CHEMISTRY LETTERS, pp. 527-528, 1986.

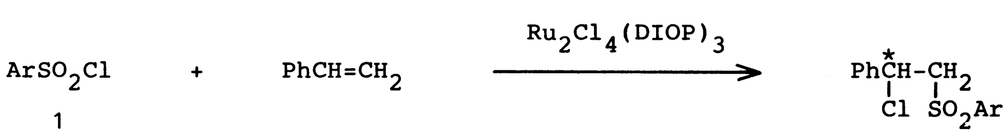
ASYMMETRIC ADDITION OF ARENESULFONYL CHLORIDES TO STYRENE CATALYZED BY A RUTHENIUM(II) CHIRAL PHOSPHINE COMPLEX

Masayuki KAMEYAMA, Nobumasa KAMIGATA,* and Michio KOBAYASHI
Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Fukazawa, Setagaya-ku, Tokyo 158

The reactions of arenesulfonyl chlorides with styrene in the presence of a ruthenium(II) chiral phosphine complex, $Ru_2Cl_4(DIOP)_3$, proceed under mild conditions to give optically active 1:1 adducts with about 20-40% enantiomeric excess.

The additions of sulfonyl chlorides to olefins, in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) under mild conditions, afford 1:1 adducts in high yield.[1)] It is proposed that sulfonyl radicals are involved as intermediate in these reactions, but their behavior differs from those initiated by photochemical or thermal reactions. The sulfonyl radicals produced from sulfonyl chlorides and ruthenium(II) phosphine complexes are considered to be confined in the coordination sphere of metal complexes.

In the presence of transition metal complexes coordinated with chiral phosphine ligands, a number of asymmetric reactions have been reported.[2)] When chiral phosphine is used instead of triphenylphosphine as ligand of ruthenium(II) complex in the above-mentioned addition reactions, an asymmetric induction is expected. We report herein the asymmetric radical additions of arenesulfonyl chlorides to styrene catalyzed by a ruthenium(II) chiral phosphine complex. Ruthenium(II) chiral phosphine complex, $Ru_2Cl_4(DIOP)_3$, was prepared according to the literature.[3)]



$$ArSO_2Cl \;+\; PhCH{=}CH_2 \xrightarrow{Ru_2Cl_4(DIOP)_3} Ph\underset{Cl}{\overset{*}{C}H}-\underset{SO_2Ar}{CH_2}$$

1 **2**

The reaction of p-toluenesulfonyl chloride (2.0 mmol) with styrene (3.0 mmol) in benzene (4 ml) in the presence of a catalytic amount of $Ru_2Cl_4[(-)\text{-DIOP}]_3$ (0.04 mmol) at 60 °C for 6 h gave 1:1 adduct (**2b**) in 92% yield (conversion 49%). The adduct (**2b**) showed a specific rotation $[\alpha]_D = +25.3°$ (c 2.7, $CHCl_3$) which corresponded to 29% enantiomeric excess of (R)-isomer. Similary, When $Ru_2Cl_4[(+)\text{-DIOP}]_3$ was used as a catalyst, the adduct (**2b**) showed $[\alpha]_D = -19.8°$ (c 2.7, $CHCl_3$) which corresponded to 24% ee of (S)-isomer. Reaction of related several arenesulfonyl chlorides with styrene was carried out in a similar way to give the corresponding adducts (**2**). The results are summarised in Table 1.

Table 1. Reaction of sulfonyl chlorides with styrene catalyzed by Ru-DIOP

Ar in 1	DIOP	Product	Abs. config.	$[\alpha]_D/°$	Optical yield/% ee
C_6H_5	(-)	2a	R	+19.5	22
C_6H_5	(+)	2a	S	-20.4	25
p-$CH_3C_6H_4$	(-)	2b	R	+25.3	29
p-$CH_3C_6H_4$	(+)	2b	S	-19.8	24
p-ClC_6H_4	(-)	2c	R	+19.3	25
p-ClC_6H_4	(+)	2c	S	-19.0	24
p-$CH_3OC_6H_4$	(-)	2d	R	+19.5	40
p-$CH_3OC_6H_4$	(+)	2d	S	-15.2	28

The enantiomeric excess and absolute configuration of 2 obtained in the present reactions were estimated by comparison with optically pure samples (2) which were prepared from optically pure mandelic acid. (R)-(+)- 2 and (S)-(-)- 2 were formed with retention from (S)-(+)-mandelic acid and (R)-(-)-mandelic acid, respectively.4)

Although the optical yields are not high, an asymmetric induction was clearly observed in the radical additions of sulfonyl chlorides to olefin catalyzed by the Ru(II)-DIOP complex. This suggests that the degree of freedom associated with the intermediate radicals is restricted compared with those in the typical free-radical reactions.5) Thus, this asymmetric induction can be taken as support for the homolytic mechanism which is operative in the coordination sphere.

References

1) N. Kamigata, J. Ozaki, and M. Kobayashi, J. Org. Chem., 50, 5045 (1985), and references cited therein.

2) H. B. Kagan and J. C. Fiaud, Top. Stereochem., 10, 175 (1978); K. Achiwa, J. Am. Chem. Soc., 98, 8265 (1976); A. Miyashita, H. Takaya, Y. Souchi, and R. Noyori, Tetrahedron, 40, 1245 (1984).

3) B. R. James, D. K. Wang, and R. F. Voight, J. Chem. Soc., Chem. Commun., 1975, 574.

4) The specific rotations of pure 2 are as follows:
(R)- 2a ; $[\alpha]_D$= +89.3° (c 2.4, $CHCl_3$), (S)- 2a ; $[\alpha]_D$= -82.7° (c 0.65, $CHCl_3$)
(R)- 2b ; $[\alpha]_D$= +87.6° (c 3.5, $CHCl_3$), (S)- 2b ; $[\alpha]_D$= -81.5° (c 3.4, $CHCl_3$)
(R)- 2c ; $[\alpha]_D$= +78.3° (c 4.4, $CHCl_3$), (S)- 2c ; $[\alpha]_D$= -79.7° (c 1.7, $CHCl_3$)
(R)- 2d ; $[\alpha]_D$= +48.3° (c 2.6, $CHCl_3$), (S)- 2d ; $[\alpha]_D$= -55.2° (c 0.94, $CHCl_3$)

5) C. Walling, "Free Radicals in Solution," Wiley, New York (1957), p. 329.

(Received January 20, 1986)