# Homogeneous Metathesis of Unsaturated Nitriles

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*Summary* Unsaturated nitriles of general formula $CH_2{=}CH[CH_2]_nCN$, where $1 \leqslant n \leqslant 4$, undergo metathesis in the presence of the catalyst system tungsten hexachloride–tetramethyltin with maximum reactivity for $n = 2$.

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The metathesis of alkenes having functional groups is a very promising synthetic application of the metathesis reaction as it opens a route to various mono- and difunctional derivatives of hydrocarbons with well defined structures. Many metathesis catalysts, however, cannot withstand the poisoning effect of a heteroatom functional group; only a few catalyst systems have been reported to cause certain functionalized alkenes, such as oxygen-containing alkenes, halogeno-alkenes, and some olefinic amines to undergo metathesis.[1]

The metathesis of unsaturated nitriles seems difficult to achieve. Nakamura *et al.*[2] reported the metathesis of a long-chain nitrile, *viz.*, octadec-9-ene nitrile, with the catalyst systems $WCl_6$–$Me_3Al_2Cl_3$ and $Mo(OEt)_2Cl_3$–$Me_3Al_2Cl_3$, but the selectivity was low (<55%). Here, we report data which show that short-chain unsaturated nitriles can be metathesised with the catalyst system $WCl_6$–$Me_4Sn$.

The metathesis of a mixture of an unsaturated nitrile, *viz.*, $CH_2{=}CH[CH_2]_nCN$, where $n$ = 1, 2, 3, or 4, and hept-3-ene was studied. Consequently, at the same time three reactions could be followed: the metathesis of hept-3-ene [reaction (1)], the metathesis of the nitrile [reaction (2)], and the co-metathesis between hept-3-ene and the nitrile [reaction (3)].

$$2CH_3CH_2CH{=}CH[CH_2]_2CH_3 \rightleftharpoons CH_3CH_2CH{=}CHCH_2CH_3 + CH_3[CH_2]_2CH{=}CH[CH_2]_2CH_3 \quad (1)$$

$$2CH_2{=}CH[CH_2]_nCN \rightleftharpoons CH_2{=}CH_2 + CN[CH_2]_nCH{=}CH[CH_2]_nCN \quad (2)$$

$$\begin{aligned} 2CH_2{=}CH[CH_2]_nCN &+ 2CH_3CH_2CH{=}CH[CH_2]_2CH_3 \\ &\rightleftharpoons CH_2{=}CHCH_2CH_3 \\ &+ CH_2{=}CH[CH_2]_2CH_3 \\ &+ CH_3CH_2CH{=}CH[CH_2]_nCN \\ &+ CH_3[CH_2]_2CH{=}CH[CH_2]_nCN \quad (3) \end{aligned}$$

The reactions were carried out in the liquid phase in a stirred glass reaction tube at 373 K. $WCl_6$ (0·1 mmol) in chlorobenzene (5 ml) was introduced into the reactor at room temperature under nitrogen, followed by $Me_4Sn$ (0·2 mmol) and equimolar amounts of *cis*-hept-3-ene and the nitrile. Then the reaction mixture was heated to the reaction temperature. For each nitrile several substrate: catalyst ratios were studied. The conversion was followed by measuring the ethylene concentration in the gas phase and by analysing the liquid phase, both by g.l.c. The reaction products in the liquid phase were identified by g.c.-m.s. There were no indications of side reactions. The reaction rate was highest in the beginning of the reaction; the highest conversion was reached within 1—2 h.

In the Table the conversions are given for the substrates used, at four different substrate: catalyst ratios, after completion of the reaction. The Table shows that for both the co-metathesis reaction and the metathesis of *cis*-hept-3-ene the order of reactivity is $n = 2 > n = 1 > n = 3 > n = 4$ and for the metathesis of the nitrile: $n = 2 > n = 3 > n =$ 1,4. It follows that the conversions pass through a maximum for $n = 2$, while they are minimal for $n = 4$. Gas-phase analyses showed that ethylene was always present [in accord with reaction (2)], although in very small amounts for $n$ = 1 or 4 (but more than in a blank experiment), while most ethylene was found for $n = 2$.

In the Table it can be seen that *cis*-hept-3-ene shows a higher reactivity towards co-metathesis than towards self-metathesis. It is also remarkable that for $n = 3$ and $n = 4$ the metathesis of hept-3-ene is almost completely suppressed. This cannot be owing to the inhibiting influence of the CN group alone since, when instead of the unsaturated nitrile a ten times greater amount of acetonitrile was present, the hept-3-ene still underwent a metathesis conversion of 31% under the same conditions (*i.e.* in this experiment the ratio alkene: acetonitrile: $WCl_6$: $Me_4Sn$ = 10: 100: 1: 2).

A model which can account for the observed reaction behaviour will be presented elsewhere.

These results show that by co-metathesis between alkenes and unsaturated nitriles new unsaturated nitriles of different

Table. Metathesis of the system *cis*-hept-3-ene/$CH_2{=}CH[CH_2]_nCN$ catalysed by $WCl_6$-$Me_4Sn$.[a]

| mmol nitrile (= mmol alkene) | Co-metathesis conversion (mol %)[b] | | | | Metathesis *cis*-hept-3-ene conversion (mol %)[c] | | | | Metathesis $CH_2{=}CH[CH_2]_nCN$ conversion (mol %)[d] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ |
| 0·5 | 52 | 65 | 14 | 4 | 24 | 24 | 5 | — | — | 6 | 2 | — |
| 1·0 | 42 | 59 | 12 | 2 | 28 | 30 | 4 | — | — | 4 | 2 | — |
| 2·0 | 22 | 43 | 6 | 2 | 26 | 27 | 2 | — | — | 5 | 1 | — |
| 4·0 | 2 | 27 | 5 | 1 | 2 | 13 | 1 | — | — | 5 | 1 | — |

[a] Conversion based on analysis of the liquid phase. [b] % co-metathesis = 100 × (mol $CH_3CH_2CH{=}CH[CH_2]_nCN$ + mol $CH_3[CH_2]_2$-$CH{=}CH[CH_2]_nCN$)/(mol starting $CH_2{=}CH[CH_2]_nCN$). [c] % metathesis *cis*-hept-3-ene = 100 × (mol $CH_3CH_2CH{=}CHCH_2CH_3$ + mol $CH_3[CH_2]_2CH{=}CH[CH_2]_2CH_3$)/(mol starting $CH_3CH_2CH{=}CH[CH_2]_2CH_3$). [d] % metathesis $CH_2{=}CH[CH_2]_nCN$ = 100 × 2 × (mol $CN[CH_2]_nCH{=}CH[CH_2]_nCN$)/(mol starting $CH_2{=}CH[CH_2]_nCN$).

chain length can be obtained, while the self-metathesis of an unsaturated nitrile offers a route for the conversion of mononitriles into dinitriles.

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[1] E. Verkuijlen and C. Boelhouwer, *Chem. Phys. Lipids*, 1979, **24**, 305, and references therein.
[2] R. Nakamura, S. Matsumoto, and E. Echigoya, *Chem. Lett.*, 1976, 1019.