

Preliminary communication

ASYMMETRIC INDUCTION IN CARBOMETHOXYLATION OF VINYLAROMATICS

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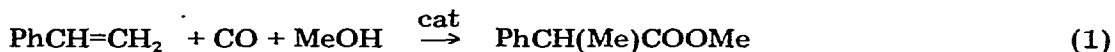
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Summary

A novel carbomethoxylation of vinylaromatics, in particular styrene, which takes place with marked asymmetric induction in the presence of a palladium catalyst and trifluoroacetic acid, is reported.

In recent years carbomethoxylation of vinylaromatics has attracted a good deal of attention [1], but as far as we are aware no optical yield higher than a few percent has been reported. We now describe a new method [2], involving carefully controlled conditions, which uses a combination of a palladium(0) complex containing neomenthyl-diphenylphosphine (NMDP) as ligand, with trifluoroacetic acid in excess and methanol as solvent.

The acid is added at 50°C under CO to the methanolic solution of styrene (or other vinylaromatics) containing the catalyst. The solution becomes dark-red and reaction 1, shown for the simplest case, takes place.



About 20 mol of product are obtained per mol of complex. After distillation of the product and the methyl trifluoroacetate, trifluoroacetic acid, styrene and methanol, a new batch of styrene can be converted. Separation of palladium black stops the catalyst-recycling process. The reaction occurs with high regioselectivity (> 94%) and with high selectivity, practically all the styrene put in reaction being recovered.

We have been able to obtain an unprecedented asymmetric induction simply by using optically active NMDP with trifluoroacetic acid in methanol; only this combination proved to be effective. In the case of styrene, using the

dextrorotatory ligand, 52% e.e. of the levorotatory methyl 2-phenylpropionate was obtained. With other phosphines, such as *sec*-butyldiphenylphosphine or DIOP, only little asymmetric induction was observed. With other acids (MeCOOH, HCOOH, HCl, HBr and many others) both the degree of conversion and the asymmetric induction were very low. Methanesulphonic acid showed activity. Another interesting effect was observed on increasing the CO pressure above 2 atm, the asymmetric induction decreasing remarkably (15.4% e.e. at 35 atm of CO).

These results are in accord with a mechanism involving formation of $\text{PdH}(\text{PR}_3)_2\text{OCOCF}_3$. By the interaction of the CF_3COOH and the palladium(0) complex a product must be formed, which is able to coordinate both styrene and CO, and to cause styrene insertion into the Pd-H bond and CO insertion into the resulting Pd-C bond.

The reason for the asymmetric induction probably lies in the faster rate of carbonylation of one of the two diastereoisomers formed by coordination of the prochiral olefin to the optically active complex. At higher CO pressure both diastereoisomers appear to undergo carbonylation at comparable rates. We have not yet been able to isolate the intermediate carbonylation complex, and it is possible that the situation is analogous to that described by Halpern [3-5] for asymmetric hydrogenation.

Carbonylation procedure

Bis(dibenzylideneacetone)palladium (0.4 g) is dissolved in styrene (15 ml) and (+)-neomenthyl-diphenylphosphine [6] (0.68 g) is added with stirring under nitrogen, followed by methanol (15 ml) and trifluoroacetic acid (3 ml). Nitrogen is replaced by CO and the solution is heated at 50°C for 4 h. The solvent and the excess styrene are distilled off and the residue is analysed by TLC on silica, using diethyl ether/*n*-hexane 1/9 as the eluent. The carbonylation product consists of methyl 2-phenylpropionate, 0.64 g (94%), and methyl 3-phenylpropionate, 0.03 g (6%). Levorotatory methyl phenylpropionate with 52% e.e. is obtained.

Similar conditions were used for other vinylaromatics. 2-Vinyl-6-methoxynaphthalene gives the levorotatory 2-(6-methoxy-2-naphthyl)propionic ester with 42% e.e.

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References

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