

## A Study of a New Catalytic System for the Metathesis of Functionalized Olefins

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Efetuoou-se o estudo sobre um novo sistema catalítico  $WCl_6.PMHS$ . Curvas de conversão, números de rotação e frequências de rotação foram comparados àqueles para os sistemas já conhecidos na literatura. Os resultados mostram que o novo sistema tem atividades análogas nas reações de metátese do 10-undecenoato de metila e 10-undecenonitrila que os sistemas conhecidos para esse tipo de reações, com a vantagem de utilizar como catalisador um composto menos tóxico e de menor custo que  $SnMe_4$  e  $Ph_2SiH_2$ .

A study of a new catalytic system  $WCl_6.PMHS$  ( $PMHS$  = polymethylhydrosiloxane) was carried out. Curves of conversion factors, turnover numbers and frequency numbers were compared with those for the systems  $WCl_6.SnMe_4$  and  $WCl_6.Ph_2SiH_2$  already described in the literature. The results show that the new system has activities in the metathesis reaction of methyl-10-undecenoate and 10-undecenonitrile similar to the typical systems used for these kind of reactions, with the advantage of using a compound which is less toxic and less expensive than  $SnMe_4$  or  $Ph_2SiH_2$  as the co-catalyst.

**Keywords:** *functionalized olefin metathesis, tungsten catalysts in metathesis, metathesis*

### Introduction

Since the discovery of the olefin-metathesis reaction for non-functionalized olefins, this research field has grown greatly and efficient systems have been developed<sup>1,2</sup>.

For functionalized olefins, this kind of reaction provides the synthesis of di-functional derivatives with well-defined structures. However, low tolerance for heteroatoms has been observed through the use of the same type of catalytic system as for non-functionalized olefins. The few systems which gave satisfactory results were those based on the use of  $WCl_6$  associated with either  $SnMe_4$  or  $Ph_2SiH_2$  (the so-called homogeneous systems), and also those based on  $Re_2O_7$  associated with  $SnMe_4$  on a solid support (the heterogeneous systems)<sup>3,4,5</sup>.

However, the recently discovered, well-defined alkylidene complexes markedly improved the yields of the metathesis reactions of functionalized olefins<sup>6,7,8</sup>. This was also the case for the  $Al_2O_3/SiO_2$  supported  $MeReO_3$  (MTO)<sup>8</sup>. A drawback of the use of the "classical systems" is the toxicity of  $SnMe_4$ , whereas the well-defined systems are problematic because they are somewhat difficult to synthesize and/or are expensive.

The purpose of the present work is to study the new catalytic system  $WCl_6.PMHS$ , where  $PMHS$  =  $Me_3SiO(MeHSiO)_nSiMe_3$ ,  $n = 35$  (polymethyl-hydrosiloxane), which avoids the use of the toxic  $SnMe_4$  and the expensive  $Ph_2SiH_2$ , in the metathesis reaction of methyl-10-undecenoate and 10-undecenonitrile. Therefore, direct comparison of this system to the known systems was carried out.

## Results

The ester:PMHS:WCl<sub>6</sub> ratio chosen for the present study was 25:4:1, which gave the best conversion factors in the preliminary study<sup>10</sup>.

The selectivity of the ester reaction was approximately 100%. Only when the reaction was performed on a large scale were traces of CH<sub>3</sub>CHCl(CH<sub>2</sub>)<sub>8</sub>COOCH<sub>3</sub> detected in addition to the expected product, as a result of the addition of HCl, formed in the reaction, to the double bond. The reactions were followed by <sup>1</sup>H-NMR spectroscopy since the olefinic protons gave signals at 4.8 (m) and 5.7 (m) ppm, for the starting ester, and at 5.25 (m) ppm for the diester. Integration of these signals directly gave the conversion factors. The reaction carried out on the nitrile was analyzed according to the same criteria, taking into account the formation of the HCl-addition product.

With either WCl<sub>6</sub> or PMHS taken separately no reaction took place. The conversion factors, turnover numbers and frequency numbers for the ester reaction with the catalytic system studied in this work are shown in Fig. 1. All of the systems were very active at the beginning of the reaction, but were deactivated after 2 h, probably as a result of the interaction of the catalytic species with the heteroatoms.

The results for the nitrile are shown in Table 1. The selectivity was poorer than for the ester reaction, in agreement to the literature for other catalytic systems. Analysis of the products, separated by silica-gel chromatography showed that in addition to 10-eicosenodinitrile, 10-undecanonitrile chloride was also formed, as a result of the addition of HCl to the double bond.

## Experimental

WCl<sub>6</sub>, SnMe<sub>4</sub>, Ph<sub>2</sub>SiH<sub>2</sub> and PMHS were purchased from Aldrich Chemical Company. Methyl-10-undecenoate was kindly supplied by ATO Chimie (France). 10-undecenonitrile was synthesized from the corresponding amide by refluxing it with thionyle chloride in benzene. The product was purified by vacuum distillation. The yield was 60%. 10-undecenonitrile: <sup>1</sup>H-NMR (δ, in CDCl<sub>3</sub>) 1.34 (m,

10H), 1.70 (m, 2H), 2.04 (m, 2H), 2.38 (t, 2H), 4.98 (t, 2H), 4.98 (t, 2H), 5.82 (m, 1H); MS (EI, 70 eV) m/z 165 (M), 136 (M-C<sub>2</sub>H<sub>5</sub>), 122 (M-C<sub>3</sub>H<sub>7</sub>); IR ν<sub>max</sub> (cm<sup>-1</sup>) 2242 (C≡N) 1635 (C=C). 10-undecenoamide was synthesized by a reaction of 10-undecenoyl-chloride (Aldrich) with NH<sub>4</sub>OH<sup>4</sup>. All of the metathesis reactions were performed under an argon atmosphere in a glove box.

In a typical reaction, 127 mg of WCl<sub>6</sub> was added to a flask containing 1.59 g of degassed methyl-10-undecenoate at 75 °C, followed by the addition of 0.081 g of degassed PMHS, making the ester:WCl<sub>6</sub>:PMHS, ratio 25:1:4. For the nitrile, the ratio was 10:1:4 and the temperature was 100 °C. The bubbling of argon into the solution was necessary in order to carry the HCl and C<sub>2</sub>H<sub>4</sub> and drive the reaction to the product. The samples collected for analysis were diluted with Et<sub>2</sub>O, filtered in microcolumns with celite 545 and analyzed by <sup>1</sup>H-NMR spectroscopy. All products were characterized by mass spectroscopy, IR and <sup>1</sup>H NMR spectroscopies: *methyl 10-undecanoyl chloride*: <sup>1</sup>H NMR (δ, in CDCl<sub>3</sub>) 1.3 (m, 12H), 1.4 (d, 3H), 1.6 (m, 2H), 2.2 (t, 2H), 3.6 (s, 3H), 3.9 (m, 1H); MS (EI, 70 eV) 203 (M), 166 (M - CH<sub>3</sub>O); IR ν<sub>max</sub> (cm<sup>-1</sup>) 1737 (C=O),

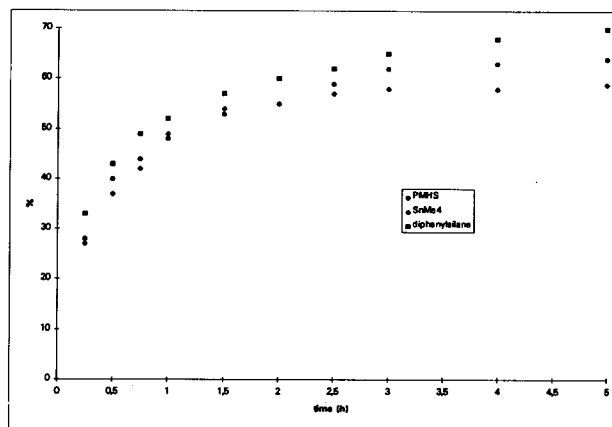


Figure 1. Conversion x time for the various catalytic systems. Errors in the data points ranged from 0-5%.

Table 1. Metathesis of 10-undecenonitrile

System	ratio*	total conversion	selectivity	yield in dinitrile	yield in chloride
WCl <sub>6</sub> -PMHS	25:1:4	-	-	14%	1%
WCl <sub>6</sub> -PMHS	10:1:4	32% ± 3	72% ± 2	23% ± 2	9% ± 2
WCl <sub>6</sub> -PMHS	7:1:4	56%	60%	34%	22%
WCl <sub>6</sub> -PMHS	6:1:4	62%	65%	40%	22%
WCl <sub>6</sub> -Ph <sub>2</sub> SiH <sub>2</sub>	25:1:2	18%	76%	14%	4%
WCl <sub>6</sub> -Ph <sub>2</sub> SiH <sub>2</sub>	10:1:2	42% ± 3	62% ± 2	26% ± 3	16% ± 2
WCl <sub>6</sub> -SnMe <sub>4</sub>	10:1:4	40% ± 2	67% ± 2	28% ± 3	12% ± 3

\* nitrile:catalyst:co-catalyst.

1736 (CH<sub>3</sub>). *Dimethyl 10-eicosenoate*: <sup>1</sup>H-NMR (δ, in CDCl<sub>3</sub>) 2.4 - 1.2 (m, 32H), 3.6 (s, 6H), 5.25 (m, 2H); MS (EI, 70 eV) 368 (M); IR ν<sub>max</sub> (cm<sup>-1</sup>) 1734 (C=O). *10-undecanonitrile chloride*: <sup>1</sup>H-NMR (δ, in CDCl<sub>3</sub>) 1.25 (m, 10H), 1.55 (d, 3H), 1.62 (m, 4H), 2.30 (t, 2H), 3.92 (m, 1H); MS (EI, 70 eV) 201 (M), 164 (M-H<sub>2</sub>Cl); IR ν<sub>max</sub> (cm<sup>-1</sup>) 2245 (C≡N), 1378 (CH<sub>3</sub>). *10-eicosenodinitrile*: <sup>1</sup>H-NMR (δ, in CDCl<sub>3</sub>) 1.30 (m, 20H), 1.68 (m, 4H), 2.0 (m, 4H), 2.35 (t, 4H), 5.4 (m, 2H); MS (EI, 70 meV) 302 (M); IR ν<sub>max</sub> (cm<sup>-1</sup>) 2250 (C≡N).

All NMR spectra were performed on a VARIAN CXR 200 MHz spectrometer using CDCl<sub>3</sub> or CCl<sub>4</sub> as solvents. The IR data were taken on a Perkin-Elmer 1430 coupled with a 483 data station. The spectra were obtained as liquid films in CsI cells. The mass spectra were made on a HP 5988 A mass spectrometer coupled to a HP 590 GC.

The conversion factors (C) were estimated from the integration of the olefinic proton signals by the equation  $C = 2D/(E_2 + 2D)$ , where D = integration of the diester or dinitrile olefinic proton signals and E<sub>2</sub> = integration of the two terminal ester or nitrile olefinic proton signals. Tests with a calibrated solution confirmed an error of 4%. Turn-over numbers were calculated by  $TN = 25C/2$  for the ester, assuming a selectivity close to 100%, and  $TN = \text{excess olefin} \times (C_{\text{dinitrile}}/2 + C_{\text{chloride product}})$ , for the nitrile, as the selectivity was not close to 100%. The C<sub>chloride product</sub> was estimated from the <sup>1</sup>H-NMR signal of the proton at 3.9 ppm. Frequency numbers were given by  $FN = TN/t$ . All the reactions were repeated at least three times, and all the data points reflect the average of the reactions.

## Discussion

The new co-catalyst PMHS is a reductor under mild conditions, but does not reduce esters, amides or nitriles *per se*<sup>11</sup>. The results obtained show that the new system WCl<sub>6</sub>.PMHS has activities strictly comparable to those of the other systems known to metathesize esters and nitriles. Previous observations demonstrated that a prerequisite for the formation of an active catalyst is the presence of one or more Si-H bonds in the co-catalyst, and also, that upon the interaction of Ph<sub>2</sub>SiH<sub>2</sub> with WCl<sub>6</sub>, reduction takes place, forming HCl<sup>4</sup>. The present results confirm these observations. Moreover, the presence of Si-O bonds does not

hinder the formation of the active species, the structure of which has yet to be established.

## Conclusion

Optimal working conditions for the very easy to use and inexpensive WCl<sub>6</sub>.PMHS system were established for the metathesis reaction of functionalized olefins. The results can be favorably compared to the "classical" systems for the metathesis of this type of olefin, and indicate that it is particularly well-suited to the synthesis of simple starting difunctionalized olefins.

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