Pergamon

Tetrahedron Letters 40 (1999) 3431–3434

TETRAHEDRON LETTERS

Participation of the Chiral Sulfinyl Functionality in Palladium-Catalyzed Asymmetric Vinylcyclopropane-Cyclopentene Rearrangements

Kunio Hiroi,* Yasuki Yoshida, and Yoko Kaneko

Department of Synthetic Organic Chemistry, Tohoku Pharmaceutical University

4-4-1 Komatsushima, Aoba-ku, Sendai, Miyagi 981-8558, Japan

Received 3 February 1999; revised 4 March 1999; accepted 5 March 1999

Abstract: Stereochemical studies on the palladium-catalyzed asymmetric 1,3-rearrangements of [4-chiral arylsulfinyl-1,3(*E* or *Z*)-butadienyl]cyclopropanes to chiral cyclopentenes are described. The plausible mechanism for the rationalization of the stereochemical outcomes is proposed.

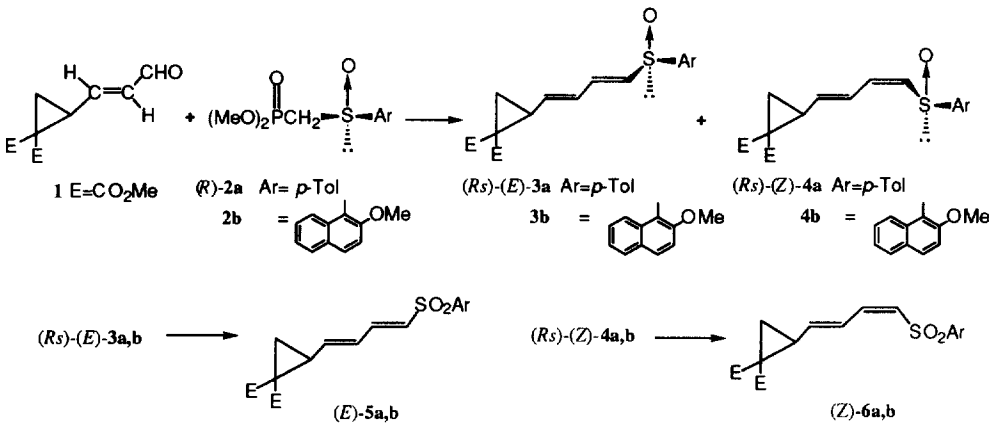
Although a vinylcyclopropane-cyclopentene rearrangement generally requires high reaction temperature,[1] a palladium catalysis facilitates the rearrangement under milder reaction conditions. Over these several years, we have undertaken stereochemical studies on palladium-catalyzed asymmetric vinylcyclopropane-cyclopentene rearrangements with chiral phosphine ligands,[2] or using vinylcyclopropanes bearing chiral sulfinyl groups on the cyclopropanes.[3] Successively, in order to reveal the participation of chiral sulfinyl groups,[4] extensive efforts have been devoted to the palladium-catalyzed asymmetric rearrangements of 1,3-butadienylcyclopropanes bearing chiral sulfinyl groups at other sites. We wish to communicate herein the stereochemistry of the palladium-catalyzed asymmetric 1,3-rearrangements of [4-chiral arylsulfinyl-1,3(*E*) or (*Z*)-butadienyl]cyclopropanes into cyclopentenes.

Dimethyl (*R*s)-2-[4-arylsulfinyl-1,3(*E*) or (*Z*)-butadienyl]cyclopropane-1,1-carboxylates (**3a,b** and **4a,b**) were prepared with a 1:1 and 2:1 ratio of the geometrical isomers of the olefin, respectively, by the condensation of aldehyde **1** (derived from dimethyl 2-formylcyclopropane-1,1-carboxylate) with Horner-Emmons reagents (*R*)-**2a,b**. Oxidation of (*R*s)-**3a,b** and (*R*s)-**4a,b** with *m*-chloroperbenzoic acid (MCPBA) afforded the corresponding sulfones (*E*)-**5a,b** and (*Z*)-**6a,b**.

The palladium-catalyzed reaction of (*R*s)-(*E*)-**3a** was carried out in toluene at room temperature for 18 h in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 equiv.) and phosphine ligands (0.2 equiv.) to give (*S*,*R*s)-(*E*)-**7a** with high diastereomeric excess (d.e.). A similar reaction of (*R*s)-(*Z*)-**4a** was carried out under the same reaction conditions to produce (*S*,*R*s)-(*Z*)-**8a** with slightly lower d.e. with unexpected retention of the (*Z*)-geometry of the starting olefin.

Introduction of a bulky substituent in the chiral sulfinyl group improved the enantiocontrol in this palladium-catalyzed rearrangement. The palladium-catalyzed reactions of (*R*s)-(*E*)-**3b** and (*R*s)-(*Z*)-**4b** were carried out in toluene at room temperature for 24 h in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 equiv.) and a phosphine ligand (0.2 equiv.) to give (*S*,*R*s)-(*E*)-**7b** and (*S*,*R*s)-(*Z*)-**8b**, respectively, with extremely high d.e.(90-94 %). The d.e. of the products **7a,b** and **8a,b** was determined by the HPLC analysis with ODS. The results obtained under

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00508-0



Scheme 1

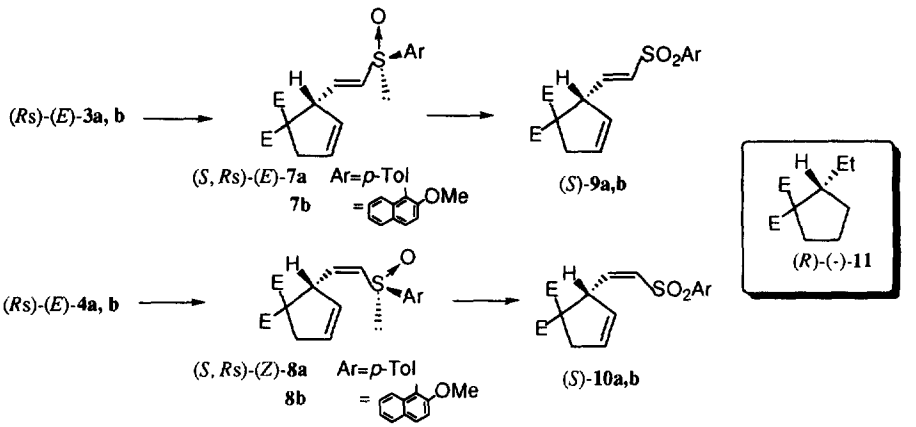
various reaction conditions are summarized in Table 1. As shown in Table 1, the chemical yields in these asymmetric 1,3-rearrangements were largely dependent on the structure of the phosphine ligands used; with triphenylphosphine and bis(diphenylphosphino)methane as ligands, the rearrangements did not occur in each substrate, whereas the use of dppe, dppp, and dppb provided high yields of the rearranged products with rather high d.e. With dpppentane, dpph, and dppf as ligands, extremely high d.e. of the rearranged products was obtained.

In contrast to these results obtained from (*R*s)-(*E*)-**3a,b** and (*R*s)-(*Z*)-**4a,b**, the palladium-catalyzed reactions of the sulfones (*E*)-**5a,b** and (*Z*)-**6a,b** under similar reaction conditions gave (*E*)-**9a,b**, which were identical with the oxidation products ((*S*)-(*E*)-**9a,b**) of (*S*,*R*s)-(*E*)-**7a,b** with MCPBA and *different from the sulfones* (*S*)-(*Z*)-**10a,b** derived from (*S*,*R*s)-(*Z*)-**8a,b**.

On the basis of these stereochemical results, it is emphasized that the chiral sulfinyl functional groups involved must participate directly with the palladium catalyst in the formation of the intermediary π-allylpalladium complexes from **4a,b**, resulting in retention of the geometry of the (*Z*) olefin, as will be discussed later.

The absolute configuration of the newly created asymmetric carbon center on the cyclopentene rings in the palladium-catalyzed rearrangements of (*R*s)-(*E*)-**3a,b** and (*R*s)-(*Z*)-**4a,b** to **7a,b** and **8a,b** was determined to be (*S*)-configuration by the chemical correlation to dimethyl (*R*)-(-)-2-ethylcyclopentane-1,1-dicarboxylate (**11**) of the known absolute configuration[3] *via* hydrogenolysis of **7a,b** and **8a,b** obtained above with Raney Ni.

The mechanism for the asymmetric induction in these palladium-catalyzed rearrangements are rationalized on the basis of the stereochemical outcome observed. It was confirmed by the HPLC analysis of the recoverd substrates prior to completion of the reactions that the asymmetric carbon center on the cyclopropane rings in the substrates used was still remained racemic during the course of the reaction. This means that these rearrangements did not result from kinetic resolution. Therefore, the stereoisomeric π-allylpalladium intermediates containing the original chiral carbons of the cyclopropyl groups should be reversiblly equilibrated. An initially-formed π-allylpalladium complex (*R*s)-**12a** derived from (*R*s)-(*E*)-**3a,b** would be equilibrated into the more stable π-allyl systems (*R*s)-**12b,c**; in the most preferred π-allyl system, (*R*s)-**12c**, with the *syn* arylsulfinyl group at C1 and the *syn* substituent at C3, the palladium-phosphine moiety is orientated at the sterically less crowded upper side (the lone pair side of the sulfinyl group) in the electronically most advantageous conformation with the sulfinyl sulfur-oxygen bond coplanar to the π-allyl system,[5] as designated in **12c**. The intramolecular substitution of the carbanion in (*R*s)-**12c** occurs at C3 allyl site from the opposite side of the palladium in a highly stereoselective



Scheme 2

Table 1. The palladium-catalyzed Asymmetric 1, 3-Rearrangements of (*R*s)-(*E*)-**3a,b** and (*R*s)-(*Z*)-**4a,b**[a)]

Substrate	Ligand[b)]	Reaction time (h)	Product	Yield (%) of **7a,b** or **8a,b**	d.e.(%) of (*Rs*, *S*)-**7a,b** or **8a,b** [c)]
3a	dppe	18	**7a**	74	70
	dppp	18	**7a**	72	68
	dppb	18	**7a**	70	73
	dpppentane	18	**7a**	16	90
	dpph	18	**7a**	12	92
	dppf	18	**7a**	43	93
3b	dppe	24	**7b**	67	92
	dppp	24	**7b**	59	87
	dppb	24	**7b**	43	92
	dpppentane	24	**7b**	7	90
	dppf	24	**7b**	5	94
4a	dppe	18	**8a**	12	79
	dppp	18	**8a**	8	79
	dppb	18	**8a**	9	55
4b	dppe	24	**8b**	26	79
	dppp	24	**8b**	18	90
	dppb	24	**8b**	21	90

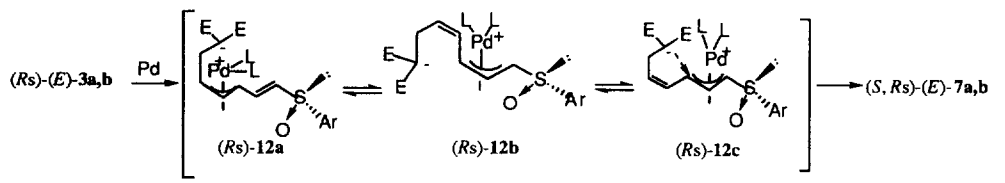
a) The 1, 3-butadienylcyclopropanes (*R*s)-(*E*)-**3a,b** and (*R*s)-(*Z*)-**4a,b** were treated with $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 equiv.) in toluene at room temperature in the presence of a phosphine ligand (0.2 equiv.).

b) dppe:1,2-bis(diphenylphosphino)ethane, dppp:1,3-bis(diphenylphosphino)propane, dppb:1,4-bis-(diphenylphosphino)butane, dpppentane:1,5-bis(diphenylphosphino)pentane, dpph:1,6-bis(diphenyl-phosphino)hexane, dppf:1,1'-bis(diphenylphosphino)ferrocene.

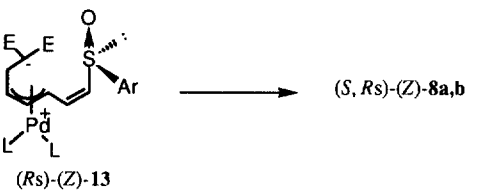
c) The diastereomeric excess (d.e.) of the products **7a,b** and **8a,b** was determined by HPLC analysis with L-column ODS.

fashion to afford (*S*,*R*s)-(*E*)-**7a,b** with high d.e.

In the case of (*R*s)-(*Z*)-**4a,b**, the direct participation of the chiral sulfinyl group to the palladium should be crucial for the rationalization of the stereochemical results; the initially-formed π-allyl-palladium complex (*R*s)-(*Z*)-**13** would be stabilized by the coordination of the sulfinyl group to the palladium. It is certainly assumed that the formation of the conformationally more stable π-allylpalladium complex with the retained (*Z*)-configuration of the olefin presumably by the coordination of the sulfinyl sulfur atom to the palladium in (*R*s)-(*Z*)-**13**,[4] followed



Scheme 3



Scheme 4

by the intramolecular nucleophilic substitution from the opposite side of the palladium, provided (*S*,*R*s)-(*Z*)-**8a,b** in a highly stereoselective fashion.

Thus, it is concluded that the palladium-catalyzed asymmetric 1,3-rearrangements of (chiral 4-arylsulfinyl-1,3-butadienyl)cyclopropanes presented a new asymmetric synthetic way to chiral cyclopentene derivatives with extremely high enantioselectivity. The plausible mechanism for these asymmetric rearrangements is proposed in terms of the direct participation of the chiral sulfinyl functionality in the formation of π-allylpalladium complexes.

References

1. Hudlicky T., Kutchan T. M., Naqvi S. M., "*Organic Reactions* ," Ed. Kende A. S., John Wiley & Sons, Inc., New York, 1985, Vol 33, Chapter 2, pp. 247-335; Goldschmidt Z., Crammer B., *Chem. Soc. Rev.*, 1988, **17**, 229.
2. Hiroi K., Arinaga Y., Ogino T., *Chem. Lett* ., **1992**, 2329; Idem, *Chem. Pharm. Bull.*, 1994, **42**, 470.
3. Hiroi K., Arinaga Y., *Tetrahedron Lett.*, 1994, **35**, 153.
4. Hiroi K., Suzuki Y., Abe I., Hasegawa Y., Suzuki K., *Tetrahedron: Asymmetry*, 1998, **9**, 3797; Hiroi K., Suzuki Y., *Tetrahedron Lett.*, 1998, **39**, 6499; Hiroi K., Suzuki Y., Kawagishi R., *ibid.*, 1999, **40**, 715.
5. Marino J. P., Laborde E., *J. Am. Chem. Soc.*, 1988, **110**, 966.