Formation of Cyclohexa-1,4-diene by Metathesis of Linoleic and Linolenic esters

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Summary The metathesis of linoleic and linolenic esters with tungsten hexachloride–tetramethyltin as catalyst yields a considerable amount of cyclohexa-1,4-diene (up to 30 mol % of the reaction mixture in the case of methyl linolenate) along with alkenes, and monocarboxylic and dicarboxylic esters.

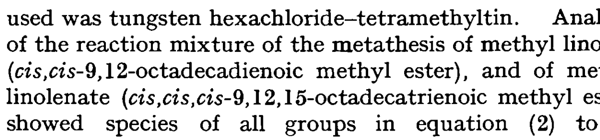
Recently Van Dam and his co-workers[1] reported the metathesis of unsaturated fatty acid esters using a tungsten hexachloride–tetramethyltin catalyst. In general metathesis of unsaturated hydrocarbons can be represented by equation (1).

$$\begin{array}{c} \mathrm{m}=\mathrm{n} \\ + \\ \mathrm{m}=\mathrm{n} \end{array} \rightleftharpoons \begin{array}{c} \mathrm{m} \\ \| \\ \mathrm{m} \end{array} + \begin{array}{c} \mathrm{n} \\ \| \\ \mathrm{n} \end{array} \qquad (1)$$

(where m and n are alkylidene groups)

It has also been shown, that the metathesis of alkadienes and higher polyenes may occur inter- or intra-molecularly resulting in acyclic alkenes and cycloalkenes, respectively.[2] By analogy with the above reaction scheme the metathesis of polyunsaturated fatty acid esters, p=q=r, can be described as a redistribution of alkylidene groups p (=CHR^1), carboxy alkylidene groups q (=CHR^{2}CO$_2$R^3), and alkyldiylidene groups r (=CHR^{4}CH=) [Equation (2)].

No work has been published so far on the formation of cyclohexa-1,4-diene by metathesis. The formation of cyclohexadienes by the metathesis of buta-1,3-diene reported by Heckelsberg and his co-workers[3] does not directly result from metathesis, but is due to cyclization of hexa-1,3,5-triene formed during the reaction.



(2)

We now report the formation of cyclohexa-1,4-diene by the metathesis of linoleic and linolenic esters. The catalyst used was tungsten hexachloride–tetramethyltin. Analysis of the reaction mixture of the metathesis of methyl linolate (*cis,cis*-9,12-octadecadienoic methyl ester), and of methyl linolenate (*cis,cis,cis*-9,12,15-octadecatrienoic methyl ester) showed species of all groups in equation (2) to be formed in the reaction. Cyclohexa-1,4-diene (r$\equiv$r) appeared to be very stable in the presence of the catalyst system; the isomer cyclohexa-1,3-diene was not observed. The statistical distribution of the terminal groups (p,q) resulting in a 1:2:1 molar ratio of the alkenes, monocarboxylic esters, and dicarboxylic esters was not disturbed by the formation of cycloalkenes.

In a typical reaction WCl$_6$ (0·114 g), and Me$_4$Sn (0·065 g) were added to methyl linolate (3·0 ml) in the absence of air and moisture. After 4 h at 353 K no further reaction was observed. Analysis of the reaction mixture showed 23 mol% alkenes, 46 mol% monocarboxylic esters, 23 mol% dicarboxylic esters, 6 mol% cyclohexa-1,4-diene, and 2 mol% higher cyclopolyenes. The conversion of the starting material was 84%. The reaction products were analysed by gas chromatography using a poly(propane-1,2-diol, 9-octadecenedioic acid)[4] stationary phase. By passing a nitrogen stream through the reaction mixture cyclohexa-1,4-diene was separated and identified by n.m.r. ($\delta_1 = 2{\cdot}66$ p.p.m., and $\delta_2 = 5{\cdot}68$ p.p.m.) and mass spectrometry ($m/e = 80$).

Under similar reaction conditions 95% methyl linolenate was converted. Analysis of the reaction mixture showed 15 mol% alkenes, 30 mol% monocarboxylic esters, 15 mol% dicarboxylic esters, 30 mol% cyclohexa-1,4-diene, and 10 mol% higher cyclopolyenes. Separation of cyclohexa-1,4-diene from the reaction mixture was difficult, because the equally volatile hex-3-ene was formed (the group p in methyl linolenate is a propylidene group).

The metathesis of linseed oil (which consists mainly of triglycerides of oleic, linoleic, and linolenic acid) gave alkenes, and cycloalkenes as the main relatively volatile products; cyclohexa-1,4-diene amounting to *ca.* 20 mol%.

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