

Summary

It has been shown that certain alkylbenzenes having a hydrogen atom on the alpha carbon atom react with maleic anhydride to form compounds analogous to the hydroperoxides produced by autoxidation of the alkylbenzenes. The structure of these products has been determined by oxidation with aqueous permanganate and the results have been applied, together with other data, to demonstrate that the reaction proceeds by a free radical chain mechanism involving the abstraction of a hydrogen atom from the alpha carbon atom. In view of the analogy between the products obtained in this investigation and in autoxidation, it is suggested that autoxidation is propagated in a similar manner.

Acknowledgment

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Autoxidation of Fats. II. Preparation and Oxidation of Methyl Oleate-Maleic Anhydride Adduct

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IN the first paper of this series (1) it was shown that maleic anhydride reacted with normal and secondary alkylbenzenes with the formation of substituted succinic acid anhydrides and that no reaction occurs with maleic anhydride and tertiary alkylbenzene. The point of attachment of maleic anhydride was found to be the alpha carbon atom of the alkyl group. Simultaneous saturation of the double bond of the maleic anhydride occurred. The configuration of these adducts is entirely analogous to the hydroperoxides formed during the autoxidation of the alkylbenzenes, namely, substitution with maleic anhydride rather than with oxygen. It was also shown that this reaction proceeded by the removal of a hydrogen atom from the alpha carbon atom propagated by a free radical chain mechanism.

A complete understanding of the autoxidation of fats cannot be expected until the products of autoxidation of the individual component fatty acids and the mechanism of their formation have been determined. The exact structure of the primary autoxidation products of methyl oleate is as yet unknown. Farmer and Sutton (2) have shown that the first isolable product is a hydroperoxide and have suggested that the —OOH group is attached to a carbon atom adjacent to a double bond. According to their original assumption, this product consisted of a mixture of C₈- and C₁₁-hydroperoxido oleates. Later, Farmer, Koch, and Sutton (3) proposed a free radical chain mechanism for this autoxidation involving a resonating 3-carbon system of the type



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and postulated that, "... there will be an approximately equal tendency for the —OOH group to appear at the positions 1 and 3 and for the double bond to remain at the original position or to appear at the adjacent C-C bond." Thus, methyl oleate should give four peroxido forms:

- (a) —C₁₁·C₁₀(OOH)·C₉:C₈—,
- (b) —C₁₁:C₁₀·C₉(OOH)·C₈—,
- (c) —C₁₁(OOH)·C₁₀:C₉·C₈—, and
- (d) —C₁₁·C₁₀:C₉·C₈(OOH)—.

Gunstone and Hilditch (4) disagree with this theory and believe that "... oxygen molecules are primarily attached to an ethenoid bond, and not to an adjacent methylene group, hydroperoxide formation finally taking place with the formation of a new ethenoid bond." If this latter assumption is correct, then only the two peroxido forms (a) and (b) mentioned above would be formed during the autoxidation of methyl oleate.

It is obvious that the solution of the problem relative to the peroxido forms produced by autoxidation of oleic acid lies in the identification of the exact position of the double bond in the hydroperoxides. The attempts to do this have not been entirely successful. Since mixtures of forms (a) and (b) yield the same products as forms (c) and (d) on oxidative fission, the work of Atherton and Hilditch (5), who used this method, only serves to prove that one or both of the above mixtures are present in the autoxidized acid or ester. Hydrogenation of both the hydroperoxide group and the double bond (2) yielded a mixture of monohydroxystearic acids which could not be separated and identified. If the peroxide group were more stable or if it were replaced by some stable group, oxidative fission would then yield the nine-carbon mono- and dicarboxylic acids from the mixture of

forms (c) and (d) but would yield the eight-carbon acids from the mixture of forms (a) and (b). Thus, fission of such a compound and identification of the mono- and dicarboxylic acids produced should clearly indicate the probable structures of methyl hydroperoxido oleate and provide information concerning the mechanism of its formation. The addition product of maleic anhydride and methyl oleate previously described by Bickford, Krauczunas, and Wheeler (6) appears to represent such a product.

There is a close analogy between the behavior of oxygen and maleic anhydride toward unsaturated compounds in general as has been pointed out by Farmer (7). Bickford *et al.* (6) demonstrated that maleic anhydride reacts with methyl oleate in a mole to mole ratio without saturating the double bond of the ester. Hoek and Lang (8) have shown that oxygen attacks alkylbenzenes, for example, ethylbenzene, in the alpha position to form a monohydroperoxide. The present authors have found that maleic anhydride also attacks, at low temperature, ethylbenzene (as well as toluene, cumene, cymene, etc.) in the position alpha to the double bond to form a substituted succinic anhydride. These observations parallel the work of Farmer (7), who found that the alpha methylene group in cyclohexene is attacked by maleic anhydride as well as by oxygen, the products being the corresponding substituted succinic anhydride and the hydroperoxide, respectively.

In brief, the salient points of similarity in the behavior of oxygen and maleic anhydride toward unsaturated compounds are (1) both reagents react with a conjugated diene to form six-membered rings, (2) both reagents are capable of inducing conjugation into a system of double bonds separated by a methylene group, (3) both reagents react with monothienoid compounds without affecting their unsaturation and yield alpha-substituted compounds, (4) both reagents react with alkylbenzenes to yield alpha-substituted products. In view of these facts it seems probable that the structures derived for maleic anhydride adducts will have a configuration analogous to those of the hydroperoxides of methyl oleate. Therefore, an account of the synthesis, properties, and structural proof of the methyl oleate-maleic anhydride adducts is presented herewith.

Before the work reported here was completed an article by Ross *et al.* (9) appeared describing an investigation of the structure of the maleic anhydride-methyl oleate adduct. In part, the present work substantiates the results of Ross *et al.*, that is, with respect to the migration of the double bond of methyl oleate during the reaction of this ester with maleic anhydride. However, the evidence presented here indicates that approximately half of the reaction product of maleic anhydride and methyl oleate is composed of two isomers in which no migration of the double bond away from the C₉-C₁₀ position occurred.

Experimental

Preparation of methyl oleate: Methyl oleate, I. V. 85.1, was prepared from pecan oil by the method of Wheeler and Riemenschneider (10)

Addition of methyl oleate to maleic anhydride: 1,600 g. (ca. 16 moles) of maleic anhydride and 450 g. (ca. 1.5 moles) of methyl oleate were mixed in a three-liter flask and the mixture was heated for 2 hours at 220°C. under a current of carbon dioxide.

After cooling to room temperature, the mixture was extracted three times with 700 ml. portions of carbon tetrachloride. After removal of the carbon tetrachloride by distillation, most of the unreacted maleic anhydride was removed by vacuum distillation. The residue, 644 g. of reddish brown viscous liquid, was esterified by refluxing for four hours with three liters of 1 N methanolic hydrogen chloride. The methanol was removed by distillation and the residue was allowed to stand overnight at room temperature. About 60 g. of dimethyl fumarate precipitated and was removed by filtration. Unesterified acids were removed by dissolving the residue in low boiling petroleum naphtha and washing the solution with 250 ml. of water, three 250-ml. portions of 2% sodium carbonate solution, and two 200-ml. portions of water. After drying over sodium sulfate the petroleum naphtha solution was distilled, first at atmospheric pressure to remove the petroleum naphtha and then at ca. 10 mm. to remove most of the dimethyl fumarate. The residue consisted of 532 g. of an orange-colored liquid.

This crude product was freed from methyl oleate and polymeric substances by fractional distillation at ca. 1 mm. pressure. The final product, 367 g., was a light yellow oil distilling at 196°-205°C. at 1 mm. pressure. Other properties of the product are given in Table 1.

TABLE 1
Properties of the Dimethyl Ester of Methyl Oleate-Maleic Anhydride Adduct

Property	Found	Calculated
Molecular weight, ¹	440	440.6
Iodine number, ²	56.7	57.7
Saponification equivalent.....	150.7	146.7
Density, g./ml.....	0.981	
Refractive index, n _D ²⁰	1.4593	
Molecular refractivity.....	122.8	122.4
Carbon, %.....	67.94	68.15
Hydrogen, %.....	9.98	10.07

¹ Molecular weight determined in benzene at several concentrations using the cryoscopic method.

² Iodine number determined by the Wijs method using a 30-minute reaction time.

Ozonization of methyl oleate-maleic anhydride adduct: 50 g. of the addition product was dissolved in 500 ml. of pentane in a 1-liter gas absorbing bottle having a fritted-glass inlet-tube. The mixture was cooled to -10°C. and maintained at this temperature while oxygen containing about 2% ozone was passed through it at the rate of 50 l. per hour for five hours. Completion of the reaction was indicated when the gas leaving the absorber rapidly liberated iodine from a potassium iodide solution. The ozonide separated as a viscous lower layer in the reaction flask.

Reductive fission of the ozonide: Sufficient alcohol (ca. 50 ml.) was added to bring the ozonides into solution in the alcohol-pentane mixture. This solution was added slowly to a suspension of 9 g. of Raney nickel in 150 ml. of pentane according to the procedure described by Cook and Whitmore (11). The temperature of the mixture was maintained at 35°C. until all the ozonide had been added, after which it was heated under reflux for two hours. Even under these reducing conditions some acids were formed and had to be separated from the aldehydes by extraction of the pentane solution with potassium bicarbonate solution. The pentane layer was then washed with dilute hydrochloric acid and water, dried with sodium

sulfate, and distilled, to remove the pentane. The neutral residue (32 g.) probably contained unreacted adduct and undecomposed ozonide in addition to aldehydes. The acid and aqueous washings were combined with the bicarbonate extracts, made strongly acid with sulfuric acid and the organic acids (23 g.) recovered by extraction with ethyl ether.

Attempts to fractionate the aldehydes were unsatisfactory. Hence, they were oxidized to the corresponding acids.

Peracetic acid oxidation of aldehydes: 135 ml. of 0.76 molar peracetic acid (dissolved in acetic acid-acetic anhydride solution) was added slowly with stirring to the above mentioned neutral product (32 g.) dissolved in 100 ml. of ether. The mixture was heated under reflux for two hours and then allowed to stand at room temperature for several days. The ether was removed under vacuum and the mixture was diluted with an equal volume of water and allowed to stand with frequent shakings until the acetic anhydride was hydrolyzed. The product, still containing any unreacted adduct, was recovered by extraction with ether. The material (24 g.) thus recovered was combined with the 23 g. of acids produced during fission.

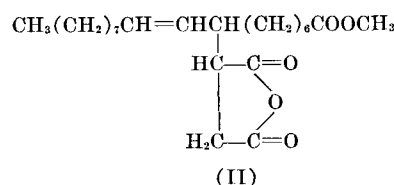
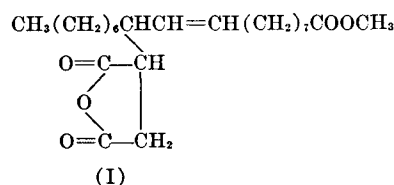
Esterification of acids: The combined product obtained as described above was dissolved in 500 ml. of absolute methanol and saturated with dry hydrogen chloride at 0°C. After standing overnight at room temperature, the solution was refluxed for 4 hours. Most of the methanol and hydrogen chloride was distilled off and the mixture diluted with twice its volume of ether, after which the unesterified acids were removed by washing with sodium bicarbonate solution and with water. The ethereal solution was dried over sodium sulfate, filtered, and evaporated under vacuum. The residual esters weighed 35 g.

Fractionation of esters: The methyl esters of the mono- and dicarboxylic acids were separated by fractional distillation from the tri- and tetracarboxylic acid esters and any unchanged adduct. Distillation was carried out with an electrically heated, air-jacketed column 40 cm. long, 1 cm. in diameter, and unobstructed except for a Nichrome spiral in contact with the wall. Four fractions were obtained corresponding to the characterizing data given in Tables 2 and 3.

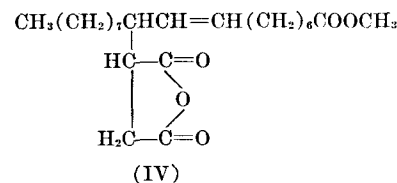
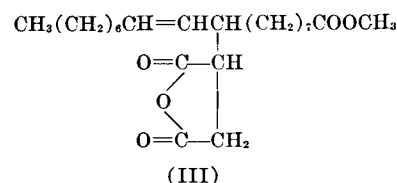
Discussion

The analytical data presented in Table 1 indicate that one mole of maleic anhydride combined under conditions specified with one mole of methyl oleate to produce a monounsaturated adduct which was isolated from the reaction mixture. The formation of nine-carbon atom acids on fission of the maleic anhydride-methyl oleate adduct indicates that part of the double bonds remained in the original C₉-C₁₀ position.

Obviously the point of attack of maleic anhydride could not have been at the C₉-C₁₀ double bond but was presumably in the alpha-position with respect to this center of unsaturation. The previous observation (1) that maleic anhydride does not attack unactivated C-H bonds would seem to exclude attack at some point farther removed from the double bond. The following are the probable structures of the adducts which yielded the nine-carbon-atom dibasic and monobasic acids.



That addition occurs between maleic anhydride and methyl oleate with attendant migration of part of the C₉-C₁₀ double bond of the oleate is confirmed by the isolation and identification of suberic and octanoic acids in the fission products of the adduct. This type of addition yields products in which the succinic acid anhydride residue is attached to the C₉- or the C₁₀-carbon atoms and the double bond of the ester has migrated to the C₁₀-C₁₁ or the C₈-C₉ positions, respectively. The configuration of these isomers may be represented as follows:



The occurrence of these two isomers does not necessarily support the theory of Gunstone and Hilditch

TABLE 2
Characteristics of Distilled Ester Fractions

Fraction No.	Boiling range at 10 mm. °C.	Wt. g.	Refractive index n _D ^{25°}	Neutral equivalent ¹	Calculated for		
					Ester	Refractive index n _D ^{25°2}	Neutral equivalent ¹
1.....	72-77	0.46	1.4170	143.4	Methyl octanoate	1.4178	144.2
2.....	87-99	0.65	1.4227	161.4	Methyl nonanoate	1.4220	153.2
3.....	118-130	1.29	1.4313	86.8	Dimethyl suberate	1.4325	87.3
4.....	133-144	1.54	1.4348	98.0	Dimethyl azelate	1.4347	94.4

¹ Neutral equivalents for corresponding free acid.

² Refractive indices calculated for 25°C. from values found in the literature.

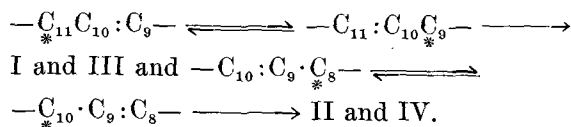
TABLE 3
 Identification of Distilled Ester Fractions

Fraction No.	Product	Identified as	M.P. °C.	Mixed m.p. ² °C.	Nitrogen	
					Found %	Calc. %
1	Methyl octanoate	Hydrazide	83.5-84.5 ¹	83.5-85.5	17.2	17.6
2	Methyl nonanoate	Hydrazide	92.5-93 ¹	91.5-93	16.4	16.3
3	Dimethyl suberate	Free acid	138.5-139.5	138.5-139.5
4	Dimethyl azelate	Free acid	99.5-120.5	99.5-102.5

¹Kyame, *et al.* (12) reported the melting point of octanoic, and nonanoic acid hydrazides to be 88.8-89°C. and 93.5-94.0°C., respectively.

²Mixed melting points determined using authentic samples of the corresponding compound.

(4) that addition occurs primarily at one of the carbon atoms attached to the double bond since only two of the four fission products isolated could be accounted for if the reaction proceeded according to their theory. The fact that compounds I, II, III, and IV are produced in nearly equal amounts, judged by the yields of the fission products, strongly supports the reaction mechanism proposed by Farmer, Koch, and Sutton (3). It appears, therefore, that the addition of maleic anhydride to methyl oleate probably proceeds by a mechanism involving the severance of one of the two activated C-H linkages adjacent to the double bond to form a resonating 3-carbon system in which there is an equal chance of addition of the maleic anhydride molecule at the 1- and 3-carbon atoms:



Forms I, II, III, and IV are analogous to the peroxido-forms (c), (d), (b), and (a), respectively. The present evidence does not indicate the mode of initiation of the reaction. In view of the similarity between the reactions of maleic anhydride and of oxygen with unsaturated compounds which are reported here and elsewhere, it is suggested that the free radical mechanism of autoxidation is correct and that four isomeric hydroperoxides are formed during the autoxidation of methyl oleate. These four isomers are represented by the forms (a), (b), (c), and (d) shown in the introduction.

Summary

The adduct of maleic anhydride and methyl oleate has been prepared and characterized. The physical

and chemical properties of the adduct indicate that it is composed of one mole of each of the reactants and that the double bond of methyl oleate has not been saturated. Oxidative fission of the adduct showed that the adduct consisted of a mixture of four isomers which yielded octanoic, nonanoic, suberic, and azelaic acids on ozonolysis. Isolation of these four acids from the fission products indicates that the addition reaction probably proceeds by a mechanism analogous to that proposed by Farmer, Koch, and Sutton for autoxidation. In view of the similarity between the reactions of maleic anhydride and oxygen with unsaturated compounds, the foregoing observations appear to support the free radical chain mechanism for the autoxidation of fats.

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