Heterogeneous Metathesis of Unsaturated Nitriles

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Unsaturated nitriles of the general formula $CH_2{=}CH[CH_2]_nCN$, where $n > 1$, undergo metathesis at room temperature in the presence of the catalyst Re_2O_7–Al_2O_3, activated with a small amount of Me_4Sn or Et_4Sn.

As part of our investigations into the activity of the catalyst system Re_2O_7–Al_2O_3 for the heterogeneous metathesis of alkenes carrying heteroatom functional groups we now report the metathesis of unsaturated nitriles. Bosma *et al.*[1] reported a systematic study of the homogeneous metathesis of short-chain unsaturated nitriles of general formula $CH_2{=}CH[CH_2]_nCN$ ($1 \leqslant n \leqslant 4$) using the catalyst system WCl_6–Me_4Sn. It was found that these nitriles could easily be cometathesized with (*Z*)-hept-3-ene, while under the conditions used a limited activity was found for self-metathesis when $n = 2$ or 3 (equation 1).

$$2\ CH_2{=}CH[CH_2]_nCN \rightleftharpoons CH_2{=}CH_2 + NC[CH_2]_nCH{=}CH[CH_2]_nCN \qquad (1)$$

For practical applications, however, heterogeneous metathesis is of particular interest owing to its obvious advantages over homogeneous metathesis, such as easy product separation and catalyst reuse. Recently, Warwel and Jansen[2] reported the cometathesis of pent-4-enenitrile ($n = 2$) with symmetrical alkenes using the heterogeneous catalyst Re_2O_7–Al_2O_3, activated with several tetra-alkyltin compounds, at 373 K. They found that no self-metathesis of the unsaturated nitrile took place. Here, we report data which show that, in contrast to these results, unsaturated nitriles of general formula $CH_2{=}CH[CH_2]_nCN$ ($2 \leqslant n \leqslant 5$) undergo self-metathesis with high conversions in the presence of the catalyst Re_2O_7–Al_2O_3, activated with a small amount of Me_4Sn or Et_4Sn.

The reactions were carried out in a glass batch reactor (30 ml) at room temperature. The Re_2O_7–Al_2O_3 catalyst (100 mg; 37 μmol of Re_2O_7) was prepared and calcined as described earlier.[3] After calcination the catalyst was introduced into the reactor under nitrogen and activated with 7 μmol of the cocatalyst (Me_4Sn or Et_4Sn) in dry, oxygen-free n-hexane (1 ml). The substrates (0.37 mmol) were added after 5 min. It appeared that the production of ethylene (equation 1) was almost complete within 4 h. The final conversions were determined after 24 h by analysing the liquid phase by g.l.c., after extraction of the catalyst with acetone.

Table 1. Metathesis of unsaturated nitriles of general formula $CH_2{=}CH[CH_2]_nCN$ catalysed by Re_2O_7–Al_2O_3, activated with Me_4Sn or Et_4Sn, at room temperature.[a]

	Conversion (mol%)	
	Me_4Sn cocatalyst	Et_4Sn cocatalyst
$CH_2{=}CHCN$	0	0
$CH_2{=}CHCH_2CN$[b]	<1	<1
$CH_2{=}CH[CH_2]_2CN$	83	91
$CH_2{=}CH[CH_2]_3CN$	91	98
$CH_2{=}CH[CH_2]_4CN$	91	98
$CH_2{=}CH[CH_2]_5CN$	80	86

[a] For conditions see text. [b] Conversion into metathesis products; under the conditions 60–70% of the substrate is isomerised into crotononitrile.

Table 1 shows the metathesis conversions of the unsaturated nitriles with two different cocatalysts, of which Et_4Sn appears to be the most effective. Substrates with $n \geqslant 2$ are very active towards metathesis. The selectivity for the primary metathesis products of these substrates was $> 98\%$. Acrylonitrile ($n = 0$) showed no activity, and allyl cyanide ($n = 1$) showed only a very small metathesis conversion. In fact, the reactivity of allyl cyanide could only be demonstrated by the enhanced production of ethylene compared with a blank experiment. Substantial isomerisation to crotononitrile took place, however.

When the amount of substrate was increased, the conversion decreased rapidly. *E.g.*, when $CH_2{=}CH[CH_2]_4CN$ was metathesized with a molar nitrile : Re_2O_7 ratio of 10 : 1, 25 : 1 or 50 : 1, using Me_4Sn as cocatalyst, the conversion decreased from 91 to 25 to 1 mol %, respectively. Apparently at high substrate concentrations the active sites on the catalyst complex so effectively with the cyano-groups that the double bond can no longer compete.

Other experiments showed that unsaturated nitriles with $n \geqslant 2$ can also very effectively be cometathesized with symmetrical alkenes [*e.g.*, (*E*)-hex-3-ene]. Again acrylonitrile showed no activity. When allyl cyanide was treated with an equimolar amount of (*E*)-hex-3-ene, both cometathesis and isomerisation to crotononitrile took place. In a typical experiment, under the same conditions as described for the self-metathesis, the total conversion of allyl cyanide was 85 mol %: 25 mol % cometathesis and 60 mol % isomerisation.

Remarkably, the reactivity of the substrates as a function of molecular structure depends on the catalyst system in use. When WCl_6–Me_4Sn is used, the (limited) activity for self-metathesis is optimal for $n = 2$ and decreases rapidly for $n = 3$ and $n = 4$.[1] With the Re_2O_7–Al_2O_3–R_4Sn catalyst system, the highest activity is found for $n = 3$ and $n = 4$. Models which account for this behaviour will be published elsewhere.

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