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Kinetic Resolution of 1,2,3,4-Tetrahydro[1]naphthyl hydroperoxide by Decomposition in the Presence of a Chiral Mn(III) Salen Complex

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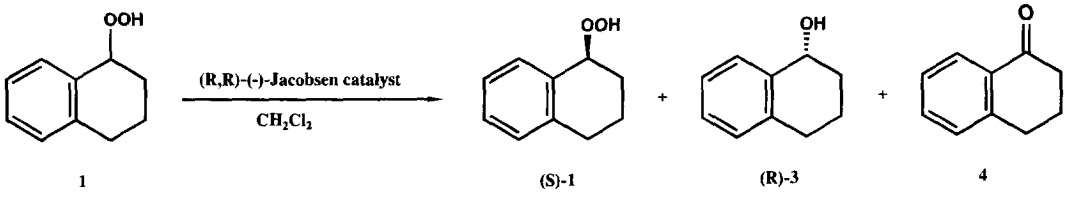
Abstract: The kinetic resolution of 1,2,3,4-tetrahydro[1]naphthyl hydroperoxide by decomposition in the presence of Jacobsen catalyst has been investigated. An enantiomeric excess up to 45% was obtained for the remaining hydroperoxide as well as for the alcohol formed.

The preparation of optically active, chiral hydroperoxides as potential stereoselective oxidizing reagents is of interest for asymmetric synthesis. Besides the analytical separation of the enantiomers on a chiral column,[1] we succeeded in resolving 1,2,3,4-tetrahydro[1]naphthyl hydroperoxide on the preparative scale.[2] Adam *et al.* [3] resolved secondary hydroperoxide by horseradish peroxidase in the presence of guaiacol. Subsequently, we have reported [4] the kinetic resolution of 1,2,3,4-tetrahydro[1]naphthyl hydroperoxide and other aralkyl hydroperoxides by three different enzymatic methods.

Here we present our first results on the kinetic resolution of 1,2,3,4-tetrahydro[1]naphthyl hydroperoxide (**THPO, 1**) by decomposition in the presence of N,N'-Bis(3,5-di-tert.-butylsalicylidene)-1,2-cyclohexane-diamino-manganese chloride (Jacobsen catalyst, **2**) .[5]

THPO is decomposed at room temperature in the the presence of Jacobsen catalyst **2** within 3 hours to nearly 40% . The main products of the decomposition are 1-tetralol **3** and 1-tetralone **4** (Scheme 1).



Scheme 1

As could be determined by HPLC on a chiral column [1,2] the remaining **THPO** as well as the corresponding alcohol **3** were obtained in nonracemic form. The absolute configuration of the **THPO** and the corresponding alcohol were assigned according to literature data. [2] The results are summarized in Table 1.

Table 1. Kinetic resolution of THPO by decomposition in the presence of Jacobsen catalyst **2** [a]

entry	catalyst	temperature °C	THPO conversion [b]	THPO % e.e. [c]	tetralol % e.e. [c]
1	(*R,R*)-(-)-**2**	RT	38	10 (*S*)-(-)	15 (*R*)-(-)
2	(*R,R*)-(-)-**2**	0	38	15 (*S*)-(-)	22 (*R*)-(-)
3	(*S,S*)-(+)-**2**	0	32	17 (*R*)-(+)	30 (*S*)-(+)
4	(*R,R*)-(-)-**2**	-20	37	26 (*S*)-(-)	36 (*R*)-(-)
5	(*R,R*)-(-)-**2**	-20	50	45 (*S*)-(-)	45 (*R*)-(-)

[a] Reaction conditions: THPO (3 mmol), (*R,R*)-(-)- or (*S,S*)-(+)- **2** (0.02 mmol) from Fluka, 10 ml dichloromethane

[b] Determined by iodometric titration; [c] Determined by HPLC using a CHIRALCEL OD column

As can be seen (R,R)-(-) Jacobsen catalyst selectively recognized the (R)-(-)-substrate enantiomer (**THPO**) which yielded consequently (R)-(-)-1-tetralol and (S)-(-) hydroperoxide (entry 1,2,4,5). On the other hand, in the presence of (S,S)-(+)-**2** nonracemic (R)-(+)-THPO and (S)-(+)-1-tetralol were obtained (entry 3). The e.e. can be increased by decreasing the reaction temperature to 0°C and -20°C, respectively. Of course the enantiomeric excess depends on the conversion of the hydroperoxide. At ca. 50% conversion 45% e.e. was determined. Unfortunately, this low value expressing the small difference of the reaction rate of the hydroperoxide enantiomers in the decomposion reaction limits the use for preparative purposes.

The decomposition of hydroperoxides in the presence of metal compounds can be usually rationalized on the basis of the Haber-Weiss mechanism.[6] Nishinaga et al.[7] found during the decomposition of 1-phenylethyl hydroperoxide with cobalt schiff base complexes an e.e. of the 1-phenylethanol formed. They assumed a prolongation of the lifetime of the (R)-1-phenylethoxyl radical by the asymmetric interaction with the optically active Co-complex , while the other enantiomer, (S)-1-phenylethoxyl radical, would be decomposed rapidly to acetophenone. An e.e. of **THPO** during the decomposition cannot be explained in this way. Studies on the reaction mechanism are under investigation.

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