

## Cometathesis of Methyl Oleate and Ethylene; a Direct Route to Methyl Dec-9-enoate

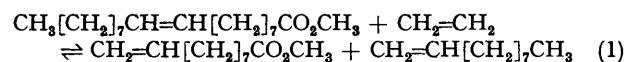
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*Summary* Methyl dec-9-enoate is obtained by cometathesis of ethylene and methyl oleate with two different catalyst systems, *viz.*  $\text{WCl}_6\text{-Me}_4\text{Sn}$  and  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3\text{-Me}_4\text{Sn}$ ; at 0.2 MPa ethylene pressure both catalyst systems show

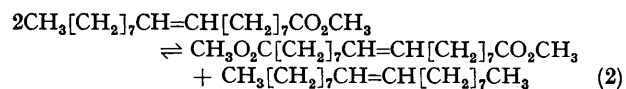
good activity at 343 K and the latter system also at room temperature.

In recent years the activity of the catalyst systems  $WCl_6-Me_4Sn$  and  $Re_2O_7-Al_2O_3-Me_4Sn$  for the homogeneous and heterogeneous metathesis of unsaturated esters and for the cometathesis of unsaturated esters with alkenes has been established,<sup>1-3</sup> although little is known so far about the cometathesis of unsaturated esters with ethylene. We now report on the activity of these catalyst systems for the cometathesis of methyl oleate (methyl *cis*-octadec-9-enoate) and ethylene (equation 1). This reaction may be important



from a synthetic point of view, since one of the product molecules is methyl dec-9-enoate, the key intermediate in the synthesis of 9-oxo-*trans*-dec-2-enoic acid, a honeybee pheromone (the 'queen substance'), and in the synthesis of 9-oxodecanoic acid, a prostaglandin intermediate.<sup>4-6</sup>

Besides the products of cometathesis (equation 1), products of self-metathesis of methyl oleate were also obtained (equation 2). Typical results with both catalyst



systems are given in the Table. It can be seen that the  $WCl_6$  catalyst shows good activity at 343 K, while the  $Re_2O_7$  catalyst shows good activity even at room temperature. From the Table it can be concluded that even at 0.2 MPa ethylene pressure more cometathesis than self-metathesis products are formed. Reducing the substrate:catalyst ratio shifts the composition of the reaction mixture in favour of products of the cometathesis reaction. From other experiments, not mentioned in the Table, it can be concluded that without a solvent the cometathesis conversion is lower. Hexane as a solvent improved the results obtained with the  $Re_2O_7$  catalyst. In order to investigate the influence of the ethylene pressure some additional experiments were carried out at 5 MPa, with the  $Re_2O_7$  catalyst at room

TABLE. Metathesis of methyl oleate (Meol) and ethylene.<sup>a</sup>

T/K	Meol/ $Re_2O_7$ or $WCl_6$	$Re_2O_7-Al_2O_3-Me_4Sn$ Conversion (mol %) <sup>b</sup>		$WCl_6-Me_4Sn$ Conversion (mol %) <sup>b</sup>	
		Cometathesis	Self-metathesis	Cometathesis	Self-metathesis
293	50	42	25	5	1
343	50	39	29	40	17
293	10	75	10	35	2
343	10	62	10	68	12

<sup>a</sup> Ethylene pressure, 0.2 MPa; solvent, chlorobenzene. <sup>b</sup> Conversion of methyl oleate, based on analysis of the liquid phase after 20 h.

With both catalyst systems the reactions were carried out in a glass batch reactor at room temperature and at 343 K, using different substrate:catalyst ratios. The ethylene pressure was kept at 0.2 MPa in most experiments. The  $Re_2O_7-Al_2O_3$  catalyst (100 mg, 37  $\mu$ mol of  $Re_2O_7$ ) was prepared and calcined as described earlier<sup>3</sup> and introduced into the reactor under nitrogen. Before activation of the catalyst with  $Me_4Sn$  (7  $\mu$ mol) in chlorobenzene (1 ml) the reaction vessel was flushed with ethylene. The methyl oleate was then added at the reaction temperature. In experiments with the homogeneous system, either 1 ml of  $WCl_6$  in chlorobenzene (37  $\mu$ mol of  $WCl_6$ ) or the same amount of freshly sublimed  $WCl_6$  was introduced into the reaction vessel under nitrogen. After flushing the reaction vessel with ethylene the catalyst was activated with  $Me_4Sn$  (37  $\mu$ mol) and the methyl oleate added at the reaction temperature. The reaction was followed by analysing the liquid phase by g.l.c. (1 m  $\times$  4 mm column, 10% UCC-W-982 on Chromosorb P, AW, DMCS treated, 149–180  $\mu$ m, 4 min hold at 100 °C, then with 30 °C min<sup>-1</sup> to 245 °C, N<sub>2</sub> carrier, flame ionisation detector).

temperature and with the  $WCl_6$  catalyst at 343 K. In all experiments the self-metathesis reaction was almost completely suppressed. After 5 h reaction time 60–70% of the methyl oleate was converted into cometathesis products with both catalyst systems.

Olive oil, which consists mainly of the triglyceride of oleic acid, also reacts with ethylene under the foregoing conditions. Both catalyst systems showed good activity, as demonstrated by the formation of large amounts of dec-1-ene.

Preliminary experiments with ethylene and other functionalised olefins showed that with these catalysts various  $\omega$ -unsaturated compounds can be obtained, which may be important from both a synthetic and technological point of view.

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