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# ASYMMETRIC AMPLIFYING PHENOMENA IN ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO BENZALDEHYDE

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Research by N. Oguni, Y. Matsuda, and T. Kaneko, J. Am. Chem. Soc. **1988**, 110, 7877

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## CONDENSATION OF THE RESEARCH

### PURPOSE OF THE STUDY

*To show that asymmetric catalysts of low enantiomeric purity can produce chiral products with high enantiomeric excess (e.e.)*

### WHAT RESEARCHERS ACCOMPLISHED

In the reaction of diethylzinc with benzaldehyde to produce ethyl phenyl carbinol (**3**), the researchers obtained an e.e. of 80–90% using 2% of a chiral amino alcohol having an e.e. of 10–20% as catalyst.

### BACKGROUND

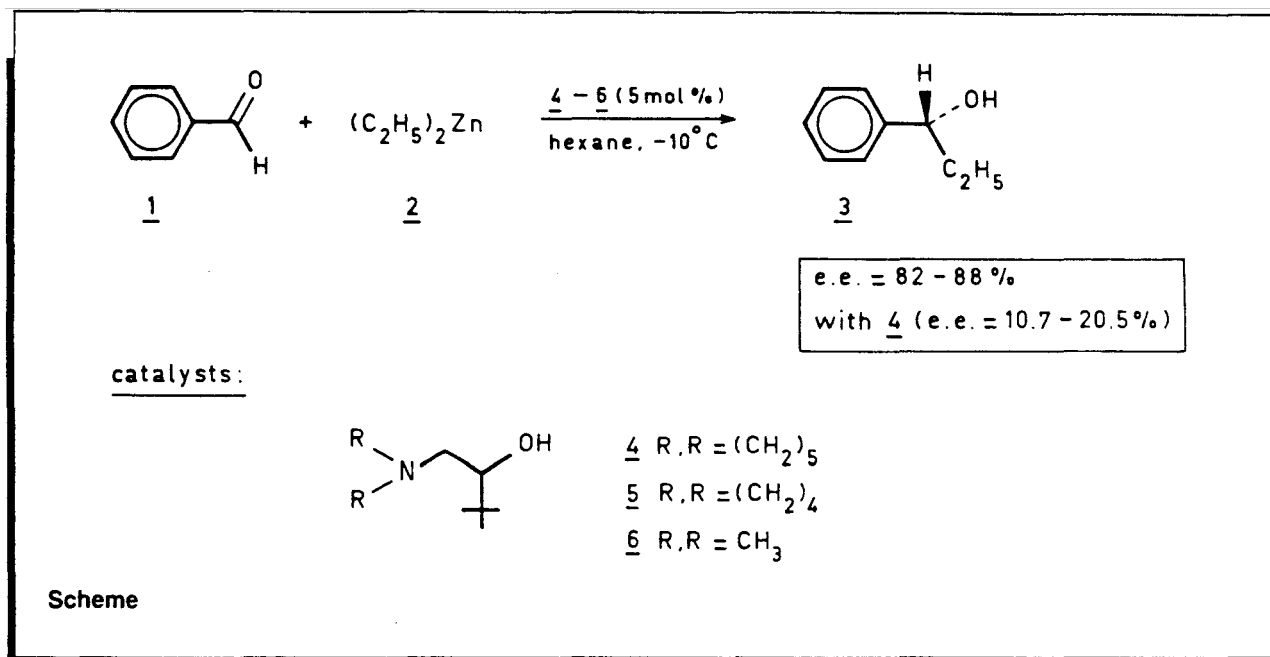
In 1986, Puchot et al.<sup>1</sup> established rigorously that the earlier proposal of Wynberg and Feringa<sup>2</sup> concerning the effect of enantiomers on one another had general validity. Puchot et al.<sup>1</sup> showed experimentally that the general assumption, namely, that products could never have an e.e. greater than that of the chiral auxiliary (catalyst, modifier, etc), was invalid. The basis for this apparent anomaly, as was discussed theoretically in 1976,<sup>2</sup> is the possible association of enantiomeric catalyst molecules with new (better *and* worse) catalyst properties. Early proof of association phenomena of chiral molecules to form diastereomers (particularly, chiral hydroxy amines) had been obtained by a classic experiment of Williams et al.<sup>3</sup> The latter showed that in a solution of enantiomerically *impure* quinine, distinct NMR absorptions could be detected for the (+) (+), (–) (–), and (+) (–) “dimeric complexes” in *achiral solvents*. It is, of course, not surprising (except in the sense that we did not recognize this much earlier!) that an efficient chiral catalyst, which by its very behavior must complex strongly with the achiral substrates, also complexes with itself. It should also come as no surprise, therefore, that such associative dimers (or trimers, etc.) might show different (better or worse) catalytic properties.

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## OBSERVATIONS

- Partial enriched aminoalcohol **4** (e.e. = 10–20%) catalyses efficiently the Et<sub>2</sub>Zn addition to benzaldehyde to yield optically active carbinol **3** (e.e. = 80–90%).
- The asymmetric amplification effect increases in the order **4** > **5** > **6** (Scheme).
- Equimolar amounts of Et<sub>2</sub>Zn and aminoalcohols **4** form dimeric complexes in solution.
- The reaction rates of the Et<sub>2</sub>Zn addition increase with the e.e. of the catalyst.

## COMMENTARY ON THE RESEARCH

This research describes the first example of a large asymmetric amplification effect in carbon–carbon bond formation chemistry, that is, the ethylation of benzaldehyde with diethylzinc. The importance of this work lies in at least two aspects: first, it provides us with a new framework for approaching asymmetric catalysis in which catalysts of low e.e give products with high e.e.'s, and second, the amplification effects as observed here might lead to useful model systems for the origin and amplification of chirality.<sup>4–7</sup>

Since complexation of a chiral catalyst and the substrate is a prerequisite for asymmetric catalysis, it follows that complexation between catalyst molecules is generally to be expected on the basis of their intrinsic structural requirements as a catalyst. Therefore, the examples of the formation of diastereomeric complexes and their influence on the selectivity of the reaction that is described here might have far-reaching consequences for the study of the mechanisms for asymmetric catalysis and for catalyst design.

## REFERENCES

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