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# The Reactions of Hydrogen Bromide with Oleic Acid and Its Esters. II. Free Radical Addition[1]

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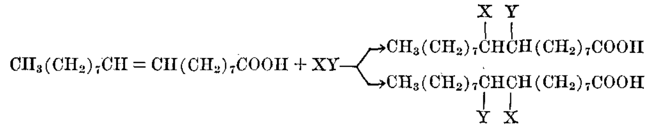
ADDITION of unsymmetrical reagents to the 9,10-double bond of oleic acid can yield a mixture of two-position isomers:



$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH + XY \rightarrow \begin{cases} CH_3(CH_2)_7\overset{X}{\overset{|}{C}}H\overset{Y}{\overset{|}{C}}H(CH_2)_7COOH \\ CH_3(CH_2)_7\underset{Y}{\underset{|}{C}}H\underset{X}{\underset{|}{C}}H(CH_2)_7COOH \end{cases}$$

In the majority of reactions with unsymmetrical reagents that have been reported the resultant mixtures were not separated. The authors assumed an even distribution at the center since the double bond was too far removed from the carboxyl group to be influenced by means of inductive or other effects. However several reports have appeared in the literature within the last few years where a difference in reactivity at the 9- and 10-carbon atom was observed with derivatives of oleic acid (1, 2, 3). The catalytic hydrogenation of 9,10-epoxystearic acid yielding only 10-hydroxystearic acid was an outstanding example of this type of reaction (4).

In the field of unsaturated fatty acids and their derivatives few investigations have been conducted to study the effect of variations of experimental conditions in addition reactions with hydrogen halides. The formation of chloro-, bromo-, and iodostearic acids by the action of the concentrated inorganic acids on either oleic or elaidic acid were first reported by Piotrowski (5) in 1890. The preparation of fluorostearic acid by the action of hydrogen fluoride in the presence of mercuric chloride was reported more recently (6). The products obtained in all of these reactions were reported as mixtures of the 9- and 10-isomers without regard to the composition of the mixture. After the discovery of the peroxide effect by Kharasch and Mayo (7) some of the simpler fatty acids with terminal double bonds were investigated in hydrogen bromide addition reactions under ionic and free radical conditions (8, 9, 10). However no investigations have been reported on the direction of addition of hydrogen halides to the naturally occurring 18-carbon unsaturated fatty acids.

It was the purpose of our investigation to examine, under closely controlled conditions, one particular addition reaction, namely, the addition of hydrogen bromide to esters of oleic acid. Hydrogen bromide was chosen since it allowed addition under both free radical and ionic conditions. In this paper we are reporting the effects of variations of solvents, dilutions, and temperature on the relative reactivity at the 9- and 10-position of a series of oleate esters when the addition is carried out under free radical conditions.

## Experimental

RAW MATERIALS. Pure *methyl oleate* was prepared by the method described by Swern (11). A major portion of the ester was converted to the urea complex for easier preservation (12).

*Anal.* Calcd. for $C_{19}H_{36}O_2$: S.E., 296; I.V. 85.6. Found: S.E., 295; I.V., 85.8.

*Oleic acid* was prepared by saponifying methyl oleate with 2 N alcoholic potassium hydroxide for two hours under nitrogen.

*Anal.* Calcd. for $C_{18}H_{34}O_2$: Neutral Equivalent 382; I.V., 90.0. Found: Neutral Equivalent, 281; I.V., 89.6.

Esters of oleic were prepared, using a Schotten-Baumann procedure by the action of oleoyl chloride on the alcohol which was dissolved in an inert organic solvent containing pyridine as the hydrogen chloride acceptor.

*Preparation of Oleoyl Chloride.* Oleic acid (84.6 g., .30 mole) was allowed to react with oxallyl chloride (95.1 g., .75 mole) at room temperature and then allowed to reflux one hour. The excess oxallyl chloride was distilled off yielding oleoyl chloride (88.0 g., .29 mole, 98%) which was then distilled, b.p. 185–190°C. at 7–10 mm.; reported b.p. 213°C. at 14.5 mm. (13).

*Anal.* Calcd. for $C_{18}H_{33}O_{10}$: % free oleic acid, 0.0. Found: % free oleic acid, 0.0 (13a).

*Preparation of Phenyl Oleate* (14, 15).

Oleoyl chloride (3 g., .01 mole) dissolved in dry ether was added slowly to phenol (0.94 g., .01 mole) and 1.65 ml. pyridine (1.60 g., 0.2 mole). A precipitate was formed and the temperature rose to *ca.* 40°C. The reaction mixture was allowed to stand for half an hour and then was filtered. Water was added and the solution extracted twice with ethyl ether. The ether solution was washed consecutively with water, dilute hydrochloride acid, water, dilute sodium hydroxide and water and then dried over anhydrous sodium sulfate. The solvent was stripped, yielding phenyl oleate (2 g., .0056 mole, 56%) and containing a trace of oleic acid. Saponification equivalent, theoretical 358, found 361.

The material had a slightly yellow color. By dissolving it in ethyl alcohol and removing a small amount of insoluble material, the ester could be recovered as a colorless oil (1.9 g., .00053 mole, 53%). Reported 55% (14).

*Anal.* Calcd. for $C_{24}H_{33}O_2$: S.E., 357; I.V., 70.9. Found: S.E., 357; I.V., 71.2.

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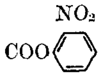
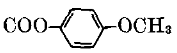
[1] This paper comprises parts of a dissertation submitted by Eric Jungermann in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

Free Radical Addition Reactions

| No. | Olefin $C_{17}H_{33}X$ X | Solvent | Dilution %* | Catalyst | Temp. °C. | Dicarboxylic acids as ml. 0.1 N NaOH | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_{10}$ | $C_9$ | $C_8$ |
| 1 | $COOCH_3$ | $C_6H_6$ | 10 | u.v.[a] | 25–30 | .311<br>.279<br>.304 | .638<br>.572<br>.604 | .317<br>.281<br>.298 |
| 2 | $COOCH_3$ | $C_6H_6$ | 5 | u.v. | 25–30 | .194<br>.321 | .399<br>.658 | .183<br>.327 |
| 3 | $COOCH_3$ | $C_6H_6$ | 2 | u.v. | 25–30 | .319<br>.278 | .647<br>.562 | .322<br>.271 |
| 4 | $COOCH_3$ | $C_6H_6$ | 1 | u.v. | 25–30 | .276<br>.309 | .571<br>.615 | .294<br>.301 |
| 5 | $COOCH_3$ | $C_6H_6$ | 0.3 | u.v. | 25–30 | .288<br>.347 | .581<br>.697 | .284<br>.348 |
| 6 | $COOCH_3$ | $C_6H_6$ | 1 | u.v. | 50–53 | .291<br>.264 | .603<br>.547 | .283<br>.262 |
| 7 | $COOCH_3$ | $C_6H_6$ | 1 | u.v. | 80 | .246<br>.312 | .693<br>.726 | .241<br>.317 |
| 8 | $COOCH_3$ | $C_6H_6$ | 1 | b.p.[b] | 25–30 | .358<br>.283 | .724<br>.576 | .355<br>.290 |
| 9 | $COOCH_3$ | $C_6H_6$ | 1 | b.p. | 25–30 | .300<br>.264 | .631<br>.541 | .318<br>.263 |
| 10 | $COOCH_3$ | None | 1 | p.b.[c] | 25–30 | .299<br>.196 | .606<br>.410 | .304<br>.203 |
| 11 | $COOCH_3$ | $C_6H_5NO_2$ | 1 | b.p. | 25–30 | .288<br>.339 | .563<br>.659 | .278<br>.342 |
| 12 | $COOCH_3$ | $C_6H_5Br$ | 1 | b.p. | 25–30 | .317<br>.293 | .643<br>.602 | .325<br>.297 |
| 13 | $COOCH_3$ | $CHCl_3$ | 1 | b.p. | 25–30 | .409<br>.279 | .783<br>.553 | .384<br>.284 |
| 14 | $COOCH_3$ | Skellysolve C | 1 | b.p. | 25–30 | .341<br>.217 | .688<br>.4333 | .345<br>.209 |
| 15 | $COOCH_3$ | None | 100 | b.p. | 25–30 | .274<br>.334 | .568<br>.713 | .273<br>.346 |
| 16 | $COOH$ | $C_6H_6$ | 1 | u.v. | 25–30 | .345<br>.269 | .701<br>.543 | .334<br>.279 |
| 17 | $COOC_6H_5$ | $C_6H_6$ | 1 | b.p. | 25–30 | .264<br>.307<br>.337 | .538<br>.624<br>.677 | .258<br>.299<br>.314 |
| 18 |  | $C_6H_6$ | 1 | b.p. | 25–30 | .283<br>.192 | .581<br>.397 | .288<br>.183 |
| 19 |  | $C_6H_6$ | 1 | b.p. | 25–30 | .281<br>.233 | .572<br>.484 | .284<br>.241 |

* % Dilution is expressed as $\frac{\text{g. olefin} \times 100}{\text{ml. solvent}}$

[a] Ultraviolet radiation (u.v.).

[b] Benzoyl peroxide (b.p.).

[c] Perbenzoic acid (p.b.).

In the above series of experiments the following variables were examined: dilution, experiments 1–5; temperature, experiments 4, 6–7; free radical catalysts, experiments 4, 8–10; solvents, experiments 4, *11–15; and ester group,* experiments 4, 16–19.

The following esters of oleic acid were prepared by the general procedure described for phenyl oleate:

| Ester | Theoretical | | | | |
|---|---|---|---|---|---|
| | S.E.[a] | I.V.[b] | %C | %H | %N |
| Benzyl | 372 | 68.2 | — | — | — |
| *p*-Methoxyphenyl | 388 | 65.4 | 72.32 | 10.30 | — |
| *p*-Nitrophenyl | 403 | 63.0 | — | — | 3.47 |
| *Tert*-butyl | 338 | 75.0 | 78.10 | 12.42 | — |
| *O*-nitrophenyl | 403 | 63.0 | — | — | 3.47 |

| Ester | Found | | | | |
|---|---|---|---|---|---|
| | S.E. | I.V. | %C | %H | %N |
| Benzyl | 370 | 68.5 | — | — | — |
| *p*-Methoxyphenyl | 389 | 64.8 | 72.15 | 10.24 | — |
| *p*-Nitrophenyl | 401 | 62.9 | — | — | 3.46 |
| *Tert*-butyl | 338 | 74.4 | 77.93 | 12.35 | — |
| *O*-nitrophenyl | 402 | 63.2 | — | — | 3.50 |

[a] S.E., saponification equivalent.
[b] I.V., iodine value.

Determination on the free acid values of purified esters indicated that no free fatty acid was present.

All the compounds were analyzed for *trans* isomer by infrared procedures (15a); it was found that they were all free of *trans* isomer.

## Method of Addition of Hydrogen Bromide Under Free Radical Conditions

The reactions were carried out in a quartz flask equipped with a fritted glass inlet tube, a thermometer and a condenser. The olefin and catalyst were dissolved in the solvent and hydrogen bromide gas was bubbled through the solution. The following example illustrates this method:

Methyl oleate (2.0 g., .0067 mole) was dissolved in 200 ml. benzene and placed in the apparatus described above. The quartz flask containing the solution was irradiated with a mercury arc lamp. Hydrogen bromide gas was bubbled through the solution for two hours keeping the temperature between 25–30°C., by external cooling. At the end of the reaction, the solution was washed with water until the washings were neutral, dried over anhydrous sodium sulfate, filtered and the solvent taken off *in vacuo*. Methyl bromostearate (2.40 g., .0064 mole, 95%) was obtained as an oil.

*Anal.* Calcd. for $C_{19}H_{37}BrO_2$: Acid value, 0; I.V., 0; Br, 21.22. Found: Acid value, 0; I.V., 1.0; Br. 21.01.

*Analysis of the Mixture of 9- and 10-Bromo-Esters.* A method for analyzing mixtures of 9- and 10-bromostearates is being submitted for publication (16). It involved the following steps.

1. Dehydrobromination by the method of Sherrill *et al.* (17).

2. Oxidation of the resultant mixed octadecenoic acids with a permanganate-periodate reagent to the mono- and dicarboxylic acids (18, 19).

3. Separation of the mono- and dicarboxylic acids followed by analysis of the mixture of dicarboxylic acids by a standard chromatographic procedure (20).

## Results and Discussion

Kharasch and Mayo (7) found that hydrogen bromide can add to a carbon-carbon double bond by either a free radical or an ionic mechanism. The duality of this mechanism helped to explain many of the deviations reported by earlier workers from the "Markownikoff rule" when hydrogen bromide was used in addition reactions with an unsymmetrical olefin.

The mechanism by which the free radical addition of hydrogen bromide to an olefin proceeds in the presence of oxygen or a peroxide is usually represented as follows:

$$HBr + O_2 \longrightarrow HOO\cdot + Br\cdot$$

$$\text{or } HBr + \text{Peroxide} \longrightarrow (H\cdot\text{peroxide}) + Br\cdot$$

$$Br\cdot + RCH = CH_2 \longrightarrow R\dot{C}H - CH_2Br$$

$$R\dot{C}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br\cdot$$

In the field of monounsaturated fatty acids, the addition of hydrogen bromide under controlled reaction conditions was investigated in only a few isolated instances. Only compounds where the double bond was at the extremes of the carbon chain (9, 10) were examined. No results are reported on compounds where the double bond is at the center of the chain. The possibility that in naturally occurring 18-carbon fatty materials some directional effects might be functioning at the center of the chain had been indicated earlier (1–4, 21, 22).

Kharasch, Mayo (7, 23) and Goering (24, 25) had carefully examined the effects of catalysts, solvent, and temperature on the free radical addition of hydrogen bromide to olefins with terminal double bonds. When hydrogen bromide is added to a double bond, two competing and independent reactions take place proceeding by two different mechanisms: free radical and ionic. Hence, when attempting examination by only one of these mechanisms, care must be taken to exclude the other mechanism as completely as possible by the use of suitable catalysts and/or inhibitors.

In studying the reaction of methyl oleate with hydrogen bromide, various free radical catalysts such as benzoyl peroxide, ultraviolet radiation, or perbenzoic acid, were used. On finding that these catalysts seemed equally efficient, the effect of variations in the solvent, the concentration, the temperature of reaction, and the ester group were evaluated. The results obtained are shown in the table below. The experiments were usually run in duplicate, occasionally in triplicate. The relative amounts of the dicarboxylic acids found are shown in terms of the total volume of N/10 sodium hydroxide required in the titration of the corresponding fractions from the chromatographic column.

One point immediately becomes clear after only a cursory examination of these results: in all oxidations essentially equal amounts of suberic and sebacic acids were formed; henceforth the original mixture of 9- and 10-bromostearates represented a 50:50 distribution of the position isomers. This indicates that the addition at the double bond was independent of the polarity of the solvent and of the configuration and electrical properties of the ester groups. Furthermore the three free radical catalysts were equally efficient. Only one result needs any amplification: in experiment No. 7, when the hydrogen bromide was added at the reflux temperature of the solvent, the reaction did not go to completion. This was indicated by the amount of azelaic acid detected which exceeded the sum of the other two dibasic acids by a considerable amount, proportional to the amount of unreacted methyl oleate.

The major conclusion that can be drawn from these free radical addition reactions is that here the 9,10-double bond is not affected by the terminal group but is similar in reactivity to the double bond in 9-octadecene. The mechanism of these free radical reactions can therefore be represented in accordance with the concepts of Kharasch (7), Mayo (23), and Waters (26).

## Summary

Oleic acid and a series of its esters were reacted with hydrogen bromide under conditions favoring addition by a free radical mechanism. Variations of the solvents, catalysts, temperatures, dilution, and the ester groups were investigated. Under all conditions a statistical 50:50 distribution of position isomers was found.

## Acknowledgment

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# Positional Isomers Formed During the Hydrogenation of Cottonseed Oil[1]

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EARLY in the history of the hydrogenation of glycerides and their derivatives one finds reports of the migration of double bonds during hydrogenation. Lewkowitsch (14) claimed that iso-oleic acid was formed by the catalytic reduction of oleic acid under certain conditions and suggested that iso-oleic acid was a positional isomer of oleic acid. Later Moore (15), Hilditch and Vidyarthi (13), and others demonstrated the presence of positional isomers in partially hydrogenated methyl oleate or oleic acid as well as in hydrogenated linoleates. Compounds having double bonds in the 8-, 10-, and 11-position were reported. Invariably it was shown that one or more positional isomers of the oleoyl group were present in the reaction products. Because of serious limitations in the methods of analysis, no attempt was made to identify all of the isomers present.

Recently with the aid of improved methods of analysis, the migration of double bonds in several unsaturated fatty acids or their methyl esters has been followed quantitatively. Boelhouwer and co-workers (8) determined the positions of the double bonds in progressively hydrogenated samples of methyl oleate, elaidinate, petroselinate, and linoleate. Allen and Kiess investigated the migration of double bonds and the formation of *trans* isomers during the hydrogenation of oleic acid and methyl oleate (3) and linoleic acid and methyl linoleate (2). In another investigation Allen (1) established the manner in which methyl *cis*-10, *cis*-12-octadecadienoate undergoes hydrogenation to form *cis*-10-, *trans*-11-, and *cis*-12-octadecenoates.

Heretofore the improved methods of analysis for establishing the position of double bonds have not been utilized to follow the hydrogenation of a natural oil or any triglyceride. While triglycerides would be expected to behave on hydrogenation like methyl esters, we have found differences (10, 11). Under comparable operating conditions triglycerides apparently hydrogenate much less rapidly than do methyl esters, and the amount of *trans* isomers formed is considerably less. In the current investigation the extent of the migration of double bonds during the hydrogenation of cottonseed oil is established. In addition, it is shown what influence the conditions of hydrogenation have on the extent of migration and the amount of *trans* isomers formed.

## Experimental

*Materials.* The cottonseed oil used in the experiments was a commercially refined, bleached, and deodorized product. It was fresh oil, being obtained from the processor shortly after its production from seed grown in the current crop year. In all respects the oil was a normal product, having the following characteristics:

| | |
|---|---|
| Iodine value | 109.7 |
| Free fatty acids, as oleic, % | 0.04 |
| Saponification value | 196.4 |
| Unsaponifiables, % | 0.48 |
| Content of linoleins, as trilinolein, % | 49.6 |
| Content of oleins, as triolein, % | 27.6 |
| Content of saturates, as trisaturates, % | 22.8 |

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