# Autoxidation of Fats. I. Preparation and Oxidation of Alkylbenzene-Maleic Anhydride Adducts

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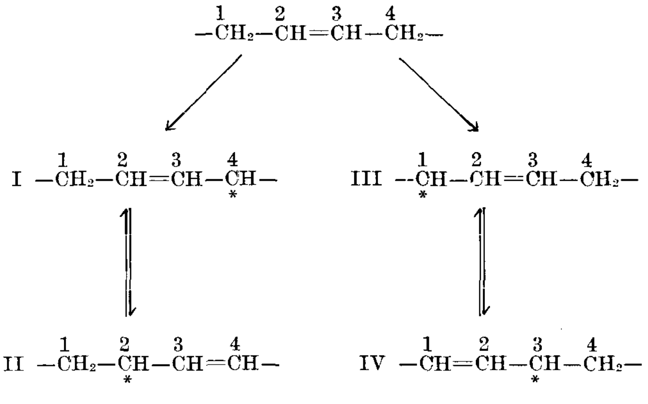
## Introduction

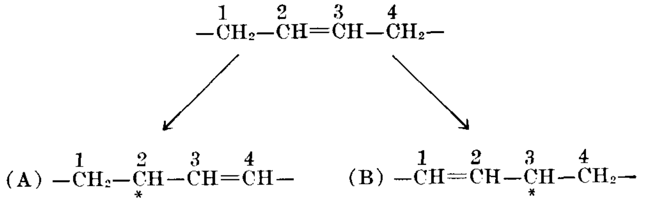
THE present and following article are concerned with the mechanism of autoxidation and its relation to autoxidizing fat systems. The results reported here and in the following article of this series proceed from an investigation of prototype double bond compounds, thence to the simplest unsaturated fatty acid (oleic) which is present in cottonseed and peanut oils, and finally to the more highly unsaturated fatty acids (linoleic and linolenic). The first report of this series is concerned with the preparation and oxidation of alkylbenzene-maleic anhydride adducts and with the interpretation of the probable mechanisms involved, especially in the light of the more recent concepts of autoxidation.

Farmer, Koch, and Sutton (1) have proposed a mechanism for autoxidation which involves the rupture of a C-H bond of an activated methylene group with the aid of energy derived from heat, light, or chemical reaction promoters. According to this concept of autoxidation, oxygen is attached to the free radical with the donation of a hydrogen atom from a nearby molecule thereby initiating a chain reaction which results in the formation of a monohydroperoxide. The hydroperoxido group (-OOH) is presumed to occupy an alpha-position with respect to the center of unsaturation. When resonance is possible these authors predicted but did not prove that four isomeric monohydroperoxides would be produced during the autoxidation of a labile system such as occurs in methyl oleate. This sequence of events may be illustrated as follows:



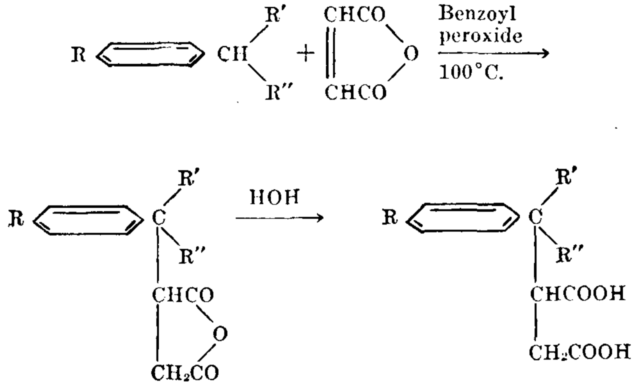
An entering substituent would attach itself to the free radical at the position holding the free electron, thus producing four isomeric addition products.

Two articles have appeared recently which assume that oxygen (2) and also maleic anhydride (3) react with alpha-methylenic compounds solely by a "shifting bond" mechanism. The proponents of this type of mechanism assume that the entering group adds directly to a double-bonded carbon atom and that the double bond then shifts away from the point of attack. This mechanism may be illustrated by the following:



Such a mechanism permits the formation of only two isomeric addition products which correspond to the free radical forms II and IV illustrated above. This mechanism cannot account for the observed reaction with methyl oleate or for any system in which there is no possibility for a displacement of the double bond.

Examples of the latter case are found in the work of Hock and Lang (4) who prepared the monohydroperoxides of ethylbenzene and xylene by autoxidation. Maleic anhydride reacts with these compounds in an analogous manner with the formation of monosuccinic anhydride derivatives. The nature of this type of reaction was established by an investigation of the reactivity of a series of alkylbenzenes having primary, secondary, and tertiary carbon atoms in the alpha position which were found to react with maleic anhydride in the presence of small amounts of benzoyl peroxide. The structure of the final products was confirmed by oxidation with aqueous permanganate. The addition reaction occurs in each case as illustrated by the following general equation:



## Experimental

*Materials:* The maleic anhydride, benzoyl peroxide, toluene, ethylbenzene, *p*-xylene, cumene, *p*-cymene, and *ter*-butylbenzene were purchased from reputable suppliers of high grade organic chemicals. The hydrocarbons which exhibited coloration in the presence of concentrated sulfuric acid were washed with cold concentrated sulfuric acid, potassium hydroxide solu-

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tion, and water, after which they were dried and fractionally distilled to obtain a constant boiling fraction.

*Preparation of adducts:* Ten grams of the maleic anhydride and a specified weight of benzoyl peroxide were dissolved in 200 ml. of the hydrocarbon. The solution was filtered into a 500-ml. round bottom flask which was then connected to a reflux condenser and maintained at the temperature of a boiling water bath. The content of free maleic anhydride was determined on 2.0 ml. samples of the reaction mixture, which were removed at regular intervals. Heating was continued until the content of the unreacted maleic anhydride indicated that the reaction had ceased. The cooled reaction mixture was transferred to a separatory funnel and extracted twice with 50 ml. portions of an aqueous solution of potassium hydroxide (15 g./100 ml. solutions). The alkaline extract was washed twice with ether to remove the unreacted hydrocarbon and then warmed on the steam bath under vacuum to remove the dissolved ether. The solution was slowly acidified with 30 ml. of concentrated hydrochloric acid and allowed to stand overnight, during which time the reaction product usually separated as a crystalline solid. The precipitate was filtered off, washed twice with 15 ml. of cold water, dried in a vacuum, and weighed. The product was then taken up in hot water or dilute alcohol, boiled with activated carbon, filtered, and allowed to stand until the product crystallized. Prior to analysis the product was recrystallized until there was no change in its melting point and neutralization equivalent. It was generally possible to recover additional but less pure crystalline reaction product by washing the mother liquor from the hydrochloric acid treatment with ether and working up the ether extract.

*Determination of maleic anhydride.* The concentration of maleic anhydride in the reaction mixture was determined iodimetrically by a method similar to that used in following the addition of maleic anhydride to fats (5, 6). The anhydrides produced in the reaction were not appreciably soluble in cold water and therefore did not interfere with the determination of maleic anhydride, which latter was true also of the small amount of benzoyl peroxide present.

*Oxidation:* The dicarboxylic acids produced by the above-described reaction were oxidized with neutral potassium permanganate. In general, two grams of the acid were refluxed for 5 hours with a solution of 14 g. of potassium permanganate in 600 ml. of water. After reduction of the excess permanganate and manganese dioxide, the product was isolated by extraction with ether. The crude product obtained by evaporating the ether was recrystallized from a suitable solvent until the melting point became constant.

## Results and Discussion

The data relative to the reaction of maleic anhydride with the various hydrocarbons are presented in Tables 1 and 2 and that for the oxidation of the resulting dicarboxylic acids appear in Table 3.

Reference to Table 1 shows the relative reactivities of the hydrocarbons toward maleic anhydride and the yield of crude product obtained in each case. The amounts of benzoyl peroxide used (usually less than 0.1 mole per mole of maleic anhydride) were those which in a preliminary investigation were found to give optimum results. Of the compounds investigated, ethylbenzene was found to be the most readily attacked. This observation parallels the experience of Hock and Lang (4), who found in a similar series of hydrocarbons the ethylbenzene was the most readily attacked by oxygen.

The neutral equivalents and elementary analyses reported in Table 2 confirm the identity of the reaction products. The fact that *ter*-butylbenzene failed to react with maleic anhydride under conditions which produced almost complete reaction with the other hydrocarbons indicates that the coupling with maleic anhydride occurs only at the carbon atom alpha to the ring and not at a nuclear or beta carbon atom. The identity of the benzylsuccinic acid was established by means of a mixed melting point with a known sample of this acid.

Further evidence that the alpha position is the point of attachment between the succinic residue and the hydrocarbon as well as for the structures of the resulting adducts was obtained by the oxidation of these compounds. As indicated in Table 3, oxidation of the adducts of both toluene and ethylbenzene gave benzoic acid while the adduct with *p*-xylene yielded terephthalic acid. These oxidation products are in accord with the structure given in Table 2.

The adduct from cumene was not oxidizable under these conditions. The fact that the unreacted reagents were recovered in this case indicates that only those compounds having a hydrogen on the alpha carbon atom are oxidized under these conditions.

*p*-Cymene contains two alpha carbon atoms which might be attacked by the maleic anhydride. If the methyl group were attacked, the reaction product would be analogous to the adduct obtained from *p*-xylene and would yield terephthalic acid on oxidation with potassium permanganate. If, however, the isopropyl group were attacked, the reaction product would be analogous to that obtained from cumene and only the methyl group would be oxidized by potassium permanganate to give a tricarboxylic acid. Since oxidation with potassium permanganate yielded the tricarboxylic acid described in Table 3 rather than terephthalic acid, it is obvious that the addition of maleic anhydride occurred at the isopropyl group.

The evidence presented here that maleic anhydride reacts with the hydrocarbons containing an alpha-methylene hydrogen and the oxidation of the resulting adducts clearly points to a mechanism involving the separation of a hydrogen from a C-H group.

The formation of 2,3-diphenyl butane during the reaction between ethylbenzene and maleic anhydride (see Table 1, footnote 2) points to the formation of the maleic anhydride adducts by a free radical reaction involving the phenethyl radical. The fact that the reaction proceeds nearly to completion in the presence of small amounts of benzoyl peroxide is indicative of a free radical chain reaction. The data on ethylbenzene correspond to chain lengths of 25 to 50, depending on the nature of the peroxide decomposition products. Further support for a free radical mechanism is furnished by the observation of Binapfl (7) that the reaction between alkylbenzenes and maleic anhydride can be promoted by high temperatures, and observations in this laboratory (8) that the reaction can also be promoted by ultraviolet light. In view of these facts it seems probable that the mechanism of the reaction can be represented by

TABLE 1

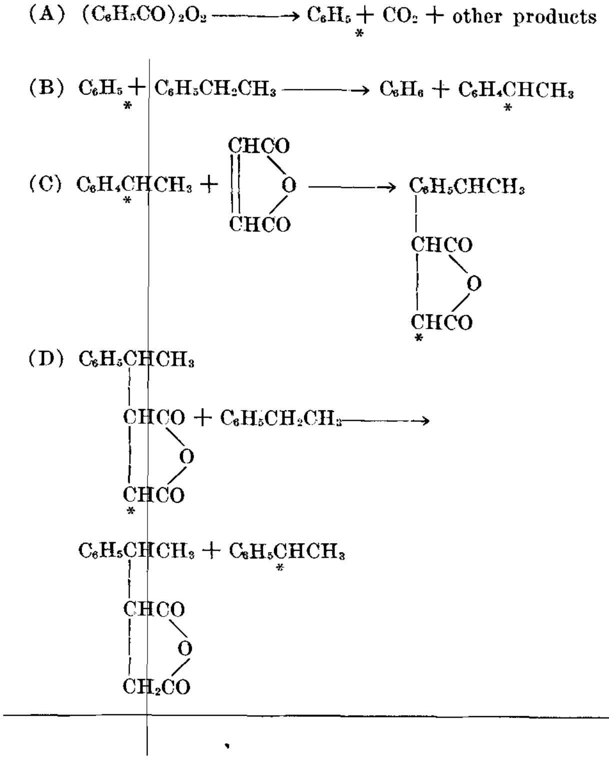
Reaction of Maleic Anhydride With Various Hydrocarbons [1]

| Hydrocarbon | Benzoyl peroxide added g. | Reaction time hrs. | Maleic anhydride reacted % | Reaction product | |
|---|---|---|---|---|---|
| | | | | Name | Yield, crude, % |
| Toluene | 5.0 | 0.0 | 0.0 | Benzylsuccinic acid | 38 |
| | | 0.50 | 36 | | |
| | | 1.0 | 73 | | |
| | | 2.0 | 81 | | |
| | | 3.0 | 84 | | |
| Ethylbenzene | 0.5 | 0.0 | 0.0 | 3-Phenyl-1,2-butanedicarboxylic acid [2] | 84 |
| | | 0.25 | 38 | | |
| | | 0.50 | 67 | | |
| | | 1.0 | 91 | | |
| | | 2.0 | 92 | | |
| *p*-Xylene | 2.0 | 0.0 | 0.0 | 3-(*p*-Tolyl)-1,2-propanedicarboxylic acid | 70 |
| | | 0.25 | 48 | | |
| | | 0.50 | 76 | | |
| | | 1.0 | 91 | | |
| | | 2.0 | 91 | | |
| Cumene | 2.0 | 0.0 | 0.0 | 3-Methyl-3-phenyl-1,2-butanedicarboxylic acid | 57 |
| | | 0.25 | 57 | | |
| | | 0.50 | 78 | | |
| | | 1.0 | 91 | | |
| | | 2.0 | 90 | | |
| Cymene | 0.5 | 0.0 | 0.0 | 3-Methyl-3-(*p*-tolyl)-1,2-butanedicarboxylic acid | 72 |
| | | 0.50 | 60 | | |
| | | 1.0 | 71 | | |
| | | 2.0 | 83 | | |
| | | 3.0 | 83 | | |
| *t*-Butylbenzene | 1.0 | 0.0 | 0.0 | none | 0 |
| | | 1.0 | 2 | | |
| | | 2.0 | 2 | | |

[1] 200 ml. hydrocarbon, 10.0 g. maleic anhydride, and benzoyl peroxide heated at 100 ± 1°C.

[2] 2,3-Diphenylbutane was also isolated from this reaction; m.p. 127°C., found carbon 91.27%, hydrogen 8.60%; calculated carbon 91.43%, hydrogen 8.57%.

the following scheme in which ethylbenzene is used for illustration:



$$\text{(A)}\quad (C_6H_5CO)_2O_2 \longrightarrow \underset{*}{C_6H_5} + CO_2 + \text{other products}$$

$$\text{(B)}\quad \underset{*}{C_6H_5} + C_6H_5CH_2CH_3 \longrightarrow C_6H_6 + \underset{*}{C_6H_4CHCH_3}$$

The chain reaction is propagated by reactions C and D, and is terminated by the reaction,

$$2\underset{*}{C_6H_5CHCH_3} \longrightarrow C_6H_5CH(CH_3)CH(CH_3)C_6H_5{}_{*}.$$

Reaction B would be favored by the large excess of hydrocarbon. Reaction of the phenethyl radical with the solvent simply results in transfer of hydrogen from one molecule to another without change in the number of free phenethyl radicals present, therefore, this radical can persist long enough to react with maleic anhydride as shown in reaction C. The stability of the phenethyl radical is also enhanced by resonance (9). Reaction D will again be favored by the large excess of hydrocarbon.

Since the products obtained by the reaction of maleic anhydride and alkyl hydrocarbons are analogous to those obtained by Hock and Lang (4) in the autoxidation of these compounds, it seems reasonable to assume that a similar free radical chain mechanism, initiated by removal of hydrogen from the alpha carbon atom, is operative in autoxidations. In view of the fact that only those compounds having a hydrogen atom on the alpha carbon atom were attacked by potassium permanganate, it seems likely that the removal of this hydrogen to form a free radical is an intermediate step even in oxidation with strong oxidizing agents.

TABLE 3

Properties of the Oxidation Products of the Dibasic Acids

| Dibasic acid | Oxidation product | | N.E. | |
|---|---|---|---|---|
| | Name | m.p. °C. | Found | Calculated |
| Benzylsuccinic | Benzoic acid | 121.6-122.2 [1] | 122.3 | 122.1 |
| 3-Phenyl-1,2-butanedicarboxylic acid | Benzoic acid | 121.6-122.2 [1] | 122.3 | 122.1 |
| 3-(*p-Tolyl*)-1,2-propanedicarboxylic acid | Terephthalic acid | Sublimes 300 [2] | 83.9 | 83.1 |
| 3-Methyl-3-phenyl-1,2-butanedicarboxylic acid | None [3] | | | |
| 3-Methyl-3-(*p-tolyl*)-1,2-butanedicarboxylic acid | 3-Methyl-3-(*p*-carboxyphenyl)-1,2-butanedicarboxylic acid | 227-228.5 | 94.4 | 93.4 |

[1] Mixed m.p. with authentic sample was 121.6-122.5°C.

[2] M.p. of dimethyl ester, 140°C.

[3] Original reagents recovered unchanged.

While it is quite possible that the autoxidation of fats may proceed by addition of oxygen at the double bond, there would appear to be no necessity for postulating such a reaction since it has been demonstrated that free radical chain reactions are readily propagated by the removal of a hydrogen from an alpha methylene group of such compounds.

TABLE 2

Properties of Dibasic Acids

| Dibasic acid | | | Found | | | Calculated | | |
|---|---|---|---|---|---|---|---|---|
| Name | Formula | m.p. °C. | N.E. | Carbon % | Hydrogen % | N.E. | Carbon % | Hydrogen % |
| Benzylsuccinic | $C_9H_{10}(COOH)_2$ | 161-161.5 [1] | 104.1 | 63.45 | 5.82 | 104.6 | 63.72 | 5.93 |
| 3-Phenyl-1,2-butanedicarboxylic | $C_{10}H_{12}(COOH)_2$ | 146-149 [1, 2] | 111.6 | 64.87 | 6.30 | 111.1 | 64.85 | 6.35 |
| 3-(*p*-Tolyl)-propanedicarboxylic | $C_{10}H_{12}(COOH)_2$ | 114-115 [1] | 112.1 | 64.85 | 6.43 | 111.1 | 64.85 | 6.35 |
| 3-Methyl-3-phenyl-1,2-butanedicarboxylic | $C_{11}H_{14}(COOH)_2$ | 150-151 [1] | 118.7 | 66.05 | 6.85 | 118.2 | 66.03 | 6.83 |
| 3-Methyl-3-(*p*-tolyl)-1,2-butanedicarboxylic | $C_{12}H_{16}(COOH)_2$ | 192-193 [3] | 125.3 | 67.25 | 7.33 | 125.2 | 67.18 | 7.25 |

[1] After recrystallization from water.

[2] Mixture of all four optical isomers.

[3] After recrystallization from ethanol-water (30:70).

### 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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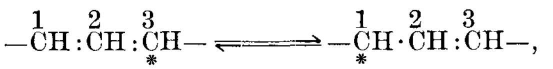
IN the first paper of this series (1) it was shown that maleic anhydride reacted with normal and secondary alkylbenzenes with the formation of substituted succinic acid anhydrides and that no reaction occurs with maleic anhydride and tertiary alkylbenzene. The point of attachment of maleic anhydride 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 $C_8$- and $C_{11}$-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



$$-\overset{1}{\mathrm{CH}}:\overset{2}{\mathrm{CH}}:\underset{*}{\overset{3}{\mathrm{C}}}\mathrm{H}- \rightleftharpoons -\underset{*}{\overset{1}{\mathrm{C}}}\mathrm{H}\cdot\overset{2}{\mathrm{CH}}:\overset{3}{\mathrm{CH}}-,$$

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) $-C_{11}\cdot C_{10}(OOH)\cdot C_9:C_8-$,
(b) $-C_{11}:C_{10}\cdot C_9(OOH)\cdot C_8-$,
(c) $-C_{11}(OOH)\cdot C_{10}:C_9\cdot C_8-$, and
(d) $-C_{11}\cdot C_{10}:C_9\cdot C_8(OOH)-$.

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 than 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

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