CATALYSTS FOR THE HOMOGENEOUS METATHESIS OF FUNCTIONALIZED OLEFINS

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1. Introduction

The metathesis of functionally substituted olefins, i.e. olefins containing one or more heteroatoms, offers many interesting possibilities for the synthesis of valuable organic products that cannot be made in any other way or only with great difficulty. Difunctional olefins, for example, that would otherwise require several reaction steps can be synthesized in one step:

\[ 2 \text{R-CH-CH-(CH}_2\text{)}_n\text{-X} \iff\text{R-CH=CH-R} + \text{X-(CH}_2\text{)}_n\text{-CH=CH-(CH}_2\text{)}_n\text{-X}, \]

in which R is an H atom or an alkyl group and X is the functional group containing the heteroatom.

For acyclic olefins with one or more functional groups the poisoning effect of the polar group on the catalyst is so great that in the first instance they could not be used as a substrate for metathesis. However, the possibility of synthesizing new compounds with different polar groups stimulated research into resistant catalysts for the metathesis of functionalized olefins.

The breakthrough came in 1972 when Van Dam et al. [1] found on performing screening experiments that a combination of WCl₆ and Sn(CH₃)₄ gave a homogeneous catalyst system that was effective in the metathesis of long-chain unsaturated fatty acid esters, i.e X = COOR, such as methyl oleate (methyl cis-9-octadecenoate).

Since the early studies of Van Dam and co-workers a growing interest has arisen in the metathesis of olefins possessing heteroatom functional groups, and this has been investigated by many workers. A great deal of research has been done into the possibilities of the homogeneous metathesis of unsaturated carboxylic esters, and other types of functionalized olefins, and has led to the synthesis of many interesting chemical compounds. In these studies the WCl₆-Sn(CH₃)₄ catalyst system plays an important role, although other effective soluble catalysts have been developed for this reaction.

Here, I would like to discuss the most relevant developments in the field of the homogeneous catalytic metathesis of acyclic functionalized olefins.
2. Oxygen-containing olefins

2.1. UNSATURATED CARBOXYLIC ESTERS

As mentioned above, the first report on the metathesis of functionalized olefins concerned the metathesis of unsaturated fatty acid esters. The first successful reaction was the metathesis of the cis and the trans isomers of methyl 9-octadecenoate (methyl oleate and methyl elaidate, respectively) into equimolar amounts of 9-octadecene and dimethyl 9-octadecenedioate:

\[
2 \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3 \iff \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 + \text{CH}_3\text{OOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3
\]

At 110 °C an equilibrium conversion of approx. 50% was reached within 2 h using a molar ratio of reactant/catalyst (WCl₆)/cocatalyst (Sn(CH₃)₄) of 75/1/1 [2]. The reaction products are stereo-isomeric mixtures, whose cis:trans ratios correspond to thermodynamic equilibria. The reactant ester also undergoes metathetical cis-trans isomerization, and the ultimate result of the reaction is independent of the conformation of the monoester. Thus, both the metathesis of methyl oleate and of methyl elaidate yield the same stereo-isomeric mixtures of products and starting esters. Double-bond isomerization did not take place, the product selectivity is very high.

Other fatty acid esters also appeared to undergo metathesis, like methyl erucate:

\[
2 \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_11\text{COOCH}_3 \iff \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3 + \text{CH}_3\text{OOC}(\text{CH}_2)_11\text{CH}=\text{CH}(\text{CH}_2)_11\text{COOCH}_3
\]

and methyl 10-undecenoate:

\[
2 \text{CH}_2=\text{CH}(\text{CH}_2)_8\text{COOCH}_3 \iff \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{OOC}(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_8\text{COOCH}_3
\]

The latter equilibrium can be shifted to the right by continually removing the volatile ethene.

The metathesis of unsaturated fatty acid esters allows the synthesis of unsaturated diesters, that can only be obtained with great difficulty via classical routes. These long-chain dicarboxylic esters are promising intermediates for the synthesis of valuable chemical products. For instance, it was shown that diethyl 9-octadecenedioate can be subjected to the Dieckmann condensation and the cyclized product can then be hydrolyzed and decarboxylated to give civetone, a 17-membered unsaturated cyclic ketone (cyclo-9-heptadecenone), whose cis form is an important base material in the perfume industry [3]. Dicarboxylic esters resulting from the metathesis of unsaturated monocarboxylic esters are also interesting starting materials for unsaturated, vulcanizable polyesters and polyamides [4].

Nakamura et al. [5,6] reported several metathetic conversions of unsaturated esters using WCl₆ or Mo(O(C₂H₅)₂Cl)₃ in combination with alkylboranes, and various other catalyst systems. Although in a few cases good conversions were obtained, rather large amounts of other olefins were produced, mainly by isomerisation and subsequent (undesirable) metathesis reactions. Only the catalyst systems WCl₆-(C₂H₅)₃B, Mo(O(C₂H₅)₂Cl)₃-(C₂H₅)₃B and WCl₆-(C₃H₇)₃Al₂Cl₃ exhibited an activity comparable with that of the WCl₆-Sn(CH₃)₄ system. Alkylaluminium and alkylborane compounds, however, behave like Grignard reagents. Consequently, they can only be applied at