METATHESIS OF METHYL ERUCATE

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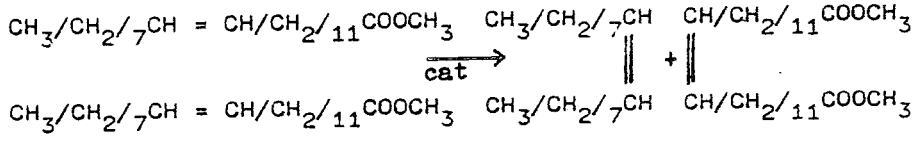
Today's rapeseed production is based mainly on the low erucic varieties, the oil obtained being more suitable for consumption. However, high erucic varieties are still cultivated, the cause being not only the climatic conditions, but - in the first place - the presence of the Δ 13-docosenoic or erucic acid, the main constituent of the high erucic oil, a valuable raw material for production of many intersting chemical products. One of the examples of application of erucic acid is the synthesis of the diester of the dicarboxylic C26 acid with one unsaturated link and of the highmolecular olefins.

These oleochemicals can be also obtained by metathesis of the methyl ester of erucic acid.

The use of metathesis reactions for processing oleochemicals was initiated in Holland by professor Boelhouwer and his team. During their extensive study of the metathesis reactions of olefins and appropriate catalysts for these reactions, P.B. Van Dam, C.Boelhouwer and M.C.Mittelmeijer /1974/ called attention to the possibility of modyfying other products containing the unsaturated links, among others also esters of the unsaturated fatty acids.

The metathesis reaction of methyl oleate is an equilibrium reaction and proceeds according to the following scheme:



methyl erucate — octadecene C18=1 — diamethyl diester of the C26=acid

This reaction proceeds at low temperatures, maximum conversion rate being about 50% /C.Boelhouwer, E.Verkuijlen, J.C.Mol, 1976, 1984/.

It has been shown that the functional groups in the olefin chain considerably influence the efficiency of the catalyst used. The same catalysts are more active in metathesis of linear olefins /C.Boelhouwer, J.C.Mol, 1984/.

On the analogy of the diester of the C18 acid obtained by metathesis of the oleic acid, the products obtained in the above discussed reaction can be a very interesting chemical raw material. Owing to the presence of three active centres in the molecule /two ester and one double link/ the long chained diester of the monounsaturated C26 acid can be a valuable raw material for the synthesis of many synthetic plastics of polyester and polyamide type. It can be used also as an intermediate product in the synthesis of aroma chemicals.

Synthetic plastics obtained from the diester of the unsaturated C18 acid show a substantially increased mechanical resistance /J.M.van Thiel, C.Boelhouwer, 1974;C.Boelhouwer, J.C.Mol, 1985/.

The subject of our work was to study the possibility of obtaining these interesting oleochemicals from the high erucic rapeseed oil using for this purpose the metathesis reaction.

The methyl ester of the erucic acid was obtained by methanolysis of the crude rapeseed oil /high erucic/ and by fractional distillation of the product. Composition and characteristics of the raw material used are given in table1.

Table 1. Characteristics of high erucic rapeseed oil.

1. Acid value		0,4
2. Moisture content, %		0,05
3. Composition of fatty acids, % /GLC/		
	C18:2	0,4
	C18:3	0,2
	C20:1	0,9
	C22:1	98,5

The following catalysts were used:

1. Homogeneous catalyst:
   - tungsten hexachloride obtained by chlorination of the metallic tungsten.
2. Heterogeneous catalysts:
   - molybdenum oxides on aluminium oxide 5, 10, 15%,
   - tungsten trichloride on silica /10% of WO_3/,
   - tungsten trichloride on aluminium oxide /10% of WO_3/,
   - a mixture of cobaltous oxide and molybdenum oxide on aluminium oxide /3,5% CoO + 10% MoO_3/, an industrial CoMo catalyst,
   - rhenium oxide on aluminium oxide /22% as Re/.

   These catalysts were obtained by impregnation of the carrier, previously calcinated during 12 hours at 600°C in air stream.

In all cases a Ziegler tetramethyl tin was used as cocatalyst.

Reaction conditions

Conditions of the metathesis reaction in case of the homogeneous catalysts are given in table 2.

Table 2.

Constant parameters		Variable parameters
Ratio WCl_6:$Sn(CH_3)_4$	= 1 : 1	Temperature, °C: 70, 120
Ratio WCl_6:ester	= 1:20	Solvent: CCl_4 or C_6H_5Cl
		Reaction time, hours: 4 and 6

When the reaction had been accomplished the catalyst was precipitated with methanol or ammonia water and filtered. In the filtrate the content of dimethyldiester of the dicarboxylic acid, olefin and methyl erucate was determined by GLC method with inner standard.

Conditions of the metathesis reaction when using a heterogeneous catalysts are given in table 3.

Table 3.

Constant parameters	Variable parameters
Activation of catalyst at 450°C 2 h	Temperature of reaction, °C - 20, 50 and 120
Cooling	Reaction time: from 15 min up to 19 h
Ratio catalyst: $Sn/CH_3/_4$ = 1 g:5 µl	Solvent: CCl_4 or chlorobenzene
Ratio catalyst: ester = 1:1,6	

The catalyst was separated by filtration and the contents of the filtrate were determined as above.
For determination a chromatograph of Carlo-Erba model GT was used; injection temperature 250-300°C. Columns with 3% of OV-17 on Gas Chrom Q 100/120 mesh, length 2 m, Ø 6/5 mm, temperature 170-250°C, program 10°C/min.
As inner standards were used: hexadecane,
sebacic acid,
palmitic acid.

Results and discussion

Results of these experiments which gave high conversion rates are shown in table 4.

Table 4. Metathesis of methyl erucate.

Catalyst	Temperature °C	Solvent	Time h	Content, % diester	Content, % olefins
WCl_6	70	CCl_4	4	52,3	8,5
	70	C_6H_5Cl	6	45,8	9,4
	110	C_6H_5Cl	6	36,6	14,1
22% Re_2O_7/Al_2O_3	20	CCl_4	18	25,8	14,2
	50	CCl_4	1	12,1	7,6
	50	CCl_4	18	9,5	4,5
	120	C_6H_5Cl	18	12,2	6,8

These results indicate a possibility of attaining the conversion equilibrium when using a homogeneous catalyst of

WCl_3 type at temperatures below 100°C and with the shortest possible time of reaction.

Heterogeneous catalysts are by far more attractive for the industrial use, but the results hitherto obtained eliminate the usability of catalyst systems other than those based on rhenium catalyst. The activity of rhenium catalysts depends on the type and method of modyfication of the carrier. Latest experiments carried out in Holland /H.Szczepańska, W.W.Niedbalska, 1986/ show that high conversion rate can be obtained with rhenium content as low as 3% when the carrier was adequately modified.

We intend to continue our work in this direction.

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