Metathesis of Unsaturated Fatty Acid Esters by a Homogeneous Tungsten Hexachloride–Tetramethyltin Catalyst

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Summary Metathesis of the methyl esters of certain unsaturated fatty acids using a tungsten hexachloride–tetramethyltin catalyst gave the expected alkenes and dicarboxylic acid dimethyl ethers.

Recently various successful attempts for the metathesis of internal alkenes and alk-1-enes have been reported.[1–4] The general scheme can be represented by reaction (1).

$$2\ R^1CH{=}CHR^2 \rightleftharpoons R^1CH{=}CHR^1 + R^2CH{=}CHR^2 \qquad (1)$$

However, the metathesis of alkenes carrying functional groups has not been described before.

We now report the metathesis of unsaturated fatty acid esters, which can be considered to be internal alkenes carrying a functional (ester) group. The catalyst used was tungsten hexachloride–tetramethyltin. In a current investigation on the catalytic properties of combinations of tungsten hexachloride with organometallic compounds this system proved to be of optimum selectivity and activity.

In the metathesis of methyl oleate (the methyl ester of *cis*-octadec-9-enoic acid) (**1**) and of methyl elaidate (the methyl ester of *trans*-octadec-9-enoic acid) (**2**), the products formed are octadec-9-ene (**3**) and the dimethyl ester of octadec-9-enedioic acid (**4**). This preparation of unsaturated symmetrical diesters (which are of importance in polymer chemistry) under mild reaction conditions from unsaturated esters may be of technological interest.

In a typical reaction, methyl oleate (**1**) [or methyl elaidate (**2**)] (3·14 ml) was added at 343 K to a mixture of chlorobenzene (14 ml), WCl_6 (0·12 g) and Me_4Sn (0·072 g). After 24 h no further conversion was observed. The results show a *ca.* 2 : 1 : 1 ratio of starting materials and products [reaction products in mol % for compound (**1**):(**1**) 50·8, (**3**) 25·7, (**4**) 23·5; for compound (**2**):(**2**) 48·0, (**3**) 25·5, (**4**) 26·5.] Reaction products were separated by gas chromatography and identified by n.m.r. and mass spectroscopy.

Under similar reaction conditions olive oil (which consists mainly of glyceryl trioleate) gives (**3**) as the main relatively volatile product. The dicarboxylic acid glyceryl esters formed are high boiling products that may consist of diglycerids (formed by *inter*molecular reaction of the starting material) or of monoglycerids (formed by *intra*molecular reaction of the starting material). The structure of these esters is under investigation. The yield of (**3**) related to the amount of oleic acid in the starting material was approximately 15 mol %.

When methyl linolate (*cis,cis*-octadeca-9,12-dienoic acid methyl ester) and methyl linolenate (*cis,cis,cis*-octadeca-9,12,15-trienoic acid methyl ester) are treated similarly almost no reaction is observed. However, equimolal mixtures of methyl linolate and methyl oleate or of methyl linolenate and methyl oleate are converted to a large extent into various reaction products. The possibility of using these reactions for the preparation of di- and tri-unsaturated hydrocarbons and dicarboxylic acid esters is being studied.

As an example of the cross reaction of methyl oleate with alkenes the reaction with hex-3-ene was studied. Apart from products resulting from the metathesis of methyl oleate the formation of dodec-3-ene and of dodec-9-enoic acid methyl ester was observed. The conversion of the starting materials amounted to 20 mol % after 18 h at 333 K.

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