

Enantioselective Alkylation of Prochiral Aldehydes by Diethylzinc Promoted by (S,S)-1,2-diphenylethan-1,2-diol

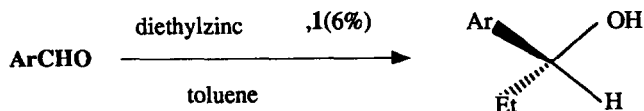
Carlo Rosini, Livia Franzini, Dario Pini, P.Salvadori *

C.N.R. Centro Studi Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 PISA, ITALY

(Received 18 July 1990)

Abstract: The title compound catalyzed reaction of diethylzinc with aromatic aldehydes provides optically active carbinols (e.e. up to 78%).

The catalytic asymmetric addition of diethylzinc to prochiral aldehydes has been widely explored employing, as chiral auxiliaries, β -aminoalcohols or diamines¹⁻¹⁹. To the best of our knowledge, simple chiral 1,2-diols have not been used, in spite of a large variety of optically active diols can be easily obtained by means of the Sharpless dihydroxylation procedure²⁰. We present here some preliminary results on the use of (S,S)-1,2-diphenylethan-1,2-diol, **1**, as chiral catalyst to obtain optically active alcohols in moderate to good enantiomeric excesses (Scheme).



Scheme

In a typical procedure, to a solution of **1** (0.0197 g, 0.092 mmol) in toluene (7 ml), diethylzinc (3 mmol, 3 ml of 1M solution in hexane) was added and the mixture stirred at room temperature for 30 min. After cooling at 0°C, 2-naphthaldehyde (0.235 g, 1.5 mmol) was introduced and the homogeneous solution stirred for 20 hrs at room temperature. The reaction was quenched adding 10% HCl. After usual work-up the residue was purified by preparative TLC (silica gel, CH₂Cl₂). As shown in the Table, aromatic aldehydes can be slowly but smoothly alkylated by diethyl zinc in the presence of **1**, the only sluggish case being that of p-methoxybenzaldehyde, for which seventy hours are required to provide a 40% yield of the corresponding carbinol²¹ (entry 8). Changing the solvent from toluene to ether does not affect the results to a great extent (entry 1 and 3). The values of the enantiomeric purities obtained are between 48% and 78%, with the R antipode always obtained in excess.

In the same reaction conditions, (R)-2-phenylethan-1,2-diol, affords the alkylation product of

2-naphthaldehyde very slowly (50% conversion after 33 hrs) and with 0% e.e.. These results show that two secondary alcoholic groups are necessary to have good chemical and optical yields in this reaction: as a matter of fact Noyori and Oguni have recently reported¹⁹ that compounds possessing primary alcoholic functions do not act as efficient catalysts of this process.

Table. Asymmetric addition of diethylzinc to ArCHO catalyzed by **1**

entry	Ar	t(h)	solvent	yield ^{1,2}	e.e. ³ (AC) ⁴
1	2-naph	20	toluene	99	72 (R)
2	"	27	ether	71	75 (R)
3	1-naph	45	toluene	40 ⁵	48 (R)
4	phenyl	69	"	99	77 (R)
5	pClC ₆ H ₄	42	"	92	68 (R)
6	oMeOC ₆ H ₄	20	"	95	78 ⁶ (R)
7	pMeOC ₆ H ₄	70	"	49 ⁷	52 (R)

1. all the runs were carried out at room temperature in the following molar ratio 1/diethyl zinc/ArCHO=1/32.6/16.3; 2. Yields determined by GLC analysis; 3. By HPLC analysis using ionic Pirkle DNBPG chiral column, unless otherwise specified; 4. Absolute configuration assigned from elution order, W.H.Pirkle, J.M.Finn, *J. Org. Chem.*, **46**, 2935 (1981); 5. 30% of aldehyde was still present together with 30% of (2-naphthyl)-carbinol; 6. Assuming, for the optically pure alcohol, $[\alpha]_D^{25} = -54$ (c=1, toluene), ref. 3; 7. 38% of aldehyde 12% of p-methoxybenzylalcohol were present.

REFERENCES AND NOTES.

- N.Oguni, T.Omi, *Tetrahedron Lett.*, 1984, **25**, 2823.
- M.Kitamura, S.Suga, R.Noyori, *J. Am. Chem. Soc.*, 1986, **108**, 6071.
- Ab.A.Smaardijk, H.Wynberg, *J. Org. Chem.*, 1987, **52**, 135.
- P.A.Chaloner, S.A.R.Perera, *Tetrahedron Lett.*, 1987, **28**, 3013.
- E.J.Corey, F.Hannon, *Tetrahedron Lett.*, 1987, **28**, 5233, 5237.
- K.Soai, A.Ookawa, T.Kaba, *J.C.S. Chem. Comm.*, 1987, 467.
- K.Soai, S.Yokoyama, K.Ebihara, T.Hayasaka, *J.C.S. Chem. Comm.*, 1987, 1690.
- K.Soai, S.Niwa, Y.Yamada, H.Inoue, *Tetrahedron Lett.*, 1987, **28**, 4841.
- G.Muchow, Y.Vannooenberghe, G.Buono, *Tetrahedron Lett.*, 1987, **28**, 6163.
- S.Itsuno, J.M.J.Frechet, *J. Org. Chem.*, 1987, **52**, 4142.
- W.Oppolzer, R.N.Radinov, *Tetrahedron Lett.*, 1988, **29**, 5645.
- N.Oguni, Y.Matsuda, T.Kaneko, *J. Am. Chem. Soc.*, 1988, **110**, 7877.
- A.van Oeveren, W.Menge, B.L.Feringa, *Tetrahedron Lett.*, 1989, **30**, 6427.
- M.Yoshioka, T.Kawakita, M.Ohno, *Tetrahedron Lett.*, 1989, **30**, 1657.
- K.Tanaka, H.Oshio, H.Suzuki, *J.C.S. Chem. Comm.*, 1989, 1700.
- M.Kitamura, S.Okada, S.Suga, R.Noyori, *J. Am. Chem. Soc.*, 1989, **111**, 4028.
- E.J.Corey, P.Yuen, F.Hannon, D.A.Wierda, *J. Am. Chem. Soc.*, 1990, **112**, 784.
- C.Bolm, M.Zehender, D.Beer, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 205.
- R.Noyori, S.Suga, K.Kawai, S.Okada, M.Kitamura, N.Oguni, M.Hayashi, T.Kaneko, Y.Masuda, *J.Organomet.Chem.*, 1990, **382**, 19.
- E.N.Jacobsen, I.Marko, W.S.Mungall, K.B.Sharpless, *J. Am. Chem. Soc.*, 1988, **1988**, 1968.
- The lower reactivity of p-methoxybenzaldehyde in catalyzed reactions with diethylzinc has been observed recently by Corey¹⁷.