

## METATHESIS OF UNSATURATED NITRILES

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### Summary

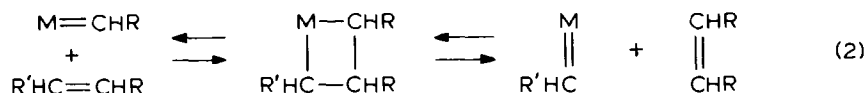
Unsaturated nitriles of the general formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  ( $n \geq 1$ ) can undergo metathesis or co-metathesis with linear alkenes in the presence of a homogeneous catalyst system, viz.  $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4$  or a heterogeneous catalyst system, viz.  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-SnR}_4$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ ), with high selectivity. The reaction temperature in the homogeneous case is 373 K, while the heterogeneous system shows high activity at room temperature. The reactivity of the unsaturated nitriles is a function of  $n$ , depending on the catalyst system in use. The results are rationalized in terms of different interactions between the substrates and the catalyst as a function of the chain length of the substrate molecule.

### Introduction

Alkene metathesis involves a catalysed reaction by which new compounds are formed via the rupture and reformation of carbon-carbon double bonds:



Both homogeneous and heterogeneous catalysts have been developed for this reaction; catalysts based on the transition metals rhenium, molybdenum or tungsten are the most active. It is now generally accepted that the reaction proceeds via a chain reaction involving metal-carbenes which react reversibly with the alkene via a metallacyclobutane intermediate:



One of the most promising synthetic applications of the metathesis reaction is to alkenes bearing heteroatom functional groups, because such reactions would allow single-step syntheses of mono- and di-functional derivatives of hydrocarbons [1]. Thus the metathesis of unsaturated nitriles should lead to interesting mono- and

di-nitriles. Moreover, since the cyano group can easily be transformed into other functional groups, metathesis of this class of compounds provides a very useful synthetic tool. An interesting possible application of the reaction should be mentioned: the dinitrile product of the metathesis reaction can be hydrogenated to the corresponding diamine, which can be used in the synthesis of polyamides and polycarbamides [2].

The first report in the open literature on the metathesis of unsaturated nitriles came from Nakamura et al. [3], who used a long-chain nitrile, viz. 9-octadecenitrile and the homogeneous catalyst system  $WCl_6 \cdot (CH_3)_3Al_2Cl_3$ . After 17 h at 333 K, a conversion of 35% was reached, but substantial double bond isomerisation had taken place, so that the selectivity was low (< 55%). Attempted metathesis of allyl cyanide with the heterogeneous catalysts  $MoO_3 \cdot CoO/Al_2O_3$  and  $WO_3/SiO_2$  [4] or a homogeneous  $WCl_6$ -based catalyst [5] failed: only isomerisation and Friedel-Crafts alkylation were observed. Recently, Warwel and Jansen [6] reported the co-metathesis of 4-pentenenitrile with symmetrical alkenes using the heterogeneous catalyst  $Re_2O_7/Al_2O_3$ , activated with various tetraalkyltin compounds, at 373 K but they found, that no self-metathesis of the unsaturated nitrile took place.

In this paper we present a systematic study of the reactivity of unsaturated nitriles of general formula  $CH_2=CH(CH_2)_nCN$  for metathesis and co-metathesis with linear alkenes, in the presence of the homogeneous catalyst system  $WCl_6 \cdot Sn(CH_3)_4$  and the heterogeneous catalyst  $Re_2O_7/Al_2O_3 \cdot SnR_4$  ( $R = CH_3$  or  $C_2H_5$ ).

## Experimental

### Chemicals

Acetonitrile, allyl cyanide and acrylonitrile (Fluka) were dried and distilled before use. All the other unsaturated nitriles were prepared from the corresponding bromide or chloride as described by Friedman and Shechter [7]. Z-3-Heptene (Fluka) was distilled from sodium wire. E-3-Hexene (Aldrich) was used without further purification. All the substrates were stored under argon. n-Hexane (Merck) and chlorobenzene (Aldrich) were distilled from sodium wire and phosphorus pentoxide, respectively. The solvents were stored over molecular sieves 3A under argon.

The  $WCl_6$  (Merck) was purified by sublimation under vacuum and kept under argon. Both tin compounds (Merck) were dried over molecular sieves 3A. The  $Re_2O_7/Al_2O_3$  catalyst was prepared by impregnation of  $\gamma-Al_2O_3$  (Ketjen CK-300,  $195 \text{ m}^2/\text{g}$ ) with an aqueous solution of ammonium perchlorate (Drijfhout), followed by drying in air at 383 K for 2 h. The catalyst was calcined in dry oxygen for 2 h at 823 K, followed by dry, oxygen-free nitrogen at the same temperature for 2 h.

### Procedure

Both the homogeneously and heterogeneously catalyzed reactions were carried out in the liquid phase in a stirred glass reactor of about 30 ml capacity. In the case of homogeneous catalysis, 5 ml of a solution of  $WCl_6$  (0.1 mmol) in chlorobenzene were first introduced into the reactor, followed by 0.2 mmol  $Sn(CH_3)_4$ . Next Z-3-heptene (in case of a co-metathesis reaction) and the unsaturated nitrile were added. All the additions were made at room temperature and under nitrogen. The reactor was then heated to 373 K on an oil bath.

In the heterogeneous case 100 mg of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (containing  $37 \times 10^{-6}$  mol of  $\text{Re}_2\text{O}_7$ ) were introduced into the reactor under nitrogen immediately after calcination. Subsequently 1 ml of n-hexane containing  $7.2 \times 10^{-6}$  mol of cocatalyst and the substrate(s) (5 minutes later) were introduced.

### Analysis

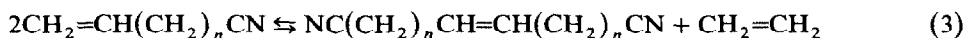
Analysis of the liquid phase of the reaction mixtures was by GLC; a glass column containing 10% UCC-W-982 on Chromosorb PAW-DMCS, 80–100 mesh, was used. Products were identified by comparison of the retention times with those of authentic samples and by GC-MS.

### Results

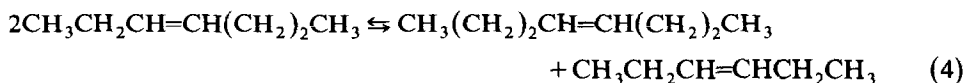
*Homogeneous metathesis and co-metathesis of unsaturated nitriles of general formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  in the presence of the catalyst system  $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4$*

(A) *Co-metathesis.* We first investigated the co-metathesis of  $\omega$ -unsaturated nitriles with Z-3-heptene, using substrates with  $n = 0-5, 8$  and 9.

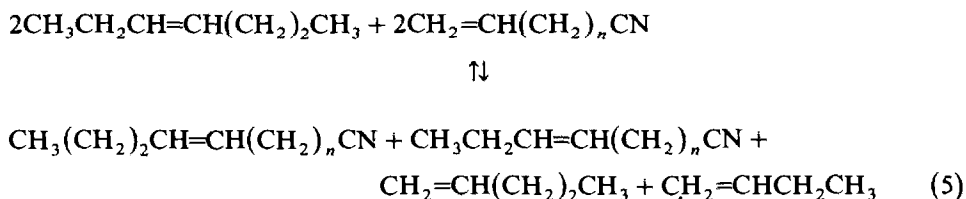
In this system three different reactions can take place; viz. self-metathesis of the unsaturated nitriles:



self-metathesis of Z-3-heptene:



and co-metathesis between the unsaturated nitrile and Z-3-heptene:



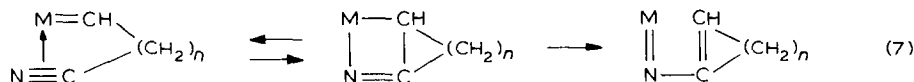
The advantages of studying the activity of a substrate under co-metathesis conditions are as follows. Some substrates are inactive in self-metathesis while showing some activity for co-metathesis (vide infra), so that co-metathesis provides a more sensitive indicator of activity than self-metathesis. Moreover, when the substrate shows no activity for both self-metathesis and co-metathesis, the self-metathesis of the Z-3-heptene indicates whether or not the catalyst is poisoned by the nitrile.

Table 1 shows the extents of conversion for the substrates used after completion of the reaction. There were no indications of side reactions. The rate was highest at the beginning of the reaction; the highest conversion was reached within 1–2 h. When the amount of substrate was increased, the conversion decreased [7].

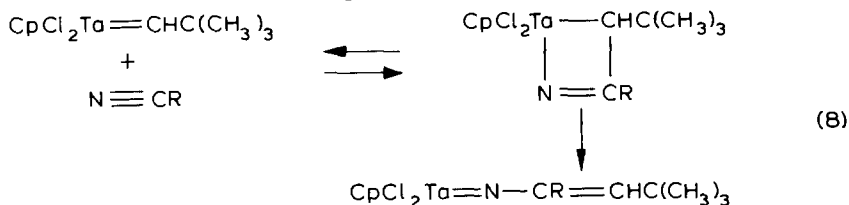
The results show that, in this system, up to  $n = 5$  the unsaturated nitriles hardly show any activity for self-metathesis. When  $n = 0$ , metathesis of Z-3-heptene is the only reaction. Table 1 shows that for  $n = 1, 2, 3$  or 4, for both the co-metathesis reaction and the self-metathesis of Z-3-heptene the order of reactivity is  $n = 2 > n =$



carbon–nitrogen triple bond, since for  $n = 3$  and  $n = 4$  the distance between the metal–carbene bond and the cyano group is too short to allow interaction by means of the lone electron pair on nitrogen. (For  $n = 0, 1$  and  $2$  this distance is too short to allow any intramolecular interaction.) Structure II, however, might react as indicated in eq. 7, leading to a destruction of the active metal–carbene structure.

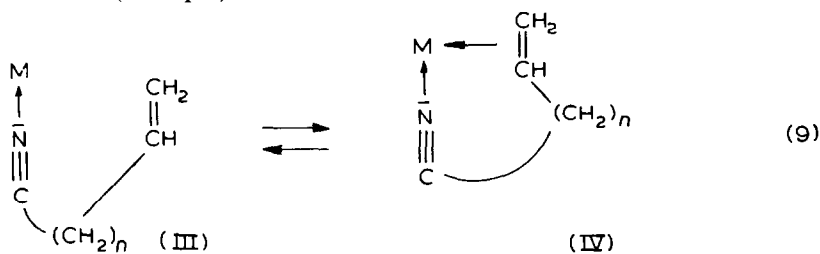


This reaction is analogous to that observed by Wood et al. [9] between a nitrile and a tantalum–carbene complex:



In this manner the low activity when  $n = 3$  and the even lower activity when  $n = 4$  can be accounted for. For  $n \geq 5$  the distance between the metal–carbene bond and the cyano group is too great to allow intramolecular interaction by means of the carbon–nitrogen triple bond. Thus the intermediate is not destroyed by side reactions, and the activity for both self- and co-metathesis increases.

The activity of *Z*-3-heptene in self-metathesis can be understood in analogous terms. When  $n = 0$  the self-metathesis conversion of *Z*-3-heptene is high because there is no competing co-metathesis reaction with the unsaturated nitrile. When  $n = 1$  or  $2$ , however, this competition occurs and the self-metathesis conversion of *Z*-3-heptene drops. When  $n = 3$  or  $n = 4$  the conversion is very low. This cannot be attributed to the inhibiting influence of the cyano group alone, since when instead of the unsaturated nitrile a ten-fold amount of acetonitrile ( $\text{CH}_3\text{CN}$ ) was present, the *Z*-3-heptene still underwent a metathesis conversion of 31% under the same conditions (i.e. in this experiment the ratio alkene/acetonitrile/ $\text{WCl}_6/\text{Sn}(\text{CH}_3)_4$  was 10/100/1/2). The explanation is that active sites are destroyed by the nitriles according to eq. 7. When  $n \geq 5$  the catalyst shows good activity for co-metathesis and self-metathesis of the unsaturated nitriles, but the self-metathesis conversion of *Z*-3-heptene is low. This can be visualized as follows: in every reaction mixture the cyano groups will complex to the vacant sites of the active catalyst structures. Up to  $n = 5$ , this makes the approach of the double bond both of *Z*-3-heptene as well as of the unsaturated nitrile more difficult, thus slowing down self- and co-metathesis of both substrates. When  $n \geq 5$ , however, the double bond and the cyano group of one and the same unsaturated nitrile molecule can be complexed to the same active structure (see eq. 9).



This reaction favours the complexation of the double bonds of those molecules which are complexed to the same active structure by means of a cyano group, and are therefore present in the immediate vicinity of the active structure. This means that the double bond of the unsaturated nitrile can approach the active structure much more easily than can the double bond of *Z*-3-heptene. In consequence, self- and co-metathesis of the unsaturated nitriles are strongly favoured compared with self-metathesis of *Z*-3-heptene.

(*B*) *Self-metathesis.* In addition to the co-metathesis experiments, the substrates were also treated under self-metathesis conditions (Table 2). The good activity of substrates with  $n \geq 5$  is in agreement with the results of the co-metathesis experiments. However, the low activity in self-metathesis displayed by the substrates with  $n = 2$  and  $n = 3$  under co-metathesis conditions is no longer evident. A possible explanation for this is that in the co-metathesis experiments *Z*-3-heptene was always added first (e.g. before the unsaturated nitrile). This means that the double bond of the *Z*-3-heptene molecules can interact with the catalyst to form active structures without the hindrance of the cyano groups. In self-metathesis experiments the cyano groups will prevent the interaction of double bonds with the catalyst, since both are introduced into the reaction mixture at the same time. This results in a much smaller number of active structures than in co-metathesis experiments. In the case of substrates with  $n \geq 5$ , however, the interaction of the catalyst with the double bond of the substrate is facilitated by the fact that the double bond and the cyano group of one and the same molecule can be complexed to the same catalyst structure (structure IV in eq. 9). This results in the formation of more active structures and, therefore, high metathesis activity.

TABLE 2

SELF-METATHESIS OF UNSATURATED NITRILES OF GENERAL FORMULA  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  WITH THE CATALYST SYSTEM  $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4$  AT 373 K (Molar ratio nitrile/ $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4 = 10/1/2$ )

$n$	Conversion (mol%)
0-4	0
5	47
8	48
9	50

TABLE 3

SELF-METATHESIS OF UNSATURATED NITRILES OF GENERAL FORMULA  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  CATALYZED BY  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  ACTIVATED WITH  $\text{Sn}(\text{CH}_3)_4$  OR  $\text{Sn}(\text{C}_2\text{H}_5)_4$  AT ROOM TEMPERATURE (Molar ratio nitrile/ $\text{Re}_2\text{O}_7 = 10/1$ )

$n$	Conversion (mol%)	
	$\text{Sn}(\text{CH}_3)_4$	$\text{Sn}(\text{C}_2\text{H}_5)_4$
0	0	0
1	1	1
2	83	91
3	91	98
4	91	98
5	80	86
8	70	
9	70	

*Heterogeneous metathesis of unsaturated nitriles of general formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  in the presence of the catalyst system  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-SnR}_4$*

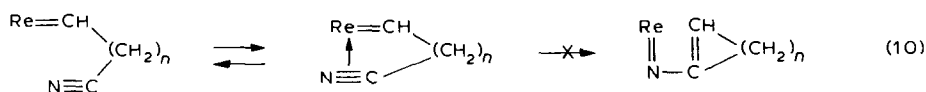
The homogeneous metathesis of unsaturated nitriles, described above, has several disadvantages for practical applications. On the other hand, heterogeneous metathesis of unsaturated nitriles would have the advantages of easy product separation and catalyst reuse. We studied the self-metathesis of unsaturated nitriles of general formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  in the presence of the catalyst  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  activated with a small amount of  $\text{Sn}(\text{CH}_3)_4$  or  $\text{Sn}(\text{C}_2\text{H}_5)_4$ .

The reactions were carried out at room temperature, and the production of ethene was almost complete within 4 h. The final conversions were determined after 24 h by analysing the liquid phase by GLC, after extraction of the catalyst with acetone. Table 3 shows the metathesis conversions of the unsaturated nitriles with two different cocatalysts, of which  $\text{Sn}(\text{C}_2\text{H}_5)_4$  appears to be the most effective. Substrates with  $n \geq 2$  are very effective towards metathesis. The selectivity for the primary metathesis products was  $> 98\%$ . Acrylonitrile ( $n=0$ ) also showed no activity with this catalyst, 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 ethene compared with blank experiments. Substantial isomerisation to crotononitrile took place, however. (Under the applied conditions, 60–70% of the substrate was isomerised to crotononitrile, while less than 1% was converted into metathesis products.)

When the amount of substrate was increased, the conversion decreased rapidly; e.g. when  $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CN}$  was metathesized with a molar nitrile/ $\text{Re}_2\text{O}_7$  ratio of 10/1, 25/1 or 50/1, using  $\text{Sn}(\text{CH}_3)_4$  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 bonds can no longer compete. (This effect might be one of the reasons why Warwel and Jansen [6] who treated  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CN}$  with symmetric alkenes in the presence of a similar catalyst at a nitrile/ $\text{Re}_2\text{O}_7$  ratio of 30/1, did not observe self-metathesis of the unsaturated nitrile. Another reason might be that co-metathesis of the nitrile was very strongly favoured over self-metathesis since the alkene/nitrile ratio used was 4/1.)

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

Remarkably, the reactivity of the substrates as a function of molecular structure differs from that observed with the  $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4$  catalyst. A possible explanation is that the side reaction destroying the active structure of the  $\text{WCl}_6\text{-Sn}(\text{CH}_3)_4$  catalyst when  $n=3$  and 4, hardly takes place, or may even be completely absent, with the rhenium-based catalyst:



The sideways complexation (with the carbon–nitrogen triple bond) of the nitrile group to the metal site would result in intramolecular stabilization of the metal–carbene intermediate: the coordinatively unsaturated rhenium is protected against impurities and against complexation with another cyano group via the lone electron pair on nitrogen. Since sideways complexation of the cyano group is much weaker than complexation via the electron pair on nitrogen, it is easier for the carbon–carbon double bond to compete with the cyano groups for the vacant sites of the rhenium. This would explain the maximum observed in metathesis activity for  $n = 3$  and 4. A maximum in the activity for metathesis of unsaturated amines and  $\omega$ -aryl alkenes has been explained analogously [10,11].

The fact that the ultimate conversion of the substrates with  $n = 8$  and 9 is slightly lower than that of the substrate with  $n = 5$  can be attributed to the fact that their molecules are larger, so that they cannot interact with active sites situated in smaller pores of the catalyst.

## Conclusions

Unsaturated nitriles undergo metathesis with high selectivity in the presence of the homogeneous or the heterogeneous catalyst system. The heterogeneous system is especially effective, showing good activity at room temperature.

When nitriles of general formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$  are metathesized or co-metathesized with alkenes their reactivity as a function of  $n$  depends on the catalyst system present. These results are rationalized in terms of different interactions between the substrate and the catalyst depending on the chain length of the substrate molecule.

Our results show that by cometathesis between alkenes and unsaturated nitriles new unsaturated nitriles of different chain length can be obtained, while self-metathesis offers an interesting way of converting mononitriles into dinitriles.

## Acknowledgement

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