

## Addition of Maleic Anhydride to Esters of Mono-unsaturated Fatty Acids

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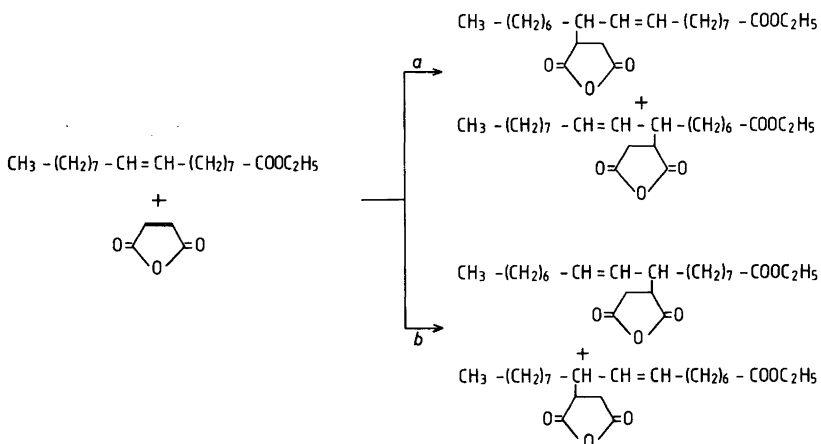
Maleic anhydride adds to ethyl oleate and ethyl elaidate at elevated temperatures to form 1:1 adducts. The product compositions of these reactions are clarified by oxidative cleavage of the remaining olefinic bond of the adducts and subsequent analysis of the products. In both cases, an addition reaction with retention of the double bond of the fatty acid competes with the ene reaction which is the expected mode of addition.

The reaction between maleic anhydride and unsaturated systems is well known and the process, when applied to fatty acids, is referred to by the term "maleinization".<sup>1</sup> The reactions which occur during maleinization fall into two major categories. With conjugated systems, capable of attaining a *cisoid* configuration of the double bonds, a Diels-Alder reaction takes place at 60–80 °C. With systems containing isolated double bonds, on the other

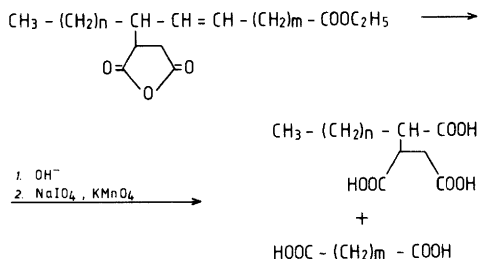
hand, temperatures around 200 °C are required and a complex mixture of products is usually obtained.

Early investigations showed that methyl oleate reacts with 1 mol, methyl linoleate with 2 mol and methyl linolenate with 2.5 mol of maleic anhydride at 200–210 °C.<sup>2</sup> Analysis indicated that the degree of unsaturation of the fatty acids was not affected by the reaction; the composition of the products, however, proved to be more difficult to elucidate.

Although the simplest maleinization, that of oleic acid, has been widely studied, neither the reaction mechanism, nor the product composition is clarified today. Two different routes leading to different reaction products have been proposed. In the first of these, the reaction occurs at the allylic positions in the fatty acid, leading to reaction products with the unsaturation retained at the 9–10-position (Scheme 1, reaction *a*).<sup>2,3</sup> By the alternative route, an ene reaction takes place, giving rise to products



Scheme 1. Maleinization of ethyl 9-octadecenoate proceeding by two different routes.



Scheme 2. Oxidative cleavage of the addition product of maleic anhydride and ethyl 9-octadecenoate.

where the double bond of the fatty acid has undergone an allylic shift (Scheme 1, reaction *b*),<sup>4,5</sup> It has also been claimed that both types of reactions take place simultaneously in the maleinization.<sup>6,7</sup> The present work aims at providing a contribution to the understanding of this process.

## RESULTS AND DISCUSSION

Ethyl oleate (ethyl *cis*-9-octadecenoate) was treated with maleic anhydride at 210 °C. The anhydride ring was opened with alkali and the reaction product was oxidized in an aqueous solution of periodate containing catalytic amounts of permanganate (Scheme 2).<sup>8</sup> Under these conditions, the olefins are readily cleaved to carboxylic acids.

If the addition of maleic anhydride proceeds according to reaction *a* of Scheme 1, the reaction sequence of Scheme 2 would give nonanoic acid and nonanedioic acid, as well as succinic acid derivatives from the substituted part of the ethyl oleate. If, on the other hand, the addition follows path *b* of Scheme 1, a mixture of octanoic acid and

octanedioic acid would be obtained along with succinic acid derivatives.

Analysis by GLC shows an approximate 1:2 ratio of cleavage products according to reactions *a* and *b* (Table 1). Obviously, the reaction is more complex than many related addition reactions.<sup>9</sup>

There seems to be two possible explanations of the product composition:

(1) The addition of maleic anhydride is purely a free radical chain reaction. Assuming a restricted rotation about the carbon-carbon bonds in the allyl radical residue,<sup>15</sup> two pairs of *cis-trans* isomers will be formed. After oxidative cleavage, a mixture of C-8 and C-9 carboxylic acids will be obtained (Scheme 3).

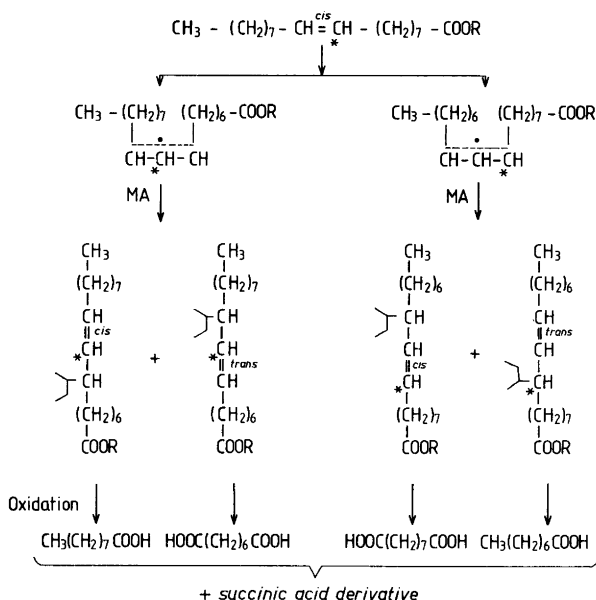
(2) An ene reaction takes place parallel to the free radical chain reaction of Scheme 3. The ene reaction gives only the cleavage products corresponding to a movement of the double bond, *i.e.* octanoic acid and octanedioic acid along with the succinic acid derivatives.

At first sight, the latter hypothesis, *i.e.* that of two simultaneous reactions, seems attractive since this would explain the predominance of the products resulting from migration of the olefinic bond in the fatty acid. However, since the double bond shifts of Scheme 3 involve changes from the original *cis* to the more stable *trans* configuration, the free radical chain route would also be expected to favour the formation of C-8 acid derivatives.

In order to obtain more information about the reaction mechanism, the maleinization was carried out with the ethyl ester of elaidic acid, the *trans* isomer of oleic acid. In a free radical chain reaction, there would, in this case, be no special driving force for a double bond shift since the double bond of the allylic starting material already possesses the *trans* configuration. Hence, if the reaction proceeds according to alternative (1) above, cleavage

Table 1. Relative amounts of C-8 and C-9 acids after maleinization of ethyl 9-octadecenoates and subsequent oxidative cleavage.

Starting products	Fission products (%)			
	Octanoic acid	Octanedioic acid	Nonanoic acid	Nonanedioic acid
Ethyl oleate	28	36	12	24
Ethyl elaidate	46	41	5	8
Ethyl oleate with radical inhibitor	41	42	6	11



Scheme 3. Addition of maleic anhydride (MA) to ethyl 9-octadecenoate by a free radical mechanism followed by oxidative cleavage of the adducts.

products derived from adducts with retention of the double bond (C-9 acids) would be expected to be at least equal in amount to those derived from adducts with an olefinic shift (C-8 acids).

In an ene reaction elaidic acid derivatives would be expected to react faster than their *cis* isomers with maleic anhydride.<sup>10</sup> Whereas the *trans* olefin can easily attain the favoured *exo* transition state, the *cis* isomer must react either *via* a sterically hindered *exo* approach or *via* an *endo* approach. This is reflected in a lower entropy of activation of the *trans* isomer.<sup>10</sup> Consequently, if the ene reaction contributes to the product composition, a higher ratio of C-8 to C-9 fission products, as compared with the reaction with ethyl oleate, would be expected.

The fission products obtained with ethyl elaidate after treatment with maleic anhydride and subsequent oxidation according to Scheme 2 appears from Table 1. In this case, the ratio of C-8 to C-9 acids is around 6:1, indicating a strong preference for the ene reaction. Although direct experimental proofs are lacking, it now seems reasonable to assume that the ene reaction contributes to the product composition also in the addition to the oleate ester. The relative amounts of ene reaction products *vs.* products from a free radical chain mechanism, however, cannot be

determined from these results.

The addition of maleic anhydride to ethyl oleate was also performed in the presence of 2,6-di-*tert*-butyl-4-methylphenol, which is known to be an efficient radical chain inhibitor. The ratio of C-8 to C-9 acids was then considerably increased compared to the reaction without inhibitor, as can be seen from Table 1. This result supports the view that the product composition is the result of two competing types of reaction. It is interesting that also in the presence of the phenolic inhibitor the free radical chain reaction takes place to a considerable extent.

Consequently, this work implies that the maleinization of the ethyl esters of 9-octadecenoic acids proceeds by two competing modes of addition: a stepwise reaction, having a free radical chain mechanism, and an ene reaction. This work does not differentiate between a concerted or a diradical mechanism of the latter reaction.

The fact that addition *via* a free radical chain mechanism competes so favourably with the ene reaction in the addition of maleic anhydride to ethyl oleate may seem surprising. Alder and coworkers, who were the first to recognize the two modes of addition, coined the terms "direkte" and "indirekte substituierende Additionen" to describe the addition

involving double bond retention and double bond shift, respectively.<sup>11</sup> They claim that "die indirekte substituierende Addition offenbar den Normalfall aller Anlagerungen von Maleinsäure-anhydrid an Monoolefin-kohlenwasserstoffe vorstellt". Even more categorical statements in favour of the ene reaction have been made by other authors.<sup>12</sup> However, the reactions described in Alder's works, as well as in later studies of the addition of maleic anhydride to monoolefins, where the product compositions have been clarified,<sup>9,13</sup> almost invariably involve olefins with terminal double bonds or with double bonds adjacent to a terminal methyl group. In both cases the ene reaction is particularly favoured: in the former structure because of reduced steric hindrance in the *suprafacial* approach of the reactants and in the latter structure because of the particular facility with which a primary hydrogen atom is abstracted.<sup>9</sup> On the other hand, the ene reaction is known to be promoted by electron-rich ene components with a high HOMO energy level, a fact which should favour disubstituted olefins.

The energy factor, however, has earlier been found to be over-shadowed by steric requirements in the formation of the transition state.<sup>10</sup> It may be that with relatively big ene components, having a *cis* double bond in a central position, the most favoured geometry of approach of the reactants is difficult to attain, thus enabling other modes of addition to take place.

The order of reactivity in the ene reaction of the *cis*- and *trans*-olefins found in this work is opposite to that suggested by Hoffmann for additions of maleic anhydride to olefins.<sup>9</sup> It is, however, in accordance with later kinetic studies of the ene reaction.<sup>10</sup>

In order to ensure that ethyl oleate does not undergo a *cis*, *trans* isomerization prior to reacting with maleic anhydride, a model experiment was carried out in which the ester was treated with phthalic anhydride under the same conditions as were used for maleic anhydride. After completed treatment, the starting materials were intact; GLC analysis showed no traces of ethyl elaidate.

## EXPERIMENTAL

*Addition of maleic anhydride to ethyl oleate and ethyl elaidate.* The ethyl ester of 9-octadecenoic acid (*cis* or *trans*, 6.21 g, 0.020 mol) was heated at 210–220 °C

with maleic anhydride (2.94 g, 0.030 mol) for 2 h in a nitrogen atmosphere under reflux.

*Oxidative cleavage of the adducts.*<sup>8</sup> The reaction product from the above addition was treated with 100 ml KOH in ethanol for 16 h at 23 °C. The solvent was evaporated, 1000 ml water was added, the pH was adjusted to 7.5–8.0 with HCl and a mixture of NaIO<sub>4</sub> (34.2 g, 0.16 mol) and KMnO<sub>4</sub> (1.69 g, 0.011 mol) was added. After 20 h at 23 °C, the solution was made acidic with 10% sulfuric acid and extracted with diethyl ether. The ether extract yielded 8.67 g of an oil.

*Analysis of the fission products.* The residue from the oxidative cleavage above was treated with ethanol (5.52 g, 0.12 mol) and dicyclohexylcarbodiimide (24.7 g, 0.12 mol) in pyridine (80 ml) in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.80 g). After 20 h at 23 °C, acetic acid (2 g) was added and the mixture was kept at 4 °C for 16 h. After the work-up procedure given in Ref. 14, an oily residue was obtained. GLC was performed using 3% SP-2310 on 100/120 mesh Supelcoport, a temperature profile of 8 °C/min and an interval of 80–200 °C. The pure ethyl esters of octanoic, nonanoic, octanedioic and nonanedioic acid were used as references.

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