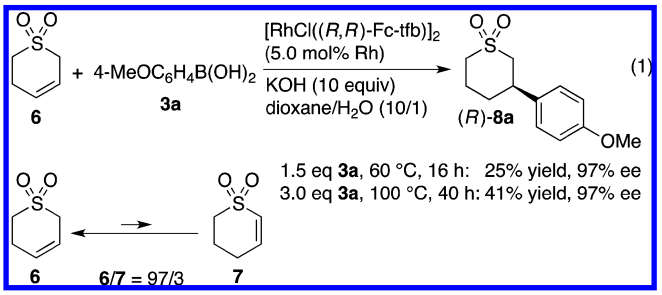
[a]Reaction conditions: 3-sulfolene (0.15 mmol), ArB(OH)$_2$ (0.23 mmol), KOH (1.5 mmol), [RhCl((*R*,*R*)-Fc-tfb)]$_2$ (5 mol % of Rh), dioxane/H$_2$O (1.0/0.1 mL) at 60 °C for 16 h. [b]Isolated yield. [c]The % ee was determined by HPLC on a chiral stationary phase. Absolute configuration of **4k** was determined to be (*R*) by X-ray crystal analysis, and other products **4** are assumed to have the same (*R*) configuration. [d]The side products, analogous to **5**, were also formed. [e]With KOH (0.75 mmol). [f]In dioxane/H$_2$O (1.0/0.2 mL). [g](*S*,*S*)-Fc-tfb was used.

Scheme 3. Proposed stereochemical pathway for the asymmetric arylation catalyzed by Rh/(*R*,*R*)-Fc-tfb

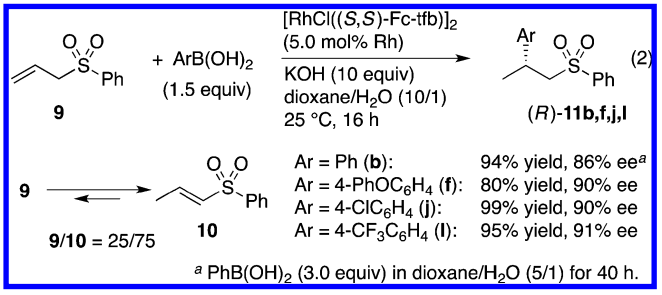


at 60 °C for 16 h) used for the reactions in Table 2, the allylic sulfone **6**[28] gave 25% yield of the arylation product **8a** with 97% ee (eq 1). The reaction with more amount of the boronic acid **3a** at a higher temperature for a longer time improved the yield of **8a** to 41%.[29]

Lautens has reported[10] that the reaction of 2-propenyl phenyl sulfone (**9**) with arylboronic acids in the presence of rhodium catalyst [Rh(OH)(binap)]$_2$ under a neutral condition



took place with high linear selectivity to give high yields of linear products, 3-arylpropyl sulfones (Scheme 1d). Under the present basic conditions with Rh/Fc-tfb as a catalyst, the isomerization–conjugate arylation sequence proceeded efficiently to completely change the regiochemistry of the carbon–carbon bond formation. Now 2-arylpropyl sulfones **11**[28] were obtained with perfect selectivity (eq 2). The equilibration of isomerization between 2-propenyl sulfone **9** and 1-propenyl sulfone **10** is on the side of **10**,[20,30] and thus the yields of **11** are generally high. The enantioselectivities are also high, around 90% ee, irrespective of the electron-donating or -withdrawing substitution on the phenylboronic acid.



In summary, we have developed a new type of rhodium-catalyzed asymmetric arylation, where 3-sulfolene is in equilibration with 2-sulfolene by a base-catalyzed isomerization under the conditions of rhodium-catalyzed arylation. The rhodium complex coordinated with Fc-tfb ligand efficiently catalyzed the arylation of 2-sulfolene under the isomerization condition to finally consume all the sulfolene isomers, and it gave a high yield of the conjugate arylation product with high enantioselectivity. This isomerization–asymmetric arylation sequence has been extended to 6-membered ring and linear allylic sulfones.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, compound characterization data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(24) The details are described in Supporting Information.

(25) The rationalization of stereochemical pathway using this type of model has been always successful (ref 17b). See also, Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508.

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(27) Equilibration experiments under the reaction conditions of the present Rh-catalyzed arylation (**6** and/or **7** with KOH in dioxane/H_2O) gave conjugate hydroxylation product, 3-hydroxytetrahydro-2*H*-thiopyran 1,1-dioxide, and therefore it is difficult to obtain the equilibrated ratio of **6**/**7**.

(28) A mixture with a small amount (ca. 10%) of **7**.

(29) The synthetic utility of the products **8** and **11** has been reported in refs 13b and c.

(30) Berranger, T.; Langlois, Y. *J. Org. Chem.* **1995**, *60*, 1720 In our experiments (with DBU in THF at 25 °C), the equilibrated ratio was 25/75 for **9**/**10**.

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