Palladium-catalysed Allylic Sulphinate–Sulphone Rearrangements; Asymmetric Induction in the Palladium-catalysed Transfer of Chiral Sulphinates to Sulphones[1]

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The rearrangement of allylic sulphinates to sulphones is facilitated by palladium catalysis, treatment of the chiral *trans*- and *cis*-allyl sulphinates (*S*)-(−)-(**1a**), -(**1c**), and -(**1e**), and (*S*)-(−)-(**1b**) and -(**1d**) with a catalytic amount of the palladium catalysts (**3**) and (**5**) providing the corresponding chiral allyl sulphones, (*S*)-(+)- and (*R*)-(−)-(**2a—c**), respectively, in good yields; exceptionally, the palladium catalysis of the rearrangement of (*S*)-(−)-(**1f**) produced (*S*)-(+)-(**2c**).

There have been many mechanistic studies on sulphinate–sulphone rearrangements.[2] Recently we found that highly stereospecific thermal rearrangements of chiral allyl sulphinates to sulphones may be accomplished by heating in *N,N*-dimethylformamide (DMF), and suggested that the reaction proceeded *via* a cyclic intramolecular transition state, *e.g.* a [2,3] sigmatropic rearrangement.[3] However, heating at high temperatures was required to complete the rearrangements, especially for allyl toluene-*p*-sulphinates bearing bulky substituents.

In order to circumvent this difficulty, we have investigated the metal-catalysed transformation of allyl sulphinates into

sulphones, and now report the applicability of palladium catalysts for this transformation.

In the attempted thermolysis of the chiral sulphinates (*S*)-(−)-(**1a—f**) in refluxing tetrahydrofuran (THF), 1,2-dimethoxyethane, benzene, and dioxane, the starting sulphinates were recovered completely; heating at 95—110 °C in DMF was required for the rearrangement to take place. However, the sulphinates (**1a—f**) could be very easily converted into the sulphones (**2a—c**) in the presence of a catalytic amount of palladium complexes. Heating of (*S*)-(−)-(**1a**) at 50 °C for 10 h in THF in the presence of tetrakis(triphenylphosphine)palladium (**3**) (0.15 equiv.) and triphenylphosphine (0.66 equiv.) provided (*S*)-(+)-(**2a**) in 74% yield with high stereospecificity (91.8%), together with the α-rearranged sulphone (**4a**) (19% yield). Furthermore, this palladium-catalysed rearrangement could be accomplished at much lower temperature than the uncatalysed reaction; *e.g.* palladium catalysis of the rearrangement of (*S*)-(−)-(**1a**) at 0 °C for 1 h led to the formation of (*S*)-(+)-(**2a**) in 69% yield with 91.9% stereospecificity. The palladium-catalysed rearrangement of the *cis*-allyl sulphinate (*S*)-(−)-(**1b**) at 50 °C in THF for 10 h resulted in a good yield of (*R*)-(−)-(**2a**) with high stereospecificity (86.4%).

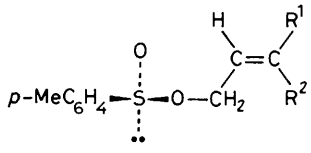
However much lower stereospecificity was observed in the palladium-catalysed rearrangement of (**1c—f**) bearing bulky substituents at the α position of the allyl groups, even at low temperatures (0 to −78 °C), as shown in Table 1. The palladium-catalysed rearrangement of the chiral allylic sulphinates, (*S*)-(−)-(**1c**), -(**1d**), and -(**1e**) was carried out in the presence of (**3**) under the conditions given in Table 1 to give the chiral allyl sulphones (*S*)-(+)-(**2b**), (*R*)-(−)-(**2b**), and (*S*)-(+)-(**2c**), respectively. Exceptionally, (*S*)-(−)-(**1f**) produced (*S*)-(+)-(**2c**). The effect of change of ligand on this asymmetric induction was investigated by using 1,2-bis(diphenylphosphino)ethane as a ligand. The rearrangement of *trans*-(*S*)-(−)-(**1c**) and *cis*-(*S*)-(−)-(**1d**) catalysed by bis[1,2-bis(diphenylphosphino)ethane]palladium (**5**)[4] provided (*S*)-(+)-(**2b**) and (*R*)-(−)-(**2b**), respectively, with almost the same stereospecificity as obtained with (**3**).

$[(Ph_3P)_4Pd)]$
(**3**)

$[(Ph_2PCH_2CH_2PPh_2)_2Pd]$
(**5**)

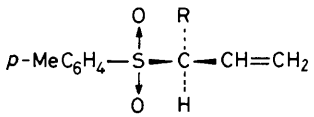
The stereospecificity of this transformation was determined by n.m.r. analysis using the shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium [Eu(hfc)$_3$]. The yields of the products (**2**) and (**4**), the ratios of (**2**) and (**4**), and the stereospecificity are summarized in Table 1.

All the chiral sulphinates employed here were prepared using methods developed by us by the boron trifluoride–diethyl ether-catalysed esterification of (*S*)-(+)-*N*,*N*-diethyltoluene-*p*-sulphinamide.[5] The absolute configurations of the starting sulphinates and also the allyl sulphones produced have already been determined.[3]



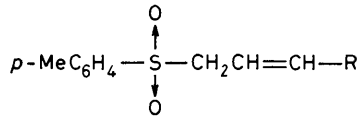
(*S*)-(−)-(**1**)

	R^1	R^2
a;	Me	H
b;	H	Me
c;	Pr^n	H
d;	H	Pr^n
e;	$[CH_2]_4Me$	H
f;	H	$[CH_2]_4Me$



(*S*)-(+)-(**2**)

	R
a;	Me
b;	Pr^n
c;	$[CH_2]_4Me$



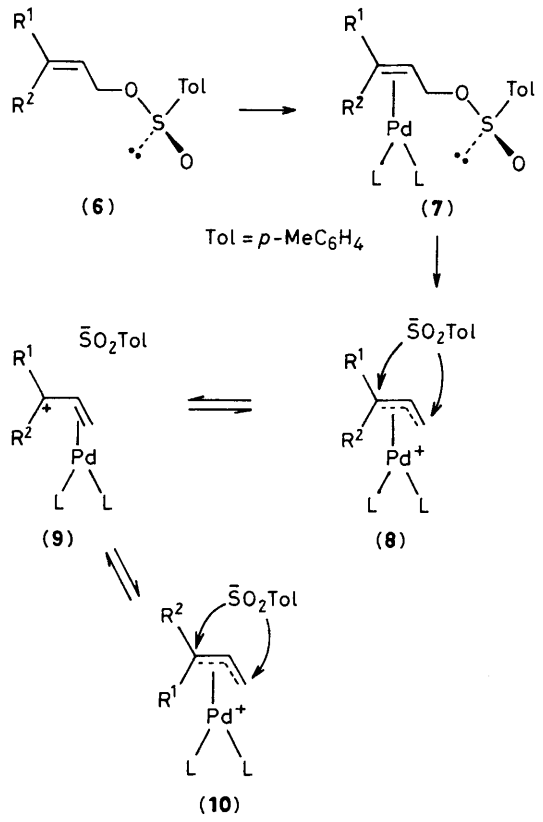
(**4**)

	R
a;	Me
b;	Pr^n
c;	$[CH_2]_4Me$

Table 1. The stereospecificity in the palladium-catalysed transformation of chiral allylic sulphinates (*S*)-(−)-(**1a—f**) into (*S*)- or (*R*)-sulphones (**2a—c**).[a]

(*S*)-(−)-(**1a—f**)	(**1a—f**) e.e.(%)[b]	Catalyst	Reaction conditions		Product yield (%) [(**2**):(**4**)]	Product (**2a—c**) $[\alpha]_D$(EtOH) (abs. confign.)	Stereospecificity (%)[c] in (**1**)→(**2**)
			Temp./°C	Time/h			
(**1a**)	58.6	(**3**)	50	10	93 [4:1]	+ 5.4° (*S*)	91.8
(**1a**)	70.7	(**3**)	0	1	86 [4:1]	+ 6.5° (*S*)	91.9
(**1b**)	49.5	(**3**)	50	10	71 [4:1]	− 4.3° (*R*)	86.4
(**1c**)	54.5	(**3**)	50	8	78 [2:3]	+ 7.9° (*S*)	38.7
(**1c**)	54.5	(**3**)	Room temp.	13.5	90 [2:3]	+ 9.5° (*S*)	46.6
(**1c**)	54.5	(**3**)	0	16.5	96 [2:3]	+ 8.7° (*S*)	42.8
(**1c**)	31.4	(**3**)	−78	6	82 [2:3]	+ 6.5° (*S*)	55.4
(**1c**)	47.0	(**5**)	50	10.5	98 [2:3]	+ 5.4° (*S*)	30.6
(**1c**)	47.1	(**5**)	Room temp.	19	76 [2:3]	+ 7.4° (*S*)	42.1
(**1c**)	47.1	(**5**)	0	66	83 [2:3]	+11.5° (*S*)	65.2
(**1d**)	61.4	(**3**)	50	10	68 [2:3]	− 7.0° (*R*)	30.3
(**1d**)	61.4	(**3**)	Room temp.	20.5	69 [2:3]	−13.2° (*R*)	57.5
(**1e**)	51.8	(**3**)	Room temp.	15.5	64 [3:7]	+ 9.6° (*S*)	51.2
(**1f**)	74.9	(**3**)	50	10	63 [3:7]	+ 7.7° (*S*)	28.4
(**1f**)	74.9	(**3**)	Room temp.	17	69 [3:7]	+14.0° (*S*)	51.7

[a] A mixture of (*S*)-(−)-(**1a—f**) (0.48 mmol), (**3**) or (**5**) (0.15 equiv.), and triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (0.66 equiv.) in THF (8 ml) was stirred under the conditions given. [b] e.e. = enantiomeric excess. [c] Calculated by n.m.r. analysis with the shift reagent [Eu(hfc)$_3$].



On the basis of the stereochemistry of the allyl sulphones (**2a**—**c**) obtained, we suggest the following mechanistic pathway for this asymmetric transfer. The lower stereospecificity of this catalysis suggests that the transition state for this transformation is somewhat ionic, involving a palladium chelate, unlike the intramolecular cyclic intermediates in [2,3] sigmatropic rearrangements.[3] The initial step is the formation of an olefin–palladium complex (**7**) from the less hindered bottom side of the most preferred conformer (**6**) in which the *p*-tolyl and the largest groups are orientated in an *anti*-coplanar conformation. The palladium complex (**7**) induces the elimination of the sulphinate group to form the ionic intermediate (**8**). In this ionic intermediate (**8**) the toluene-*p*-sulphonyl group would attack the γ- or α-carbon atoms of the allyl unit, the stereochemistry being retained by chelation with the palladium catalyst, from the opposite side of the palladium–carbon bond, consequently producing (*S*)-(+)-(**2a**—**c**) from (*S*)-(−)-(**1a**), -(**1c**), and -(**1e**), and (*R*)-(−)-(**2a**) and -(**2b**) from (*S*)-(−)-(**1b**) and -(**1d**). In the case of (**1f**), (**8**) would be transformed into (**10**) by rapid equilibration *via* (**9**), because of the severe steric interference between the pentyl group and the olefin–palladium co-ordinated unit orientated in the *syn*-conformation. Therefore palladium catalysis of the rearrangement of (*S*)-(−)-(**1f**) led to the formation of (*S*)-(+)-(**2c**), exceptionally, by the γ-sulphonylation of (**10**).

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1 Preliminary results were presented at the Second I.U.P.A.C. Symposium on Organometallic Chemistry Directed toward Organic Synthesis, Dijon, France, August 1983.
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