

# Homogeneous Catalytic Metathesis of Unsaturated Fatty Esters: New Synthetic Method for Preparation of Unsaturated Mono- and Dicarboxylic Acids

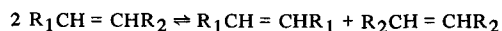
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## ABSTRACT

The catalytic metathesis of unsaturated fatty esters is a new, versatile method for the synthesis of a variety of fatty derivatives and alkenes. Monounsaturated esters are converted into unsaturated dicarboxylic esters which might be important technologically for the production of new polyesters and polyamides, and for the synthesis of civetone-type perfumes. Metathesis of linoleate and linolenate leads to a variety of hydrocarbons and mono- and dicarboxylates of different unsaturation. Joint reactions of unsaturated esters and alkenes are a useful means for the synthesis of homologues of oleic acid and other fatty acids. Metathesis of unsaturated fatty oils (olive, soybean, linseed, etc.) leads to the formation of high molecular dicarboxylic acid glyceryl esters with improved drying properties.

## INTRODUCTION

The catalytic metathesis of alkenes was first described by Banks and Bailey (1). The homogenous metathesis of alkenes and of alkenes carrying functional groups, represented by:



has been fostered by the discovery of several catalyst systems (2), which, under very mild reaction conditions, allow a high degree of conversion of the reactants, and the reactions are usually very selective. In this article, the homogenous metathesis of a number of unsaturated fatty esters which can be considered as alkenes with a functional (ester) group, is described as a method for the synthesis of (symmetrical) unsaturated dicarboxylic acids and their esters and of the corresponding alkenes.

The unsaturated dicarboxylic acids obtained may be important, because: (A) they could be starting material for the preparation of new unsaturated polyesters and polyamides with the alkene function offering the opportunity to produce three dimensional structures by cross linking reactions; (B) hydrogenation of the alkene function allows the synthesis of saturated dicarboxylic acids. Both the unsaturated and saturated dicarboxylic acids cannot be ob-

tained easily by other ways. Condensation reactions of these dicarboxylic acids have been described for the synthesis of civetone-type perfumes (3-8). In a previous article (9), some preliminary experiments concerning the homogenous metathesis of unsaturated fatty esters and of fatty oils were described. In the meantime, by some changes in the techniques used, considerable improvements of the results have been achieved.

Metathesis reactions of unsaturated fatty esters, joint reactions of these esters with alkenes and with other esters were carried out during this investigation. Table I gives a survey of a number of reactions performed with tungsten hexachloride-tetramethyl tin as a homogenous catalyst.

## EXPERIMENTAL PROCEDURES

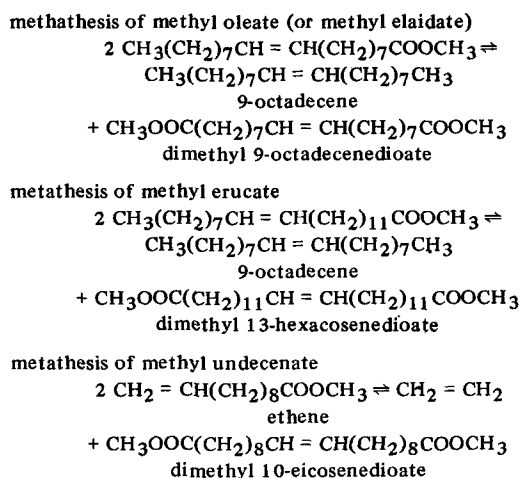
*Metathesis of some unsaturated fatty esters:* Starting materials were methyl oleate and methyl elaidate, methyl erucate, and methyl undecenate. Reactions were performed under an atmosphere of dried, pure nitrogen in a glass apparatus, provided with silicone-rubber septa, through which the reactants were injected by means of hypodermic syringes. The reaction vessels were dried carefully to exclude traces of moisture. The reactions were performed with a reactant-catalyst ratio of 75:1, and the catalyst components tungsten hexachloride and tetramethyl tin were present in equimolar quantities. The great sensitivity of tungsten hexachloride towards moisture makes working under dry nitrogen necessary to obtain a good reproducibility of the reaction. During the initial experiments, chlorobenzene was used as a solvent. This solvent has a favorable influence on the selectivity (10) of the homogeneous metathesis reaction.

Later, the experiments were carried out without solvent and on a larger scale, with as much as 1 kg of the starting material. The results showed that neither the rate of reaction nor the selectivity decreased when comparative reaction conditions were chosen. Moreover, the absence of a low boiling solvent has the advantage that it is possible to work at more elevated temperatures which considerably shortens the reaction time and facilitates separation and purification of reaction products. The following reactions were carried out:

TABLE I  
Homogeneous Metathesis of Unsaturated Fatty Esters with Tungsten Hexachloride-Tetramethyltin as Catalyst

| Starting material                    | Reaction conditions |         | Percentage of starting material converted | Reaction products formed                                |   | Selectivity of <sup>a</sup> reaction (%) |
|--------------------------------------|---------------------|---------|---|---|---|--|
|                                      | Time hr             | Temp. K |   | Methyl esters of  | Hydrocarbons                            |  |
| Methyl oleate                        | 2                   | 383     | 50  | 9-Octadecenedioic acid                                  | 9-Octadecene                            | 100                                      |
| Methyl elaidate                      | 2                   | 383     | 50  | 9-Octadecenedioic acid                                  | 9-Octadecene                            | 100                                      |
| Methyl erucate                       | 2                   | 383     | 50  | 13-Hexacosenedioic acid                                 | 9-Octadecene                            | 100                                      |
| Methyl undecenate                    | 10                  | 383     | 89  | 10-Eicosenedioic acid                                   | Ethene                                  | 100                                      |
| Methyl linoleate                     | 6                   | 353     | 60  | Variety of unsaturated mono- and dicarboxylic acids id. | Variety of unsaturated hydrocarbons id. |  |
| Methyl linolenate                    | 6                   | 353     | 68  |   |   |  |
| Methyl oleate + 3-Hexane (equimolar) | 10                  | 333     | 33  | 9-Octadecenedioic acid<br>9-Dodecenoic acid             | 3-Dodecene<br>9-Octadecene              | 100                                      |

<sup>a</sup>Percentage of reaction products mentioned in the two preceding columns.



After each experiment, the reaction mixture was dissolved in an excess of petroleum ether. To this solution, an excess of strong ammonium hydroxide was added, and the mixture was stirred vigorously during which operation the metallic derivatives of the catalyst system were precipitated. With this technique, the problem of separation of the catalyst from the reaction products was solved quite easily. After filtration of the precipitate, a bright, yellow solution resulted which, apart from a small fraction of impurities, contained only the unconverted starting material and the reaction products. The diesters were crystallized from the solution at 253 K. The crystals were separated and the mother liquor was concentrated by evaporation to half of the original volume, and a second fraction of diester was obtained in the same way.

The diesters were recrystallized from petroleum ether. Table II shows some physical constants of the reaction products. The mother liquor was concentrated and saponified with potassium hydroxide solution. The soap formed was dissolved in an excess of water. The water layer was extracted with petroleum ether and the ether layer concentrated, whereafter 9-octadecene could be distilled as main product. The soap solution was treated with dilute sul-

phuric acid and the fatty acids formed were esterified to be used again as starting material. From the diesters, the corresponding dicarboxylic acids were prepared by saponification and acidification. Some data of these acids also are represented in Table II and the results of their ultimate analysis in Table III.

The composition of the reaction intermediates and the end products was investigated by means of gas liquid chromatography. Analytical conditions: gas chromatograph, Hewlett-Packard HP 5750 G; detector, double flame ionization; column, 2 m, 1.3% Apiezon L on Chromosorb P, AW/DMCS, 100-120 mesh; column temperature, 520-570 K; detector temperature, 720-770 K; injection port temperature, 720-770 K; and carrier gas, helium, 100 ml/min.

IR spectra of the diesters showed that both *cis*- and *trans*-configurations were present; their separation and identification are still in progress. As follows from gas liquid chromatographic analysis shifting of the double bond does not occur under the conditions of the metathesis experiments; this would have resulted in the formation of a variety of unsaturated dicarboxylic esters and hydrocarbons of different mol wt besides the products mentioned in Table II.

The conversions mentioned in Table I indicate that, with methyl oleate (elaidate) and methyl erucate, equilibrium is obtained; with methyl undecenate, the reaction proceeds beyond 50% conversion, because the ethene formed was blown off during the synthesis and this allowed the reaction to proceed.

*Joint reactions of methyl oleate with alkenes:* Joint reactions of unsaturated esters with alkenes open the possibility of synthesizing homologues of these esters in a simple and convenient way. As an example the reaction of methyl oleate and 3-hexene is given:

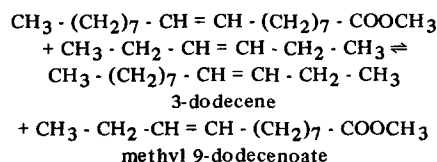


TABLE II

Physical Data of Some Dicarboxylic Acids and Esters and of 9-Octadecene Obtained by Metathesis of Unsaturated Fatty Esters<sup>a</sup>.

| Dimethylester, acid or alkene | Mol wt | Melting point (K) | n <sub>D</sub> <sup>50</sup> | Iodine value |              | Acid value  |              |
|-------------------------------|--------|-------------------|------------------------------|--------------|--------------|-------------|--------------|
|                               |        |                   |                              | Theoretical  | Experimental | Theoretical | Experimental |
| 9-Octadecenedioate            | 340    | 305               | 1.4474                       | 75           | 74±1         | -           | -            |
| 13-Hexacosenedioate           | 452    | 320               | 1.4509                       | 56           | 57±1         | -           | -            |
| 10-Eicosenedioate             | 368    | 319               | 1.4472                       | 69           | 70±1         | -           | -            |
| 9-Octadecene                  | 252    | 274.5             | 1.4341                       | 101          | 98±1         | -           | -            |
| 9-Octadecenedioic acid        | 312    | 361               | -                            | -            | -            | 359         | 356±6        |
| 13-Hexacosenedioic acid       | 424    | 369               | -                            | -            | -            | 264         | 254±6        |
| 10-Eicosenedioic acid         | 340    | 381               | -                            | -            | -            | 330         | 324±6        |

<sup>a</sup>Mass spectrometrical data of the dicarboxylic esters showed the expected parent peaks at m/e 340, 452, and 368 and the diagnostic peak for aliphatic esters at m/e 74.

TABLE III

Ultimate Analyses of Dicarboxylic Acids Obtained by Metathesis of Some Unsaturated Fatty Esters

| Dicarboxylic acid       | Percentage, carbon |              | Percentage, hydrogen |              | Percentage, oxygen |              |
|-------------------------|--------------------|--------------|----------------------|--------------|--------------------|--------------|
|                         | Theoretical        | Experimental | Theoretical          | Experimental | Theoretical        | Experimental |
| 9-Octadecenedioic acid  | 69.20              | 69.17        | 10.32                | 10.42        | 20.49              | 20.48        |
| 10-Eicosenedioic acid   | 70.55              | 70.34        | 10.66                | 10.54        | 18.79              | 19.09        |
| 13-Hexacosenedioic acid | 73.54              | 73.33        | 11.39                | 11.26        | 15.07              | 15.20        |

It is clear that, besides 3-dodecene and 9-dodecenoate, the products of metathesis of methyl oleate (viz. 9-octadecene and 9-octadecene dioic ester) also will be present in the reaction product; their separation and purification, however, did not give rise to difficulties. When reacting methyl oleate with nonsymmetrical alkenes, the reaction mixture will be more complicated as a consequence of the increased number of possible products of metathesis; reactions with symmetrical alkenes, therefore, should be preferred.

*Metathesis of some multiple unsaturated fatty esters:* Initial experiments on the metathesis of methyl linoleate and methyl linolenate showed almost no conversion of the starting material. Later experiments, however, gave fairly good results by omitting the chlorobenzene and elevating the reaction temperature.

The higher degree of unsaturation of the esters gives rise to a great number of products; preliminary results have shown the presence of the expected hydrocarbons, mono-carboxylic esters, and dicarboxylic esters.

The complexity of the reaction mixture and the relatively high degree of unsaturation of several of the reaction products makes the isolation and identification of these compounds rather difficult; this part of investigation is still in progress.

*Metathesis of fatty oils:* Like methyl esters of unsaturated fatty acids, glyceryl triesters of these acids can be converted by homogenous metathesis. The metathesis of olive oil (consisting of ca. 75% of glyceryl trioleate) has been described before (9). Further experiments have been performed with soybean oil (25% oleate, 55% linolate, 8% linolenate) and with linseed oil (18% oleate, 21% linolate, 45% linolenate).

Under the reaction conditions mentioned above, olive oil yielded 9-octadecene as relatively volatile compound beside a mixture of di- and trimeric glycerids. Mass spectrometry showed peaks at  $m/e = 885$  and  $1520$ , corresponding with triolein and the dimeric glyceride formed by metathesis, and large peaks of fragments of  $m/e = 1237$  and  $1209, 956$  and  $929, 899, 675,$  and  $642$ ; furthermore, a large number of peaks up to  $m/e = 2000$ , the limit of the range of the spectrometer.

Schematically, the reaction can be seen in Figure 1. With the intramolecular reaction, the metathesis occurs between fatty acid groups of the same molecule (which does not result in a larger molecule); however, with the intermolecular reaction molecule enlargement does take place. Stereochemical considerations indicate a strong domination of the intermolecular reaction over the intramolecular one. In this connection, the molecular enlargement in the thermal polymerization of linseed oil should be mentioned, during which reaction probably the multiple unsaturated fatty acid

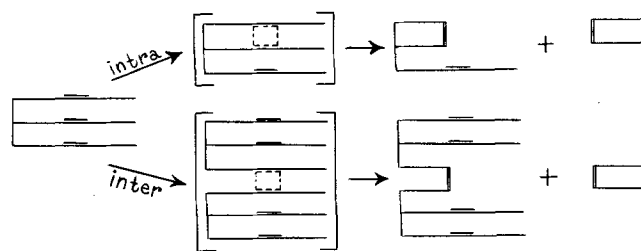


FIG. 1. Possible metathesis reactions of tri-olein.

groups react, after conjugation, according to an intermolecular Diels-Alder reaction (12).

An essential difference between the thermal polymerisation and the molecule enlargement by metathesis is the preservation of double bonds. While the thermal polymerisation lowers the iodine value considerably, this is not the case with metathesis, as no double bonds are consumed during this reaction. The iodine value might decrease when low boiling unsaturated hydrocarbons, formed during the reaction, escape from the reaction vessel. Table IV lists some physical data of fatty oils before and after metathesis and of the reaction products after removal of the alkenes. A significant decrease in drying time is affected by the metathesis of linseed oil.

DISCUSSION

The examples reported in this article show that the homogeneous metathesis of unsaturated fatty esters offers versatile possibilities for the synthesis of unsaturated symmetrical dicarboxylic acids and their derivatives. Joint reactions of unsaturated esters with alkenes allow the direct synthesis of their homologues. In this article, only the metathesis of some abundantly occurring esters has been discussed as examples for much wider and more general applications, for example: the synthesis of branched fatty acids by joint reactions of unsaturated esters with branched alkenes; reactions of low mol wt esters (acrylic, crotonic, vinylacetic, allylacetic, etc.); reactions of unsaturated dicarboxylic esters (maleic, fumaric, hydromuconic, etc.); and reactions of specific naturally occurring fatty esters (licanic, isanic, eleostearic, ricinoleic, sterculic, etc.).

These reactions, and the technological applicability of the reaction products, are now the subject of intensive research in our Institute.

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TABLE IV

Metathesis of Fatty Oils<sup>a</sup>

| Product                                   | $n_D^{20}$ | $d_4^{20}$ | Specific refraction | Iodine value | Saponific value | Drying time hr |
|---|------------|------------|---------------------|--------------|-----------------|----------------|
| Olive oil                                 | 1.4688     | 0.9132     | 0.3049              | 80           | 193             | -              |
| Id., after metathesis                     | 1.4688     | 0.9255     | 0.3008              | 72           | 193             | -              |
| Id., after distilling hydrocarbons formed | 1.4733     | 0.9393     | 0.2988              | 75           | 215             | -              |
| Soybean oil                               | 1.4749     | 0.9224     | 0.3052              | 136          | 191             | -              |
| Id., after metathesis                     | 1.4742     | 0.9258     | 0.3037              | 130          | 191             | -              |
| Id., after distilling hydrocarbons formed | 1.4757     | 0.9301     | 0.3031              | -            | 196             | -              |
| Linseed oil                               | 1.4811     | 0.9282     | 0.3067              | 190          | 195.5           | 150            |
| Id., after metathesis                     | 1.4800     | 0.9279     | 0.3062              | 185          | 195.5           | 100            |
| Id., after distilling hydrocarbons formed | 1.4820     | 0.9326     | 0.3057              | 181          | 205.5           | 50             |

<sup>a</sup>Reactions were carried out with 1.3% of an equimolar  $WCl_6 - Sn(CH_3)_4$  catalyst and heated for 2 hr at 383 K.

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