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ASYMMETRIC INDUCTION IN THE PALLADIUM-CATALYZED SULFONYLATION OF ALLYLIC SULFINATES AND ACETATES WITH CHIRAL PHOSPHINE LIGANDS

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Treatment of allylic (±)-p-toluenesulfinates with tetrakis-(triphenylphosphine)palladium in the presence of chiral phosphine ligands underwent allylic sulfinate-sulfone rearrangements to give the corresponding optically active allylic sulfones in high optical yields. The palladium-catalyzed reactions of readily obtainable allylic acetates with sodium p-toluenesulfinate in the presence of chiral phosphine ligands provided a new entry to optically active allylic sulfones with high enantiomeric excess.

Recently we have reported the stereochemistry of thermal[1] and palladium-catalyzed chiral allylic sulfinate-sulfone rearrangements.[2] During these investigations, however, some difficulties have been encountered in improving the chemical yields and the stereospecificities, and much efforts have been made to overcome these difficulties.

We wish to communicate herein asymmetric induction in the palladium-catalyzed sulfinate-sulfone rearrangement and the palladium-catalyzed sulfonylation of allylic acetates, using chiral phosphine ligands.

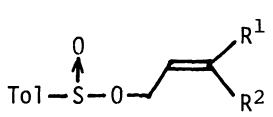
trans-2-Butenyl (±)-p-toluenesulfinate (1a) was treated with tetrakis(triphenylphosphine)palladium (0.15 equiv.) in the presence of (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)[3] (0.60 equiv.) in tetrahydrofuran (THF) at 0 °C for 14 h, to afford (R)-(-)-1-buten-3-yl p-tolyl sulfone (2a)[1] in 77% yield with 87.0% enantiomeric excess, together with an α-rearranged product, 2-butenyl p-tolyl sulfone (3a) (15% yield).
The palladium catalysis of cis-2-butenyl (±)-p-toluenesulfinate (1b) under the same conditions gave an 86.0% enantiomeric excess of allylic sulfone (R)-(-)-2a

of the same absolute configuration as obtained above. This would be rationalized by transformation of the cis-allylic intermediate (5b) into the more stable one (5a) in the equilibrium mediated by the palladium catalyst.

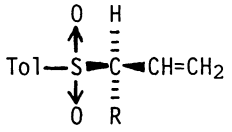
The results of the transformation of (±)-1a into (R)-(-)-2a employing other chiral ligands such as neomenthyldiphenylphosphine (NMDPP)[4] and (S)-(2-methylbutyl)diphenylphosphine (MBDPP) are summarized in Table 1. Among them, the use of (-)-DIOP as a chiral ligand led to the formation of (R)-(-)-2a with the highest enantiomeric excess (87.0%). The palladium catalysis of other allylic sulfinates (±)-1c,d was carried out in the presence of (-)-DIOP under the same conditions and the results are summarized in Table 1. With the bulkier substituents (R^1 or R^2) in 1a-d, the ratios of α- to γ-rearranged allylic sulfones were increasing in the above palladium catalysis.

No equilibrium exists between 2a-c and 3a-c in this palladium-catalyzed transformation under the conditions using THF as a solvent without methanol, as described above, which is quite different from the case reported earlier.[5] This was confirmed by the complete recovery of the starting chiral allylic sulfones (R)-(-)-2a-c without any conversion into γ-rearranged products (3a-c), retaining the optical activity completely, upon treating (R)-(-)-2a-c with tetrakis(triphenylphosphine)palladium in THF at 0-60 °C.

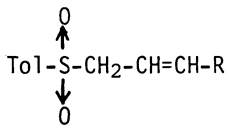
For much easier access to chiral allylic sulfones, readily obtainable allylic acetates were used instead of the allylic sulfinates in the above reactions.[5]



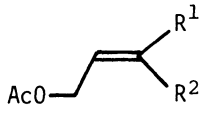
1a R^1=CH_3, R^2=H
b =H, =CH_3
c =n-C_3H_7, =H
d =n-C_5H_{11}, =H



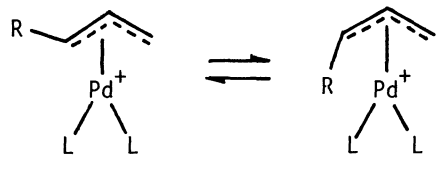
(R)-(-)-2a R=CH_3
b =n-C_3H_7
c =n-C_5H_{11}



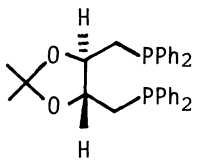
3a R=CH_3
b =n-C_3H_7
c =n-C_5H_{11}



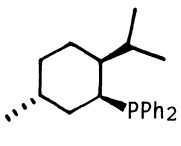
4a R^1=CH_3, R^2=H
b =H, =CH_3
c =n-C_3H_7, =H
d =H, =n-C_3H_7
e =n-C_5H_{11}, =H



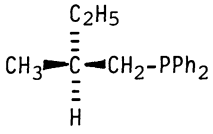
5a ⇌ 5b



(-)-DIOP



NMDPP



(S)-MBDPP

Table 1. The Palladium Catalysis of the Allylic (±)-Sulfinates (1a-d) with Chiral Ligands[a)]

Sulfinates 1a-d	Ligands (equiv.)	Yields of 2 /%	$[\alpha]_D$(EtOH) of 2	e.e.(%) of 2[b)]	Yields of 3 /%
1a	(-)-DIOP (0.6)	77	-8.7°	87.0	15
1a	NMDPP (1.2)	74	-7.6°	76.0	15
1a	(S)-MBDPP(1.2)	72	-7.3°	73.0	14
1b	(-)-DIOP (0.6)	73	-8.6°	86.0	15
1c	(-)-DIOP (0.6)	37	-29.7°	78.5	55
1d	(-)-DIOP (0.6)	17	-30.4°	83.0	70

a) The allylic (±)-sulfinates (1a-d) were treated with tetrakis(triphenylphosphine)palladium (0.15 equiv.) in the presence of the chiral ligands in THF at 0 °C for 14 h.

b) The enantiomeric excess (%) was calculated by their optical rotations.[1)]

The palladium-catalyzed reaction of trans-2-butenyl acetate (4a) with sodium p-toluenesulfinate was performed in the presence of tetrakis(triphenylphosphine)-palladium (0.15 equiv.) and (-)-DIOP (0.6 equiv.) in THF at room temperature for 6 h, to give (R)-(-)-2a in 73% yield with 88.0% enantiomeric excess. The reaction of cis-2-butenyl acetate (4b) with sodium p-toluenesulfinate under the same conditions provided the allylic sulfone (R)-(-)-2a of the same absolute configuration as obtained in the trans system (4a), with 88.0% enantiomeric excess.

The palladium-catalyzed reactions of both trans- and cis-2-hexenyl acetate (4c and 4d) with sodium p-toluenesulfinate produced (R)-(-)-1-hexen-3-yl p-tolyl sulfone (2b) in 39 and 38% yields with 78.8 and 70.3% enantiomeric excess, besides with 2-hexenyl p-tolyl sulfone (3b) (59 and 58% yields), respectively. This would be reasonably explained by the equilibrium between 5a and 5b, in the same way as mentioned above in the catalysis of the sulfinates 1a,b.

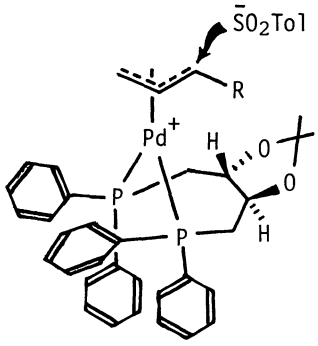
The mechanistic pathway for this asymmetric induction with (-)-DIOP would be presented as follows. In the presence of (-)-DIOP, a seven-membered intermediate would be formed by replacement of the ligand with (-)-DIOP and coordination of the palladium catalyst with the allylic systems. The more preferable conformations in the intermediary palladium complex would be the diagonally coordinated states 6a and 6b. In these states, the more severe steric interference is observed in 6a between the substituent R and one of the oxygen moieties in the part of (-)-DIOP. Therefore, the p-toluenesulfonyl group reacts from the top side of the most preferable intermediate 6b, resulting in formation of (R)-(-)-2a-c with high enantiomeric excess.

Table 2. The Palladium-catalyzed Asymmetric Sulfonylation of the Allylic Acetates 4a-e[a)]

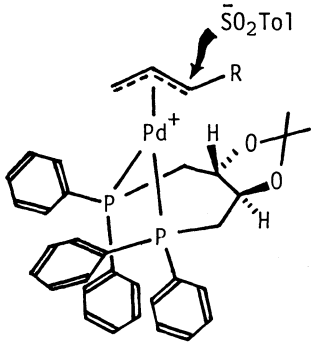
Acetates 4a-e	Reaction time h	Yields of 2 /%	$[\alpha]_D$(EtOH) of 2	e.e.(%) of 2[b)]	Yields of 3 /%
4a	6	73	-8.8°	88.0	24
4b	8	70	-8.8°	88.0	23
4c	6	39	-29.5°	78.8	59
4d	7	38	-26.3°	70.3	58
4e	8	21	-25.3°	69.6	74

a) The allylic acetates 4a-e were reacted with sodium p-toluenesulfinate (2.0 equiv.) in the presence of tetrakis(triphenylphosphine)palladium (0.15 equiv.) and (-)-DIOP (0.6 equiv.) in THF at room temperature.

b) The enantiomeric excess (%) was calculated by their optical rotations.[1)]



6a



6b

Thus, this novel method provides a new entry to synthetically valuable optically active allylic sulfones. Its synthetic application to asymmetric synthesis of biologically active substances is now in progress.

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References

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