The Oxidation of Monoethenoid Fatty Acids and Esters. Catalytic Oxidation of n-*Propyl Oleate. The Oxidation Products.*

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The products of catalytic oxidation at 55°, 85°, and 120° of *n*-propyl oleate by gaseous oxygen have been resolved. The main products resulting from transformation or decomposition of the initially formed hydroperoxides are 9 : 10-epoxy- and 9 : 10-dihydroxy-stearic acids, unsaturated keto-esters, and the scission fragments nonanoic, decanoic, suberic, and azelaic acid. With increasing temperature and duration of oxidation, the unsaturated keto-esters tend to dimerise and form oils and resins that still retain their ketonic character.

The observed rapid loss of unsaturation at the higher temperatures, and the formation of appreciable quantities of epoxy- and dihydroxy-stearic acid derivatives, are compatible with a mechanism involving direct attack on ethenoid linkages by free hydroxyl radicals generated by thermal homolytic fission of the initially formed hydroperoxides.

Feuell and Skellon (*J.*, 1952, 59) found that, on the catalytic oxidation of *n*-propyl oleate by gaseous oxygen, maximum peroxidation with rapid loss of unsaturation occurred at 85—120°. Detailed investigation of the numerous products of similar oxidations is now described.

Purified *n*-propyl oleate (Feuell and Skellon, *loc. cit.*) was catalytically oxidised, with high oxygen dispersion and uranium oleate as catalyst (Skellon and Spence, *J. Soc. Chem. Ind.*, 1948, **67**, 365; Skellon and Thruston, *J.*, 1953, 138) to achieve rapid peroxidation. The conditions were generally similar to those previously employed (Feuell and Skellon, *loc. cit.*), but the oxidations extended over longer periods to secure reasonable yields of the end-products resulting from hydroperoxide decomposition. The oxidation products were separated by solvent fractionation, crystallisation, and distillation, methods previously described being suitably modified (Skellon, *J. Chem. Soc. Ind.*, 1931, **50**, 382T; *J.*, 1948, 343; Ellis, *Biochem. J.*, 1936, **30**, 753; 1950, **46**, 129).

Carbon dioxide was evolved during the oxidations, but even under the most stringent conditions the amount of chain degradation ($CH_2 \longrightarrow CO_2 + H_2O$) was small, corresponding to less than 0·5 atom of carbon per molecule of ester. The quantities of water were in all cases considerably in excess of those equivalent to the amount of carbon dioxide required by the above reaction, and apparently resulted from hydroperoxide decomposition to αβ-unsaturated ketones or to epoxide formation from dihydroxystearic acid derivatives.

The principal substances obtained were 9 : 10-epoxy- and 9 : 10-dihydroxy-stearic acids, oily and resinous ketonic products, and the scission fragments nonanoic, decanoic, suberic, and azelaic acids. The dihydroxy-stearic acid was isolated principally as the *threo*-isomer (m. p. 95°), but after prolonged oxidation (18 hr.) at 120°, much of this compound was obtained initially in the form of a complex of high molecular and equivalent weight that was converted into the *erythro*-isomer (m. p. 132°) by strong alkaline hydrolysis.

There was evidence for the presence of polymerised semi-aldehydes of suberic and azelaic acid. Small amounts of volatile lower fatty acids were detected. Prolonged oxidation at 120° resulted in the formation of a little hydroxyoxostearic acid (mixture of 9 : 10- and 10 : 9-isomers). Mild alkaline hydrolysis of the oxidised esters gave small yields of a mixture of nonanal and nonan-2-one, affording evidence for the presence of unsaturated

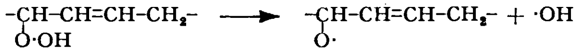
(I) $CH_3{\cdot}[CH_2]_6{\cdot}CO{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2Pr$ $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}CO{\cdot}[CH_2]_6{\cdot}CO_2Pr$ (II)

keto-esters (I and II), as suggested by Ellis (*loc. cit.*). Hydrolysis of (I) yields azelaic ester semialdehyde and nonan-2-one, while (II) gives nonanal and 8-oxononanoic ester. The yields of the principal end-products resolved are given in the Table.

Products of catalytic oxidation of n-*propyl oleate* (g. per 100 g. of oxidised ester).

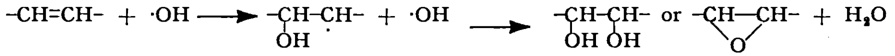
Temperature	55°	85°	120°	120°
Time of oxidation (hr.)	50	45	8	18
Products :				
9 : 10-Dihydroxystearic acid	3·1	9·6	7·4	17·1
9 : 10-Epoxystearic acid	8·3	4·1	2·2	9·5
9 : 10- and 10 : 9-Hydroxyoxostearic acid	—	—	—	2·1
Nonanoic acid	0·8	3·7	1·4	3·1
Decanoic acid	—	1·3	3·1	3·1
Suberic acid	—	1·4	0·7	1·8
Azelaic acid	0·3	2·4	1·0	2·2
αβ-Unsaturated keto-esters	0·4	1·6	1·8	1·5
Ketonic oils (sol. in light petroleum)	6·3	14·8	12·3	3·4
Ketonic resins (insol. in light petroleum)	1·4	16·9	22·7	28·8

The results are compatible with Waters's suggestion (*Ann. Reports*, 1945, 134) that during oxidations, particularly at the higher temperatures, some of the hydroperoxide formed initially by the α-methylenic chain-reaction sequence (Farmer, *Trans. Faraday Soc.*, 1946, **42**, 233; Bawn, *J. Oil Col. Chem. Assoc.*, 1953, **36**, 443) undergoes homolytic fission :



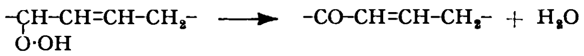
$$\underset{O\cdot OH}{-CH}-CH{=}CH-CH_2- \longrightarrow \underset{O\cdot}{-CH}-CH{=}CH-CH_2- + \cdot OH$$

The observed rapid loss of unsaturation at high temperatures, and the formation of appreciable quantities of 9 : 10-epoxy- and 9 : 10-dihydroxy-stearic acid, are explained by the attack on ethenoid linkages by the free hydroxyl radicals so formed :



$$-CH{=}CH- + \cdot OH \longrightarrow \underset{OH}{-CH}-\underset{\cdot}{CH}- + \cdot OH \longrightarrow \underset{OH}{-CH}-\underset{OH}{CH}- \text{ or } \underset{O}{-CH{-}CH-} + H_2O$$

The process of thermal catalytic oxidation appears to involve : (1) Decomposition of the hydroperoxides in the presence of the metallic catalyst (uranium), yielding αβ-unsaturated ketonic esters (cf. Cook, *J.*, 1938, 1774; Paquot, *Bull. Soc. chim.*, 1945, **12**, 120) :



$$\underset{O\cdot OH}{-CH}-CH{=}CH-CH_2- \longrightarrow -CO-CH{=}CH-CH_2- + H_2O$$

(2) Fission of the isomeric hydroperoxides to mono- and di-basic acids and the semi-aldehydes of the latter (Gibson, *J.*, 1948, 2275). The αβ-unsaturated ketonic esters may subsequently dimerise or polymerise to form the oily resins that are always obtained in appreciable quantities from such oxidations.

EXPERIMENTAL

Preparation of n-*Propyl Oleate*.—Purified oleic acid was prepared from olive oil (Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 131T) and converted into the *n*-propyl ester (Feuell and Skellon, *loc. cit.*) (Found : sap. val., 175·0; I val., 75·7. Calc. for $C_{21}H_{40}O_2$: sap. val., 172·9; I val., 78·2).

Catalytic Oxidations.—General. Oxygen at 18 mm. pressure was passed into the ester (45 g.) contained in a small bulb fitted with a stopper through which passed a No. 4 sintered-glass bubbler (for oxygen), a thermometer, a stoppered tube (for a sampling pipette), and an exit tube. The apparatus was placed in a thermostatically controlled oven, and the exit gases were passed through a weighed U-tube cooled in ice and through concentrated sodium hydroxide solution. All oxidations were carried out in the presence of 0·05% of uranium (as uranyl oleate dissolved in the ester).

Oxidation at 55°. The ester was oxidised for 50 hr. Water (0·093 g.) and a trace of sharp-smelling oil were collected in the U-tube. Carbon dioxide (0·122 g.) was evolved steadily throughout. Changes in peroxide content were :

Time (hr.)	4	8	22	32	46	50
Active O (%) *	0·098	0·137	0·273	0·314	0·423	0·465

* Method of Skellon and Wills (*Analyst*, 1948, **73**, 78).

The oxidised product had the following characteristics : sap. val., 183·1; acid val., 9·1; I val., 65·6; *M* (Rast), 330; CO (Method of Skellon and Feuell, *Analyst*, 1953, **78**, 135), 1·62%.

Oxidation at 85°. The ester was oxidised for 45 hr. Water (0·87 g.) and a trace of aldehyde (Schiff's test) were collected. Carbon dioxide (1·56 g.) was evolved throughout, the evolution being greater during the later stages. Changes in peroxide content were :

Time (hr.)	4	12	20	24	37	45
Active O (%)	0·397	0·964	1·230	1·218	0·775	0·621

The oxidised product had the following characteristics : sap. val., 261·5; acid val., 70·5; I val., 16·3; CO, 2·76%; *M* (Rast), 374.

Oxidation at 120°. The ester was oxidised for 8 and 18 hr. In the first run, 1·30 g. of water were collected, and in the second 3·43 g. Carbon dioxide (0·94 and 2·84 g. respectively) was evolved, the evolution being greatest after 8—12 hours' oxidation. Changes in peroxide content were :

Time (hr.)	1	2	3	4	6	8	12	18
Active O (%) (8 hr.)	0·471	0·621	0·604	0·585	0·435	0·318	—	—
,, (18 hr.)	—	0·618	—	0·640	0·562	—	0·440	0·258

The oxidised products from the 8 and the 18 hr. runs had the following characteristics, respectively : sap. val., 250·0, 311·2; acid val., 58·1, 58·0; I val., 26·0, 8·7; CO, 1·70, 1·42%; *M* (Rast), 368, 405.

Detailed Analysis of the Oxidised Esters.—(a) *Resolution into acidic and neutral fractions.* The products (*ca.* 40 g.) from the four oxidations [denoted below as : 55°, A; 85°, B; 120° (8 hr.) C; 120° (18 hr.) D] in ether (100 ml.) were extracted thrice with 20% sodium carbonate solution. After being washed with ether, the alkaline extracts were refluxed with excess of alcoholic N-potassium hydroxide, then acidified with hydrochloric acid, and the mixed liberated acids extracted with ether. Material A yielded 1·3 g., B 7·25 g., C 7·9 g., and D 7·6 g., of brown acids (Found, respectively : equiv., 235·1, 138·6, 263·5, 149·3; I val., 63·0, 11·8, 18·3, 9·5). The aqueous layer after extraction of these acids was neutralised, re-acidified with sulphuric acid, and distilled in steam; the distillates from B, C, and D were sharp-smelling and required for neutralisation, respectively, 4·2, 6·3, 7·1 ml. of 0·05N-alkali. On recovery of the neutral oxidation products, A afforded 33·7 g., B 28·6 g., C 27·0 g., and D 31·6 g. of yellow oils (Found, respectively : sap. val., 175·2, 204·0, 190·5, 241·4; I val., 65·7, 17·4, 30·8, 7·7). During extraction, ether-insoluble *n*-propyl dihydroxystearate separated : B gave 0·61 g. and C 0·7 g. of the *threo*-isomer, m. p. (recrystallised) and mixed m. p. 58—59° (lit., 59°) (Found, respectively : sap. val., 156·5, 159·9. Calc. for $C_{21}H_{42}O_4$: sap. val., 156·5); hydrolysis gave *threo*-9 : 10-dihydroxystearic acid, m. p. and mixed m. p. 94—95° (lit., 95°) (Found : equiv., 315·5. Calc. for $C_{18}H_{36}O_4$: equiv., 316·5). Material D gave 2·0 g. of impure *erythro*-isomer, m. p. (recrystallised) and mixed m. p. 92—93° (lit., 94°) (Found : sap. val., 158·6); hydrolysis gave *erythro*-9 : 10-dihydroxystearic acid, m. p. and mixed m. p. 132° (lit., 132°) : impure *threo*-isomer (0·2 g.), m. p. 65—68°, was obtained from the mother-liquor after recrystallisation.

(b) *Separation of the acidic products.* The acids were refluxed four times with light petroleum (b. p. 40—60°), and the combined concentrated extracts cooled at 0° : the precipitates of impure dibasic acids (A 0·07 g., B 1·1 g., C 0·4 g., D 1·2 g.) were removed by filtration. Extraction of the light-petroleum-insoluble residues with hot 25% ethanol gave further small yields of impure dibasic acids that were combined with the main precipitates and purified with ethanol and chloroform, affording suberic and azelaic acids : B gave 0·7 g. of suberic acid, C 0·2 g., D 0·5 g., having, respectively, m. p. (recrystallised) and mixed m. p., 139°, 140°, 139—140°

(lit., 140°) (Found, respectively: equiv., 88·5, 88·0, 87·8. Calc. for $C_8H_{14}O_4$: equiv., 87·1); A gave 0·07 g. of azelaic acid, B 1·2 g., C 0·3 g., D 0·8 g., having, respectively, m. p. (recrystallised) and mixed m. p. 104—105°, 106°, 105—106°, 105—106° (lit., 106°) (Found, respectively: equiv., 94·1, 94·9, 93·9, 94·0. Calc. for $C_9H_{16}O_4$: equiv., 94·1).

The light petroleum liquors gave, on evaporation, sharp-smelling yellow oils, which were steam-distilled. The oily distillates, extracted with ether, afforded an acid: from A 0·2 g., B 1·1 g., C 0·2 g., D 0·7 g. (Found, respectively: equiv., 160·0, 155·7, 160·0, 156·2. Calc. for $C_9H_{18}O_2$: equiv., 158·2), presumed to consist mainly of nonanoic acid. The oily residues not volatile in steam, by treatment with 40% ethanol, yielded decanoic acid and some unchanged oleic acid: B gave 1·1 g. of impure decanoic acid, C 1·1 g., D 0·77 g., having, respectively, f. p. (purified) 29—30°, 30—32°, 30—31° (lit., 31·5°) (Found, respectively: equiv., 174·0, 170·5, 173·0. Calc. for $C_{10}H_{20}O_2$: equiv., 172·2); A gave 0·5 g. of oleic acid, B 0·8 g., C 2·7 g. (Found, respectively: equiv., 283·8, 278·5, 280·5; I val., 89·9, 85·7, 87·8. Calc. for $C_{18}H_{34}O_2$: equiv., 282·5; I val., 89·9).

The acids insoluble in hot light petroleum, after extraction with 25% ethanol, formed brown resins (thought to be polymers of azelaic semialdehyde): from B 1·98 g., C 2·3 g., D 2·5 g. [Found, respectively: equiv., 156·6, 164·7, 190·4; *M* (Rast), 612, 807, 461; OH, 4·7, 4·7, 4·2; CO, 3·7, 3·3, 2·9; C, 66·8, 63·1, 62·3; H, 10·3, 8·8, 9·1%. Calc. for $(C_9H_{16}O_3)_n$: equiv., 172·2; M ($n = 4$), 688·8; OH, 7·41; CO, 4·1; C, 62·8; H, 9·3%].

(c) *Resolution of the neutral substances.* The neutral oils (*ca.* 30 g.) were refluxed with 0·05N-sodium hydroxide (750 ml.) for 2 hr. (Ellis, *Biochem. J.*, 1950, **46**, 129), and the small yields of volatile products were collected [see (d) below]. The esters recovered from this mild hydrolysis were completely saponified with N-potassium hydroxide in 50% alcohol, and after acidification and ether-extraction yielded mixed free acids: from A 28 g., B 27 g., C 22 g., D 13 g. (Found, respectively: equiv., 282·1, 274·4, 271·2, 287·4; I val., 80·7, 28·3, 30·6, 10·1). Material D also gave 2 g. of an ether-insoluble white solid, m. p. 175—180° (Found: equiv., 664), which after hydrolysis with alcoholic 3N-potassium hydroxide for 3 hr. afforded *erythro*-9 : 10-dihydroxystearic acid, m. p. and mixed m. p. 131—132° (lit., 132°) (Found: equiv., 315·7. Calc. for $C_{18}H_{36}O_4$: equiv., 316·5).

The mixed free acids were dissolved in 3—4 times their bulk of 96% methanol and cooled at 0°. The precipitates were fractionated with *n*-hexane into insoluble and soluble fractions, consisting of 9 : 10-epoxystearic and unchanged oleic acid respectively. Material A gave 2·9 g. of epoxide, B 1·4 g., C 1·7 g., D 2·2 g., m. p.s 53—54° (lit., 55°) (Found, respectively: equiv., 298·5, 297·8, 297·2, 298·0. Calc. for $C_{18}H_{34}O_3$: equiv., 298·5) [partly hydrolysed by 40% potassium hydroxide to *erythro*-9 : 10-dihydroxystearic acid, m. p. 131° (lit., 132°)]. The yields of oleic acid were: from A 2·0 g., B 1·5 g., C 0·9 g., D 0·2 g. (Found, respectively: equiv., 283·1, 281·1, 283·3, —; I val., 87·2, 88·4, 88·4, 86·9. Calc. for $C_{18}H_{34}O_2$: equiv., 282·5; I val., 89·9).

The methanolic filtrates remaining after removal of the impure epoxide precipitates were carefully diluted with warm water, and the separated oils washed with dilute methanol and hot water, all washings being bulked. At this stage, 0·8 g. of *threo*-9 : 10-dihydroxystearic acid was deposited from D; it had m. p. (recrystallised) and mixed m. p. 94° (lit., 95°) (Found: equiv., 314·8. Calc. for $C_{18}H_{36}O_4$: equiv., 316·5). The combined dilute methanolic liquors were made just alkaline, concentrated, acidified with sulphuric acid, and steam-distilled; the oily distillates, extracted with ether, yielded nonanoic acid: from A 0·08 g., B 0·2 g., C 0·3 g., D 0·06 g. (Found, respectively: equiv., 163·7, 160·5, 159·7, 163·9. Calc. for $C_9H_{18}O_2$: equiv., 158·2). The solid residues not volatile in steam were extracted with hot benzene and gave small yields of impure dibasic acids (suberic and azelaic acids): from B 0·3 g., C 0·5 g., D 0·3 g. (Found, respectively: equiv., 92·7, 91·8, 98·1. Calc. for $C_8H_{14}O_4$: equiv., 87·1. Calc. for $C_9H_{16}O_4$: equiv., 94·1). The separated and washed oils after drying (from A 20·5 g., B 18·2 g., C 18·0 g., D 9·9 g.) were refluxed four times with light petroleum (b. p. 40—60°), and the combined concentrated extracts cooled at 0°; the precipitates of impure *threo*-9 : 10-dihydroxystearic acid were removed by filtration: A gave 1·1 g., B 1·9 g., C 1·6 g., D 1·5 g., m. p. (recrystallised) and mixed m. p. 93—95° (lit., 95°) (Found, respectively: equiv., 315·1, 316·9, 315·7, 317·1. Calc. for $C_{18}H_{36}O_4$: equiv., 316·5). The precipitate from material D only, on treatment with light petroleum and chloroform (King, *J.*, 1936, 1788) gave 0·5 g. of hydroxyoxostearic acid, m. p. 62—63°, mixed m. p. 63—64° (lit., 64—65°) (mixture of 9 : 10- and 10 : 9-isomers) (Found: equiv., 313·1. Calc. for $C_{18}H_{34}O_4$: equiv., 314·5); it gave mixed semicarbazones of m. p. 135—138° (lit., 130—140°).

The light petroleum mother-liquors afforded, on evaporation, pale yellow oils: from A

19·0 g., B 8·9 g., C 6·2 g., D 0·8 g. These oils, by repeated treatment with acetone at −20°, were separated into unchanged oleic acid and ketonic oils of dimeric nature. Material A yielded 15·0 g. of oleic acid, B 3·1 g., C 1·3 g. (Found, respectively : equiv., 283·3, 284·0, 280·3; I val., 87·1, 87·4, 87·9. Calc. for $C_{18}H_{34}O_2$: equiv., 282·5; I val., 89·9). The yields of ketonic oils were : from A 2·2 g., B 5·1 g., C 4·4 g., D 0·8 g. These oils were subjected to steam-distillation and extraction with 30% ethanol to remove monomeric products before analysis [Found, respectively : equiv., 323·4, 337·0, 289·5, 288·5; I val., 48·7, 42·3, 39·3, 18·7; OH, 0·71, 0·90, 0·87, 1·41%; CO, 2·03, 1·48, 2·27, 2·47%; *M* (Rast), 402, 443, 458, 471].

The residues insoluble in hot light petroleum after extraction with 30% alcohol formed brown resins : from A 0·5 g., B 5·8 g., C 8·1 g., D 6·7 g. [Found, respectively : equiv., 323·1, 293·6, 268·5, 324·0; I val., 42·0, 33·3, 28·8, 15·3; OH, —, —, 5·23, 5·96; CO, 1·93, 1·79, 1·93, 1·34%; *M* (Rast), 474, 504, 423, 519].

(d) *Examination of volatile products of mild hydrolytic distillation.* The volatile products from the initial mild hydrolysis of the neutral substances were sharp-smelling oils : from A 0·04 g., B 0·18 g., C 0·21 g., D 0·15 g.; they gave positive Schiff's tests and formed 2 : 4-dinitrophenylhydrazones of m. p., respectively, 57—59°, 70—73°, 67—70°, 72—75°. A similar oily distillate (2·5 g.) from the hydrolysis of 100 g. of *n*-propyl oleate oxidised at 85° for 28 hr. contained 8·3% of free acid calculated as nonanoic acid; it yielded a 2 : 4-dinitrophenylhydrazone of m. p. 72—75°. This oil was treated with excess of moist silver oxide, made alkaline, and extracted with ether; on evaporation 0·9 g. of nonan-2-one was obtained; the m. p. and mixed m. p. of the derived semicarbazone was 119° (lit., 119°), and of the 2 : 4-dinitrophenylhydrazone 37—39° (authentic specimen, 39°). The alkaline liquors after ether-extraction were acidified and steam-distilled; the volatile product (1·2 g.) consisted of nonanoic acid (Found : equiv., 157·9. Calc. for $C_9H_{18}O_2$: equiv., 158·2); it formed a zinc salt having m. p. and mixed m. p. 131—132° (lit., 130—132°).

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