

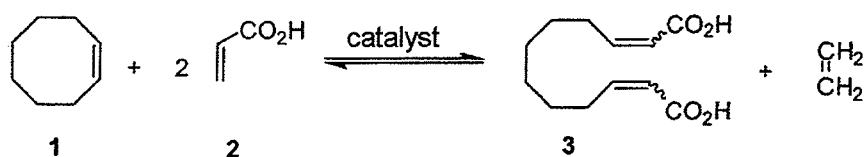
Method for producing dodeca-2,10-diene-1,12-dicarboxylic acid or 1,12-dodecane-dicarboxylic acid by way of ring-opening cross metathesis (ROCM) of cyclooctene with acrylic acid

Alkyldicarboxylic acids are important compounds for the preparation of plastics such as polyesters and polyamides. Particular mention may be made of high-performance plastics based on polyamides, as are used, for example, for the production of fuel lines. One of these dicarboxylic acids is 1,12-dodecanedicarboxylic acid (DDA). As industrial processors for preparing DDA, particular mention may be made of:

- cleavage of cyclododecanol by means of concentrated nitric acid; Invista and Degussa
- oxidative coupling and opening of cyclohexanone by means of H_2O_2 ; Ube
- biotechnological processes in which *n*-dodecane is terminally oxidized to form DDA; Cathay Biotechnology and others.

These processes are energy-intensive and produce large quantities of waste which is expensive to dispose of. In addition, the selectivity is often not high. Thus, for example, in the oxidative cleavage of cyclododecanol by means of nitric acid, the formation of short-chain "breakup acids" by oxidative degradation is a problem.

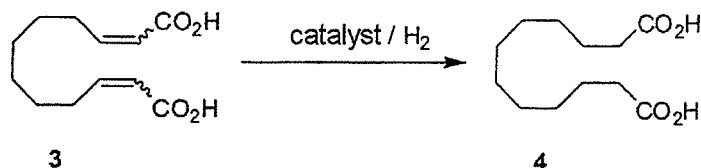
A new approach to the preparation of dicarboxylic acids is metathesis. A combination of ring-opening metatheses (ROM) with cross metathesis (CM) makes it possible to prepare aliphatic α,β -unsaturated dicarboxylic acids in one step from cycloalkenes and acrylic acid using suitable precatalysts. If cyclooctene (1) as starting material is reacted with acrylic acid (2), dodecane-2,10-diene-1,12-dicarboxylic acid (3) is obtained (**scheme 1**). The combination of the two reaction steps is also referred to as ROCM (ring-opening cross metathesis) or ROX metathesis.



Scheme 1: Reaction of COE with acrylic acid to form compound 3.

The α,β -unsaturated dicarboxylic acid obtained can be hydrogenated in a second step to give the

desired 1,12-dodecanedicarboxylic acid (4) (scheme 2).



Scheme 2: Hydrogenation of dodeca-2,10-diene-1,12-dicarboxylic acid to DDA.

Moreover, it is also conceivable to use the unsaturated dicarboxylic acid as monomer for the preparation of unsaturated polyamides or polyesters. The polymers obtained in this way can subsequently be crosslinked, which is of interest for many applications.

Metathesis reactions are equilibrium reactions giving a corresponding product distribution. The above-described reaction can take various reaction paths. Thus, the cycloalkene can react in a ring-opening metathesis polymerization to form a polyolefin. Furthermore, formation of various telechelic oligomers can occur. These secondary reactions have an adverse effect on the yield of desired product and also make work-up of the reaction mixture difficult. The formation of ethylene, which can be taken off as gas from the liquid phase, results in a shift of the equilibrium in the direction of the product. However, this effect is not sufficient to suppress secondary reactions such as polymerization completely.

Prior art

In the prior art to date,

(Morgan, John, P., Morrill, Christie; Grubbs, Robert, H.; Choi, Tae-Lim WO 02/079127 A1,

Choi, T-L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* 2001, 123, 10417-10418,

Randl, S.; Cannon, S. J.; Blechert, S. *J. Chem. Soc., Chem. Commun.* 2001, 1796-1797), the reaction is carried out in dilute solutions ($c \sim 0.2$ M) in order to push the reaction in the direction of the low molecular weight products. Column chromatography using silica gel is predominantly employed for working up the reaction mixture and separating off the catalyst. Furthermore, dichloromethane, which is considered to be problematical for an industrial

reaction, is predominantly used as solvent. Working at a high dilution, the consumption of large amounts of solvents in the work-up and the use of solvents which are hazardous to health stand in the way of the concept of a durable process which is to form the basis of industrial implementation.

It has now surprisingly been found that a process according to the claims makes it possible to shift the equilibrium completely in the direction of the desired product without working at a high dilution. In addition, the process described makes effective recycling of the catalyst possible. This is achieved by, in contrast to previous practice, working at high substrate concentrations up to reactions in bulk. During the course of the reaction, the α,β -unsaturated dicarboxylic acid precipitates when the solubility product is exceeded and is thus removed from the equilibrium (in the homogeneous phase). This adds a second positive effect to the shifting of the equilibrium in the direction of the desired product by formation of gaseous ethylene.

A further challenge is separating off and, if appropriate, recycling the catalyst. The catalyst often has to be separated off by column chromatography in a complicated operation, which makes industrial implementation uneconomical.

As a result of the product being obtained as a solid in the process described here, this can easily be filtered off, purified and the catalyst dissolved in the filtrate can be recycled.

The reaction described is carried out at temperatures of from 10 to 100°C, preferably from 20 to 80°C and particularly preferably from 20 to 60°C.

The reaction described can be carried out in bulk or using a solvent. Suitable solvents are acyclic and also cyclic hydrocarbons. Aromatic halogenated hydrocarbons are particularly suitable and aromatics having alkyl groups are very particularly suitable.

When the reaction is carried out in solution, cyclooctene concentrations of > 1 M are preferred. Particular preference is given to cyclooctene concentrations of from 1 to 2 M and very particular preference is given to cyclooctene concentrations of from 2 to 4 M, based on the solvent.

In the process described, the catalyst is used in amounts of from 5 to 0.0001 mol%, based on the amount of cyclooctene. Preference is given to amounts of from 2 to 0.001 mol% and particular preference is given to amounts of from 1 to 0.5 mol% of catalyst, based on the molar amount of cyclooctene used.

To obtain the α,β -unsaturated dicarboxylic acid in polymer grade quality, purification by crystallization, distillation or a combination of the two is possible.

Suitable catalysts are ruthenium-carbene complexes which, as one of the characteristic features, bear an N-heterocyclic carbene ligand. Examples of preferred catalysts are shown in **Figure 1**. Particular preference is given to catalysts of the type 7, with an electron-withdrawing group R' on the benzylidene ligand.

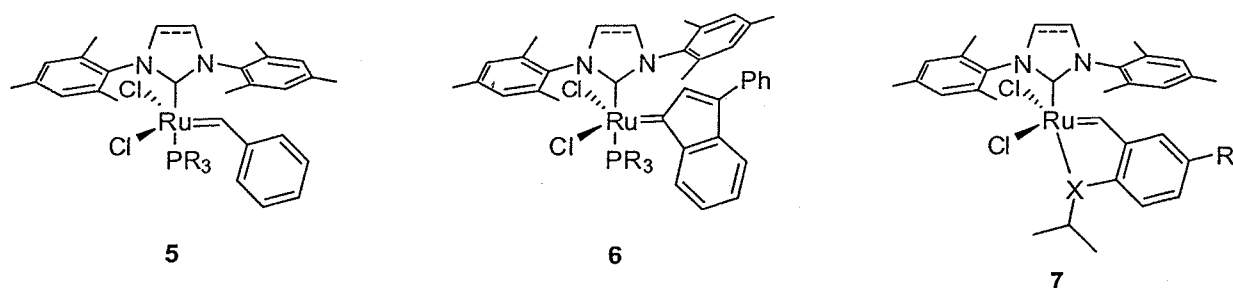


Figure 1: Examples of ruthenium catalysts used.

Examples:

1. 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulphonyl)phenyl]methylen ruthenium(II) dichloride (0.333 g, 0.45 mmol) is placed together with acrylic acid (13.09 g, 0.182 mol) under argon in a three-necked flask provided with reflux condenser and the mixture is heated to 60°C. Cyclooctene (10 g, 0.091 mol) is added dropwise over a period of 20 minutes. After 1.5 hours, the reaction mixture is allowed to cool to room temperature and is admixed with toluene (200 ml). It is briefly heated to boiling and subsequently cooled slowly while stirring. The solid which has precipitated is filtered off and washed with cold toluene (3 × 10 ml). After drying under reduced pressure, the product is obtained as a white solid (10.2 g, 50%). According to

NMR analysis, the product has a purity of > 99%.

2. A mixture of cyclooctene (10 g, 0.091 mol) and acrylic acid (13.09 g, 0.182 mol) in toluene (20 ml) was heated to 60°C. 10 ml of a solution of 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulphonyl)phenyl]methylenruthenium(II) dichloride (0.667 g, 0.00091 mol) in toluene (25 ml) are firstly added and the remaining 15 ml are added dropwise over a period of one hour. After the addition is complete, the mixture is stirred at the indicated temperature for one hour and is then cooled. The precipitated solid is filtered off and washed with cold toluene (3 × 5 ml). After drying under reduced pressure, the product is obtained as a white solid (10.2 g, 50%). According to NMR analysis, the product has a purity of > 99%.

Claims:

1. Process for preparing dodeca-2,10-diene-1,12-dicarboxylic acid, characterized in that cyclooctene and acrylic acid are reacted by means of a metathesis reaction in the presence of a ruthenium catalyst at high substrate concentrations up to reactions in bulk, with the dicarboxylic acid formed precipitating.
2. Process according to Claim 1, characterized in that the unsaturated dodeca-2,10-diene-1,12-dicarboxylic acid obtained is hydrogenated to 1,12-dodecanedicarboxylic acid in a second step.
3. Process according to Claim 1, characterized in that cyclooctene is present in concentrations of > 1 mol/l when the reaction is carried out in solution.
4. Process according to Claim 1, characterized in that cyclooctene is present in concentrations of from 2 to 4 mol/l when the reaction is carried out in solution.
5. Process according to any of the preceding claims, characterized in that ruthenium-carbene complexes which bear an N-heterocyclic ligand are used as catalysts.
6. Process according to any of the preceding claims, characterized in that the ruthenium catalysts are used in amounts of from 5 to 0.0001 mol% based on the molar amount of cyclooctene.

7. Process according to any of the preceding claims,
characterized in that
the ruthenium catalysts are used in amounts of from 2 to 0.001 mol% based on the molar
amount of cyclooctene.
8. Process according to any of the preceding claims,
characterized in that
the ruthenium catalysts are used in amounts of from 1 to 0.5 mol% based on the molar
amount of cyclooctene.
9. Process according to any of the preceding claims,
characterized in that
acyclic or cyclic hydrocarbons are used as solvents.
10. Process according to any of the preceding claims,
characterized in that
aromatic halogenated hydrocarbons are used as solvents.
11. Process according to any of the preceding claims,
characterized in that
the ruthenium catalysts dissolved in the filtrate are recycled.
12. Process according to any of the preceding claims,
characterized in that
the unsaturated dicarboxylic acid obtained is purified by crystallization, distillation or a
combination of the two.